Chapter 2

Different Theories of Dielectrics

2.1 Introduction:

This chapter contains different theories proposed for dielectrics. The polar nature of dielectric material is measured in terms of its permanent molecular dipole moment. The Dielectric constant of material depends on dipole moment and ability of dipoles to align in the direction of applied field. When the electric field is applied to dielectric, the molecular charges get displaced. The total charge passing through unit area within the dielectric, perpendicular to the direction of applied field is called as polarization. There are three types of polarization –

a) *Electronic Polarization* (Pe): This is due to the displacement of electrons with respect to the atomic nucleons and occurs in atoms, in all dielectrics. It takes very small interval of time of the order of $10^{-15}$ sec., which is corresponds to period of ultraviolet light.

b) *Atomic Polarization* (Pa): This is due to mutual displacement of atoms or group of atoms. It takes a short time of the order of $10^{-13}$ to $10^{-12}$ sec., which corresponds to period of infrared light.

c) *Orientation Polarization* (Po): This is property of the polar molecules. It is due to rotation of permanent dipoles of dielectric
medium. The molecular dipoles orient in the direction of the applied field. It is function of molecule size, viscosity, temperature, and frequency of applied field. It takes a time of the order of $10^{-12}$ to $10^{-10}$ sec., which corresponds to period of microwave frequency region.

Thus the total polarization is $\text{Pt} = \text{Pe} + \text{Pa} + \text{Po}$

Thus the polar materials have greater permittivity than the non-polar, because of additional polarization due to orientation.

**Theories of Dielectric Relaxation:**

Theories of dielectric relaxation $^{[1,2]}$ are based on

1) **Static permittivity:** When the polar dielectric material having permanent dipole moment is placed in steady electric field, so that all types of polarization can maintain equilibrium. Permittivity of dielectric material under this condition is called static permittivity ($\varepsilon_0$).

2) **Dynamic permittivity:** When dielectric material is placed in electric field which changes with frequency of applied field, such frequency dependent permittivity of material is called dynamic permittivity.
2.2 Theories of Static Permittivity:

Consider two point charges $q$ and $q'$, separated by distance $'r'$ in a homogeneous dielectric, then the dielectric constant may be expressed in terms of the force $'F'$ between two charges

$$F = \frac{qq'}{\varepsilon r^2} \quad (2.1)$$

Where $\varepsilon$ is the static dielectric constant, a characteristic of the medium between the two charges. It is also defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. For a capacitor if $'A'$ is area of each plate at a potential $'V'$ the capacity is given by-

$$C = \frac{q}{V} \Rightarrow \frac{\varepsilon A}{4\pi} \quad (2.2)$$

The static dielectric constant $'\varepsilon'$ is the ratio of the dielectric constant of the medium between the plates to that of free space.

The intensity of electric field is perpendicular to the plates of charged capacitor in vacuum.

$$E_0 = 4\pi \delta \quad (2.3)$$

Where, $\delta$ is the surface charge density. If the space between the plates is filled with a homogeneous dielectric material of dielectric constant $\varepsilon$, the field strength decreases to-

$$E = \frac{4\pi \delta}{\varepsilon} \quad (2.4)$$
The same amount of decrease in field strength will occur, if the charge density is reduced by \( \delta = \left( \frac{1 - \varepsilon}{\varepsilon} \right) = P \), where \( P \) is surface charge density.

The electric displacement, vector \( \mathbf{D} \) is defined as

\[
\mathbf{D} = 4\pi\delta
\]  
(2.5)

So that \( \mathbf{D} = \varepsilon\mathbf{E} = \mathbf{E} + 4\pi\mathbf{P} \)  
(2.6)

\[
(\varepsilon - 1) = \frac{4\pi\mathbf{P}}{\mathbf{E}}
\]  
(2.6a)

\[
\varepsilon = 1 + \frac{4\pi\mathbf{P}}{\mathbf{E}}
\]  
(2.7)

This eq. gives relation between dielectric constant or permittivity and applied electric field[1].

The charge + PA on one surface of the dielectric material and PA on the opposite surface, resulting from a displacement of charge throughout the dielectric, gives an electric moment \((\mathbf{P}\mathbf{A})(r)\), where ‘\( r \)’ being the thickness.

\[
\mathbf{M} = \mathbf{P}\mathbf{A}\ r
\]

Let \( \mathbf{A}\ r = \mathbf{V} \), volume of the Slab,

\[
\mathbf{M} = \mathbf{P}\ \mathbf{V}
\]  
(2.8)

Thus polarization \( \mathbf{P} \) can be defined as electric moment per unit volume. The polarized slab behaves like an assembly of electric dipoles parallel to one another.
i) **Clausius mossotti equation:**

A sphere of continuous isotropic dielectric of suitable size, which is large compared to molecular dimensions but small as compared to distance between plates. A homogeneous field is established in the dielectric when the plates are uniformly charged with a surface density $\delta$. If the actual intensity of the electric field acting on single molecule is $F$, then under influence of this force, molecules posses an electric moment which is given by

$$m = \alpha_0 F$$  \hspace{1cm} (2.9)

Where $\alpha_0$ is polarizability of the molecule. Dipole moment may be permanent or induced. The average moment in the direction of field is given by [1]

$$\bar{M} = \frac{\mu^2 \cos^2 \theta}{K T} F + e r$$  \hspace{1cm} (2.10)

In this equation first term indicates moment due to dipole moment and second term indicates moment due to displacement of elastically bound charges.

This equation shows that permanent dipole moment contributes to polarization and hence dielectric constant is temperature dependent, while the moment induced by the displacement is independent of temperature.
If ‘F’ actual force with unit positive charge in the medium to be enclosed by a small sphere. This force may be treated as consisting of three components.

1) The force \( F_1 \) due to charges of surface density \( \delta \) on plates.

2) The force \( F_2 \) due to polarization of medium outside the small sphere.

3) The force \( F_3 \) due to medium contained in the small sphere.

\[
F = F_1 + F_2 + F_3 \quad \text{(2.11)}
\]

\[
F = 4\pi \delta \quad \text{(2.12)}
\]

And
\[
F_2 = 4\pi P + \left(4\pi P / 3\right) \quad \text{(2.13)}
\]

The \( F_2 \) can be obtained by considering that the matter within the small sphere is to be removed. This force is made up of two parts, first due to layers of induced charges on the dielectric facing the conducting plates and seconds the layer of charge on surface of small spherical cavity. \( P \) is polarization of the medium i.e. the electric moment per unit volume set up in the dielectric.

A general expression for \( F_3 \) cannot be given but it may be evaluated in special cases. It may be shown that in a cubic crystal \( F_3 \) is zero. This is true in gases and for those liquids in which molecules are moving totally independent of each other. By assuming \( F_3 = 0 \) the total force ‘F’ is given by,
\[ F = 4\pi \delta - 4\pi P + \left(\frac{4\pi P}{3}\right) \]

But \[ D = 4\pi \delta \] and \[ D = E + 4\pi P \]

\[ F = E + 4\pi P - 4\pi P + \left(\frac{4\pi P}{3}\right) \]

\[ F = E + \left(\frac{4\pi P}{3}\right) \] (2.14)

But \[ \varepsilon E = E + 4\pi P \]

\[ E(1 - \varepsilon) = 4\pi P \] (2.15)

\[ F = E + E(1 - \varepsilon)/3 \] (2.16)

\[ F = E(\varepsilon + 2)/3 \] (2.17)

This is the relation existing between the actual force \( F \) and electric field \( E \), from the electrostatic calculations. \[ ^{[6]} \]

Let \( N_1 \) be the number of molecules per cubic centimeter, then by definition of polarization.

\[ P = N_1 m = N_1 \alpha_o F \] (2.18)

From eq. (2.17)

\[ P = N_1 \alpha_o \left(\frac{\varepsilon + 2}{3}\right) \] (2.19)

By using equation (2.15) & (2.19), we get

The relation between dielectric constant \( \varepsilon \) and molecular polarizability \( \alpha_o \) as

\[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{4\pi}{3} N_1 \alpha_o \] (2.20)

In pure substance \( N_1 = \frac{Nd}{M} \), where \( M \) is molecular weight, \( d \) is density and \( N \) is number of molecules per mole.
\[
\frac{(\varepsilon - 1)M}{(\varepsilon + 2)d} = \frac{4\pi}{3} N\alpha_o \tag{2.21}
\]

This equation is known as Clausius Mossitti Equation[1]. The right hand side of above equation indicates the molar polarization and is given by

\[
p = \frac{4\pi}{3} N\alpha_o \tag{2.22}
\]

The molar polarization is purely molecular quantity giving some information about electric properties of the molecule. Using equation (2.21) & (2.22)

\[
p = \frac{(\varepsilon - 1)M}{(\varepsilon + 1)d} \tag{2.24}
\]

The molar polarization is different from the \(P\) used to denote the electric moment per unit volume.

The permittivity depends on the amount of polarization. In non polar molecules this polarizability arise in two ways i.e. electric polarization and atomic polarization when electric field is applied to polar material, the permanent dipole tends to align themselves parallel to field. Polarizability is a function of the frequency of the applied field.

When the frequency of the applied field is sufficiently low, all types of polarization can reach the steady field value to the instantaneous value of the alternating field. At higher and higher frequencies there will
be less polarization and therefore permittivity value decreases with increase in frequency.

ii) **Debye theory of static permittivity:**

Debye[2] put the theory of static permittivity by using (i) dipolar Polarizability which was calculated by Langevin to find the mean magnetic moment parallel to applied field having permanent magnetic moments and (ii) the expression for Local field calculated by Lorentz.

To derive the relation for static permittivity, field at a single molecule is considered by imagining a spherical surface of molecular dimension in the dielectric medium. Consider the medium inside the sphere is made up of individual molecules and outside the sphere is a medium of homogeneous permittivity. The field at the center of sphere can be divided into three parts.

1) The field due to charges from outside the sphere and applied field.
2) The field due to polarization charges on the spherical surface.
3) The field due to molecules inside the spherical region

Debye’s theory depends on following assumptions.

A) No local directional forces due to neighbors act on the dipoles, so that they are distributed according to Langevin’s Law.

B) The field component due to molecules inside the spherical region is zero.

With these assumptions, the equation given by Debye is
\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{4\pi N_1 \left( \alpha + \frac{\mu^2}{3KT} \right)}{3\varepsilon}
\]

(2.25)

Where \( N_1 \) – Number of molecules per unit volume.
\( \alpha \) - Polarizability \( (\alpha = \alpha_{\text{electronic}} + \alpha_{\text{atomic}}) \)
\( \mu \) - Dipole moment
\( K \) – Boltzmann constant
\( \varepsilon_0 \) - Static Permittivity
\( \varepsilon \) - Permittivity of free space.

If material has molecular weight \( M \) and density \( p \), then \( N_1 = \frac{Np}{M} \), \( N \)
is Avogadro Number.

Therefore, equation (2.25) can be written as

\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \times \frac{M}{p} = \frac{4\pi N \left( \alpha + \frac{\mu^2}{3KT} \right)}{3\varepsilon}
\]

(2.26)

In this expression, \( \left( \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \times \frac{M}{p} \right) \) is called the molar polarization.

The following conclusions can be drawn from Debye’s theory[2].

1) For non polar material, the molar polarizability should be constant independent of temperature and pressure. An increase in density of such substances will lead to an increase in the permittivity.

2) For polar substance the polarizability will fall with temperature because thermal agitation decreases the dipolar polarization.
3) The molar polarization tends to \( \frac{M}{p} \) as \( \varepsilon \) tends to infinity and if contribution of \( \alpha \) is neglected, then right hand side reached to \( \frac{M}{p} \) at temperature

\[
T = \frac{4\pi N \rho \mu}{9MK \varepsilon}
\]

(2.27)

Below this temperature, the polarization becomes so large and it causes large internal field that the molecules will spontaneously align themselves parallel to one another even in the absence of an external field and the material becomes ferroelectrics.

There are some limitations in equation (2.25) due to assumptions made by Debye in deriving above equation.

1. The validity of equation is restricted to fluids due to first assumptions so that it would be not justified in crystalline material.

2. The second assumption is of doubtful validity except in the case of gases at moderately low densities and possibly of dilute solutions of polar molecules in nonpolar solvents.

According to Debye theory, liquids act as ferroelectrics material when \( T < T_c \) but the phenomenon of ferroelectricity is not common and certain does not occur in water. This failure of Debye equation is because of assumption that the force due to medium inside the spherical sphere is
zero, which is almost certainly not valid. Because of this Onsager\textsuperscript{[3,4]} has given his theory on following assumptions.

iii) **Onsager Theory:**

Onsager\textsuperscript{[3,4]} considered the local field at molecule and given a model for permittivity. He treated a molecule as a polarizability point at the center of a spherical cavity of molecular dimension in a continuous medium of static permittivity $\varepsilon_0$. The molecule is a polar molecule, which is spherical in form with molecular radius ‘a’ and is given by the equation

$$a^3 = \frac{3}{4\pi N_1}$$

i.e. the sum of the volumes of the spherical cavities equal to the total volume of the material. There are no local direction forces due to their neighbors on the molecules.

The internal field in molecule consists of two parts

1) The spherical cavity field $G$, produced in the empty cavity by the external applied field given by

$$G = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} E = gE \quad \text{where } g = \frac{3\varepsilon_0}{2\varepsilon_0 + 1}$$

2) The reaction field $R$ setup in the cavity by polarization induced by dipole in its surrounding, given by

$$R = \frac{2(\varepsilon_0 - 1) m_i}{(2\varepsilon_0 + 1) a^3}$$

Where $m_1$ is total moment of the molecule.
The total internal field acting on a spherical polar molecule is

\[ F = G + R \]

\[ = \frac{3\epsilon_0}{2\epsilon_0 + 1}E + \frac{2(\epsilon_0 - 1)}{2\epsilon_0 + 1} \frac{m_1}{a^3} \]

\[ F = gE + r \frac{m_1}{a^3} \quad \text{where} \quad r = \frac{2(\epsilon_0 - 1)}{2\epsilon_0 + 1} \quad (2.28) \]

From above equation it is clear that when \( \epsilon_0 \to \infty \), Onsager’s internal field tends to finite value while in Debye equation it tends to infinity.

The total moment \( m \) of the molecule is the vector sum of its permanent moment \( \mu \) and induced moment \( \alpha F \) by the local field.

\[ m = \mu + \alpha F \]

\[ = \mu + \alpha \left[ gE + r \frac{m_1}{a^3} \right] \]

\[ = \mu + \alpha gE + \alpha r \frac{m}{a^3} \]

\[ = \frac{(\mu + \alpha gE)}{\left(1 - \frac{r \alpha}{a^3}\right)} \]

The mean moment parallel to the field is given by

\[ \bar{m} \left( \frac{g}{1 - \frac{r \alpha}{a^3}} \right) \times \frac{\mu^2}{3kT} + \frac{\alpha g}{\left(1 - \frac{r \alpha}{a^3}\right)} \]

By using this equation in \( P = N_1 \bar{m} \) we get

\[ \frac{\epsilon_0 - 1}{4\pi} = \frac{N_1 g}{\left(1 - \frac{r \alpha}{a^3}\right)} \times \left[ \alpha + \frac{1}{\left(1 - \frac{r \alpha}{a^3}\right)} \times \frac{\mu^2}{3kT} \right] \quad (2.29) \]
But Onsager defined polarizability $\alpha$ in an internal refraction index by

$$\alpha = \frac{n^2 - 1}{n^2 + 2} \times a^3$$

By substituting for $\alpha$, $a^3$, $g$ and $r$ in above equation we get

$$\frac{\varepsilon_0 - n^2}{\varepsilon_0} \times \frac{2\varepsilon_0 + n^2}{n^2 + 2} = \frac{4\pi N_\mu^2}{9 \epsilon_0 K T \varepsilon}$$

This is Onsager equation. As $\varepsilon_0$ increases the Lorentz field $F$ increases without limit, but in Onsager’s cavity field tends to limit $(3E / 2)$, while the factor $A$ due to the reaction field never exceeds $n^2 + 2 / 3$. This equation does not predict the occurrence of ferroelectricity.

Debye’s theory and Onsager’s theory might be called semi statistical theories where macroscopic arguments are used to obtain the expression for local field. Kirkwood$^{[1]}$ and later Frohlich set out a rigorous expression to obtain the static permittivity using statistical methods.

iv) **Kirkwood Theory:**

Kirkwood$^{[1-5]}$ considered a specimen of the material containing $N$ dipoles of moment $\mu$ enclosed in a spherical volume $V$ and this spherical volume is situated in a uniform external field. Using this assumption Kirkwood’s equation for non-polarizable dipole is

$$\frac{\varepsilon_0 - 1}{3\varepsilon_0} \times \frac{2\varepsilon_0 + 1}{\varepsilon_0} = \frac{4\pi N_\mu^2}{v \epsilon_0} \times \frac{g \mu^2}{3 K T}$$

(2.31)
Where ‘g’ is correlation parameter which is a measure of local ordering in the material. The correlation parameter g will have the value unity if the average moment of spherical volume is same to the moment of individual molecule at the center of sphere. It will have greater than one if dipoles in spherical volume line up in parallel direction and the value of ‘g’ will be less than one if the dipoles are line up in antiparallel direction. The Factor he introduced a polarizability $\alpha$ to each dipole and approximated the local field acting on a dipole obtained an expression.

$$\frac{\varepsilon_0 - 1}{\varepsilon_0} \frac{2\varepsilon_0 + 1}{3\varepsilon_0} = \frac{4\pi N}{v_e} \times \left( \alpha + \frac{g\mu^2}{3KT} \right)$$  \hspace{1cm} (2.32)

v) Frohlich’s Theory

Frohlich’s\cite{1-7} theory is similar to Debye’ theory, Frohlich considered a spherical region of macroscopic dimensions within an infinite specimen which is treated as continuous medium. He obtained an equation for non polarizable dipoles as

$$\frac{\varepsilon_0 - 1}{\varepsilon_0} \frac{2\varepsilon_0 + 1}{3\varepsilon_0} \frac{M}{d} = 4\pi N \frac{(\bar{m}\bar{m})}{3KT}$$  \hspace{1cm} (2.33)

It can be observed from this equation that if $m$ is defined as $\mu$ & $\bar{m}$ is written as $g$, this equation is identical with Kirkwood’s equation (2.32)

Further, by taking into account the distortion polarization, Frohlich obtained an expression as
\[
\varepsilon_0 - \frac{n^2}{n^2 + 2^2} \frac{2\varepsilon_0 + n^2}{\varepsilon_0} \frac{M}{d} = 4\pi N \frac{g\mu^2}{9KT} \tag{2.34}
\]

vi) **Cole Theory:**

Cole\textsuperscript{[1]} proposed a theory of static permittivity which is similar to the theory of Kirkwood, but only differs in the treatment of direction of polarization. He obtained an expression for static permittivity as

\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} = \frac{n^2 - 1}{n^2 + 2} + \frac{4\pi N}{3\varepsilon \varepsilon_0} \times \frac{3\varepsilon_0}{\varepsilon_0 + 2} \frac{n^2 + 2}{2\varepsilon_0 + n^2} \times \frac{g\mu^2}{3KT} \tag{2.35}
\]

Which reduces to

\[
\frac{\varepsilon_0 - n^2}{\varepsilon_0} \frac{2\varepsilon_0 + n^2}{n^2 + 2^2} = \frac{4\pi N}{3\varepsilon} \frac{g\mu^2}{3KT} \tag{2.36}
\]

### 2.3 Theories of Dynamic Permittivity:

When an alternating field with high frequency is applied to a dielectric material, the dipolar polarization can not reach its equilibrium value fast enough or follow the polarizing field. So that, dipole moment per unit volume decreases with increase in frequency and hence there will be decrease in permittivity. When a field \( E \) is applied to a dielectric, the distortion polarization, which will represent by \( P_1 \) will establish very quickly compared with the time intervals in which we are interested, but remaining dipolar part of polarization, \( P_2 \) takes some time to reach its equilibrium value. If we assume that it increases at a rate proportional to its departure from its equilibrium value.
\[ i.e \quad \frac{dP_2}{dt} = \frac{P - P_1 - P_2}{\tau} \quad (2.37) \]

where, \( P \) is equilibrium value of total polarization

\( \tau \) is a constant which is the dimensions of time and is called the macroscopic relaxation time.

The above equation can be written as

\[ \frac{dP_2}{P - P_1 - P_2} = \frac{dt}{\tau} \quad (2.38) \]

After solving this equation we get

\[ \ln(P - P_1 - P_2) = \frac{-t}{\tau} + C \quad (2.39) \]

\( C \) is constant. If we assume the field \( E \), have been suddenly applied at \( t=0 \), then \( P_2=0 \) at \( t=0 \)

\[
C = \ln(P - P_1) \\

P_2 = P - P_1 \left( 1 - e^{\frac{t}{\tau}} \right) 
\]

If a polarization \( P \) is established due to a steady field \( F \) and the field is switched off at \( t = 0 \), \( P_1 \) falls immediately to zero \( P_2 \) approaches its equilibrium value according to exponential law with time constant \( \tau \)

\[ \frac{dP_2}{dt} = -\frac{P_2}{\tau} \]

Solution of this equation is

\[ P_2 = (P - P_1) e^{\frac{t}{\tau}} \]

Consider the applied field alternates with angular frequency \( \omega \), we can represent such field by

\[ E = E_0 e^{i\omega t} \]
The static permittivity and refractive index are defined in terms of \( P \) and \( P_1 \) by

\[
4\pi P = \varepsilon (\varepsilon_\omega - 1)E \quad \text{as } \omega \to 0;
\]

i.e.

\[
P = \varepsilon \frac{(\varepsilon_\omega - 1)}{4\pi} E
\]

and

\[
4\pi P_1 = \varepsilon (n^2 - 1)E \quad \text{as } \omega \to \infty
\]

i.e.

\[
P_1 = \varepsilon \frac{(n^2 - 1)E}{4\pi}
\]

Where \( n \) is the refractive index. Using the values of \( P, P_1 \) in eq. (2.37) we get-

\[
\frac{dP_2}{dt} = \frac{P - P_1 - P_2}{\tau}
\]

\[
= \frac{(\varepsilon_\omega - n^2)}{4\pi \tau} E - \frac{P_2}{\tau}
\]

\[
= \frac{(\varepsilon_\omega - n^2)}{4\pi \tau} E e^{i\omega t} - \frac{P_2}{\tau}
\]

The solution of this equation is

\[
P_2 = \frac{\varepsilon (\varepsilon_\omega - n^2)E}{4\pi (1 + i\omega \tau)}
\]

In this equation, \( P_2/E \) has become a complex quantity. This means that dipolar part of the polarization is not in phase with the applied field \( E \). We can express polarization as –

\[
P^* = p' - ip'' = P_1 + P_2
\]

\[
= \varepsilon \frac{(n^2 - 1)E}{4\pi} + \frac{\varepsilon (\varepsilon_\omega - n^2)E}{4\pi (1 + i\omega \tau)} \quad (2.40)
\]

When polarization becomes complex, the permittivity must also become complex, and eq. (2.7) can be written as –
\[ \varepsilon' = \varepsilon' - i\varepsilon'' = 1 + \frac{4\pi P}{E} \]

Substituting the values of \( P^* \) from eq. (2.40) we get-

\[ \varepsilon' = \varepsilon' - i\varepsilon'' = n^2 + \frac{\left(\varepsilon_0 - n^2\right)}{1 + i\omega \tau} \tag{2.41} \]

Therefore, \( \varepsilon' = n^2 + \frac{\varepsilon_0 - n^2}{1 + \omega^2 \tau^2} \)

and \( \varepsilon' = \frac{\varepsilon_0 - n^2}{1 + \omega^2 \tau^2} \omega \tau \)

These are known as Debye or the Debye-Drube equations. The real part of complex permittivity is also called as dielectric dispersion and imaginary part is called as dielectric loss. The dielectric loss becomes maximum

\[ \left( \varepsilon_{\text{max}} = \frac{\varepsilon_0 - n^2}{2} \right) \text{ at frequency } \omega = \frac{1}{\tau} \tag{2.42} \]

The phase lag between the polarization and the applied field leads to absorption of energy in the dielectric. The maximum energy will be absorbed at \( \omega = \frac{1}{\tau} \) i.e. maximum dielectric loss.
2.4 Different Models of Dynamic Permittivity:

There are different models used to describe the permittivity in terms of frequency. Some of the popular models are described below.

1) The Debye Model:

Debye[2] gave a model for complex permittivity and dielectric loss by equation

\[
\varepsilon' = \varepsilon'_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + j\omega\tau}
\]

Where \( \varepsilon' = \varepsilon' - j\varepsilon'' \) is complex permittivity, \( \varepsilon' \) is known as dielectric dispersion, \( \varepsilon'' \) is known as dielectric loss, \( \varepsilon_0 \) is static permittivity, and \( \varepsilon_{\infty} \) permittivity at infinite frequency. \( \omega \) is angular frequency and \( \tau \) is relaxation time.

The physical significance of these equations is that at frequency for which \( \omega\tau \ll 1 \) i.e below the absorption curve, equilibrium will be set up in a short time compared with that for which the field is in one direction. In this case the maximum value of permittivity is obtained and little energy will be absorbed. When the frequency approaches that for which \( \omega\tau = 1 \), the field will reverse in time comparable with \( \tau \), then polarizatin will not have time to reach the maximum. Thus the energy absorbed per cycle will be maximum. At frequencies for which \( \omega\tau \gg 1 \), there is no significant
orientation of dipoles in each cycle and the measured permittivity does not contain a contribution from this particular polarization.

The variation of $\varepsilon'$ and $\varepsilon''$ with frequency is as shown in fig. below. These curves are known as dispersion and absorption curves respectively.

![Dispersion and Absorption Curves](image)

**Plot of $\varepsilon'$ and $\varepsilon''$ versus frequency in GHz**

The dielectric loss approaches to zero for small and for large values of $\omega\tau$ while it is maximum for $\omega\tau = 1$ i.e. $\varepsilon_{\text{max}} = \frac{\varepsilon_{0} - n^2}{2}$ at a frequency $\omega = \frac{1}{\tau}$ and falls to half its maximum when $\omega\tau = \frac{1 + \omega^2\tau^2}{4}$.

Another way to represent the experimental result is to construct a diagram by plotting $\varepsilon'$ against $\varepsilon''$ at same frequency. The above equations for $\varepsilon'$ and $\varepsilon''$ are parametric equations of a circle. On eliminating $\omega, \tau$ and rearranging we obtain
\[
\left( \varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2} \right)^2 + \varepsilon'' = \left( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \right)^2
\]

Which is the equation of a circle with center \( \left[ \frac{\varepsilon_0 + \varepsilon_\infty}{2}, 0 \right] \) and radius \( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \). Thus by plotting \( \varepsilon' \) against \( \varepsilon'' \) a semicircle is obtained as shown in fig. below called as Debye semicircle. The method has the disadvantage that the frequency, which is the independent variable and the one whose value is most accurately known, is not explicitly shown.

The Cole-Cole model:

The experimental observations on many materials, which have particularly long chain molecules and polymers, show a broader
dispersion curve and the maximum loss at lower frequency compare to that would be expected from the Debye relationship. According to Cole-Cole[3], in such cases permittivity might follow the empirical equation

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

Where \(\alpha\) represents the symmetrical distribution parameter of relaxation time and it lies in between 0 to 1 i.e. \(0 \leq \alpha < 1\). In the limit when \(\alpha = 0\), above equation reduces to Debye equation. The plotted curve of \(\varepsilon'\) Vs \(\varepsilon''\) obeys an equation of a circle

\[
\left[\frac{1}{2} \varepsilon_0 + n^2 \varepsilon - \varepsilon_0\right] + \left[\varepsilon' + \frac{1}{2} \varepsilon_0 - n^2 \tan\left(\frac{\pi\alpha}{2}\right)\right]^2
\]

\[
\frac{1}{4}(\varepsilon_0 - n^2)\sec^2\left(\frac{\pi\alpha}{2}\right)
\]

(2.43)

With center at

\[
\left\{\frac{1}{2} \varepsilon_0 + n^2, -\frac{1}{2} \varepsilon_0 - n^2 \tan\left(\frac{n\alpha}{2}\right)\right\}
\]

and radius

\[
\frac{1}{2}(\varepsilon_0 - n^2)\sec\left(\frac{n\alpha}{2}\right)
\]
In this cases, $\varepsilon'$ Vs $\varepsilon''$ curve falls inside the Debye semicircle as shown in fig. Below

![Cole-Cole plot](image)

This semi circle is called as Cole-Cole arc or Cole-Cole plot. The Cole-Cole arc is symmetrical above the line through the center.

3) **The Davidson – Cole Relaxation model:**

The Cole-Cole arc is symmetrical about a line through the center parallel to Y-axis, Cole and Davidson found that the experimental results for certain materials do not have this symmetry in $\varepsilon'$ Vs $\varepsilon''$ plots, but they follows a skewed arc.

Davidson and Cole\(^6\)\(^7\) suggested a model in which an equation for complex permittivity can be written as
\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j\omega \tau)^\beta} \]  

(2.44)

Where \( \beta \) is the Davidson-Cole distribution parameter, which lies in the limit 0 to 1 i.e. \( 0 < \beta \leq 1 \). In the limiting condition at \( \beta = 1 \), above reduces to the Debye equation. As \( \beta \) decreases the arc of plot of \( \varepsilon' \) Vs \( \varepsilon'' \) becomes progressively more asymmetric as shown in fig. below.

Rationalization of equation above yields dispersion and absorption equations

\[ \frac{\varepsilon' - n^2}{\varepsilon_0 - n^2} = \cos^\beta \theta \cdot \cos \beta \theta \]

and

\[ \frac{\varepsilon'' - n^2}{\varepsilon_0 - n^2} = \cos^\beta \theta \cdot \sin \beta \theta \]

This value of \( \beta \) determines the angle at which the arc cuts the \( \varepsilon' \) axis at the high frequency end.
4) The Havriliak – Negami Model:

To explain behavior of $\varepsilon'' - \varepsilon'$ plot, Cole-Cole and Davidson-Cole models are useful, but in some liquids this curve deviates from the Cole-Cole and Davidson-Cole curves. Hence, Havriliak and Negami[8] has suggested an expression for complex permittivity which includes Cole-Cole and Davidson-Cole functions given as

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

(2.45)

Where $\alpha$ and $\beta$ are constants having values $0 \leq \alpha < 1$ and $0 < \beta \leq 1$.

This equation represents Cole-Cole model when $\beta = 1$, Davidson-Cole model when $\alpha = 0$ and Debye model for $\alpha = 0$, $\beta = 1$. The $\alpha$ and $\beta$ has no physical significance because it is a purely empirical factor to describe the appearance of the experimentally obtained complex plots.

2.5 Dielectric Study of Biological systems:

The dielectric properties of biological systems are very remarkable. They typically display extremely high dielectric permittivity at low frequencies, falling off in more or less distinct steps with increasing frequency. Their frequency dependence permits identification and investigation of a number of completely different underlying
mechanisms, and hence, dielectric studies of biomaterials have long been
important in biophysics. Dielectric spectroscopy has been used as a tool
to investigate the dielectric properties of cells and organelles. Following
on from the pioneering works of Debye[1], Onsager[2] and Kirkwood [5]
on polar molecules, Oncley [9], investigated the dielectric properties of
globular proteins in aqueous solutions. Since then the dielectric properties
of proteins have been extensively studied by a number of workers[10-15]
and the observed dielectric behavior has generally been interpreted as
arising from Brownian rotation of the protein macromolecule as a whole
although subsidiary dispersion due to bound water or local chain motion
exists. The application of the time domain dielectric spectroscopy
generally called time domain spectroscopy was successful in obtaining
new information on the structural and dynamic parameters of biological
systems. Schwan amongst others [16-20] laid the foundations for the
understanding of the dispersion of a biological cell suspended in an
electrolyte according to the theories of Maxwell and Wagner. Since then
the dielectric properties of cells and bacteria have been extensively
studied by a number of workers [21-30] and the observed dielectric data
has generally been interpreted as arising from interfacial polarization. In
general, starting from the pioneer works of Schwan, the properties of
biological materials are characterized by three major dispersions, which
he termed $\alpha, \beta, \gamma$ different mechanisms account for low frequency,
radio frequency, and microwave frequency. Additional fine structure effects lead to further differentiation since the low frequency, radio frequency, and microwave effects in turn exhibit multiple relaxation behavior. Cell suspensions will typically exhibit a significant dispersion in the radio frequency range.

The dielectric properties and conductivities of whole blood in in frequency range of 0.2 to 10MHz has been reported by H.Beving[31]. Yoshihito Hayashi [32] has recently introduces the dielectric coagulometry approach to estimate the risk of venous thrombosis. The electrical impedance of human blood has been studied by Hakan[33] . The Time domain dielectric spectroscopy study of biological systems has been reported by Yuri Feldman[34]. The different dielectric models are used for the analysis of the dielectric properties of cells in suspension. The mixture model and single and double shell models of spherical cells are used depending on the concentration, shape and conductivity parameters are considered to apply these models. The Maxwell-Wagner model describes the suspension dielectric spectrum as a function of the dielectric properties of the suspending medium and cell using equation
where \( p \) is the volume fraction of cell, \( \varepsilon_{\text{mix}}^* \) is the effective complex dielectric permittivity of the whole mixture, \( \varepsilon_{\text{sup}}^* \) is the complex dielectric permittivity of the supernatant, \( \varepsilon_{c}^* \) is the effective complex dielectric permittivity of the average cell.

By incorporating conductivity, the complex permittivity can be written as

\[
\varepsilon_{i}^*(\omega) = \varepsilon_{i} - j \frac{\sigma_{i}}{\varepsilon_{0}\omega}
\]

where \( \varepsilon_{i} \) is static permittivity and \( \sigma_{i} \) is conductivity of cell phase.

To understand human metabolism at the cellular level, influence of glucose on the dielectric parameters of erythrocytes has been studied by many researchers[35-40]. The time domain spectroscopy has been used for comparative study of normal, transformed and cancerous cells. Theoretical analysis and measurement techniques for dielectric spectroscopy of biological cells in radio frequency range has been reported by K.Asami[41].

The literature survey shows that, time domain dielectric spectroscopy is the new approach to study biological systems. The main
advantage of this method is the time required for measurement and coverage of wide range of frequencies. In some cases, very small quantity of sample required for analysis is also the advantage of this method.

2.6 Dielectric Properties of Blood:

Electrorotation of fixed red blood cells has been investigated by Georgieva et. al.[42] in the frequency range between 16 Hz and 30 MHz. The rotation was studied as a function of electrolyte conductivity and surface charge density. Between 16 Hz and 1 kHz, fixed red blood cells undergo cofield rotation. The maximum of cofield rotation occurs between 30 and 70 Hz. The position of the maximum depends weakly on the bulk electrolyte conductivity and surface charge density. Below 3.5 mS/m, the cofield rotation peak is broadened and shifted to higher frequencies accompanied by a decrease of the rotation speed. Surface charge reduction leads to a decrease of the rotation speed in the low frequency range. These observations are consistent with the recently developed electroosmotic theory of low frequency electrorotation. It is shown that a rigid correlation between electrorotation and the dielectric dispersion of a suspension of the same particles should exist [43,44]. This line of reasoning is in good agreement with many experimental findings at higher field frequencies reported by others [45-48]. The equivalency between electrorotation and impedance measurements at high frequencies
means that the information, which can be obtained by both methods, is equivalent. The advantage of electrorotation is that dielectric properties of single particles can be studied.

For the interrogation of biological systems, the microwave region of electromagnetic spectrum has many advantages as a choice of radiant energy[49]. The measurement of dielectric properties at microwave frequencies allows inferences to be made concerning the tertiary structure of bio-molecules, at least with respect to hydration and their associated functions. At microwave frequencies the dominant molecular species contributing to the dielectric constant of bio-systems is water. Likewise, water and electrolytes dominate the dielectric losses in bio-systems. Electromagnetic radiation and propagation characteristics in media (fluid) depends upon the propagation constant $\gamma$. The propagation constant reveals the nature of the media in which the wave is propagating, which is a complex number. The real part of it is attenuation constant $\alpha$, and the imaginary part of it is phase shift constant $\beta$.

The microwave dielectric measurements were performed in the frequency range fro 1MHz to 30 GHz using TDR for emulsion and gel using flat ended sample cell [50].

Thermally Stimulated Current (TSC) analysis is an extensive tool to understand the charge storage, charge relaxation and electrets behavior of organic dielectrics and biomaterials. M. S. Gaur et. al. studied the TSC
behavior of blood and tried to correlate with blood sugar level and blood group [51]. The TSC is recorded for the blood of different groups donated by healthy donator, are characterized by positive and negative peaks at temperature ranging 46-60°C and 90-110°C respectively. However, the TSC of blood donated by diabetic patient is showing interesting behavior and characterized by two peaks of positive polarity. The positive current peak position is subjected to glucose concentrations.

The TSC spectra are affected by various factors such as glucose concentration, water content, protein concentration, blood group, concentration of red and white blood cells etc. The study of TSC was undertaken on known blood group and concentration of glucose. However, there is little existing literature on TSC behavior of healthy and diabetic patient blood sample. It is expected that this approach of blood diagnosis will give new information’s about the health of human being.

Work has been done in exploring the possibilities of application of microwaves in the diagnosis of blood[52]. When a person is suffering from any disease, there will be a change in the constituents of blood. Such a change in the constituents of blood leads to a change in the electromagnetic properties of blood from which the disease can be diagnosed. The electromagnetic properties that help in the diagnosis of blood are its dielectric constant, ionic density, collision frequency etc.
The dielectric constant can be chosen as the main parameter in the diagnosis of blood which in turn depends on the relative amounts of its various constituents. It has been observed that the electrolyte and protein composition in blood plasma varies with age and also varies with the type of food intake because the salts present in water vary with geographical locations. Such a variation in blood plasma leads to a change in dielectric constant of the blood. Thus the dielectric constant of blood sample from one healthy person is not exactly same as that from another healthy person. Thus a study of blood is useful to make an estimation of its constituents for a normal human as well as for the specific cases of disease.

Waveguides systems have been used to obtain measurements for the complex permittivity of human blood in the frequency range 29-90 GHz. Alison[53] compared and analysed data in conjunction with lower frequency work, in particular that of Wei. There are two distinct regimes of behavior in the obtained spectra.

The study related to the effects of the blood-microstructure on the electrical conduction from two different but correlated properties: Electrical and mechanical (viscosity) revealed interesting results[54]. They derived useful parameters for the evaluation of electrical conduction as a function of the blood viscosity, ac-conductivity and dielectric
constant of normal and diabetic blood are measured in the frequency range 10 kHz–1 MHz at the room temperature. An empirical relation relating the resistivity and viscosity of the blood has been presented[54].

Based on electrorotation studies, Becker et.al[55] demonstrated that the dielectric properties of the metastatic human breast cancer cell line MDA231 were significantly different from those of erythrocytes and T lymphocytes. These dielectric differences were exploited to separate the cancer cells from normal blood cells by appropriately balancing the hydrodynamic and dielectrophoretic forces acting on the cells within a dielectric affinity column containing a microelectrode array. The operational criteria for successful particle separation in such a column are analyzed and their findings indicate that the dielectric affinity technique may prove useful in a wide variety of cell separation and characterization applications.

Dielectric permittivity and conductivity data for human erythrocytes exhibit two consecutive dispersions with frequency in the range from 0.1 to 250 MHz[56]. The dispersion observed above 50 MHz yields a circle in the complex impedance plane with its center on the real axis, suggesting a Debye relaxation, for the erythrocyte interior medium, centered in the microwave frequency range as for bulk water. Moreover, the Maxwell mixture equation, indicates that this "free" water forms most of the suspending medium of hemoglobin macromolecules. These results
extend to lower frequencies with biological tissues such as muscle, skin, or liver at microwaves frequencies.

Ismail et.al.[57] studied the design and development of a non-destructive method for measuring the complex permittivity of human blood from healthy volunteers using rectangular dielectric waveguide (RDWG) measurement system in the frequency range of 9 – 12 GHz. The human blood is placed in a Plexiglas sample holder and values of the complex permittivity of samples were computed from measured reflection and transmission coefficients. They used TRL calibration technique and time-domain gating feature in the vector network analyzer to eliminate errors due to multiple reflections in the RDWG measurement system.

F.Jaspard [58] have investigated the haematocrit dependence of the electrical parameters (relative permittivity and conductivity) of blood. The measuring set-up, composed of an impedancemeter (HP 4291A), an open-ended coaxial line and a temperature controlling set, was designed for dielectric measurements in the 1 MHz to 1 GHz frequency range. Measurements were performed on ex vivo animal (cow and sheep) blood at 37°C. The two dielectric parameters appeared to be strongly dependent on the haematocrit. The conductivity increases in the whole frequency range when the haematocrit decreases.
Dielectric properties of blood have been of interest due to its application in medicine, health and related areas, particularly for the analysis of blood from the point of view of pathological testing. For this purpose different techniques and approaches were used based on the parameter of interest. Park et. al.[59] designed, developed fabricated a new needle-type sample cell to investigate the correlation between blood glucose and electrical parameters using an impedance analyzer. The characteristics of the measurement cells were optimized to give high sensitivity. They showed that the values of the real (ε’) and the imaginary (ε”) dielectric constant increase with decreasing glucose contents in the water/glucose system, and that the value of ε’ in hamster tail changes according to the variation in blood glucose. It is likely that there is a correlation between blood glucose and the value of ε’, the electrical parameter.

Latest continuous glucose monitoring systems depends on the accurate relationship between the glucose concentration and the dielectric properties of the blood plasma. In a study, Karacolak et.al[60] studied the dielectric properties of 10 blood plasma samples, they studied measurements for various glucose levels in the frequency range of 500 MHz to 20 GHz. To relate the glucose concentration with the dielectric properties, first an accurate Cole-Cole model is used to fit the dielectric
properties as a function of frequency and then the Cole-Cole parameters are defined as a function of glucose using a polynomial fitting.

Our aim is to use this technique for development of pathological test equipment for analysis of blood, urine, salvia and cells.

The main focus is to use small quantity of sample and reduce measurement and analysis time so that the development equipment can be used as screening test equipment to be used for analysis of large number of samples. We are also focusing on the portability and easy handling of the developed equipment.

The details of development stages are explained in next chapter.
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