2.1 Introduction:

According to the classical model an atom may be conceived of as consisting of a tightly bound positively charged nucleus surrounded by a diffused electron cloud having a charge equal and opposite to that of the nucleus. Under the influence of an external electric field, the centroids of the electron clouds of the atom or molecules may become displaced from the centroids of the nuclei due to the coulomb forces acting on the charges, thereby giving rise to microscopic electric dipoles. The atoms or molecules are then said to be polarized by the interaction of the applied electric field. As a result of the formation of such atomic or molecular dipoles and the alignment of these dipoles with respect to the direction of the applied electric field, the material will be polarized on a macroscopic scale as well. Such a polarization of the material is called the electronic polarization.
The atoms or group of atoms are also displaced relative to each other causing atomic polarization \( P_a \). These two polarization are collectively called distortion polarization \( P_d \). The electric dipole produced in this manner is called induced dipole and its moment, \( \mu_i \), is proportional to the applied field \( E \).

\[
\mu_i \propto E
\]

\[
\mu_i = \alpha E
\]

The constant \( \alpha \) is the property of the atom called the atomic polarizability. The induced dipole moment will remain till the external electric field is present.

There are certain dielectric materials, whose atoms or molecules possess permanent electric dipoles, but, in the normal circumstances, these
atomic or molecular dipoles are randomly oriented such that the material is not polarized on a macroscopic scale. If an electric field is applied to such a material, the electric field produces torque on the atomic or molecular dipoles, converting there by the initially random polarization into a partially coherent one along the field, on a macroscopic scale. The material is then said to be polarized and such phenomenon is known as orientational polarization. The orientational polarization is in addition to the distortion polarization $P_d$. Thus the total polarization $P_t$ and polarizability $\alpha_t$ is given by

$$P_t = P_d + P_0$$

$$\alpha_t = \alpha_d + \alpha_o$$

(2.2)

The electronic and atomic polarizability depends only upon atomic configuration and almost independent of the temperature, while, the orientational polarizability is inversely proportional to absolute
temperature T, because the increasing thermal motion reduces the alignment of the permanent dipoles by the electric field. Therefore, orientational polarization is strongly temperature dependant. The permittivity of polar materials is obviously higher than non-polar ones. The temperature dependence of the permittivity of polar materials also differs from that of the non-polar materials. In non-polar materials change of temperature has only small effect, while the permittivity of polar materials falls very rapidly than that of a non-polar material. All three atomic, electronic and orientational polarizations, is a function of frequency which provides a means to study the molecular behaviour. The various theories which explain the experimental data are reviewed in the following sections.

2.2 Theories of Static Permittivity:

When an isotropic polar material is placed in an electric field, which is either constant or a low frequency field, all types of polarizations attain equilibrium with the applied field. The permittivity under this condition is called static permittivity and denoted by $\varepsilon_0$. Debye was first
to derive an equation connecting permittivity of a liquid to its dipole moments. In his treatment, he assumed that the internal field acting on the molecule subjected to a macroscopic electric field $\vec{E}$ can be represented by the Lorentz field,

$$\vec{E} = \vec{E} + \left( \frac{4\pi}{3} \right) \vec{P}$$

(2.3)

where $\vec{P}$ is the polarization vector, that is, electric moment per unit volume of the specimen. If $\alpha_d$ is the polarizability of the molecule and $\mu$ its permanent dipole moment, one can write $\vec{P}$ in terms of equation (2.3) as,

$$\vec{P} = n \left( \alpha_d + \frac{\mu^2}{3kT} \right) \left( \vec{E} + \frac{4\pi}{3} \vec{P} \right)$$

(2.4)

where $n$ is the number density of molecules at temperature $T^\circ K$. By using the fundamental electrostatic equation,

$$\vec{P} = \left( \frac{\varepsilon_0 - 1}{4\pi} \right) \vec{E}$$

(2.5)

equation (2.4) can be written in the form,

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left( \alpha_d + \frac{\mu^2}{3kT} \right)$$

(2.6)
where \( N \) is the Avogadro number, \( \rho \) is the density, \( M \), the molecular weight and \( \varepsilon_0 \) is the dielectric constant of the liquid. The above equation can be written as,

\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{4\pi N}{3V} \left( \alpha_d + \frac{\mu^2}{3kT} \right) \tag{2.7}
\]

where \( \frac{\rho}{M} = V \), molar volume. Equation (2.7) is the extension of the well known Clausius-Mossotti equation for non-polar liquids to the polar liquids.

At very high frequencies only distortion polarization remains and orientational polarization becomes zero, so equation (2.7) reduce to the form,

\[
\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi N}{3V} \alpha_d \tag{2.8}
\]

where \( \varepsilon_\infty \) is the high frequency permittivity.

From equations (2.7) and (2.8),

\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi N \mu^2}{9kT}\quad V \tag{2.9}
\]

The equation (2.9) gives a relation between permittivity and dipole moment and therefore, can be used for calculating the molecular dipole moment.
from measurement of static permittivity. Measurements performed in the gaseous phase and in dilute solutions of polar compounds in non-polar solvents give comparable values of the dipole moment. But the values calculated from measurements on concentrated solutions and on pure polar liquids do not, however, agree with the gas values. Moreover equation (2.7) predicts a Curie point, that is infinite dielectric constant at a temperature $T_C$. This becomes evident when neglecting the induced polarization, and writing equation (2.7) in the form,

$$\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{4\pi N \mu^2}{9 k T V} = \frac{T_C}{T} \quad (2.10)$$

where

$$\frac{4\pi N \mu^2}{9 k V} = T_C \quad (2.11)$$

Thus, according to equation (2.10), for $T = T_C$, $\varepsilon_0$ should be large, that is, $T_C$ is a Curie point. Vanvleck$^3$ tried to explain this anomalous situation by stating that this does not necessarily mean that the dielectric constant must really increase without limit. Rather, at temperature below $T_C$ the polarization can not be treated as linearly
dependent upon field strength as assumed in the derivation of the Debye equation. Therefore, the theory predicts a saturation or a stable state of permanent electric polarization analogous to the familiar ferromagnetic state in some types of solids. In other words, below \( T_C \), the material should exhibit a spontaneous polarization. But no such ferroelectric behavior has been found in liquids though as per calculations based on equation (2.11), most of the liquids are expected to show this type of behavior under normal conditions. Among pure solid substances, this effect has so far been observed in few solids available in natural form\(^4\). This failure of Debye equation is not surprising because it is applied to a case where the assumption, that the local field due to molecule is zero, is almost not valid, but it does emphasize the inadequacy of the Lorentz field as a measure of the local field in a dipolar dielectric.

Several modifications of the Debye equation were proposed by many workers\(^5-8\), but because of either restricted applicability or lack of sound
theoretical foundation none of them gained general acceptance. Onsager treated the molecule as a polarizable dipole at the centre of a spherical cavity of molecular dimension in a continuous medium of static permittivity $\varepsilon_0$. The internal field in the cavity consists of two parts: (i) that produced due to external applied field in the empty cavity called the cavity field, (ii) the reaction field set-up in the cavity by the polarization which the dipole induces in the surroundings.

The Onsager's equation for static permittivity is

$$\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + \varepsilon)^2} = \frac{4\pi N \mu^2}{9kT\nu}$$

Equation (2.12) makes it possible to compute the permanent dipole moment of a molecule from the measurement of permittivity of the pure liquid, if the density and $\varepsilon_\infty$ are known. For the derivation of this equation it is supposed that the molecules are spherical and that no specific molecular interaction between the molecules occur, i.e., the dipoles are distributed according to Langevin's
law. Except for some specific classes of compounds, Onsager's theory accounted for most of the deviations from the Debye equation in the case of polar liquids. For gases and dilute solutions of polar compounds in non-polar solvents, the results of Debye's theory are only slightly affected when the reaction field is taken into account. The Onsager equation made it possible to determine the permanent dipole moment from measurements on concentrated solutions and pure polar liquids. Some further improvements were obtained when the non-spherical shape of the molecules were incorporated into Onsager's theory by Buckley, Buckingham, Abbott, Ross and Scholte.

The Onsager equation generally does not hold good for associated liquids, e.g. Carboxylic acids, alcohols etc. A theory, relating the deviation from the Onsager equation in the case of associating liquids to the orientation correlation of neighbouring molecules as a result of short range specific interaction, was given by Kirkwood. Kirkwood and later Frohlich using statistical method throughout
obtained rigorous expression for static permittivity. The Kirkwood-Frohlich equation is

\[
\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + 2)^2} = \frac{4\pi N}{3V} \cdot \frac{g \mu^2}{3kT} \tag{2.13}
\]

where \( g \) is called correlation parameter and is a measure of the relative orientation of neighbouring dipoles as influenced by specific short range forces such as intramolecular hydrogen bonding. It is possible to calculate \( g \) if the structure of the material is known, otherwise it is an empirical parameter which can be calculated from the permittivity of the material and the dipole moment of the molecules. If there are no specific correlations one has \( g = 1 \) and the Kirkwood-Frohlich equation reduces to the Onsager equation (2.12); the value of \( g \) is greater than unity is indicative of an average parallel alignment of near neighbour dipoles while the value of \( g \) less than unity is indicative of an average antiparallel alignment.

It has been observed that the description of dielectric behaviour of associated compounds
like alcohols, water, nitriles and even polymers in terms of Kirkwood correlation factor has generally proved useful. However, in a number of cases the application of the theory is hampered by lack of knowledge of the molecular configuration or the mode of association. Moreover, the equation also contains the approximation involved in treating the polar molecules as spheres.

Cole obtained an expression for static permittivity similar to Frohlich expression, but his theory differs from the theories of Kirkwood and Frohlich in the treatment of distortion polarization. The method has a special interest because Cole has generalised it to the case of an alternating field. His treatment of distortion polarization is based on the method developed by Van Vleck to calculate the permittivity of non-polar liquids. The state of liquid can be described by a set of displacement vectors and the corresponding moments. The displacement can be calculated statistically from the external field and the dipole-dipole forces, assuming the charges to be harmonically bound to their equilibrium position. The expression given by Cole is:
\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{4\pi N}{3} \cdot \frac{3\varepsilon_0 (\varepsilon_\infty + 2)}{(\varepsilon_0 + 2)(2\varepsilon_0 + \varepsilon_\infty)} \cdot \frac{9\mu^2}{3kT} 
\]

which reduce to,

\[
\frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0 (\varepsilon_\infty + 2)^2} = \frac{4\pi N}{3} \cdot \frac{9\mu^2}{3kT} 
\]

in agreement with the Frohlich equation (2.13).

2.3 Macroscopic Theory of Dielectric Dispersion:

In the previous section, permittivity has been calculated for the case where the applied field is either steady or frequency of applied field is low. In this section we shall study the effect of high frequency electric field to the dielectrics.

At low frequency all the types of polarization can reach the value they would have had in the steady field equal to the instantaneous value of the alternating field, but as the frequency is raised the polarization no longer has time to reach its steady value. The orientation polarization is the first to be affected. This type of polarization takes a time
of the order $10^{-12}$ to $10^{-10}$ sec. to reach its equilibrium value in liquids and solids with moderately small molecules and at normal temperatures (much longer in polymers); consequently, when the applied field has a frequency of $10^{10}$ to $10^{12}$ cycles per second, the orientation polarization fails to reach its equilibrium value and contributes less and less to the polarization as the frequency rises. It is this fall of polarizability from $\xi = \xi_e + \xi_a + \xi_0$ to $\xi = \xi_e + \xi_a$ with its related fall of permittivity and occurrence of absorption that constitutes dielectric dispersion. The frequency range in which the dielectric dispersion occurs, $\xi_e$ and $\xi_a$ remain unchanged, since the distortion polarization of a molecule takes much less time to reach equilibrium with an applied field than the orientation polarization does.

This lag in response of orientation polarization to the applied electromagnetic field is commonly referred to as relaxation, which may be defined as the lag in the response of the system to the change in the force i.e., the applied field. The dielectric relaxation occurs when a dielectric material is
polarized by the external field and then it relaxes on removal of the field. The orientation polarization decays exponentially with time; the characteristic time of this exponential decay is called relaxation time which is defined as the time in which this polarization reduces to \(1/e\) times its original value.

In the presence of relaxation effects the dielectric constant may conveniently be written as complex quantity,

\[
\varepsilon^* = \varepsilon' - j \varepsilon''
\]

(2.16)

where \(\varepsilon'\) is dielectric constant and \(\varepsilon''\) is dielectric loss. The loss tangent is defined by,

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]

(2.17)

Debye equation as derived by Frohlich for complex permittivity is,

\[
\varepsilon^* = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + j \omega \tau_{m}}
\]

(2.18)

separating into real and imaginary parts one obtains,

\[
\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + \omega^2 \tau_{m}^2}
\]

(2.19)
\[ \varepsilon^\| = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau_m^2} \cdot \omega \tau_m \]  

(2.20)

where \( \tau_m \) is the macroscopic relaxation time. The variation of \( \varepsilon^1 \) and \( \varepsilon^\| \) with frequency is shown in Fig. 2.1, the frequency being displayed on the logarithmic scale. The dielectric dispersion covers a wide range of frequency. It reaches its maximum

\[ \varepsilon^\|_{\text{max}} = \frac{\varepsilon_0 - \varepsilon_\infty}{2} \]  

(2.21)

at a frequency \( \omega_m = \frac{1}{\tau_m} \) and falls off to half its maximum when

\[ \omega \tau_m = \frac{1 + \omega^2 \tau_m^2}{4} \]  

(2.22)

\[ = 0.27 \approx 0.373 \]

The dielectric loss is thus considerable over frequencies varying in value by a factor more than 10.

Another way which is generally used to represent experimental results is to construct ARGAND diagram or complex plane locus in which the imaginary part
Fig. 2.1 Variation of $\varepsilon'$ and $\varepsilon''$ with frequency

Fig. 2.2 Debye semicircle
\( \varepsilon'' \) of the complex permittivity is plotted against the real part \( \varepsilon' \), each point corresponding to one frequency. From equations (2.19) and (2.20) one gets

\[
\left( \varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2} \right)^2 + \varepsilon''^2 = \left( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \right)^2 \tag{2.23}
\]

Thus by plotting \( \varepsilon'' \) against \( \varepsilon' \) a semicircle is obtained, as shown in Fig.2.2, with radius \( \varepsilon_0 - \varepsilon_\infty/2 \), its centre being on the abscissa at a distance \( \left( \frac{\varepsilon_0 + \varepsilon_\infty}{2} \right) \) from the origin. The intersection points with the abscissa are characterised by \( \varepsilon' = \varepsilon' \) and \( \varepsilon' = \varepsilon_\infty \) respectively. An interesting point is that for a given value of \( \varepsilon_0 \) and \( \varepsilon_\infty \) the \( \varepsilon'' \), \( \varepsilon' \) curve is completely defined provided the equations (2.19) and (2.20) are valid, whereas the frequency range in which the dispersion occurs has no influence on \( \varepsilon'' \), \( \varepsilon' \) curve. Thus \( \varepsilon'' \), \( \varepsilon' \) curve is independent of the value of the relaxation time.

The Debye equation (2.19) and (2.20) have been successful in representing accurately the dielectric behaviour of a number of spherical molecules. Most of the commonly observed deviation occurs in the case of polymers which do not fit in the Debye equations.
K.S. Cole and R.H. Cole suggested that in this case the permittivity might follow the empirical relation,

\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega \tau_0)^{1-\alpha}} \]  

(2.24)

where \( \alpha \) is a constant having values between 0 and 1 and is called distribution parameter. It is a measure of the width of the distribution. Rationalising this expression and using

\[ j \frac{\Gamma (1-\alpha)}{2} = \exp \left[ \frac{i\pi (1-\alpha)}{2} \right] \],

one obtains,

\[ \frac{\varepsilon_1 - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1 + (\omega \tau_0)^{1-\alpha} \sin(\pi \alpha/2)}{1 + (\omega \tau_0)^{2(1-\alpha)} + 2(\omega \tau_0)^{1-\alpha} \sin(\pi \alpha/2)} \]  

(2.25)

and

\[ \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{(\omega \tau_0)^{1-\alpha} \cos(\pi \alpha/2)}{1 + (\omega \tau_0)^{2(1-\alpha)} + 2(\omega \tau_0)^{1-\alpha} \sin(\pi \alpha/2)} \]  

(2.26)

The locus on the complex plane of which these are the parameteric equations can be obtained by eliminating \( \omega \tau_0 \). The equation of the locus is
\[
\left[ \frac{1}{2} (\varepsilon_0 + \varepsilon_\infty) - \varepsilon^1 \right]^2 + \left[ \varepsilon^{\prime\prime} + \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) \tan (\pi \omega/2) \right]^2 \\
= \frac{1}{4} (\varepsilon_0 - \varepsilon_\infty)^2 \sec^2 (\pi \omega/2)
\]  

(2.27)

This is the equation of a circle with its centre at

\[
\left[ \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) , \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) \tan (\pi \omega/2) \right]
\]

and radius \( \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) \sec (\pi \omega/2) \)

when \( \varepsilon^{\prime\prime} \) is plotted as ordinate against \( \varepsilon^1 \) as abscissa for different frequencies, an arc of a circle is obtained as shown Fig.2.3, whose centre lies below the real axis. This type of curve shows a continuous symmetrical distribution of relaxation times. The diameter of the circle, drawn from the point where \( \varepsilon^1 = \varepsilon_\infty \), makes an angle \( \propto \pi/2 \) with the abscissa.

In the limit \( \omega = 0 \), the Cole-Cole curve reduces to the Debye semicircle.

A number of cases have been reported in which the arc is somewhat skewed (Fig.2.4). Davidson and Cole\textsuperscript{19-21} suggested a new empirical relation to account for such behaviour. The Cole-Davidson equation is
Fig. 2.3 Cole-Cole arc

Fig. 2.4 Cole-Davidson arc
\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + \frac{j}{\omega \tau_0})^\beta} \]  

(2.28)

where \( \beta \) is an empirical parameter having values between 0 and 1 and is called the distribution parameter. The shape of the arc for different values of \( \beta \) is shown in Fig. 2.5. Rationalising and putting \( \tan \phi = \omega \tau_0 \), one gets,

\[ \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \cos^\beta \phi \cos^\beta \phi \]  

(2.29)

\[ \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \cos^\beta \phi \sin^\beta \phi \]  

(2.30)

The value of \( \beta \) determines the angle at which the arc cuts the \( \varepsilon' \) axis at high frequency end. The tangent at the high frequency end makes an angle \( \beta \pi/2 \) with the abscissa. This equation has been successful in representing the behaviour of substances at low temperatures. As the temperature is raised, \( \beta \to 1 \) and the arc tends to a Debye semicircle.

In certain cases there are two distinct relaxation processes which occur simultaneously. If \( \tau_1 \) and \( \tau_2 \) are the two relaxation times, \( \varepsilon' \) and \( \varepsilon'' \) are given by equations.\(^{22}\)
Fig. 2.5 Normalized Cole-Davidson arcs for different values of $\beta$

Fig. 2.6 Multiple relaxation processes
\[
\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{C_1}{1 + (\omega \tau_1)^2} + \frac{C_2}{1 + (\omega \tau_2)^2} \tag{2.31}
\]

\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{C_1}{1 + (\omega \tau_1)^2} \omega \tau_1 + \frac{C_2}{1 + (\omega \tau_2)^2} \omega \tau_2 \tag{2.32}
\]

where \(C_1\) and \(C_2\) are the relative weights of each relaxation term and \(C_1 + C_2 = 1\). Similarly in some cases, even if there are multiple relaxation processes but they are distinctly separated, a curve is obtained which can be analysed into separate Pellat-Debye curves Fig.2.6.

2.4 Distribution of Relaxation Times:

The Cole-Cole and Cole-Davidson types of behaviour can be understood as arising from the existence of a continuous spread of relaxation times, each of which alone would give rise to a Debye type of behaviour. Let \(G(\tau)\) be the distribution function of relaxation time, \(G(\tau) d\tau\) be the fraction of the molecules associated at a given instant with relaxation times between \(\tau\) and \(\tau + d\tau\). For such a distribution of relaxation time equation (2.18) must be extended to,
\[ \varepsilon^* = \varepsilon_\infty + (\varepsilon_\infty - \varepsilon_0) \int_0^\infty \frac{G(\tau)}{1 + j\omega \tau} \, d\tau \quad (2.33) \]

From its definition it follows that \( G(\tau) \) satisfies the normalisation condition,

\[ \int_0^\infty G(\tau) \, d\tau = 1 \quad (2.34) \]

starting from (2.33) following equations are obtained,

\[ \varepsilon' = \varepsilon_\infty + (\varepsilon_\infty - \varepsilon_0) \int_0^\infty \frac{G(\tau)}{1 + \omega^2 \tau^2} \, d\tau \quad (2.35) \]

and

\[ \varepsilon'' = (\varepsilon_\infty - \varepsilon_0) \int_0^\infty \frac{\omega \tau}{1 + \omega^2 \tau^2} G(\tau) \, d\tau \quad (2.36) \]

The special form for the distribution function \( G(\tau) \) was first introduced by Wagner \( ^{23} \) who assumed that an infinite number of independent causes disturb an original relaxation time \( \tau_0 \). This assumption leads to Gaussian probability function,

\[ G(\tau) \, d\tau = \frac{b}{\sqrt{\pi}} e^{-b^2 y^2} \, dy \quad (2.37) \]

where \( b \) is a constant and \( y = \ln \frac{\tau}{\tau_0} \). Unfortunately
Gaussian distribution does not lend itself to simple evaluation.

Fuoss and Kirkwood$^{24}$ suggested an expression for dielectric loss, applicable in particular to polymeric polar molecules in a non-polar solvent. They found that the results of loss measurements on polymers may be represented very successfully by the empirical relation,

$$\varepsilon'^{\|} = \frac{\varepsilon'^\text{max}}{\cosh (\beta \ln \omega/\omega_m)}$$  \hspace{1cm} (2.38)

where $\beta$ is a distribution parameter ($\beta = 1$ corresponds to Debye equation) and $\omega_m$ is the angular frequency corresponding to maximum value $\varepsilon'^\text{max}$ of $\varepsilon'^{\|}$. The value of $\varepsilon'^\text{max}$ is chosen by trial and error to give the best straight line on a plot of $\cosh^{-1} (\varepsilon'^\text{max}/\varepsilon'^{\|})$ against $\log\omega$ whose gradient is $2.30 \beta$ and whose intercept on the $\log \omega$ axis gives $\omega_m$. The Fuoss-Kirkwood function corresponds to a logarithmic distribution function.
The relaxation time $\tau$ is given by
$$ \tau = \frac{1}{\omega_m} $$

The Cole-Cole equation for complex permittivity gives a distribution function,
$$ F(S) = \frac{1}{2\pi} \frac{\sin \alpha \pi}{\cos \pi (1-\alpha) S - \cos \alpha \pi} $$

where $S = \ln \omega/\omega_m$

This function is in practice not very different from Gaussian distribution. The equations (2.37) and (2.40) can be made to coincide fairly close to each other by a suitable choice of the parameters $b$ and $\alpha$.

The Cole-Cole distribution falls off more slowly towards extreme values of $S$ than the Gaussian distribution. The Cole-Cole distribution is a useful representation for many experimental results and appears to be reasonable in view of its similarity to Gaussian distribution.

Poley gave the relation between the Fuoss-Kirkwood $\beta$ and the Cole-Cole $\alpha$ factors as,
$$ \beta \sqrt{2} = \frac{1 - \alpha}{\cos \pi (1-\alpha) \frac{\pi}{4}} $$
The distribution function for skewed arc behaviour is given by

\[ F(\tau / \tau_0) = \frac{\sin B \tau}{\pi} \left( \frac{\tau}{\tau_0 - \tau} \right)^{\beta} \quad \text{for } \tau < \tau_0 \quad (2.42) \]

\[ F(\tau / \tau_0) = 0 \quad \text{for } \tau > \tau_0 \quad (2.43) \]

Higasi has proposed a distribution function,

\[ f(\tau) = \frac{1}{A \tau} \quad ; \quad \tau_1 < \tau < \tau_2 \quad (2.44) \]

where \( \tau_1 \) and \( \tau_2 \) are the two limiting values of relaxation times. Further,

\[ \tau_2 = \sqrt{\tau_1 \tau_2} = \frac{1}{\cos m} = \tau_1 \exp(A/2) = \tau_2 \exp(-A/2) \quad (2.45) \]

\[ \frac{\varepsilon_1}{\varepsilon_0 - \varepsilon_\infty} = \frac{2}{A} \tan^{-1}(\tanh A/4) \quad (2.46) \]

Higasi has pointed out that the more general version

\[ f(\tau) = \frac{1}{A \tau^\eta} \quad ; \quad 0 < \eta < \infty \quad (2.47) \]
Fröhlich considers the case of a molecule which changes its direction by large jumps over a potential barrier rather than in small steps of Debye's diffusive model. He supposes that the heights of potential barriers are uniformly distributed between $H=H_0$ and $H=H_0+V_0$ so that the fraction of dipoles for which the barrier height lies in the range $d\gamma$ about $H_0 + V$ is $d\gamma/V_0$. The relaxation time for a molecule for which the barrier height is $(H_0+V)$ is,

$$\tau_i = A \exp \left[ \frac{(H_0 + V)}{kT} \right] = \tau_0 \exp \left( \frac{\gamma}{kT} \right)$$

(2.48)

where $\tau_0 = A \exp \left( \frac{H_0}{kT} \right)$

and the relaxation time ranges from $\tau_0$ to $\tau_i$, where $\tau_i = \tau_0 \exp \left( \frac{V_0}{kT} \right)$. If distribution of relaxation times is described by the function $f(\tau')$, where $f(\tau') d(\ln \tau')$ is the fraction of molecules which have relaxation times between $\tau$ and $\tau' + \sigma \tau'$, then,
The logarithmic function of \( \tau \) is, therefore, a rectangular function. The interesting feature of Fröhlich's Law is that it predicts the temperature-variation of the width of the distribution. If \( V_0 \) varies only slowly with temperature, the distribution will become narrower as the temperature increases, tending to a \( \delta \)-function as \( T \) tends to infinity. This corresponds qualitatively to the behaviour found in practice.

If the internal field correction is negligible, as will be the case if the polar substance is in dilute solution in a non-polar solvent, the molecular and macroscopic relaxation times are equal, and the complex permittivity is given by

\[
\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty \frac{f(\tau') \, d(\ln \tau')}{1 + \frac{\omega \tau'}{V_0}}
\]

(2.54)
On separating the real imaginary parts and integrating, one obtains,

\[\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = 1 - \frac{KT}{2\nu_0} \ln \left( \frac{1 + \omega^2 \tau^2}{1 + \omega^2 \tau_0^2} \right) \quad (2.56)\]

and

\[\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{KT}{\nu_0} \left[ \tan^{-1}(\omega \tau_1) - \tan^{-1}(\omega \tau_0) \right] \quad (2.57)\]

2.5 Molecular Theories of Dielectric Dispersion:

Debye has given an elegant discussion of dielectric relaxation of polar molecules in liquids. His central results is that the orientational part of the polarizability depends on the applied frequency \(\omega\) as, for alternating field

\[\alpha(\omega) = \frac{\alpha_0}{1 - j\omega \tau} \quad (2.58)\]

where \(\tau\) is the relaxation time and \(\alpha_0\) is the static
orientational polarizability. In liquids the relaxation time is related to the viscosity \( \eta \) by the approximate relation

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

(2.59)

where \( a \) is the radius of the molecule, supposed to be spherical. According to Debye the expression for complex permittivity is,

\[
\varepsilon^* - 1 = \frac{4\pi N}{3} \alpha_d + \frac{4\pi N \mu^2}{9kT} \frac{1}{1 + j\omega \tau}
\]  

(2.60)

At very high frequencies equation (2.60) reduces to,

\[
\frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha_d
\]  

(2.61)

Similarly, at low frequencies equation (2.60) reduces to,

\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha_d + \frac{4\pi N \mu^2}{9kT}
\]  

(2.62)

Substituting these values in equation (2.60) one obtains,

\[
\frac{\varepsilon^* - 1}{\varepsilon^* + 2} - \frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} = \left[ \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} \right] \cdot \frac{1}{1 + j\omega \tau}
\]  

(2.63)

On solving the above equation for \( \varepsilon^* \) one gets,
Separating into real and imaginary parts, the following expressions are obtained,

\[ \frac{\varepsilon^1 - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + x^2} \]  \hspace{1cm} (2.65)

\[ \frac{\varepsilon^{11}}{\varepsilon_0 - \varepsilon_\infty} = \frac{x}{1 + x^2} \]  \hspace{1cm} (2.66)

where \( x = \frac{\varepsilon_0 + \omega}{\varepsilon_\infty + \omega} \).

Equations (2.65) and (2.66) differ from equations (2.19) and (2.20) only in containing the quantity \( \tau (\varepsilon_0 + \omega)/(\varepsilon_\infty + \omega) \) instead of \( \tau_m \). The difference arises because the relaxation time, which Fröhlich uses, is for macroscopic relaxation processes, while the relaxation time used by Debye is that of the microscopic or molecular processes.

Hence  \[ \tau_m = \frac{\varepsilon_0 + \omega}{\varepsilon_\infty + \omega} \tau \]  \hspace{1cm} (2.67)
Debye theory gives the same form for the frequency dependence of the permittivity as the macroscopic theory, but shows that the macroscopic relaxation time is in all cases larger than the microscopic relaxation time.

Debye's theory fails to explain the dielectric behaviour of majority of liquids. The failure is due to over simplified model used in the theory and inadequacy of the Lorentz field as a measure of internal field in a dipolar-dielectric. By considering Onsager's model Collie et al. obtained the result,

\[
\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + 1)}{\varepsilon^*} = \frac{(2\varepsilon + 1)(\varepsilon + 2)}{2\varepsilon_0 + \varepsilon_\infty} \cdot \frac{4\pi N \mu^2}{27kTv} \cdot \frac{1}{1 + j\omega \tau^{(2,68)}}
\]

In this theory it is assumed that the dielectric is able to respond completely to thermal motion of the dipoles.

Eyring considered dielectric relaxation as a rate phenomenon like one for viscosity and diffusion, the concept of transition of a dipole over a certain potential barrier was used. A dipole in liquid may have two equilibrium positions which are separated
by a barrier of definite height. Before the dipole is able to jump to the next equilibrium position it must acquire an excess of energy over the average thermal energy from thermal fluctuations. Eyring's theory leads to the following expressions for dielectric relaxation and viscous flow

\[ \tau = \left( \frac{h}{kT} \right) \exp \left( \frac{\Delta F_\varepsilon^*}{kT} \right) \]  

(2.69)

\[ \eta = \left( \frac{hN}{V} \right) \exp \left( \frac{\Delta F_\eta^*}{kT} \right) \]  

(2.70)

where \( \Delta F_\varepsilon^* \) and \( \Delta F_\eta^* \) are the free energies of activation for dielectric relaxation and viscous flow respectively and \( V \) is the molar volume. A further development of Eyring's theory has been given by Kauzmann. He showed that a distribution of relaxation times according to Cole-Cole can easily be understood by it. Due to thermal fluctuations the conditions in the neighbourhood of all the molecules at a given moment are not at all identical. Thus the free energy of activation required for a molecule to overcome a potential barrier varies, i.e., there is a distribution of free energies of activation. Such a distribution is a symmetrical one about the mean value and
thus accounts for symmetrical $\varepsilon^1$, $\log \omega$; and $\varepsilon^{11}$, $\log \omega$ curves, since the relaxation rate depends exponentially on the free energy.

In the recent years theories of dielectric relaxation have only attempted correlation of particular parameters. Cole, Fatuzo-Mason, Klug et al., Fulton, Titular and Deutch, Sullivan and Deutch, Nee and Zwanizing, Tjia, Bordewijk and Bottcher, and many others have made further contribution to the theory of dielectric relaxation. In the work of these authors the sample geometry received particular attention as in the Kirkwood-Fröhlich theory of static dielectric constant. Titular and Deutch made an analysis of the conflicting expressions between the frequency dependent dielectric constant $\varepsilon(\omega)$ and the embedded sphere correlation proposed by Fatuzo-Mason and Glarum and opined that the Fatuzo-Mason expression is correct.

Sullivan and Deutch established an alternative formal relation for $\varepsilon(\omega)$ of polar media. In contrast to expressions for $\varepsilon(\omega)$ in terms of dipole-dipole correlation function, the Sullivan and Deutch expression
contains no shape dependent terms and therefore reveals more directly the dependence of $\varepsilon'(\omega)$ on short ranged molecular quantities. A term for the long range correlation between the dipoles in the embedded region and those in the surrounding is also developed. The relation between short range and long range time dependent correlation in the dipolar medium agrees with the results presented by Fulton\textsuperscript{36} though from a somewhat different standpoint. This theory can be the starting point for introducing refined relaxation models, but there is no evidence of its application to practical problems as yet. Moreover, no quantitative expressions have been developed for dielectric relaxation time basing on this molecular theory.

Kivelson and Madden\textsuperscript{41} also proposed a theory for $\varepsilon(\omega)$ relating it to a truly single particle correlation function for suitable sample geometry. The polarization is related, using linear response theory to a many particle correlation function which has the same form as a true single particle correlation function. A relation between single particle relaxation time and the observed many particle relaxation time is derived which allows the dielectric relaxation
data to be compared with reorientation relaxation time from light scattering and magnetic resonance experiments.

Zwanzing \(^{42}\) first introduced and then Nee and Zwanzig \(^{43}\) elaborated the concept of dielectric friction. The effect is expressed by slowing down of molecular rotation by a torque resulting from the dipole-dipole interactions. Tjia et al. \(^{40}\) pointed out certain inconsistencies in their derivation. Yet they also agreed that the rate of the average local field calculation justifies the slowing down of dielectric relaxation. The work of these authors indicated that the dielectric relaxation time depended on the dipole moment value.

In view of these considerations the application of dielectric relaxation to practical problems is still based on Debye\(^{1,5}\), and Cole-Cole\(^{18,44,45}\) relations.
REFERENCES: