DIELECTRIC PROPERTIES OF PURE LIQUIDS[1]

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1. There are now no essential difficulties in understanding the dielectric properties of gases at sufficiently low pressures, if one takes into account the fact that the molecules are not only polarizable but can also be oriented because of the existence of a permanent electric dipole. The same situation exists also for dilute solutions of polar molecules in non-polar solvents, if we neglect small corrections arising from the effect of the solvent. The situation is quite different, however, when one tries to understand on the basis of the theory developed for gases the dielectric properties of the common pure liquids in which the molecules approach each other closely. Particularly impressive is this complication in the case of liquids with relatively small, highly polar molecules. However, it must be stressed that the complications are not confined to this particular limiting case. They appear, even if not in such a striking fashion, in the case of all liquids, even the non-polar ones, and clearly have as their origin the mutual influences of the neighboring molecules, which are not necessarily connected with the existence of permanent dipoles.

2. It is clear then that the main problem in the understanding of pure liquids is the interpretation of the mutual interactions between the molecules. A very striking example of these general considerations is water. The molecule H_2O is polar and has a dipole moment equal to 1.84×10^{-18} electrostatic units, according to measurements made with water vapor. This enables one to calculate the molecular orientation-polarization, with the aid of the well-known equation

$$P_0 = \frac{4\pi}{3} N \frac{\mu^2}{3kT} \tag{1}$$

in which N is the Avogadro number, μ is the moment, k is the Boltzmann constant, and T is the absolute temperature. Thus the theoretical value

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of P_0 is equal to 71 cc. The experiments with liquid water give, however, a dielectric constant $\epsilon = 81$, and from this, using the equation

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} \qquad (2)$$

one obtains for liquid water the total molecular polarization $P = 17$ cc. In this equation M is the molecular weight and d is the density. Part of this value is to be ascribed to the polarizability of the molecules and not to their orientations. This amounts, as one knows from the optical refractive index measurements, to about 4 cc. Hence in contrast to the calculated value $P_0 = 71$ cc., one obtains from the experiments for the liquid only $P_0 = 13$ cc. as the orientation-polarization. One cannot believe that the dielectric properties of a water molecule can be influenced to such an extent by the close proximity of the other molecules. It is much more natural to believe that in the liquid the orientation of a molecule is influenced by its neighbors while measurements in the electric field are being made. Accordingly, equation 1, which presupposes completely free rotation, should not be applied to liquids without large corrections. A very beautiful example of how such corrections become of practical importance when the molecules approach each other is to be found in the measurements of the dielectric constant of sulfur dioxide at high densities by Eversheim (1902). At a temperature of 150°C. and a density of $\delta = 0.76$ g. per cubic centimeter a value $P_0 = 33$ cc. is found for the orientation-polarization, whereas from the known dipole data one calculates $P_0 = 37$ cc. Here the two values are still quite close together. However, at a temperature of 14.5°C. and a density of $\delta = 1.39$ g. per cubic centimeter the value $P_0 = 27$ cc. is obtained, while the theoretical value is $P_0 = 55$ cc.

A study of the electric double refraction (Kerr effect) shows very clearly that also in the case of non-polar liquids the free rotation is considerably inhibited, as has been mentioned before. As an example of such molecules we mention carbon disulfide. From measurements of the electric double refraction in the vapor phase one calculates for the three polarizabilities of the molecule, $\alpha_1 = 15.1 \times 10^{-24}$ in the direction of the S—C—S molecular axis and $\alpha_2 = \alpha_3 = 5.54 \times 10^{-24}$ in the directions perpendicular to the molecular axis. From these data one calculates for the Kerr constant of the liquid, according to the equation

$$\frac{n_p - n_s}{n_0} = K \mathscr{E}^2 \qquad (3)$$

the value $K = 19.7 \times 10^{-12}$. In the equation n_p is the refractive index parallel to the field, n_s is the refractive index perpendicular to the field,

n_s is the normal refractive index, and $\mathscr{E}$ is the field strength in electrostatic units. Direct measurements with the liquid give instead a value 40 per cent lower, namely $K = 11.8 \times 10^{-12}$. Nevertheless, the average polarizability of the molecule, $\alpha = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3)$, is not affected by the change to the liquid state, as one can conclude from the comparison of the refractive indices of the gas and the liquid using the Lorenz–Lorentz equation. One has, therefore, the alternative either of assuming that the differences in the polarizabilities of the molecule in different directions have been decreased on a change to the liquid state, while their sum remains unchanged, or that in the liquid the molecule is no longer free to orient itself in the external field as it is in the gas. Obviously the second alternative is to be selected.

3. Through these preliminary considerations we are led to concentrate our attention on the binding which exists between the molecules in a liquid. Such binding is quite familiar to us from the study of the solid state, where it is responsible for the elastic properties of crystals. From the point of view of the van der Waals continuity between gases and liquids, understanding of these forces is more difficult. However, even from the point of view of the classical theory one can raise the question as to how far the transition to the solid state has been achieved in the liquids. Indeed, within the last few years a variety of experiments has demonstrated that one is justified in discussing the quasi-crystalline structure of liquids. After the first joint experiments of the speaker and Scherrer had demonstrated (1916) that one obtains interference maxima in the scattering of x-rays by liquids, many experiments of other investigators, among which should be mentioned the studies of Keesom on liquefied gases and the extended and beautiful investigations of Stewart (Iowa), have clearly interpreted the origin of the main interference maxima. There must exist in the liquids small regions of space within which the relative orientation of molecules approximates very nearly the perfectly regular arrangement in the solid cluster, the only difference between the two being that in liquids this orientation depends on time. A particularly clear understanding of the situation is obtained from the study of the scattering of x-rays by monatomic liquids, as, for instance, mercury. Where the single atoms give an intensity of scattered rays which monotonously decreases with increasing angle between the primary and the secondary ray, the same atom present as a liquid produces very noticeable interference maxima and minima. In this particular case it is even possible to determine the mutual orientation and the preferred distances between the atoms from a probability curve to be deduced from the scattering measurements. It thus becomes clear that in molecular orientation the liquids behave as quasi-crystals.

As the experiments with the scattering of light of ordinary frequencies

demonstrate, there exists a similarity between the liquids and the crystals not only in the orientation but also in the types of allowed molecular motions. If one studies monochromatic light scattered by a liquid with the aid of an apparatus with high resolving power, such as an echelon-grating, one finds that the originally monochromatic line has been split into a narrow triplet due to the process of scattering. The magnitude of the separation of the triplet components depends on the direction at which the observation is made, and is the greatest at a scattering angle of 180°. The central line of the triplet has the same frequency as the original light. The separation of the two exterior symmetric components of the triplet is the larger, the higher the sound velocity in the liquid. These facts, which have been established in experiments of Gross, Meyer, Raman, and others, would be entirely incomprehensible if the molecules in the liquid had freedom of motion independently of each other. In that case the molecular motions would produce not a splitting of the original line into a triplet but merely a broadening of it. We know that in an ideal solid body the motions of an atom are to be understood as superposition of motions which produce a very large number of thermal sound waves which are propagated through the body in all directions. The correctness of the T^3 law for the specific heat of solid bodies at low temperatures is the experimental proof of this. L. Brillouin has investigated in a theoretical work the scattering of light in an ideal solid body, and finds that this scattering must be considered as a Bragg reflection by the sound waves and that in consequence of the coöperation of the Doppler effect the primary spectral line must be split into a doublet.

Liquids do not exhibit a broadening but a splitting. From this we conclude, following Brillouin's calculation, that the motions of neighboring molecules are strongly coupled in liquids also, just as in solid bodies. The fact that in addition to the doublet of the Brillouin theory, one observes with liquids the third, unshifted line is obviously to be explained as meaning that a liquid is not an ideal solid body. As is well known even for crystals the ideal solid body is only a limiting case which can never be realized in practice, because it cannot have any heat expansion. Reasoning in this manner Placzek and Landau have recently interpreted, in a short letter to the author, the intensity of the middle component of the scattered light as connected with the difference of heat capacities of liquids at constant pressure and of constant volume. Recent experiments carried out in Leipzig have indeed confirmed this interpretation of the intensity distribution among the three lines of the scattered light. Altogether one can conclude with complete certainty that the orientation and coupling of molecules in liquids are very similar to the binding of molecules in solid crystals.

4. In order to obtain an idea as to the mode of motion of an atom in a monatomic liquid by using the concepts which we have now developed, we make the following statements. The atom is vibrating very much as in a solid crystal, and therefore has on the average approximately the same amount of kinetic as well as potential energy. However, and this is typical of the liquid, the center of vibrations is not stationary but instead moves slowly through the liquid as in Brownian motion. In perfect agreement with this is the observation that the heat capacity of liquid mercury has very nearly the value required by the Dulong–Petit law. Of far greater interest to us is, however, the behavior not of monatomic liquids but of liquids consisting of rather complex molecules. In this case we are much more interested not in translational motions of the center of gravity of a molecule, but in rotations of the molecule. One is tempted to form a picture of this motion which is very similar to that developed for the translations. It should not be considered a free rotation but rather a kind of torsional vibration, the axis of which undergoes a slow rotation in space instead of being rigidly fixed as it is in the case of torsional vibrations in crystals.

When one tries to apply these ideas to the mathematical problem of the dipole orientation in liquids, one concludes that the molecules are influenced in liquids by two kinds of forces. First, the molecule is exposed to the usual couple due to the external electric field; and second, there exists a potential energy which acts to hold the molecule in its instantaneous position fixed by its surroundings. For this potential energy one can assume as the very simplest approximation an expression of the form

$$u = - E \cos \theta \qquad (4)$$

where θ is the angle between the axis of the permanent electric moment and the instantaneous axis fixed by the surroundings. It is quite obvious that an equation of the form 4 is not capable of representing the detailed behavior in all special cases. However, one can regard equation 4 as the first term in a series of spherical harmonics, and hope that even this first term is a good approximation to reality. The total energy of a dipole in a field F is to be obtained by adding to the energy given by equation 4 also the field energy $-\mu F \cos \theta'$, where θ' is the angle between the dipole axis and the external field. One can readily calculate the average component of the dipole in the direction of the field F. However, this will depend to a great extent on the angle between the field and the axis, which is fixed by the surroundings of the molecule. The final average observable moment in the direction of F is then to be obtained by averaging over all such orientations caused by the molecular surroundings. The quantitative expression representing this average moment in the direction of F is given by

$$m = \frac{\mu^2}{3} \frac{E}{kT} [1 - L^2(\beta)] \tag{5}$$

in which β is an abbreviation for $\beta = \frac{E}{kT}$, and L is the well-known function of Langevin so useful in the theory of magnetization, namely

$$L(\beta) = \coth \beta - \frac{1}{\beta} \tag{5'}$$

Equation 5 shows, according to our expectations, that the interactions between the molecules of a liquid interfere with the orientation of the dipoles in an external field. The classical value

$$m = \frac{\mu^2 F}{3kT}$$

which one obtains for the completely freely rotating molecules, is now to be multiplied by a factor $[1 - L^2(\beta)]$, less than unity. In the case of small binding forces $(E \ll kT)$ this factor is very nearly unity, and in the cases of large binding forces $(E \gg kT)$ it tends towards the value

$$\frac{2}{\beta} = \frac{2kT}{E}$$

which it reaches for very large values of binding energy E, so that then the effect of permanent dipoles is completely eliminated. One can estimate this factor as equal to unity less the ratio of the value of the average moment in the direction of the instantaneous axis in the absence of the external field to the absolute value of the moment. It is most noteworthy that this result holds irrespective of the special assumptions involved in defining equation 4, and is valid for any arbitrary law of force.

Let us now consider the applications of equation 5 and start by considering the case of water. The experimentally determined molecular orientation polarizability was 13 cc., whereas the theoretically calculated one for the case of freely rotating molecules is 71 cc. Thus the experimental reduction factor is $13/71 = 2/11$. According to the above theory this reduction factor for the case of strong binding forces, which are obviously present here, is equal to $2/\beta$. We will obtain an agreement with experiment, therefore, if we assign to the binding energy in liquid water, in agreement with the definition of β, the value $E = 11\ kT$. This is an extremely large value; it produces a hindering of orientation such as would be produced by a field of some 72,000,000 volts per centimeter. From a molecular point of view, however, this magnitude of energy is quite understandable, since a

field strength of 72,000,000 volts per centimeter would be produced by a water dipole at a distance of 2.5×10^{-8} cm. Approximately the same value of E is observed for instance in the case of nitrobenzene, whereas for the liquid diethyl ether the reduction factor is almost unity, so that E is almost equal to zero and the molecules must have an almost free rotation. In between these extremes are to be found the alcohols. Thus for ethyl alcohol the reduction factor is 0.56, which means, according to equations 5 and 5′, that the binding energy is $E = 2.9\,kT$. With increasing length of the carbon chain in alcohols this binding energy decreases.

5. The preceding estimates indicate that the magnitude of the binding energy E is an excellent measure of the extent of that type of association in liquids which affects the orientation. The representation of the binding energy through an equation as simple as equation 4 and the use made of it in the following calculations is, of course, to be regarded as the first rather crude approximation to reality. In this connection it becomes of considerable interest to see how far this representation is capable of explaining other, thus far not considered, properties of liquids. A phenomenon which is very characteristic of the dipole orientation is the decrease in dielectric constant observed with a strong external field. It is particularly in the case of the saturation that enormous differences between theory and experiment are to be observed with associated liquids. The first accurate measurements of the saturation effect were made on ethyl ether by Herweg. His measurements corrected for electric double refraction and electrostriction were discussed by means of a formula derived from the dipole theory adapted to molecules with free rotation. It was

$$\epsilon = \epsilon_0 - \frac{4\pi}{15}\,n\,\frac{\mu^4}{k^3T^3}\left(\frac{\epsilon_0 + 2}{3}\right)^4 \mathscr{E}^2 \qquad (6)$$

In this formula ϵ is the dielectric constant measured in the field $\mathscr{E}$ and n is the number of molecules per cubic centimeter in the liquid. For ethyl ether, the only substance used in his experiments, there was perfect agreement between theory and experiment. Later on Malsch thought that the experiment would be easier working with liquids of high dielectric constant, for in this case the inner field strength is greater than the external field strength by the factor

$$\frac{\epsilon_0 + 2}{3}$$

There were some difficulties, derived from the fact that all liquids with high dielectric constants are conducting, but these difficulties were overcome by a special method. The results of the experiment were in com-

plete disagreement with the theory. Thus, for instance, one obtains from equation 6 that for water

$$\frac{\epsilon - \epsilon_0}{\epsilon_0} = -3.9\left(\frac{\mathscr{E}_v}{100,000}\right)^2$$

if the external field strength $\mathscr{E}_v$ is measured in volts per centimeter. On the contrary, the experimental results gave

$$\frac{\epsilon - \epsilon_0}{\epsilon_0} = -1.1 \times 10^{-3}\left(\frac{\mathscr{E}_v}{100,000}\right)^2$$

It is seen that for water the experimental effect is 3500 times smaller than that calculated. In other cases similar, although not so enormous, differences occur; thus for instance in the case of ethyl alcohol the observed effect is fourteen times smaller than the calculated.

The question arises whether these differences can be understood as a result of the quasi-crystalline structure of the liquids and whether they can be explained quantitatively with the help of our former assumptions. By assuming for the binding energy the same formula as before, i.e., $u = -E\cos\theta$, and by calculating the orientation-polarization to a higher approximation, the result is that in equation 6 the second member has to be multiplied by a reduction factor R. This factor can be represented by the formula

$$R(\beta) = 3\left[(1 - 4L^2 + 3L^4) + 4\frac{L}{\beta}(2L^2 - 1) + 6\frac{L^2}{\beta^2}\right] \qquad (7)$$

in which again L represents Langevin's function. For large values of $\beta = E/kT$, R is given by

$$R(\beta) = 3/\beta^4 \qquad (7)$$

Now if for water Malsch's results are adopted, $3/\beta^4 = 1/3500$ and $\beta = 10$, that is to say $E = 10\,kT$. This means that the same binding energy which had to be assumed to understand the value of the orientation-polarization, which is 5.5 times smaller than the calculated value, explains at the same time why the saturation effect is found experimentally to be 3500 times smaller than the one calculated. It is true that a small difference exists, in that $E = 11\,kT$ has been derived from the orientation-polarization, whereas in this case $E = 10\,kT$ is found, but this difference is within the experimental error of the Malsch measurements. The results found in the cases of ethyl alcohol and ethyl ether are also satisfactory. In the first case, in which the saturation effect has been found to be fourteen times smaller than that calculated, it follows that $\beta = 2.9$. This is

in accordance with the value derived for β from the orientation-polarization. In the second case we know that the orientation-polarization nearly equals the value calculated for free molecules and we understand, therefore, why Herweg could represent his experimental results by means of equation 6 without introducing any reduction factor at all.

6. Another phenomenon which is characteristic of substances with polar molecules is the anomalous dispersion and absorption in the range of long electric waves, which was discovered by Drude. The theory, which so far has only been applied to the case of free dipoles, gives an explanation of this effect by stating that at high frequencies a phase difference exists between the electric field and the dipole orientation. This can be expressed formally by an equation giving the average moment m in a field of the strength $Fe^{i\omega t}$ as follows:

$$m = \frac{\mu^2}{3kT} \frac{Fe^{i\omega t}}{1 + \dfrac{i\rho\omega}{2kT}} \tag{8}$$

The constant ρ of this formula is a measure of the friction opposing rotation, and if the molecule is represented by a sphere of the radius a, and if η is the coefficient of viscosity of the liquid,

$$\rho = 8\pi\eta a^3 \tag{8'}$$

In this way we not only express that the dispersion and absorption effect is limited to the case of polar liquids, but also that the frequency at which these effects occur is intimately connected with the viscosity of the liquid. Many observers have made experiments which indicate that this connection between viscosity and frequency is qualitatively correct, but in certain cases it was necessary to introduce a molecular radius, a, smaller than the value known to be correct. A very characteristic example of such a case is glycerin. It can be said that for particles of molecular dimensions we have no experience as to their frictional constants and that it is not impossible that in such a case Stokes' formula, containing the ordinary viscosity constant, does not hold. On the other hand, it is not to be forgotten that the temperature variation of the dispersion and absorption effect is closely related to the temperature variation of the viscosity. From this point of view it seems interesting to calculate how much the theoretical result will be influenced by the fact that the molecules are not free but that we have to deal with a quasi-crystalline structure.

The calculations are much more complicated than those we had to deal with; it will be sufficient here to give only the main outline. An equation has to be found for the distribution function f of the dipole axis, the latter

being at the same time under the influence of the molecular binding energy u_0, and the variable field $Fe^{i\omega t}$ causing an energy of orientation

$$u_1 = -\mu Fe^{i\omega t}\cos \theta'$$

As in the case of free dipoles an equation for Brownian motion of rotation can be used. If, moreover, the effect is taken into account, the external field can only create a very small orientation effect, and the problem can be formulated as follows.

If the total energy of a dipole as it is influenced by its surroundings and by the electrical field can be represented by

$$u = u_0 + u_1 e^{i\omega t}$$

and if we assume

$$f = f_0 + f_1 e^{i\omega t}$$

we obtain

$$f_0 = C \cdot e^{-\frac{u_0}{kT}}$$

and the function f_1 is found as a solution of the equation

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \left[\frac{\partial f_1}{\partial \theta} + \frac{f_1}{kT} \frac{\partial u_0}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{\partial f_1}{\partial \phi} + \frac{f_1}{kT} \frac{\partial u_0}{\partial \phi} \right] - \frac{i\omega\rho}{kT} f_1$$
$$= -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \left[\frac{f_0}{kT} \frac{\partial u_1}{\partial \theta} \right] - \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{f_0}{kT} \frac{\partial u_1}{\partial \phi} \right] \tag{9}$$

in which θ and ϕ are the ordinary spherical coördinates.

The solution of the problem can be represented in the following way. Starting with the equation,

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \left[\frac{\partial X_n}{\partial \theta} + \frac{X_n}{kT} \frac{\partial u_0}{\partial \theta} \right] + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi} \left[\frac{\partial X_n}{\partial \phi} + \frac{X_n}{kT} \frac{\partial u_0}{\partial \phi} \right] + \lambda_n X_n = 0 \tag{10}$$

one has to find first of all such values of λ_n that the functions X_n can be considered as eigenfunctions on the sphere. Thus we have obtained a generalization of the ordinary spherical harmonics which represent the X_n for $u_0 = 0$ with $\lambda_n = n(n + 1)$. If then these functions are known, the right-hand term in equation 9 can be represented by an expansion in series of the form

$$\Sigma c_n X_n$$

and we find

$$f_1 = \sum \frac{c_n X_n}{\lambda_n + \dfrac{i\omega\rho}{kT}}$$

This is the way that was followed, assuming equation 4 for the binding energy. However, it was only possible to represent the functions by expanding them in powers of

$$\beta = \frac{E}{kT}$$

For small values of β, and at the same time for small values of $\omega\rho/kT$, the average moment, m, is given by the expression

$$m = \frac{\mu^2 F e^{i\omega t}}{3kT} \left[\left(1 - \frac{\beta^2}{9} \right) - \frac{i\omega\rho}{2kT} \left(1 - \frac{11}{54} \beta^2 \right) \right] \qquad (12)$$

For large values of β calculations are much simpler, because in this case the motion of the dipole can be approximated by a simple vibration about an axis defined by the interaction of the surrounding molecules. In this limiting case the result is

$$m = \frac{\mu^2 F e^{i\omega t}}{3kT} \cdot \frac{1}{\dfrac{\beta}{2} + \dfrac{i\rho\omega}{2kT}} \qquad (12')$$

It is very simple to judge the results to be drawn from these formulas for the limiting cases $\beta = 0$ and $\beta \gg 1$. If they are represented as in

$$m = \frac{\mu^2 F e^{i\omega t}/3kT}{1 + \dfrac{i\rho\omega}{2kT}} \ (\beta = 0); \qquad m = \frac{\mu^2 F e^{i\omega t} \Big/ 3\dfrac{E}{2}}{1 + \dfrac{i\rho\omega}{2\dfrac{E}{2}}} \ (\beta \gg 1) \quad (12'')$$

it is seen that the transition from the case of that of free dipoles to strongly bound dipoles can be performed by replacing the thermal energy kT by the much larger energy $E/2$. It follows then from the formulas for the dielectric losses and for the dispersion effect that we have at the same time a diminution of the dipole action to be observed both in the dielectric constant itself and in the losses. The binding energy is acting (in the case of large values of β) just as if the constant

$$\rho = 8\pi\eta a^3$$

had been diminished, and this can be interpreted by saying either that the viscosity is less than normal or that the molecular radius is smaller than would be expected.   Further experiments are still necessary, but the fact that the greatest differences between experiment and theory occur for highly associated liquids makes it probable that also in this case the difficulties will be overcome by taking account of their quasi-crystalline structure.