

PHYS 342/555

Introduction to solid state physics

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Chapter 13: Dielectrics and ferroelectrics

Lecture in pdf format will be available at:

<http://www.phys.utk.edu>

Polarization

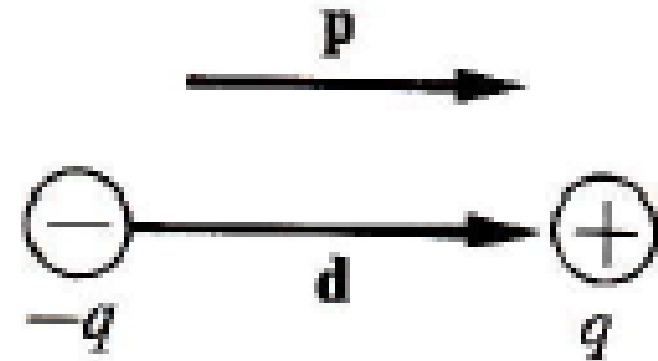
The polarization \mathbf{P} is defined as the dipole moment per unit volume, averaged over the volume of a cell. The total dipole moment,

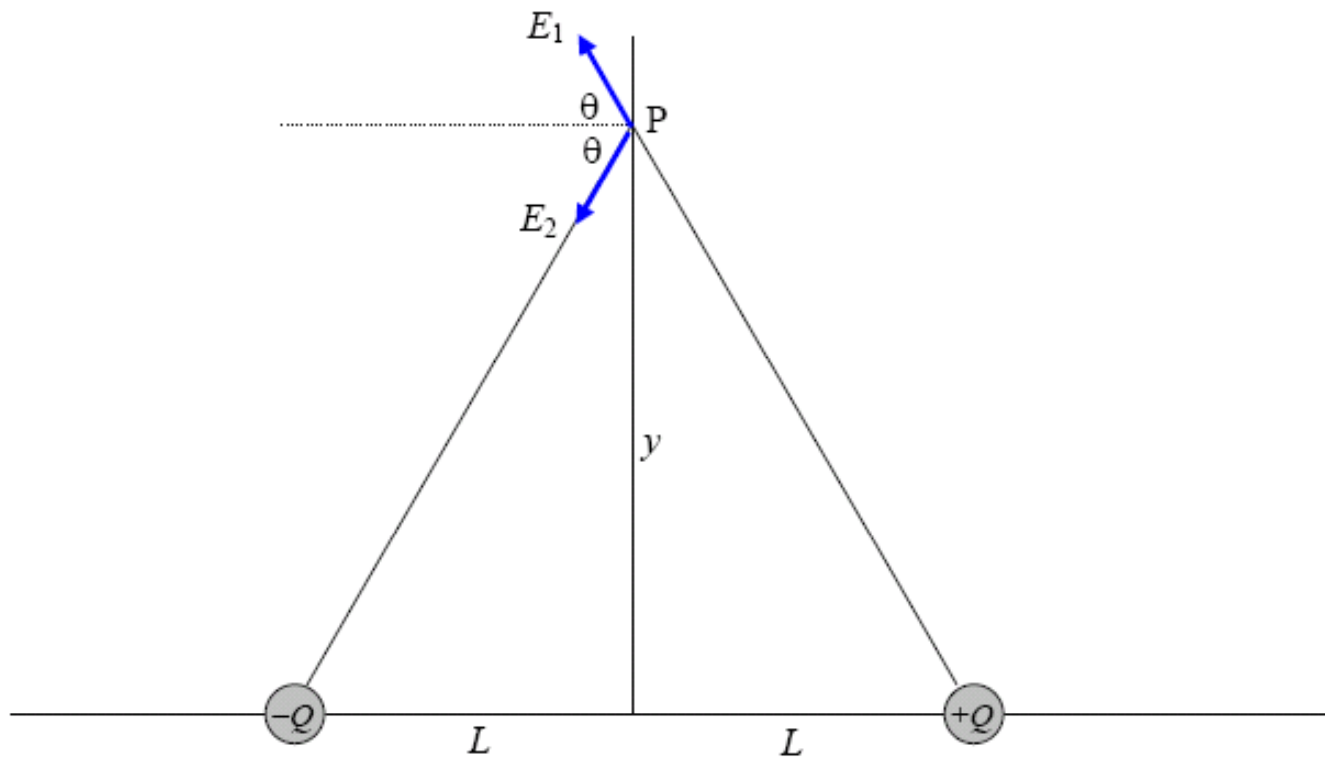
$$\vec{p} = \sum q_n \vec{r}_n,$$

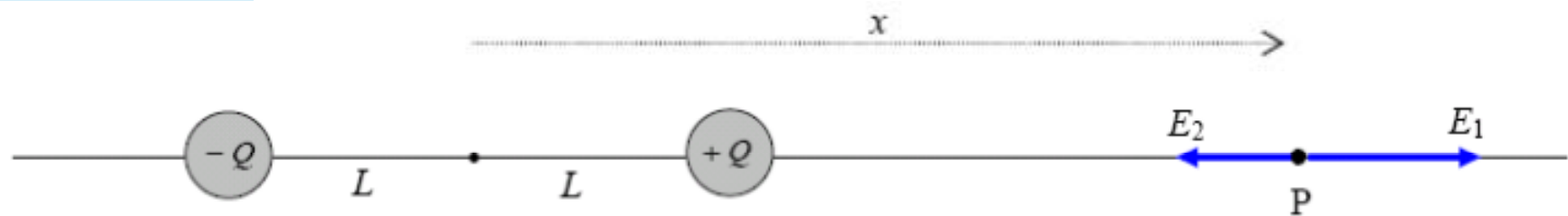
The electric field at a point \vec{r} from a dipole moment \vec{p} is:

$$\vec{E}(\mathbf{r}) = \frac{3(\vec{p} \cdot \vec{r})\vec{r} - r^2 \vec{p}}{r^5}$$

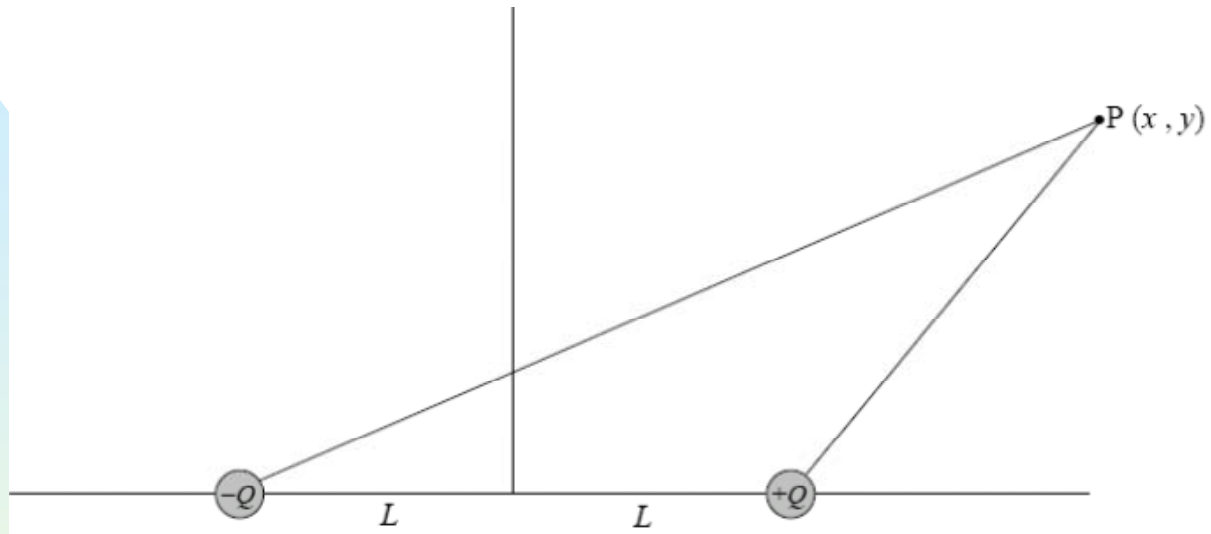
$$\mathcal{E} = \frac{1}{4\pi\epsilon_0} \frac{3(\mathbf{p} \cdot \mathbf{r})\mathbf{r} - r^2\mathbf{p}}{r^5},$$



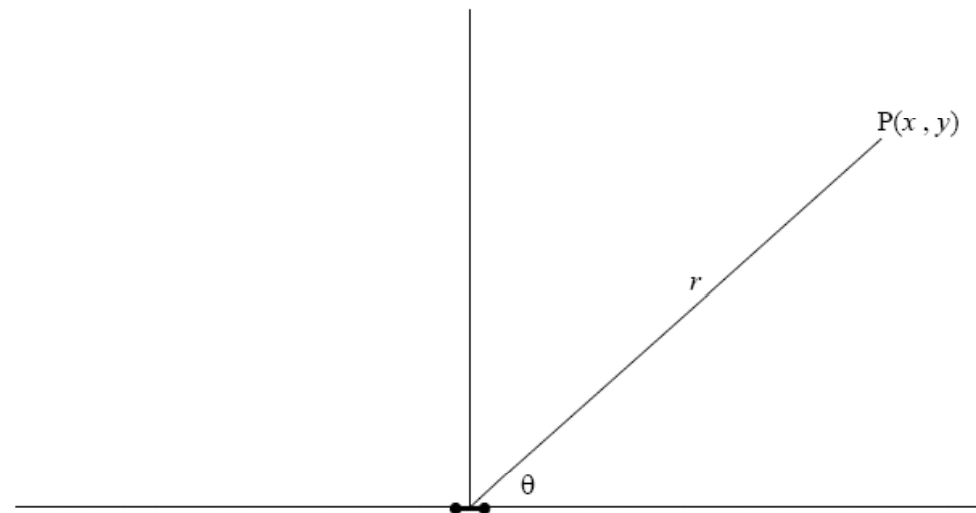




$$E = E_1 - E_2 = \frac{Q}{4\pi\epsilon_0} \left(\frac{1}{(x-L)^2} - \frac{1}{(x+L)^2} \right).$$



$$V = \frac{Q}{4\pi\epsilon_0} \left(\frac{1}{\{(x-L)^2 + y^2\}^{1/2}} - \frac{1}{\{(x+L)^2 + y^2\}^{1/2}} \right).$$



$$V = \frac{Q}{4\pi\epsilon_0} \left(\frac{1}{(r^2 - 2Lx)^{1/2}} - \frac{1}{(r^2 + 2Lx)^{1/2}} \right) = \frac{Q}{4\pi\epsilon_0 r} \left((1 - 2Lx/r^2)^{-1/2} - (1 + 2Lx/r^2)^{-1/2} \right).$$

When a dipole is placed in an external electric field, it interacts with the field. The field exerts a torque on the dipole which is given by

$$\boldsymbol{\tau} = \mathbf{p} \times \boldsymbol{\mathcal{E}}, \quad (8.3)$$

where $\boldsymbol{\mathcal{E}}$ is the applied field (Fig. 8.2). The magnitude of the torque is $\tau = p\mathcal{E} \sin \theta$, where θ is the angle between the directions of the field and the moment, and the direction of $\boldsymbol{\tau}$ is such that it tends to bring the dipole into alignment with the field. This tendency toward alignment is a very important property, and one which we shall encounter repeatedly in subsequent discussions.

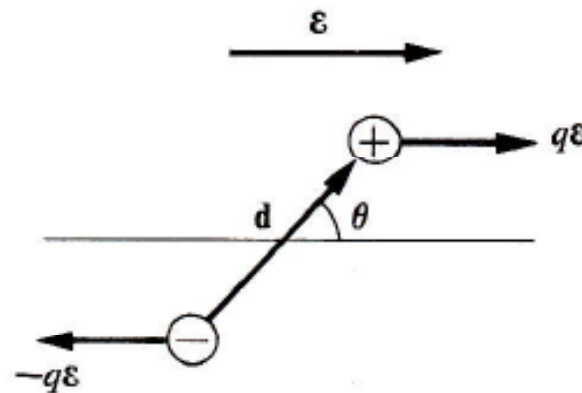


Fig. 8.2 The torque exerted on one dipole by an electric field. Vectors $q\boldsymbol{\mathcal{E}}$ and $-q\boldsymbol{\mathcal{E}}$ represent the two forces exerted by the field on the point charges of the dipole.

Another, and equivalent, way of expressing the interaction of the dipole with the field is in terms of the potential energy. This is given by

$$V = - \mathbf{p} \cdot \mathcal{E} = - p\mathcal{E} \cos \theta , \quad (8.4)$$

which is the potential energy of the dipole. We can see that the energy depends on θ , the angle of orientation, and varies between $-p\mathcal{E}$, when the dipole is aligned with the field, and $p\mathcal{E}$, when the dipole is opposite to the field. Because the energy is least when the dipole is parallel to the field, it follows that this is the most favored orientation, i.e., the dipole tends to align itself with the field. This is, of course, the same conclusion reached above on the basis of torque consideration.

In discussing dielectric materials, we usually talk about the *polarization* \mathbf{P} of the material, which is defined as the dipole moment per unit volume. If the number of molecules per unit volume is N , and if each has a moment \mathbf{p} , it follows that the polarization is given by†

$$\mathbf{P} = N\mathbf{p}, \quad (8.5)$$

where we have assumed that all the molecular moments lie in the same direction.

When a medium is polarized, its electromagnetic properties change; this is expressed through the well-known equation

$$\mathbf{D} = \epsilon_0 \mathcal{E} + \mathbf{P}, \quad (8.6)$$

where \mathbf{D} is the electric displacement vector and \mathcal{E} the electric field in the medium.

It is also well known that the displacement vector \mathbf{D} depends only on the *external* sources producing the external field, and is completely unaffected by the polarization of the medium.† It follows that the external field \mathcal{E}_0 , that is, the field outside the dielectric, satisfies the relation

$$\mathbf{D} = \epsilon_0 \mathcal{E}_0. \quad (8.7)$$

When we compare this with (8.6), we find that

$$\mathcal{E} = \mathcal{E}_0 - \frac{1}{\epsilon_0} \mathbf{P}, \quad (8.8)$$

showing that the effect of the polarization is to modify the field inside the medium. In general, this results in a reduction of the field.

Equation (8.6) is usually rewritten in the form

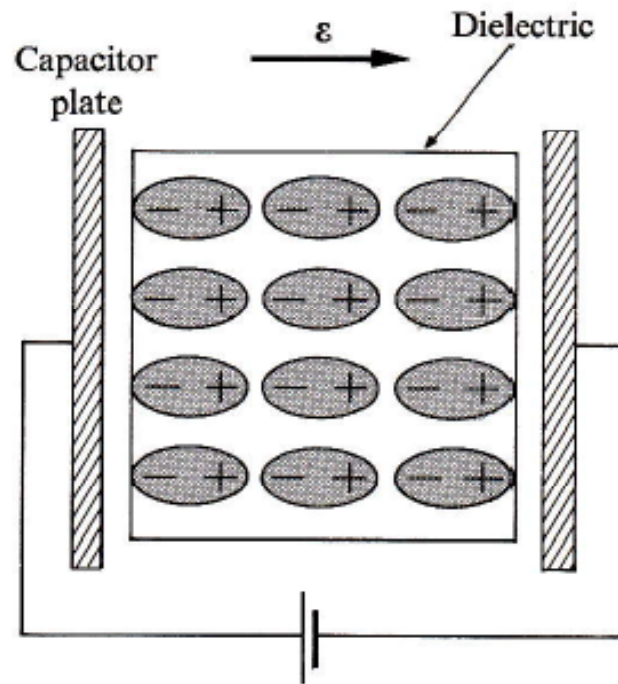
$$\mathbf{D} = \epsilon \mathcal{E} = \epsilon_0 \epsilon_r \mathcal{E}, \quad (8.9)$$

where the *relative dielectric constant*

$$\epsilon_r = \epsilon/\epsilon_0 \quad (8.10)$$

expresses the properties of the medium. All the dielectric and optical characteristics of the substance are contained in this constant, and indeed much of this chapter is concerned with evaluating it under a variety of circumstances. Thus it follows that we can gain much information about a medium by measuring its dielectric constant. From this point on, we shall refer to the relative dielectric constant ϵ_r as simply the dielectric constant, since we rarely need to use the actual dielectric constant $\epsilon = \epsilon_0 \epsilon_r$.

$$\mathcal{E}_0 = V_0/L,$$



medium—i.e., the lining up of the dipole moments along the field—which, in turn, modifies the field to a new value \mathcal{E} . This new field can be determined by measuring the new potential difference V by a voltmeter, and using the relation

$$\mathcal{E} = V/L. \quad (8.12)$$

The dielectric constant is given in terms of the fields \mathcal{E}_0 and \mathcal{E} by the relation

$$\epsilon_r = \mathcal{E}_0/\mathcal{E}, \quad (8.13)$$

as can be seen by comparing (8.9) with (8.10). It follows, therefore, that

$$\epsilon_r = V_0/V, \quad (8.14)$$

Since the polarization of a medium—i.e., the alignment of the molecular moment—is produced by the field, it is plausible to assume that the molecular moment is proportional to the field. Thus we write

$$\mathbf{p} = \alpha \mathcal{E}, \quad (8.15)$$

where the constant α is called the *polarizability* of the molecule. The expression (8.15) is expected to hold good, except in circumstances in which the field becomes very large, in which case other terms must be added to (8.15) to form what is, in effect, a Taylor-series expansion of \mathbf{p} in terms of \mathcal{E} . Equation (8.15) may be regarded as the first term in this expansion. (Higher-order terms lead to nonlinear effects.)

The polarization \mathbf{P} can now be written as

$$\mathbf{P} = N\alpha\mathcal{E}, \quad (8.16)$$

which, when substituted into (8.6), yields

$$\mathbf{D} = \epsilon_0\mathcal{E} + N\alpha\mathcal{E} = \epsilon_0 \left(1 + \frac{N\alpha}{\epsilon_0} \right) \mathcal{E}. \quad (8.17)$$

Comparing this result with (8.9), one finds

$$\epsilon_r = 1 + (N\alpha/\epsilon_0), \quad (8.18)$$

The *electric susceptibility* χ of a medium is defined by the relation

$$\mathbf{P} = \epsilon_0 \chi \mathcal{E}, \quad (8.19)$$

which relates the polarization to the field. By comparing this equation with (8.16), we find that the susceptibility and polarizability are interrelated by

$$\chi = \frac{N\alpha}{\epsilon_0}, \quad (8.20)$$

and hence Eq. (8.18) may be written simply as

$$\epsilon_r = 1 + \chi. \quad (8.21)$$

Thus the departure of the dielectric constant from unity, the value for vacuum, is equal to the electric susceptibility.† (If several gaseous species are present, then the factor $N\alpha$ in (8.20) should be replaced by $\sum_i N_i \alpha_i$.)

Equation (8.18) may also be written in terms of the density of the medium by noting that $N = \rho N_A / M$, where ρ is the density, M the molar mass, and N_A Avogadro's number. Thus

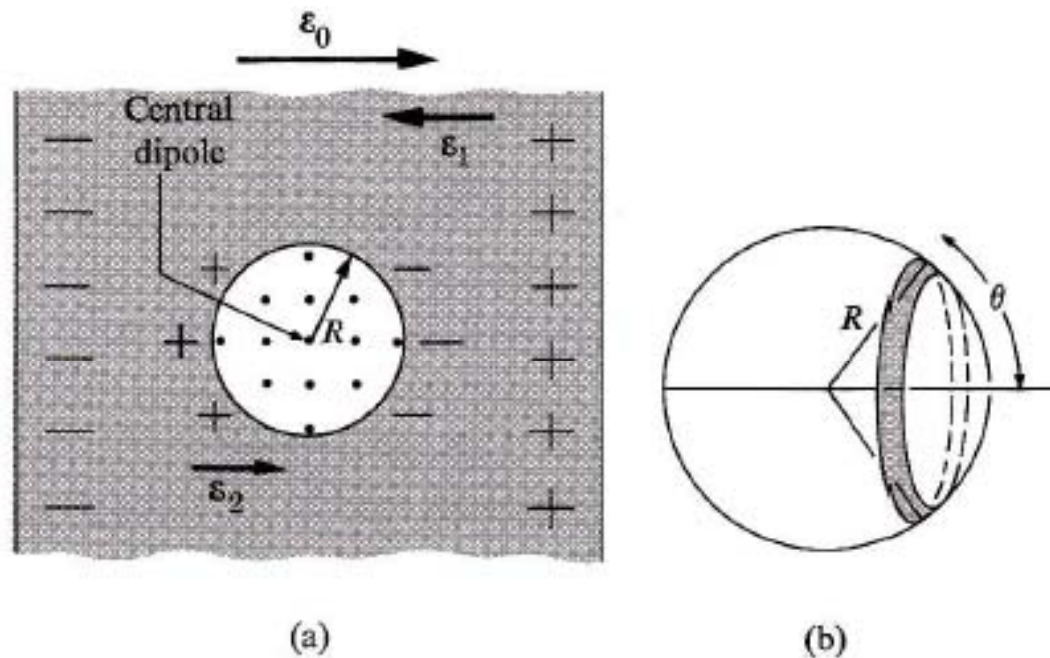
$$\epsilon_r = 1 + (\rho N_A / \epsilon_0 M) \alpha. \quad (8.22)$$

This expression, indicating that ϵ_r increases linearly with density, holds in gases, in which density can be conveniently varied over a wide range. This fact lends support to the argument used in the derivation of (8.19), and in particular to (8.15).

Experiments do show, however, that Eqs. (8.18) or (8.22) do not hold well in liquids or solids, i.e., in condensed physical systems. This point is important to us here, as our primary interest lies in describing solid substances, and we must therefore seek a better expression for the dielectric constant than (8.18). The root of the difficulty lies in (8.15). It is implied here that the field acting on and polarizing the molecules is equal to the field \mathcal{E} , but a closer examination reveals that this is not necessarily so. If it develops that the polarizing field is indeed different from \mathcal{E} , relation (8.15) should then be replaced by

$$\mathbf{p} = \alpha \mathcal{E}_{\text{loc}}, \quad (8.23)$$


where \mathcal{E}_{loc} is, by definition, the polarizing field—also called the *local field*.



concerned (Fig. 8.5). 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

$$\mathcal{E}_{\text{loc}} = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{E}_2 + \mathcal{E}_3, \quad (8.24)$$

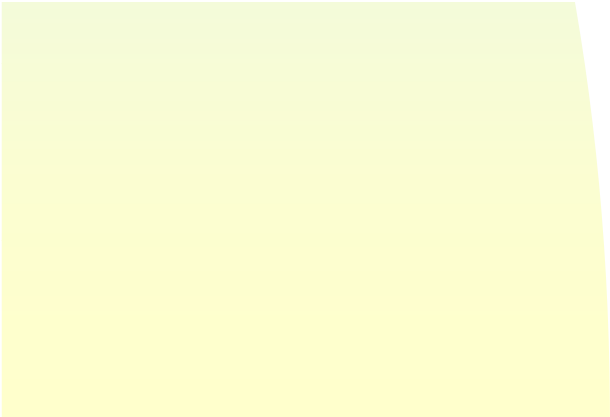
where \mathcal{E}_0 is the external field, \mathcal{E}_1 the field due to the polarization charges lying at the external surfaces of the sample, \mathcal{E}_2 the field due to the polarization charges lying on the surface of the Lorentz sphere, and \mathcal{E}_3 the field due to other dipoles lying within the sphere. Note that the part of the medium between the sphere and the external surface does not contribute anything since, in effect, the volume polarization charges compensate each other, resulting in a zero net charge in this region.



\mathcal{E}_1 : This field, due to the polarization charges on the external surface, is also known as the *depolarization field*, since it is obviously opposed to the external field. The value of this field depends on the geometrical shape of the external surface, and for the simple case of an infinite slab is given by

$$\mathcal{E}_1 = -\frac{1}{\epsilon_0} \mathbf{P}, \quad (8.25)$$

which you may confirm by using Gauss' law. The depolarization fields for other geometrical shapes can be found in the references (Kittel, 1971), as well as in the problems.



\mathcal{E}_2 : The polarization charges on the surface of the Lorentz cavity may be considered as forming a continuous distribution (recall that the cavity is large)

whose density is $-P \cos \theta$. The field due to the charge at a point located at the center of the sphere is, according to Coulomb's law, given by

$$\mathcal{E}_2 = \int_0^\pi \left(-\frac{P \cos \theta}{4\pi\epsilon_0 R^2} \right) \cos \theta (2\pi R^2 \sin \theta d\theta), \quad (8.26)$$

where the additional factor $\cos \theta$ is included because we are, in effect, evaluating only the component of the field along the direction of \mathbf{P} (other components vanish by symmetry), and the factor $2\pi R^2 \sin \theta d\theta$ is the surface element along the sphere (see Fig. 8.5b). Integration of (8.26) leads to the simple result

$$\mathcal{E}_2 = \frac{1}{3\epsilon_0} \mathbf{P}, \quad (8.27)$$

a field in the same direction as the external field.

\mathcal{E}_3 : This field, which is due to other dipoles in the cavity, may be evaluated by summing the fields of the individual dipoles using (8.2). The result obtained depends on the crystal structure of the solid under consideration, but for the case of a cubic structure it may readily be shown that the sum vanishes. That is,

$$\mathcal{E}_3 = 0, \quad (8.28)$$

If the various fields are now substituted into (8.24), one finds that

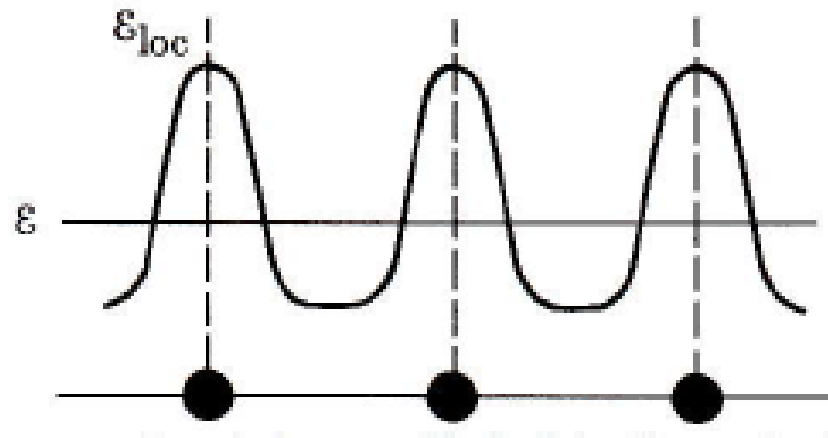
$$\mathcal{E}_{\text{loc}} = \mathcal{E}_0 - \frac{2}{3\epsilon_0} \mathbf{P}, \quad (8.29)$$

which gives the polarizing field in terms of the external field and the polarization.

We may compare the value of \mathcal{E}_{loc} obtained above with that of \mathcal{E} in (8.8). We discover that

$$\mathcal{E}_{\text{loc}} = \mathcal{E} + \frac{1}{3\epsilon_0} \mathbf{P}, \quad (8.30)$$

which shows that \mathcal{E}_{loc} is indeed different from \mathcal{E} , as we have suspected. The former field is, in fact, larger than the latter, so the molecules are more effectively polarized than our earlier discussions have indicated. Equation (8.30) is known as the *Lorentz relation*.



Let us now evaluate the dielectric constant. The polarization, according to (8.23) and (8.16), is given by

$$\mathbf{P} = N\alpha\mathcal{E}_{\text{loc}}, \quad (8.31)$$

which, when used in conjunction with (8.30), yields

$$\mathbf{P} = \left(\frac{N\alpha}{1 - \frac{N\alpha}{3\epsilon_0}} \right) \mathcal{E}. \quad (8.32)$$

Dielectric constant and polarizability

The dielectric constant ϵ of an isotropic medium relative to vacuum is defined as

$$\epsilon \equiv \frac{E + 4\pi P}{E} = 1 + 4\pi\chi$$

The polarizability α of an atom is defined in terms of the local electric field at the atom:

$$p = \alpha E_{local}$$

The polarization of a crystal is then

$$P = \sum_j N_j p_j = \sum_j N_j \alpha_j E_{local}(j).$$

If the local field is given by the Lorentz relation, then

$$P = \sum_j N_j \alpha_j \left(E + \frac{4\pi}{3} P \right) = \left(\sum_j N_j \alpha_j \right) \left(E + \frac{4\pi}{3} P \right).$$

$$\chi = \frac{P}{E} = \frac{\sum_j N_j \alpha_j}{1 - \frac{4\pi}{3} \sum_j N_j \alpha_j}.$$

The total polarizability can be separated into three parts:

1. electronic: arises from the displacement of the electron shell relative to a nucleus.
2. ionic: comes from the displacement of a charged ion with respect to other ions.
3. dipolar: from molecules with a permanent electric dipole moment that can change orientation in an applied electric field.

8.4 SOURCES OF POLARIZABILITY

There are different types of polarization processes, depending on the structure of the molecules which constitute the solid. If the molecule has a *permanent moment*, i.e., a moment even in the absence of an electric field, we speak of a *dipolar molecule*, and a *dipolar substance*.

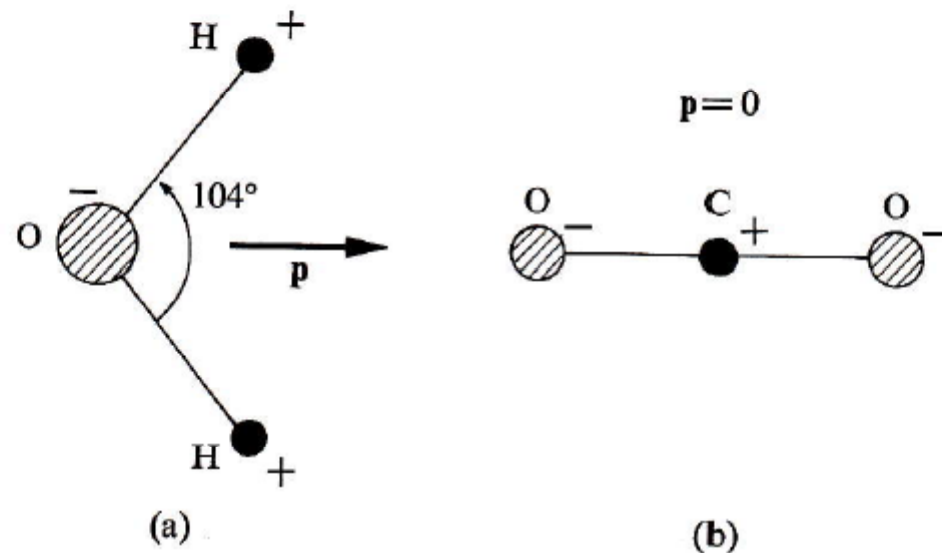


Fig. 8.7 (a) The water molecule and its permanent moment. $p = 1.9$ debye units (1 debye = 10^{-29} coul·m). (b) CO₂ molecule.

If the molecule contains ionic bonds, then the field tends to stretch the lengths of these bonds. This occurs in NaCl, for instance, because the field tends to displace the positive ion Na^+ to the right (see Fig. 8.8), and the negative ion Cl^- to the left, resulting in a stretching in the length of the bond. The effect of this change in length is to produce a net dipole moment in the unit cell where previously there was none. Since the polarization here is due to the relative displacements of oppositely charged ions, we speak of *ionic polarizability*.

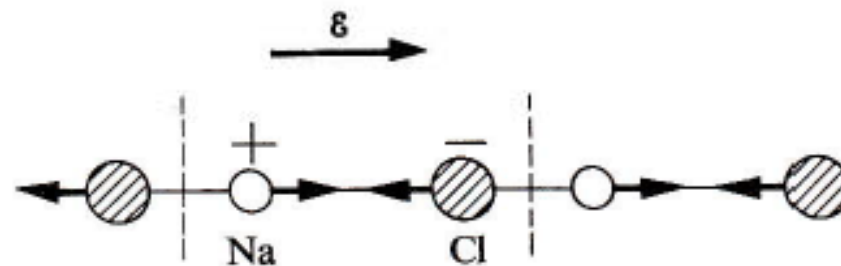


Fig. 8.8 Ionic polarization in NaCl. The field displaces the ions Na^+ and Cl^- in opposite directions, changing the length of the bond.

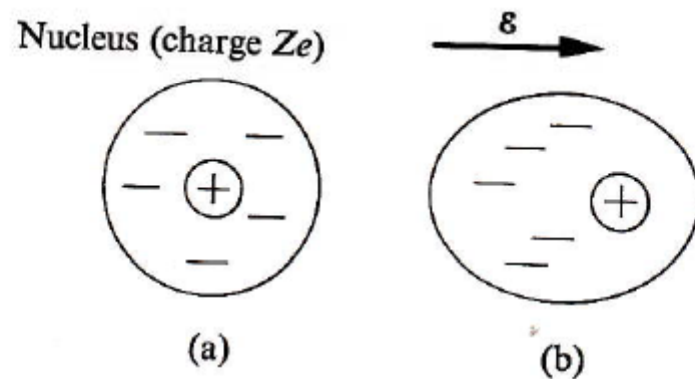
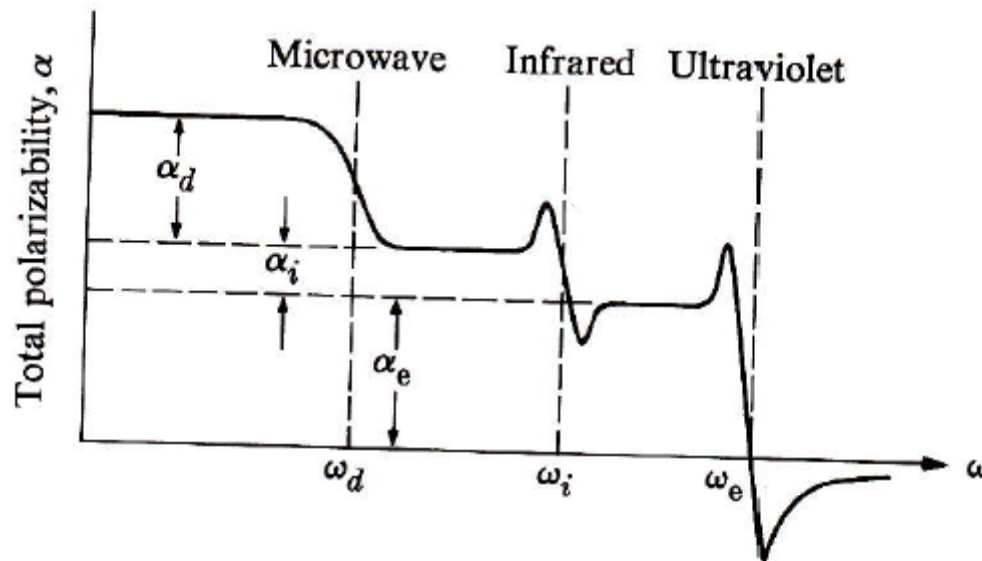


Fig. 8.9 Electronic polarization. (a) Unpolarized atom. (b) Atom polarized as a result of the field.

In general, therefore, we may write for the total polarizability

$$\alpha = \alpha_e + \alpha_i + \alpha_d, \quad (8.36)$$

which is the sum of the various contributions; α_e , α_i , and α_d are the electronic, ionic, and dipolar polarizabilities, respectively. The electronic contribution is present in any type of substance, but the presence of the other two terms depends on the material under consideration. Thus the term α_i is present in ionic substances, while in a dipolar substance all three contributions are present. In covalent crystals such as Si and Ge, which are nonionic and nondipolar, the polarizability is entirely electronic in nature.



violet region. It can be seen that in the range $\omega = 0$ to $\omega = \omega_d$, where ω_d (d for dipolar) is some frequency usually in the microwave region, the polarizability is essentially constant. In the neighborhood of ω_d , however, the polarizability decreases by a substantial amount. This amount corresponds precisely, in fact, to the dipolar contribution α_d . The reason for the disappearance of α_d in the frequency range $\omega > \omega_d$ is that the field now oscillates too rapidly for the dipole to follow, and so the dipoles remain essentially stationary.

The polarizability remains similarly unchanged in the frequency range ω_d to ω_i , and then plummets at the higher frequency. The frequency ω_i lies in the infrared region, and corresponds to the frequency of the transverse optical phonon in the crystal ω_t (Section 3.12). For the frequency range $\omega > \omega_t$, the ions with their heavy masses are no longer able to follow the very rapidly oscillating field, and consequently the ionic polarizability α_i vanishes, as shown in Fig. 8.10.

Polarizability of atomic hydrogen. Consider a semiclassical model of the ground state of the hydrogen atom in an electric field normal to the plane of the orbit (Fig. 25), and show that for this model $\alpha = a_H^3$, where a_H is the radius of the unperturbed orbit. *Note:* If the applied field is in the x direction, then the x component of the field of the nucleus at the displaced position of the electron orbit must be equal to the applied field. The correct quantum-mechanical result is larger than this by the factor $\frac{9}{2}$. (We are speaking of α_0 in the expansion $\alpha = \alpha_0 + \alpha_1 E + \dots$.) We assume $x \ll a_H$. One can also calculate α_1 on this model.

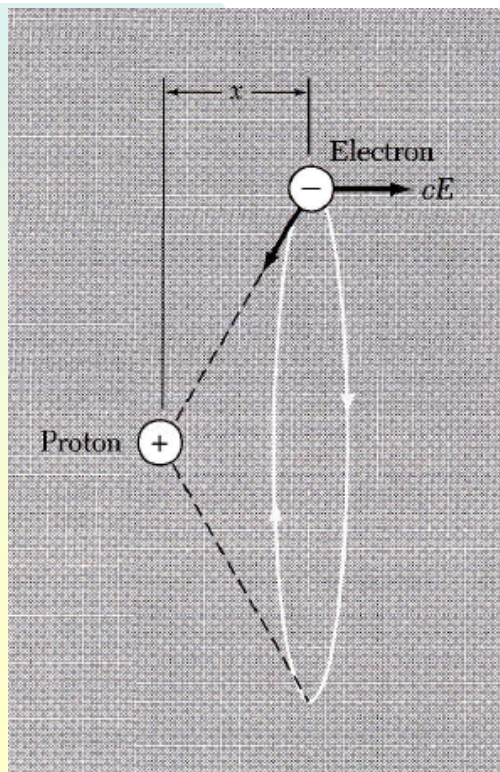
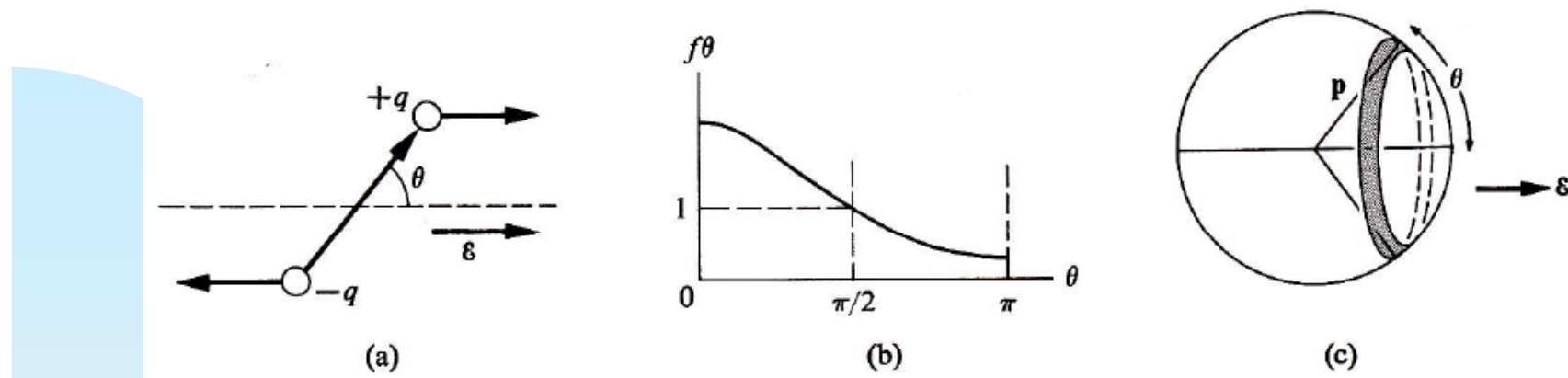


Figure 25 An electron in a circular orbit of radius a_H is displaced a distance x on application of an electric field E in the $-x$ direction. The force on the electron due to the nucleus is e^2/a_H^2 in CGS or $e^2/4\pi\epsilon_0 a_H^2$ in SI. The problem assumes $x \ll a_H$.

8.5 DIPOLAR POLARIZABILITY



Suppose the field is along the x -direction. The potential energy of the dipole is given, according to (8.4), by

$$V = -\mathbf{p} \cdot \mathcal{E} = -p \mathcal{E} \cos \theta, \quad (8.37)$$

where θ is the angle made by the dipole with the x -axis (Fig. 8.11). The dipole is no longer oriented randomly. The probability of finding it along the θ -direction is given by the distribution function

$$f = e^{-V/kT} = e^{p\mathcal{E} \cos \theta/kT}. \quad (8.38)$$

This expression is simply the Boltzmann factor, well known from statistical mechanics, with the potential energy being the orientational energy of (8.37). This distribution function, shown in Fig. 8.11(b), indicates that the dipole is more likely to lie along the field $\theta \simeq 0$ than in other directions, in agreement with the picture developed previously.

The average value of p_x , the x -component of the dipole moment, is given by the expression

$$\bar{p}_x = \frac{\int p_x f(\theta) d\Omega}{\int f(\theta) d\Omega}, \quad (8.39)$$

where the integration is over the solid angle, whose element is $d\Omega$. By carrying out the integration over the whole solid angle range (Fig. 8.11c), we take into account all the possible orientations of the dipole. The function $f(\theta)$ is the distribution function of (8.38) with its dependence on θ indicated, and the denominator in (8.39) is included for a proper normalization of this distribution function. In evaluating expression (8.39), we use the formulas $p_x = p \cos \theta$, $d\Omega = 2\pi \sin \theta d\theta$

(where the factor 2π arises from the integration over the azimuthal angle ϕ), $f(\theta)$ taken from (8.38), and the limits on the integrals $\theta = 0$ and $\theta = \pi$. Thus

$$\bar{p}_x = \int_0^\pi p \cos \theta e^{p\mathcal{E} \cos \theta/kT} 2\pi \sin \theta d\theta \bigg/ \int_0^\pi e^{p\mathcal{E} \cos \theta/kT} 2\pi \sin \theta d\theta,$$

which, when evaluated, yields†

$$\bar{p}_x = p L(u), \quad (8.40)$$

where

$$L(u) = \text{Coth}(u) - \frac{1}{u} \quad \text{and} \quad u = \frac{p\mathcal{E}}{kT}. \quad (8.41)$$

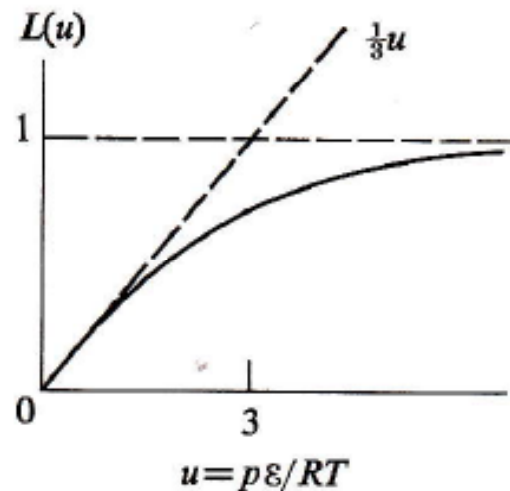


Fig. 8.12 The Langevin function $L(u)$ versus u .

The function $L(u)$, known as the *Langevin function*, is plotted in Fig. 8.12. Near the origin the function increases *linearly*, and one may show that $L(u) \simeq \frac{1}{3} u$. As u increases, the function continues to increase, monotonically, eventually saturating at the value unity as $u \rightarrow \infty$. The dipole moment \bar{p}_x , as a function of $p\mathcal{E}/kT$, has the same shape as Fig. 8.12, except for a change of the vertical scale by a constant p . Thus, for small values of the field, \bar{p}_x increases linearly, while at very high field, \bar{p}_x saturates at the maximum value p . This shows that at very high field the dipole points exactly along the field, which is a plausible result.

In most experimental situations, the ratio $u = p\mathcal{E}/kT$ is very small. For example, if we take $p \simeq 10^{-29}$ coul·m, $\mathcal{E} = 10^5$ V/m, and $T = 300^\circ\text{K}$, we find $u \simeq 10^{-4}$, which is very small indeed compared with unity. Thus we may use the low-field approximation

$$\bar{p}_x = \frac{p^2}{3kT} \mathcal{E}. \quad (8.42)$$

The result (8.42) may also be obtained from the following physical argument. As we know, the effect of a field is to align the dipoles, whereas the effect of temperature is to oppose this and to randomize the direction of the dipoles. Therefore one may write

$$\bar{p}_x = p \frac{\text{orientational energy}}{\text{thermal energy}}.$$

If we substitute the values orientational energy = $p\mathcal{E}$ and thermal energy $\simeq kT$, we obtain

$$\bar{p}_x = p \frac{p\mathcal{E}}{kT} = \frac{p^2\mathcal{E}}{kT},$$

Dipolar polarizability, on the basis of (8.42), is given by

$$\alpha_d = \frac{p^2}{3kT}. \tag{8.43}$$

8.6 DIPOLAR DISPERSION

The equation we shall use to describe the motion of the dipolar polarization is

$$\frac{dp_d(t)}{dt} = \frac{1}{\tau} \left[p_{ds}(t) - p_d(t) \right], \quad (8.45)$$

where $p_d(t)$ is the actual dipolar moment at the instant t , while $p_{ds}(t)$ is the saturated (or equilibrium) value of the moment, which would be the value approached by $p_d(t)$ if the field were to retain its instantaneous value for a long time. We have assumed that the rate of increase of $p_d(t)$ is proportional to the departure of this moment from its equilibrium value, and the quantity τ is called the *relaxation time*, also referred to as the *collision time*.

Let us illustrate the meaning of (8.45) in a very simple situation. Suppose that a static field is applied at the instant $t = 0$. In that case, $p_{ds}(t) = \alpha_d \mathcal{E} = p_0$ (p_0 is the permanent moment of the molecule), because this is the value reached

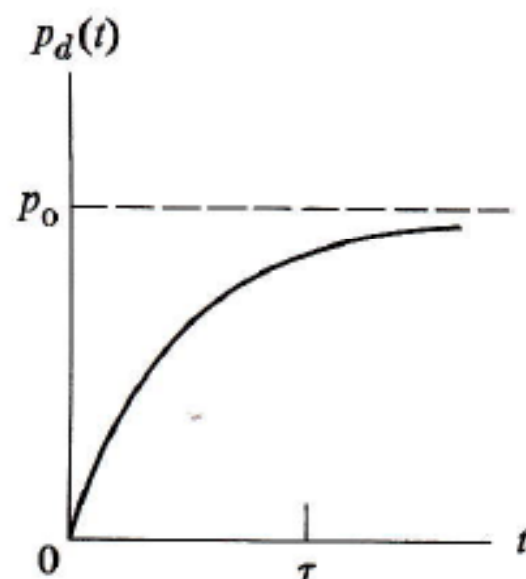
by the moment long after the application of the field, where α_d is the static polarizability calculated in Section 8.5. Equation (8.45) now reduces to


$$\frac{dp_d}{dt} + \frac{p_d(t)}{\tau} = \frac{p_0}{\tau}, \quad (8.46)$$

which, as a first-order linear differential equation, can be readily solved, yielding

$$p_d(t) = p_0(1 - e^{-t/\tau}). \quad (8.47)$$

Thus the moment rises toward its equilibrium value in an exponential fashion, (Fig. 8.15), much like the direct-current rise in an R–L electrical circuit (of time constant τ) when the battery has just been connected.





Let us now apply (8.45) to the case of an ac field

$$\mathcal{E}(t) = A e^{-i\omega t}. \quad (8.49)$$

The equilibrium moment is given by

$$p_{ds}(t) = \alpha_d(0)\mathcal{E}(t) = \alpha_d(0)A e^{-i\omega t}, \quad (8.50)$$

where $\alpha_d(0)$ is the static dipolar polarizability discussed in Section 8.5. Clearly the expression (8.50) is the value which would be reached by $p_d(t)$ if the field were

to remain equal to $\mathcal{E}(t)$ at all subsequent times (that is, for $t' > t$). Equation (8.45) now reduces to

$$\frac{dp_d(t)}{dt} + \frac{p_d(t)}{\tau} = \frac{\alpha_d(0)}{\tau} \mathcal{E}(t). \quad (8.51)$$

Since the driving term on the right is varying harmonically in time, as indicated by (8.49), we try a solution of the form

$$p_d(t) = \alpha_d(\omega) \mathcal{E}(t) = \alpha_d(\omega) A e^{-i\omega t}, \quad (8.52)$$

where $\alpha_d(\omega)$ is, by definition, the ac polarizability. When this is substituted into (8.51), one readily arrives at

$$\alpha_d(\omega) = \frac{\alpha_d(0)}{1 - i\omega\tau}. \quad (8.53)$$

It can be seen that the ac polarizability is now a complex quantity, indicating that the polarization is no longer in phase with the field. This gives rise to energy absorption, as we shall see shortly.

To derive the corresponding expression for the dielectric constant $\epsilon_r(\omega)$, we write

$$\epsilon_r(\omega) = 1 + \chi_e(\omega) + \chi_d(\omega),$$

where $\chi_e(\omega)$ and $\chi_d(\omega)$ are the electronic and dipolar susceptibilities, respectively. We have assumed for simplicity that the ionic contribution is sufficiently small to be negligible, and we have also ignored the local field correction, i.e., we have used (8.18). Now in the frequency region in which dipolar dispersion is significant—i.e., the microwave region—the electronic susceptibility is constant because the electrons, being so light, can respond to the field essentially instantaneously. We may therefore write the above equation as

$$\epsilon_r(\omega) = n^2 + \chi_d(\omega), \quad (8.54)$$

where $n^2 = 1 + \chi_e$ is the optical dielectric constant and n is the index of refraction.

The dipolar contribution $\chi_d(\omega) = \epsilon_r(\omega) - n^2$ does not follow the field instantaneously. There is a phase lag, as implied by the complex polarizability of (8.53). Since χ_d is proportional to α_d (see 8.20), it follows that $\chi_d(\omega)$ has the same complex form as $\alpha_d(\omega)$ in (8.53), and one may then write (8.54) in the form

$$\epsilon_r(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 - i\omega\tau}, \quad (8.55)$$

where the numerator on the right gives the static value of the dipolar susceptibility, that is, $\chi_d(0) = \epsilon_r(0) - n^2$. Equation (8.55) is the expression we have been

seeking for the dielectric constant. This quantity is clearly frequency dependent, signifying that the medium exhibits *dispersion*.

This dielectric constant, being a complex quantity, can be written as

$$\epsilon_r(\omega) = \epsilon_r'(\omega) + i\epsilon_r''(\omega), \quad (8.56)$$

yielding for the real and imaginary parts

$$\epsilon_r'(\omega) = n^2 + \frac{\epsilon_r(0) - n^2}{1 + \omega^2\tau^2}, \quad (8.57a)$$

and

$$\epsilon_r''(\omega) = \frac{\epsilon_r(0) - n^2}{1 + \omega^2\tau^2} \omega\tau, \quad (8.57b)$$

which are known as *Debye's equations*.

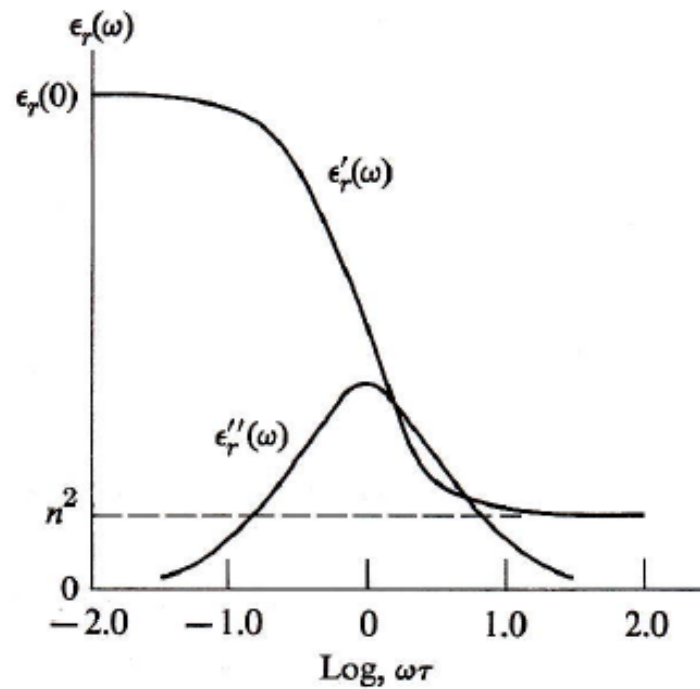


Fig. 8.16 Real and imaginary parts $\epsilon_r'(\omega)$ and $\epsilon_r''(\omega)$ versus $\log(\omega\tau)$ for a dipolar substance.

The rate of energy loss in the system may be calculated as follows:
The polarization current density is

$$J = \frac{dP}{dt}, \quad (8.58)$$

and therefore the rate of joule heating per unit volume is given by

$$Q = J\mathcal{E}. \quad (8.59)$$

The polarization vector is given in terms of the dielectric constant by the relation

$$\begin{aligned} P(t) &= \epsilon_0 [\epsilon_r(\omega) - 1] \mathcal{E}(t) \\ &= \epsilon_0 [(\epsilon_r'(\omega) - 1) + i\epsilon_r''(\omega)] \mathcal{E}(t), \end{aligned} \quad (8.60)$$

which can also be written as

$$P(t) = \epsilon_0 \epsilon_r^*(\omega) e^{i\phi} \mathcal{E}(t), \quad (8.61)$$

where $\epsilon_r^*(\omega) = [(\epsilon_r(\omega) - 1)^2 + \epsilon_r''^2(\omega)]^{1/2}$ and ϕ is an angle given by

$$\tan \phi = \frac{\epsilon_r''(\omega)}{\epsilon_r'(\omega) - 1}. \quad (8.62)$$

It is evident from (8.61) that the polarization lags behind the field by an angle ϕ (recall that $\mathcal{E}(t) \sim e^{-i\omega t}$).


The density of the polarization current is now given according to (8.58) and (8.61) by

$$\begin{aligned} J &= -i\omega\epsilon_0\epsilon_r^*(\omega) e^{i\phi} \mathcal{E}(t) \\ &= \omega\epsilon_0\epsilon_r^*(\omega) e^{i(\phi-\pi/2)} \mathcal{E}(t), \end{aligned} \quad (8.63)$$

which precedes the field by a phase angle $\phi' = (-\phi + \pi/2)$. [Draw the figure.] If we now substitute this value into (8.59) and determine the time average, we obtain

$$\begin{aligned} Q &= \frac{1}{2} |J| |\mathcal{E}| \cos \phi' \\ &= \frac{1}{2} \epsilon_0 \omega \epsilon_r^*(\omega) \sin \phi |\mathcal{E}|^2 \\ &= \frac{1}{2} \epsilon_0 \omega \epsilon_r''(\omega) |\mathcal{E}|^2, \end{aligned} \quad (8.64)$$

where we have used (8.62) in the last equation. Note that the loss rate is proportional to $\omega \epsilon_r''(\omega)$, that is, essentially to $\epsilon_r''(\omega)$. Thus the loss rate is greatest near the collision frequency.



Measuring the dielectric constant enables us to determine the relaxation time, as we have just seen. This time depends on the interaction between the dipolar molecule and the fluid in which it rotates. Debye has shown that, when we treat the surrounding medium as a viscous fluid, the relaxation time for a spherical molecule is given by

$$\tau = \frac{4\pi\eta R^3}{kT}, \quad (8.65)$$

where η is the viscosity of the fluid and R the radius of the molecule. For water at room temperature, $\eta \simeq 0.01$ poise, $R \simeq 2\text{\AA}$, leading to $\tau \simeq 2.5 \times 10^{-11}\text{s}$, in approximate agreement with experiment.

The time τ increases as the temperature is lowered both because of T in the denominator and because viscosity increases as temperature decreases. For example, the relaxation time in ice at -20°C is of the order of 10^{-7}s , which is five orders of magnitude greater than the value at room temperature. Table 8.2 lists relaxation times for a few simple liquids at room temperature.

Table 8.2
Relaxation Times at 20°C

Substance	τ
Water	9.5×10^{-11}
Alcohol	13
Chloroform	7.5
Acetone	0.33
Chlorobenzene	0.12
Toluene	0.75
<i>t</i> -butyl chloride	0.48

8.9 ELECTRONIC POLARIZABILITY

Now that we have discussed dipolar and ionic polarizabilities, let us look at electronic polarizability and dispersion. We shall give a classical treatment first as a preliminary to the quantum discussion to follow.

Classical treatment

To find the static polarizability, we assume that the electrons form a uniform, negatively charged sphere surrounding the atom. It can be shown through the laws of electrostatics that when a field \mathcal{E} is applied to this atom, the nucleus is displaced from the center of the sphere by a distance

$$x = \left(\frac{4\pi\epsilon_0 R^3}{Ze} \right) \mathcal{E}, \quad (8.76)$$

where R is the radius of the sphere (the atomic radius), and Ze the nuclear charge (see the problem section). The atom is thus polarized, and the dipole moment, $p = Zex$, yields the electronic polarizability

$$\alpha_e = 4\pi\epsilon_0 R^3. \quad (8.77)$$

If we substitute the typical value $R = 10^{-10}$ m, we find that $\alpha_e \simeq 10^{-41}$ farad \cdot m², in an order of magnitude which has actual polarizabilities given in Table 8.4.

To find the ac polarizability, we assume that the electrons in the atom experience an elastic restoring force corresponding to a resonant frequency ω_0 .†

Table 8.4

Electronic Polarizabilities for Some Inert Gases and Closed-Shell Alkali and Halogenic Ions (in units of 10^{-40} farad m^2).

Inert gases		Alkali cores		Halogenic closed-shell	
He	0.18	Li ⁺	0.018	F ⁻	0.76
Ne	0.35	Na ⁺	0.20	Cl ⁻	2.65
Ar	1.74	K ⁺	0.86	Br ⁻	3.67
Kr	2.2	Rb ⁺	1.34	I ⁻	5.5
Xe	3.6	Cs ⁺	2.20		

When the ac field is polarized in the x -direction, the appropriate equation of motion for the electron is

$$m \frac{d^2 x}{dt^2} + m\omega_0^2 x = -e \mathcal{E}. \quad (8.78)$$

Assuming an ac field $\mathcal{E} = \mathcal{E}_0 e^{-i\omega t}$, one can readily solve for x and the polarization. The polarizability is found to be

$$\alpha_e(\omega) = \frac{e^2/m}{\omega_0^2 - \omega^2}. \quad (8.79)$$

If there are Z electrons per atom and N atoms per unit volume, the resulting electric susceptibility is

$$\chi_e(\omega) = \frac{NZe^2/\epsilon_0 m}{\omega_0^2 - \omega^2}, \quad (8.80)$$

and the index of refraction is given by

$$n^2(\omega) = 1 + \frac{NZe^2/\epsilon_0 m}{\omega_0^2 - \omega^2}. \quad (8.81)$$

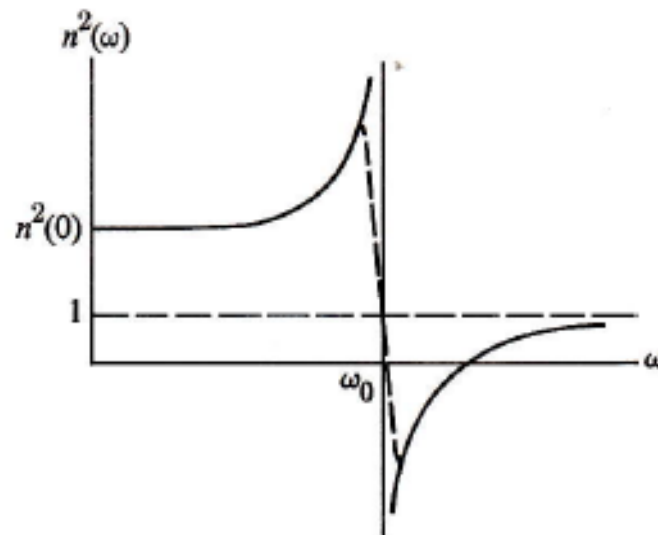


Fig. 8.21 Square of index of refraction $n^2(\omega)$ versus frequency, illustrating dispersion in ultraviolet region due to motion of electrons.

Figure 8.21 plots the function $n^2(\omega)$ versus ω , and shows strong dispersion at the resonance frequency ω_0 . Such behavior is typical of all resonant systems, and reflects the strong interaction between the driving field and the system when the frequency-matching condition is satisfied, that is, when $\omega \simeq \omega_0$. The annoying divergence at $\omega = \omega_0$ can be removed by including a collision term in Eq. (8.78), as we did in Section 4.11. [Indeed, the results thus obtained should

Show that the polarizability of a conducting metallic sphere of radius a is $\alpha = a^3$.

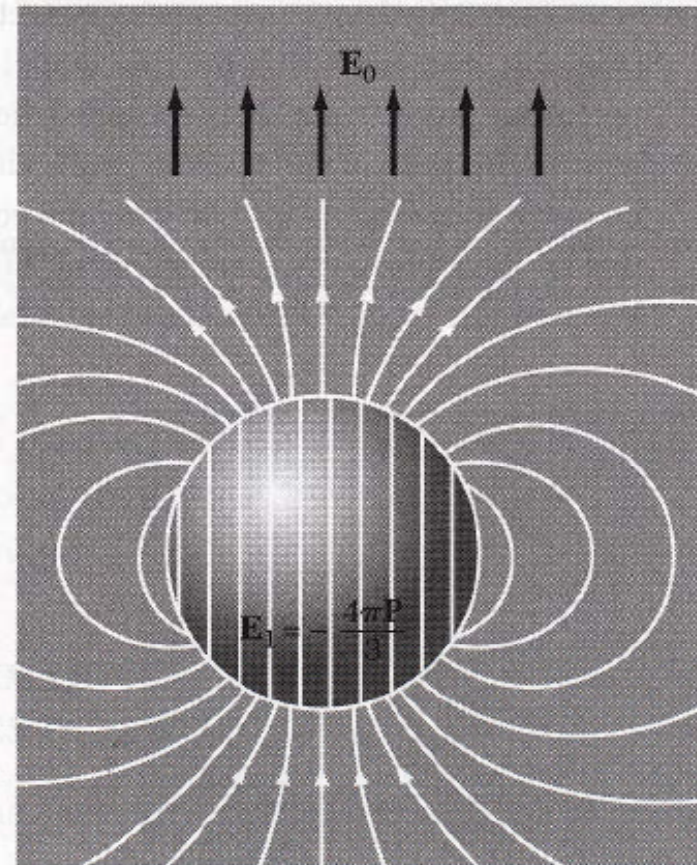


Figure 26 The total field inside a conducting sphere is zero. If a field \mathbf{E}_0 is applied externally, then the field \mathbf{E}_1 due to surface charges on the sphere must just cancel \mathbf{E}_0 , so that $\mathbf{E}_0 + \mathbf{E}_1 = \mathbf{0}$ within the sphere. But \mathbf{E}_1 can be simulated by the depolarization field $-4\pi\mathbf{P}/3$ of a uniformly polarized sphere of polarization \mathbf{P} . Relate \mathbf{P} to \mathbf{E}_0 and calculate the dipole moment \mathbf{p} of the sphere. In SI the depolarization field is $-\mathbf{P}/3\epsilon_0$.

Structural phase transitions

The stable structure at a temperature T is determined by the minimum of the free energy $F = U - TS$.

Ferroelectric crystals

A ferroelectric state is a state where the center of positive charge of the crystal does not coincide with the center of negative charge.

Ferroelectricity disappears above a certain temperature, where the crystal is in the paraelectric state.

■ Ferroelectricity

- Ferroelectricity is an electrical phenomenon whereby certain materials may exhibit a **spontaneous dipole moment**, the direction of which can be switched between equivalent states by the application of an external electric field.
- The internal electric dipoles of a ferroelectric material are physically tied to the material lattice so anything that changes the physical lattice will change the strength of the dipoles and cause a current to flow into or out of the capacitor even without the presence of an external voltage across the capacitor.

■ Ferroelectric properties

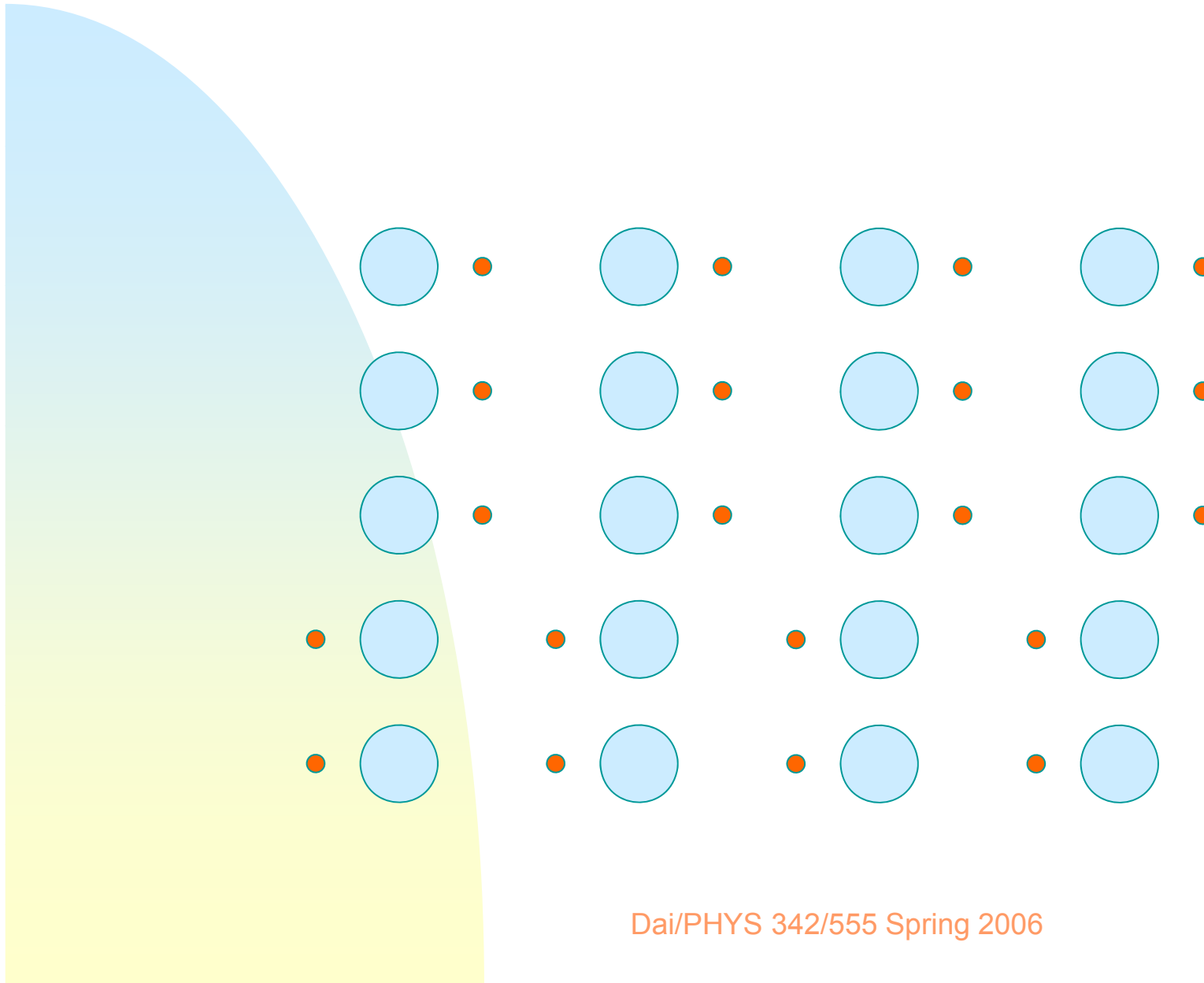
- Most ferroelectric materials undergo a structural phase transition from a high-temperature nonferroelectric (or paraelectric) phase into a low-temperature ferroelectric phase.
- The paraelectric phase may be piezoelectric or nonpiezoelectric and is rarely polar.
- The symmetry of the **ferroelectric phase** is always lower than the symmetry of the **paraelectric phase**.

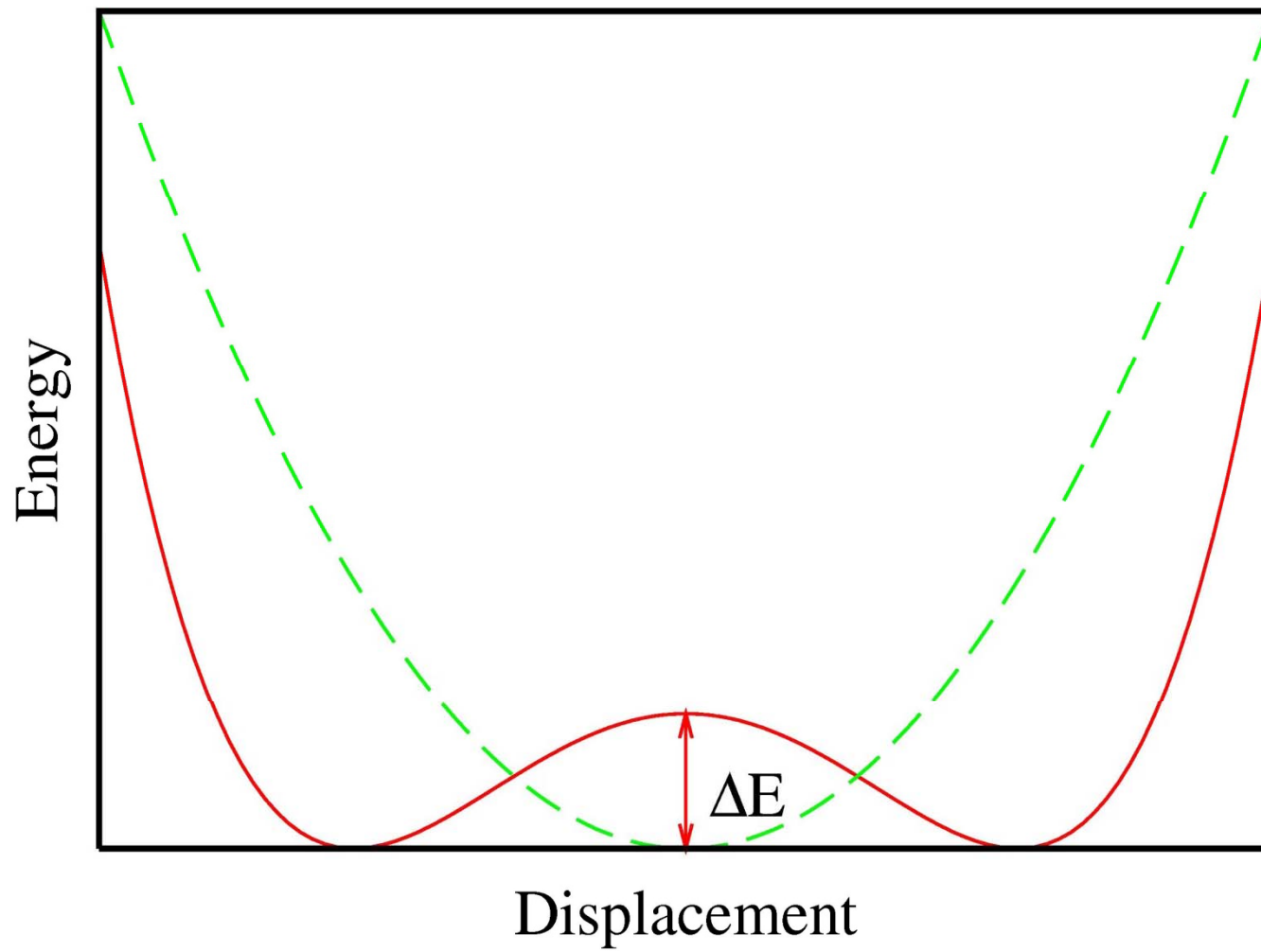
- The temperature of the phase transition is called the **Curie point, T_C** .
- Above the Curie point the dielectric permittivity falls off with temperature according to the Curie–Weiss law

$$\epsilon = \epsilon_0 + \frac{C}{T - T_0} \approx \frac{C}{T - T_0}$$

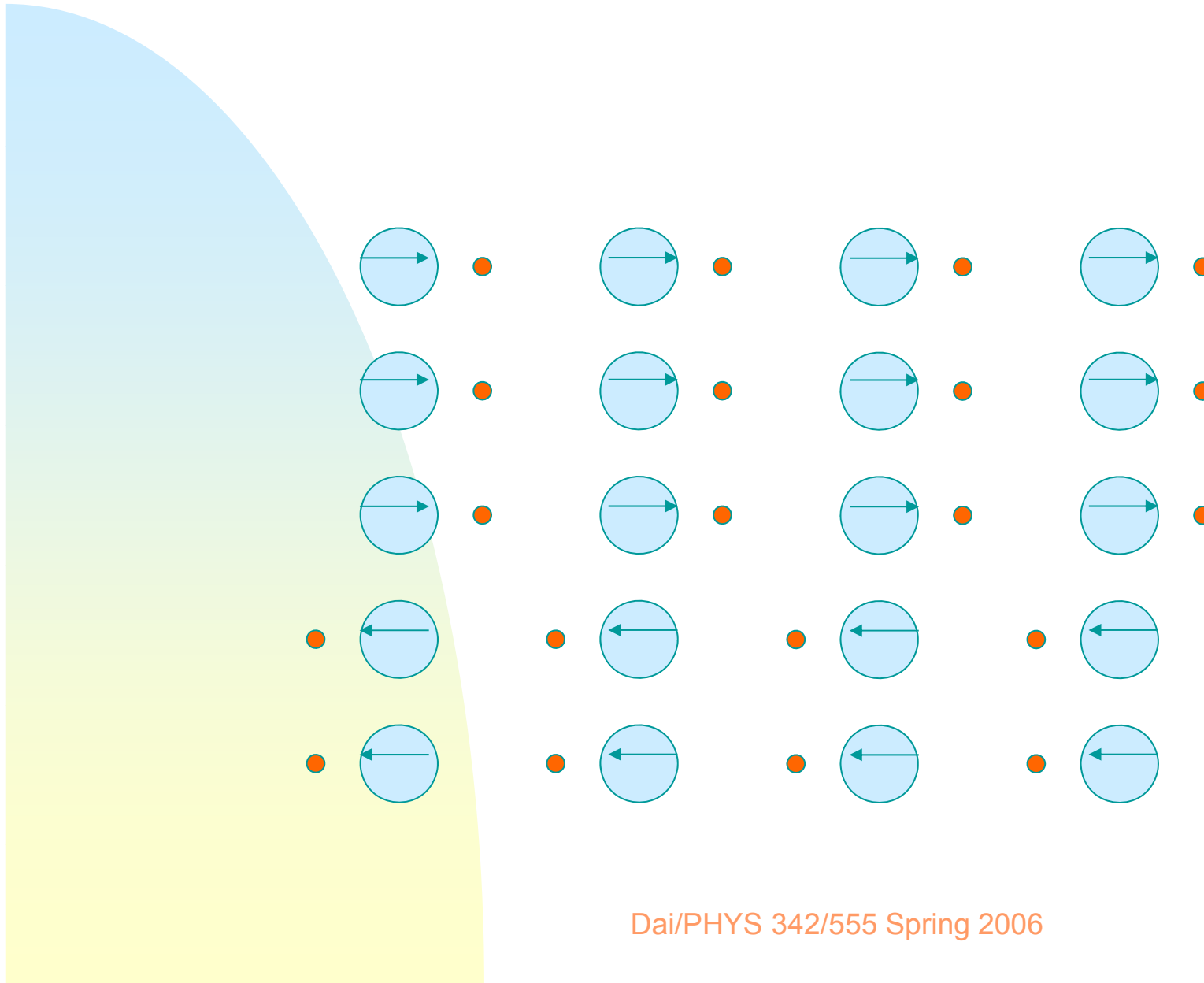
- ◆ where C is the Curie constant, T_0 ($T_0 \leq T_C$) is the Curie–Weiss temperature.
- Some ferroelectrics, such as BaTiO_3 , undergo **several phase transitions into successive ferroelectric phases.**

- A naïve picture

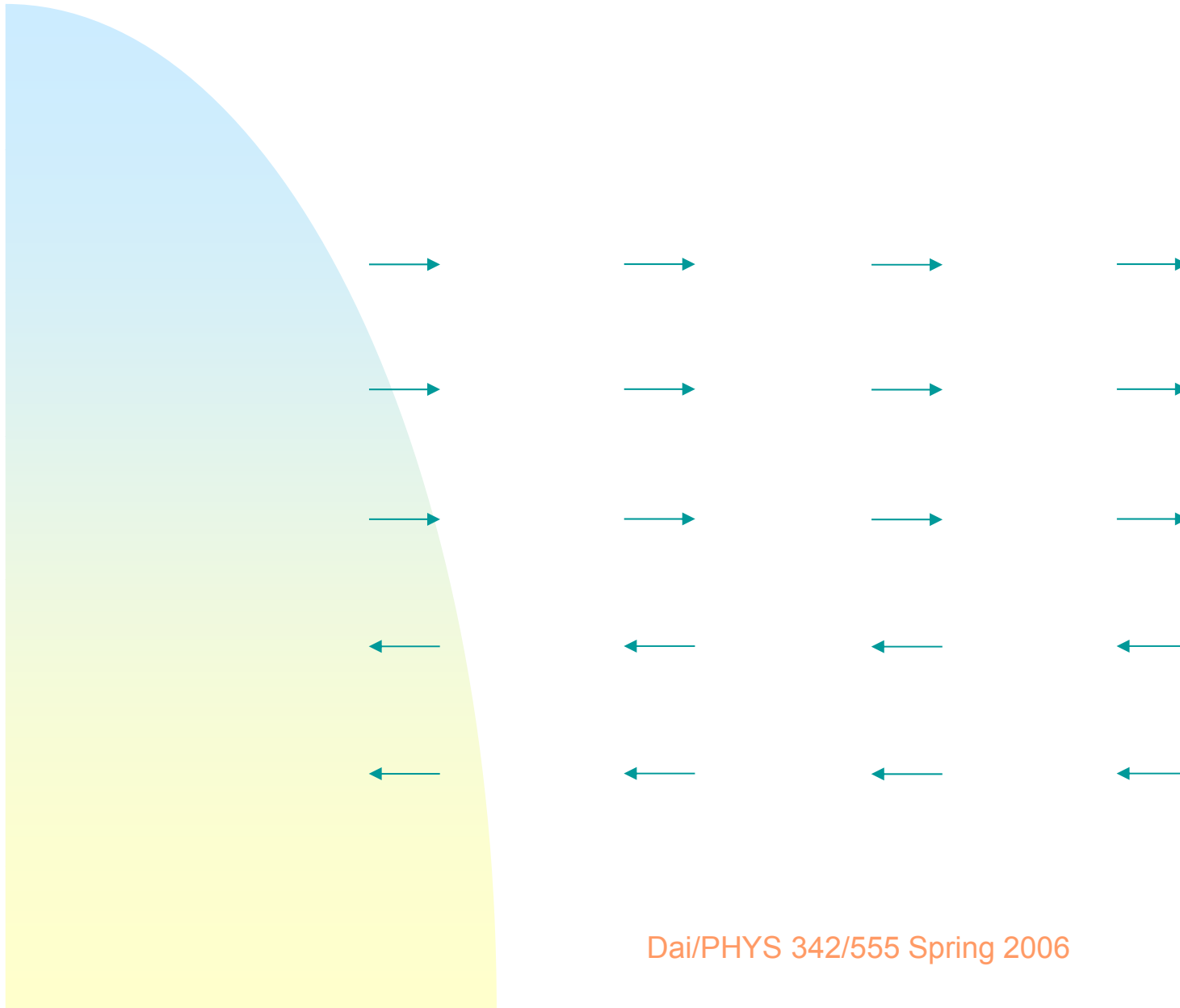




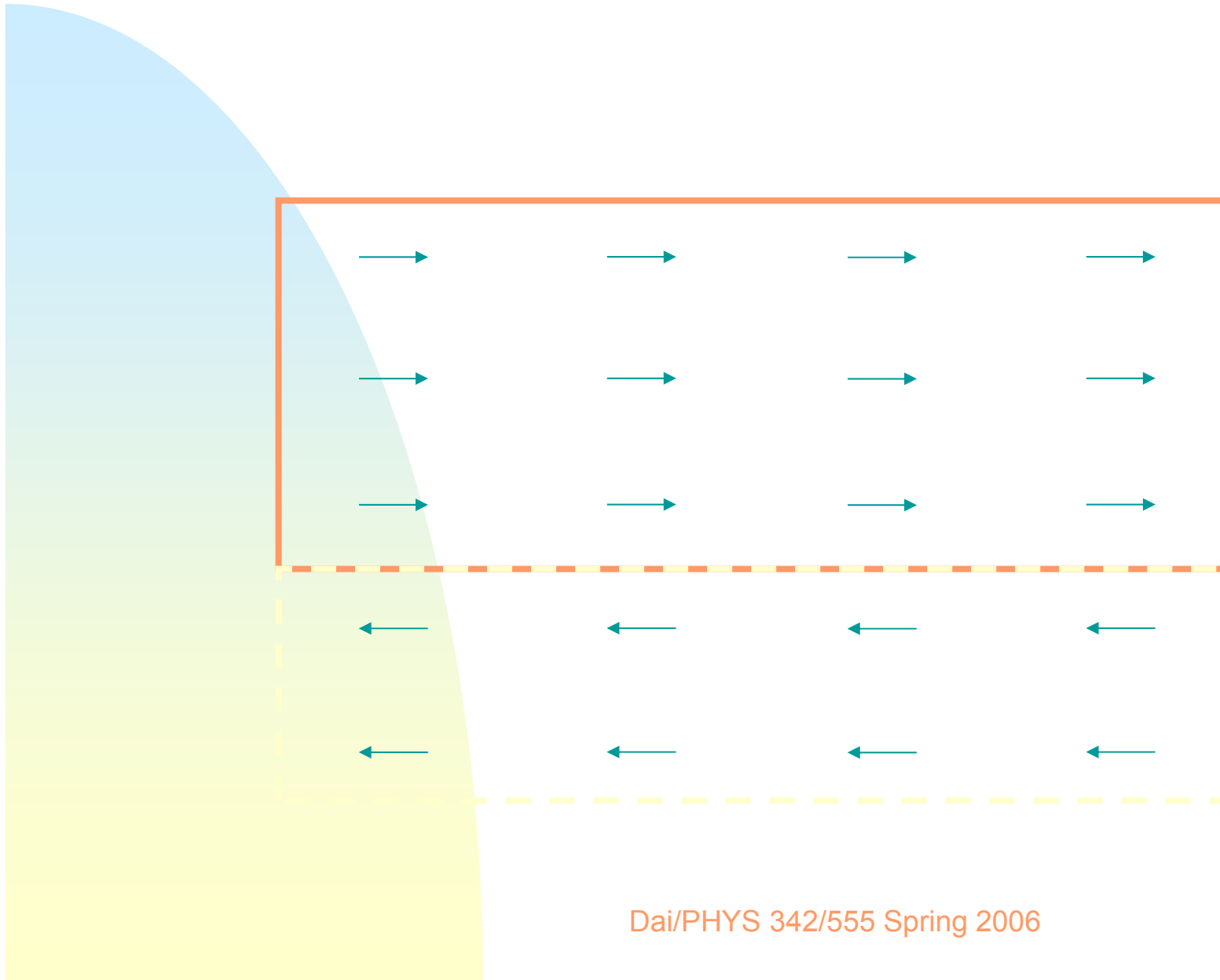
■ A naïve picture



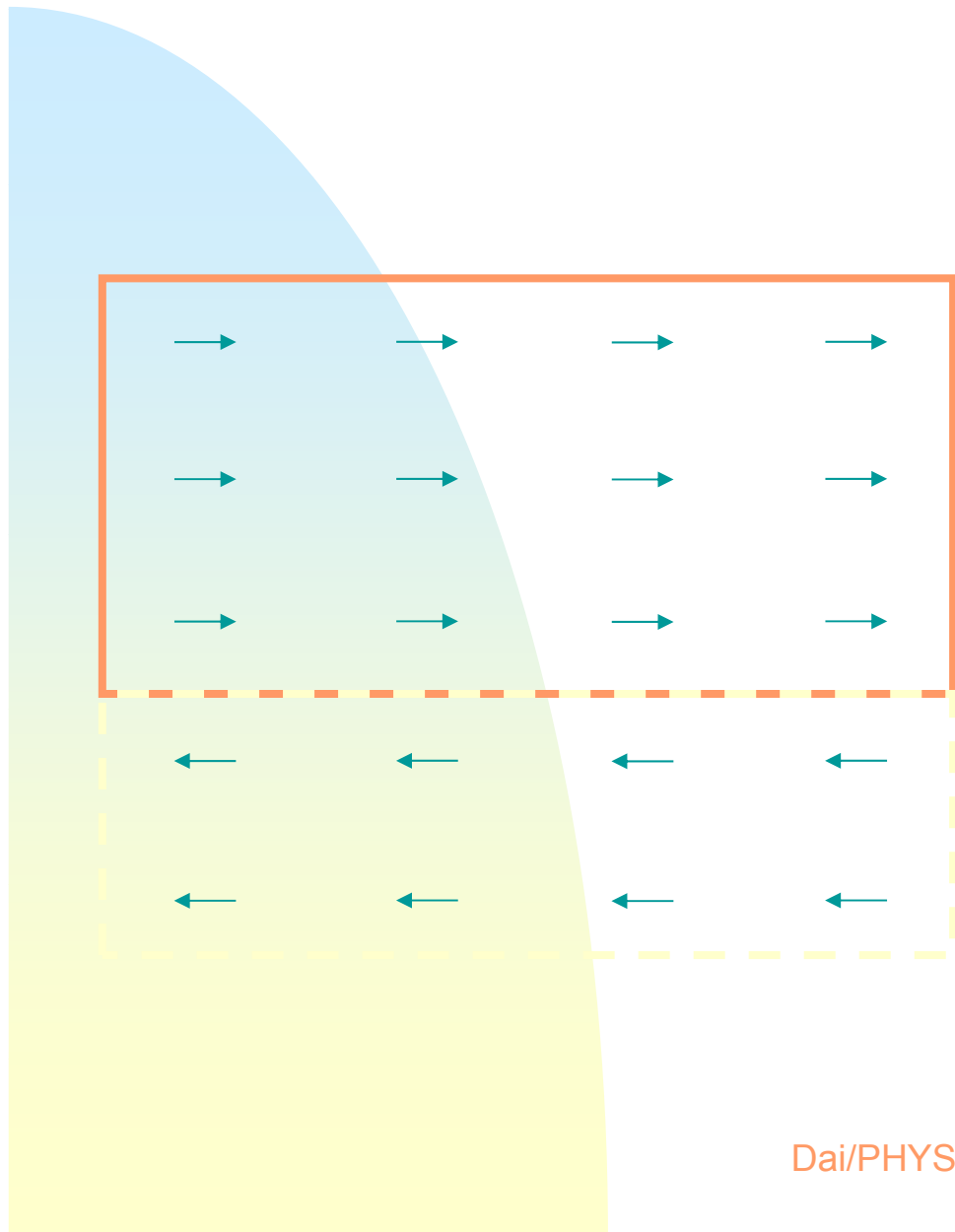
- A naïve picture



- A naïve picture



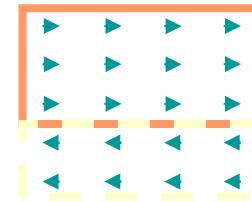
- A naïve picture



- The local alignment of dipoles can exist over any length scale.
- Different regions may exist with different polarisation orientations:
 - ◆ Call these “domains” in line with magnetic materials.
 - ◆ In contrast with magnetism, domain walls are abrupt.

- Applied field

- Suppose we now apply an electric field, horizontal in the figure.
- If it is of sufficient strength, the small ions will be able to overcome the barrier and dipoles will switch direction
 - ◆ The dipoles are polarised by the applied field.
 - ◆ Domain walls move.



- Polarisation vs. E-field

- Suppose we start with a material where there are **many domains** which are **aligned randomly**.

- ◆ What is the initial polarisation?

- Polarisation vs. E-field

- If we apply a small electric field, such that it is not able to switch domain alignments, then the material will behave as a normal dielectric:

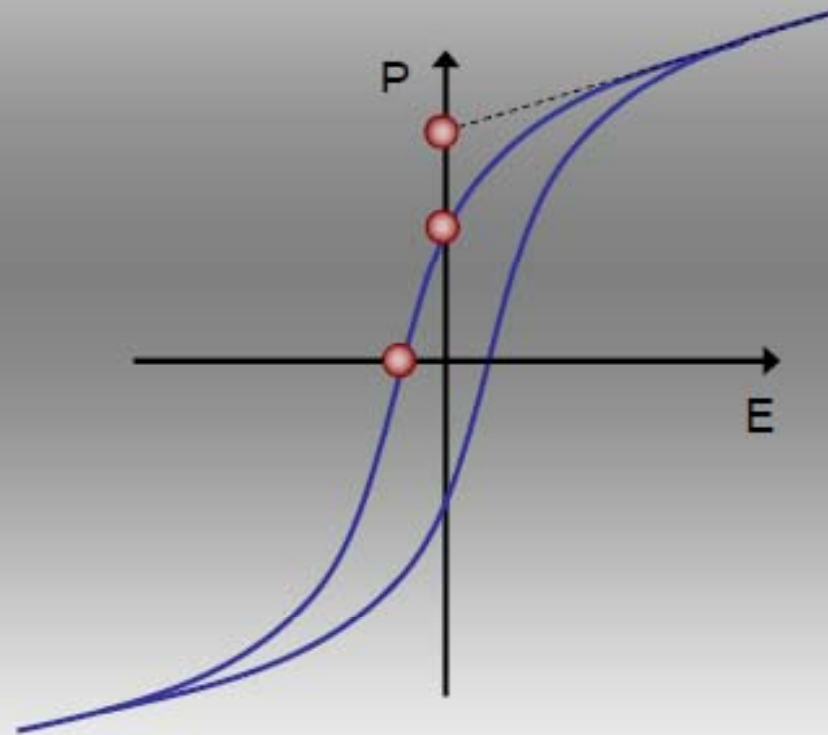
- ◆ $P \propto E$

- As E is increased, we start to flip domains and rapidly increase P .
- When all domains are switched, we reach saturation.
- What happens if the E-field is now removed?

- Polarisation vs. E-field

- The value at zero field is termed the ***remnant polarisation***.
- The value of P extrapolated back from the saturation limit is the ***spontaneous polarisation***.
- Reversal of the field will eventually remove all polarisation
 - ◆ The field required is the ***coercive field***.
- Further increasing the reverse field will completely reverse the polarisation, and so a hysteresis loop is formed...

Polarisation hysteresis

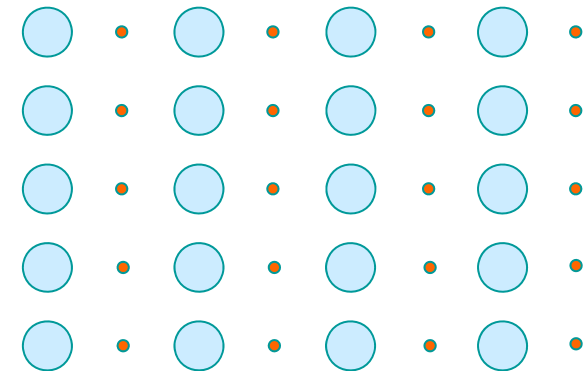
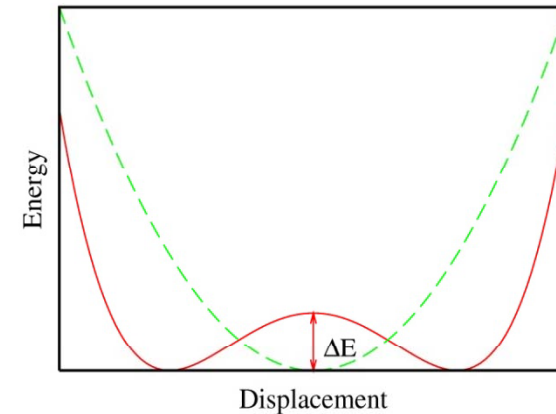


- Polarisation hysteresis
- The essential feature of a ferroelectric is ***not*** that there is a spontaneous polarisation, but that ***the spontaneous polarisation can be reversed by the application of an electric field.***
- Now, ΔE is small enough for the applied field to reverse the direction of the dipoles, i.e. move the atoms within the crystal, what else might affect this change?
- What are the relative sized of ΔE and $k_B T$?
- What will happen if $\Delta E \leq k_B T$?

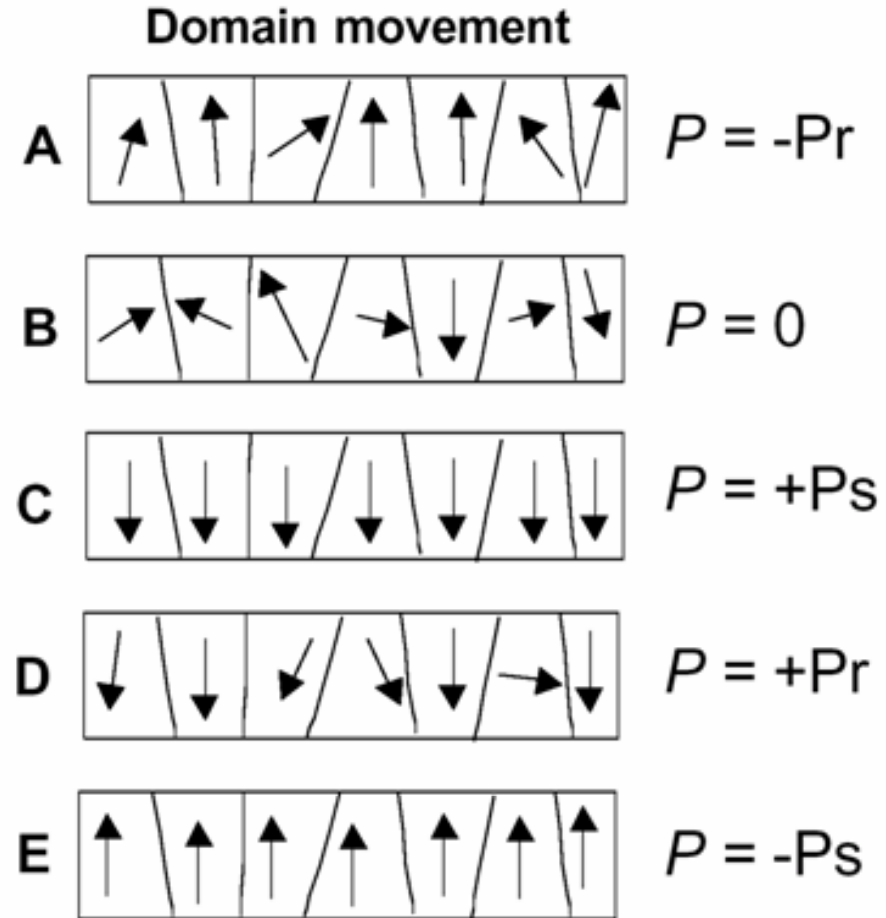
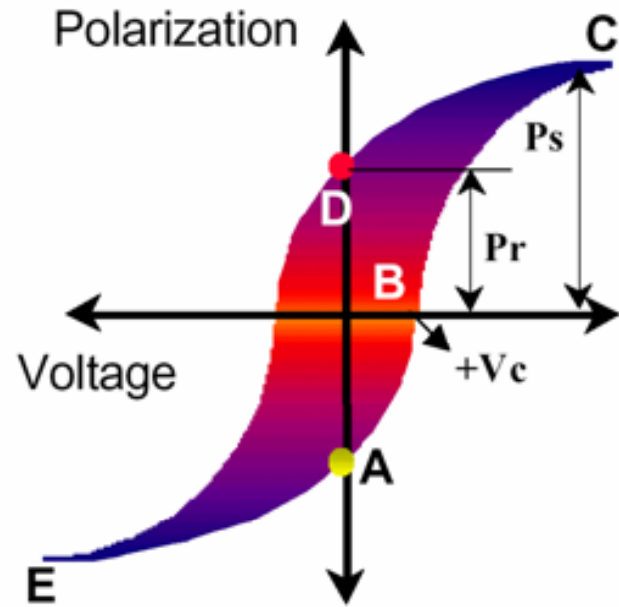
- Curie temperature

- Above a *critical temperature* the spontaneous polarisation will be lost due to one of two effects:

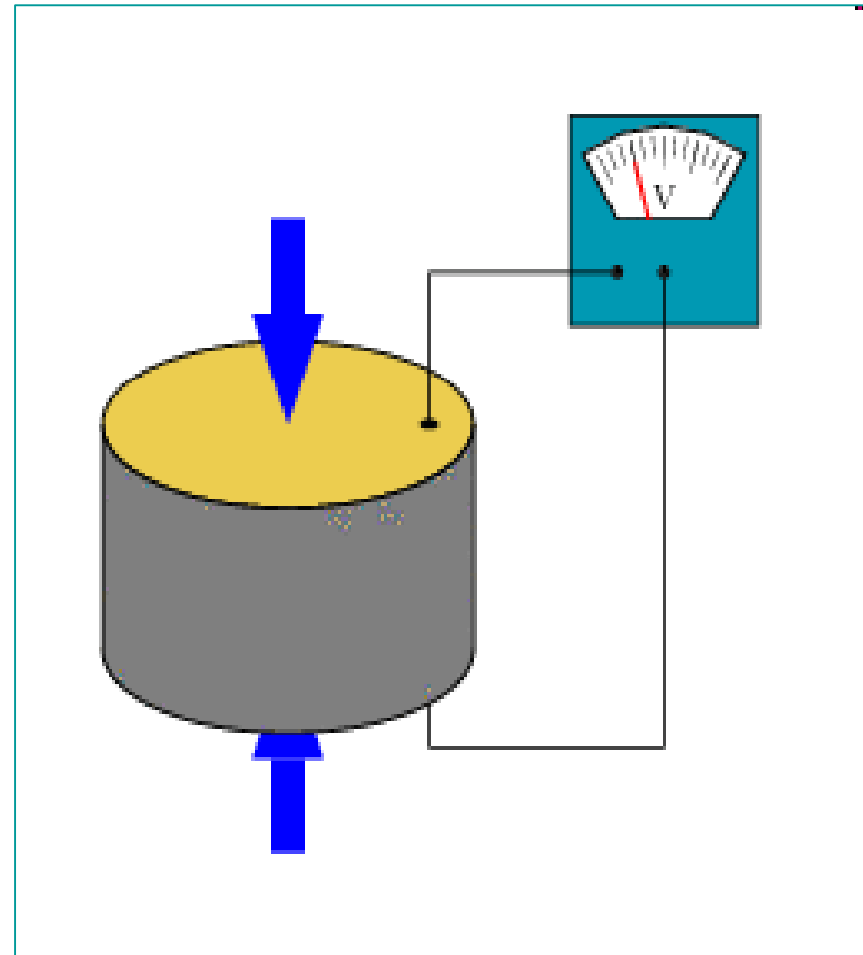
- ◆ A change of structure such that there is a single minimum in the energy mid-way between sites
- ◆ The rate that the small ions hop is so high that on average there is no net polarisation



Domain Wall Movement



- Piezoelectric effect
- The application of an electric field induces a geometrical change.
- Alternatively, a distortion of the material induces a potential difference.
- Used in many electrical devices, e.g. sound-to-electricity



8.10 PIEZOELECTRICITY

In this and the following sections we turn to certain phenomena associated with ionic polarization. The term *piezoelectricity* refers to the fact that, when a crystal is strained, an electric field is produced within the substance. As a result of this field, a potential difference develops across the sample, and by measuring this potential one may determine the field. The inverse effect—that an applied field produces strain—has also been observed. (It was discovered in about 1880.)

The piezoelectric effect is very small. A field of 1000 V/cm in quartz produces a strain of only 10^{-7} . That is, a rod 1 cm long changes its length by 10 Å. Conversely, even small strains can produce enormous electric fields.

The piezoelectric effect is often used to convert electrical energy into mechanical energy, and vice versa; i.e., the substance is used as a *transducer*. For instance, an electric signal applied to the end of a quartz rod generates a mechanical strain, which consequently leads to the propagation of a mechanical

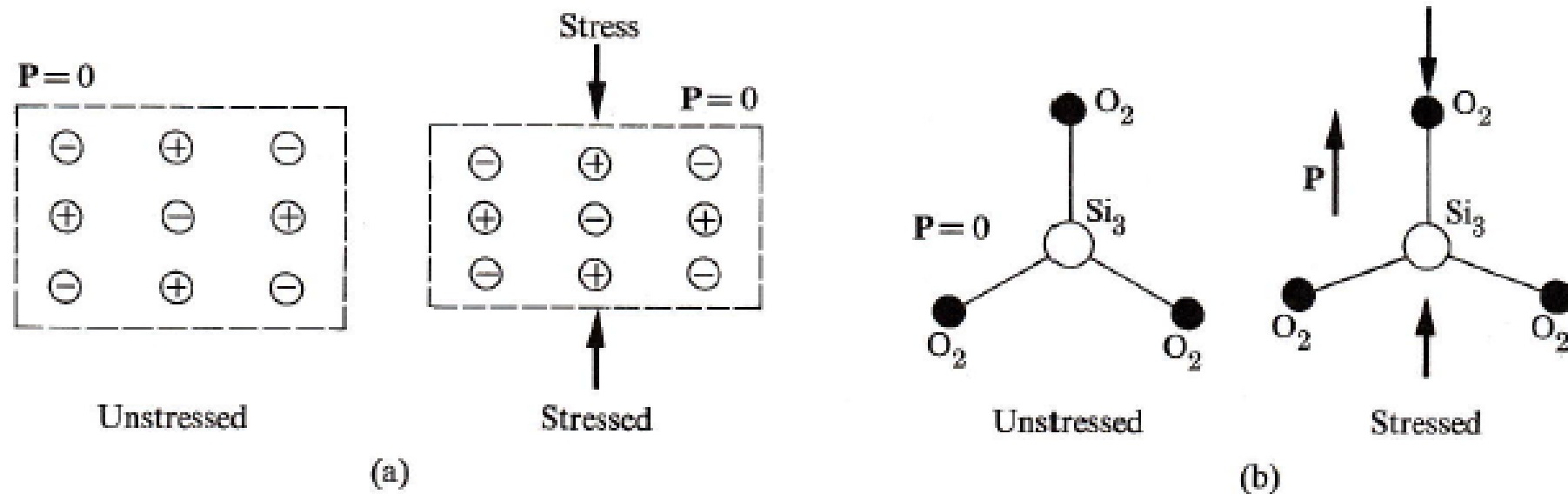


Fig. 8.24 Crystal with center of inversion exhibits no piezoelectric effect. (b) Origin of piezoelectric effect in quartz: crystal lacks a center of inversion.

It follows that a substance can be piezoelectric only if the unit cell *lacks a center of inversion*. Figure 8.24(a) shows this, and demonstrates that if a center of inversion *is* present, it persists even after distortion, and consequently the polarization remains zero. However, when there is no center of inversion, as in Fig. 8.24(b), distortion produces a polarization. We can now understand, for example, why no regular cubic lattice can exhibit piezoelectricity.

■ Crystallography and ferroelectrics

- The crystal classification of a material has immediate implications for ferroelectric effects
 - ◆ There are 32 crystal classes
 - ◆ 11 of them have a centre of symmetry (centrosymmetric) and cannot support ferroelectricity
 - ◆ Of the remaining 21, the O-point group (432) also excludes ferroelectricity.
 - ◆ The remaining 20 classes all exhibit the **piezoelectric effect**
 - ◆ Of these, 10 have a unique polar direction.

- $T T_h O T_d O_h$
- $C_4 S_4 C_{4h} D_4 C_{4v} D_{2d} D_{4h}$
- $D_2 C_{2v} D_{2h}$
- $C_2 C_s C_{2h}$
- $C_1 C_i$
- $C_3 S_6 D_3 C_{3v} D_{3d}$
- $C_6 C_{3h} C_{6h} D_6 C_{6v} D_{3h} D_{6h}$

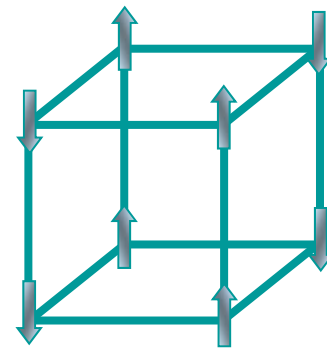
■ Classification of ferroelectrics

- i. “Crystal-chemical”: hydrogen-bonded (e.g. KH_2PO_4) or otherwise (e.g. double oxides).
- ii. No. of polarisation directions: single direction (e.g. PbTa_2O_6), several equivalent directions (e.g. BaTiO_3).
- iii. Centrosymmetric non-polar phase: E.g. Rochelle salts exhibit piezoelectric phase above T_c , whereas BaTiO_3 is centrosymmetric.
- iv. First vs. second order phase change at T_c . It turns out this corresponds to the value of the Curie constant (C), one group being of the order of 10^3K , and the other 10^5K .

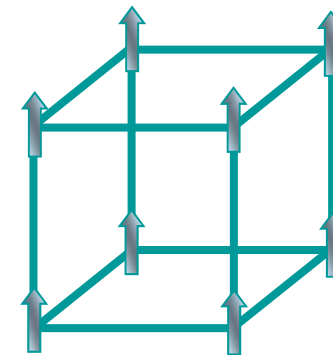
These four classifications do not necessarily coincide.

- Antiferroelectrics

- If the free energy of an antipolar phase is comparable to the polar state then the material is termed **antiferroelectric**.
- If a material exhibits ferroelectric effects in one polar direction, and antiferroelectric effects perpendicular, it may be termed **ferrielectric**.



Antipolar

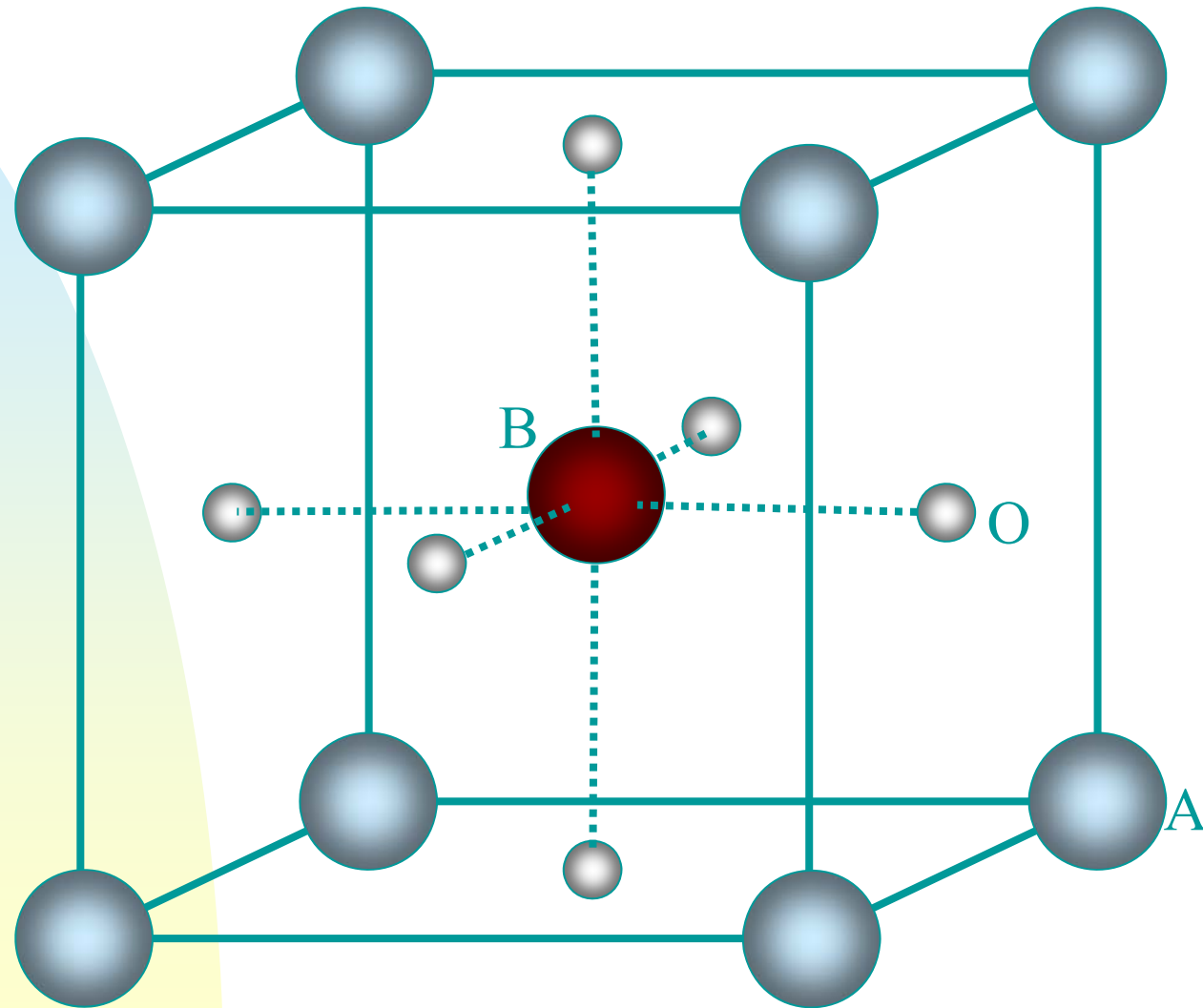


Polar

■ Perovskites

- Perovskite is a naturally occurring mineral with chemical formula CaTiO_3 .
- This is a prototype for many ABO_3 materials which are very important in ferroelectrics.
- These materials may be envisaged by consideration of a non-polar, cubic basic building block...

■ Perovskites

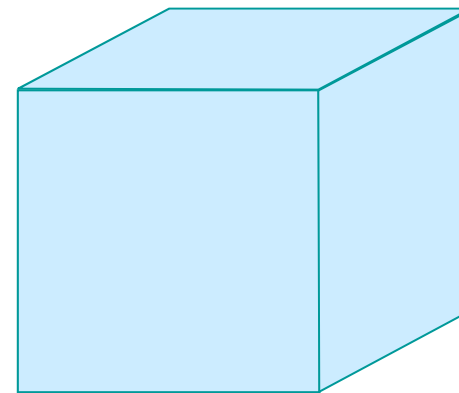
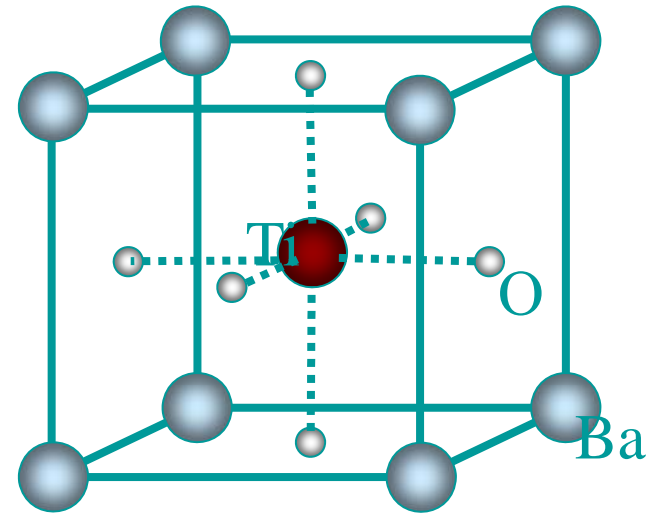


■ Perovskites

- Below the Curie temperature, these crystals undergo symmetry lowering distortions. We'll initially focus up the distortions of BaTiO_3 .
- There are three phase transitions in order of decreasing temperature: 120°C , 5°C , and -90°C .

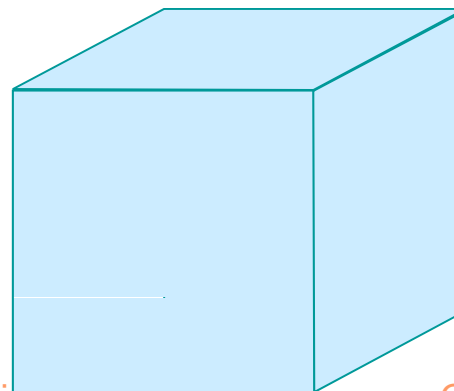
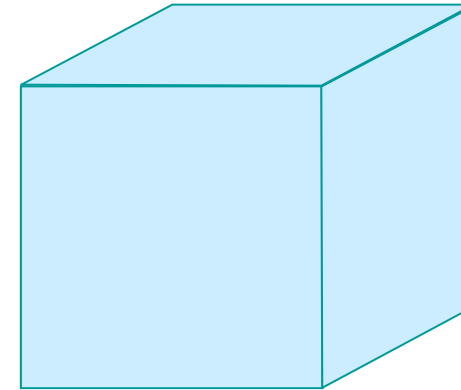
- BaTiO_3

- Above 120°C BaTiO_3 is cubic (non-polar)



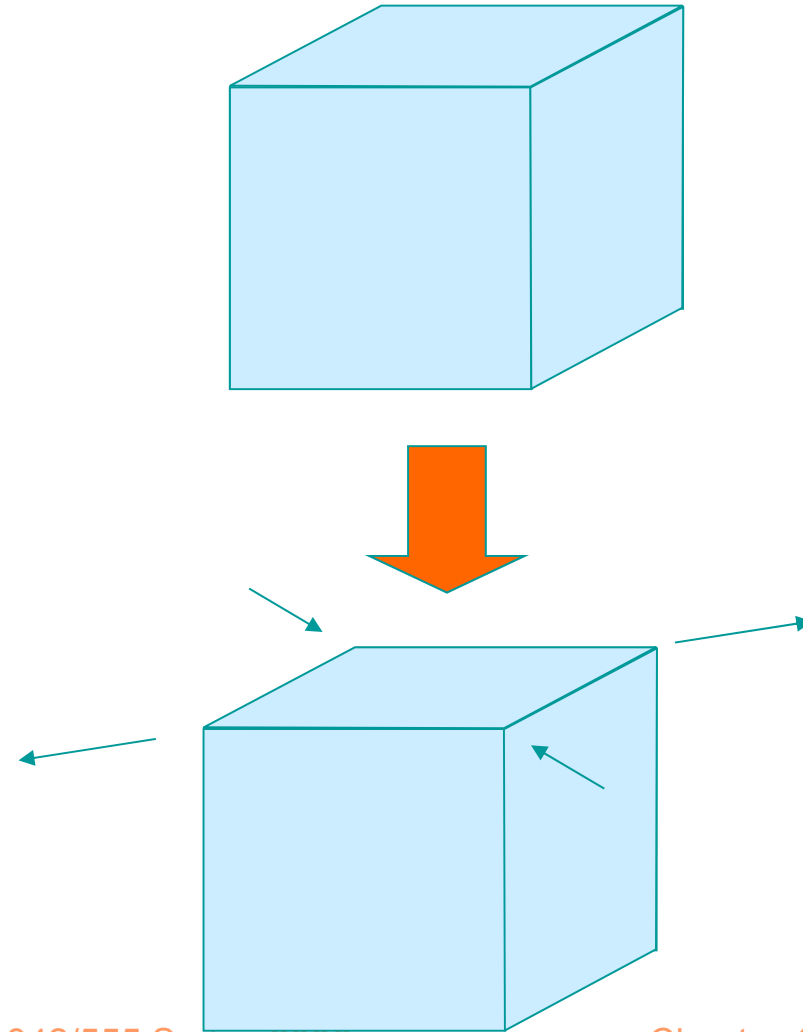
- BaTiO_3

- From 120°C down to $\sim 5^\circ\text{C}$, there is a distortion to a tetragonal phase.
- All of the cube directions can undergo this type of distortion: this leads to complexity in domain formation.



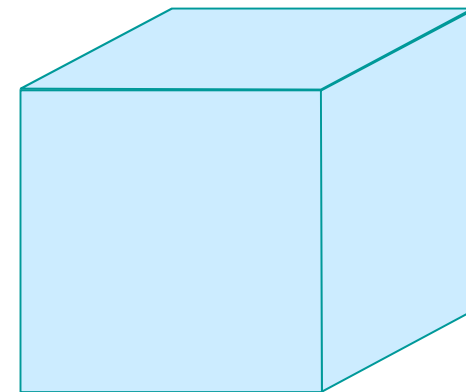
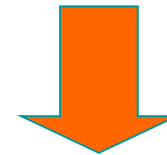
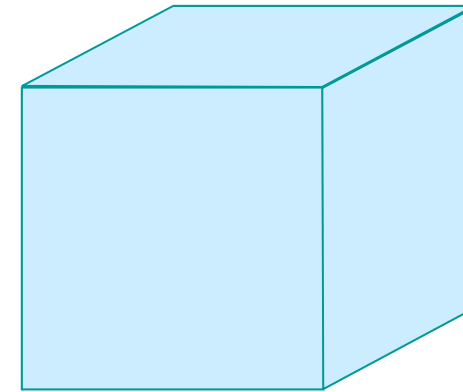
- BaTiO_3

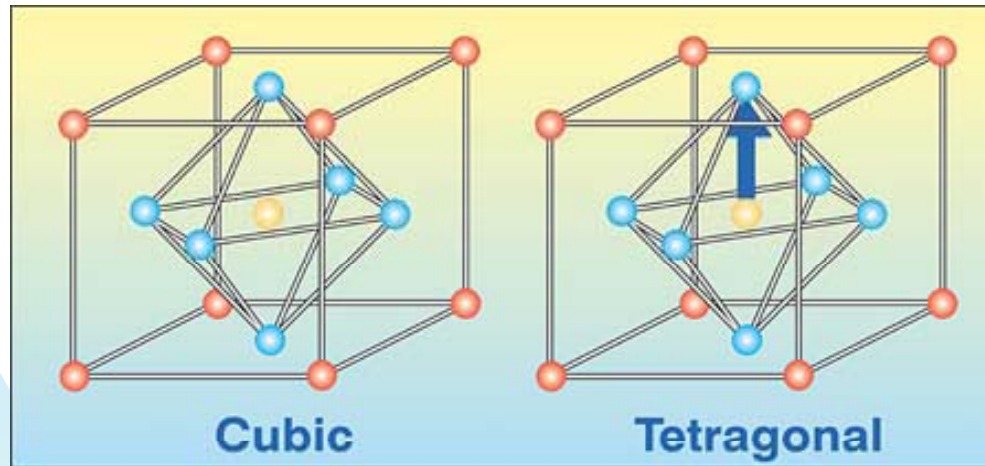
- From 5°C down to around -90°C the structure is orthorhombic by dilation along $[110]$ directions and contraction along $[1-10]$.



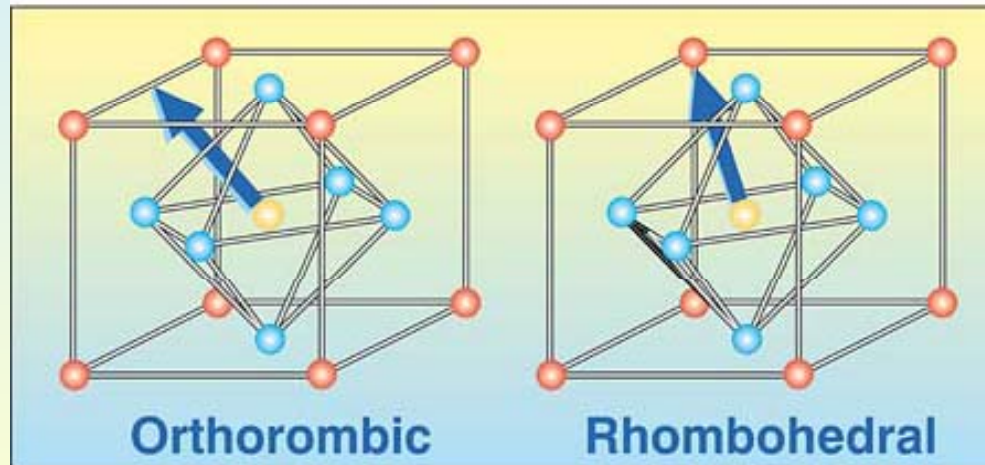
- BaTiO_3

- Finally the lowest temperatures yield rhombohedra (distortions along the body diagonal).
- There are therefore 8 equivalent distortion directions





[001]
directions



[110]
directions

[111]
directions

The phase transition sequence in perovskites

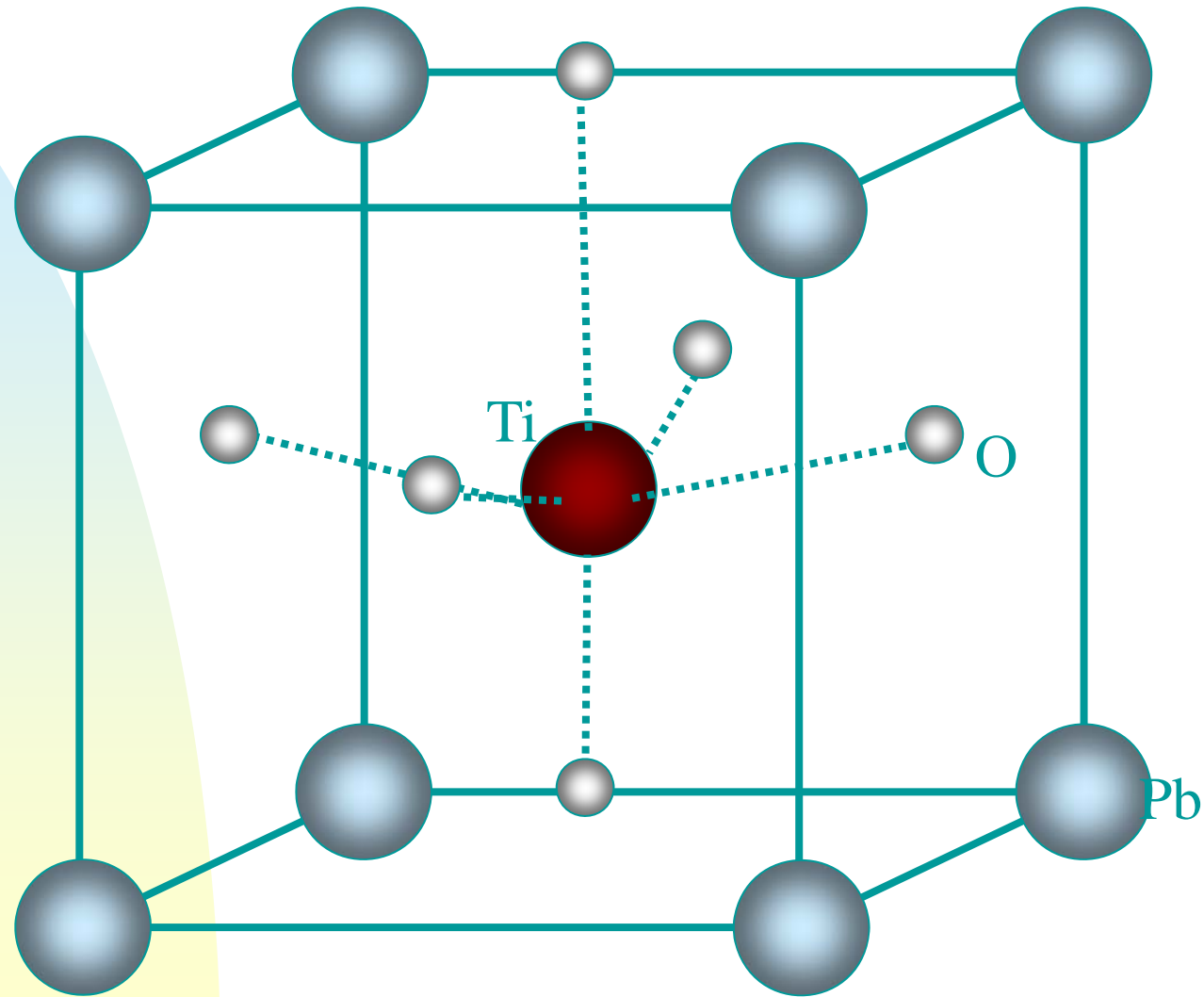
- PbTiO_3 internal structure

- The foregoing analysis of BaTiO_3 focuses on the shape of the unit cell. However, for the ferroelectric effect, we also require internal structural changes.
- In light of current interest in Cu-related defects in lead titanium tri-oxide, we'll review this tetragonal system at room temperature...

■ PbTiO_3 internal structure

- X-ray and neutron scattering yield the internal structure:
- $a=3.904\text{\AA}$, $c=4.150\text{\AA}$, so that $c/a=1.063$.
- Taking the Pb site as the origin, the displacements are
 - ◆ $\delta z_{\text{Ti}}=+0.040$
 - ◆ $\delta z_{\text{OI}}=+0.112$
 - ◆ $\delta z_{\text{OII}}=+0.112$
- Here OI are the polar O-sites, and OII are the equatorial.
- Thus, since the oxygen atoms are all displaced by the same amount, the oxygen cage remains intact, and shifts relative to the Ti and Pb sites.

■ PbTiO_3



- PbTiO_3

- It should be clear that this system has a net dipole in each unit cell, and furthermore that the distortion can be along any of the x, y and z directions.
- In real PbTiO_3 , there is a non-trivial role for point defects, especially O-vacancies.

Classification of ferroelectric crystals

Ferroelectric crystals can be classified into two main groups: order-disorder and displacive transition.

