

Dielectric Properties of Insulators

Syllabus: Electric dipole moment, Dielectric constant, Polarizability, Electric susceptibility, Displacement vector, Electronic, Ionic, and Orientational polarization, Internal fields in solids, Piezoelectricity, Pyroelectricity, Ferroelectricity.

References: i). Solid State Physics by A J Dekker
ii). The Feynman Lectures on Physics, Vol. 2

1. Introduction: Most objects - two classes $\begin{cases} \text{Conductors} \\ \text{Insulators or dielectrics} \end{cases}$

Conductors - 'free' charges that can move about through the material.

Dielectrics - All charges attached to specific atoms or molecules - they are on a tight leash, and all they can do is move a bit within the atom or molecule. Their cumulative effects account for the characteristic behaviour of dielectric materials.

2. Polarization \vec{P} : Response of a dielectric when placed in an electric field \vec{E} is the creation of a net dipole moment per unit volume, \vec{P} , within the material induced by the field. Polarization vector $\vec{P} = N \vec{p}$: N - number of atoms/molecules per unit volume.

\vec{p} - induced dipole moment per atom/molecule. We will consider electrostatic fields only.

Three types of polarization $\begin{cases} \text{Electronic} - \text{electronic displacements within comprising atom due to field} \\ \text{Ionic} - \text{atomic or ionic displacements within the molecule (changes in bond angles and interatomic distances due to the field)} \\ \text{Orientational} - \text{molecules with permanent dipole moments tending to orient along the field.} \end{cases}$ Ref. p 137 Dekker.

Note: Two equal and opposite charges ($q, -q, q > 0$) separated by a small distance (S) form an electric dipole with the corresponding dipole moment being given by $\vec{p} = q \vec{S}$ $\begin{matrix} \vec{S} \rightarrow \\ -q \quad q \end{matrix}$

The vector points from the negative to the positive charge of the dipole.

$$\vec{p} = q \vec{S}, \quad \vec{P} = N \vec{p} \equiv N q \vec{S} \quad (1)$$

where in (1), $\vec{p} = q \vec{S}$ - induced dipole moment per atom (or molecule); in each atom there are charges ' q ' separated by a distance S . \vec{P} - induced dipole moment per unit volume of the dielectric. ('Field' implies electric field here in this chapter.)

It seems reasonable that, if the field is not too high, the amount of induced dipole moment will be proportional to the field. That is, a small field will displace the charges a little bit and a larger field will displace them further - and in proportion to the field - unless the displacement gets too large. For the remainder of this chapter, we will assume that the field is not too high, so that the dipole moment ^(\vec{P}) is exactly proportional to the field, i.e. $\vec{P} \propto \vec{E}$. For a linear, isotropic dielectric, the induced dipole

moment vector \vec{p} and the field \vec{E} are in the same direction, and they are related through a proportionality constant ' α_p ' ; i.e.,

$$\vec{p} = \alpha_p \vec{E}$$

(2) (α_p is positive.)
Why?

' α_p ' is known as the polarizability of the dielectric material. (Note: For a linear, anisotropic dielectric, α_p is a tensor.) Since $\vec{P} = N\vec{p}$, \vec{P} is also proportional to the electric field \vec{E} . We write, for a linear isotropic dielectric,

$$\vec{P} = \chi \epsilon_0 \vec{E}$$

(3)

where ϵ_0 - permittivity of free space; the proportionality constant is $\chi \epsilon_0$ where χ is known as the electric susceptibility of the material of the dielectric ($\chi > 0$).
Why?

Comparing (2) and (3), & with $\vec{P} = N\vec{p}$,

$$\alpha_p = \frac{\chi \epsilon_0}{N}$$

(4)

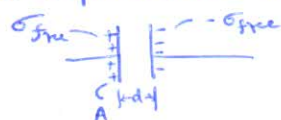
$$(\because P = \chi \epsilon_0 E = Np = N\alpha_p E)$$

(χ - a measure of the 'ease' with which induced dipoles are created.)

3. Polarization charges

What actually determines how χ behaves, how accurately it is constant for very large fields, and what is going on inside different materials - some of these issues will be discussed in class later. For the present, we will simply suppose that there exists a mechanism by which a dipole moment is induced which is proportional to the electric field. Our discussions will also remain confined to the case of linear isotropic dielectrics only. We will first consider a parallel-plate capacitor without a dielectric.

For this parallel-plate capacitor, we assume that the two plates carry charges with surface densities ' σ_{free} ' and ' $-\sigma_{free}$ ' respectively ($\sigma_{free} > 0$); each plate has an area ' A ' & the interplate separation is ' d '. We will study this first under 'open circuit' conditions \rightarrow



The electric field between the plates is

(5)

$$\boxed{E_0 = \frac{\sigma_{free}}{\epsilon_0}}$$

It points from left to right in the above figure. Note: We refer to the surface charge on the capacitor plates as σ_{free} (or σ_{free}) because they can move 'freely' anywhere on the conductor; for example, they can be easily removed by discharging the capacitor. The (magnitude of) the charge on each plate of the capacitor is

$$Q = \sigma_{free} A,$$

(6)

and the voltage drop across the plates is,

$$V_0 = E_0 \cdot d = \frac{\sigma_{\text{free}} d}{\epsilon_0} \quad (7)$$

The capacitance of this capacitor without any dielectric between the plates is,

$$C_0 = \frac{Q}{V_0} = \frac{\sigma_{\text{free}} A}{E_0 \cdot d} = \frac{\sigma_{\text{free}} A}{\frac{\sigma_{\text{free}} d}{\epsilon_0}} = \frac{\epsilon_0 A}{d} \quad (8)$$

C_0 - sometimes referred to as the geometrical capacitance.

We now put a dielectric (of susceptibility χ) between the plates of the above capacitor so that it covers all the space between the plates. The dielectric (of effective area 'A', and thickness 'd') becomes polarized with the development of a net induced dipole moment per unit volume, \vec{P} . We suppose that \vec{P} is uniform (students, explain why this assumption is valid.), so that net polarized charges only appear at the surfaces of the dielectric that are in contact with the plates of the capacitor. At the surface that is in contact with the positively charged plate of the capacitor the negative charges, the electrons, have effectively moved out a distance δ thereby creating an effective surface density of ^{negative} charge. At the other surface (in contact with the negative capacitor plate), the electrons in the dielectric have moved in, leaving some positive charge effectively out a distance δ , thereby creating an effective surface density of positive charge - see Figure 1. These are the so-called surface polarization charges.

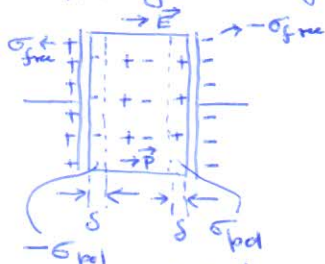


Figure 1. A dielectric slab in a uniform electric field.
 $\sigma_s > 0$, $\sigma_p > 0$.

This charge can be calculated as follows. If A is the area of the plate, the number of electrons that appear at the surface is the product of A and N, the number per unit volume, and the ^{magnitude} displacement δ , which we assume here is perpendicular to the surface. Therefore the ^{magnitude} total charge within a distance δ from the plate is $NASq_e$, where q_e is the electronic charge magnitude. To get the surface density of polarization charge induced on the surface we divide this quantity (i.e., $NASq_e$) by A. The magnitude of the surface charge density is then given by

$$\sigma_{\text{pol}} = Nq_e \delta \quad (9)$$

But this is just equal to the magnitude P of the polarization vector in Eq. (1):

$$\sigma_{\text{pol}} = P \quad (10)$$

The surface density of charge is equal to the polarization inside the material. The surface charge is, of course, positive on one surface and negative on the other.

Students, it is essential that you remember σ_{pol} exists only because of σ_{free} .

If σ_{free} is removed by discharging the capacitor, then σ_{pol} will disappear (explain how σ_{pol} will disappear).

Now because of the presence of σ_{pol} , the 'effective' surface density of charge on each plate will have the magnitude $\sigma_{free} - \sigma_{pol}$ (since at a given plate σ_{free} and σ_{pol} have opposite signs). Then the electric field between the plates (i.e., the electric field in the dielectric) becomes

$$E = \frac{\sigma_{free} - \sigma_{pol}}{\epsilon_0} \equiv \frac{\sigma_{free} - P}{\epsilon_0} \quad (11)$$

From (3), $P = \chi \epsilon_0 E$, so that

$$E = \frac{\sigma_{free} - \chi \epsilon_0 E}{\epsilon_0} \Rightarrow \boxed{E = \frac{\sigma_{free}}{\epsilon_0} \cdot \frac{1}{(1 + \chi)}} \quad (12)$$

Comparing Eqs. (5) and (12), it is clear that for the same surface density of 'free' charges on the plates, the electric field between the plates is reduced by a factor of $1 + \chi$ in the presence of the dielectric between the plates.

The voltage between the plates is

$$V = E \cdot d = \frac{\sigma_{free} \cdot d}{\epsilon_0 (1 + \chi)} \quad (13)$$

The charge on each plate is still given by (6), i.e., by $Q = \sigma_{free} \cdot A$, so the capacitance of the capacitor with the dielectric between the plates is

$$C = \frac{Q}{V} = \frac{\cancel{\sigma_{free}} \cdot A \cdot \epsilon_0 (1 + \chi)}{\cancel{\sigma_{free}} \cdot d} = \frac{\epsilon_0 (1 + \chi) A}{d}$$

i.e.,

$$C = \frac{\epsilon_0 (1 + \chi) A}{d} \equiv \frac{\epsilon_0 \epsilon_r A}{d} = \frac{\epsilon A}{d} \quad (14)$$

$$(15)$$

where

$$\epsilon_r = 1 + \chi, \quad \epsilon = \epsilon_0 \epsilon_r = \epsilon_0 (1 + \chi)$$

ϵ_r is known as the relative permittivity, or dielectric constant of the material; and $\epsilon (= \epsilon_0 \epsilon_r)$ is called the permittivity of the material. Equation (14), when compared to Eq. (8), shows that when a parallel-plate capacitor is filled with a dielectric, the capacitance is increased by the factor $\epsilon_r = \epsilon_0 (1 + \chi)$. To better understand this consider two identical parallel plate capacitors (i.e., same A, d),

where one capacitor (call it 'a') is without dielectric and the other (call it 'b') has a dielectric (of dielectric constant ϵ_r) filling up the space between the plates. Suppose both these capacitors are separately connected to two identical voltage sources... 'V' - see

Figure 2.

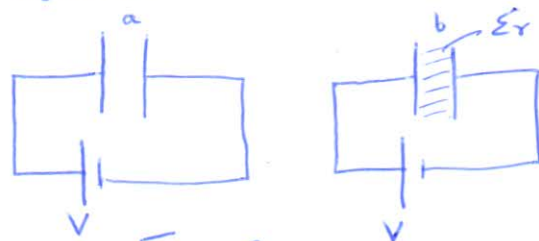


Figure 2

For capacitor 'a' (without dielectric), the capacitance is simply,

$$C_a = \frac{\epsilon_0 A}{d} \equiv \frac{Q_{free}^a}{V} \quad (16)$$

where Q_{free}^a is the total free charge on the plates,

i.e., $Q_{free}^a = \sigma_{free}^a \cdot A$; $\sigma_{free}^a \rightarrow$ surface charge density of free charges on the plates.

For capacitor 'b' (with dielectric), the capacitance is

$$C_b = \frac{\epsilon_r \epsilon_0 A}{d} \equiv \frac{Q_{free}^b}{V} \quad (17)$$

where $Q_{free}^b (\equiv \sigma_{free}^b \cdot A)$ - total free charge on the plates of a 'b' capacitor. From (16) & (17),

$$\frac{C_b}{C_a} = \epsilon_r = \frac{Q_{free}^b}{Q_{free}^a} \left(\equiv \frac{\sigma_{free}^b}{\sigma_{free}^a} \right), \quad (18)$$

i.e.,

$$Q_{free}^b = \epsilon_r Q_{free}^a \quad \left(\text{or } \sigma_{free}^b = \epsilon_r \sigma_{free}^a \right) \quad (19)$$

Equation (19) shows that the 'capacity' of a capacitor to hold free charge increases by a factor of ϵ_r , if a dielectric (of constant ϵ_r) is inserted between the plates.

4. The Electric Displacement (\vec{D}): It is defined as

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} \quad (20)$$

For a linear isotropic dielectric, $\vec{P} = \chi \epsilon_0 \vec{E}$ (3) $\rightarrow \vec{P}$ & \vec{E} - same direction.

$$\therefore \vec{D} = \epsilon_0 (1 + \chi) \vec{E} = \epsilon_0 \epsilon_r \vec{E} = \epsilon \vec{E} \quad (21) \rightarrow \vec{D} \text{ & } \vec{E} \text{ - same direction}$$

Also since \vec{D} , \vec{E} , \vec{P} have same directions in this case we can write,

$$D = \epsilon_0 E + P = \epsilon_0 (1 + \chi) E = \epsilon E \quad (22)$$

Now for a parallel plate capacitor without a dielectric, $P = 0$ & $E = \frac{\sigma_{free}}{\epsilon_0}$ (or $\chi = 0$)

Then

$$D = \epsilon_0 E + P = \epsilon_0 \cdot \frac{\sigma_{free}}{\epsilon_0} + 0 = \sigma_{free},$$

i.e.,

$$D = \sigma_{free} \quad (23)$$

For a parallel plate capacitor with a dielectric, $D = \epsilon_0 E + P = \epsilon E + \chi \epsilon_0 E = \epsilon_0 (1 + \chi) E$.

But $E = \frac{\sigma_{\text{free}}}{\epsilon_0} \cdot \frac{1}{(1+\chi)}$, from (12).

$$\therefore D = \epsilon_0 (1+\chi) \cdot E = \cancel{\epsilon_0 (1+\chi)} \cdot \frac{\sigma_{\text{free}}}{\cancel{\epsilon_0 (1+\chi)}} = \sigma_{\text{free}}.$$

So once again,

$$D = \sigma_{\text{free}} \quad (24)$$

In this context, one point should be emphasized. An equation like $\vec{D} = \epsilon \vec{E}$ is an attempt to describe a property of matter. But matter is extremely complicated, and such an equation does not always hold. For instance, if \vec{E} gets too large, then \vec{D} is no longer proportional to \vec{E} . For some substances, the proportionality breaks down even with relatively small fields. Also ϵ may depend on how fast \vec{E} changes with time. Therefore this kind of equation is a kind of approximation, like Hooke's law. It cannot be a deep and fundamental equation. The fundamental equations dealing with charges, currents, and fields are the Maxwell's equations which you may study elsewhere.

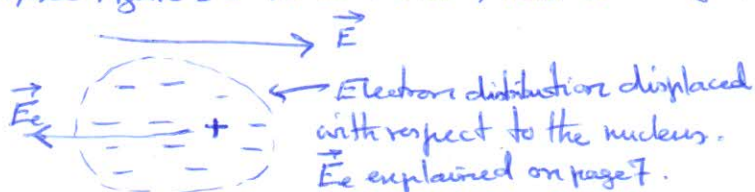
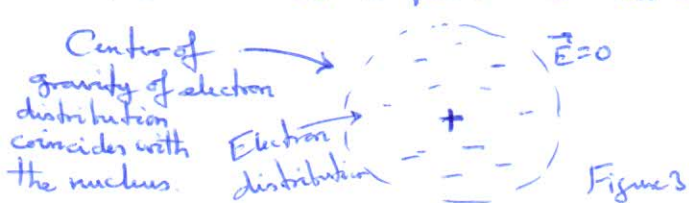
The term 'polarization' refers to the response of a dielectric to an applied electric field, which is the creation of induced dipole moments within the dielectric. At this point we will consider the behaviour of free atoms and molecules in an external field. The term "free" refers to a system in which to a good approximation the mutual interaction between the particles may be neglected, as in a gas of low density. If the external field is \vec{E} , the polarization \vec{P} is, $\vec{P} = \chi \epsilon_0 \vec{E}$. But $\vec{P} = N \vec{p}$ where \vec{p} - average induced dipole moment per molecule, i.e., $\vec{P} = \chi \epsilon_0 \vec{E} = N \vec{p}$, so that

$$\vec{p} = \frac{\chi \epsilon_0}{N} \vec{E} = \alpha_p \vec{E}; \quad \alpha_p = \frac{\chi \epsilon_0}{N} \quad (2) \text{ \& (4)}$$

where α_p is known as the polarizability of the dielectric. (Students, you must note again that $\vec{P} = \chi \epsilon_0 \vec{E}$ does not always hold good, even for a given dielectric.) We now discuss the mechanisms through which polarization can take place.

A. Electronic Polarization

We will first discuss the polarization of nonpolar molecules. Consider the simplest case of a monoatomic gas (for instance, helium). When an atom of such a gas is in an electric field, the electrons are pulled one way by the field while the nucleus is pulled the other way; see Figure 3. As a result, there is a slight



net displacement of the centers of positive and negative charge with respect to each other, and a dipole moment is induced (see Fig. 3). For small fields, the amount of displacement, and so also the dipole moment, is proportional to the electric field. The displacement of the electron distribution which produces this kind of induced dipole moment is called electronic polarization. The proportionality constant (when it exists) between the induced dipole moment \vec{p} and the electric field \vec{E} is known as the electronic polarizability, α_e :

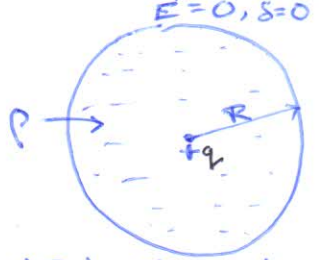
$$\vec{p} = \alpha_e \vec{E} \quad (25)$$

Let us now consider in a bit more details about what exactly happens during electronic polarization. As mentioned above when a free neutral, atom is subjected to an electric field, the nucleus is pushed in the direction of the field, and the electrons the opposite way. An equilibrium is soon established. The two opposing forces - \vec{E} pulling the electrons and nucleus apart and their mutual attraction drawing them back together - reach a balance, leaving the atom polarized with an induced dipole moment given by Eq. (25). \vec{p} is in the same direction as \vec{E} (i.e. $\alpha_e > 0$). So if $q (= Ze; Z - \text{atomic number, } e - \text{magnitude of electronic charge} = 1.6 \times 10^{-19} \text{ C})$ is the total charge on the nucleus, then, at equilibrium, the total force on the nucleus is zero, i.e.,

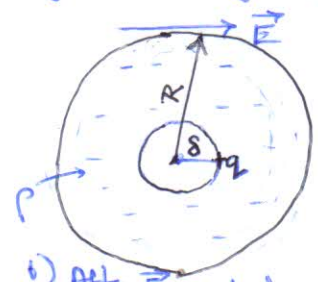
$$\left. \begin{aligned} q\vec{E} + q\vec{E}_e &= 0 \\ \Rightarrow \vec{E} &= -\vec{E}_e \end{aligned} \right\} \quad (26)$$

where \vec{E}_e is the electric field at the site of the nucleus due to the net attractive force caused by the electron cloud (which has shifted relative to the nucleus in a direction opposite to \vec{E}). (See Figure 3.)

To obtain an idea of the magnitude of α_e , consider the following simplified model: Suppose the atom is represented by a nucleus of charge q ($q = Ze$) and a homogeneous negative charge distribution ^{of density ρ} inside a sphere of radius R . So,



a) Before \vec{E} applied
Figure 4



b) After \vec{E} applied.

$$\rho = \frac{-q}{\frac{4}{3}\pi R^3} \quad (27)$$

[Students, explain the minus sign in (27)]

On the application of the electric field \vec{E} to the right, we assume that the entire spherical negative charge distribution (of radius R & density ρ) shifts to the left and the nucleus

to the right (see Figure 4(b)) thereby creating a net distance δ between the centers of gravity of the negative and positive charges. Then Eqs. (26) hold, and we now need to derive an expression for E_e .

Contribution to E_e (i.e., electric field at the location of the nucleus due to excess electrons on the left of the nucleus - see Fig. 4b) will come only from the spherical distribution of negative charge of radius δ . If q_e is the total negative charge within this sphere (of radius δ), then, Why??

$$q_e = \frac{4\pi}{3} \delta^3 \rho, \quad (28)$$

and

$$E_e = \frac{q_e}{4\pi \epsilon_0 \delta^2} \quad (29)$$

Substituting for ρ and q_e from Eqs. (27) and (28) in (29) we get,

$$E_e = \frac{1}{4\pi \epsilon_0 \delta^2} \times \frac{4\pi}{3} \delta^3 \times \frac{-q}{\frac{4\pi}{3} R^3} = \frac{-q\delta}{4\pi \epsilon_0 R^3} \quad (30)$$

Therefore, from (26), $\therefore E = -E_e$,

$$E = \frac{q\delta}{4\pi \epsilon_0 R^3} \quad (31)$$

But $q\delta \equiv p$, the magnitude of the induced dipole moment.

$$\therefore E = \frac{p}{4\pi \epsilon_0 R^3}$$

$$\Rightarrow p = 4\pi \epsilon_0 R^3 E \equiv \alpha_e E \quad (32)$$

i.e.,

$$\boxed{\alpha_e = 4\pi \epsilon_0 R^3} \quad (33)$$

which gives the expression for the electronic polarizability for this simple model.

The atomic volume, V , can be written here as,

$$V = \frac{4\pi}{3} R^3, \quad (34)$$

Then,

$$\alpha_e = 4\pi \epsilon_0 R^3 = 3\epsilon_0 V \quad (35)$$

i.e., for this model of the atom, the electronic polarizability is proportional to the

atomic volume. Although this atomic model is extremely crude, the result (35) is not too bad and is accurate to within a factor of four or so for many simple atoms.

Estimation of α_e and δ : $R \approx 1 \text{ \AA} = 10^{-10} \text{ m}$, $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 / \text{Nm}^2$

$$\alpha_e \approx 4\pi \times 8.85 \times 10^{-12} \times (10^{-10})^3 = 10^{-40} \text{ F.m}^2$$

[Students, show that the unit of α_e is F.m^2]

Then, for an electric field of 10^4 V/m , $q \approx 1.6 \times 10^{-19} \text{ C}$,

$$p = q\delta = \alpha_e E \Rightarrow \delta \approx \frac{\alpha_e E}{q} \sim \frac{10^{-40} \times 10^4}{10^{-19}} = 10^{-17} \text{ m}$$

$$\text{So } \frac{\delta}{R} \sim 10^{-7} \text{, i.e., } \delta \ll R.$$

For each atom or ion one may associate a certain electronic polarizability, α_e . In general, atoms with many electrons tend to have a larger electronic polarizability than those with few electrons. Electrons in the outer electronic shells will contribute more to α_e than do electrons in the inner shells, because the former are not so strongly bound to the nucleus as the latter. See Dekker for more details.

B. Ionic Polarization: In molecules as well as in atoms an external electric field will displace the electrons with respect to the corresponding nuclei. Over and above this, however, a displacement of atoms or ions within the molecule may be caused by an external field. For example in an HCl molecule an external field will change the internuclear distance to some extent, leading to a change in the dipole moment. Similarly, in a molecule like CCl_4 (which has no permanent dipole moment) a change in the bond angles between the C-Cl groups will produce a dipole moment because each of these groups by itself does have a dipole moment. This kind of induced polarization is called ionic polarization because it is a consequence of the displacement of atoms within the molecule. The induced electric dipole moment resulting from elastic displacements of ions within the molecule may again be represented by an expression of the type (25), by replacing α_e by the ionic polarizability α_i . For most molecules, $\alpha_i \approx 0.1 \alpha_e$. See Dekker, p.137.

In this section we shall consider the polarizability of a molecule in a static electric field, resulting from its permanent dipole moment (e.g., HCl , H_2O , etc.).

Consider a gas containing a large number of identical molecules, each with a permanent dipole moment of magnitude p_0 . ^{Without} an external electric field, the dipoles will be oriented at random and the gas as a whole will have no resulting dipole moment. An external field \vec{E} will exert a torque on each dipole and will tend to orient the dipoles in the direction of the field - see Figure 5.

On the other hand, this ordering influence of the electric field will be counteracted by the thermal motion of the particles. However the ordering influence will have a finite nonzero effect on the molecules. A vector sum of the dipole moments of all the molecules will now yield a net dipole moment (and hence polarization) in the direction

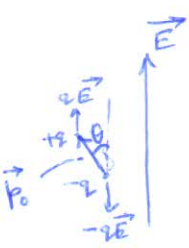


Figure 5

of \vec{E} . In other words, \vec{P} (along \vec{E}) will be non-zero and with $P = Np$, the average induced dipole moment, p , per molecule will be non-zero. Hence in the context of the present discussion,

$$p = \langle p_0 \cos \theta \rangle = p_0 \langle \cos \theta \rangle \quad (36)$$

where θ is the angle between \vec{p}_0 and \vec{E} as shown in Figure 5. Calculation of the average value of $\cos \theta$ (i.e., $\langle \cos \theta \rangle$) is a simple problem in statistical mechanics with the assumption that the dipoles may rotate freely. If $P(\theta)d\theta$ is the probability of finding the dipole between an angle θ and $\theta + d\theta$, then, $\langle \cos \theta \rangle = \int_0^\pi \cos \theta P(\theta) d\theta$ (36a)

Now, $P(\theta)d\theta \propto e^{-U/KT} \quad (37)$

where $U = -\vec{p}_0 \cdot \vec{E} = -p_0 E \cos \theta$ is the potential energy of the dipole in the electric field corresponding to the angle θ , k - Boltzmann constant, T - temperature in K . Secondly $P(\theta)d\theta$ is also proportional to the number of ways in which the dipole can make an angle between θ and $\theta + d\theta$ with \vec{E} , i.e.,

$$P(\theta)d\theta \propto 2\pi \sin \theta d\theta \quad (38)$$

which is the solid angle subtended by the space between two right circular cones with angles θ and $\theta + d\theta$. From (37) and (38),

$$P(\theta)d\theta = C \cdot e^{-U/KT} \cdot 2\pi \sin \theta d\theta, \quad (39)$$

where C is the constant of proportionality which can be determined by using the condition.

$$\int_0^\pi P(\theta) d\theta = 1. \quad (40)$$

From (39) and (40),

$$C \cdot \int_0^\pi e^{-u/kT} \sin\theta d\theta = 1, \text{ i.e., } C = \frac{1}{2\pi \int_0^\pi e^{-u/kT} \sin\theta d\theta} \quad (41)$$

$$P(\theta) d\theta = \frac{e^{-u/kT} \sin\theta d\theta}{\int_0^\pi e^{-u/kT} \sin\theta d\theta}, \quad (42)$$

$u = -p_0 E \cos\theta$

\therefore From (36a) and (42),

$$\langle \cos\theta \rangle = \frac{\int_0^\pi \cos\theta e^{p_0 E \cos\theta / kT} \sin\theta d\theta}{\int_0^\pi e^{p_0 E \cos\theta / kT} \sin\theta d\theta} \quad (43)$$

Change of variables: $a = \frac{p_0 E}{kT} = \text{constant for given } p, E, T.$ Set $x = \frac{p_0 E \cos\theta}{kT}$

i.e., $x = a \cos\theta \rightarrow \text{For } \theta = 0, x = a \text{ \& for } \theta = \pi, x = -a$

$dx = -a \sin\theta d\theta \Rightarrow \sin\theta d\theta = -\frac{dx}{a}$

(44)

\therefore From (43) & (44),

$$\langle \cos\theta \rangle = \frac{\int_a^{-a} \frac{x}{a} e^x \cdot \frac{-dx}{a}}{\int_a^{-a} e^x \cdot \frac{-dx}{a}} = \frac{1}{a} \frac{\int_{-a}^a x e^x dx}{\int_{-a}^a e^x dx} \quad (45)$$

$$\Rightarrow \langle \cos\theta \rangle = \frac{1}{a} \frac{[x e^x - e^x]_{-a}^a}{[e^x]_{-a}^a} = \frac{1}{a} \frac{[a e^a - e^a] - [-a e^{-a} - e^{-a}]}{[e^a - e^{-a}]}$$

$$= \frac{1}{a} \left[\frac{a(e^a + e^{-a}) - (e^a - e^{-a})}{e^a - e^{-a}} \right] = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a}$$

i.e.,

$$\langle \cos\theta \rangle = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} = \coth a - \frac{1}{a} \equiv L(a), \quad \left. \begin{array}{l} \text{Langevin} \\ \text{function} \end{array} \right\} \quad (46)$$

where, $a = p_0 E / kT$

• For a plot of $L(a)$ vs a , see DeKker, p. 139. Try to reproduce the plot using Excel or any other graphing software.

From (36) and (46), the average induced dipole moment per molecule is given by,

$$p = p_0 \langle \cos\theta \rangle = p_0 \left[\frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \right] = p_0 L(a) \quad (47)$$

where $a = \frac{p_0 E}{kT}$

Case 1: $a \gg 1$, i.e., $p_0 E \gg kT$. Then, $e^a \gg e^{-a}$, so that,

$$L(a) = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \approx \frac{e^a}{e^a} - \frac{1}{a} = 1 - \frac{1}{a} \approx 1, \quad (48)$$

i.e.,
$$p = p_0 L(a) \approx p_0 \quad (a \gg 1) \quad (49)$$

In other words if the ordering influence of the electric field \gg 'disordering' influence of the thermal motion of the molecules, this situation would correspond to complete alignment of the dipoles in the field direction.

Case 2: $a \ll 1$, i.e., $p_0 E \ll kT$ - this approximation holds as long as the field strength is not too high and the temperature is not too low. Then,

$$e^a \approx 1 + a + \frac{a^2}{2} + \frac{a^3}{6}, \quad e^{-a} \approx 1 - a + \frac{a^2}{2} - \frac{a^3}{6},$$

so that,

$$L(a) = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \approx \frac{2 + a^2}{2a + \frac{a^3}{3}} - \frac{1}{a} \approx \frac{a}{3} \quad (50)$$

i.e.,

$$p = p_0 L(a) = p_0 \cdot \frac{a}{3} = p_0 \cdot \frac{p_0 E}{3kT} = \frac{p_0^2 E}{3kT}$$

So

$$p = \frac{p_0^2}{3kT} E \quad \text{for } p_0 E \ll kT. \quad (51)$$

Suppose $E \sim 10^5 \text{ V/m}$. We know, $p_0 \sim 10^{-30} \text{ C.m}$. $\therefore p_0 E \sim 10^{-25} \text{ J}$.

At room temperature, $kT \sim 10^{-21} \text{ J}$. Comparing, $\frac{p_0 E}{kT} \sim 10^{-4} \ll 1$.

From (51), we can write the orientational polarizability as,

$$\alpha_o = \frac{p_0^2}{3kT} \quad (52)$$

Summarizing, one may conclude that the electric properties of a molecule may be characterized by the following three quantities:

- α_e , representing the polarizability due to electronic displacements within the composing atoms (or ions).
- α_i , representing the polarizability due to atomic or ionic displacements within the molecule (changes in bond angles and interatomic distances).
- a permanent dipole moment p_0 .

6. Dielectric constant of gases

Suppose \vec{E} - applied electric field, N - number of gas molecules per unit volume; $\alpha_e, \alpha_i, \alpha_o$ are the respective electronic, ionic & orientational polarizabilities of the gas molecules. Then, from (2), the average dipole moment per molecule will be,

$$\vec{p} = \alpha_p \vec{E} = (\alpha_e + \alpha_i + \alpha_o) \vec{E} = \left(\alpha_e + \alpha_i + \frac{p_o^2}{3kT} \right) \vec{E} \quad (53)$$

$$\therefore \vec{P} = N \vec{p} = N \left(\alpha_e + \alpha_i + \frac{p_o^2}{3kT} \right) \vec{E} \quad (54)$$

Note that only the permanent dipole moment gives a temperature dependent contribution (to the polarization vector, \vec{P}), because α_e and α_i are essentially independent of T . Now,

$$\vec{P} = \chi \epsilon_0 \vec{E} = (\epsilon_r - 1) \epsilon_0 \vec{E} \quad (55)$$

\therefore From (54) and (55),

$$\epsilon_r - 1 = \frac{N}{\epsilon_0} \left(\alpha_e + \alpha_i + \frac{p_o^2}{3kT} \right) \quad (56)$$

For a plot of $\epsilon_r - 1$ vs $\frac{1}{T}$ for various gases, see Fig. 6.6, p. 141, Dekker. The plots are seen to be straight lines in agreement with (56). From the slope of the lines and a knowledge of N , p_o may be obtained. Also the extrapolated intercept of the line with the ordinate will give the value of $(\alpha_e + \alpha_i)$. The determination of dipole moments has contributed a great deal to our knowledge of molecular structure. For example, CCl_4 and CH_4 , according to Fig. 6.6, do not possess permanent dipole moments, in agreement with the symmetric structure of these molecules. Similarly, the fact that H_2O has a dipole moment of 1.84 D, whereas CO_2 has no dipole moment, indicates that the CO_2 molecule has a linear structure, whereas in H_2O the two OH bonds must make an angle different from 180° with each other.

It must be noted that only electrostatic fields have been considered in the above discussion. Further the value of N is considered sufficiently low so that the interaction between the gas molecules could be neglected. In that case, the field acting at the location of a particular molecule is to a good approximation equal to the applied field \vec{E} .

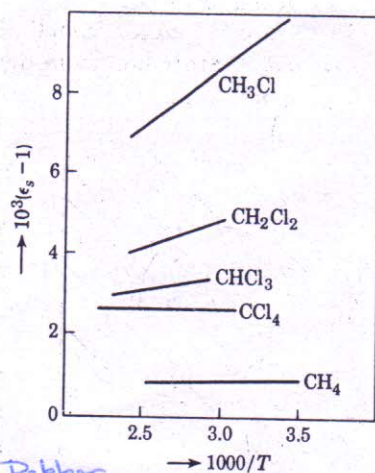


Fig. 6-6. Temperature variation of the static dielectric constant of some vapors.

7. Problems

1. Calculate the induced dipole moment per unit volume of He gas if it is placed in an electric field of 6000 V/cm. Given $\alpha_{\text{He}} = 0.18 \times 10^{-40} \text{ F.m}^2$ and $\text{density} = 2.6 \times 10^{25} \frac{\text{atoms}}{\text{m}^3}$.
2. For argon, electric polarizability is $1.43 \times 10^{-40} \text{ F.m}^2$. Find the dielectric constant given gas density is 1.8 g/cm^3 and atomic mass of argon is 39.95 g/mole .
3. A parallel plate capacitor of area $4 \times 5 \text{ sq. cm}$ is filled with mica ($\epsilon_r = 6$). The distance between the plates is 1 mm , and the capacitor is connected to a 100 V battery. Calculate (a) the capacitance of the capacitor, (b) the free charge on the plates, (c) the polarized charge surface density. Repeat the calculation for a dielectric with $\epsilon_r = 5$. Explain the difference in results in the two cases.
4. Calculate the field strength required to reach 0.1 per cent of the saturation value of the orientational polarization of a dipolar gas at room temperature if the dipoles have a strength of 1 Debye unit.
5. A hydrogen atom (with the Bohr radius of 0.5 \AA) is situated between two metal plates 1 mm apart, which are connected to opposite terminals of a 500 V battery. What fraction of the atomic radius does the separation distance S amount to, roughly? Estimate the voltage you will need with this apparatus to ionize the atom.