

# Dispersion and Absorption in Dielectrics

## I. Alternating Current Characteristics\*

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The dispersion and absorption of a considerable number of liquid and dielectrics are represented by the empirical formula

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) / [1 + (i\omega\tau_0)^{1-\alpha}]. \quad (1)$$

In this equation,  $\epsilon^*$  is the complex dielectric constant,  $\epsilon_0$  and  $\epsilon_\infty$  are the "static" and "infinite frequency" dielectric constants,  $\omega = 2\pi$  times the frequency, and  $\tau_0$  is a generalized relaxation time. The parameter  $\alpha$  can assume values between 0 and 1, the former value giving the result of Debye for polar dielectrics. The expression (1) requires that the locus of the dielectric constant in the complex plane be a circular arc with end points on the axis of reals and center below this axis.

If a distribution of relaxation times is assumed to account for Eq. (1), it is possible to calculate the necessary distribution function by the method of Fuoss and Kirkwood. It is, however, difficult to understand the physical significance of this formal result.

If a dielectric satisfying Eq. (1) is represented by a three-element electrical circuit, the mechanism responsible for the dispersion is equivalent to a complex impedance with a phase angle which is independent of the frequency. On this basis, the mechanism of interaction has the striking property that energy is conserved or "stored" in addition to being dissipated and that the ratio of the average energy stored to the energy dissipated *per cycle* is independent of the frequency.

## I. INTRODUCTION

IT is a familiar fact that the dielectric constants of many liquids and solids depend markedly on the frequency of measurement. The dependence is in general found to be a decrease from a static value  $\epsilon_0$  at low frequencies to a smaller limiting value  $\epsilon_\infty$  at higher frequencies. In the transition region of anomalous dispersion there is an "absorption conductivity" and the situation may be described in terms of a complex dielectric constant  $\epsilon^* = \epsilon' - i\epsilon''$ .

The classical theory of the effect for polar liquids is due to Debye.<sup>1</sup> In this theory the difference between the values  $\epsilon_0$  and  $\epsilon_\infty$  is attributed to dipole polarization. The orientation of polar molecules in an alternating-current field is opposed by the effects of thermal agitation and molecular interactions. Debye represents the second effect by a picture of viscous damping, the molecules being regarded as spheres in a continuous medium having the macroscopic viscosity. The theoretical analysis in this case leads to the

equation<sup>2</sup>

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) / (1 + i\omega\tau_0), \quad (1)$$

which can be written

$$\begin{aligned} \epsilon' - \epsilon_\infty &= (\epsilon_0 - \epsilon_\infty) / [1 + (\omega\tau_0)^2], \\ \epsilon'' &= (\epsilon_0 - \epsilon_\infty) \omega\tau_0 / [1 + (\omega\tau_0)^2], \end{aligned} \quad (2)$$

where  $\omega = 2\pi \cdot$  frequency and the parameter  $\tau_0$  is a characteristic constant which may be called the relaxation time.<sup>3</sup>

Dispersion and absorption can also occur in nonhomogeneous dielectrics. The possibility of absorption in a double-layer dielectric if the ratios of conductivities and dielectric constants of the two layers are not equal was first pointed out by Maxwell.<sup>4</sup> Wagner<sup>5</sup> has derived expressions for  $\epsilon'$ ,  $\epsilon''$  in the case of spheres dispersed in a uniform dielectric medium. These expressions are

<sup>2</sup> Reference 1, p. 94.

<sup>3</sup> This constant  $\tau_0$  is not the same as the relaxation time as defined by Debye, differing from it by a constant factor which depends on the theory assumed for the static dielectric constant, cf. R. H. Cole, *J. Chem. Phys.* **6**, 385 (1938). The distinction is unimportant for the present discussion.

<sup>4</sup> J. C. Maxwell, *Electricity and Magnetism* (Oxford Press, London, 1892), Vol. I.

<sup>5</sup> K. W. Wagner, *Ann. d. Physik* **40**, 817 (1913).

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<sup>1</sup> P. Debye, *Polar Molecules* (Chemical Catalogue Company, New York, 1929).

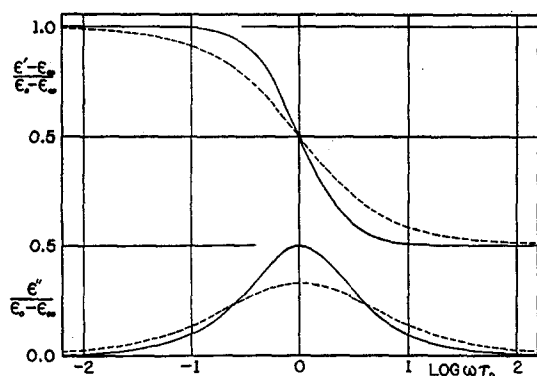


FIG. 1. Real and imaginary parts of the dielectric constant plotted against frequency. The solid curves are for the Debye Eqs. (2), the dashed curves indicate the type of behavior frequently found experimentally.

identical in form with Eqs. (2), differing only in the significance of the parameters  $\epsilon_0$ ,  $\epsilon_\infty$ , and  $\tau_0$ .

Theories of other types of dispersion phenomena also lead to equations of the same type form. The simple theories of paramagnetic dispersion as developed by Gorter and Kronig,<sup>6</sup> and Casimir and du Pre,<sup>7</sup> are examples. The same frequency dependence of elastic dispersion and damping in metals subjected to alternating stress is predicted by the theory of Zener.<sup>8</sup>

One might thus expect these relations to have a very general validity as a description of dispersion processes. Nevertheless, there is a considerable amount of experimental evidence to indicate that Eqs. (2) are not a correct description of the observed frequency dependence in such processes. The observed behavior is rather generally found to consist in a considerably broader frequency range of dispersion and absorption together with a smaller maximum value of  $\epsilon''$  than is predicted by Eqs. (2). This is particularly true in the case of liquid and solid dielectrics, and it is the purpose of the present paper to present the results of an analysis of representative experimental data.

The steady state response of a dielectric or other dispersion system to a sinusoidal force as a function of frequency is formally related to the transient response to an applied force as a function of time by a Fourier integral. A com-

plete knowledge of either response is sufficient to determine the other. The discharge of a condenser containing a dielectric described by Eq. (1) follows the familiar exponential decay curve. If Eq. (1) is not an adequate description of the steady state properties, it follows that the transient response must differ from the predicted exponential time dependence and vice versa. Such deviations are indeed found experimentally in many cases. The significance of the observed behavior and its relation to the steady state characteristics will be considered in a later paper.<sup>9</sup>

## II. REPRESENTATION OF DISPERSION DATA

Before discussing the applicability of Eq. (2) to dielectric constant data it is worth while to consider the possible representations of such data. Ordinarily it is customary to plot  $\epsilon'$  and either  $\epsilon''$  or the loss factor  $\tan \delta (= \epsilon''/\epsilon')$  against the frequency or wave-length. If the Debye Eqs. (2) are valid, one obtains the solid curves of Fig. 1, the symmetry resulting from the logarithmic frequency scale. The experimental data often possess this same type of logarithmic symmetry but with the important differences that the frequency range of dispersion is broader and the absorption smaller in maximum value. This behavior is indicated by the dashed curves in Fig. 1.

The experimental data are not readily analyzed by such a representation nor is the significance of departures from the expected behavior easily appreciated. A more convenient basis for discussion is the Argand diagram or complex plane locus in which the imaginary part of the complex dielectric constant is plotted against the real part, each point being characteristic of one frequency of measurement. The locus of Eqs. (2) in this representation is a semicircle with its center on the real ( $\epsilon'$ ) axis and intercepts at  $\epsilon_0$  and  $\epsilon_\infty$  on this axis. This is easily shown from Eq. (1) which can be written in the form  $u + v = \epsilon_0 - \epsilon_\infty$ , where  $u = \epsilon^* - \epsilon_\infty$ ,  $v = i\omega\tau_0(\epsilon^* - \epsilon_\infty)$ . The quantities  $u$ ,  $v$ , considered as vectors in the complex plane are perpendicular, their vector sum being the constant real quantity  $\epsilon_0 - \epsilon_\infty$ . The right angle in-

<sup>6</sup> C. J. Gorter and R. de L. Kronig, *Physica* **3**, 1009 (1936).

<sup>7</sup> H. B. G. Casimir and F. K. du Pre, *Physica* **5**, 507 (1938).

<sup>8</sup> C. Zener, *Phys. Rev.* **53**, 90 (1938).

<sup>9</sup> "Dispersion and absorption in dielectrics. II. Direct current characteristics," to be submitted to this journal.

cluded by these vectors is therefore inscribed in a semicircle of diameter  $\epsilon_0 - \epsilon_\infty$ , as shown in Fig. 2 (a) (the imaginary part of  $\epsilon^*$  is plotted as positive). This semicircle is then the locus of the dielectric constant as  $\omega$  varies from 0 to  $\infty$ . This circle diagram has proved a very convenient representation of dispersion data in general.<sup>10</sup> Its usefulness for the present subject of discussion will be evident from what follows.

The complex plane locus suffers from the seeming disadvantage that both real and imaginary parts of the dielectric constant must be known if the data are to be analyzed in this fashion. This difficulty is more apparent than real, however, as an experimental method suitable for determination of either component usually involves a determination of the other as well. It is important, moreover, to realize that one cannot say whether or not the Debye equations are in adequate description of the facts unless these data or their equivalent are available (see, however, under IV). The discussion of the following section is therefore concerned with an analysis of some reasonably complete dispersion and absorption data in the literature. The conclusions which can be drawn from less complete data will be considered in V.

### III. EXPERIMENTAL EVIDENCE

#### A. Liquids

The original Debye theory of dispersion and absorption was developed for polar gases and

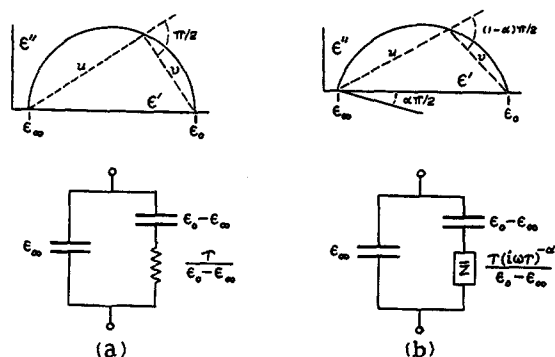


FIG. 2. Theoretical complex plane loci of the complex dielectric constant and equivalent circuits for dielectrics; (a) Debye theory, (b) as required by experimental evidence.

<sup>10</sup> See, for example, K. S. Cole, *J. Gen. Physiol.* **12**, 29 (1928); *ibid.* **15**, 641 (1932).

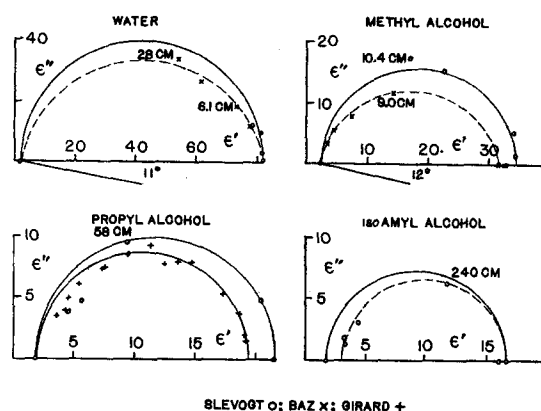


FIG. 3. Complex dielectric constants of water and alcohols.

dilute solutions of polar liquids, but has been extensively applied to results on pure polar liquids. The major difficulty in testing it adequately lies in the technical problem of making measurements at the necessary frequencies of  $10^8$  to  $10^{11}$  cycles for simple polar liquids. It is important to note that for liquids one usually knows both  $\epsilon_0$  and  $\epsilon_\infty$ , the former from low frequency measurements and the latter by extrapolation to zero frequency of the optical index of refraction.<sup>11</sup> If these end points are known, the semicircle is completely defined, except that knowledge of  $\epsilon_0$  and  $\epsilon_\infty$  obviously does not determine the frequency range in which the effects occur.

Bätz,<sup>12</sup> and Slevogt,<sup>13</sup> have made measurements on water, methyl and ethyl alcohols over the frequency ranges  $3 \times 10^9$ – $10^{10}$  c and  $10^8$ – $3 \times 10^9$  c, respectively. The dielectric constant data for water and methyl alcohol are plotted in the complex plane in Fig. (3). It is evident that the data are not in good agreement nor do they establish the validity of the theoretical semicircle. The same thing is true of the results for ethyl alcohol. Slevogt has also measured several of the higher alcohols. His data for propyl alcohol, together with values given by Girard,<sup>14</sup> are plotted in Fig. (3). The internal consistency and

<sup>11</sup> This procedure is not without uncertainty because of the possibility of atomic polarization giving rise to absorption in the infra-red and a related dispersion of which this extrapolation takes no account. In the absence of definite information on this point, one can do no better than to ignore the difficulty. The error should not, in most cases, be serious.

<sup>12</sup> G. Bätz, *Physik. Zeits.* **40**, 394 (1939).

<sup>13</sup> K. E. Slevogt, *Ann. d. Physik* **36**, 141 (1939).

<sup>14</sup> P. Girard, *Trans. Faraday Soc.* **30**, 763 (1934).

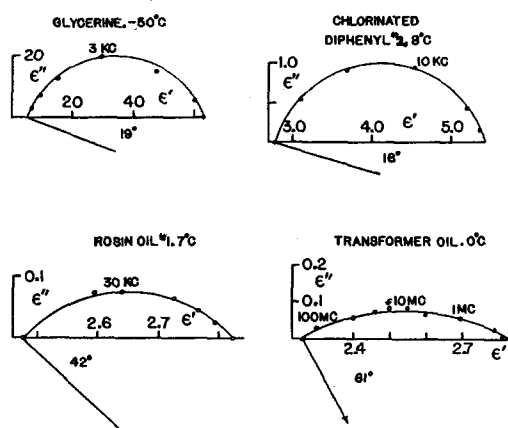
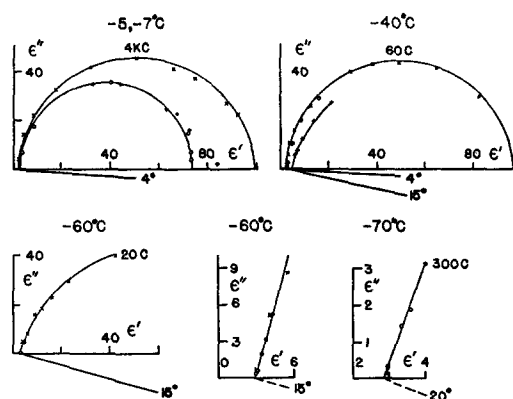


FIG. 4. Complex dielectric constants of liquids.

agreement of the two sets of data are seen to be rather poor in this case also. Slevogt's results for *n*-amyl alcohol, as plotted in Fig. 3, can be fitted by a semicircle only if  $\epsilon_\infty$  is taken to be 3.1 rather than the value 1.9 corresponding to the square of the optical index of refraction. This difference can be plausibly explained as being due to atomic polarization. However, the internal consistency of the data is sufficiently poor that this explanation is only a tentative one. This effect is not indicated for methyl and ethyl alcohols on the basis of Báz' data and it is not possible to fit a semicircle to his results. They can, however, be represented quite well by a circular arc with center below the  $\epsilon'$  axis as shown in Fig. 3. This type of departure from the predictions of the simple dispersion theories is characteristic of a large number of dielectrics, as will be evident from the discussion of the succeeding sections. It is apparent that no definite conclusions are justified in the case of polar liquids on the basis of data similar to those discussed in this section. There is, therefore, a great need for reliable values of  $\epsilon'$  and  $\epsilon''$  for polar liquids at frequencies which cover the major part of the dispersion range.

On the basis of the Debye theory one should expect the dispersion range to occur at much lower frequencies for viscous liquids, as the relaxation time is proportional to the quotient  $\eta/T$ , where  $\eta$  is the macroscopic viscosity and  $T$  is the absolute temperature. This type of dependence is found experimentally in many cases. The dispersion effect may thus occur in a much



MURPHY X, SMYTH AND HITCHCOCK O, WINTSCH +.

FIG. 5. Complex dielectric constants of ice at various temperatures.

more convenient frequency range and quite complete data exist in the literature for liquids such as glycerine and various glycols which are extremely viscous at sufficiently low temperatures. The dispersion range for insulating oils may also occur at experimentally convenient frequencies. In some cases, it is doubtful as to whether the dispersion for such liquids is due to dipole polarization. Examples of this latter type need not be excluded from the present discussion because, as already mentioned, all the simple dispersion theories predict the same frequency dependence. A detailed theory must, of course, take this difference into account.

Morgan,<sup>15</sup> has measured  $\epsilon'$ ,  $\epsilon''$  for glycerine at temperatures down to  $-70^\circ\text{C}$  and over the frequency range 30c–10<sup>5</sup>c. The complex plane locus at  $-50^\circ\text{C}$  is plotted in Fig. 4 from data obtained by interpolation on his published plots of  $\epsilon'$ ,  $\epsilon''$  against the temperature. It is apparent that the experimental results cannot be represented satisfactorily by a semicircle but that a circular arc with depressed center is a good approximation.

Data of White and Morgan,<sup>16</sup> for a chlorinated diphenyl, also plotted in Fig. 4, were obtained in the same way and show the same effect. The characteristic departure from the semicircle is found to an even greater extent in data for a

<sup>15</sup> S. O. Morgan, Trans. Electrochem. Soc. **65**, 109 (1934).

<sup>16</sup> A. H. White and S. O. Morgan, J. Frank. Inst. **216**, 635 (1933).

rosin oil<sup>17</sup> and a transformer oil,<sup>18</sup> which are also plotted in Fig. 4. It is to be noted that the dispersion range of frequencies is much wider and the maximum absorption much smaller in such cases.

The circular arc locus is found to be an excellent representation of data on a considerable number of other liquids for which data are available. It is useful to have some simple measure of the departure of such arcs from a semicircle. This is conveniently taken to be the angle between the  $\epsilon'$  axis and the radius of the arc drawn to the point  $\epsilon_\infty$ , and the value of this angle is indicated on the plots in Figs. 3 and 4.

## B. Solids

One should expect the parameter  $\tau_0$  to be much larger for polar solids than for polar liquids and the frequency range of dispersion to be a more convenient one as a result. Experimentally, however, the situation often turns out to be no simpler because this frequency range is often as awkwardly low as that for liquids is high. In such cases there is a difficulty not found for liquids in that the static dielectric constant is now an unknown quantity the value of which can be inferred only by extrapolation of the dispersion curve to zero frequency. There are, however, some reasonably complete data on dispersion in crystalline polar solids which are suitable for the present purpose.

Dielectric constants for ice have been determined over a considerable temperature and frequency range by Wintsch,<sup>19</sup> Smyth and

Hitchcock,<sup>20</sup> and Murphy.<sup>21</sup> Some of their results are plotted in Fig. 5. The data of Wintsch and of Murphy extend to lower frequencies so that a more complete picture of the dispersion is afforded than by the results of Smyth and Hitchcock. It is again evident from these graphs that a circular arc rather than a semicircle is consistent with the experimental data, particularly at the lower temperatures. The data of Smyth and Hitchcock at temperatures below  $-30^\circ\text{C}$  are not complete enough to permit one to infer the nature of the complete locus. It is, however, significant that the data are not consistent with the assumption of a semicircle. It is seen from Fig. 5 that the data require that the dielectric constant locus approach the  $\epsilon'$  axis at an angle of somewhat less than  $90^\circ$ . At these "low" frequencies the data are thus consistent with the circular arc locus found in the other examples.

White, Biggs and Morgan,<sup>22</sup> have shown that several crystalline benzene derivatives exhibit dispersion and absorption in the frequency range 1 to 100 kc. Some of their data at temperatures for which this frequency range gives a fairly complete picture are plotted in Fig. 6. In these cases also, the circular arc is an excellent representation of the data. All the data of these workers which show appreciable dispersion also show considerable deviations from the semicircular locus. These deviations increase with decreasing temperature and, as far as can be determined

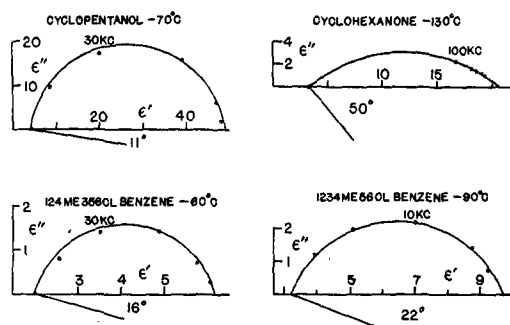


FIG. 6. Complex dielectric constants of organic crystalline solids.

<sup>17</sup> S. O. Morgan and A. H. White, *J. Frank. Inst.* **213**, 313 (1932).

<sup>18</sup> H. Rieche, *Zeits. f. Physik* **95**, 158 (1935).

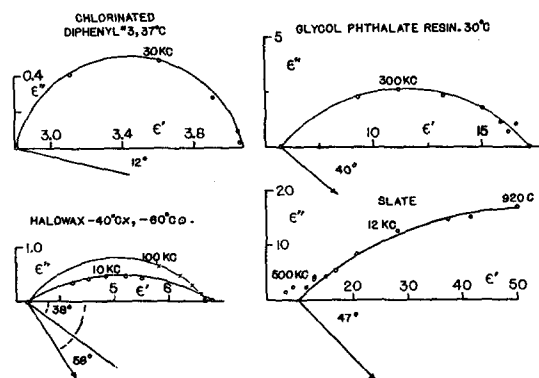


FIG. 7. Complex dielectric constants of solids.

<sup>19</sup> H. Wintsch, *Helv. Phys. Acta* **5**, 126 (1932).

<sup>20</sup> C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.* **54**, 4631 (1932).

<sup>21</sup> E. J. Murphy, *Trans. Electrochem. Soc.* **65**, 309 (1934).

<sup>22</sup> A. H. White, S. S. Biggs and S. O. Morgan, *J. Am. Chem. Soc.* **62**, 16 (1940).

from the data presented graphically, the results are well fitted by a circular arc.

White and Bishop<sup>23</sup> have made measurements on a large number of organic crystals and have found dispersion in many cases. Their values for cyclopentanol at  $-70^{\circ}\text{C}$  and cyclohexanone at  $-130^{\circ}\text{C}$  are plotted in Fig. 6 and again one finds that circular arcs are required to fit the data. Other results reported in the same paper show similar dispersion characteristics, and it is reasonable to conclude that the circular arc is an excellent analytic representation of the dispersion in a variety of organic crystals.

Data are available in the literature for a number of solid dielectrics of interest in insulation problems. These dielectrics are usually of complex and uncertain molecular composition, and one might not expect to find any very close similarities in their dispersion characteristics. It turns out, however, that the circular arc locus is a very general expression of data for these dielectrics. Four examples are shown in Fig. 7.<sup>24</sup>

No detailed comment is necessary on the general characteristics, which are sufficiently evident from Fig. 7. It should, however, be pointed out that for such dielectrics as these the departures from the semicircle are very great in many cases, but that these departures are nevertheless represented by a circular arc. It is thus evident from these examples and the ones previously discussed that this type of locus is characteristic of a large number of otherwise dissimilar dielectrics.

#### IV. OTHER STATEMENTS OF THE EXPERIMENTAL RESULTS

##### A. Analytic formulation

The analytical expression for the circular arc locus is easily deduced by consideration of Fig. 2. From simple geometry the angle  $(1-\alpha)\pi/2$  between the vectors  $u$  and  $v$  in the complex plane is independent of the frequency and equal to half the central angle subtended by the arc. It therefore follows that

$$u+v=u[1+f(\omega)e^{i(1-\alpha)\pi/2}]=\epsilon_0-\epsilon_\infty, \quad (3)$$

<sup>23</sup> A. H. White and W. S. Bishop, J. Am. Chem. Soc. **62**, 8 (1940).

<sup>24</sup> The sources of the data are: chlorinated diphenyl, reference 16; glycol phthalate resin, W. A. Yager, Physics **7**, 434 (1936); Halowax, reference 15; slate, G. E. Bairsto, Proc. Roy. Soc. **96**, 363 (1920).

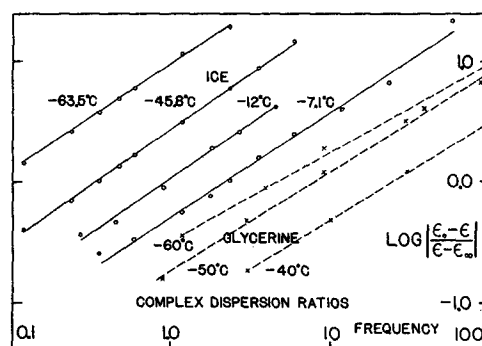


FIG. 8. Frequency dependence of the complex dielectric constants of ice and glycerine, as explained in the text. The logarithmic scales of frequency have been shifted by arbitrary amounts.

where  $f(\omega)$  is a (real) undetermined function of the frequency and other parameters. From the relation  $e^{i(1-\alpha)\pi/2} = i^{(1-\alpha)}$  this can be written

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) / [1 + i^{(1-\alpha)} f(\omega)], \quad (4)$$

as the complex quantity  $u$  is simply  $\epsilon^* - \epsilon_\infty$ , where  $\epsilon^*$  is the complex dielectric constant.

The dependence of the function  $f(\omega)$  on the frequency is undetermined by this geometrical argument. From general considerations one can expect that this dependence will be of the form  $\omega^{1-\alpha}$ , as the complex form of  $\epsilon^*$  results from the initial hypothesis of an applied field  $E = E_0 e^{i\omega t}$ . Any theory in which  $\omega$  appears as the result of linear operations on the complex exponential must lead to the same functional dependence on  $\omega$  as on the unit imaginary  $i$  so that

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) / [1 + (i\omega\tau_0)^{1-\alpha}], \quad (5)$$

where the parameter  $\tau_0$  is left undetermined.

This dependence of  $f(\omega)$  on  $\omega$  is easily verified from the experimental data by plotting the logarithm of the ratio  $|v/u|$  against the logarithm of the frequency. It is easily shown from Eq. (5) that

$$|v/u| = (\omega\tau_0)^{1-\alpha}, \quad (6)$$

and the locus of  $\log_e |v/u|$  plotted against  $\log_e \omega$  is a straight line of slope  $1-\alpha$ .<sup>25</sup> As an illustration, these quantities are plotted from the data of Murphy for ice and of Morgan for glycerine in Fig. 8. It is seen that the locus is indeed a straight line of slope less than unity as required by Eq. (6). Furthermore, the values of  $\alpha$

<sup>25</sup> K. S. Cole, J. Gen. Physiol. **12**, 29 (1928).

so obtained are in agreement with the values required by the circular arc loci.

The real and imaginary parts  $\epsilon'$ ,  $\epsilon''$  of the complex dielectric constant as a function of frequency are given by

$$\begin{aligned}\epsilon' - \epsilon_\infty &= \frac{(\epsilon_0 - \epsilon_\infty)[1 + (\omega\tau_0)^{1-\alpha} \sin \frac{1}{2}\alpha\pi]}{1 + 2(\omega\tau_0)^{1-\alpha} \sin \frac{1}{2}\alpha\pi + (\omega\tau_0)^{2(1-\alpha)}} \\ &= \frac{1}{2}(\epsilon_0 - \epsilon_\infty) \left[ 1 - \frac{\sinh(1-\alpha)x}{\cosh(1-\alpha)x + \cos \frac{1}{2}\alpha\pi} \right], \\ \epsilon'' &= \frac{(\epsilon_0 - \epsilon_\infty)(\omega\tau_0)^{1-\alpha} \cos \frac{1}{2}\alpha\pi}{1 + 2(\omega\tau_0)^{1-\alpha} \sin \frac{1}{2}\alpha\pi + (\omega\tau_0)^{2(1-\alpha)}} \\ &= \frac{\frac{1}{2}(\epsilon_0 - \epsilon_\infty) \cos \frac{1}{2}\alpha\pi}{\cosh(1-\alpha)x + \sin \frac{1}{2}\alpha\pi},\end{aligned}\quad (7)$$

where  $x = \log_e(\omega\tau_0)$ . It is easily seen that Eqs. (7) reduce to the Debye expressions (2) for  $\alpha=0$ . For values of  $\alpha$  greater than zero the dispersion region is broader and the maximum value of  $\epsilon''$  for  $\omega = 1/\tau_0$  decreased.

If data are available only for  $\epsilon'$  or  $\epsilon''$  alone as a function of frequency, the applicability of Eq. (5) can be determined by some such method as comparison with standard curves for Eq. (7). It should be noted that  $\epsilon'$  and  $\epsilon''$  are uniquely determined if either  $\epsilon'$  or  $\epsilon''$  is known over the entire frequency range for which dispersion and absorption occur. The general relations

$$\begin{aligned}\epsilon'(\omega) - \epsilon_\infty &= -\frac{2}{\pi} \int_0^\infty \frac{\epsilon''(\nu) \nu d\nu}{\nu^2 - \omega^2}, \\ \epsilon''(\omega) &= \frac{2}{\pi} \int_0^\infty \frac{[\epsilon'(\nu) - \epsilon_\infty] \omega d\nu}{\nu^2 - \omega^2},\end{aligned}\quad (8)$$

were given by Kramers<sup>26</sup> and are easily shown to follow from the fact that  $\epsilon'$  and  $\epsilon''$  are conjugate functions. It is readily verified that the relations (8) are satisfied by the explicit forms of  $\epsilon'$  and  $\epsilon''$  given in Eqs. (7).

### B. Equivalent circuits

It is often convenient to represent the properties of dielectrics exhibiting dispersion by means of an equivalent electrical circuit. Such a

network for a dielectric described by an equation of the Debye form is shown in Fig. 2(a). In this circuit the capacity  $\epsilon_\infty$  represents the polarization which is established even at very high frequencies, while the capacity  $\epsilon_0 - \epsilon_\infty$  corresponds to the polarization set up only for low frequencies of the field. The mechanism which acts to prevent this polarization from being established at higher frequencies is represented by the resistance  $\tau_0/(\epsilon_0 - \epsilon_\infty)$ .

If the experimental data require the circular arc locus and Eq. (5) as an expression of the dispersion, the resistance of Fig. 2(a) is replaced by a complex impedance  $Z = \tau_0(i\omega\tau_0)^\alpha/(\epsilon_0 - \epsilon_\infty)$ . This impedance has the striking property that, while the resistance and reactance components are functions of the frequency, the phase angle is a constant independent of the frequency and equal to  $\frac{1}{2}\alpha\pi$ .

Since the angle between the  $\epsilon'$  axis and the radius vector to the point  $\epsilon_\infty$  of the circular arc in the complex plane locus is also equal to  $\frac{1}{2}\alpha\pi$ , the properties of a dielectric with a locus of this kind may be stated equally well in terms of this phase angle or in terms of the index  $\alpha$ . It must be understood that the use of the complex impedance  $Z$  is merely one way of expressing the experimental facts and that it and its real and imaginary parts have no conventional meaning.

### V. INTERPRETATION OF LESS COMPLETE DISPERSION DATA

In many cases dispersion data given in the literature are not sufficiently complete to determine uniquely the complete dependence of the complex dielectric constant on the frequency. It is, however, possible in some cases to show definitely that such data are consistent with Eq. (5) and not with Eq. (1).

#### A. The complex plane locus for very low or high frequencies

Because of technical difficulties, experimental values of  $\epsilon'$  and  $\epsilon''$  are sometimes known only near the low or high frequency limit of the dispersion range so that the complete dielectric constant locus cannot be plotted. In these cases it is possible only to determine whether Eqs. (1) or (5) are consistent with the data. If Eq. (1) is valid, the locus approaches the  $\epsilon'$  axis for  $\omega=0$  or

<sup>26</sup> H. A. Kramers, *Atti Congr. dei Fisici, Como*, 545, 1927. See also reference 6.

TABLE I. Constants of dispersion and absorption for various dielectrics.\*

	$T^{\circ}\text{C}$	$\epsilon_0$	$\epsilon_{\infty}$	$a$	$b$	$\alpha$	REFER- ENCE
<b>A: Liquids</b>							
Water	19	81	1.8	9.4	12	0.09	12
Water	19	81	1.8	—	—	(0.0)	13
Methyl alcohol	19	31.8	2.0	6.4	11	0.13	12
	19	(33.2)	2.0	5.9	11	(0.0)	13
Ethyl alcohol	20	25.8	1.85	9.4	11	0.15	12
	19	26.0	1.85	1.3	10	(0.0)	13
Propyl alcohol	?	19.2	1.9	3.2	10	(0.0)	14
	19	21.3	1.9	3.2	10	(0.0)	13
<i>n</i> -Butyl alcohol	19	19.1	(3.2)	6.4	10	(0.0)	13
Iso-amyl alcohol	19	(16.1)	(3.1)	1.0	9	(0.0)	13
Glycerine	-50	63	5.0	6.9	5	0.21	15
	-60	69	5.0	1.2	3	0.21	15
Rosin oil No. 1	7	2.825	2.475	3.8	6	0.46	17
	-1	2.840	2.475	1.9	5	0.51	17
	-5	2.858	2.475	6.4	5	0.53	17
Rosin oil No. 2	-40	2.67	2.48	2.9	5	0.37	17
	-50	—	2.48	—	—	(0.64)	17
Transformer oil	0	2.82	2.26	2.0	8	0.63	18
Chlorinated	-25	7.10	2.76	4.3	5	0.27	16
diphenyl No. 1	-30	(7.44)	2.76	3.6	4	0.31	16
<b>B: Solids</b>							
Ice	-1	74	3.0	2.0	5	0.03	20
	-5	75	3.0	3.1	5	0.00	20
	-6	80	3.0	3.1	5	(0.08)	19
	-7.1	98	2.0	4.0	5	0.04	21
	-20	82	3.0	1.4	4	0.02	20
	-20	82	3.5	1.0	4	0.07	19
	-40	(81)	3.0	—	—	0.02	20
	-40	—	3.5	—	—	0.16	19
	-45.8	97	2.0	2.7	3	0.07	21
	-50	—	3.02	—	—	0.12	20
	-60	—	3.00	—	—	0.17	20
	-63.5	(117)	3.0	(1.6)	2	0.17	21
1,2,4-Trimethyl	-70	—	2.90	—	—	0.22	20
	-60	7.16	3.0	8.8	6	0.19	22
3,5,6-Trichloro- benzene	-80	7.85	3.0	8.4	5	0.31	22
Methylpenta- chlorobenzene	0	5.36	3.10	3.2	7	0.11	22
	-18	5.54	3.10	1.6	6	0.13	22
	-40	5.94	3.10	1.4	5	0.24	22
1,2,3,4-Tetra- methyl 5,6-di- chlorobenzene	-77	9.65	3.02	2.1	6	0.22	22
	-88	9.70	3.00	1.1	5	0.25	22
Pentamethyl- chlorobenzene	-111	9.80	2.92	6.1	5	0.31	22
	-61	7.34	2.94	5.9	6	0.18	22
	-70	8.00	3.00	1.8	5	0.21	22
	-79	8.60	2.92	5.0	5	0.26	22
Cyclopentanol	-70	48	4.3	7.6	6	0.12	23
Cyclohexanone	-130	20.9	3.3	1.6	8	0.55	23
Abietic acid	86.8	3.72	2.81	2.2	6	0.40	24
Chlorinated	14	5.20	2.82	1.6	6	0.12	16
diphenyl No. 2	5	5.49	2.82	2.8	5	0.20	16
	-1	(5.73)	2.82	—	—	0.28	16
Chlorinated	37	4.06	2.80	3.5	6	0.13	16
diphenyl No. 3	27.5	4.23	2.80	7.2	5	0.25	16
Plasticized poly- vinyl chloride	25	(10.0)	3.04	1.3	4	0.61	32
Glycol phthalate	30	17.2	5.8	5.7	7	0.44	24
Phenol formalde- hyde resin	70	8.25	3.40	1.1	5	0.60	33
Vinsol	98	8.48	3.42	1.2	4	0.61	24
Halowax	-40	6.70	3.40	4.8	7	0.42	15
	-50	6.75	3.40	2.4	6	0.54	15
	-60	6.80	3.40	3.5	5	0.64	15
Paraffin	21	—	—	—	—	(0.85)	27
Ceresin	21	—	—	—	—	(0.86)	27
Rubber, 20% sulphur	75	4.85	2.70	1.1	5	0.64	34
Rubber, 32% sulphur	135	5.70	2.70	5.3	5	0.68	34
Pyrex	21	—	—	—	—	(0.885)	27
Mica	21	—	—	—	—	(0.88)	27
Slate	?	(98)	8.0	2.7	4	0.53	24

\* Values of  $\epsilon_0$ ,  $\epsilon_{\infty}$ ,  $\tau_0$ ,  $\alpha$  and the temperature of measurement are listed, together with the source of the data. Values which are doubtful because of inadequate frequency range or lack of consistency of the data are enclosed in parentheses. The values of  $\alpha$  listed in such cases do not necessarily apply to the entire frequency range. The absence of an entry indicates that the data do not permit even an approximate estimate. The entries for  $\tau_0$  are given as values for  $a$  and  $b$ , respectively, in the equation  $\tau_0 = a \cdot 10^{-b}$  sec.

$\infty$  at right angles to the axis. If Eq. (5) is satisfied, the limiting slope of the locus is not infinite but rather  $\tan \frac{1}{2}(1-\alpha)\pi$  as is evident from Fig. 2(b).

The latter behavior is found to be the general rule. An example is found in the data of Smyth and Hitchcock for ice at temperatures below  $-30^{\circ}\text{C}$  as plotted in Fig. 5. As the temperature decreases, the limiting slopes show an increasing departure from the value of unity demanded by the Debye theory. At these lower temperatures it is clearly impossible to do more than guess at the nature of the dispersion except at the high frequency limit, and one can only suspect that, as in many other cases, the locus may well be a circular arc. It is still less possible to determine the value of the static dielectric constant, and one can only venture the opinion that it must be very large and attained only at extremely low frequencies.

MacLeod<sup>27</sup> has obtained data on several solid dielectrics which show the same characteristic. This observer determined the equivalent series

<sup>27</sup> H. J. MacLeod, Phys. Rev. **21**, 53 (1923).

resistance  $R_s$  and capacity  $C_s$  of glass, paraffin, ceresin wax, and mica over the frequency range 500c–10<sup>6</sup>c and found that the data could be represented by equations of the form  $R_s = a\nu^{-k}$ ,  $C_s = b(1 + c\nu^{n-1})$ . It is readily shown from Eqs. (7) that for  $\omega\tau_0 \gg 1$  one obtains relations of this form and that  $k = 2 - \alpha$ ,  $n = \alpha$ . From this it is also seen that  $n + k = 2$ , which MacLeod found to be the case to within 0.5 percent. These results are particularly interesting because they show that for these dielectrics a frequency of 500c is near the infinite frequency end of the dispersion range. Furthermore, the values of  $\alpha$  lie between 0.85 and 0.90 so that the dispersion range is very wide and the static value of the dielectric constant is attained only at extremely low frequencies.

## B. Maximum value of the absorption

The second of Eqs. (7) predicts that the maximum value of  $\epsilon''$  for  $\omega = 1/\tau_0$  is

$$\epsilon''_{\max} = \frac{1}{2}(\epsilon_0 - \epsilon_{\infty}) \tan [(1-\alpha)\pi/4]. \quad (9)$$

Data tabulated by Morgan<sup>28</sup> show that for a

<sup>28</sup> S. O. Morgan, J. Ind. and Eng. Chem. **30**, 273 (1938).



considerable number of alcohols, glycols, various chlorinated compounds, rosins and solids the value of  $\epsilon''_{\max}$  is considerably less than  $\frac{1}{2}(\epsilon_0 - \epsilon_\infty)$ . This is, from Eq. (8), consistent with the circular arc locus and values of  $\alpha$  greater than zero, although one is not, of course, entitled to deduce from these data alone that the dispersion is described by Eq. (5).

### C. Dependence of the absorption conductivity on the frequency

Data in the literature on the "absorption conductivity"<sup>29</sup> of dielectrics as a function of frequency give further evidence consistent with Eqs. (7) for  $\alpha > 0$ . This conductivity  $\sigma$  is from elementary considerations equal to  $\epsilon''\omega$ . At very low frequencies Eq. (7) gives

$$\epsilon = (\epsilon_0 - \epsilon_\infty)(\omega\tau_0)^{2-\alpha}\cos\frac{1}{2}\alpha\pi. \quad (10)$$

Thus, if  $\omega \ll 1/\tau_0$ ,  $\sigma$  should be proportional to a power of  $\omega$  between 1 and 2 for values of  $\alpha$  between 1 and 0. An example of departures from the limiting square law frequency dependence is found in data of Dahms,<sup>30</sup> on aqueous sugar solutions. These experiments gave an absorption conductivity proportional to a power of  $\omega$  between 1.88 and 1.56. From Eq. (9) these results correspond to values of between 0.12 and 0.44.

Schmale,<sup>31</sup> has measured  $\sigma$  for water, nitrobenzol, chlorobenzol, and acetone for wavelengths from 10 m to 20 m. He found that the absorption conductivity was proportional to  $\omega^2$  in all cases, in agreement with the Debye theory. Because of the rather limited frequency range and the discrepancies between data of B  z and Slevogt on polar liquids, this evidence cannot be regarded as conclusive.

It is clear from the examples which have been discussed in this section that the circular arc locus and the equivalent analytic representation of Eq. (5) are an excellent description of the dispersion in a large number of dielectrics. This description requires the introduction of the single parameter  $\alpha$  in addition to the constants  $\epsilon_0$ ,  $\epsilon_\infty$ ,  $\tau_0$ .

<sup>29</sup> It should be emphasized that this "absorption conductivity" refers only to the conductivity associated with dispersion. It does not include any "direct current" steady-state conductivity as will be discussed in a later paper (reference 6).

<sup>30</sup> W. Dahms, *Physik. Zeits.* **37**, 158 (1936). See also: M. Wien, *Physik. Zeits.* **37**, 870 (1936).

<sup>31</sup> K. Schmale, *Ann. d. Physik* **35**, 671 (1939).

The experimental results are thus completely described by these four quantities and the values found for the examples considered in the present work are listed in Table I.<sup>32-34</sup>

## VI. PROPOSED MODIFICATIONS OF THE SIMPLE DISPERSION THEORIES

The fact that a considerable amount of experimental data can be represented by Eq. (5) with  $\alpha > 0$  does not of course explain why this kind of result should occur. It has long been recognized that the Debye Eqs. (1) are not valid in many cases, and various explanations have been put forward to account for the observed deviations. The fact that so many of these deviations are represented analytically by Eq. (5), graphically by the circular arc locus, or electrically by a complex impedance with phase angle independent of the frequency has not previously been brought out.<sup>35</sup> It is therefore of importance to examine whether this characteristic behavior is accounted for by any of the proposed explanations.

### A. Hindered rotation

The hypothesis of hindered rotation has been applied to the problem of the static dielectric constant of polar liquids by Debye,<sup>36</sup> and to dispersion in polar liquids by Debye and Ramm.<sup>37</sup> The difficulties with the concept in the two cases have been discussed elsewhere.<sup>38</sup> For the sake of completeness, the relation of the theory of Debye and Ramm to the experimental results on dispersion will be outlined briefly.

If the effect of the assumed hindered rotation is small, the term  $1/(1+i\omega\tau_0)$  in Eq. (1) is replaced by a series of the form

$$\sum \frac{c_n}{1+i\omega\tau_0/\lambda_n}, \quad (11)$$

and the frequency dependence of  $\epsilon^*$  is modified.

<sup>32</sup> W. A. Yager, *Trans. Electrochem. Soc.* **74** (preprint) (1938).

<sup>33</sup> L. Hartshorn, N. J. L. Megson, and E. Rushton, *Proc. Phys. Soc.* **52**, 796 (1940).

<sup>34</sup> A. H. Scott, A. T. McPherson, and H. L. Curtis, *Bur. Stand. J. Research* **11**, 173 (1933).

<sup>35</sup> See, however, reference 10.

<sup>36</sup> P. Debye, *Physik. Zeits.* **36**, 100, 193 (1935).

<sup>37</sup> P. Debye and W. Ramm, *Ann. d. Physik* **28**, 28 (1937).

<sup>38</sup> See, for instance, J. H. Van Vleck, *J. Chem. Phys.* **5**, 556 (1937), and reference 3.

The experimental deviations from Eq. (1), for polar liquids, however, occur in strongly polar liquids for which the theory predicts only a single dispersion term of the form (10). Furthermore, the departures increase with decreasing temperature, a behavior which is again contrary to the theory.

The series (11) cannot in any case reasonably be expected to account for Eq. (5). The nature of the difficulty is readily seen by considering the expression (7) for  $\epsilon''$ . This expression is logarithmically symmetrical in the frequency about the value  $\omega = 1/\tau_0$ . The series (11) must then give this same characteristic symmetry which can be the case only if the constants  $c_n$  have the same value for  $\lambda_n = 1/n$  as for  $\lambda_n = n$ . It is difficult to see any reason for such a symmetrical distribution of the  $c_n$ . Furthermore, this distribution must be a very broad one to account for values of  $\alpha$  much greater than zero (cf. under C). In addition, the distribution must approximate a continuous one as otherwise the limiting behavior at very low or very high frequencies will be given essentially by a single term of the series. This would require limiting  $90^\circ$  angles of approach to the  $\epsilon'$  axis of the complex plane locus. As is evident from the discussion in III and V, this behavior is not found experimentally.

### B. Effect of molecular shape

In the original Debye treatment for polar molecules the molecules are assumed to be spherical. If a more general assumption of an ellipsoidal form is made, one obtains instead of a single relaxation time three related in terms of the axial ratios of the ellipsoid.<sup>39</sup> A series of the form (11) with three terms is then obtained. The difficulties with this hypothesis as a general explanation are then covered in the discussion under A.

### C. Distribution of relaxation times

The concept of a distribution of relaxation times was first introduced by von Schweidler.<sup>40</sup> Later Wagner<sup>5</sup> proposed the use of a logarithmic Gaussian distribution of the form

$$F(s)ds = (b/\pi^{1/2})\exp(-b^2s^2)ds, \quad (12)$$

<sup>39</sup> J. Perrin, *J. de phys. et rad.* [7] **5**, 497 (1934); A. Budo, *Physik. Zeits.* **40**, 603 (1939).

<sup>40</sup> E. von Schweidler, *Ann. d. Physik* **24**, 711 (1907).

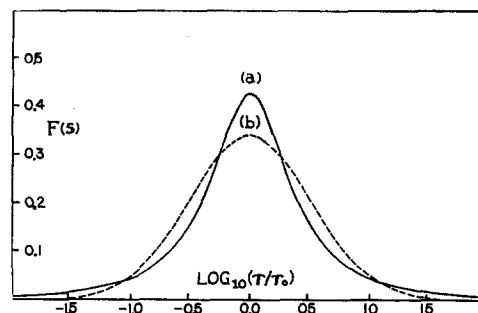


FIG. 9. Distribution of relaxation times  $F(s)$ , where  $s = \log_e(\tau/\tau_0)$ ; (a) calculated from circular arc locus for  $\alpha = 0.23$ , (b) logarithmic Gaussian distribution for  $b = 0.6$ .

where  $s = \log_e(\tau/\tau_0)$  and  $b$  determines the breadth of the distribution. As Fuoss and Kirkwood<sup>41</sup> have shown, it is possible to calculate the distribution necessary to account for any given experimental results from the observed  $\epsilon''$ -frequency relation. If the general relation (7) for  $\epsilon''$  is used, their analysis is easily shown to give the result

$$F(s)ds = \frac{1}{2\pi} \cdot \frac{\sin \alpha \pi}{\cosh(1-\alpha)s - \cos \alpha \pi} ds. \quad (13)$$

It is interesting to compare this result with Eq. (12). Yager<sup>24</sup> has evaluated  $\epsilon'$  and  $\epsilon''$  from Eq. (12) by numerical integration and from his values it is possible to find the value of  $b$  which corresponds most closely to a given  $\alpha$ . As an example the two distributions for  $b = 0.6$  and the corresponding value 0.23 of  $\alpha$  are plotted in Fig. 9. It is evident that the Gaussian distribution (dashed curve) requires too great a concentration of relaxation times for values of  $\tau$  which are comparatively close to  $\tau_0$  and that the distribution (13) is considerably broader. The necessary breadth increases rapidly for larger values of  $\alpha$  and the Gaussian distribution (12) is an increasingly poorer approximation. For  $\alpha = 0.5$ , 95 percent of the relaxation times are included in the range  $0.001 < \tau/\tau_0 < 1000$ , while for  $\alpha = 0.75$  only 72 percent are included in the same range.

Although the distribution (13) is formally an exact representation of the circular arc locus and Eq. (5), there remains the difficulty of accounting for such a broad distribution as is required in many cases. An even greater difficulty is en-

<sup>41</sup> R. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.* **63**, 385 (1941).

countered in attempting to account for the essential logarithmic symmetry of this distribution. In the absence of any satisfactory explanation of these features, the distribution function is nothing more than a means of expressing the experimental results which is equivalent to the circular arc locus or Eq. (5).

#### D. Complex coefficient of viscosity

Gemant<sup>42</sup> has suggested that, by analogy with observed elastic effects in solid friction, one might expect in the case of polar dielectrics a complex coefficient of viscosity or solid friction in the relaxation time of Eq. (1). This viscosity  $\eta^*$  must be of the form

$$\eta^* = \eta_0(i\omega)^{-\alpha},$$

$\eta_0$  being a constant, if Eq. (5) is to result.

An assumption of this kind does not, of course, explain the experimental results but merely restates the problem in terms of a concept which itself remains to be explained. There is therefore little to be gained by this approach.

#### E. Other suggested modifications

Gemant has also proposed that the dispersion term  $1/(1+i\omega\tau_0)$  in Eq. (1) be replaced by an expression of the form  $[1-(i\omega\tau_0)^g]/[1-(i\omega\tau_0)^h]$ , where  $g=(4j\pm1)/(4k\pm1)$ ,  $h=(4l+2)/(2m+1)$ , with  $j, k, l, m$  integers. This expression reduces properly to  $1/[1+(i\omega\tau_0)^{1-\alpha}]$  only if  $g=\frac{1}{2}h=1-\alpha$ . In the absence of a fundamental basis for the suggested expression, this procedure offers nothing in the way of explanation for Eq. (5).

Other modifications of the simple dispersion theories which have been suggested either have no effect on the frequency dependence or are incapable of accounting for the particular type of dispersion found experimentally as expressed by Eq. (5).

### VII. CONCLUSION

The experimental data which have been discussed are believed to be representative of a considerable number and variety of dielectrics. There is no doubt that dispersion and absorption in these dielectrics may be due to one or more of several types of polarization. The remarkable fact is that the experimental results are so generally expressed by an empirical formula involving a single new constant  $\alpha$ .

The hypothesis of a distribution of relaxation times, although a natural one to consider, leads to a general distribution formula with the one disposable parameter  $\alpha$ . Both the breadth and form of this distribution are difficult to understand. The fact that so many otherwise dissimilar dielectrics exhibit the same characteristic form of dispersion suggests that a more general fundamental mechanism or process must be involved.

The ordinary mechanisms proposed to explain dielectric absorption (e.g., viscous damping, direct current conductivity) have the common feature that they are purely dissipative in character. This is represented in the equivalent circuit of the dielectric by a pure resistance. The actual behavior of dielectrics, however, requires that the dispersion mechanism be equivalent to a complex impedance as shown in Fig. 2 (b). It therefore implies a conservation or "storage" of energy in addition to dissipation of energy in the mechanism of molecular interaction responsible for the dispersion. The characteristic feature of the equivalent complex impedance, a phase angle which is independent of frequency, has a very simple statement in terms of energy. Namely, the ratio of the average energy stored to the energy dissipated *per cycle* in the form of heat is a constant independent of the frequency. The simplicity of this result suggests that the problem may profitably be considered from this viewpoint.

<sup>42</sup> A. Gemant, Physics 7, 311 (1936).