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THEORY OF DIELECTRIC RELAXATION*

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1. INTRODUCTION

The theory of dielectric relaxation proposed in 1913 by Debye has been extremely useful in accounting for many experimental observations. However with the development of submillimetre spectroscopy the Debye theory became inadequate. During the period 1974-1980 theoretical investigations of dielectric relaxation based on rotational Brownian motion were carried out at the Dublin Institute for Advanced Studies. The present lectures give a summary of these investigations and of their implications for dielectric relaxation experiments. A fuller account with detailed explanations and calculations, together with a bibliography, may be found in ref. 1.

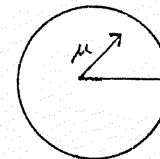
In the next section basic physical quantities encountered in the study of dielectric relaxation will be defined. In section 3 the Debye theory is described and in section 4 a summary is given of mathematical formulae required for a discussion of Brownian motion. These are applied to the calculation of complex permittivity for orientational polarization in section 5. In the following section the relation between theoretical and experimental results is considered, and the final section consists of a brief conclusion.

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2. DEFINITIONS

We begin by explaining what is meant by dielectric relaxation¹⁾. Suppose that we have a molecule like Na Cl (common salt) or CH Cl₃ (chloroform) or CH₃ C Cl₃ (methyl chloroform) that has a permanent electric dipole. We call such a molecule a polar molecule.

In the case of methyl chloroform the molecule is approximately a sphere. Let us therefore put down a sphere, and suppose that the dipole has strength μ and that its axis lies along a radius. Imagine that the sphere is being tossed around by random couples, as happens if it is in Fig.1. A polar spherical molecule. a heat bath. We denote by $\underline{n}(t)$ a unit vector in the direction of the dipole moment at time t , so that the dipole moment vector $\underline{\mu}(t) = \mu \underline{n}(t)$.



Next let us consider a dielectric composed of polar molecules. If a constant electric field has been applied in a fixed direction for a long time, the dipoles will tend to orient themselves somewhat in the same direction. In order to keep the picture as simple as possible we assume that we have a spherical portion of the dielectric, that the material is isotropic, that it is uniformly polarized and that electric fields are so weak that we may employ a linear theory. Then the induced moment of the dielectric will be in the direction of the constant field. At time $t=0$ the field is removed and the system under the influence of the thermal motion of the environment tends to revert to a random arrangement.

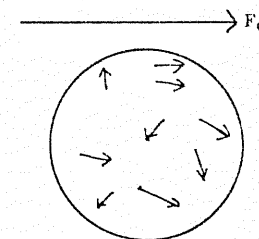


Fig. 2. Orientation of dipoles influenced by a static field F_0 .

This process is called dielectric relaxation. If we assume that each polar molecule relaxes independently of its neighbours, the quantity $(\underline{\mu}(0) \cdot \underline{\mu}(t))$

or $(\underline{n}(0) \cdot \underline{n}(t))$ will be a measure of the relaxation of the molecule. On averaging over all the molecules of the system it will follow that the relaxation of the whole dielectric sample will be related to $\langle (\underline{n}(0) \cdot \underline{n}(t)) \rangle$, the mean value of $(\underline{n}(0) \cdot \underline{n}(t))$. We call $\langle (\underline{n}(0) \cdot \underline{n}(t)) \rangle$ the autocorrelation function of $\underline{n}(t)$.

The next idea that we introduce is permittivity for an isotropic medium. As you know from the theory of electrostatics, there is associated with a static field F_0 in a fixed direction an electric displacement D_s given by

$$D_s = \epsilon_s F_0$$

The factor of proportionality ϵ_s is the static relative permittivity. The electric displacement due to a periodic field in a fixed direction $F_0 \cos \omega t$ which has been applied for a long time will have frequency $\frac{\omega}{2\pi}$ but will be a linear combination of $\cos \omega t$ and $\sin \omega t$. To obtain this combination we may put $F_0 e^{i\omega t} = F$, write

$$D = \epsilon(\omega) F \quad (1)$$

and equate real parts on each side. We call $\epsilon(\omega)$ the complex relative permittivity and, to conform with the convention adopted by engineers, we write

$$\epsilon(\omega) = \epsilon'(\omega) - i \epsilon''(\omega).$$

When $\omega = 0$, we have the static case and so

$$\epsilon'(0) = \epsilon_s, \quad \epsilon''(0) = 0.$$

There is another constant permittivity denoted by ϵ_∞ that will appear later in our calculations. When the frequency $\frac{\omega}{2\pi}$ is sufficiently high, the dipole axis will not rotate. By ϵ_∞ we mean the permittivity for a frequency just sufficiently high to prevent this rotation.

The quantity $\epsilon'(\omega)$ is called the relative permittivity, and $\epsilon''(\omega)$ is called the loss factor because it is related to the loss of electromagnetic radiation in its passage through a dielectric. If for different values of ω we plot the points $(\epsilon'(\omega), \epsilon''(\omega))$ as cartesian coordinates referred to rectangular axes, we shall obtain a curve called the Cole-Cole plot due to the brothers K.S. and R.H. Cole. This plot is often used by experimentalists.

We shall now relate complex permittivity to the absorption and dispersion of electromagnetic radiation in a dielectric. According to Maxwell's equations the quantities F and D in (1) satisfy

$$\nabla^2 F - \frac{1}{c^2} \frac{\partial^2 D}{\partial t^2} = 0. \quad (2)$$

On taking a plane wave solution of this equation it is found that the index of refraction is a function $n(\omega)$ of the angular frequency given by

$$n(\omega) = \sqrt{\frac{|\epsilon(\omega)| + \epsilon'(\omega)}{2}}, \quad (3)$$

where $|\cdot|$ denotes absolute value. This gives the dispersion effect in the dielectric, that is, the way in which the index of refraction depends on the frequency. Secondly we may deduce from (2) how electromagnetic radiation is absorbed when it passes through the dielectric. Indeed we find that the intensity of radiation decreases by a factor e in a distance $\frac{1}{a(\omega)}$ given by

$$a(\omega) = \frac{\sqrt{2}\omega}{c} \sqrt{|\epsilon(\omega)| - \epsilon'(\omega)}. \quad (4)$$

We call $a(\omega)$ the absorption coefficient. It is usually expressed in neper cm^{-1} . This is the reciprocal of the number of centimetres in which the intensity drops by a factor e . The graph of $a(\omega)$ as a function of ω , or of frequency $\frac{\omega}{2\pi}$ or of wave number $\frac{\omega}{2\pi c}$, which is just the reciprocal of the wave length, is called an absorption curve and a similar graph of $n(\omega)$ is called a dispersion curve.

In future when speaking of the polarization of dielectrics we shall confine our attention almost entirely to orientational polarization, that is, the polarization caused by the rotation of permanent dipoles in molecules. If we assume that the polar molecules relax independently of one another, then for orientational polarization the complex permittivity $\epsilon(\omega)$ is connected with the autocorrelation function of $\underline{n}(t)$ by the Kubo relation

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = 1 - i\omega \int_0^\infty \langle (\underline{n}(0) \cdot \underline{n}(t)) \rangle e^{-i\omega t} dt, \quad (5)$$

where the mean value $\langle \dots \rangle$ is taken when the constant field has been switched off and the system has reverted to a steady state.

As an illustration of the Kubo relation let us suppose that the autocorrelation function $\langle (\underline{n}(0) \cdot \underline{n}(t)) \rangle$ decays exponentially with time, so that

$$\langle (\underline{n}(0) \cdot \underline{n}(t)) \rangle = e^{-\lambda t} \quad (6)$$

Then, from (5),

$$\frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{1 + \frac{i\omega}{\lambda}} \quad (7)$$

By equating real and imaginary parts of both sides of this equation and employing (3) and (4) we may deduce the values of $\epsilon'(\omega)$, $\epsilon''(\omega)$, $\alpha(\omega)$, $n(\omega)$.

3. DEBYE THEORY

Having dealt with these preliminaries we proceed to an exposition of the theory of dielectric relaxation starting with the investigations of Debye, who about 1913 developed the idea that dielectrics contain polar molecules. Neglecting the mutual interaction of these molecules he considered the statistical behaviour of a single molecule. Debye took the molecule to be a sphere with a dipole of moment μ at its centre. If an electric field of intensity F in a fixed direction acts on the molecule and if θ is the angle between the directions of the dipole axis and the field, the equation of motion may be written

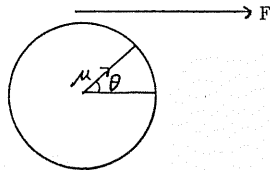


Fig. 3. A polar molecule influenced by an electric field F .

$$I\ddot{\theta} = -IB\dot{\theta} - \mu F \sin\theta + \text{thermal couple.} \quad (8)$$

In this equation I is the moment of inertia of the molecule. The external field produces a moment $-\mu F \sin\theta$. The environment produces a thermal couple and this gives rise to a frictional couple proportional to the angular velocity $\dot{\theta}$, provided that the Rayleigh - Stokes law holds. This assumes that the environment consists of particles whose linear dimensions are small compared with the radius of the molecule. It also assumes that the macroscopic laws of hydrodynamics are applicable to a microscopic system.

Let us look at (8). We have for convenience written the frictional couple as $IB\dot{\theta}$. On comparing the first two terms of (8) we see that B has the dimensions of a reciprocal time and we therefore define a friction time τ_F by

$$\tau_F = \frac{1}{B}.$$

Another quantity with the dimensions of time is τ_D defined by

$$\tau_D = \frac{IB}{2kT}, \quad (9)$$

where k is the Boltzmann constant and T is the absolute temperature. We call τ_D the Debye time and we see that the product of the two times,

$$\tau_F \tau_D = \frac{I}{2kT}, \quad (10)$$

whose value is known once we know the moment of inertia I of the polar molecule.

Then

$$\frac{\tau_F}{\tau_D} = \frac{2kT}{IB^2},$$

a quantity which is found from experiment to be of order 10^{-2} , so that

$$\tau_F \ll \tau_D. \quad (11)$$

In order to solve (8) Debye neglected the $I\ddot{\theta}$ - term saying that the acceleration effect is negligibly small. We shall not enter into the details of his calculation, and we shall express his result in the notation that we have been employing above. Essentially the result is

$$\langle (n(\omega) \cdot n(t)) \rangle = e^{-\frac{t}{\tau_D}}. \quad (12)$$

On comparing this with (6) we deduce from (7) that the complex permittivity is given by

$$\frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{1 + i\omega \tau_D}. \quad (13)$$

Writing as before $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ we obtain

$$\begin{aligned} \epsilon'(\omega) &= \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau_D^2} \\ \epsilon''(\omega) &= \frac{(\epsilon_s - \epsilon_{\infty}) \omega \tau_D}{1 + \omega^2 \tau_D^2}. \end{aligned} \quad (14)$$

From these equations we find that the Cole-Cole plot is a semi-circle in the upper half plane with centre at $(\frac{1}{2}(\epsilon_s + \epsilon_\infty), 0)$ and radius $\frac{1}{2}(\epsilon_s - \epsilon_\infty)$, so that it intersects the $\epsilon'(\omega)$ -axis at ϵ_∞ and ϵ_s . The highest point of the semi-circle is reached when ω satisfies $\omega\tau_p = 1$. When $n(\omega)$ and $a(\omega)$ are calculated from (3), (4) and (14), the dispersion and absorption curves are as shown below.

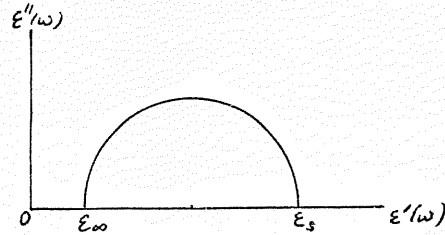


Fig. 4. The Cole-Cole plot in the Debye theory.

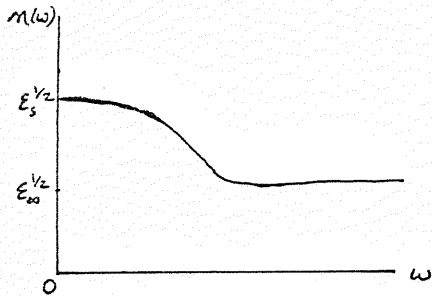


Fig. 5. The dispersion curve in the Debye theory.

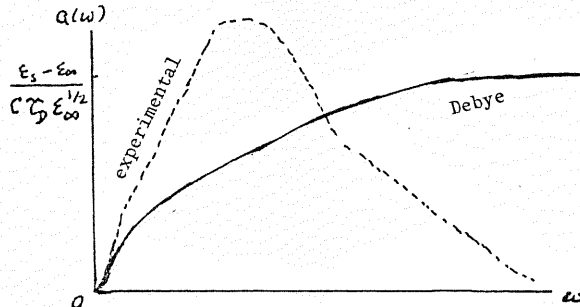


Fig. 6. The absorption curve in the Debye theory and the corresponding experimental curve.

One should note the behaviour of the theoretical Debye absorption curve, especially for large ω . There the curve flattens out to what is called the Debye plateau. In fact experiments on dielectric absorption give curves which agree well with the Debye curve at low frequencies but rise to a maximum greater than the height of the Debye plateau and then drop down to zero.

4. INTRODUCTORY INERTIAL THEORY

We now attempt to develop a theory of dielectric relaxation based on rotational Brownian motion that is valid at high frequencies and is applicable to non-spherical rigid polar molecules. Solutions of different aspects of this problem were published in a number of papers that appeared in the period 1974-1979

as a result of collaboration between G.W. Ford, J.T. Lewis, J. McConnell and B.K.P. Scaife. For the relaxation process we may put $F=0$ in (8), so that we have for a spherical molecule

$$I \ddot{\theta} = -IB\dot{\theta} + \text{thermal couple.} \quad (15)$$

As we have mentioned, Debye omitted the term on the left hand side saying that the angular acceleration $\ddot{\theta}$ is small. The neglect of $I \ddot{\theta}$ could also be interpreted as the neglect of the moment of inertia of the molecule; that is to say, as the neglect of inertial effects. We want to construct a theory in which $I \ddot{\theta}$ is retained. Now this causes mathematical difficulties. In fact the action of the thermal couple is envisaged as producing a quick succession of discontinuous changes in $\dot{\theta}$. Since $\dot{\theta}$ is discontinuous, $\ddot{\theta}$ does not exist and equation (15) as it stands is meaningless.

To derive an expression for the thermal couple in (15) one has to study in some detail random processes and in particular Markov processes. It is found that we may express the thermal couple as $I \frac{dW(t)}{dt}$, where $W(t)$ satisfies

$$\left\langle \frac{dW(t)}{dt} \frac{dW(t')}{dt'} \right\rangle = \sigma^2 \delta(t-t'), \quad (16)$$

σ is a constant and $\delta(t-t')$ is a Dirac delta function. $W(t)$ is called a Wiener process. We therefore rewrite (15) as

$$I \frac{d\omega}{dt} = -IB\omega + I \frac{dW}{dt} \quad (17)$$

with $\omega = \frac{d\theta}{dt}$. This is called a Langevin equation.

We must then solve the equation for angular velocity $\omega(t)$,

$$\frac{d\omega}{dt} = -B\omega + \frac{dW}{dt}, \quad (18)$$

and we recall that $\frac{d\omega}{dt}$ does not exist. To give the last equation a meaning we adopt the procedure of Doob. For our purposes this means that we interpret (18) as signifying that for $f(t)$ any non-stochastic, that is, non-random,

continuous function of t

$$\int_a^b f(t) d\omega(t) = -B \int_a^b f(t) \omega(t) dt + \int_a^b f(t) dW(t). \quad (19)$$

On employing (16) and putting $f(t) \equiv e^{Bt}$ it is found that

$$\langle \omega(t) \omega(s) \rangle = \frac{kT}{I} e^{-B|t-s|}. \quad (20)$$

This important result implies that, when the molecule is spherical, $\omega(t)$ is a Gaussian random variable.

In the study of rotational Brownian motion and its application to dielectric relaxation a key rôle is played by the rotation operator. If M_x, M_y, M_z are the cartesian components of the quantum-mechanical orbital angular momentum of a particle, we define J_x, J_y, J_z by

$$M_x = \hbar J_x, \quad M_y = \hbar J_y, \quad M_z = \hbar J_z.$$

If a rigid body is rotated through an angle χ about an axis whose direction cosines are n_x, n_y, n_z , the corresponding rotation operator $R(t)$ is given by

$$R(t) = \exp[-i\chi(\underline{n} \cdot \underline{J})]. \quad (21)$$

Since $\frac{d\chi}{dt} = \omega(t)$, the angular velocity about the axis of rotation, we deduce from (21) that

$$\frac{dR(t)}{dt} = -i(\underline{J} \cdot \underline{\omega}(t))R(t). \quad (22)$$

When the motion is Brownian, the value of $R(t)$ is random. Thus $R(t)$ is a stochastic function of the time: it is called the stochastic rotation operator and it obeys the nonlinear stochastic differential equation (22).

To link $R(t)$ with dielectric relaxation we recall that the rotation of a rigid body is specified by Euler angles whose values at time t we denote by $\alpha(t), \beta(t), \gamma(t)$. In the three-dimensional representation for which the basis elements are the spherical harmonics $Y_{1,-1}, Y_{10}, Y_{11}$

$$R'_{m'm}(t) = D'_{m'm}(\alpha(t), \beta(t), \gamma(t)),$$

where D denotes a Wigner function. In particular

$$R'_{00}(t) = D'_{00}(\alpha(t), \beta(t), \gamma(t)) = \cos \beta(t).$$

When considering dielectric relaxation we interpret $\beta(t)$ as the angle between $\underline{n}(0)$ and $\underline{n}(t)$, so that

$$\langle (\underline{n}_{10} \cdot \underline{n}(t)) \rangle = \langle \cos \beta(t) \rangle = \langle R(t) \rangle'_{00}$$

and the Kubo relation (5) is expressible as

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = 1 - i\omega \int_0^\infty \langle R(t) \rangle'_{00} e^{-i\omega t} dt. \quad (23)$$

Thus we require only the value of $\langle R(t) \rangle'_{00}$, where $R(t)$ obeys (22).

5. COMPLEX PERMITTIVITY FOR ORIENTATIONAL POLARIZATION

Before proceeding to solve (22) we must know the angular velocity variable $\underline{\omega}(t)$. When we were dealing with the sphere, we saw that it obeyed the Langevin equation (17), that $\omega(t)$ is a Gaussian random variable and that it satisfies (20).

However we shall be concerned also with the case of a rigid polar molecule which has no axis of symmetry. We then take rotating axes of coordinates through the centre of mass and in the directions of the principal axes of inertia; call them O_1, O_2, O_3 . We suppose that the dipole axis is along a line through the centre of mass and that it has components

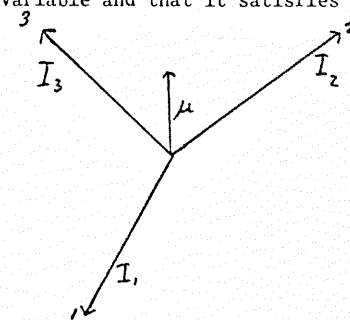


Fig. 7. The asymmetric rotator.

$\mu n_1, \mu n_2, \mu n_3$ referred to the above coordinate frame. Let I_1, I_2, I_3 be the

principal moments of inertia and $\omega_1, \omega_2, \omega_3$ the components of angular velocity. We assume that the frictional couple has moments proportional to $\omega_1, \omega_2, \omega_3$ and write them $I_1 B_1 \omega_1, I_2 B_2 \omega_2, I_3 B_3 \omega_3$. We express the components of the thermal couple as $I_1 \frac{dW_1}{dt}, I_2 \frac{dW_2}{dt}, I_3 \frac{dW_3}{dt}$. Then the equations expressing the law that the rate of change of angular momentum is equal to the sum of the moments of the impressed couples are

$$\begin{aligned} I_1 \dot{\omega}_1 - (I_2 - I_3) \omega_2 \omega_3 &= -I_1 B_1 \omega_1 + I_1 \frac{dW_1}{dt} \\ I_2 \dot{\omega}_2 - (I_3 - I_1) \omega_3 \omega_1 &= -I_2 B_2 \omega_2 + I_2 \frac{dW_2}{dt} \\ I_3 \dot{\omega}_3 - (I_1 - I_2) \omega_1 \omega_2 &= -I_3 B_3 \omega_3 + I_3 \frac{dW_3}{dt} \end{aligned} \quad (24)$$

We call these the Euler-Langevin equations. We need not delay over the method of solution of these equations, since it is essentially the same as that which we shall explain presently for the solution of (22). For our purposes the important results are

$$\begin{aligned} \langle \omega_1(t) \omega_1(s) \rangle &= \frac{kT}{I_1} e^{-B_1 |t-s|} + \frac{(I_2 - I_3)^2 (kT)^2 e^{-B_1 |t-s|}}{I_1^2 I_2 I_3 (B_2 + B_3 - B_1)^2} \\ &\quad \times [1 - (B_2 + B_3 - B_1) |t-s| - e^{-(B_2 + B_3 - B_1) |t-s|}] + \dots \quad (25) \\ \langle \omega_2(t) \omega_3(s) \rangle &= 0, \text{ etc.} \end{aligned}$$

On account of the second term on the right hand side of (25) the components of angular velocity are not Gaussian variables.

To return to the solution of (22), we employ a method that goes back to Krylov and Bogoliubov in the 1930's and was later expounded by Bogoliubov and Mitropolsky, by K.M. Case and by N.G. Van Kampen. We shall follow the exposition of G.W. Ford. The solution consists of a slowly varying ensemble average $\langle R(t) \rangle$, about which there are random fluctuations, and the solution

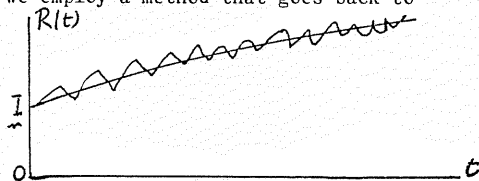


Fig. 8. The fluctuation of $R(t)$ about $\langle R(t) \rangle$.

is expressed by

$$R(t) = (\underline{I} + \varepsilon F^{(1)}(t) + \varepsilon^2 F^{(2)}(t) + \dots) \langle R(t) \rangle, \quad (26)$$

where \underline{I} is the identity operator and ε a small dimensionless parameter. The non-stochastic $\langle R(t) \rangle$ obeys an equation

$$\frac{d\langle R(t) \rangle}{dt} = (\varepsilon \mathcal{J}^{(1)}(t) + \varepsilon^2 \mathcal{J}^{(2)}(t) + \varepsilon^3 \mathcal{J}^{(3)}(t) + \dots) \langle R(t) \rangle. \quad (27)$$

Employing (25) we may deduce from (26) and (27) expressions for $\varepsilon F^{(1)}(t), \varepsilon^2 F^{(2)}(t), \dots, \varepsilon \mathcal{J}^{(1)}(t), \varepsilon^2 \mathcal{J}^{(2)}(t), \dots$ for substitution into (26) and (27). The final result for $\langle R(t) \rangle$, which is all that is required for (23), is given by

$$\langle R(t) \rangle = (\underline{I} + \varepsilon^2 \mathcal{V}^{(2)}(t) + \varepsilon^4 \mathcal{V}^{(4)}(t) + \dots) \exp([\varepsilon^2 \mathcal{G}^{(2)} + \varepsilon^4 \mathcal{G}^{(4)} + \dots]t), \quad (28)$$

where $\mathcal{V}^{(2)}, \mathcal{V}^{(4)}, \dots, \mathcal{G}^{(2)}, \mathcal{G}^{(4)}, \dots$ are determined operators.

We substitute (28) into (23) and after lengthy calculations obtain for an asymmetric molecule

$$\frac{\varepsilon_s - \varepsilon_\omega}{\varepsilon_s - \varepsilon_\omega} = \frac{n_1^2}{D_2 + D_3 + i\omega} \left\{ \frac{D_2(D_2 + D_3 + B_2)}{D_2 + D_3 + B_2 + i\omega} + \frac{D_3(D_2 + D_3 + B_3)}{D_2 + D_3 + B_3 + i\omega} \right\} + \dots + \dots \quad (29)$$

In this equation

$$D_i = \frac{kT}{I_i B_i} + \text{a term of small order of magnitude.} \quad (30)$$

On account of the three friction constants B_1, B_2, B_3 it will be difficult to assess the experimental implications of (29).

Let us therefore take the special case of a polar molecule that is symmetric about the third axis. By symmetry the dipole lies along this axis and (29)

reduces to

$$\frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{\left(1 + \frac{i\omega}{2D_1}\right) \left(1 + \frac{i\omega}{B_1 + 2D_1}\right)} \quad (31)$$

We see from (30) that to a first approximation

$$\frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{(1 + i\omega\tau_D)(1 + i\omega\tau_F)} \quad (32)$$

where

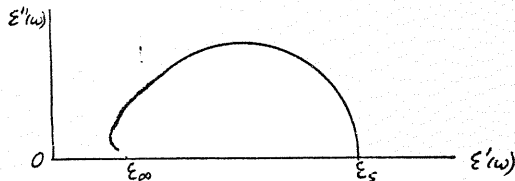
$$\tau_D = \frac{I, B_1}{2kT}, \quad \tau_F = \frac{1}{B_1} \quad (33)$$

and, from (11), we know that $\tau_F \ll \tau_D$. We call (32) the Rocard relation. It is essentially the same as a result deduced in 1933 by Rocard from a differential equation which contained an $I\ddot{\theta}$ - term and so gave rise to the difficulties mentioned with regard to equation (15). The result (32) for a symmetric rotator will hold for the special cases of a polar molecule that is a spherical rotator or a linear rotator.

From (32) we deduce for $\omega\tau_F \ll 1$ that

$$\begin{aligned} \epsilon'(\omega) &= \epsilon_{\infty} + \frac{(\epsilon_s - \epsilon_{\infty})(1 - \omega^2\tau_D\tau_F)}{1 + \omega^2\tau_D^2 + \omega^4\tau_D^2\tau_F^2} \\ \epsilon''(\omega) &= \frac{(\epsilon_s - \epsilon_{\infty})(\tau_D + \tau_F)\omega}{1 + \omega^2\tau_D^2 + \omega^4\tau_D^2\tau_F^2} \end{aligned} \quad (34)$$

If we draw the Cole-Cole plot, we find that the semicircular shape persists throughout the first quadrant, that for large values of ω the curve bends backwards, and that the minimum value of $\epsilon'(\omega)$ is Fig. 9. The Cole-Cole plot for the Rocard relation, less than ϵ_{∞} . This type of behaviour has been found experimentally by



Goulon et al.²⁾, who investigated absorption through liquid chloroform at 25°C.

6. THEORY AND EXPERIMENT

We shall now say something about the applicability of the theory that has been outlined above to dielectrics in different phases. It has been assumed that the mutual interaction of the dipoles in polar molecules may be neglected. This situation may be realised for a dielectric in the gaseous phase. It may also be realised for a liquid dielectric which is in dilute solution in a nonpolar solvent. It has also been assumed in this case that the linear dimensions of the particles in the solvent are small compared with the dimensions of the solute particles, so that it may not be too implausible to suppose that the frictional couple is proportional to the angular velocity.

With regard to applications to solid dielectrics^{3,4)}, it is known from experiment that there are crystals which when raised above a certain temperature enter the rotator solid phase in which reorientation of the molecules is possible. Examples of such molecules are CHCl₃ (chloroform), CH₃CCl₃ (1,1,1-trichloroethane or methyl chloroform), HBr (hydrogen bromide), HI (hydrogen iodide). The orientation is due to thermal motion communicated through Van der Waals forces with a Lennard-Jones or Stockmayer potential. The same forces will also produce a frictional drag. Hence it is reasonable to apply our theory to polar crystals in the rotator solid phase. Thus, for example, McLellan and Walker⁵⁾ found rather similar absorption curves for methyl chloroform in the rotator solid phase at 227K and in the liquid phase at 242K. Molecular reorientation also occurs for clathrate hydrates of polar compounds.

Let us now consider how a quantitative comparison may be instituted between the theory that we have expounded and experiments on dielectric absorption. For reasons explained earlier we confine our attention to dielectrics whose polar molecules have an axis of symmetry. This allows us to employ the Rocard relation for the permittivity $\epsilon(\omega)$. In order to calculate $\epsilon'(\omega)$ and $\epsilon''(\omega)$ from (32) or (34) we must know the values of the constants $\epsilon_s, \epsilon_{\infty}, \tau_D, \tau_F$. In Debye's theory τ_F is found by relating it to the macroscopic viscosity of the surrounding

fluid in accordance with the Rayleigh-Stokes theory. There are two objections to this procedure, viz., (i) macroscopic laws may not be applied to microscopic situations, (ii) in actual cases it is found to give a result which is wrong. An alternative procedure is to regard $\epsilon_s, \epsilon_\infty, \tau_D, \tau_F$ as four parameters to be determined by experiment or, more precisely, from the Cole-Cole plot. Since the semicircular shape of the plot persists for more than half of the semicircle, we can complete the semicircle. The value of ϵ_s is the greater intercept on the $\epsilon''(\omega)$ -axis, ϵ_∞ is the lesser intercept and τ_D is the reciprocal of the value of ω at the highest point. Since, as in (10),

$$\tau_F \tau_D = \frac{I_1}{2kT},$$

we can deduce the value of τ_F and we are in a position to calculate $\epsilon'(\omega)$ and $\epsilon''(\omega)$.

To illustrate this let us return to the experiment of Goulon *et al.*²⁾ on neat chloroform at 25°C. Clearly it would be better from the theoretical viewpoint if the chloroform were in dilute solution but the amount of experimental information that we have about dielectric absorption is not very great and we must make the best use of what information is available. The moment of inertia of the CHCl₃ molecule is 2.7×10^{-38} g cm². It is stated in their paper that $\tau_D = 6.36 \times 10^{-12}$ sec. Hence, from (33),

$$B_1 = \frac{2kT\tau_D}{I_1} = 1.93 \times 10^{13} \text{ sec}^{-1} = 19.3 \text{ THz}.$$

It follows that

$$\tau_F = \frac{1}{B_1} = 5.18 \times 10^{-14} \text{ sec},$$

so that

$$\frac{\tau_F}{\tau_D} = 8.1 \times 10^{-3} \ll 1.$$

From the Cole-Cole plot we read off the value of ϵ_s as 4.72 and the value of ϵ_∞ as 2.08. We may now calculate $\epsilon'(\omega), \epsilon''(\omega)$ from (34) and substituting into (4) obtain the absorption coefficient $a(\omega)$. We plot $a(\omega)$ as a function of the wave number. For comparison we draw the corresponding absorption curve as given

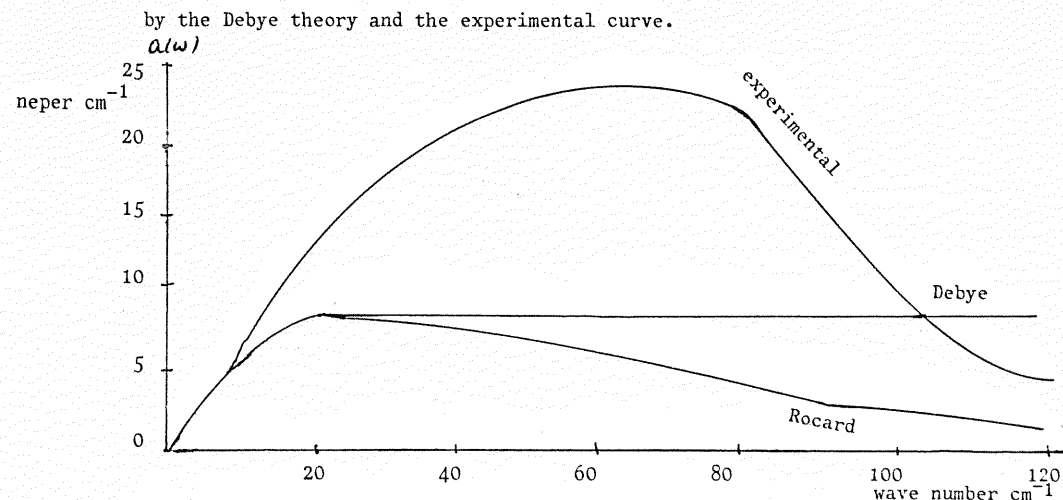


Fig. 10. Theoretical and experimental absorption curves for neat chloroform at 25°C

The experimental curve has a peak much higher than the maximum of the Rocard curve. This extra absorption is called Poley absorption. No quantitative explanation of this absorption has so far been forthcoming. Nonpolar liquids also show absorption in the submillimetre region, though this absorption is about one order of magnitude smaller than that for polar liquids. It is thought that for nonpolar liquids the absorption is collision induced but so far the theory of collision induced absorption has been established only for gases with simple molecular systems like He-Ar, Ne-Ar, H-D, N₂⁶⁾.

Cole-Cole plots may also be employed to make comparisons between theory and experiment for dielectric relaxation, but their usefulness in the submillimetre region is rather limited. Thus in the above case of chloroform at 25°C the highest point on the plot is reached at a frequency of about 30 GHz, that is, at a wave number of about 1 cm^{-1} . For higher wave numbers the points become rather crowded together.

In the above theory no attempt has been made to take account of the mutual interactions between neighbouring polar molecules, be they dipolar interactions, quadrupolar interactions etc.. Thus we have no complete theory either of Poley absorption or of Cole-Cole plots. However several empirical generalizations

of (13) are employed in order to fit experimental points⁴). Thus K.S. Cole and R.H. Cole proposed

$$\frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{1 + (i\omega\tau_0)^{1-\alpha}}, \quad (0 \leq \alpha < 1) \quad (35)$$

It may be shown that this gives the arc of a circle such that the lines joining a point on it to $(\epsilon_s, 0)$, $(\epsilon_{\infty}, 0)$ include an angle $\frac{1}{2}(1-\alpha)\pi$. Then R.H. Cole and D.W. Davidson proposed the relation

$$\frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{(1 + i\omega\tau_0)^{\beta}}, \quad (0 < \beta \leq 1) \quad (36)$$

This gives an asymmetric (ϵ', ϵ'') plot. Moreover it leads not just to a single relaxation time but to a distribution of such times. Both (35) and (36) may be included in the more general equation

$$\frac{\epsilon(\omega) - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{[1 + (i\omega\tau_0)^{1-\alpha}]^{\beta}} \quad (37)$$

When the relaxation times are widely distributed, eq. (36) is not too accurate and it is found better to employ the Fuoss-Kirkwood formula for the loss factor $\epsilon''(\omega)$,

$$\frac{\epsilon''(\omega)}{\epsilon_m''} = \operatorname{sech} \left[\beta \log \left(\frac{\omega}{\omega_m} \right) \right], \quad (38)$$

where ϵ_m'' is the maximum value of $\epsilon''(\omega)$, ω_m is the angular frequency at which this maximum occurs and β is a parameter to be determined by the results of the experiments in question. There is an extensive literature on the interpretation by (35)-(38) and some other formulae of the experimental results for dielectric relaxation of both solids and liquids.

7. CONCLUSION

It will appear from the above condensed account that some initial progress has been made in setting up a theory of dielectric relaxation. It has been seen that much more experimental information on dielectric absorption is required¹). When such information is available, we shall be able to look again at some of the suppositions on which the present theory has been established and may hope to formulate a more satisfactory theory.

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