

## ANOMALOUS DISPERSION OF DIELECTRIC CONSTANT

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**ABSTRACT.** A new equation based on the ideas of hindered rotation and preferred orientation in quasi-crystalline liquids and solids has been derived in order to quantitatively account for the dispersion and absorption of polar substances. The existing relationships of Debye, Cole and Cole and others have been critically reviewed. The new expression for  $\epsilon'$  the dielectric constant and  $\epsilon''$  the dielectric loss are

$$\epsilon' = \epsilon_s + \frac{(\epsilon_0 - \epsilon_s)}{1 + \omega^2\tau^2} \quad ; \quad \epsilon'' = \frac{(\epsilon_0 - \epsilon_s)\omega\tau}{1 + \omega^2\tau^2}$$

The new equations for dispersion and absorption have been extended to binary solutions of polar components and a general equation has been derived for the dielectric constant and dielectric loss in terms of the relaxation times of the two components.

## INTRODUCTION

The phenomenon by which there occurs a marked decrease of the dielectric constant with increasing frequencies of the applied field accompanied by a strong absorption of electric waves is referred to as anomalous dispersion. This effect in liquids was first observed experimentally by Drude (1897). Debye (1929) based his explanation for anomalous dispersion on the idea of the existence of polar molecules. At sufficiently low frequencies when the period of the field is large compared to  $\tau$ , the time of relaxation of the polar substance, the molecules can follow the field with ease and consequently the material has high static dielectric constant. When the frequency of the field is of a magnitude comparable to relaxation time the dielectric constant falls gradually with increasing frequencies. Finally at very high frequencies, *i.e.*, when the period of the field is very small compared to  $\tau$  the dipoles reach such a state wherein they do not show any response to the applied field. Thus the polar material here is characterised by a constant high frequency dielectric constant. The extent and the range of dielectric dispersion is a function of the internal forces in the substance such as the viscosity and also depends upon the nature of the dipoles of which the molecules of the substance are constituted.

## POLAR LIQUIDS AND SOLIDS

Debye (*loc. cit.*) was the first to derive a quantitative expression to account for the dispersion and absorption of polar substances. He wrote for the

molecular polarisation in the dispersion region as follows

$$P_{(\omega)} = \frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{M}{d} = \frac{4\pi N}{3} \left( \alpha_p + \frac{\mu^2}{3kt} \frac{1}{1 + i\omega\tau} \right) \quad \dots (1)$$

The equation of Debye is based on the validity of the Clausius-Mosotti relationship which has been found to be a failure when applied to concentrated solutions and pure liquids and has got limited application even in the case of dilute solutions. This failure is inherent in the assumption of a spherical cavity in evaluating the internal field and the postulate of a dipole having all possible orientation in space.

It is of interest to note that Debye has derived a formula for the average electric moment of a molecule in solids assuming that the molecule can point with its moment only in two definite directions, the direction of  $F$  and the opposite.

The mean moment of a molecule in the direction of  $F$  is

$$\bar{m} = \frac{1}{1 + i\omega\tau} \frac{\mu^2 F_0 e^{i t}}{kT} = \frac{1}{1 + i\omega\tau} \frac{\mu^2 F}{kT}$$

The expression on right hand side can be derived in a very simple manner as follows. The general distribution function in a variable field has been given by Debye as

$$f = A \left( 1 + \frac{1}{1 + i\omega\tau} \frac{\mu F}{kT} \cos \theta \right) \quad \dots (2)$$

where  $\theta$  is the angle ' $\mu$ ' makes with  $F$ . The Boltzmann's distribution function gives for  $n_1$  and  $n_2$  the number of molecules following the two possible orientations one along and the other opposite to the field

$$n_1 = A \left( 1 + \frac{\mu F}{kT} \frac{1}{1 + i\omega\tau} \right)$$

$$n_2 = A \left( 1 - \frac{\mu F}{kT} \frac{1}{1 + i\omega\tau} \right)$$

obtained by putting  $\cos \theta = \pm 1$  in Debye's expression (2)

$$\begin{aligned} \text{the mean moment } \bar{m} &= \mu(n_1 - n_2) / (n_1 + n_2) \\ &= \frac{2A(\mu^2 F / kT)}{2A} \left( \frac{1}{1 + i\omega\tau} \right) \end{aligned}$$

$$i.e. \bar{m} = \frac{\mu^2 F}{kT} \frac{1}{(1 + i\omega\tau)}$$

This expression for  $\bar{m}$  for solids differs from that derived earlier for the case of gases by a factor  $1/3$  since in the former case, only the directions parallel and anti-parallel to the field are considered. Proceeding as before Debye has obtained the same expressions for  $\epsilon'$  and  $\epsilon''$  as for the case of gases. This is because, firstly he has used the same Clausius-Mosotti

relationship  $\frac{(\epsilon - 1)M}{(\epsilon + 2)d}$  to hold good and secondly the modified expression for  $\bar{m}$  for solids has been eliminated in the initial stages of the derivation by being expressed in terms of  $\frac{(\epsilon - 1)M}{(\epsilon + 2)d}$  and hence becomes ineffective to modify the expressions for  $\epsilon'$  and  $\epsilon''$ .

THE NEW EQUATION

It has been found by Jatkar, Iyengar and Sathe, (1946) that the polarisation of liquids and solids in a static field is given by

$(\epsilon - 1)M/d = 4\pi N(\alpha_k + \mu^2/kT)$  instead of the classical expression

$$\frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{M}{d} = \frac{4\pi N}{3} (\alpha_k + \mu^2/3kT).$$

The former equation has been derived using a new internal field based on the concept of a thin long cylindrical cavity which is in conformity with the anisotropy of the dipole, and also on the consideration of preferred orientation along and opposite to the direction of the applied field. This equation has been found applicable to a large number of polar liquids and solids. Extending the new relationship to the case of a variable field, the polarisation  $P_{(\omega)}$  at frequency  $\omega$  is given by

$$P_{(\omega)} = \frac{(\epsilon - 1)M}{d} = 4\pi N \left( \alpha_k + \frac{\mu^2}{kT} \frac{1}{1 + i\omega\tau} \right)$$

Defining

$$(\epsilon_\infty - 1)M/d = 4\pi N\alpha_k \text{ and } (\epsilon_0 - 1)M/d = 4\pi N \left( \alpha_k + \frac{\mu^2}{kT} \right)$$

we have

$$P_{(\omega)} = M/d \left\{ (\epsilon_\infty - 1) + \frac{1}{(1 + i\omega\tau)} [(\epsilon_0 - 1) - (\epsilon_\infty - 1)] \right\} = \frac{(\epsilon - 1)M}{d}$$

whence

$$\begin{aligned} \epsilon &= \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + i\omega\tau} \\ &= \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)(1 - i\omega\tau)}{1 + \omega^2\tau^2} \end{aligned}$$

*i.e.*,

$$\epsilon = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + \omega^2\tau^2} - i\omega\tau \frac{(\epsilon_0 - \epsilon_\infty)}{1 + \omega^2\tau^2}$$

Writing

$$\epsilon = \epsilon' - i\epsilon''$$

$$\epsilon' = \frac{(\epsilon_0 - \epsilon_\infty)}{1 + \omega^2\tau^2} + \epsilon_\infty \quad \text{and} \quad \epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}$$

These expressions are very similar to the classical expressions but for a factor  $\frac{(\epsilon_0 + 2)}{(\epsilon_\infty + 2)}$  which comes associated with  $\omega\tau$  in the latter case. It is note-

worthy that the two expressions are identical when  $\frac{(\epsilon_0 + 2)}{(\epsilon_\infty + 2)} = 1$ , i.e., when the high frequency dielectric constant does not very much differ from the static dielectric constant.

Wyman's (1936) and Onsager's (1936) expressions for the polarization lead to the same equations for  $\epsilon'$  and  $\epsilon''$  as given by the application of the new equation. For a modified form of Onsager's equation

$$\frac{(\epsilon - 1)}{(\epsilon + 2)} - \frac{(\epsilon_\infty - 1)}{(\epsilon_\infty + 2)} - \beta = q \left\{ \frac{3}{2} \frac{(\epsilon_\infty + 2)}{(\epsilon + 2)} - 1 \right\}$$

where 'q' is an empirical constant; (the case  $q = 1$  corresponding to Onsager's equation). Cole (1938) has shown that

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + Z^2} \quad \text{and} \quad \epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)}{1 + Z^2} \cdot Z$$

where

$$Z = \frac{\omega\tau}{1 - \delta} \quad [\delta \text{ being a constant} = \frac{1}{3}, \frac{4\pi N\mu^2}{9kT} \frac{(\epsilon_\infty + 2)}{(\epsilon_0 + 2)} (1 - q)]$$

The application of experimental data has shown that 'δ' is indeed small, (i.e.,  $Z = \omega\tau$ ) so that the expressions for  $\epsilon'$  and  $\epsilon''$  correspond to the new equation.

The maximum in  $\epsilon''$  as well as the maximum slope of the  $\epsilon' - \omega$  curve occur at a frequency  $\omega_c$  the condition for which is given according to (1) Debye's expression as  $\omega_c\tau = \frac{(\epsilon_\infty + 2)}{(\epsilon_0 + 2)}$ , (2) Onsager's  $\omega_c\tau = 1$ , (3) the modified Onsager's equation  $\frac{\omega_c\tau}{1 - \delta} = 1$  and (4) the new equation  $\omega_c\tau = 1$ . Thus the relaxation times obtained from the observed values of  $\omega_c$  are always smaller by a factor  $\frac{(\epsilon_\infty + 2)}{(\epsilon_0 + 2)}$  in Debye's case as compared with the correct value calculated from the new equation.

#### SOLUTIONS

##### (a) Nonpolar:

Since the Clausius-Mosotti expression is considered to be valid for dilute solutions in nonpolar solvents, it is expected that Debye's dispersion equation derived on the basis of this hypothesis should be applicable to measurements in dilute solutions of nonpolar solvents. The extension of Debye's dispersion equation to a binary system has been made by Williams (1934) who has considered a solution in which there are  $n_2$  polar molecules/c.c. each having electronic polarisability  $\alpha_{L_2(0)}$  and moment  $\mu_2$  dissolved in  $n_1$  mols./c.c. of the

nonpolar solvent each having electronic polarisability  $\alpha_{11(0)}$  and zero electric moment. Thus the polarisation per c.c. of the mixture

$$P_{12(\omega)} = \frac{(\epsilon_{12} - 1)}{(\epsilon_{12} + 2)} = \frac{4\pi}{3} \left\{ \alpha_{11(0)}n_1 + \alpha_{22(0)}n_2 + \frac{n_2\mu^2}{3kT} \frac{1}{(1 + i\omega\tau_2)} \right\}$$

$$= \frac{(\epsilon_{12(\infty)} - 1)}{(\epsilon_{12(\infty)} + 2)} + \frac{1}{1 + i\omega\tau_2} \left\{ \frac{(\epsilon_{12(0)} - 1)}{(\epsilon_{12(0)} + 2)} - \frac{(\epsilon_{12(\infty)} - 1)}{(\epsilon_{12(\infty)} + 2)} \right\}$$

$\epsilon_{12(\infty)}$  = high frequency dielectric constant and  $\epsilon_{12(0)}$  = static dielectric constant of solution and  $\tau_2$  = relaxation time of the polar solute molecules. Writing  $\epsilon_{12} = \epsilon_{12}' - i\epsilon_{12}''$  and separating the real and imaginary parts

$$\epsilon_{12}' = \epsilon_{12(\infty)} + \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{1 + \lambda^2} - \lambda \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{1 + \lambda^2}$$

whence

$$\epsilon_{12} = \epsilon_{12(\infty)} + \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{1 + \lambda^2} \quad \text{and} \quad \epsilon_{12}'' = \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{1 + \lambda^2} \cdot \lambda$$

$$\left( \lambda = \omega\tau_2 \frac{(\epsilon_{12(0)} + 2)}{(\epsilon_{12(\infty)} + 2)} \right)$$

These expressions which are very similar to those given by Debye for gases were derived on the basis of Clausius-Mosotti expression for total polarisation. The usage of the correct expression for polarisation  $(\epsilon - 1)M/d$  gives expressions for  $\epsilon'$  and  $\epsilon''$  very similar to those derived above except that in the former case the factor  $\frac{(\epsilon_{12(\infty)} + 2)}{(\epsilon_{12(0)} + 2)}$  does not occur. In fact in dilute solutions of nonpolar solvents  $\epsilon_{12(0)} \approx \epsilon_{12(\infty)}$  so that the factor  $\frac{(\epsilon_{12(\infty)} + 2)}{(\epsilon_{12(0)} + 2)}$  fortuitously becomes unity and hence Debye's expression coincides with the new equation.

(b) Polar:

Oncley (1938) has attempted to interpret the dispersion of polar binary solutions using Wyman's (1936) empirical equation for polarisation. No rigorous theoretical treatment of the subject is available in literature. On the basis of the new equation for molecular polarisation  $(\epsilon - 1)M/d$ , the expression for the molecular polarisation  $P_{12(\omega)}$  of the solution at  $\omega$  frequency can be written as,

$$P_{12(\omega)} = P_{1(\omega)}f_1 + P_{2(\omega)}f_2$$

where  $P_{1(\omega)}$  and  $P_{2(\omega)}$  are the molecular polarisations of the two polar components at  $\omega$  frequency.

Now 
$$P_{12(\omega)} = \frac{(\epsilon_{12} - 1)(M_1f_1 + M_2f_2)}{d_{12}} = \frac{(\epsilon_1 - 1)M_1f_1}{d_1} + \frac{(\epsilon_2 - 1)M_2f_2}{d_2}$$

Writing for the sake of simplicity in terms of specific polarisations

$$p_2 \left( = \frac{(\epsilon_r - 1)}{d_r} \right)$$

$$p_{12(\omega)} = \frac{(\epsilon_{12} - 1)}{d_{12}} = \frac{(\epsilon_1 - 1)}{d_1} \omega_1 + \frac{(\epsilon_2 - 1)}{d_2} \omega_2; \omega_1 \text{ and } \omega_2$$

being weight fractions.

$$\text{i.e.} \quad \epsilon_{12} = 1 + d_{12} \{ p_{1(\omega)} \omega_1 + p_{2(\omega)} \omega_2 \}$$

where

$$p_1(\omega) = \frac{(\epsilon_1 - 1)}{d_1} = \frac{(\epsilon_{1(\infty)} - 1)}{d_1} + \frac{1}{1 + i\omega\tau_1} \frac{(\epsilon_{1(0)} - \epsilon_{1(\infty)})}{d_1}$$

and

$$p_2(\omega) = \frac{(\epsilon_2 - 1)}{d_2} = \frac{(\epsilon_{2(\infty)} - 1)}{d_2} + \frac{1}{1 + i\omega\tau_2} \frac{(\epsilon_{2(0)} - \epsilon_{2(\infty)})}{d_2}$$

$\tau_1$  and  $\tau_2$  being the relaxation times and  $\epsilon_{1(0)}$  and  $\epsilon_{2(0)}$  the static dielectric constants of the two polar components. Substituting these values of  $p_1(\omega)$  and  $p_2(\omega)$  we get

$$\begin{aligned} \epsilon_{12} = 1 + d_{12} \left\{ \frac{(\epsilon_{1(\infty)} - 1)}{d_1} \omega_1 + \frac{(\epsilon_{2(\infty)} - 1)}{d_2} \omega_2 \right. \\ \left. + \frac{(\epsilon_{1(0)} - \epsilon_{1(\infty)})}{1 + i\omega\tau_1} \frac{\omega_1}{d_1} + \frac{(\epsilon_{2(0)} - \epsilon_{2(\infty)})}{1 + i\omega\tau_2} \frac{\omega_2}{d_2} \right\} \end{aligned}$$

Since

$$\frac{(\epsilon_{12(\infty)} - 1)}{d_{12}} = \frac{(\epsilon_{1(\infty)} - 1)}{d_1} \omega_1 + \frac{(\epsilon_{2(\infty)} - 1)}{d_2} \omega_2$$

and

$$\frac{(\epsilon_{2(0)} - \epsilon_{2(\infty)})}{d_2} \omega_2 = \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{d_{12}} - \frac{(\epsilon_{1(0)} - \epsilon_{1(\infty)})}{d_1} \omega_1$$

$$\begin{aligned} \epsilon_{12} = \epsilon_{12(\infty)} + \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{1 + i\omega\tau_2} \\ + d_{12} \left[ - \frac{(\epsilon_{1(0)} - \epsilon_{1(\infty)})}{d_1} \omega_1 \left\{ \frac{1}{(1 + i\omega\tau_1)} - \frac{1}{(1 + i\omega\tau_2)} \right\} \right] \end{aligned}$$

Separating  $\epsilon_{12}$  into its real and imaginary parts and comparing with

$$\epsilon_{12} = \epsilon_{12}' - i\epsilon_{12}''$$

we get

$$\begin{aligned} \epsilon_{12}' = \epsilon_{12(\infty)} + \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{1 + \omega^2\tau_2^2} \\ + \frac{(\epsilon_{1(0)} - \epsilon_{1(\infty)})}{d_1} d_{12}\omega_1 \left\{ \frac{1}{(1 + \omega^2\tau_1^2)} - \frac{1}{(1 + \omega^2\tau_2^2)} \right\} \end{aligned}$$

$$\text{and } \epsilon_{12}'' = \frac{(\epsilon_{12(0)} - \epsilon_{12(\infty)})}{1 + \omega^2 \tau_2^2} \omega \tau_2 + \frac{(\epsilon_{1(0)} - \epsilon_{1(\infty)})}{d_1} d_{12} \omega_1 \left\{ \frac{\omega \tau_1}{(1 + \omega^2 \tau_1^2)} - \frac{\omega \tau_2}{(1 + \omega^2 \tau_2^2)} \right\}$$

For a nonpolar solvent  $\epsilon_{1(0)} \approx \epsilon_{1(\infty)}$  so that the above equations reduce to the expression derived earlier for nonpolar solutions.

#### MOLECULAR RADIUS

Debye considered the rotation of a molecule amidst its surroundings analogous to a sphere carrying a dipole, rotating in a viscous medium. According to this analogy it is seen that a torque is necessary to rotate the molecule against the inner friction of the medium in which it is suspended. Stokes has calculated that this inner frictional force is given by  $\zeta = 8\pi\eta a^3$  where  $\eta$  is the inner friction constant of the surrounding medium in which the sphere of radius 'a' is rotating. From his considerations of Brownian motion, Debye has deduced that the relaxation times  $\tau = \zeta/2kT$ . Substituting  $8\pi\eta a^3$  for  $\zeta$  we get

$$\tau = \frac{4\pi\eta a^3}{kT}$$

Thus a knowledge of  $\tau$  from the observed critical frequency will enable the calculation of 'a', the radius of the molecule of an assumed spherical shape rotating in a medium of known viscosity  $\eta$ . It is evident that a considerable number of molecules do not fall in conformity with the picture of a rotating sphere. The long zig-zag chain type of molecules which are often met with scoop out a disc-like rather than a spherical cavity when they rotate. It will be thus interesting to investigate the frictional forces in conformity with this picture. In fact, Stokes has dealt with such a two dimensional rotation about an axis and has calculated the frictional torque as  $4\pi\eta a^2 h$  where 'a' is the radius of the disc cavity and 'h' its thickness. Here  $\zeta$  is equal to  $\tau/kT$  corresponding to the case of a rotation in one plane, as has been derived by Debye (1913) in an earlier paper. Thus a knowledge of the thickness 'h' of a rotating chain enables one to determine 'a' the radius of the disc. 'a' then should correspond to half the length of the molecule or any unit thereof which is executing rotation.

#### DISTRIBUTION OF RELAXATION TIME

In the case of compounds involving complex molecular structure, e.g., the high polymers it was found that there was a considerably broader frequency range of dispersion and absorption together with a smaller maximum value of  $\epsilon''$  than predicted by Debye's equation. This discrepancy was thought to be due to the fact, that the polarisation was wrongly assumed to have a single unique relaxation time. Wagner (1913) assumed a distribution

of relaxation time about some probable value and proposed the use of a logarithmic Gaussian distribution. Yager (1936) predicted that  $\epsilon''_{\max}$  is  $< \frac{(\epsilon_0 - \epsilon_\infty)}{2}$  by an amount depending upon the density of distribution. Fuoss and Kirkwood (1941) have also deduced an empirical formula to determine the distribution function of relaxation times.

Cole and Cole (1941) gave an expression for the complex dielectric constant

$$\epsilon = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + (\omega\tau_0)^{1-n}}$$

by their study of dispersion in the light of the Argand diagram or the complex plane locus. If this  $\epsilon$  is resolved into its real and imaginary component  $\epsilon' - \epsilon''$  then

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + (\omega\tau)^{2(1-n)}} \quad \text{and} \quad \epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)(\omega\tau)^{1-n}}{1 + (\omega\tau)^{2(1-n)}}$$

Even on this basis the condition at critical frequency  $\omega_c$  remains the same as calculated on the basis of the new equation for a single  $\tau$ , viz.,  $\omega_c\tau = 1$  as can be easily obtained by finding out the  $\frac{d\epsilon''}{d\omega}$  and equating it to zero. In fact, the assumption of any distribution co-efficient or parameter does not change the position of the critical frequency but has the effect of changing the shape of the  $\epsilon'$  and  $\epsilon''$  curves.

Cole and Cole (1941) have discussed the representation of dispersion data on the basis of the Argand diagram or complex plane locus in which  $\epsilon''$  the imaginary part of the complex dielectric constant is plotted against  $\epsilon'$  the real part at various frequencies. The locus of such a plot, on the basis of a single relaxation time, has been shown to be a semi-circle with the centre on the  $\epsilon'$  axis by a consideration of vectors in complex plane. The locus could as well be deduced in a very simple manner from the expressions for  $\epsilon'$  and  $\epsilon''$  by a mere elimination of the frequency factor as follows

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{1 + \lambda^2} \dots\dots(1) \quad \text{and} \quad \epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\lambda}{1 + \lambda^2} \dots\dots(2); \quad \lambda = \omega\tau$$

according to the new equation and is  $\omega\tau \frac{(\epsilon_\infty + 2)}{(\epsilon_0 + 2)}$  according to Debye.

$$\begin{aligned} \text{From (2)} \quad \epsilon''^2 &= \frac{(\epsilon_0 - \epsilon_\infty)^2}{(1 + \lambda^2)^2} \cdot \lambda^2 \\ &= \frac{(\epsilon_0 - \epsilon_\infty)^2}{(1 + \lambda^2)^2} \cdot \lambda^2 + \frac{(\epsilon_0 - \epsilon_\infty)}{(1 + \lambda^2)^2} - \frac{(\epsilon_0 - \epsilon_\infty)^2}{(1 + \lambda^2)^2} \end{aligned}$$

$$\text{Using (1)} \quad \epsilon''^2 = (\epsilon' - \epsilon_\infty) (\epsilon_0 - \epsilon_\infty) - (\epsilon' - \epsilon_\infty)^2$$

$$\text{i.e.,} \quad \epsilon''^2 = (\epsilon' - \epsilon_\infty) (\epsilon_0 - \epsilon_\infty)$$



Geometrically this condition means that the rectangle contained by two segments of a diameter equal to  $(\epsilon' - \epsilon_x)$  and  $(\epsilon_0 - \epsilon')$  equals the square of a chord  $\epsilon''$  cutting the diameter perpendicularly. This means that  $\epsilon' - \epsilon''$  curve is a semi-circle with centre on the  $\epsilon'$  axis. Cole and Cole, however, found that experimental data do not justify this semi-circular plot in a number of cases but could be represented by a circular arc characterised by an angle  $\alpha\pi/2$  which is a measure of the deviation from the semicircle, being equal to the angle between the  $\epsilon'$  axis and the radius through  $\epsilon_\infty$ . This circular arc again has been given a theoretical basis by Cole and Cole using complex plane loci. The significance of this angle can be obtained in a very simple way as follows. Considering the circular arc it is seen from figure 1

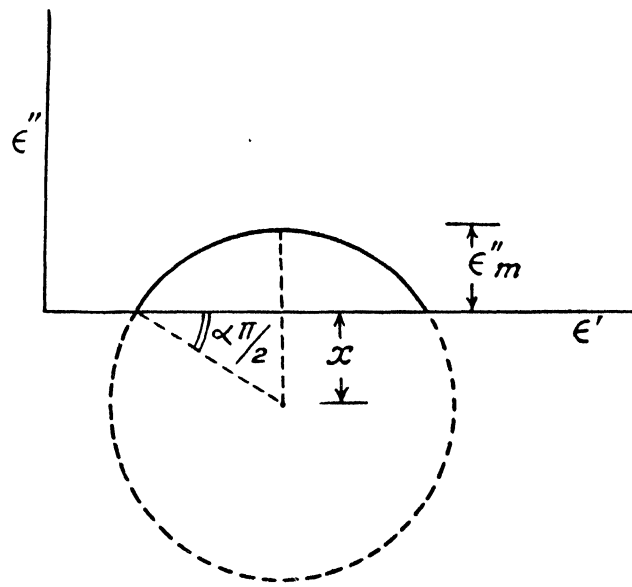


FIG. 1

$$\epsilon''_m(\epsilon''_m + 2\lambda) = \frac{(\epsilon_0 - \epsilon_\infty)^2}{4} \quad \text{Since } \lambda = \frac{(\epsilon_0 - \epsilon_\infty)}{2} \tan \alpha\pi/2$$

$$\epsilon''_m^2 + (\epsilon_0 - \epsilon_\infty) \tan \alpha\pi/2 \epsilon''_m - \frac{(\epsilon_0 - \epsilon_\infty)^2}{4} = 0$$

$$\epsilon''_m = \frac{(\epsilon_0 - \epsilon_\infty) \tan \alpha\pi/2 \pm (\epsilon_0 - \epsilon_\infty) \sec \alpha\pi/2}{2}$$

Discarding the negative solution for  $\epsilon''_m$

$$\begin{aligned} \epsilon''_m &= (\epsilon_0 - \epsilon_\infty) (\sec \alpha\pi/2 - \tan \alpha\pi/2) / 2 \\ &= (\epsilon_0^2 - \epsilon_\infty) k / 2 \end{aligned}$$

'k' being a constant characteristic of the substance. Thus the parameter 'alpha' introduced serves to increase the  $\epsilon''_{max}$  value which usually falls short of

the value  $\frac{(\epsilon_0 - \epsilon_\infty)}{2}$  as evaluated on the basis of a single relaxation time. Cole and Cole have given on the basis of their complex plane locus the equation for  $\epsilon''_m$  as  $\epsilon''_m = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \tan (1 - \alpha)\pi/4$

This is identical with the equation derived above since

$$\begin{aligned} \tan (1 - \alpha) \frac{\pi}{4} &= \frac{(\cos \alpha\pi/4 - \sin \alpha\pi/4)}{\cos \alpha\pi/4 + \sin \alpha\pi/4} = \frac{(1 - 2 \cos \alpha\pi/4 \sin \alpha\pi/4)}{(\cos^2 \alpha\pi/4 - \sin^2 \alpha\pi/4)} \\ &= \frac{(1 - \sin \alpha\pi/2)}{\cos \alpha\pi/2} = (\sec \alpha\pi/2 - \tan \alpha\pi/2) \end{aligned}$$

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