

6-3. Orientational polarization

In this section we shall consider the polarizability of a molecule in a static field, resulting from its permanent dipole moment. Consider, for example, a gas containing a large number of identical molecules, each with a permanent dipole moment μ . Without an external field, the dipoles will be oriented at random and the gas as a whole will have no resulting dipole moment. An external field E will exert a torque on each dipole and will tend to orient the dipoles in the direction of the field (see Fig. 6-4). On the other hand, this ordering influence of the external field will

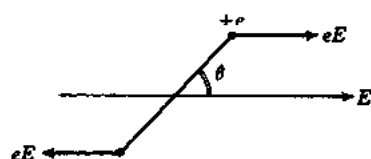


Fig. 6-4. Illustrating the torque exerted on a dipole by an external field.

be counteracted by the thermal motion of the particles. The problem therefore may be stated as follows: What is the average component of the dipole moment per molecule in the direction of the applied field at a temperature T ? To answer this question it will be assumed that the dipoles may rotate freely. We then have before us a simple problem in statistical mechanics.

Let us define the potential energy of a dipole making a 90° angle with the external field as zero. The potential energy corresponding to an angle θ between μ and E is then equal to

$$-\mu E \cos \theta = -\mu \cdot E \quad (6-12)$$

According to statistical mechanics, the probability for a dipole to make an angle between θ and $\theta + d\theta$ with the electric field is then proportional to

$$2\pi \sin \theta d\theta \exp [(\mu E \cos \theta)/kT]$$

where $2\pi \sin \theta d\theta$ is the solid angle between θ and $\theta + d\theta$. Hence the average component of the dipole moment along the field direction is equal to

$$\mu \langle \cos \theta \rangle = \frac{\int_0^\pi \mu \cos \theta \sin \theta d\theta \exp [(\mu E \cos \theta)/kT]}{\int_0^\pi \sin \theta d\theta \exp [(\mu E \cos \theta)/kT]} \quad (6-13)$$

To evaluate the integrals, let

$$(\mu E/kT) \cos \theta = x \quad \text{and} \quad (\mu E/kT) = a \quad (6-14)$$

We then obtain

$$\langle \cos \theta \rangle = \frac{1}{a} \frac{\int_{-a}^{+a} x e^x dx}{\int_{-a}^{+a} e^x dx} = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} = L(a) \quad (6-15)$$

The function $L(a)$ is called the Langevin function, since this formula was first derived by Langevin in 1905 in connection with the theory of paramagnetism.³ In Fig. 6-5, $L(a)$ has been plotted as a function of $a = \mu E/kT$. Note that for very large values of a , i.e., for high field strengths, the function approaches the saturation value unity. This situation would correspond to complete alignment of the dipoles in the field direction, because then $\mu \langle \cos \theta \rangle = \mu$.

As long as the field strength is not too high and the temperature is not too low, the situation may be strongly simplified by making the approximation $a \ll 1$ or $\mu E \ll kT$. Under these circumstances the Langevin function $L(a) = a/3$, so that then

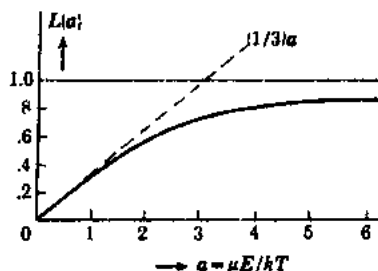


Fig. 6-5. The Langevin function $L(a)$. For $a \ll 1$, the slope is $1/3$.

$$\mu \langle \cos \theta \rangle = (\mu^2/3kT)E \quad \text{for } \mu E \ll kT \quad (6-16)$$

As an example of the condition implied in (6-16), consider a field of 3000 volts per cm. The dipole moment μ of a molecule is of the order of 10^{-10} esu of charge times 10^{-8} cm, i.e., about 10^{-18} cgs units,⁴ so that $\mu E \approx 10^{-17}$ in cgs units. On the other hand, kT at room temperature is of the order of 10^{-14} erg and for this example the condition is certainly satisfied. In this example saturation would be approached only in the vicinity of 1°K . It may be noted that the quantum mechanical treatment of this problem leads essentially to the same results as obtained here.⁵

The existence of electric dipoles in molecules was first postulated by Debye in 1912;⁶ this concept has contributed a great deal to the present understanding of dielectrics as well as to our knowledge of molecular structure. We shall now see how the molecular quantities α_e , α_s , and μ enter in the description of the macroscopic dielectric constant.

³ P. Langevin, *J. Physique*, 4, 678 (1905).

⁴ 10^{-18} esu cm is called a "Debye unit."

⁵ See, for example, P. Debye, *Polar Molecules*, Dover, New York, 1945.

⁶ P. Debye, *Phys. Z.*, 13, 97 (1912).

6-4. The static dielectric constant of gases

We are now in a position to give an atomic interpretation of the static dielectric constant of a gas. It will be assumed that the number of molecules per unit volume is small enough so that the interaction between them may 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 E . Suppose the gas contains N molecules per unit volume; the properties of the molecules will be characterized by an electronic polarizability α_e , an atomic polarizability α_a , and a permanent dipole moment μ . From the discussions in the preceding two sections it follows that, as a result of the external field E , there will exist a resulting dipole moment per unit volume:

$$P = N(\alpha_e + \alpha_a + \mu^2/3kT)E \quad (6-17)$$

Note that only the permanent dipole moment gives a temperature-dependent contribution, because α_e and α_a are essentially independent of T . If the gas fills the space between two capacitor plates of area A and separation d , the total dipole moment between the plates will be equal to

$$M = PAD$$

This simple relation shows immediately that the same total dipole moment would be obtained by assuming that the dielectric acquires an induced surface charge density P at the boundaries facing the capacitor plates, as discussed in Sec. 6-1. Hence the quantity P introduced here as the dipole moment per unit volume is identical with the quantity P introduced in Sec. 6-1, where it represented the induced surface charge density at the dielectric-plate interface. Therefore, combination of (6-17) and (6-6) leads immediately to the Debye formula for the static dielectric constant of a gas.⁶

$$\epsilon_s - 1 = 4\pi P/E = 4\pi N(\alpha_e + \alpha_a + \mu^2/3kT) \quad (6-18)$$

As an example of an application of this formula, we show in Fig. 6-6 the temperature dependence of some organic substances in the gaseous state.⁷ Note that $(\epsilon_s - 1)$ has been plotted versus the reciprocal of the absolute temperature, leading to straight lines, in agreement with formula (6-18). From the slope of the lines and a knowledge of the number of molecules per unit volume, the dipole moment μ may be obtained. Also, from the extrapolated intercept of the lines with the ordinate, one can calculate $(\alpha_e + \alpha_a)$. The determination of dipole moments has contributed a great deal to our knowledge of molecular structure. For example, CCl_4 and

⁷ R. Sanger, *Phys. Z.*, **27**, 556 (1926).

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 Debye units, 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.⁸

6-5. The internal field according to Lorentz

The theory of the dielectric constant of solids and liquids is much more complicated than that for gases. In gases one may, to a good approximation, assume that the field acting on the particles is equal to the externally applied field E . (In solids and liquids, however, a given molecule or atom "sees" not only the external field, but the fields produced by the dipoles on other particles as well. As a result of the long range of Coulomb forces, the latter contribution can no longer be neglected. The central problem in the theory of the dielectric constant of liquids and solids is therefore the calculation of the field at the position of a given atom. This field is called the internal or local field and is different from the externally applied field E .)

(To calculate the internal field, the following method was suggested by Lorentz:⁹ Select a small spherical region from the dielectric with the atom for which the local field must be calculated at the center (see Fig. 6-7).) The radius of the sphere is chosen large enough to consider the region outside the sphere as a continuum of dielectric constant ϵ_1 . For the region inside the sphere, however, the actual structure of the substance must be taken into account. The following contributions to the internal field at the location of the atom then arise:

- (i) The contribution from the charge density on the plates, giving $4\pi q = D$.

⁸ For a table of dipole moments of a large number of molecules, see, for example, the article on dielectric polarization by O. Fuchs and K. L. Wolf, *Hand- und Jahrbuch der chemischen Physik*, Vol. 6, Leipzig, 1935.

⁹ H. A. Lorentz, *The Theory of Electrons*, Teubner, Leipzig, 1909, Sec. 117.

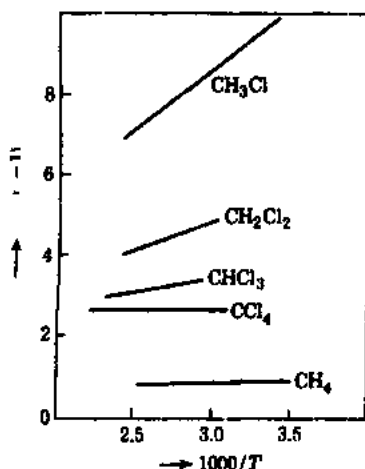


Fig. 6-6. Temperature variation of the static dielectric constant of some vapors. [After Sanger, ref. 7]