whence the required capacitance is

$$C = C_0 + a^3\varepsilon_1(\varepsilon_2 - \varepsilon_1)/(2\varepsilon_1 + \varepsilon_2)h^2.$$

§13. Dielectric properties of crystals

In an anisotropic dielectric medium (a single crystal) the linear relation between the electric induction and the electric field is less simple, and does not reduce to a simple proportionality.

The most general form of such a relation is

$$D_i = D_{0i} + \varepsilon_{ik}E_k, \tag{13.1}$$

where $\mathbf{D}_0$ is a constant vector, and the quantities ε_{ik} form a tensor of rank two, called the *permittivity tensor* (or the *dielectric tensor*). The inhomogeneous term $\mathbf{D}_0$ in (13.1) does not, however, appear for all crystals. The majority of the types of crystal symmetry do not admit this constant vector (see below), and we then have simply

$$D_i = \varepsilon_{ik}E_k. \tag{13.2}$$

The tensor ε_{ik} is symmetrical:

$$\varepsilon_{ik} = \varepsilon_{ki}. \tag{13.3}$$

In order to prove this, it is sufficient to use the thermodynamic relation (10.10) and to observe that the second derivative $-4\pi\partial^2\tilde{F}/\partial E_k\partial E_i = \partial D_i/\partial E_k = \varepsilon_{ik}$ is independent of the order of differentiation.

For $\tilde{F}$ itself we have (when (13.2) holds) the expression

$$\tilde{F} = F_0 - \varepsilon_{ik}E_iE_k/8\pi. \tag{13.4}$$

The free energy F is

$$F = \tilde{F} + E_iD_i/4\pi = F_0 + \varepsilon^{-1}{}_{ik}D_iD_k/8\pi. \tag{13.5}$$

Like every symmetrical tensor of rank two, the tensor ε_{ik} can be brought to diagonal form by a suitable choice of the coordinate axes. In general, therefore, the tensor ε_{ik} is determined by three independent quantities, namely the three principal values $\varepsilon^{(1)}, \varepsilon^{(2)}, \varepsilon^{(3)}$. All these are necessarily greater than unity, just as $\varepsilon > 1$ for an isotropic body (see §14).

The number of different principal values of the tensor ε_{ik} may be less than three for certain symmetries of the crystal.

In crystals of the triclinic, monoclinic and orthorhombic systems, all three principal values are different; such crystals are said to be *biaxial*.† In crystals of the triclinic system, the directions of the principal axes of the tensor ε_{ik} are not uniquely related to any directions in the crystal. In those of the monoclinic system, one of the principal axes must coincide with the twofold axis of symmetry or be perpendicular to the plane of symmetry of the crystal. In crystals of the orthorhombic system, all three principal axes of the tensor ε_{ik} are crystallographically fixed.

Next, in crystals of the tetragonal, rhombohedral and hexagonal systems, two of the

† This name refers to the optical properties of the crystals; see §§98, 99.

three principal values are equal, so that there are only two independent quantities; such crystals are said to be *uniaxial*. One of the principal axes coincides with the fourfold, threefold or sixfold axis of crystal symmetry, but the directions of the other two principal axes can be chosen arbitrarily.

Finally, in crystals of the cubic system all three principal values of the tensor ε_{ik} are the same, and the directions of the principal axes are entirely arbitrary. This means that the tensor ε_{ik} is of the form $\varepsilon\delta_{ik}$, i.e. it is determined by a single scalar ε. In other words, as regards their dielectric properties, crystals of the cubic system are no different from isotropic bodies.

All these fairly obvious symmetry properties of the tensor ε_{ik} become particularly clear if we use a concept from tensor algebra, the *tensor ellipsoid*, the lengths of whose semiaxes are proportional to the principal values of a symmetrical tensor of rank two. The symmetry of the ellipsoid corresponds to that of the crystal. For instance, in a uniaxial crystal the tensor ellipsoid degenerates into a spheroid completely symmetrical about the longitudinal axis; it should be emphasized that, as regards the physical properties of the crystal which are determined by a symmetrical tensor of rank two, the presence of a threefold or higher axis of symmetry is equivalent to complete isotropy in the plane perpendicular to this axis. In cubic crystals, the tensor ellipsoid degenerates into a sphere.

Let us now examine the dielectric properties of crystals for which the constant term $\mathbf{D}_0$ appears in (13.1). The presence of this term signifies that the dielectric is spontaneously polarized even in the absence of an external electric field. Such bodies are said to be *pyroelectric*. The magnitude of this spontaneous polarization is, however, in practice always very small (in comparison with the molecular fields). This is because large values of $\mathbf{D}_0$ would lead to strong fields within the body, which is energetically very unfavourable and therefore could not correspond to thermodynamic equilibrium. The smallness of $\mathbf{D}_0$ also ensures the legitimacy of an expansion of $\mathbf{D}$ in powers of $\mathbf{E}$, of which (13.1) represents the first two terms.

The thermodynamic quantities for a pyroelectric body are found by integrating the relation $-4\pi\partial\tilde{F}/\partial E_i = D_i = D_{0i} + \varepsilon_{ik}E_k$, whence

$$\tilde{F} = F_0 - \varepsilon_{ik}E_iE_k/8\pi - E_iD_{0i}/4\pi. \tag{13.6}$$

The free energy is

$$\begin{aligned} F = \tilde{F} + E_iD_i/4\pi &= F_0 + \varepsilon_{ik}E_iE_k/8\pi \\ &= F_0 + \varepsilon^{-1}{}_{ik}(D_i - D_{0i})(D_k - D_{0k})/8\pi. \end{aligned} \tag{13.7}$$

It should be noted that the term in $\tilde{F}$ linear in E_i does not appear in F.†

The total free energy of a pyroelectric can be calculated from formula (11.12) by substituting (13.7) and (13.1). If there is no external field, $\mathfrak{E} = 0$, and we have simply

$$\mathscr{F} = \int [F_0 - (\mathbf{E}\cdot\mathbf{D}_0/8\pi)]\,\mathrm{d}V. \tag{13.8}$$

It is remarkable that the free energy of a pyroelectric in the absence of an external field depends, like the field $\mathbf{E}$, not only on the volume of the body but also on its shape.

† It should also be noted that in these formulae we neglect the *piezoelectric effect*, i.e. the effect of internal stresses on the electric properties of a body; see §17. The formulae given here are therefore, strictly speaking, applicable only when the fields are uniform throughout the body, and internal stresses do not arise.

As has already been pointed out, the phenomenon of pyroelectricity is not possible for every crystal symmetry. Since, in any symmetry transformation, all the properties of the crystal must remain unchanged, it is clear that the only crystals which can be pyroelectric are those in which there is a direction which is unchanged (and, in particular, not reversed) in all symmetry transformations, and that this will be the direction of the constant vector $\mathbf{D}_0$.

This condition is satisfied only by those symmetry groups which consist of a single axis together with planes of symmetry which pass through the axis. In particular, crystals having a centre of symmetry certainly cannot be pyroelectric. We may enumerate those out of the 32 crystal classes in which pyroelectricity occurs:

triclinic system: C_1
monoclinic system: C_s, C_2
orthorhombic system: C_{2v}
tetragonal system: C_4, C_{4v}
rhombohedral system: C_3, C_{3v}
hexagonal system: C_6, C_{6v}.

There are, of course, no pyroelectric cubic crystals. In a crystal of class C_1 the direction of the pyroelectric vector $\mathbf{D}_0$ is not related to any direction fixed in the crystal; in one of class C_s, it must lie in the plane of symmetry. In all the remaining classes listed above the direction of $\mathbf{D}_0$ is that of the axis of symmetry.†

It should be mentioned that, under ordinary conditions, pyroelectric crystals have zero total electric dipole moment, although their polarization is not zero. The reason is that there is a non-zero field $\mathbf{E}$ inside a spontaneously polarized dielectric. Since a body usually has a small but non-zero conductivity, the presence of a field gives rise to a current, which flows until the free charges formed on the surface of the body annihilate the field inside it. The same effect is produced by ions deposited on the surface from the air. Experimentally, pyroelectric properties are observed when a body is heated and a change in its spontaneous polarization is detected.

PROBLEMS

PROBLEM 1. Determine the field of a pyroelectric sphere in a vacuum.

SOLUTION. The field inside the sphere is uniform, and the field and induction are related by $2\mathbf{E} = -\mathbf{D}$ (as follows from (8.1) when $\mathfrak{E} = 0$, i.e. when there is no applied external field). Substituting in (13.1), we obtain the equation $2E_i + \varepsilon_{ik}E_k = -D_{0i}$. We take the coordinate axes to be the principal axes of the tensor ε_{ik}. Then this equation gives $E_i = -D_{0i}/(2+\varepsilon^{(i)})$. The polarization of the sphere is $P_i = (D_i - E_i)/4\pi = 3D_{0i}/4\pi(2+\varepsilon^{(i)})$. The field outside the sphere is that of an electric dipole with moment $\mathscr{P} = \mathbf{P}V$.

PROBLEM 2. Determine the field of a point charge in a homogeneous anisotropic medium.‡

SOLUTION. The field of a point charge is given by the equation div $\mathbf{D} = 4\pi e\delta(\mathbf{r})$ (the charge being at the origin). In an anisotropic medium $D_i = \varepsilon_{ik}E_k = -\varepsilon_{ik}\partial\phi/\partial x_k$; taking the coordinate axes x, y, z along the principal axes of the tensor ε_{ik}, we obtain for the potential the equation

$$\varepsilon^{(x)}\partial^2\phi/\partial x^2 + \varepsilon^{(y)}\partial^2\phi/\partial y^2 + \varepsilon^{(z)}\partial^2\phi/\partial z^2 = -4\pi e\,\delta(\mathbf{r}).$$

† In referring to symmetry conditions, we are regarding the crystal as an infinite medium. For a finite crystal, the exact value of the total dipole moment may depend (in an ionic crystal) on which crystal planes form its faces and whether these planes contain ions of only one sign or are electrically neutral. However, in macroscopic electrodynamics, which implies averaging over physically infinitesimal volumes, it is reasonable to consider that the position of the faces relative to the crystal lattice is averaged also. In consequence of this averaging, $\mathbf{D}_0$ vanishes in any non-pyroelectric finite crystal, and in a pyroelectric one is independent of the face configuration.

‡ In Problems 2–6 the anisotropic dielectric is assumed to be non-pyroelectric.

By the introduction of new variables

$$x' = x/\sqrt{\varepsilon^{(x)}}, \quad y' = y/\sqrt{\varepsilon^{(y)}}, \quad z' = z/\sqrt{\varepsilon^{(z)}}, \tag{1}$$

this becomes

$$\Delta'\phi = -\frac{4\pi e}{\sqrt{(\varepsilon^{(x)}\varepsilon^{(y)}\varepsilon^{(z)})}}\,\delta(\mathbf{r}')$$

which formally differs from the equation for the field in a vacuum only in that e is replaced by $e' = e/\sqrt{(\varepsilon^{(x)}\varepsilon^{(y)}\varepsilon^{(z)})}$. Hence

$$\phi = \frac{e'}{r'} = \frac{e}{\sqrt{(\varepsilon^{(x)}\varepsilon^{(y)}\varepsilon^{(z)})}}\left[\frac{x^2}{\varepsilon^{(x)}} + \frac{y^2}{\varepsilon^{(y)}} + \frac{z^2}{\varepsilon^{(z)}}\right]^{-\frac{1}{2}}$$

In tensor notation, independent of the system of coordinates chosen, we have

$$\phi = e/\sqrt{(|\varepsilon|\varepsilon^{-1}{}_{ik}x_i x_k)},$$

where $|\varepsilon|$ is the determinant of the tensor ε_{ik}.

PROBLEM 3. Determine the capacitance of a conducting sphere, with radius a, in an anisotropic dielectric medium.

SOLUTION. By the transformation shown in Problem 2, the determination of the field of a sphere with charge e in an anisotropic medium reduces to the determination of the field in a vacuum due to a charge e' distributed over the surface of the ellipsoid $\varepsilon_{ik}x'_i x'_k = \varepsilon^{(x)}x'^2 + \varepsilon^{(y)}y'^2 + \varepsilon^{(z)}z'^2 = a^2$. Using formula (4.14) for the potential due to an ellipsoid, we find the required capacitance to be given by

$$\frac{1}{C} = \frac{1}{2\sqrt{(\varepsilon^{(x)}\varepsilon^{(y)}\varepsilon^{(z)})}}\int_0^\infty \left[\left(\xi + \frac{a^2}{\varepsilon^{(x)}}\right)\left(\xi + \frac{a^2}{\varepsilon^{(y)}}\right)\left(\xi + \frac{a^2}{\varepsilon^{(z)}}\right)\right]^{-\frac{1}{2}} d\xi.$$

PROBLEM 4. Determine the field in a flat anisotropic plate in a uniform external field $\mathfrak{E}$.

SOLUTION. From the condition of continuity of the tangential component of the field it follows that $\mathbf{E} = \mathfrak{E} + A\mathbf{n}$, where $\mathbf{E}$ is the uniform field inside the plate, $\mathbf{n}$ a unit vector normal to its surface, and A a constant. The constant is determined from the condition of continuity of the normal component of the induction, $\mathbf{n}\cdot\mathbf{D} = \mathbf{n}\cdot\mathfrak{E}$, or $n_i\varepsilon_{ik}E_k = n_i\varepsilon_{ik}\mathfrak{E}_k + A\varepsilon_{ik}n_i n_k = \mathfrak{E}_i n_i$. Hence $A = -(\varepsilon_{ik} - \delta_{ik})n_i\mathfrak{E}_k/\varepsilon_{lm}n_l n_m$.

In particular, if the external field is along the normal to the plate (the z-direction), we have

$$A = \mathfrak{E}(1 - \varepsilon_{zz})/\varepsilon_{zz}.$$

If it is parallel to the plate and in the x-direction, then

$$A = -\mathfrak{E}\varepsilon_{zx}/\varepsilon_{zz}.$$

PROBLEM 5. Determine the torque on an anisotropic dielectric sphere, with radius a, in a uniform external field $\mathfrak{E}$ in a vacuum.

SOLUTION According to (8.2) we have for the field inside the sphere $E_x = 3\mathfrak{E}_x/(\varepsilon^{(x)}+2)$, and similarly for E_y, E_z. Here the axes of x, y, z are taken to be the principal axes of the tensor ε_{ik}. Hence the components of the dipole moment of the sphere are

$$\mathscr{P}_x = \frac{4}{3}\pi a^3 P_x = \frac{\varepsilon^{(x)} - 1}{\varepsilon^{(x)} + 2}a^3\mathfrak{E}_x, \text{ etc.}$$

The components of the torque on the sphere are

$$K_z = (\mathscr{P}\times\mathfrak{E})_z = 3a^3\mathfrak{E}_x\mathfrak{E}_y(\varepsilon^{(x)} - \varepsilon^{(y)})/(\varepsilon^{(x)}+2)(\varepsilon^{(y)}+2),$$

and similarly for K_x, K_y.

PROBLEM 6. An infinite anisotropic medium contains a spherical cavity with radius a. Express the field in the cavity in terms of the uniform field $E^{(e)}$ far from the cavity.

SOLUTION. The transformation (1) of Problem 2 reduces the equation for the field potential in the medium to Laplace's equation for the field in a vacuum. The equation for the field potential in the cavity is transformed into that for the potential in a medium with permittivities $1/\varepsilon^{(x)}$, $1/\varepsilon^{(y)}$, $1/\varepsilon^{(z)}$. Moreover, the sphere is transformed into an ellipsoid with semiaxes $a/\sqrt{\varepsilon^{(x)}}$, $a/\sqrt{\varepsilon^{(y)}}$, $a/\sqrt{\varepsilon^{(z)}}$. Let $n^{(x)}$, $n^{(y)}$, $n^{(z)}$ be the depolarizing factors of such an ellipsoid (given by formulae (4.25)). Applying formula (8.7) to the field of this ellipsoid, we obtain the relation

$$(1-n^{(x)})\frac{\partial\phi^{(i)}}{\partial x'}+\frac{n^{(x)}}{\varepsilon^{(x)}}\frac{\partial\phi^{(i)}}{\partial x'}=\frac{\partial\phi^{(e)}}{\partial x'},$$

and similarly for the y' and z' directions. Returning to the original coordinates, we have $\partial\phi/\partial x' = \sqrt{\varepsilon^{(x)}}\partial\phi/\partial x = -\sqrt{\varepsilon^{(x)}}E_x$, so that the field in the cavity is

$$E^{(i)}{}_x = \frac{\varepsilon^{(x)}}{\varepsilon^{(x)}-n^{(x)}(\varepsilon^{(x)}-1)}E^{(e)}{}_x.$$

§14. The sign of the dielectric susceptibility

To elucidate the way in which the thermodynamic quantities for a dielectric in a field depend on its permittivity, let us consider the formal problem of the change in the electric component of the total free energy of the body when ε undergoes an infinitesimal change.

For an isotropic (not necessarily homogeneous) body we have by (10.20) $\mathscr{F}-\mathscr{F}_0 = \int(D^2/8\pi\varepsilon)\mathrm{d}V$. When ε changes, so does the induction, and the variation in the free energy is therefore

$$\delta\mathscr{F} = \int\frac{\mathbf{D}\cdot\delta\mathbf{D}}{8\pi\varepsilon}\mathrm{d}V - \int\frac{D^2}{8\pi\varepsilon^2}\delta\varepsilon\,\mathrm{d}V.$$

The first term on the right is the same as (10.2), which gives the work done in an infinitesimal change in the field sources (i.e. charges on conductors). In the present case, however, we are considering a change in the field but no change in the sources. This term therefore vanishes, leaving

$$\delta\mathscr{F} = -\int(\delta\varepsilon/\varepsilon^2)(D^2/8\pi)\mathrm{d}V = -\int\delta\varepsilon(E^2/8\pi)\mathrm{d}V. \tag{14.1}$$

From this formula it follows that any increase in the permittivity of the medium, even if in only a part of it (the sources of the field remaining unchanged), reduces the total free energy. In particular, we can say that the free energy is always reduced when uncharged conductors are brought into a dielectric medium, since these conductors may (in electrostatics) be regarded as bodies whose permittivity is infinite. This conclusion generalizes the theorem (§2) that the energy of the electrostatic field in a vacuum is diminished when an uncharged conductor is placed in it.

The total free energy is diminished also when any charge is brought up to a dielectric body from infinity (a process which may be regarded as an increase of ε in a certain volume of the field round the charge). In order to conclude from this that any charge is attracted to a dielectric, we should, strictly speaking, prove also that $\mathscr{F}$ cannot attain a minimum for any finite distance between the charge and the body. We shall not pause here to prove this statement, especially as the presence of an attractive force between a charge and a dielectric may be regarded as a fairly evident consequence of the interaction between the charge and the dipole moment of the dielectric, which it polarizes.

We can deduce immediately from formula (14.1) the direction of motion of a dielectric body in an almost uniform electric field, i.e. one which may be regarded as uniform over the dimensions of the body. In this case E^2 is taken outside the integral, and the difference $\mathscr{F}-\mathscr{F}_0$ is a negative quantity, proportional to E^2. In order to take a position in which its free energy is a minimum, the body will therefore move in the direction of E increasing.

It can be shown independently of (14.1) that the total change in the free energy of a dielectric when it is placed in an electric field is negative.† This can be done by the use of thermodynamic perturbation theory, the change in the free energy of the body being regarded as the result of a perturbation of its quantum energy levels by the external electric field. According to this theory we have

$$\mathscr{F}-\mathscr{F}_0 = \overline{V}_{nn} - \frac{1}{2}\sum_n\sum_m{}'\frac{|V_{nm}|^2(w_m-w_n)}{E_n^{(0)}-E_m^{(0)}} - \frac{1}{2T}\overline{(V_{nn}-\overline{V}_{nn})^2}; \tag{14.2}$$

see *SP* 1, (32.6). Here $E_n^{(0)}$ are the unperturbed levels, V_{mn} the matrix elements of the perturbing energy, and the bar denotes a statistical averaging with respect to the Gibbs distribution $w_n = \exp\{(\mathscr{F}_0 - E_n^{(0)})/T\}$.

The term $\overline{V}_{nn}$ in formula (14.2), which is linear in the field, is zero except in pyroelectric bodies. The quadratic change in the free energy, which is of interest here, is given by the remaining terms. It is evident that they are negative.

On the other hand, it is clear from the derivation of (14.2) that the total free energy $\mathscr{F}$ must be taken in this formula as described in §11, omitting the energy of the field which would exist in the absence of the body. The difference $\mathscr{F}-\mathscr{F}_0$ is therefore given by the thermodynamic formula (11.7). Let us consider a long narrow cylinder placed parallel to a uniform external field $\mathfrak{E}$. The field within the cylinder is then $\mathfrak{E}$ also, and its polarization $\mathbf{P} = (\varepsilon-1)\mathfrak{E}/4\pi$, so that

$$\mathscr{F}-\mathscr{F}_0 = -(\varepsilon-1)V\mathfrak{E}^2/8\pi.$$

Thus $\mathscr{F}-\mathscr{F}_0$ is negative only if $\varepsilon > 1$. This leads to the conclusion mentioned in §7 and already made use of, namely that the permittivity of all bodies exceeds unity, and the dielectric susceptibility $\kappa = (\varepsilon-1)/4\pi$ is therefore positive.

In the same way we can prove the inequalities $\varepsilon^{(i)} > 1$ for the principal values of the tensor ε_{ik} in an anisotropic dielectric medium. To do so, it is sufficient to consider the energy of a field parallel to each of the three principal axes in turn.

§15. Electric forces in a fluid dielectric

The problem of calculating the forces (called *ponderomotive* forces) which act on a dielectric in an arbitrary non-uniform electric field is fairly complicated and requires separate consideration for fluids (liquids or gases) and for solids. We shall take first the simpler case, that of fluid dielectrics. We denote by $\mathbf{f}\,\mathrm{d}V$ the force on a volume element $\mathrm{d}V$, and call the vector $\mathbf{f}$ the *force density*.

It is well known that the forces acting on any finite volume in a body can be reduced to forces applied to the surface of that volume (see *TE*, §2). This is a consequence of the law of conservation of momentum. The force acting on the matter in a volume $\mathrm{d}V$ is the change in its momentum per unit time. This change must be equal to the amount of momentum entering the volume through its surface per unit time. If we denote the momentum flux

† The change proportional to the square of the field is meant. It may be recalled that, in pyroelectric bodies, the change in the free energy contains also a term linear in the field, which is of no interest here.