

For an estimate of the natural frequency  $\omega_0$ , we can set this energy equal to  $\hbar\omega_0$ —the energy of an atomic oscillator whose natural frequency is  $\omega_0$ . We get

$$\omega_0 \approx \frac{1}{2} \frac{me^4}{\hbar^3}.$$

If we now use this value of  $\omega_0$  in Eq. (11.7), we find for the electronic polarizability

$$\alpha \approx 16\pi \left[ \frac{\hbar^2}{me^2} \right]^3. \quad (11.12)$$

The quantity  $(\hbar^2/me^2)$  is the radius of the ground-state orbit of a Bohr atom (see Chapter 38, Vol. I) and equals 0.528 angstroms. In a gas at standard pressure and temperature (1 atmosphere, 0°C) there are  $2.69 \times 10^{19}$  atoms/cm<sup>3</sup>, so Eq. (11.9) gives us

$$\kappa = 1 + (2.69 \times 10^{19})16\pi(0.528 \times 10^{-8})^3 = 1.00020. \quad (11.13)$$

The dielectric constant for hydrogen gas is measured to be

$$\kappa_{\text{exp}} = 1.00026.$$

We see that our theory is about right. We should not expect any better, because the measurements were, of course, made with normal hydrogen gas, which has diatomic molecules, not single atoms. We should not be surprised if the polarization of the atoms in a molecule is not quite the same as that of the separate atoms. The molecular effect, however, is not really that large. An exact quantum-mechanical calculation of  $\alpha$  for hydrogen atoms gives a result about 12% higher than (11.12) (the  $16\pi$  is changed to  $18\pi$ ), and therefore predicts a dielectric constant somewhat closer to the observed one. In any case, it is clear that our model of a dielectric is fairly good.

Another check on our theory is to try Eq. (11.12) on atoms which have a higher frequency of excitation. For instance, it takes about 24.5 volts to pull the electron off helium, compared with the 13.5 volts required to ionize hydrogen. We would, therefore, expect that the absorption frequency  $\omega_0$  for helium would be about twice as big as for hydrogen and that  $\alpha$  would be one-quarter as large. We expect that

$$\kappa_{\text{helium}} \approx 1.000050.$$

Experimentally,

$$\kappa_{\text{helium}} = 1.000068,$$

so you see that our rough estimates are coming out on the right track. So we have understood the dielectric constant of nonpolar gas, but only qualitatively, because we have not yet used a correct atomic theory of the motions of the atomic electrons.

### 11-3 Polar molecules; orientation polarization

Next we will consider a molecule which carries a permanent dipole moment  $p_0$ —such as a water molecule. With no electric field, the individual dipoles point in random directions, so the net moment per unit volume is zero. But when an electric field is applied, two things happen: First, there is an extra dipole moment induced because of the forces on the electrons; this part gives just the same kind of electronic polarizability we found for a nonpolar molecule. For very accurate work, this effect should, of course, be included, but we will neglect it for the moment. (It can always be added in at the end.) Second, the electric field tends to line up the individual dipoles to produce a net moment per unit volume. If all the dipoles in a gas were to line up, there would be a very large polarization, but that does not happen. At ordinary temperatures and electric fields the collisions of the molecules in their thermal motion keep them from lining up very much. But there is some net alignment, and so some polarization (see Fig. 11-2). The polarization that does occur can be computed by the methods of statistical mechanics we described in Chapter 40 of Vol. I.

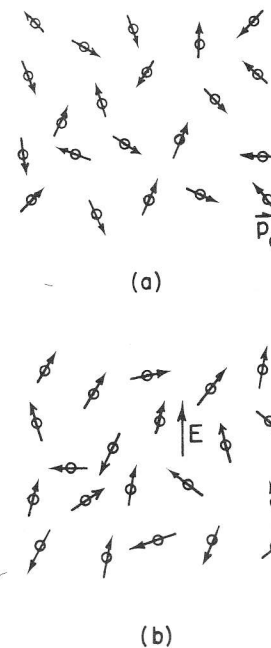


Fig. 11-2. (a) In a gas of polar molecules, the individual moments are oriented at random; the average moment in a small volume is zero. (b) When there is an electric field, there is some average alignment of the molecules.

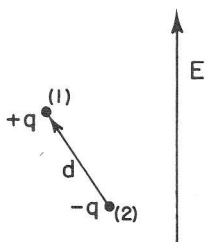


Fig. 11-3. The energy of a dipole  $\mathbf{p}_0$  in the field  $\mathbf{E}$  is  $-\mathbf{p}_0 \cdot \mathbf{E}$ .

To use this method we need to know the energy of a dipole in an electric field. Consider a dipole of moment  $\mathbf{p}_0$  in an electric field, as shown in Fig. 11-3. The energy of the positive charge is  $q\phi(1)$ , and the energy of the negative charge is  $-q\phi(2)$ . Thus the energy of the dipole is

$$U = q\phi(1) - q\phi(2) = qd \cdot \nabla\phi,$$

or

$$U = -\mathbf{p}_0 \cdot \mathbf{E} = -p_0 E \cos \theta, \quad (11.14)$$

where  $\theta$  is the angle between  $\mathbf{p}_0$  and  $\mathbf{E}$ . As we would expect, the energy is lower when the dipoles are lined up with the field.

We now find out how much lining up occurs by using the methods of statistical mechanics. We found in Chapter 40 of Vol. I that in a state of thermal equilibrium, the relative number of molecules with the potential energy  $U$  is proportional to

$$e^{-U/kT}, \quad (11.15)$$

where  $U(x, y, z)$  is the potential energy as a function of position. The same arguments would say that using Eq. (11.14) for the potential energy as a function of angle, the number of molecules at  $\theta$  per unit solid angle is proportional to  $e^{-U/kT}$ .

Letting  $n(\theta)$  be the number of molecules per unit solid angle at  $\theta$ , we have

$$n(\theta) = n_0 e^{+p_0 E \cos \theta / kT}. \quad (11.16)$$

For normal temperatures and fields, the exponent is small, so we can approximate by expanding the exponential:

$$n(\theta) = n_0 \left( 1 + \frac{p_0 E \cos \theta}{kT} \right). \quad (11.17)$$

We can find  $n_0$  if we integrate (11.17) over all angles; the result should be just  $N$ , the total number of molecules per unit volume. The average value of  $\cos \theta$  over all angles is zero, so the integral is just  $n_0$  times the total solid angle  $4\pi$ . We get

$$n_0 = \frac{N}{4\pi}. \quad (11.18)$$

We see from (11.17) that there will be more molecules oriented along the field ( $\cos \theta = 1$ ) than against the field ( $\cos \theta = -1$ ). So in any small volume containing many molecules there will be a net dipole moment per unit volume—that is, a polarization  $P$ . To calculate  $P$ , we want the vector sum of all the molecular moments in a unit volume. Since we know that the result is going to be in the direction of  $\mathbf{E}$ , we will just sum the components in that direction (the components at right angles to  $\mathbf{E}$  will sum to zero):

$$P = \sum_{\text{unit volume}} p_0 \cos \theta_i.$$

We can evaluate the sum by integrating over the angular distribution. The solid angle at  $\theta$  is  $2\pi \sin \theta d\theta$ , so

$$P = \int_0^\pi n(\theta) p_0 \cos \theta 2\pi \sin \theta d\theta. \quad (11.19)$$

Substituting for  $n(\theta)$  from (11.17), we have

$$P = -\frac{N}{2} \int_0^\pi \left( 1 + \frac{p_0 E}{kT} \cos \theta \right) p_0 \cos \theta d(\cos \theta),$$

which is easily integrated to give

$$P = \frac{N p_0^2 E}{3kT}. \quad (11.20)$$

be zero. The field inside the slot must give a contribution which just cancels the part from the field outside. Therefore the field  $E_0$  actually found in the center of a long thin slot is equal to  $E$ , the average electric field found in the dielectric.

Now consider another slot whose large sides are perpendicular to  $E$ , as shown in part (c) of Fig. 11-5. In this case, the field  $E_0$  in the slot is not the same as  $E$  because polarization charges appear on the surfaces. If we apply Gauss' law to a surface  $S$  drawn as in (d) of the figure, we find that the field  $E_0$  in the slot is given by

$$E_0 = E + \frac{P}{\epsilon_0}, \quad (11.22)$$

where  $E$  is again the electric field in the dielectric. (The gaussian surface contains the surface polarization charge  $\sigma_{\text{pol}} = P$ .) We mentioned in Chapter 10 that  $\epsilon_0 E + P$  is often called  $D$ , so  $\epsilon_0 E_0 = D_0$  is equal to  $D$  in the dielectric.

Earlier in the history of physics, when it was supposed to be very important to define every quantity by direct experiment, people were delighted to discover that they could define what they meant by  $E$  and  $D$  in a dielectric without having to crawl around between the atoms. The average field  $E$  is numerically equal to the field  $E_0$  that would be measured in a slot cut parallel to the field. And the field  $D$  could be measured by finding  $E_0$  in a slot cut normal to the field. But nobody ever measures them that way anyway, so it was just one of those philosophical things.

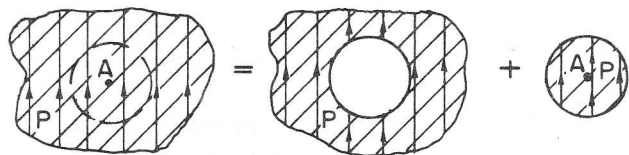


Fig. 11-6. The field at any point  $A$  in a dielectric can be considered as the sum of the field in a spherical hole plus the field due to a spherical plug.

For most liquids which are not too complicated in structure, we could expect that an atom finds itself, on the average, surrounded by the other atoms in what would be a good approximation to a *spherical hole*. And so we should ask: "What would be the field in a spherical hole?" We can find out by noticing that if we imagine carving out a spherical hole in a uniformly polarized material, we are just removing a sphere of polarized material. (We must imagine that the polarization is "frozen in" before we cut out the hole.) By superposition, however, the fields inside the dielectric, before the sphere was removed, is the sum of the fields from all charges outside the spherical volume plus the fields from the charges within the polarized sphere. That is, if we call  $E$  the field in the uniform dielectric, we can write

$$E = E_{\text{hole}} + E_{\text{plug}}, \quad (11.23)$$

where  $E_{\text{hole}}$  is the field in the hole and  $E_{\text{plug}}$  is the field inside a sphere which is uniformly polarized (see Fig. 11-6). The fields due to a uniformly polarized sphere are shown in Fig. 11-7. The electric field inside the sphere is uniform, and its value is

$$E_{\text{plug}} = -\frac{P}{3\epsilon_0}. \quad (11.24)$$

Using (11.23), we get

$$E_{\text{hole}} = E + \frac{P}{3\epsilon_0}. \quad (11.25)$$

The field in a spherical cavity is greater than the average field by the amount  $P/3\epsilon_0$ . (The spherical hole gives a field 1/3 of the way between a slot parallel to the field and a slot perpendicular to the field.)

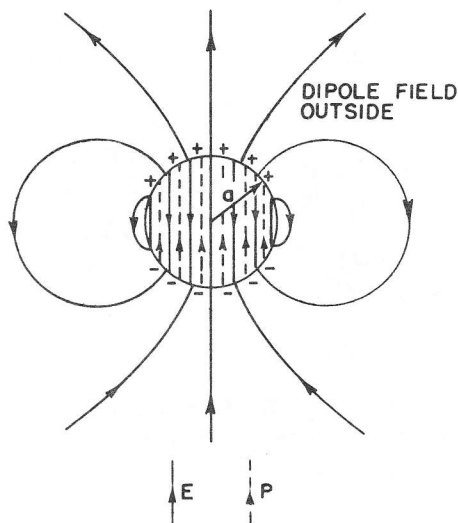
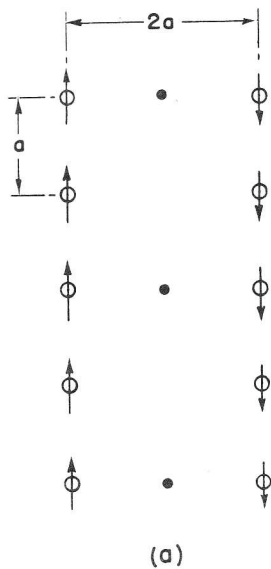


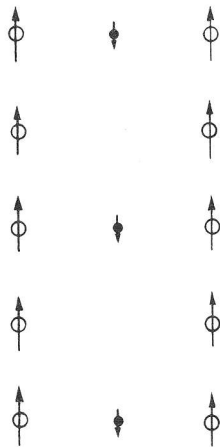
Fig. 11-7. The electric field of a uniformly polarized sphere.

### 11-5 The dielectric constant of liquids; the Clausius-Mossotti equation

In a liquid we expect that the field which will polarize an individual atom is more like  $E_{\text{hole}}$  than just  $E$ . If we use the  $E_{\text{hole}}$  of (11.25) for the polarizing field



(a)



(b)

Fig. 11-10. Models of a ferroelectric: (a) corresponds to an antiferroelectric, and (b) to a normal ferroelectric.

to pick out chains of ions along vertical lines. One of them consists of alternating oxygen and titanium ions. There are other lines made up of either barium or oxygen ions, but the spacing along these lines is greater. We make a simple model to imitate this situation by imagining, as shown in Fig. 11-10(a), a series of chains of ions. Along what we call the main chain, the separation of the ions is  $a$ , which is half the lattice constant; the lateral distance between identical chains is  $2a$ . There are less-dense chains in between which we will ignore for the moment. To make the analysis a little easier, we will also suppose that all the ions on the main chain are identical. (It is not a serious simplification because all the important effects will still appear. This is one of the tricks of theoretical physics. One does a different problem because it is easier to figure out the first time—then when one understands how the thing works, it is time to put in all the complications.)

Now let's try to find out what would happen with our model. We suppose that the dipole moment of each atom is  $p$  and we wish to calculate the field at one of the atoms of the chain. We must find the sum of the fields from all the other atoms. We will first calculate the field from the dipoles in only one vertical chain; we will talk about the other chains later. The field at the distance  $r$  from a dipole in a direction along its axis is given by

$$E = \frac{1}{4\pi\epsilon_0} \frac{2p}{r^3}. \quad (11.32)$$

At any given atom, the dipoles at equal distances above and below it give fields in the same direction, so for the whole chain we get

$$E_{\text{chain}} = \frac{p}{4\pi\epsilon_0} \frac{2}{a^3} \cdot \left( 2 + \frac{2}{8} + \frac{2}{27} + \frac{2}{64} + \dots \right) = \frac{p}{\epsilon_0} \frac{0.383}{a^3}. \quad (11.33)$$

It is not too hard to show that if our model were like a completely cubic crystal—that is, if the next identical lines were only the distance  $a$  away—the number 0.383 would be changed to  $1/3$ . In other words, if the next lines were at the distance  $a$  they would contribute only  $-0.050$  unit to our sum. However, the next main chain we are considering is at the distance  $2a$  and, as you remember from Chapter 7, the field from a periodic structure dies off exponentially with distance. Therefore these lines contribute much less than  $-0.050$  and we can just ignore all the other chains.

It is necessary now to find out what polarizability  $\alpha$  is needed to make the runaway process work. Suppose that the induced moment  $p$  of each atom of the chain is proportional to the field on it, as in Eq. (11.6). We get the polarizing field on the atom from  $E_{\text{chain}}$ , using Eq. (11.32). So we have the two equations

$$p = \alpha\epsilon_0 E_{\text{chain}}$$

and

$$E_{\text{chain}} = \frac{0.383}{a^3} \frac{p}{\epsilon_0}.$$

There are two solutions:  $E$  and  $p$  both zero, or

$$\alpha = \frac{a^3}{0.383},$$

with  $E$  and  $p$  both finite. Thus if  $\alpha$  is as large as  $a^3/0.383$ , a permanent polarization sustained by its own field will set in. This critical equality must be reached by barium titanate at just the temperature  $T_c$ . (Notice that if  $\alpha$  were larger than the critical value for small fields, it would decrease at larger fields and at equilibrium the same equality we have found would hold.)

For  $\text{BaTiO}_3$ , the spacing  $a$  is  $2 \times 10^{-8}$  cm, so we must expect that  $\alpha = 21.8 \times 10^{-24}$  cm<sup>3</sup>. We can compare this with the known polarizabilities of the individual atoms. For oxygen,  $\alpha = 30.2 \times 10^{-24}$  cm<sup>3</sup>; we're on the right track. But for titanium,  $\alpha = 2.4 \times 10^{-24}$  cm<sup>3</sup>; rather small. To use our model we should probably take the average. (We could work out the chain again for alternating