Chapter-2

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2.1 Dielectric Polarization

A dielectric is an insulator that can be polarized by an applied electric field. When a dielectric is placed in an electric field, electric charges do not flow through the material, but only slightly shift from their average equilibrium positions causing dielectric polarization. The response of the dielectric material to electric field depends on the nature of its molecules. The molecules of a dielectric may be of two types: polar molecule and non-polar molecule. The molecules can be classified into polar and non-polar depending upon their symmetry and centre of gravity of positive and negative charges. A polar molecule is one in which the centre of gravity of positive charges and negative charges do not coincide and is separated by a distance of molecular dimensions. They have an asymmetrical distribution of charges and have permanent dipole moment. The magnitude of the dipole moment depends on the size and symmetry of the molecule [1]. In a system of polar molecules, the molecules are oriented in random direction in the absence of electric field so that the net dipole moment of the system is zero. If such a system of molecules is subjected to the varying electromagnetic field, then it gets polarized. On the other hand, when the centres of gravities of positive and negative charges coincide, they are known as non-polar molecules. Non-polar molecules may acquire a dipole moment in the presence of electric field. This is because the electric field causes distortion in their electronic distribution.

A dielectric is chiefly characterized by relative permittivity. Permittivity is a physical quantity that describes how an electric field affects and is affected by a dielectric medium and is determined by the ability of a material to polarize in response to the field. Higher the permittivity of the material, greater will be the polarizability of the molecules.

The application of the electric field to a dielectric produces a displacement of charge within through a progressive orientation of intrinsic or induced dipoles. This is known as dielectric polarization. Dielectric polarization is of three types. Starting from high frequencies these are electronic polarization, atomic polarization and orientation polarization. The polar molecules have all the three types of polarization whereas non-polar molecules have only electronic and atomic polarization.
2.1.1 Electronic Polarization

This is the polarization that results from the displacement of the electron clouds of atoms, molecules and ions with respect to the heavy fixed nuclei in response to an applied electric field to a distance that is less than the dimensions of the atoms, molecule, or ions. The magnitude of the electronic polarization depends upon the strength of the electric field and is independent of the temperature. Electronic polarizability exists in all atoms and molecules of both polar and non-polar dielectrics, regardless of the possibility of the appearance of other types of polarizability in the dielectric. The electronic polarization sets in a very short period of time, of the order of $10^{-14}$ to $10^{-16}$ seconds. This time period is comparable to the period of luminous vibrations.

2.1.2 Atomic Polarization

Atomic polarization results from the elastic displacement of the atomic nuclei relative to one another in a molecule of the dielectric on the application of electric field. The time required for this type of polarization lies in the infrared region of the electromagnetic radiation spectrum. Atomic polarization is slower than electronic polarization, as the displacement involved here is slower than electronic polarization, as the displacement involved here is that of much heavier ion. It takes $10^{11}$ to $10^{14}$ seconds to build up and is influenced by temperature.

Both electronic and atomic polarizations are collectively called as the distortion polarization and are common to polar and non-polar molecules.

2.1.3 Orientation Polarization

The orientation polarization is characteristic of polar dielectrics which consist of molecules having a permanent dipole moment. In the absence of external field, the dipoles are all randomly oriented and resulting in zero polarization. When an external field is applied, the dipoles rotate about their axis of symmetry and tend to align in the direction of the applied field. The polarization due to alignment is called orientation polarization. Orientation polarization is strongly dependent on temperature. Orientation polarization is slower than the electronic and atomic polarizations as the process of orientation involves the rotation of molecules. The build up time is of the order of $10^{-10}$ or more. This type of polarization lies in the microwave region of the electromagnetic
spectrum. Time required establishing orientation polarization depends upon number of
factors like the dimensions of the molecule, molecule-molecule interaction and the
viscosity of the medium.

**Theory of orientation polarization**
The theory of orientation polarization for polar molecules must account for
- The tendency of dipoles to orient in the direction of external electric field and
- Opposition to the orienting molecules by viscosity of the medium and thermal motion
  of the molecules [2].

On the basis of statistical theory of Langevin [3], and using Clausius-Mossoti
equation [4], and taking into account the internal field approach of Lorentz [5], Debye
developed the theory of polarization for polar molecules in the electric field. The
equation developed by him is known as the Debye equation and can be written as:

\[
P = \frac{M}{d} \left( \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \right) \cdot \frac{4\pi N}{3} \left( \alpha_E + \alpha_A + \frac{\mu^2}{3kT} \right)
\]

where \(M\) is the molecular weight, \(d\) is the density of the substance and \(N\) is the
Avogadro’s number. \(P\) means total polarization and is equal to the sum of electronic,
atomic and orientation polarization.

i.e. \(P = P_E + P_A + P_O\)

where \(P_E = \frac{4\pi N}{3} \alpha_E\), \(P_A = \frac{4\pi N}{3} \alpha_A\) and \(P_O = \frac{4\pi N}{3} \left( \frac{\mu^2}{3kT} \right)\)

The Debye equation (2.1) has two assumptions:

1. No local directional forces due to neighbouring molecules act on the dipoles, so
   that they are distributed according to Langevin’s law and the field is isotropic.
2. The component \(F_3\) of the local field due to the molecules in the spherical region
   of cavity is zero.

The first assumption restricts the validity of Debye’s equation to fluids, and second to
gases at low densities and to dilute solutions of polar molecules in non-polar solvents.
Many research workers on well-founded criticism have objected the applicability of
Debye’s equation to polar liquids. Ansel’m [6] proved that the Debye’s assumption of
isotropcity of the internal field created by the dipolar molecules on the application of
external field was not substantial and could lead to serious error. Debye theory applied to water molecules shows that water has Curie point at 1100°K and so be ferroelectric through the whole of its liquid range. This failure of Debye equation is not surprising, since we are here applying it to a case where the second assumption is almost certainly not valid. This failure of Debye theory which led Onsagar to find a relation between permittivity and dipole moment of a polar molecule.

Onsagar [7] assume the polar molecule as a polarizable point dipole at the center of a spherical cavity of molecular dimensions in a continuous medium of static permittivity \( \varepsilon_0 \). The radius \( a \) of this cavity is defined by:

\[
\frac{4\pi Nd}{3M} a^3 = 1
\]

i.e. the sum of volumes of the spherical cavities is equal to the total volume of the material. This assumption that the cavity in which the molecule lies can be treated as a sphere in a homogeneous medium limits the validity of the theory to material in which there are no strong local forces. The internal field could be represented by two parts:

- The cavity field \( G \), produced in the empty cavity by the external applied field; and
- The reaction field \( R \) set up in the cavity by the polarization which the dipole induces in its surroundings.

Calculating fields \( G \) and \( R \) on purely electrostatic basis, Onsagar established a relation between dielectric constant of a polar liquid with the dipole moment of its molecules, by means of following equation:

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

This equation is known as the Onsagar’s equation for the static permittivity. Where \( V \) is the molar volume and \( \varepsilon_0 \) is static dielectric constant of pure polar liquid.

Onsagar theory avoids Debye’s assumption that the part \( F_3 \) of the local field is zero. However, he adopted the other assumption that no local directional forces due to neighbouring molecules act on the dipoles, so that they are distributed according to Langevin’s law. Therefore Onsagar’s theory will apply to fluids, but without the restriction on density for the Debye’s theory. Onsagar’s theory is in good agreement with
the experimental results for the weak polar liquids. The application of Onsagar's theory to strong polar liquids and solids is restricted because of following limitations:

1. Onsagar's model is the over simplification of the actual complex phenomenon.
2. The environment of the molecule is supposed to be a continuous sphere with a constant static permittivity $\varepsilon_0$. In practice, polar liquids having strong local forces, the molecular cavity cannot be spherical one and may show directional behaviour.
3. The interaction of a molecule with its surroundings is considered only through the reaction field $R$. It is parallel to the direction of a particular molecule, so it cannot change its orientation.

Both Debye's theory and Onsagar's theory might be called as 'semi-statistical' theories as they use a statistical argument to solve first part of the problem i.e. the calculation of dipolar polarizability, but makes use of microscopic arguments to obtain expression for the local field. Kirkwood [8] obtains an expression for the static permittivity by using statistical methods and avoiding the neglect of local forces which limits the validity of Debye's and Onsagar's theories to fluids. By considering the spherical region of radius ‘r’ of the dielectric containing a large number of molecules, he obtained the following expression for static permittivity:

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} = \frac{4\pi N}{V}\left(\alpha_0 + \frac{\mu^2 g}{3kT}\right)$$

where $g$ is the correlation parameter and is a measure of the local ordering in the material. The correlation parameter has value unity if the average moment of a finite spherical region about one fixed molecule in an infinite specimen of the same material, is just the moment of the fixed molecule. The value of $g$ greater than unity indicates an average parallel alignment of neighbouring dipoles while the value of $g$ less than unity indicates that the neighbouring dipoles are aligned in an anti-parallel direction.

If the structure of the material is known, it is possible to calculate the value of $g$, otherwise, it becomes an empirical parameter and can be calculated from dipole moment and permittivity of the material. The correlation parameter helps to know the structure and local forces in the material. When the effect of distortion polarization is included, it is very difficult to calculate the parameter $g$ from experimental results of dipole moment and dielectric constant of the medium. This restricts its applicability. Fröhlich [9]
followed a model similar to Debye's and established a statistical relation connecting
dipole moment of a molecule with the dielectric constant of the polar medium as:
\[
\frac{(\varepsilon_0 - \varepsilon_m)(2\varepsilon_0 + \varepsilon_m)}{\varepsilon_0(\varepsilon_0 + 2)} = \frac{4\pi N (\mu^2 g)}{3V} \left( \frac{1}{3kT} \right)
\]

For \( g = 1 \), this equation reduces to Onsagar's equation (2.2).

Attempts have been made to extend Fröhlich theory to anisotropic molecules by
different research workers [10-15]. Dipole-dipole interactions for spherical molecules has
been included by Omini [16] and found to be in good agreement with the experimental
results.

In all the above discussed theories dipole moment is model dependent and no model
is completely adequate. At present there is a need of a theory to account for all aspects of
dielectric polarization of polar liquids, solids, and gases.

2.2 Dielectric Dispersion

Each of the three types of polarizations is a function of the frequency of the applied
field. Because polarization cannot follow an electric field in a high-frequency field,
permittivity has a dependence on the frequency. This dependence of the permittivity of a
dielectric material on the frequency of an applied electric field is called Dielectric
dispersion [17].

At d.c. field (for frequency \( \omega = 0 \)) all the three types of polarizations i.e. electronic,
atomic and orientation are present. As the frequency increases from zero, the total
polarization changes very little at the beginning. When the frequency becomes higher the
dielectric dispersion arises.

- In the microwave region around \( 10^{10} \) Hz, it becomes impossible for orientation
  polarization to follow the electric field. This is because in this range of frequency
  natural time of orientation of polar molecules becomes more than the time period of
  the applied field and molecules are not able to reorient as quickly as field alternates.
  Hence, the orientation polarization no longer contributes to the total polarization and
  the total polarization consists of atomic and electronic polarization only. It is this fall
  of polarization, with its related fall of permittivity and occurrence of absorption that
  constitutes dielectric dispersion.
• In the infrared or far-infrared region around $10^{13}$ Hz, atomic polarization loses the response to the electric field and further dispersion regions will occur.
• Electronic polarization loses its response in the UV region around $10^{15}$ Hz. Thus electronic polarization, a fast process exist upto very high frequency fields.

The frequency dependence of polarization is shown in fig. 2.1.

![Fig. 2.1: Frequency Dependence of Polarization](image)

In the lower frequency range of the external field, the total polarization ($P = P_e + P_A + P_O$) remains in phase with the applied field. With the increase in frequency, orientation polarization lags behind, whereas electronic and atomic polarizations do continue to remain in phase with the external applied field. In this way total polarization get a component, which lags behind the polarizing field and accounts for the absorption of energy or dielectric loss. In this frequency range, the total permittivity can be considered as a complex quantity defined by:

$$\varepsilon' = \varepsilon' - j\varepsilon''$$

2.5
where $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts of the complex permittivity and accounts for dielectric constant and dielectric loss respectively. The loss tangent can be defined by

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$  \hspace{1cm} (2.6)

Relation for $\varepsilon'$ and $\varepsilon''$ can be derived by using macroscopic consideration. When alternating electric field $E$ is applied to the dielectric medium, the distortion polarization $P_d$ will be established in the microwave frequency range instantaneously, whereas the orientation polarization $P_o$ takes time to reach its equilibrium value. If the rate of increase of $P_o$ is proportional to its departure from its equilibrium value, then we can write:

$$\frac{dP_o}{dt} = \frac{P - P_d - P_o}{\tau'}$$  \hspace{1cm} (2.7)

where $P$ is the equilibrium value of total polarization and $\tau'$ is a constant, having the dimensions of time and is called as macroscopic relaxation time. The above equation can be rewritten as:

$$\frac{d(P - P_d - P_o)}{P - P_d - P_o} = \frac{dt}{\tau'}$$

On integration, we get the solution as:

$$\ln(P - P_d - P_o) = -\frac{t}{\tau'} + C_1$$  \hspace{1cm} (2.8)

where $C_1$ is a constant. If we assume that field $E$ is suddenly applied at $t = 0\, \text{s}$, $P_o = 0$ at $t = 0\, \text{s}$, and from above relation we have

$$\ln(P - P_d) = C_1$$

Putting this value of $C_1$ in equation (2.8), we get

$$\ln(P - P_d - P_o) = -\frac{t}{\tau'} + \ln(P - P_d)$$

$$\ln \left[ 1 - \frac{P_o}{P - P_d} \right] = -\frac{t}{\tau'}$$

and

$$P_o = (P - P_d) \left[ 1 - \exp \left(-\frac{t}{\tau'}\right) \right]$$  \hspace{1cm} (2.9)
This means that $P_o$ approaches equilibrium value exponentially (Fig. 2.2(a)).

Similarly assuming that the total polarization $P$ is established in a steady electric field $E$ and the polarizing field is suddenly removed at $t = 0$, then $P_d$ and $P$ are also zero at $t = 0$ and equation (2.7) reduces to

\[
\frac{dP_o}{dt} = \frac{P_o}{\tau'}
\]

\[
\frac{dP_o}{P_o} = \frac{dt}{\tau'}
\]

Integrating, we have

\[
\ln P_o = -\frac{t}{\tau'} + C_2
\]  \hspace{1cm} (2.10)

\[\text{Fig. 2.2}\]

here $C_2$ is a constant of integration. Its value can be found from initial conditions i.e. at $t = 0$, $P_o = P - P_d$

Therefore from above equation, we have

\[
C_2 = \ln(P - P_d)
\]

If we put it in equation (2.10), we get

\[
P_o = (P - P_d) \exp\left(-\frac{t}{\tau'}\right)
\]  \hspace{1cm} (2.11)

Above equation shows that $P_o$ also falls exponentially (Fig. 2.2(b)).
The constant $\tau'$ is called the relaxation time and is defined as the time during which the polarization of the medium after the removal of external electric field decreases by a factor $1/e$ relative to its original value (\(e\) being the natural logarithmic base).

Now consider the case when the applied field changes with frequency $f$, circular frequency $2\pi f = \omega$. Such a field can be represented by

$$E = E_0 \exp(j\omega t).$$

Substituting the value of $P$ and $P_d$ in equation (2.7), we get

$$\frac{dP_o}{dt} = \frac{\epsilon}{4\pi \tau'}(\epsilon_0 - \epsilon_m)E_0 \exp(j\omega t) - \frac{P_o}{\tau'}$$

Assuming the solution of this equation of the form $P_o = A \exp(j\omega t)$, we get

$$A = \frac{\epsilon(\epsilon_0 - \epsilon_m)E_0}{4\pi(1 + j\omega \tau')}$$

$$P_o = \frac{\epsilon(\epsilon_0 - \epsilon_m)E_0}{4\pi(1 + j\omega \tau')}$$

From the above equation, it is clear that $\frac{P_o}{E}$ becomes a complex quantity, indicating that, orientation polarization is out of phase with the external applied field. We may write:

$$P_d + P_o = P' - jP^* = \frac{\epsilon(\epsilon_0 - 1)E}{4\pi} + \frac{\epsilon(\epsilon_0 - \epsilon_m)E}{4\pi(1 + j\omega \tau')}$$

where both $P'$ and $P^*$ are real. When the polarization becomes complex, the permittivity also becomes complex and we can write:

$$\epsilon^* = \epsilon' - j\epsilon^* = 1 + 4\pi \left(\frac{P' - jP^*}{\epsilon E}\right)$$

$$= \epsilon_m + \frac{\epsilon_0 - \epsilon_m}{1 + j\omega \tau'}$$

The simultaneous solution of above equation gives the following values for real component $\epsilon'$ and imaginary component $\epsilon^*$:

$$\epsilon' = \epsilon_m + \frac{\epsilon_0 - \epsilon_m}{1 + \omega^2 \tau'^2}$$

$$\epsilon^* = \frac{\epsilon_0 - \epsilon_m}{1 + \omega^2 \tau'^2} \omega \tau'$$
Variation of $\varepsilon'$ and $\varepsilon''$ with frequency is shown in fig. 2.3.

At frequency $\omega = \frac{1}{\tau'}$, the dielectric constant and dielectric loss reaches its maximum and can be given as:

\[
\varepsilon'_{\text{max}} = \frac{\varepsilon_0 + \varepsilon_\infty}{2} \quad 2.15
\]

\[
\varepsilon''_{\text{max}} = \frac{\varepsilon_0 - \varepsilon_\infty}{2} \quad 2.16
\]

$\varepsilon''$ is sometimes called as the dielectric loss factor, because it controls the rate at which electric energy is converted into heat in the medium. The quantity loss tangent is given by:

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 + \varepsilon_\infty} \quad 2.17
\]

By comparison with the experimental results, it is possible to calculate $\tau'$. This can be easily done from the maximum of $\varepsilon''$ curve, which gives $\tau' = \frac{1}{\omega}$. Another method is by plotting $\varepsilon'$ against $\varepsilon''$ for various values of $\omega$. Simultaneous solution of equations (2.13) and (2.14) leads to the expression

\[
\left(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2}\right)^2 + \varepsilon''^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2 \quad 2.18
\]
This is the equation of a circle in $\varepsilon', \varepsilon''$ plane with center $\left(\frac{\varepsilon_0 + \varepsilon_m}{2}, 0\right)$ and radius $\frac{\varepsilon_0 - \varepsilon_m}{2}$ and is shown in fig. 2.4. A fair agreement between the theoretical and experimental results based upon above analysis in case of n-propanol [18], nitrobenzene [19] having only single relaxation time have been reported.

![Debye Curve - Complex Plane Plot](image)

**Fig 2.4 Debye Curve – Complex Plane Plot**

Hennelly et. al.[20] found that the experimental plots for $\varepsilon'$ versus $\log \omega$ and $\varepsilon''$ versus $\log \omega$ differ considerably from the corresponding theoretical plots and $\varepsilon''$, $\varepsilon'$ plot is more complex than the simple semicircle above $\varepsilon'$ line. Three different types of $\varepsilon''$, $\varepsilon'$ curves in addition to Debye’s semicircle behaviour may be recognized.

- **Cole-Cole arc.** The center of which lies below the actual axis showing a symmetric distribution of relaxation times (Fig.2.5).
- **Davidson-Cole arc.** A skewed arc plot showing an asymmetric distribution of relaxation times (Fig.2.6).
- **A curve possessing number of circular plots, indicating multiple relaxation times** (Fig.2.7).

The deviation of experimental plots for $\varepsilon''$, $\varepsilon'$ from Debye’s semicircle plot is because of the existence of distribution of relaxation times. Due to thermal influences, directing forces, and changing interaction forces, the local environment of each polar
molecule in a system of polar molecules may change with space and time resulting in its own relaxation time.

For a system, depending upon the molecular structure, there may be more than one relaxation mechanism, each having characteristic relaxation time. In the measurement of relaxation time taken over spatial conditions, contributions from all above mechanisms also get measured and the resulting measurement of relaxation time shows a continuous spread of relaxation times about most probable value. This range of distribution of relaxation times is quite wide for polymeric compounds [21-22].

![Fig. 2.5: Cole-Cole Arc Plot](image)


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

where \(\alpha\) (distribution parameter) is a constant having value between 0 and 1. \(\tau_0\) is the most probable relaxation time about which other relaxation times are symmetrically distributed. In the limit \(\alpha = 0\), the Cole-Cole curve reduces to the Debye semicircle. According to Cole-Cole method, the plot of \(\varepsilon'\) and \(\varepsilon^\ast\) is an arc of a circle whose center lies below the actual axis (Fig.2.5). A diameter of this circle will cut the \(\varepsilon'\) axis at \(\varepsilon_{\infty}\).
making an angle of $\left( \frac{\tau(\alpha)}{2} \right)$. From this Cole-Cole arc plot, distribution parameters ($\alpha$) and relaxation time ($\tau_0$) can be calculated.

Cole and Davidson [19] explained skewed arc plot of fig. 2.5 with the help of following equation:

$$\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1}{(1 + j\omega\tau')^\alpha}$$

Rationalizing above equation to find $\varepsilon'$ and $\varepsilon''$ yields

$$\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{(1 - j\omega\tau')^\alpha}{(1 + \omega^2\tau'^2)^{\alpha/2}}$$

$$= \frac{(\cos \phi - j\sin \phi)^\alpha}{(1 + \omega^2\tau'^2)^{\alpha/2}}$$

$$= \frac{\exp(-j\alpha\phi)}{(1 + \tan^2 \phi)^{\alpha/2}}$$

where $\tan \phi = \omega\tau'$.

Fig. 2.6: Davidson Cole or Skewed Arc Plot
Therefore, \[
\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \cos^a \phi \cos \alpha \phi
\]
and
\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \cos^a \phi \sin \alpha \phi
\]
As temperature increases \(a \to 1\), and the arc tends to the Debye Semicircle.

In multiple relaxation time plot (Fig 2.7), each semicircle represents Debye type of relaxation time and the system have multiple relaxation mechanisms, each having characteristics relaxation time.

Bergmann et. al. [26] gave expressions for \(\varepsilon'\) and \(\varepsilon''\) for a system having two distinct relaxation mechanisms

\[
\varepsilon' = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \left[ \frac{C_1}{1 + (\omega \tau_1)^2} + \frac{C_2}{1 + (\omega \tau_2)^2} \right]  \tag{2.21}
\]

\[
\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty) \left[ \frac{C_1 \omega \tau_1}{1 + (\omega \tau_1)^2} + \frac{C_2 \omega \tau_2}{1 + (\omega \tau_2)^2} \right]  \tag{2.22}
\]

where \(C_1\) and \(C_2\) are the relative weights of each relaxation mechanism and \(C_1 + C_2 = 1\).
Many research workers had made frequent attempts to solve the problem arising from associating different relaxation times with different relaxation mechanisms of the system [27-31].

2.3 Dielectric Relaxation

Relaxation is a process. The term applies, strictly speaking, to linear systems where a response and a stimulus are proportional to one another in equilibrium. Relaxation is a delayed response to a changing stimulus in such a system. Dielectric relaxation occurs in dielectric that is in insulating materials with negligible or small conductivity. The stimulus is almost always an electric field, the response a polarization. The time lag between electrical field and polarization implies an irreversible degradation of free heat. This relaxation is often described in terms of permittivity as a function of frequency.

Every system in this universe has a tendency to remain in its state of thermal equilibrium unless not disturbed by an external force. When some external forces are applied, it tends to drift the system away from its thermal equilibrium state. As soon as the external forces are applied, the internal effects and surrounding environment type of forces acts to bring the system back to the thermal equilibrium state. These forces are called restoring forces. The system attains a final balancing state under the action of these two types of forces acting in opposite directions. On the application of external applied forces the system does not return to its original thermal equilibrium state immediately, but takes some time to do so. Similarly, on the removal of external applied forces, the system takes some time to return to its original thermal equilibrium state. This lag in the attainment of final equilibrium state is known as the phenomenon of relaxation and the time taken by the system to return to its original equilibrium state is known as the relaxation time. In case of polar molecules, when an external electromagnetic field is applied, the molecule tends to orient themselves in the direction of applied field. Restoring forces arising from the thermal effects and interaction of polarizing molecules with their surrounding comes to play so as to appose the polarizing tendency of the molecules. The polar system attains a balancing equilibrium state under the action of these two types of forces. On the removal of external field, the polarized molecule tends to attain their original thermal equilibrium position of random distribution. Because here
also a restoring force comes into play, the system takes some time to attain that state. This phenomenon of polarization lagging behind the polarizing field is known as the dielectric relaxation and the time taken by polarization of the system to fall to its $1/e^\text{th}$ value of maximum polarization on the removal of polarizing field is known as the relaxation time. Relaxation time and dipole moment measurements give important information about the structure of the polar molecules.

A number of theories have been put forward by many research workers to account for the dielectric relaxation process in the molecular system. One of them is discussed below.

**Debye’s Diffusive Theory of Relaxation:**

Debye’s Diffusive Theory is based upon Einstein’s theory of Brownian motion, according to which the molecules of a medium are always in Brownian motion and follows a diffusive law. Debye supposed that the rotation of molecules on the application of external applied field is constantly interrupted by collisions with the neighbours. The effect of these collisions may be described by a resistive couple which is proportional to the angular velocity of the molecules. Here the method of W. F. Brown [32] has been followed, according to which in the absence of an applied field the molecules must follow a diffusive law, whereas in Debye’s original theory, he derived this assumption.

Suppose the orientation of a molecule be specified by angles $\theta$ and $\phi$ on the application of an electric field. Let $f(\theta,t)\,d\Omega$ be the fraction of the molecules whose dipole moments lie in an element of solid angle $d\Omega$ about the direction $(\theta,\phi)$. Since in the presence of applied electric field, orienting molecular dipoles have tendency to orient themselves in the direction of applied field, the function $f(\theta,t)$ will be dependent on $\theta$, the angle between the dipole moment and the field and on time $t$, it will be independent of $\phi$. This distribution i.e. $f(\theta,t)$, can be represented by a distribution of points on a unit sphere. Let $J_\theta$ be the net number of representative points passing in unit time across unit length of latitude $\theta = \text{const.}$ on this sphere in the direction of increasing $\theta$ [Fig. 2.8]. Then the mathematical expression for it can be written as:

$$J_\theta = -K \frac{\partial f}{\partial \theta} + f(\theta)$$

2.23
The first term in the right hand side of equation (2.23) represents the diffusive process and the second term represents the effect of applied field. The negative sign is due to the reason that these two processes are in opposite directions. As the external electric field is applied, the molecules are set in rotation with an average terminal angular velocity \( \langle \dot{\theta} \rangle \) dependent on orienting couple and the resistive constant \( (\xi) \).

\[
\xi \langle \dot{\theta} \rangle = -\frac{\partial U}{\partial \theta}
\]

Fig. 2.8: Distribution of Points on a Unit Sphere

where \( U = -\mu F \cos \theta \) is the potential energy of the molecule due to the applied field. At the equilibrium state, \( J_\theta = 0 \) and the equation (2.23) becomes
0 = -K \frac{\partial f}{\partial \theta} + f(\dot{\theta})

This can be written as:

- \frac{K \frac{\partial f}{\partial \theta}}{\xi} = -f(\dot{\theta}) = \frac{f}{\xi} \frac{\partial U}{\partial \theta}

Solution of this equation can be written as

f = A \exp\left(-\frac{U}{K\xi}\right)

where A is a constant. In equilibrium the molecules follow Boltzmann distribution law i.e.

f = A \exp\left(-\frac{U}{kT}\right)

Therefore from equation (2.26) and (2.27), one can write:

K = \frac{kT}{\xi}

Substituting equations (2.24) and (2.28) in equation (2.23), we get

J_\theta = -\frac{kT}{\xi} \frac{\partial f}{\partial \theta} - \frac{\mu F \sin \theta}{\xi} f

In non-equilibrium case, total number of representative points crossing any line \( \theta = \text{const.} \) is \( 2\pi \sin \theta J_\theta \) per second in the direction of increasing \( \theta \). Similarly the total number of representative points crossing any line \( \theta = \text{const.} + d\theta \) is

\( \left\{ 2\pi \sin \theta J_\theta + \frac{\partial}{\partial \theta} (2\pi \sin \theta J_\theta) d\theta \right\} \) per second in the direction of increasing \( \theta \). The difference between these two numbers gives the rate of increase in the number of representative points in the element of sphere between \( \theta \) and \( \theta + d\theta \). Therefore,

\[ \frac{\partial}{\partial t} (2\pi \sin \theta f d\theta) = -\frac{\partial}{\partial \theta} (2\pi \sin \theta J_\theta) d\theta \]

On solving, we get

\[ \frac{\partial f}{\partial t} = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta J_\theta) \]

Substituting the value of \( J_\theta \) from equation (2.29), we have
\[
\frac{\partial f}{\partial t} = -\frac{1}{\xi \sin \theta} \frac{\partial}{\partial \theta} \left( kT \sin \theta \frac{\partial f}{\partial \theta} + f \mu F \sin^2 \theta \right)
\]

2.30

When the field is alternating with frequency \( \omega \), equation (2.30) can be solved and its solution can be written as

\[
f = A \left( 1 + \frac{1}{1 + j \omega \tau'} \frac{\mu F \cos \theta}{kT} \right)
\]

2.31

where \( \tau' = \frac{\xi}{2kT} \) is called the microscopic relaxation time because it depends upon the average resistive force experienced by the individual molecules. The average moment in the direction of the field is

\[
\langle \mu \cos \theta \rangle = \frac{\int_0^\pi A \cos \theta \left( 1 + \frac{\mu F \cos \theta}{kT(1 + j \omega \tau')} \right) 2\pi \sin \theta d\theta}{\int_0^\pi A \left( 1 + \frac{\mu F \cos \theta}{kT(1 + j \omega \tau')} \right) 2\pi \sin \theta d\theta} = \frac{\mu^2 F}{3kT(1 + j \omega \tau')}
\]

2.32

Let us assume that, \( F \) is the Lorentz field with permittivity \( \varepsilon' \) and \( \mu \) be the permanent dipole moment of a molecule which has polarizability \( \alpha \). The equation for permittivity can be written as:

\[
\frac{\varepsilon' - 1}{\varepsilon' + 2 \rho} = \frac{4\pi N}{3\varepsilon} \left( \alpha + \frac{1}{j \omega \tau' \frac{3kT}{\mu^2}} \right)
\]

2.33

At low frequency, when \( \omega \tau' << 1 \), the above equation reduces to Debye's equation for static permittivity as:

\[
\frac{\varepsilon' - 1}{\varepsilon' + 2 \rho} = \frac{4\pi N}{3\varepsilon} \left( \alpha + \frac{1}{3kT} \frac{\mu^2}{\omega^2 \tau'^2} \right)
\]

At high frequency, when \( \omega \tau' >> 1 \), the distortion polarization makes their full contribution, while the contribution of orientation polarization falls to zero. Such a frequency occurs in far infra-red region. In this region the equation (2.33) reduces to

\[
\frac{\varepsilon' - 1}{\varepsilon' + 2 \rho} = \frac{4\pi N \alpha}{3\varepsilon}
\]

The equation (2.33) can be rearranged to give [33]
Thus Debye's theory shows that macroscopic relaxation time $\tau$ is always longer than the microscopic relaxation time $\tau'$. 

The assumption of Lorentz field imposes a severe limitation on the validity of Debye's equation. Onsagar's model also has limitations; it nevertheless gives a better representation of the properties of liquids. Therefore Onsagar's model was extended to frequency region where dispersion occurs. This has been done by Collie et. al. by considering the contribution due to cavity field and reaction field[34]. The following equation can be derived:

$$\epsilon^* - \epsilon_m = \frac{1}{\epsilon_m - \epsilon_m} \frac{1}{1 + j\omega \tau'}$$

where

$$\tau = \frac{\epsilon_m + 2}{\epsilon_m + 2} \tau'$$

Debye's diffusive theory assumes that orientation polarization approaches its equilibrium value at a rate proportional to its departure from equilibrium. It is the simplest type of relaxation process. Rocard [35] however showed that, this assumption breaks down at higher frequencies and the molecule rotate with their terminal velocity. He showed that this assumption of Debye's theory is valid only if

$$\omega \tau / 2\pi << 1$$

where $\tau_c = I / \xi$ is the characteristic time. $I$ and $\xi$ represents the moment of inertia and resistive constant of the molecule, respectively.

In Debye's diffusive model molecules are supposed to change their orientation in series of small steps under the effect of varying field. Such a model is appropriate to liquids, but is unlikely to be appropriate to solids, because of the reason that a molecule in solid has a number of equilibrium positions corresponding to the minima of potential energy. Many research workers have proposed a number of barrier models of relaxation to study this type of process. Following Fröhlich theory of static permittivity, in which
each molecule has two equilibrium positions, the expression for decay of polarization may be derived as:

\[ P = P_0 \exp(-t/\tau') \]  \hspace{1cm} 2.37

where \( \tau' \) is the microscopic relaxation time and is given by

\[ \tau' = A \exp(H/kT) \]  \hspace{1cm} 2.38

where \( A \) has the dimensions of time and is temperature dependent; \( H \) is the height of potential barrier separating the two equilibrium positions. Scaife [36] has given a good account of the number of attempts made to modify the Debye's model. Scaife [37-38] following the Langevin's method has obtained the following expression for the complex permittivity of polar liquids

\[
\left( \varepsilon - \varepsilon_m \right) \left( 2\varepsilon + 1 \right) \left( 2\varepsilon^* + \varepsilon_m \right) = \frac{4\pi \mu^2 (\varepsilon_m + 2)^2}{3kT\varepsilon} \frac{1}{1 + j\omega \tau} \]  \hspace{1cm} 2.39

Lots of work has been done on polar molecules. Recently many research workers [39-45] have studied the dielectric relaxation of polar liquids.

### 2.4 Dielectric Relaxation as a Rate Process

The phenomena of dielectric relaxation as a rate process was explained by Eyring et al. [46] by considering the dipole orientation in analogy with a chemical rate process. Eyring begins by considering a chemical reaction of the type \( A + B \rightarrow C \) and assume that for this reaction to take place \( A \) and \( B \) must first form an activated complex \( AB^* \). In our case of binary mixtures, let a chemical reaction between an atom \( A \) and the diatomic molecule of atoms \( B \) and \( C \) to give a diatomic molecule \( AB \) and atom \( C \) be represented by the equation

\[ A + BC \rightarrow AB + C \]  \hspace{1cm} 2.40

The rate of a chemical reaction \( R \) is proportional to the concentration of atom \( A(C_A) \) and the concentration of molecule \( BC(C_{BC}) \).

Mathematically, the rate of a chemical reaction can be written as
\[ R \propto C_A C_{BC} \]

or \[ R = k_tC_A C_{BC} \]  \hspace{1cm} (2.41)

where \( k_t \) is the constant of proportionality and is called as the specific reaction rate. For simplifying mathematical calculations, let us assume that during the chemical reaction, atoms \( A, B \) and \( C \) always remain in straight line. The progress of the reaction may be followed by noting the inter-atomic distances \( X_{AB} \) and \( X_{BC} \). Where \( X_{AB} \) represents the distance between atoms \( A \) and \( B \) and \( X_{BC} \) represents the distance between atoms \( B \) and \( C \).

Before collision between atom \( A \) and diatomic molecule \( BC \), the inter-atomic distance \( X_{BC} \) is found to be less than \( X_{AB} \). If a chemical reaction takes place during collision, then after the collision \( X_{AB} \) is found to be less than \( X_{BC} \). Under these circumstances during collision, all the atoms are very near to each other. This state may be recognized as the activated state and the combined molecule may be called as the collision complex \([(ABC)^*]\). The overall chemical reaction can be written as:

\[ A + BC \leftrightarrow (ABC)^* \rightarrow AB + C \]  \hspace{1cm} (2.42)

Figure 2.9 represents the progress of the above reaction on potential energy surface; the upper lift triangle represents the initial state \( A + BC \), the activated state \((ABC)^*\) is represented by the middle region and the lower triangle on right hand side represents the final state of the reaction i.e. \( AB + C \). The reaction co-ordinates are represented by the dotted lines. The reaction mechanism can also be followed from the cross section of the potential energy surface along the reaction coordinates (Fig. 2.10). The reaction rate \( (R) \) depends upon the probability \( (k) \) of the occurrence of reaction in activated state, average number of molecules \( (n^*) \) in the activated state, and the average velocity \( (\bar{v}) \) per unit width with which the molecules pass through the activated state. Mathematically, the reaction rate can be written as:
\[ R = n (\frac{v}{\omega}) \]

Taking into account the statistical mechanics considerations, the specific reaction rate constant can be written as:

\[ K' = \left( \frac{kT}{h} \right) \exp \left( \frac{-\Delta F}{RT} \right) \]

where \( k \), \( h \), and \( R \) represent Boltzmann’s constant, Planck’s constant and gas constant respectively. \( \Delta F \) represents the free energy of activation and is the difference between the free energy of activated and inactivated states. This equation is known as the Eyring’s equation for the chemical reaction rate.

Dielectric relaxation process can also be treated as a rate process by considering two different equilibrium states for the dipole orientations as two states of the reaction i.e. state \( A+BC \) and state \( AB+C \). The state at which the orienting dipoles have sufficient energy to cross the potential energy barrier and to pass to the other equilibrium state may be taken as the activated state \( [(ABC)^*] \).

Number of times per second that a dipole acquires sufficient energy to pass over the potential barrier from one equilibrium position to the other may be taken as the specific reaction rate ‘\( k \)’ of a rate process. Hence we can write:

\[ \tau = \frac{h}{kT} \exp \left( \frac{\Delta F}{RT} \right) \]

According to Eyring’s rate equations the expression for the viscosity of a liquid in terms of reaction rates can be written as:

\[ \eta = \frac{N \hbar}{V} \exp \left( \frac{\Delta F_{\eta}}{RT} \right) \]

here \( V \) is the molar volume and \( \Delta F_{\eta} \) is the change in free energy of activation.
Fig. 2.9: Potential Energy Surface for the Reaction of A with BC in One Dimension

Fig. 2.10: Potential Energy as a function of Distance along the Reaction Coordinate
The equations (2.45) and (2.46) shows that the plots of $\log(\tau T)$ versus $10^3/T$ and $\log \eta$ versus $10^3/T$ should be straight lines.

The expression for free energy of activation ($\Delta F_\eta$) in terms of entropy of activation ($\Delta S_\eta$) and enthalpy of activation ($\Delta H_\eta$) can be written as:

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta$$  \hspace{1cm} 2.47

Substituting equation (2.47) in equation (2.46), we get

$$\eta = \frac{hN}{V} \exp\left(-\frac{\Delta S_\eta}{R}\right) \exp\left(\frac{\Delta H_\eta}{RT}\right)$$  \hspace{1cm} 2.48

### 2.5 Viscous Flow as a Rate Process

Eyring's rate equation could be used for the description of rate process and the evaluation of energy parameters. For describing viscous flow process as a rate process the following theoretical model could be given.

The viscous flow process involves translational as well as rotational motion of molecules. This is concerned with the relative motion of the molecules among themselves under the action of externally applied field. From the crystalline point of view the liquid state is found to preserve short-range crystalline order and completely missing long-range order. The short-range crystalline order is due to the neighbouring molecular interactions.

The vacant molecular sites similar to that in crystalline structure are also present in the liquid and are shown in fig.2.11. Let $a$ and $\delta$ be the distances between the lattice sites and adjacent planes of the molecules respectively. Let us assume the motion of the molecule to the neighbouring vacant site as the fundamental rate process. During the course of this process, the wandering molecule is to pass through the region of high potential energy because of the presence of neighbouring molecules. The potential energy curve will be
symmetrical about the potential hill in the absence of external applied force. The motion of the molecules in the direction of applied force could be recognized as the forward process and motion of molecules in the direction opposite to the applied force could be recognized as reverse process.

Figure 2.11 shows two states corresponding to the two minima in the potential energy curve and could be recognized as two stable states. The state corresponding to the potential hill in the potential energy curve may be taken as the activated state. If \( K_f \) and \( K_r \) are the frequencies of the forward and reverse processes respectively, then the net velocity of the fluid flow with respect to the lattice site in the direction of applied force can be written as:

\[
\nu_0 = a(K_f - K_r)
\]

Let \( F \) be the force per unit area acting to displace one layer of the molecule with respect to the other layer. The force acting on the molecule to move it in forward direction can be written as \( \frac{F}{n\delta} \). \( K_f \) and \( K_r \) could be given by Eyring's rate equations (equation 2.46 and 2.47). The free energy of activation for the forward process and reverse process is different because the forward process is easier than the reverse process. The force \( \frac{F}{n\delta} \) acts to decrease the free energy of activation for a jump in the direction of force and increase the free energy of activation for a jump in the direction opposite to the direction of force. Taking the activated state in between the two lattice sites, the work done by the external force to move the molecule to a distance \( a/2 \) into the activated state can be written as \( \frac{1}{2} \left( \frac{aF}{n\delta} \right) \) and this represents the change in free energy of activation of the two processes.
Fig 2.11 Fundamental rate process involved in viscous flow

Therefore, $K_f$ and $K_r$ could be written as:

$$K_f = K_0 \exp \left( \frac{aF}{2\delta nKT} \right)$$  \hspace{1cm} 2.50

$$K_r = K_0 \exp \left( - \frac{aF}{2\delta nKT} \right)$$  \hspace{1cm} 2.51

Putting the value of $K_f$ and $K_r$ in equation (2.49), we have

$$v_o = a (K_f - K_r) = 2aK_0 \sinh \left( \frac{aF}{2\delta nKT} \right)$$  \hspace{1cm} 2.52

From elementary considerations, the coefficient of viscosity could be written as:
\[ \eta = \frac{F}{\nu_0/\delta} = \frac{F\delta}{2aK_0 \sinh \left( \frac{aF}{2\delta nKT} \right)} \]  

The linear variation of \( \log(\tau T) \) versus \( 10^3/T \) and \( \log \eta \) versus \( 10^3/T \) have been experimentally observed by many research workers [47-52] and it is concluded that the process of dielectric relaxation and viscous flow can be treated as a rate process.
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