Chapter

2

Theoretical Backgrounds

Contents

2.1 Introduction

For better understanding of dielectric behaviour of any materials, a detailed theoretical background is required. Materials can be divided into three main types based on their ability to conduct electricity: conductors, semiconductors, and insulators. Dielectric and insulating materials are often used interchangeably, although dielectric materials form a significant part of insulators. The dielectric materials become polarized when exposed to an electric field allowing an electrostatic field to form within them. As a result the positive charges within dielectric materials move towards the direction of the field, while the negative charges move in the opposite direction, form of a dipole. This polarization leads to the separation of positive and negative charges within each small volume of the material, while the material as a whole remains electrically neutral. Dielectric materials play a crucial role in enhancing the storage capacity of capacitors by neutralizing charges at the electrode surfaces. This prevents them from significantly contributing to the external electric field [1]. In this chapter, various topics related to dielectric materials are discussed in detail, including theories of polarization, their electrochemical impedance spectroscopy and Physical and chemical properties (Density, Ultrasonic velocity, Viscosity and FTIR study).

2.1.1 Polar and Non polar

The arrangement of atoms within a molecule provides insight into its polarity. A molecule is deemed polar if it possesses two distinct centers where positive and negative electric charges are distributed unevenly across different ends of the molecules. Conversely, a nonpolar molecule features two centers where the distribution of positive and negative charges coincides at the same point within the molecule.

Polarity means charges separated in a molecule. Polar molecules have a dipole moment showing this separation, while nonpolar ones don't have much charge separation. Polar substances usually interact with other polar ones, while nonpolar molecules interact less. Table 2.1 gives a list of polar and nonpolar liquids.

Table 2.1 Features of polar and non-polar binary liquids.

Features	Polar	Nonpolar
Definition	Polar substances have a positive charge and a negative charge within their structure,	Nonpolar substances don't have a significant separation of charges within their structure

	creating a separation of charges	
Movement	Nonpolar substances do not have an electrical dipole moment because they lack a significant separation of charges.	Nonpolar substances do not have an electrical dipole moment because the distribution of charges within the molecule is symmetrical, resulting in a cancellation of any dipole moment.
Charge separation	There is separation of charge	There is separation of no charge
Interaction	Polar substances tend to interact with other polar substances due to their opposite charges.	Nonpolar substances do not typically interact strongly with polar substances
Example	Methanol, Hexanol, Acetone, DMF	Oil, Benzene, CCl_4, n-Heptane

2.1.2 Dipole moment molecule or Electric moment

The dipole moment measures the overall polarity of a molecule. If a molecule has polar bonds that aren't evenly distributed around its center, it results in an unequal charge across the molecule. This uneven charge distribution makes the molecule polar, showing a significant difference in electrical charge.

A dipole moment measures the distance between two opposite electric charges (+q and -q), as illustrated in Figure 2.1. It's a vector quantity, meaning it has both magnitude and direction. The magnitude equals the charge multiplied by the distance between the charges, and the direction is from the negatively charged end to the positively charged end as given below.

$$\mu = qr \qquad (2.1)$$

Where μ represents the dipole moment, q stands for the magnitude of the separated charge and r denotes the distance between the charges.

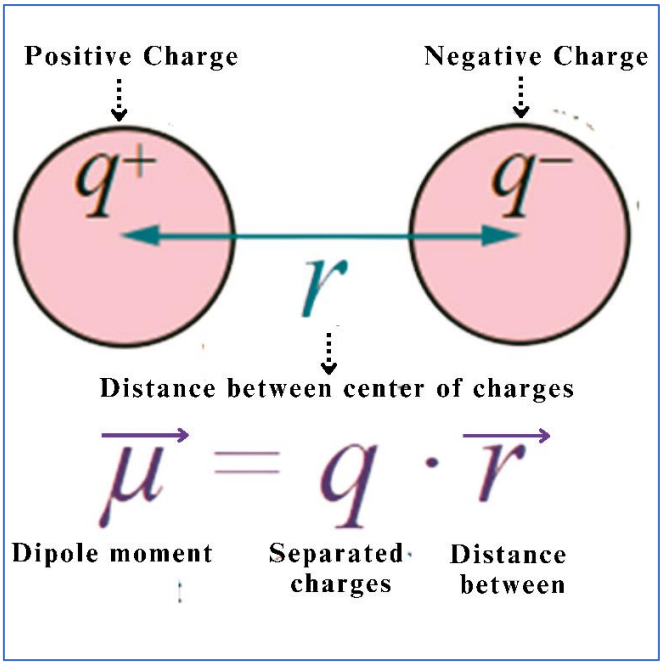

Fig. 2.1 Separation of two opposite charge (+q and -q) carriers with a distance (r).

The dipole moment is represented by an arrow, indicating the direction from the positive to the negative end of the dipole. In a molecule, the magnitude of the separated charge (q) is typically on the order of 10^{-10} electrostatic units (e.s.u.), and the distance (r) between the charges is on the order of 10^{-8} centimeters (cm). Therefore, the unit of dipole moment is 10^{-18} e.s.u.cm, also known as "Debye" (abbreviated as D). In present study use of liquids dipole moment is n-Hexanol (1.60 D), n-Octanol (1.68 D) and N, N-Dimethylformamide (3.86 D) respectively. The dielectric constant of a material depends on the dipole moments and the ability of these dipoles to align in the direction of the applied electric field.

2.2 Polarization

When an external electric field is applied to a dielectric material, all the bound charges within it align themselves in the direction of the applied electric field. This alignment of bound charges is known as polarization (P). In many dielectric materials, the degree of polarization is directly proportional to the strength of the applied alternating current (AC) electric field.

$$\vec{P} = \alpha\vec{E} \qquad (2.2)$$

Where α is the is known as polarizability of the material.

Polarization can also be defined as the total charge passing through a unit area within a dielectric, perpendicular to the direction of the applied electric field. There are different

types of polarization that occur in dielectric materials, including electronic polarization ($\vec{P}e$), ionic polarization ($\vec{P}i$), orientation polarization ($\vec{P}o$) and interfacial or space-charge polarization ($\vec{P}s$). In a polarization mechanism, the total polarization is the sum of all these individual polarizations (Fig. 2.2).

$$\vec{P}_{Total} = \vec{P}_E + \vec{P}_I + \vec{P}_O + \vec{P}_S \quad (2.3)$$

Where, ($\vec{P}_E$) Electronic, ($\vec{P}_I$) Ionic, ($\vec{P}_O$) Orientation, and ($\vec{P}_S$) Interfacial or space-charge polarization are polarizations due to electronic, ionic, orientation and interfacial or space-charge polarization movements of the system.

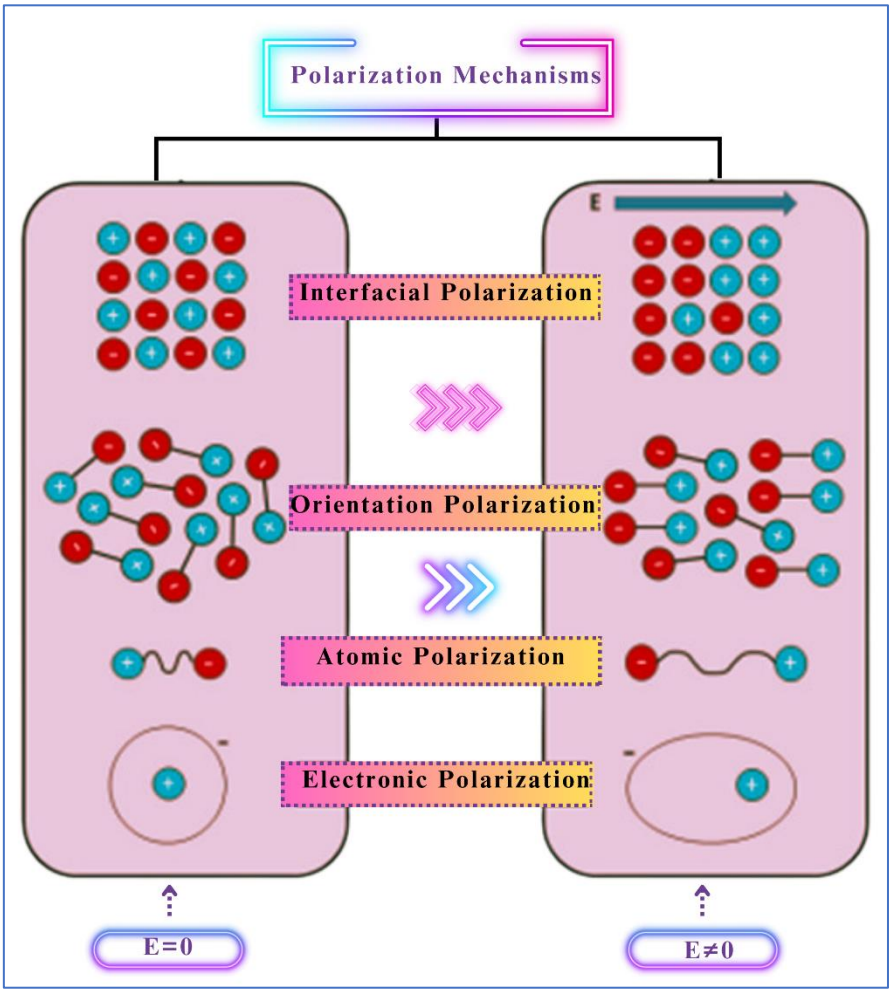

Fig. 2.2 Different polarization mechanisms in the absence and presence of an electric field.

As discussed earlier, polarization is directly proportional to the applied electric field, hence polarizability (α) is also expressed as follows.

$$\alpha_{Total} = \alpha_E + \alpha_I + \alpha_O + \alpha_S \quad (2.4)$$

Where, Electronic represents the electronic polarizability (α_E), which arises due to the displacement of the electron relative to the positive nuclei. Ionic represents the ionic

polarizability (α_I), which occurs due to the displacement of anions and cations in opposite directions from each other. Orientation represents the orientation polarizability (α_O), which arises due to the alignment of dipoles in the presence of an electric field. Interfacial or Space-charge represents the interfacial or space-charge polarizability (α_S), which occurs due to the diffusion of ions in the presence of an external electric field.

Four types of polarizations are explained as follows:

2.2.1 Dielectric Polarization of material

The dielectric constant, also known as permittivity, is a property of a dielectric material. It's equal to the ratio of the capacitance when a dielectric medium filled with the given material to the capacitance of an ideal capacitor in a vacuum. These constant measures the ability of a material to store electric charge under the influence of an electric field. It's an expression of how much a material concentrates electric flux and serves as the electric equivalent of relative magnetic permittivity.

Different materials may exhibit various types of dielectric mechanisms or polarization effects, which contribute to their overall permittivity. In dielectric materials, electric charge carriers are arranged in such a way that they can move in the presence of an applied electric field. These charge carriers become polarized to counteract the electric field, with positive and negative carriers moving in opposite directions. At zero frequency, the value of polarization ($\vec{P}_O$) reaches its maximum. However, due to the inertia of the charge carriers, the polarization mechanism takes time, causing the polarization (P) to generally not be in phase with the electric field (E). Therefore, frequency-dependent complex dielectric permittivity spectra $\varepsilon^*(f) = \varepsilon'(f) - j\varepsilon''(f)$ are used to provide both amplitude and phase information. The spectra of polarization mechanisms often take the form of relaxation or resonance. A resonance spectrum occurs when charge is moved against a restoring force [3-4].

2.2.2 Electronic Polarization

The electronic polarization mechanism arises from a shift in the center of mass of the negative electron charge surrounding the positive atomic nucleus when an electric field is applied (as shown in Fig. 2.3). Because electrons are lighter, they respond rapidly to the applied electric field. This displacement of the center of negative charge relative to the positive atomic nucleus creates a dipole moment in the presence of the electric field.

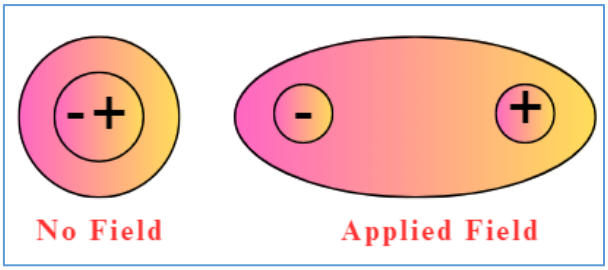

Fig. 2.3 Electronic polarization without field and with application of field.

Electronic polarization is a common phenomenon observed in most materials. It is of the order of 10^{-15} s, which corresponds to time period at optical frequencies. It can be expressed in terms of the dipole moment of the material and its unit volume as follows:

$$P = \frac{\mu}{V} \tag{2.5}$$

where P is the polarization, μ is dipole moment and V is unit volume.

2.2.3 Atomic Polarization

In materials, atomic polarization can occur in atoms with different structural properties. When an atom's electron cloud is influenced by an external charge, it becomes polarized, causing the electron cloud to shift away from the nucleus's center. The arrangement of atoms in a molecule result in the displacement of the electron cloud towards the atom with stronger binding. Initially, the atom contains charges of opposite polarity, and when an external field is applied to these charges, it changes the equilibrium positions of the atoms, leading to charge displacement. Atomic polarization differs slightly from electronic polarization. In atomic polarization, there's a relative motion of atoms due to the application of an external field. On the other hand, electronic polarization involves the shift of the charge cloud surrounding atoms when an external field is applied. Both these polarizations are instantaneous, meaning they're fully formed in a very short amount of time.

2.2.4 Orientation polarization

In orientation polarization, a material contains built-in dipoles that are independent of each other, allowing them to rotate freely. A primary example is liquid water, where each water molecule has a small dipole that can orient itself in any direction with respect to other molecules. Additionally, the orientation of these dipoles changes continuously because the molecules are in constant motion. Orientation polarization is therefore primarily observed in liquids, where the molecules have the freedom to move and reorient themselves.

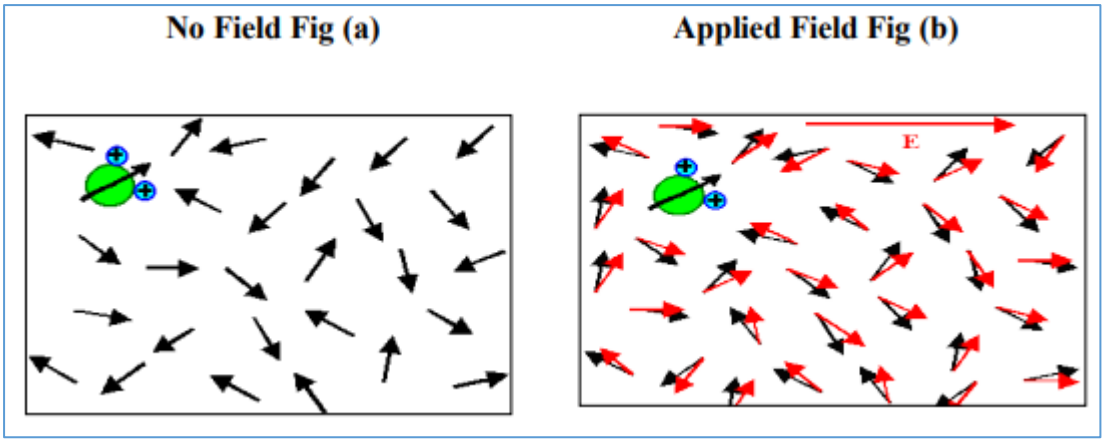

Fig. 2.4 Orientation polarization without field and with application of field.

Figure 2.4 (a) illustrates the graphical representation of molecules in a liquid without an external field. It depicts that at any given moment, all dipoles in the liquid are oriented in a particular direction. Figure 2.4 (b) exhibits a scan of molecules in a liquid with an applied external field. It reveals a cluster of molecules in the liquid, each of which forms a natural dipole due to the difference in the centers of charge between the negatively and positively charged atoms within the molecule. As a result, each molecule carries a dipole moment.

Orientation polarization is indeed slower than distortion polarization. The relaxation time for this type of polarization typically ranges from 10^{-12} to 10^{-10} seconds, falling within the microwave region of the electromagnetic spectrum. The time needed to establish orientation polarization depends on several factors, including molecular size, molecule-molecule interactions, temperature, and the viscosity of the medium.

2.2.5 Interfacial or Space-charge Polarization

In a crystal with an equal number of mobile positive ions and fixed negative ions, in the absence of an electric field, there is no net separation between all the positive charges and all the negative charges. This equilibrium state results in no overall electric dipole moment.

When an external electric field is applied between two electrodes of a capacitor, all the positive charge carriers are repelled by the positive charge on one electrode and move towards the negative charge on the other electrode. Similarly, all the negative charge carriers are repelled by the negative electrode and move towards the positive electrode. As a result of the application of electrical energy, all the charge carriers are attracted to the electrodes, leaving no charge in the space between them. This phenomenon is known as interfacial or space charge polarization, as depicted in Fig. 2.5.

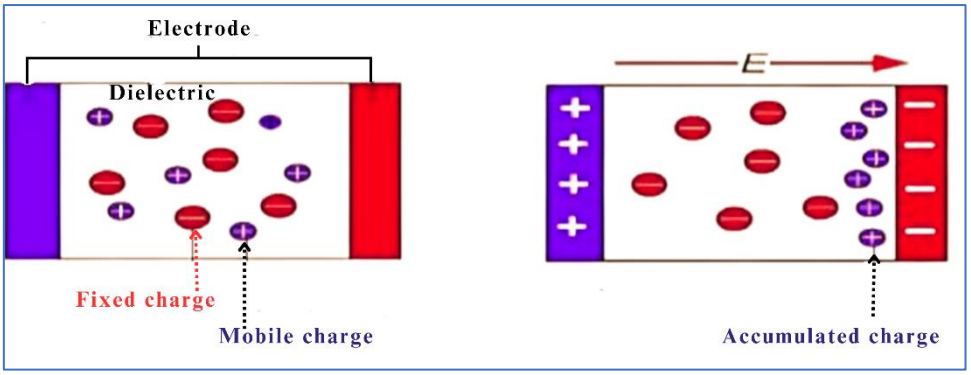

Fig. 2.5 Interfacial Polarization without field and with application of field.

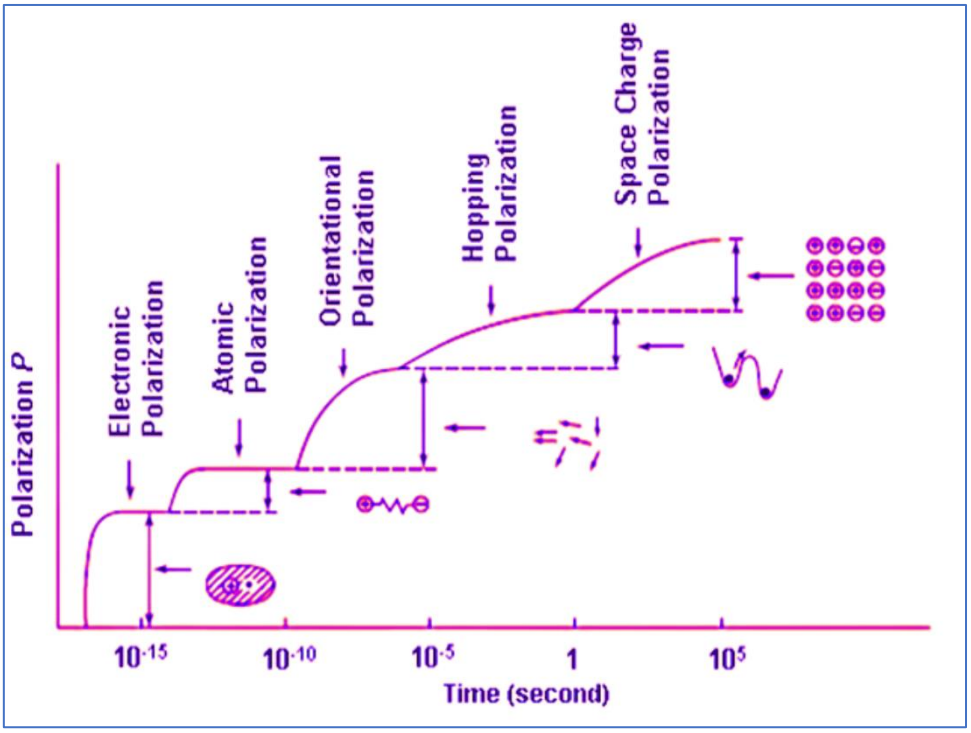

Fig. 2.6 Contribution to the time dependent dielectric constant from different charge configuration.

All these processes of polarization can occur in homogeneous pure materials, except for interfacial polarization. Interfacial polarization requires either various stages or mixtures of pure materials to occur.

2.3 Frequency Response of Dielectric Mechanism

All four types of polarizations are influenced by the frequency of the applied electric field, as depicted in Figure 2.6. At lower frequencies, all polarizations can reach their maximum values, similar to what they would achieve under a constant electric field equal to the instantaneous value of the alternating field. However, as the frequency increases, there is less time for polarization to reach its maximum value. Orientation

polarization depends on factors such as molecular size, viscosity, temperature, and excitation frequency of the applied field. Its relaxation time ranges from 10^{-12} to 10^{-10} seconds, similar to the time span of the microwave region (Figure 2.7). Ionic polarization occurs due to the displacement of positive and negative charges, and it has a relatively short relaxation time on the order of 10^{-13} to 10^{-12} seconds, comparable to the time period of infrared light. Electronic polarization results from the displacement of electrons, which respond quickly to changes in the electric field due to their light mass. Its relaxation time is on the order of 10^{-15} seconds, corresponding to the time period of optical frequencies [5].

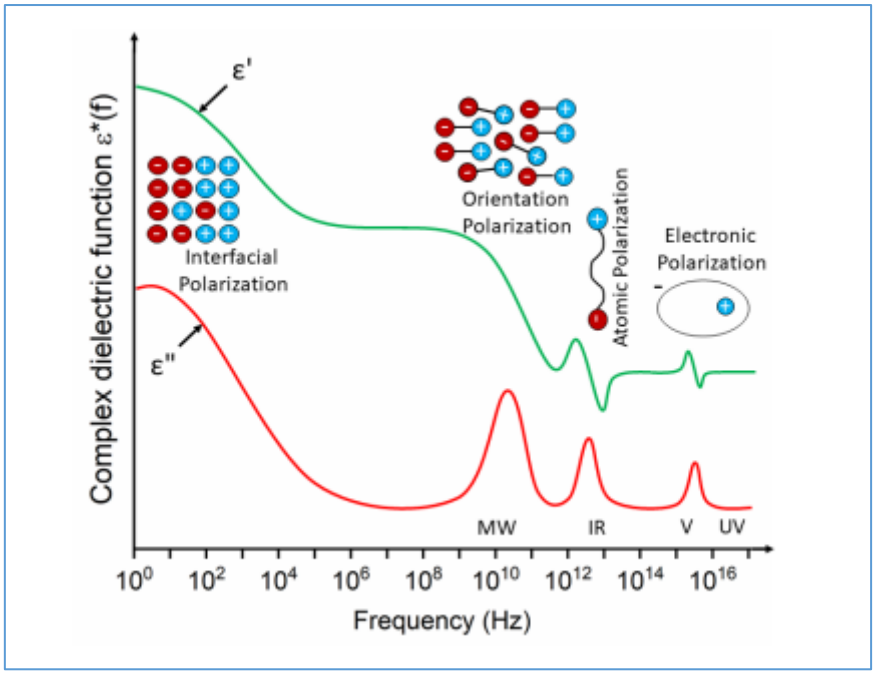

Fig. 2.7 Complex permittivity and polarization mechanisms as function of frequency.

At the microscopic level, several dielectric ssprocesses contribute to the behavior of materials. At microwave frequencies, there's a strong interaction between dipole orientation and ionic conduction. Polar molecules, like water, have a permanent dipole moment that rotates to align with an alternating electric field. These processes result in significant losses, which is why microwave ovens heat food. Atomic and electronic processes in the microwave region are weaker and usually continuous. Each dielectric process has a "cut-off frequency" characteristic. As the frequency increases, slower processes decrease in significance, while quicker ones contribute more to the overall permittivity (ε′). The loss factor (ε′′) peaks at each critical frequency accordingly. The

magnitude and cut-off frequency of each mechanism are distinctive for different materials.

For example, water has a significant dipolar effect at low frequencies, but it diminishes rapidly around 22 GHz [5]. In contrast, Teflon doesn't exhibit dipolar processes, and its permittivity remains relatively stable in the millimeter-wave region.

2.3.1 Resonant Frequency

Electronic or atomic polarization tends to exhibit a resonant effect. In the infrared and visible light regions, the inertia of orbiting electrons becomes significant and should be considered. Atoms can be conceptualized as oscillators with damping effects akin to mechanical spring and mass systems [show in fig. 2.7]. At frequencies other than the resonant frequency, the oscillation amplitude remains low. Below resonance, electronic and atomic processes contribute only minimally to ε', displaying nearly lossless behavior. The resonant frequency is established by a resonant response in ε' and a maximum absorption peak in ε". Contributions from all these mechanisms vanish beyond the resonance.

2.4 Theories of Dielectric Relaxation

Theories of dielectric relaxation can be broadly classified into two categories: static permittivity theories and dynamic permittivity theories. In static permittivity theories, the focus lies on elucidating the behavior of polar dielectric materials with permanent dipole moments when subjected to a constant electric field, resulting in the maintenance of equilibrium under various polarizations. The permittivity of the material under such conditions is termed static permittivity (ε_0). Conversely, dynamic permittivity theories examine the change in permittivity of dielectric materials when exposed to an electric field varying in frequency. With increasing frequency of the applied field, molecular dipoles within the material are unable to reorient quickly enough to align with the changing field, leading to a decrease in the material's permittivity. These theories aim to describe the frequency-dependent behavior of the material's permittivity. Understanding both static and dynamic permittivity is crucial for comprehensively characterizing the dielectric properties of materials under different electrical conditions.

2.4.1 Relaxation Time

In orientation polarization, a relaxation effect is typically observed, characterized by a relaxation time (τ) that describes the time required for dipoles to align in the presence of an electric field or to return to their original disordered state after the field is removed [6]. This time constant is a measure of the mobility of molecules, or dipoles, within a

material. In liquids and solids, where molecules are in a condensed state with limited freedom to move, the application of an electric field induces slow rotation of the molecules due to constant collisions, leading to internal friction [7]. Over time, the molecules exponentially approach their final oriented state, with the relaxation time constant (τ) governing this process. When the electric field is switched off, the molecules return to their random distribution with the same time constant. The relaxation frequency (fc) is inversely proportional to the relaxation time (τ):

$$\tau = \frac{1}{2\times\pi\times f} \tag{2.6}$$

At frequencies below relaxation, the alternating electric field changes slowly enough for the dipoles to keep up with the shifts. The loss factor (ε") increases directly with frequency (as shown in Fig. 2.8) because polarization can fully develop. However, as the frequency increases, ε" continues to rise while the storage factor (ε') starts to decrease due to a lag in dipole alignment with the electric field. Beyond the relaxation frequency, both ε" and ε' decrease because the electric field changes too quickly for the dipoles to rotate effectively, causing the orientation polarization to disappear. [5]

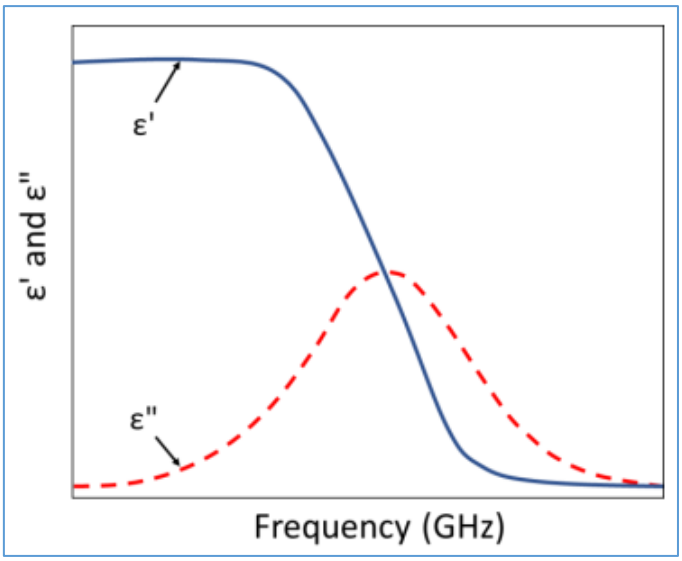

Fig. 2.8 Variation of ε' and ε" as a against frequency for Debye relaxation

The dipole moment of the molecule of a substance influences its permittivity and measurement of permittivity can be used to calculate the dipole moment. At low frequency electromagnetic field of moderate intensity, all types of polarizations attain equilibrium with the applied field in an isotropic polar material and the permittivity of the material is called static permittivity (ε_0). For investigating the molecular structure and for the study of high frequency dielectric behavior, the static permittivity is very

much useful. Various theories have been developed to express the relation between permittivity and dipole moment.

2.5 Theories of Static Permittivity

Dielectric constant of the material is a measure of the degree to which the electric charge distribution in the material can be polarized by the application of an electric field. Theories of permittivity are in view of the response of charge distribution to the applied electric field.

When considering a parallel plate capacitor in a vacuum with surface area A and distance between plates d, if the capacitor is charged such that one plate carries a charge q_1 (measured in electrostatic units, e.s.u.) and the other plate carries a charge q_2 (measured in electrostatic units, e.s.u.), then the force between these charges is determined by Coulomb's law.

$$\mathbf{F} = \left[\frac{1}{4\pi\varepsilon_v}\right]\left[\frac{q_1 q_2}{\varepsilon r^3}\right] r \tag{2.7}$$

When q_1 and q_2 are measured in Coulombs (C), F in Newtons (N), and r in meters. ε_v represents the vacuum permittivity, which is approximately 8.85×10^{-12} farads per meter (F/m). In the electrostatic system of units, $4\pi\varepsilon v$ is normalized to 1. Thus, in this system, ε becomes a dimensionless quantity, commonly used in dielectric theory.

Considering the above conditions Coulomb's law can be written as,

$$\mathbf{F} = \left[\frac{q_1 q_2}{\varepsilon r^3}\right]\mathbf{r} \tag{2.8}$$

When considering the force F (in dyne) of repulsion between two like charges q_1 and q_2 (measured in Coulombs) separated by a distance r (in centimeters) within a dielectric material. When there is a vacuum between the plates, the electric field E is

$$\vec{\mathbf{E}}_{\text{Vacuum}} = 4\pi q \tag{2.9}$$

When a dielectric material with a dielectric constant ε is inserted between the plates of a capacitor, the electric field between the plates decreases due to polarization. Thus, the electric field becomes

$$\vec{\mathbf{E}} = \frac{4\pi q}{\varepsilon} \tag{2.10}$$

The amount of polarization charge can be written as

$$\vec{\mathbf{P}} = q\left(1 - \frac{1}{\varepsilon}\right) \tag{2.11}$$

The impact of the electric field on the dielectric is proportionate to charging of two surfaces of the dielectric with charges of inverse sign to those causing on the field. The surface density of these opposite sign charges on the surface of dielectric is $\vec{\mathbf{P}}$, and is

known as polarization [8]. It is the aggregate charge going through any unit area inside the dielectric (parallel) to the plates.

The electric displacement D is defined in terms of the original applied charge density:

$$\vec{\mathbf{D}} = 4\pi q \tag{2.12}$$

$$\vec{\mathbf{D}} = \varepsilon\vec{E} = \vec{E} + 4\pi\,\vec{\mathbf{P}} \tag{2.13}$$

It can be also written as:

$$\varepsilon - 1 = \frac{4\pi\vec{P}}{\vec{E}} \tag{2.14}$$

The relationship between the capacitance (C) of a parallel plate capacitor, the charge (Q) on its plates, and the applied potential difference (V) across the plates is given by the equation:

$$Q = CV \tag{2.15}$$

Neglecting edge effects, the capacitance of a pair of parallel plates, each of area A and containing materials of dielectric constant ε is

$$C = \frac{\varepsilon A}{4\pi d} \tag{2.16}$$

Measuring this capacity results in an understanding of the static dielectric constant. The static dielectric constant for a specified substance is the ratio of a condenser's ability to that substance as the dielectric medium to the ability of the same vacuum condenser as the dielectric medium:

$$\varepsilon_0 = \frac{C}{C_0} \tag{2.17}$$

Relative permittivity (Dielectric constant) is a function of temperature and frequency and also a dimensionless quantity.

Therefore, polarization [7] is also defined as the dipole moment per unit volume.

$$\vec{P} = \frac{\mu}{V} \tag{2.18}$$

Polarization [7] is also defined as the charge per unit area.

$$\vec{P} = \frac{Q}{A} \tag{2.19}$$

Polarizations in the dielectric materials can be calculated using different theories and different theories for calculating the amount of polarization are discussed in the latter part of the section.

2.5.1 Clausius-Mossotti Equation

Consider a sizable, isotropic dielectric sphere, much larger than atomic dimensions yet significantly smaller than the distance between the plates. In this setup, the dielectric

experiences a uniform electric field when the plates are uniformly charged with a surface charge density (σ). If the electric field's actual intensity acting on an individual molecule is expressed as $\vec{F}$, it induces an electric moment within the atomic groups, which can be expressed as:

$$\mathbf{m} = \vec{\mathbf{F}}\alpha_0 \tag{2.20}$$

Where α_0 represents the polarizability of the molecule.

Hence, the total average moment aligned with the applied field [9] can be expressed by the following equation.

$$\mathbf{m} = \frac{\mu^2 \cos^2\theta}{TK}\,\vec{\mathbf{F}} + \text{er} \tag{2.21}$$

In the given equation, the first term signifies the permanent dipole moment of the molecules, while the second term represents the displacement caused by the flexibility of bound charges. This indicates that the permanent dipole moment contributes to the polarization effect, making the dielectric constant dependent on temperature. Conversely, the moment resulting from the displacement of bound charges remains unaffected by temperature changes. $\vec{\mathbf{F}}$ can be conveniently understood by envisioning a positive unit charge enclosed within a small sphere, relatively larger than molecular dimensions but smaller than the distance between the plates. This approach allows for the breakdown of the force acting on this unit charge into three components:

- The force $\vec{\mathbf{F}}_1$ arises from the interaction between the unit charge and the surface charge density σ on the plates.
- The force $\vec{\mathbf{F}}_2$ arises from the polarization of the medium surrounding the small sphere.
- The force $\vec{\mathbf{F}}_3$ is generated by the medium contained within the small sphere.

$$\vec{\mathbf{F}}_{\text{total}} = \vec{\mathbf{F}}_1 + \vec{\mathbf{F}}_2 + \vec{\mathbf{F}}_3 \tag{2.22}$$

The force due to surface charge density ($\boldsymbol{\sigma}$) is denoted as $\vec{\mathbf{F}}_1$, and mathematically expressed as

$$\vec{\mathbf{F}}_1 = 4\pi\boldsymbol{\sigma} \tag{2.23}$$

To calculate $\vec{\mathbf{F}}_2$ we can consider removing the matter within the small sphere. $\vec{\mathbf{F}}_2$ consists of two components: the force resulting from layers of induced charges on the dielectric facing the conducting plates, and the charge layer on the surface of the small spherical cavity.

$$\vec{\mathbf{F}}_2 = -4\pi\vec{\mathbf{P}} + \left(\frac{4\pi}{3}\,\vec{\mathbf{P}}\right) \tag{2.24}$$

Where $\vec{\mathbf{P}}$ represents the polarization of the material, indicating the dipole moment per unit volume within the dielectric material.

$\vec{\mathbf{F}}_3$ represents the force due to the material contained within the small sphere, and its determination relies entirely on the material's structure. Obtaining a valid expression for it is generally not feasible. Lorentz [10] proposed that in a cubic crystal lattice, the dipoles within the material experience no net force, leading to $\vec{\mathbf{F}}_3$being zero. This theory applies to gases and certain liquids where molecules are randomly oriented in the absence of an electric field. Hence, due to this rationale, the force $\vec{\mathbf{F}}_3$ is considered zero. Consequently, the total force is expressed by the following formula:

$$\vec{\mathbf{F}}_{\text{total}} = 4\pi\boldsymbol{\sigma} - 4\pi\vec{\mathbf{P}} + \left(\frac{4\pi}{3}\vec{\mathbf{P}}\right) \tag{2.25}$$

But $D = 4\pi\sigma$ and $D = E + 4\pi\vec{\mathbf{P}}$ So, Eq. (2.25) becomes,

$$\vec{\mathbf{F}}_{\text{total}} = E + 4\pi\vec{\mathbf{P}} - 4\pi\vec{\mathbf{P}} + \left(\frac{4\pi}{3}\vec{\mathbf{P}}\right) \tag{2.26}$$

$$\vec{\mathbf{F}}_{\text{total}} = E + \left(\frac{4\pi}{3}\vec{\mathbf{P}}\right) \tag{2.27}$$

But $D = E + 4\pi\vec{\mathbf{P}}$ and from this we can write the following equation.

$$E(\varepsilon - 1) = 4\pi\vec{\mathbf{P}} \tag{2.28}$$

Force ($\vec{\mathbf{F}}_{\text{total}}$) is given by:

$$\vec{\mathbf{F}}_{\text{total}} = E + \left(\frac{E(\varepsilon-1)}{3}\right) \tag{2.29}$$

$$\vec{\mathbf{F}}_{\text{total}} = \left(\frac{E(\varepsilon+2)}{3}\right) \tag{2.30}$$

This equation signifies the relation between electric field (E) and actual force ($\vec{\mathbf{F}}$). Let N_1 be the number of molecules per cubic centimeter, then by definition of polarization. This equation establishes the relationship between the electric field (E) and the actual force ($\vec{\mathbf{F}}$). Let N_1 denote the number of molecules per cubic centimeter [11]. Then, according to the definition of polarization:

$$\vec{\mathbf{P}} = N_1 m = N_1\alpha_0\vec{\mathbf{F}} \tag{2.31}$$

Substituting the value of $\vec{\mathbf{F}}$ from the Eq. (2.30) we get,

$$\vec{\mathbf{P}} = N_1\alpha_0\left(\frac{E(\varepsilon+2)}{3}\right) \tag{2.32}$$

By using the Eq. (2.31) and Eq. (2.32), we get the relation between polarizability (α_0) and dielectric constant (ε).

$$\frac{(\varepsilon-1)}{(\varepsilon+2)} = \frac{4\pi}{3} N_1\alpha_0 \quad (2.33)$$

For a pure molecule, $N_1 = \frac{Nd}{M}$, where N represents the number of molecules per mole, d denotes the density, and M signifies the molecular weight, we can substitute the value of N_1 above the equation:

$$\frac{(\varepsilon-1)M}{(\varepsilon+2)d} = \frac{4\pi}{3} N\alpha_0 \quad (2.34)$$

This equation (2.34) is known as Clausius- Mossotti Equation.

2.5.2 Debye Theory of Static Permittivity

Debye's hypothesis [12], applies dipolar polarizability and Langevin's method to determine the mean magnetic moment parallel to an applied field for gas particles with permanent magnetic moments. Debye also incorporates Lorentz's interpretation of the locally calculated field. This hypothesis relies on two key assumptions: (a) The molecule is considered as rigid system of charges (b) The external field is supposed to induce no charge at all. These assumptions provide the foundation for Debye's exploration of gas particle behavior in response to magnetic fields.

The molecules are classified into two distinct groups.

(1) Molecules with normal values of molar polarization

(2) Molecules with abnormally large values of polarization

With these classifications, the mean electric moment $\bar{\mathbf{m}}$ can generally be expressed as:

$$\bar{\mathbf{m}} = \left[\alpha_0 + \frac{\mu^2}{3KT}\right] \vec{\mathbf{F}} \quad (2.35)$$

Where α_0 represents the polarizability due to distortion, and $\frac{\mu^2}{3KT}$ represents the polarizability due to the orientation of dipoles in the field, and it is added to the induced moment. Thus, the total polarizability is:

$$\alpha = \left[\alpha_0 + \frac{\mu^2}{3KT}\right] \quad (2.36)$$

A more general expression than Eq. (2.34) is obtained by replacing α_0 with the value indicated by Eq. (2.36) in Eq. (2.34), resulting in:

$$\frac{(\varepsilon-1)M}{(\varepsilon+2)d} = \frac{4\pi}{3} N\alpha = \frac{4\pi P}{3}\left[\alpha_0 + \frac{\mu^2}{3KT}\right] \quad (2.37)$$

Debye's derivation provides a more general equation by expressing α_0 as the average of the three polarizabilities along the three axes of the molecule, which is considered as an ellipsoid of polarization.

The conclusion of the Debye hypothesis is as follows [13]:

(a) For non-polar materials, the molar polarizability should remain constant, unaffected by changes in temperature and pressure. An increase in the density of such a substance will result in a corresponding increase in permittivity.

(b) For polar substances, the molar polarizability decreases with increasing temperature. This is because thermal agitation reduces dipolar polarization.

The linear dependence of polarization on the reciprocal of absolute temperature is assumed for gases where molecular freedom is present.

The application of the Debye equation to polar liquids becomes evident when polarization due to distortion is neglected. Thus, we can write:

$$\frac{(\varepsilon-1)}{(\varepsilon+2)} = \frac{4\pi N\mu^2 d}{9KTM} \tag{2.38}$$

and considering

$$\frac{4\pi N\mu^2 d}{9KM} = T_c \tag{2.39}$$

So that equation becomes,

$$\frac{(\varepsilon-1)}{(\varepsilon+2)} = \frac{T_c}{T} \tag{2.40}$$

When temperature (T) is equal or less than then permittivity (ε) becomes infinitely large and that value of should be consider as Curie temperature. Van Vleck [14] pointed out that this does not mean that the dielectric constant really must increase without limit, but rather that at temperatures below the polarization can not be treated as linearly dependent on the field strength, as assumed in the derivation of the Debye equation, since saturation effects should occur, producing electricity along ferromagnetism, i.e. a stable state of permanent electric polarization.

2.5.3 Onsager Theory of Static Permittivity

Debye's hypothesis suggests that liquids behave like ferroelectric materials when the temperature is below a critical point (Tc). However, ferroelectricity is rare and certainly not observed in water [15]. The failure of the Debye equation stems from the assumption that the third order electric field term ($\mathbf{F_3}$) is always zero, which might not be true in all cases. To calculate the local field acting on a single molecule, which depend on the polarization of the neighboring molecules, Onsager [16,17] adopted the following model.

The molecule is treated as a polarizable point dipole and a sphere about this point having radius ‘a’, of the molecular dimensions is assumed. The radius ‘a’ of this sphere is given by

$$\mathbf{a}^3 = \frac{a}{4\pi N_1} \tag{2.41}$$

That is, the sum of the volumes of spherical cavities is equal to the total volume of the material. The material outside the sphere is treated as a homogeneous medium of permittivity ε_0. The material inside the sphere is considered as made up of individual molecules. Now, the internal field in the cavity consists of two parts:

(1) The cavity field $\vec{\mathbf{G}}$, which would be produced in the empty cavity by the external field

$$\vec{\mathbf{G}} = \frac{3\varepsilon_0}{2\varepsilon_0+1} E = g\vec{\mathbf{E}} \tag{2.42}$$

Where $\frac{3\varepsilon_0}{2\varepsilon_0+1} = g$, ε_0 represent the static permittivity of the material and E is external applied field.

The external field comes from charges on the capacitor plates and nearby dielectric surfaces. The field in the empty spherical region, without polarizable molecules, is called the cavity field '$\vec{\mathbf{G}}$'.

The reaction field $\vec{\mathbf{R}}$ established in the cavity is generated by the polarization induced by dipoles surrounding it.

$$\vec{\mathbf{R}} = \left(\frac{2(\varepsilon_0-1)}{2\varepsilon_0+1}\right)\left(\frac{\mathbf{m}}{a^3}\right) = r\left(\frac{\mathbf{m}}{a^3}\right) \tag{2.43}$$

Where $\left(\frac{2(\varepsilon_0-1)}{2\varepsilon_0+1}\right) = r$ and ε_0 represent the static permittivity of the material.

The formula for the total internal field acting on a spherical polar molecule is given by:

$$\vec{\mathbf{F}} = \vec{\mathbf{G}} + \vec{\mathbf{R}} \tag{2.44}$$

$$\vec{\mathbf{F}} = \frac{3\varepsilon_0}{2\varepsilon_0+1} E + \left(\frac{2(\varepsilon_0-1)}{2\varepsilon_0+1}\right)\left(\frac{\mathbf{m}}{a^3}\right) \tag{2.45}$$

$$\vec{\mathbf{F}} = gE + r\left(\frac{\mathbf{m}}{a^3}\right) \tag{2.46}$$

From equation 2.45, it can be observed that when static permittivity of the material is 0, 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 combination of its permanent moment '$\vec{\boldsymbol{\mu}}$' and the induced moment '$\alpha\vec{\mathbf{F}}$' generated by the local field.

$$\mathbf{m} = \vec{\boldsymbol{\mu}} + \alpha\vec{\mathbf{F}} \tag{2.47}$$

$$\mathbf{m} = \vec{\boldsymbol{\mu}} + \alpha\left[gE + r\left(\frac{\mathbf{m}}{a^3}\right)\right] \tag{2.48}$$

$$\mathbf{m} = \frac{(\vec{\boldsymbol{\mu}}+\alpha gE)}{\left(1-\frac{r\alpha}{a^3}\right)} \tag{2.49}$$

The mean moment parallel to the field can be expressed as

$$\mathbf{m} = \frac{g}{\left(1-\frac{r\alpha}{a^3}\right)}\frac{\vec{\mu}^2 E}{3KT} + \frac{ag}{\left(1-\frac{r\alpha}{a^3}\right)} \tag{2.50}$$

By using this equation in $\vec{\mathbf{P}} = N_1\,\mathbf{m}$ we get

$$\frac{(\varepsilon_0-1)}{4\pi} = \left(\frac{N_1 g}{\left(1-\frac{r\alpha}{a^3}\right)}\right)\left[a + \frac{1}{\left(1-\frac{r\alpha}{a^3}\right)}\frac{\vec{\mu}^2}{3KT}\right] \tag{2.51}$$

Onsager defined the polarizability 'α' in terms of the refractive index as follows:

$$\alpha = \frac{n^2-1}{n^2+2}a^3 \tag{2.52}$$

By substituting for α, a^3, g, and r in the above equation, we obtain

$$\frac{(\varepsilon_0-n^2)(2\varepsilon_0+n^2)}{\varepsilon_0(n^2+2)^2} = \frac{4\pi N_1\vec{\mu}^2}{9KT} \tag{2.53}$$

Onsager's mathematical statement for static permittivity suggests that as the estimation of ε_0 increases, the Lorentz field '$\vec{\mathbf{F}}$' grows unbounded. However, in the Onsager cavity field, it tends toward a limit of $\frac{3E}{2}$, whereas the response field tends toward a limit of $\left(\frac{n^2+2}{3}\right)$. Consequently, the Onsager equation does not predict the occurrence of ferroelectricity.

Debye's and Onsager's theories are semi-statistical in nature. Debye relies on statistical arguments, while Onsager's approach involves macroscopic reasoning to derive expressions for the local field. In contrast, Kirkwood and later Frohlich developed a more thorough and rigorous statistical method to calculate static permittivity.

2.5.4 Kirkwood Theory of Static Permittivity

Kirkwood [18] presents an example where a material with N dipoles of moment μ is confined in a spherical volume V and exposed to a uniform external field. With this assumption, a comparison for non-polarizable dipoles is given by

$$\frac{(\varepsilon_0-n)(\varepsilon_0+2)}{3\varepsilon_0}\frac{m}{d} = 4\pi N\frac{g\mu^2}{3KT} \tag{2.54}$$

Where 'g' represents a correlation parameter that quantifies the degree of local ordering present in the material. The estimation of g is one, if average moment of the finite spherical region around one atom, which is held settled, is equivalent to the moment of fixed molecule.

When neighboring atoms' dipoles align parallel to the fixed atom's dipole, 'g' is greater than one. Conversely, when neighboring molecules' dipoles orient anti-parallel to the fixed molecule's dipole, 'g' is less than one. Kirkwood introduces distortion polarization by assigning a polarizability, α, to each dipole. Kirkwood has generalized the Onsager's

hypothesis by eliminating the approximation of uniform local dielectric constant identical with macroscopic dielectric constant of the medium.

$$\frac{(\varepsilon_0-n)(\varepsilon_0+2)}{3\varepsilon_0}\frac{m}{d} = 4\pi N\left[\alpha + \frac{g\mu^2}{3KT}\right] \quad (2.55)$$

2.5.5 Frohlich's Theory of Static Permittivity

Frohlich [19] considered a spherical region of macroscopic dimensions within an infinite specimen, which is treated as a continuous medium. He calculated the static permittivity using statistical methods. According to Frohlich, the equation for non-polarizable dipoles is...

$$\frac{(\varepsilon_0-n)(\varepsilon_0+2)}{3\varepsilon_0}\frac{m}{d} = 4\pi N\left[\frac{m\vec{m}}{3KT}\right] \quad (2.56)$$

This equation reveals that if we identify 'm' as 'μ' and '$\vec{m}$' as 'gμ', it becomes identical to Kirkwood's equation 2.55. Frohlich takes the distortion polarization into account by imagining non polarizable dipole units to be embedded in polarizable continuum of permittivity n^2.

Therefore, Frohlich's equation is...

$$\frac{(\varepsilon_0-n^2)(2\varepsilon_0+n^2)}{\varepsilon_0(n^2+2)^2}\frac{m}{d} = 4\pi N\frac{g\mu^2}{9KT} \quad (2.57)$$

Except for interaction of correlation parameters, the equation is identical with Onsager's equation 2.53.

2.6 Theories of Dynamic Permittivity:

An alternating electric field of an appropriate frequency induces dielectric dispersion. The trademark orientational movements of the dipoles bring about a frequency variation of the dielectric constant, and the presence of 'dielectric losses' more than a broad band of frequencies. At the point when the bearing of the field is changing sufficiently quick, the sub-atomic strengths obstructing the dipole orientation dominate and the dipole gets to be not able to take after the progressions at these frequencies and the orientation of permanent dipoles no more add to the dielectric constant. In addition, in a certain frequency band a phase lag between the field and dipole orientation creates and vitality is drawn from the electrical source by the material and is dissipated as heat. This phenomenon is depicted by a complex representation of the dielectric constant.

$$\varepsilon^*(f) = \varepsilon'(f) - j\varepsilon''(f) \quad (2.58)$$

The real part of permittivity $\varepsilon'(f)$ signifies the dielectric constant, while the imaginary part of permittivity, $\varepsilon''(f)$ represents the dielectric loss.

At the point when a dielectric is set in static electric field, all the three segments of aggregate polarization are in phase with the applied field. However, as the frequency increases, the bulky nature of dipoles prevents them from staying in phase with the applied electric field. This leads to an associated loss, hence the dielectric constant is treated as a complex quantity (ε″). When the external field is switched on or off, the rate of change of polarization is given by

Case-1: When the field is switched on, the rate of change of polarization is given by

$$\vec{\mathbf{P}} = \overrightarrow{\mathbf{P_1}} + \overrightarrow{\mathbf{P_2}} \tag{2.59}$$

Where $\vec{\mathbf{P}}$ represents the total polarization, $\overrightarrow{\mathbf{P_1}}$ signifies the distortion polarization (aligned with the applied field), and $\overrightarrow{\mathbf{P_2}}$ indicates the dipolar polarization (the out-of-phase component).

$$\frac{d\overrightarrow{\mathbf{P_2}}}{dt} \alpha (\vec{\mathbf{P}} - \overrightarrow{\mathbf{P_1}}) \tag{2.60}$$

$$\frac{\mathrm{d}|(\vec{\mathbf{P}}-\overrightarrow{\mathbf{P_1}}-\overrightarrow{\mathbf{P_2}})|}{|(\vec{\mathbf{P}}-\overrightarrow{\mathbf{P_1}}-\overrightarrow{\mathbf{P_2}})|} = -\frac{\mathrm{dt}}{\tau} \tag{2.61}$$

In the provided equation, τ represents the macroscopic relaxation time necessary for the polarization to decrease to a value equal to 1/e (approximately 37%) of its initial value when the external field is switched off. Solving this equation with the boundary condition that at t=0, $\overrightarrow{\mathbf{P_2}}$= 0, we obtain

$$\overrightarrow{\mathbf{P_2}} = (\vec{\mathbf{P}} - \overrightarrow{\mathbf{P_1}})(1 - \mathrm{e}^{\frac{\mathrm{t}}{\tau}}) \tag{2.62}$$

This solution can be represented graphically as depicted in Figure 2.9.

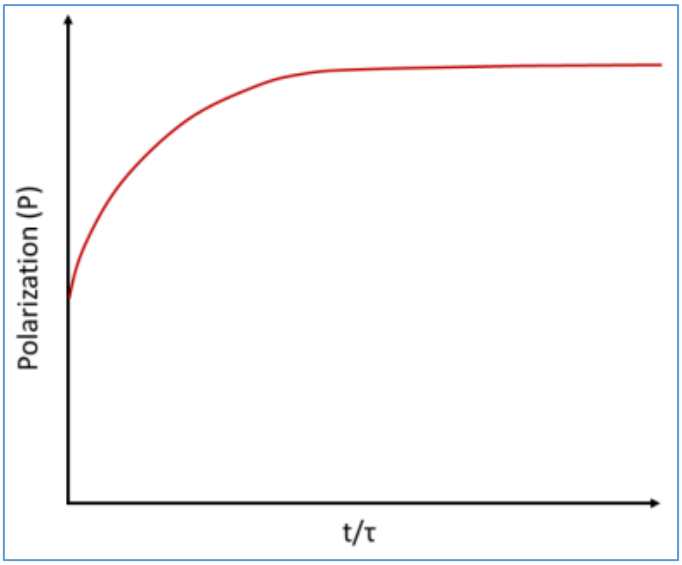

Fig. 2.9 Growth of polarization with respect to $\frac{t}{\tau}$.

Case -2: When the field is switched off.

$$\frac{d\overrightarrow{P_2}}{dt} = -\frac{(\vec{P}-\overrightarrow{P_1}-\overrightarrow{P_2})}{\tau} \quad (2.63)$$

when t = 0, $\overrightarrow{P_2} = (\vec{P} - \overrightarrow{P_1})$ from which we obtain

$$\overrightarrow{P_2} = (\vec{P} - \overrightarrow{P_1})(1 - e^{-\frac{t}{\tau}}) \quad (2.64)$$

which can be represented graphically as depicted in Figure 2.10.

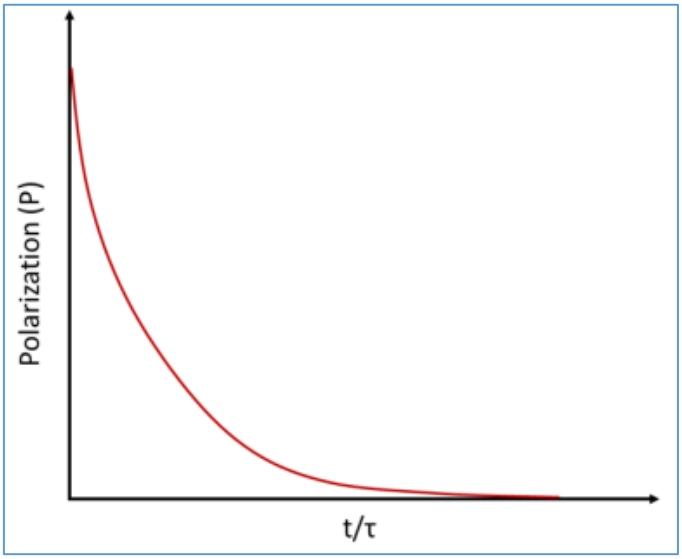

Fig. 2.10 Decay of polarization with respect to $\frac{t}{\tau}$.

At low frequency region $4\pi\vec{P} = \varepsilon(\varepsilon_0 - 1)E$ (2.65)

As $\omega \rightarrow 0$, Since above Eq. (2.59) written as $\vec{P} = \overrightarrow{P_1} + \overrightarrow{P_2}$

The contribution due to both exists only at very low frequencies but at high frequencies,

$$4\pi\overrightarrow{P_1} = (\varepsilon_0 - 1)E \quad (2.66)$$

As $\omega \rightarrow \infty$ and $\varepsilon_\infty = n_2$, Because at high frequency $\overrightarrow{P_2} = 0$

From the rate Equation (2.63)

$$\frac{d\overrightarrow{P_2}}{dt} = -\frac{(\vec{P}-\overrightarrow{P_1}-\overrightarrow{P_2})}{\tau}$$

$$\frac{d\overrightarrow{P_2}}{dt} = \frac{\varepsilon}{4\tau}(\varepsilon_0 - n^2)E_0 e^{j\omega t} - \frac{\overrightarrow{P_2}}{t}m \quad (2.67)$$

In steady state the solution to above equation is given by,

$$\overrightarrow{P_2} = \frac{\varepsilon(\varepsilon_0 - n^2)}{4\pi(1+j\omega\tau)} E \quad (2.68)$$

$$\overrightarrow{P_1} + \overrightarrow{P_2} = \vec{P}' - j\vec{P}'' \quad (2.69)$$

$$\frac{d\overrightarrow{P_2}}{dt} = \frac{\varepsilon}{4\tau}(\varepsilon_0 - n^2)E + \frac{\varepsilon(\varepsilon_0 - n^2)}{4\pi(1+j\omega\tau)} E \quad (2.70)$$

As $\varepsilon^*(f) = \varepsilon'(f) - j\varepsilon''(f)$

$$1 + \frac{4\pi}{\varepsilon E}\vec{P}' - j\vec{P}'' = n^2 + \frac{(\varepsilon_0 - n^2)}{(1+j\omega\tau)} \quad (2.71)$$

ε'(f) and ε"(f) are given by

$$\boldsymbol{\varepsilon'(f)} = n^2 + \frac{(\varepsilon_0 - n^2)}{1+\omega^2\tau^2} \tag{2.72}$$

$$\boldsymbol{\varepsilon''(f)} = \frac{(\varepsilon_0 - n^2)}{1+\omega^2\tau^2} \tag{2.73}$$

$$\boldsymbol{\tan\delta} = \left[\frac{\frac{(\varepsilon_0 - n^2)}{1+\omega^2\tau^2}}{n^2+\frac{(\varepsilon_0 - n^2)}{1+\omega^2\tau^2}}\right] = \frac{\varepsilon''}{\varepsilon'} \tag{2.74}$$

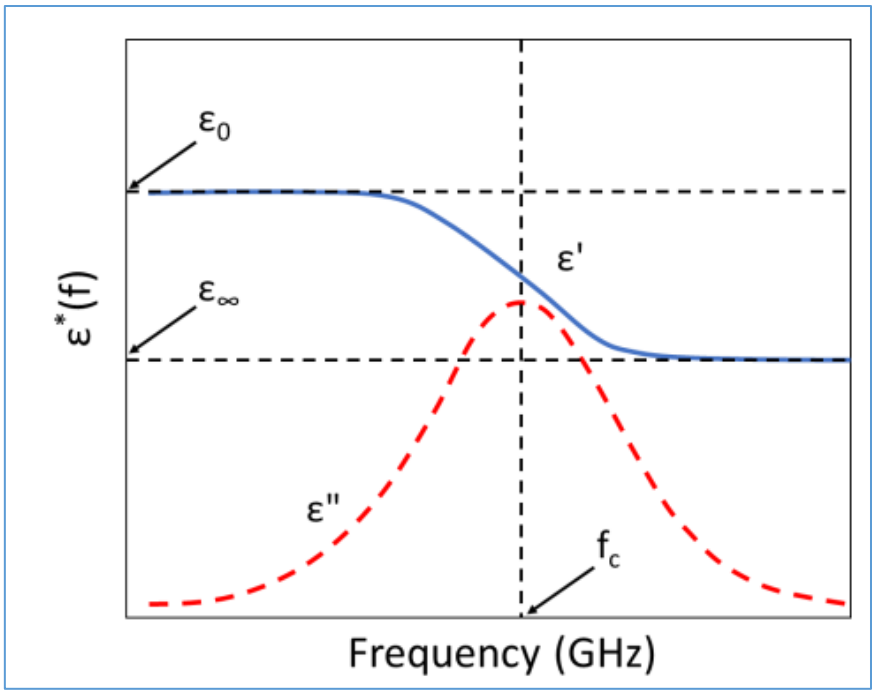

Fig. 2.11 Variation of ε'(f) and ε"(f) with frequency.

The dielectric constant is strictly not a constant but varies with many physical parameters of which frequency and temperature are of prime importance. The variation of ε'(f) and ε"(f) with frequency can be represented graphically as illustrated in Fig. 2.12.

2.6.1 Theory of Debye Relaxation Model

The frequency-dependent dielectric constant at any angular frequency ω is described by the Debye equation is [7,12]

$$\boldsymbol{\varepsilon^*(f)} = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1+j\omega\tau)} \tag{2.75}$$

Where ε_∞ represent the high frequency limiting dielectric constant closely related to the refractive index ($\varepsilon_\infty = n^2$) and ε_0 represent the dielectric constant, measured for static electric field. The real(ε′(f)) and imaginary parts (ε′′(f)) of the complex dielectric constant are then given by.

$$\boldsymbol{\varepsilon'(f)} = n^2 + \frac{(\varepsilon_0 - n^2)}{1+\omega^2\tau^2} \quad \text{and} \tag{2.76}$$

$$\boldsymbol{\varepsilon''(f)} = \frac{(\varepsilon_0 - n^2)}{1+\omega^2\tau^2} \tag{2.77}$$

ε' is known as dielectric constant and ε" is dielectric loss.

In the above Eq. τ is called the macroscopic relaxation time and corresponds to the time required for the polarization of the dielectric to decrease or to relax 1/e of its value after the removal of the field. This relaxation time, which decreases with temperature, is related to the physical properties of the polar molecule and their environments. It may also be seen.

$$\boldsymbol{\varepsilon''_{max}} = \frac{(\varepsilon_0 - \varepsilon_\infty)}{2} \tag{2.78}$$

When the frequency $\boldsymbol{\omega = \tau^{-1}}$

The equations for ε' and ε'' provided earlier can be rearranged and written as follows.

$$\left(\frac{(\varepsilon_0 - \varepsilon_\infty)}{2}\right)^2 = \left(\boldsymbol{\varepsilon'} \frac{(\varepsilon_0 + \varepsilon_\infty)}{2}\right)^2 + \boldsymbol{\varepsilon''^2} \tag{2.79}$$

This is the equation of a circle in ε′, ε″ with center at ($\frac{(\varepsilon_0+\varepsilon_\infty)}{2}$, 0) and radius equal to ($\frac{(\varepsilon_0-\varepsilon_\infty)}{2}$).

Dielectric measurements are depicted by plotting ε'' against ε' in an Argand diagram, where data points typically form a semi-circle positioned above the ε' axis. This graphical representation, as illustrated in Fig. 2.13, facilitates the analysis of dielectric properties and reveals the material's frequency-dependent behavior.

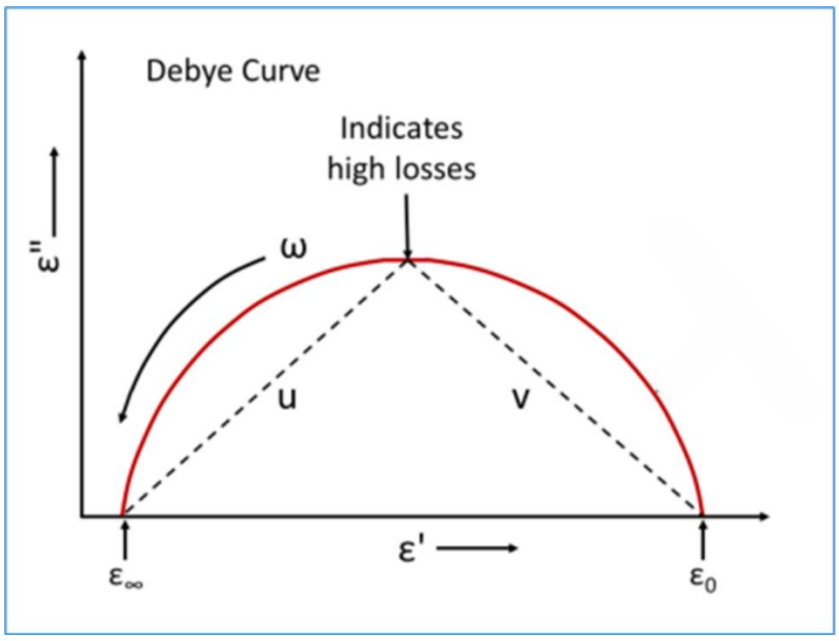

Fig. 2.12 Debye semi-circle.

2.6.2. Theory of Cole-Cole Relaxation Model

Cole and Cole [11] observed that in various materials, the locus of ε' follows an arc of a semicircle, following the empirical equation.

$$\boldsymbol{\varepsilon^*(f) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1+j\omega\tau)^\alpha}, 0 \le \alpha \le 1} \quad (2.80)$$

Where α represents a constant known as the distribution parameter, it quantifies the degree of deviation of the dispersion from the typical Debye type.

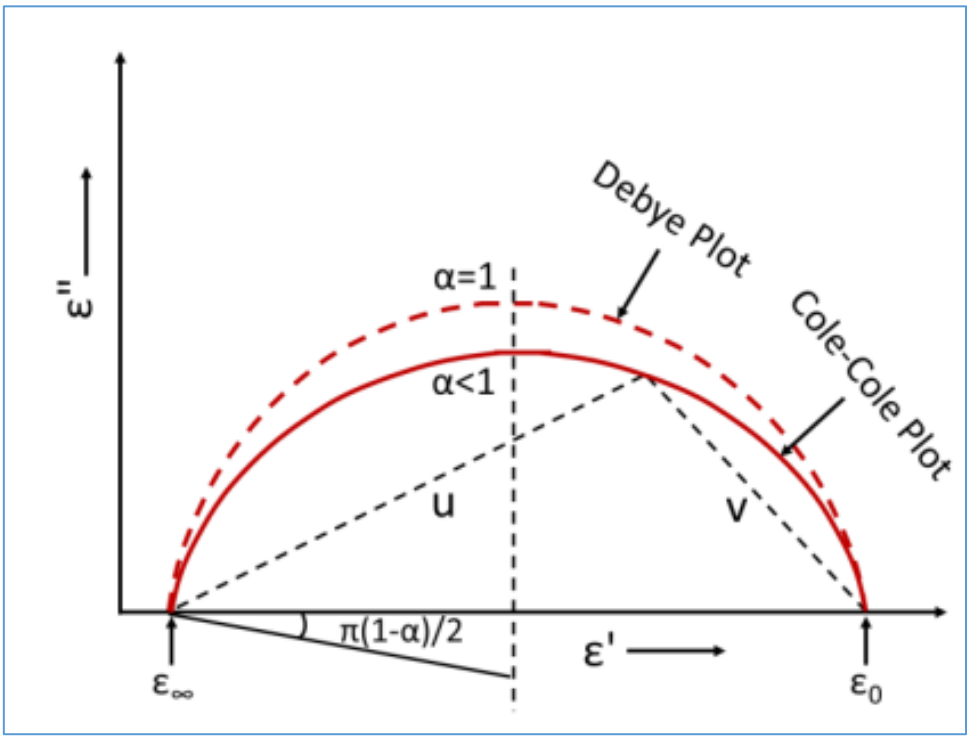

Fig. 2.13 Cole-Cole depressed arc.

The real and imaginary parts are derived by rationalizing this expression and employing appropriate mathematical methods.

$$\boldsymbol{j^\alpha} = \exp\left[\frac{j\alpha\pi}{2}\right] \quad (2.81)$$

$$\frac{(\varepsilon' - \varepsilon_\infty)}{(\varepsilon_0 - \varepsilon_\infty)} = \left[\frac{1+(\omega\tau)^\alpha \sin\left(\frac{\pi(1-\alpha)}{2}\right)}{1+(\omega\tau)^{2\alpha}+2(\omega\tau)^\alpha \sin\left(\frac{\pi(1-\alpha)}{2}\right)}\right] \quad (2.82)$$

$$\frac{\varepsilon''}{(\varepsilon_0 - \varepsilon_\infty)} = \left[\frac{(\omega\tau)^\alpha \cos\left(\frac{\pi(1-\alpha)}{2}\right)}{1+(\omega\tau)^{2\alpha}+2(\omega\tau)^\alpha \sin\left(\frac{\pi(1-\alpha)}{2}\right)}\right] \quad (2.83)$$

The locus of these parametric equations in the complex plane can be determined by

$$\left[\frac{1}{2}(\varepsilon_0 + \varepsilon_\infty) - \varepsilon'\right]^2 + \left[\varepsilon''^2 + \frac{1}{2}(\varepsilon_0 - \varepsilon_\infty) - \tan\left(\frac{\pi(1-\alpha)}{2}\right)\right]^2 = \frac{1}{4}\left[(\varepsilon_0 - \varepsilon_\infty)^2 sec^2\left(\frac{\pi(1-\alpha)}{2}\right)\right]$$

This is the equation of a circle with its center at

$$\left\{\frac{1}{2}(\varepsilon_0+\varepsilon_\infty)\right\},\left\{\frac{1}{2}(\varepsilon_0-\varepsilon_\infty)\tan\left(\frac{\pi(1-\alpha)}{2}\right)\right\}$$

And radius is given by.

$$\frac{1}{2}\left[(\varepsilon_0-\varepsilon_\infty)^2\sec\left(\frac{\pi(1-\alpha)}{2}\right)\right]$$

The angle θ in the Debye dispersion and Cole-Cole arc dispersion, as depicted in Fig. 2.14, can be determined using the following relation [20].

$$\boldsymbol{\theta}=\left(\frac{\pi(1-\alpha)}{2}\right)$$

$$\boldsymbol{\tan\theta}=\frac{\sin h(\alpha Y)}{\cos\left(\frac{\pi(1-\alpha)}{2}\right)} \qquad (2.84)$$

$$Y=\log\frac{\lambda}{\lambda_c}$$

The relaxation time τ can be determined from the arc plot by utilizing [11,16,17].

$$(\omega\tau)=(v(u^{-1}))^{\alpha} \qquad (2.85)$$

(Where u and v are depicted in Fig. 2.12 and 2.13, respectively)

As the temperature decreases, the value of α generally increases. When α equals 1, the Cole-Cole arc transforms into the Debye semicircle. Subsequently, Kastha [21] attempted to offer a physical rationale for the adoption of the Cole-Cole relation.

2.6.3 Theory of Davidson-Cole Relaxation Model

The Cole-Cole arc is symmetrical about a line passing through the center parallel to the Y-axis, Cole and Davidson discovered [11,22] that the experimental findings for some materials do not have this symmetry in plots of ε " vs. ε ', but they follow a skewed arc. Davidson and Cole [11,22], introduced a model that represents the equation for complex permittivity as follows.

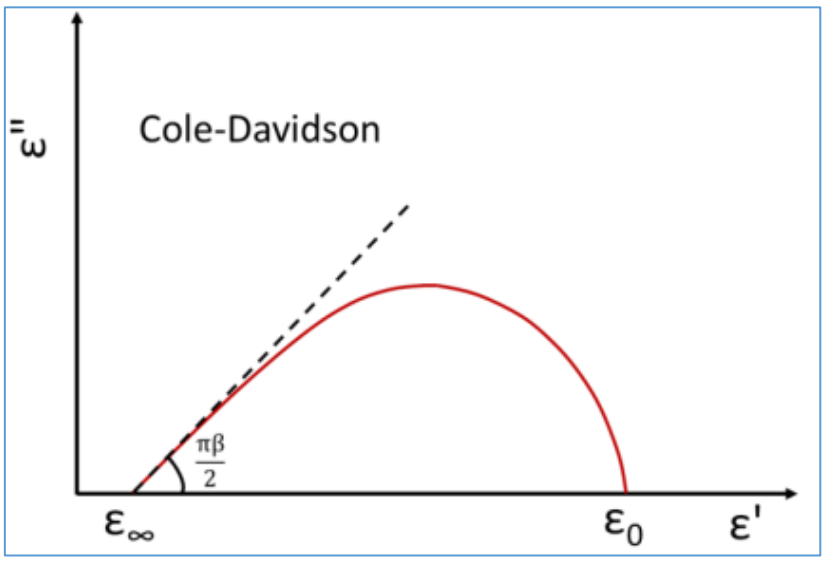

Fig. 2.14 Cole-Davidson arc.

$$\boldsymbol{\varepsilon^*(f) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1+j\omega\tau)^\beta}, 0 < \beta \leq 1} \quad (2.86)$$

Rearranging the above Eq. (2.86)

$$\frac{(\varepsilon^* - \varepsilon_\infty)}{(\varepsilon - \varepsilon_\infty)} = \frac{1}{(1+j\omega\tau)^\beta} \quad (2.87)$$

The rationalization of the equation mentioned above leads to the derivation of dispersion and absorption equations.

The Davidson-Cole distribution parameter, denoted as β, ranges between 0 and 1, satisfying $\boldsymbol{0 < \beta \leq 1}$ .When β=1 the equation reduces to the Debye equation. As β decreases, the plot of ε" versus ε′ becomes increasingly asymmetric, as depicted in Figure 2.14.

$$\frac{(\varepsilon' - n^2)}{(\varepsilon - n^2)} = \cos^\beta\varphi\cos\beta\varphi \quad (2.88)$$

$$\frac{\varepsilon''}{(\varepsilon - n^2)} = \cos^\beta\varphi\sin\beta\varphi \quad (2.89)$$

At the high frequency end, the value of β determines the angle at which the arc intersects the axis of ε′. Differentiating the above two equations with respect to φ give

$$\frac{d\varepsilon''}{d\varepsilon'} = \frac{\left(\frac{d\varepsilon''}{d\varphi}\right)}{\left(\frac{d\varepsilon'}{d\varphi}\right)} = -\cot(\beta + 1)\varphi \quad (2.90)$$

In the high frequency limit, $\omega\tau \to \infty$, $\varphi = \tan^{-1}(\omega\tau) = \frac{\pi}{2}$,

$$\frac{d\varepsilon''}{d\varepsilon'} = \tan\left[\frac{\beta\pi}{2}\right] \quad (2.91)$$

This equation is very effective in representing the behavior of substances at low temperatures. As the temperature is increased by $\beta \to 1$, so the arc tends to be a Debye arc.

2.6.4 Theory of Havriliak-Nigami Relaxation Model

The dielectric functions discussed earlier were found inadequate in accurately representing the spectral response observed in several polar materials. There are many examples of dielectric behaviour, which cannot be described by the Cole-Cole [11] and Davidson-Cole [22] expressions, both containing only one variable parameter to describe the shape of the plot ε" against ε' . Havriliak-Negami [23] generalized the expression, which composed of a giving of the expression Cole-Cole and Davidson-Cole as illustrated below.

$$\boldsymbol{\varepsilon^*(f) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1+j\omega\tau^\alpha)^\beta}} \quad (2.92)$$

The expression incorporates the Cole-Cole model when β = 1, the Davidson-Cole model when α = 1, and both α and β equal 1, representing the Debye model.

2.7 Dielectric Parameters Related to Molecular Behavior

There are distinctive formulae with which one can associate dielectric parameters with sub-atomic activities in liquid. The relationship between dielectric parameters and sub-atomic interactions and the structural changes in mixture can be investigated to some degree by utilizing different hypotheses. In the absence of precise theories addressing these quantities, existing theories with certain assumptions can offer insights into the trends concerning interactions and structural changes.

2.7.1 Kirkwood Correlation Factor

The modified Kirkwood-Frohlich correlation factor can be employed to describe the molecular interactions between a polar solute and a non-polar solvent. The Kirkwood-Frohlich theory [24], incorporates short-range interactions by introducing the dimensionless correlation factor g. This factor provides insights into the orientation of electric dipoles within polar liquids. The Kirkwood correlation factor (g) for pure liquids is determined by the expression.[25]

$$\left(\frac{4\pi N\mu^2\rho}{9KTM}\right)\mathbf{g} = \frac{(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty+2)^2} \qquad (2.93)$$

Here, N is Avogadro's number, μ is the dipole moment of the molecules forming the liquid, ρ is density of the liquid at temperature T in the kelvin scale. M is the molecular weight, ε_∞ and ε_0 are the square of the refractive index and the complex permittivity

For a mixture of two polar liquids, say '1' and '2' the equation 2.93 could be modified [20], as under [26].

(I) Assuming g^{eff} represents the effective correlation factor for the mixture, the Kirkwood equation for the mixture can be expressed as follows:

$$\frac{4\pi N}{9KT}\left(\frac{\mu_1^2\rho_1}{M_1}X_1 + \frac{\mu_2^2\rho_2}{M_2}X_2\right)\mathbf{g^{eff}} = \frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \qquad (2.94)$$

(II) Assuming that the dipole moments of both liquids are affected by the same amount g^f, the Kirkwood equation for the mixture is modified as:

$$\frac{4\pi N}{9KT}\left(\frac{\mu_1^2\rho_1 g_1}{M_1}X_1 + \frac{\mu_2^2\rho_2 g_2}{M_2}X_2\right)\mathbf{g^F} = \frac{(\varepsilon_{0m}-\varepsilon_{\infty m})(2\varepsilon_{0m}+\varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m}+2)^2} \qquad (2.95)$$

Where X_1 and X_2 are the mole fractions of liquids 1 and 2 in the mixture, respectively, and the suffixes 1, 2, and m represent liquid 1, liquid 2, and mixture, respectively.

The Kirkwood correlation factor g serves as a measure of the molecular association of a reference molecule with its nearest neighbors. Deviations of g from unity indicate the degree of molecular association.

I. A Kirkwood correlation factor g =1 signifies an equilibrium state between the multimers or non-association among the dipoles.

II. A Kirkwood correlation factor g >1 suggests a parallel orientation among the dipoles.

III. A Kirkwood correlation factor g <1 indicates an anti-parallel orientation among the dipoles of the liquid.

In equation 2.94, the value of g^{eff} varies between g_1 and g_2 for associative and non-associative mixtures as the concentration (mole fraction) of liquid 2 increases from 0 to 100%. In equation 2.95, the value of g^f is unity for pure polar liquids and approaches unity when there is little to no interaction. The deviation of the g^f value from unity signifies the interaction between liquids 1 and 2.

2.8 Bruggeman Factor

The static permittivity of a two-component mixture must fall between the extremes represented by the static permittivity of the two individual liquids. To understand the dipole interaction in the mixture of two liquids, various mixture formulae have been proposed [26,27].

The Bruggeman factor (f_B) formula [28,29] serves as an initial indicator of molecular interaction in binary mixtures and is expressed as follows:

$$f_B = \left(\frac{\varepsilon_{0m}-\varepsilon_{02}}{\varepsilon_{01}-\varepsilon_{02}}\right)\left(\frac{\varepsilon_{01}}{\varepsilon_{0m}}\right)^{\frac{1}{3}} = (1-\Phi_2) \qquad (2.96)$$

Where Φ_2 is the volume fraction of liquid 2 in liquid 1. If interactions exist between the components, the Bruggeman Factor (f_B) varies nonlinearly with Φ_2. However, if there are no interactions between the components in the mixture, f_B should vary linearly with the volume fraction Φ_2.

To fit the experimental data equation 2.96 has been modified [24] as;

$$f_B = 1 - [a - (a-1)\Phi_2]\Phi_2 \qquad (2.97)$$

Where 'a' represents the Bruggeman parameter, providing insight into the interaction between components in the mixtures. This parameter quantifies the interaction in terms of changes in volume.

A value of a=1 indicates the absence of interaction between the components in the mixture. A value of a<1 corresponds to a reduction in the effective volume occupied by

component '1' due to the presence of component '2'. Conversely, values of a >1 correspond to an increase in the effective volume of component '1' due to the presence of component '2'.[20]

2.9 Thermodynamic Parameters

according to Eyring, the relaxation process in dielectrics can be understood as the movement of a dipole across a potential barrier that separates energy minima [29,30]. In order to determine the activation enthalpy, from the theory of rate process, Kauzamann [31] gained from the relaxation time.

$$\boldsymbol{\tau_d} = \frac{h}{KT}\exp\frac{\Delta G}{RT} = \frac{h}{KT}\exp\left(\frac{\Delta H - T\Delta S}{RT}\right) \quad (2.98)$$

In the context of the dipole reorientation process, ΔG represents the activation free energy, ΔH signifies the molar enthalpy of activation, and ΔS denotes the molar entropy of activation. These parameters characterize the energy and entropy changes associated with the activation of dipole movement. ΔH, the molar enthalpy of activation, is determined from the slope of the plot of the natural logarithm of the relaxation time (τ) against the reciprocal of temperature (1/T). This relationship allows for the estimation of the energy required for the activation of the dipole reorientation process. When ΔH and ΔS are independent of temperature, the plot of log(τ) versus 1/T will be linear. This linearity indicates that the enthalpy and entropy of activation remain constant over the temperature range being considered. The height of the potential barrier, representing ΔH, can be determined using the tangent of the slope of the plot of log(τ) versus 1/T.

$$\boldsymbol{\Delta H} = R\frac{d(\log\tau T)}{d\left[\frac{1}{T}\right]} = R\frac{d(\log\tau)}{d\left[\frac{1}{T}\right]} - RT \quad (2.99)$$

The calculated ΔS may require absolute significance, but the order of magnitude of the activation enthalpy (ΔH) provides insight into the molecular energy involved in the relaxation process. Exploring the thermodynamic parameters of polar mixtures can offer valuable insights into understanding how dipoles behave under the influence of an applied field. This investigation helps in assessing the conditions under which dipoles are affected by external fields. A subjective methodology is conceivable as several complicated functions are included in the relaxation procedure; however, the discourse has its own utility in that. It provides a superior representation of the dielectric behavior of the particle.

2.10 Modeling Electrode Polarization in Dielectric Spectroscopy

Electrode polarization is the polarization effect resulting from the movement of charge carriers under an electric field in materials with blocking electrodes.

Electrode polarization, the incident by which ions build up at electrodes under low frequency electric fields is particularly considered as a nuisance in the analysis of dielectric data [32]. Based on the work of Macdonald [33] and modifications by Coelho [34], Klein developed a method of analysis that models the frequency dependency of complex dielectric permittivity (ε*f) data to basically and precisely extract both ion mobility and mobile ion concentrations [35]. Klein model electrode polarization in the case of ionomers with anions fixed along the polymer chains and the cations as mobile counterions [35].

In the Klein model, we analyze a material sample with a thickness L and a neutral medium permittivity ε. In the neutral medium of the Klein model, negative charges are stationary or fixed in place [33,34]. Attached to the fixed negative charges in the neutral medium are mobile positive charges. The concentration of mobile positive charge carriers is denoted as p, and they possess a mobility represented by μ. Here in this, the negative charge carriers are immobile and ionic generation and recombination to have reached equilibrium, and thus the concentration of negative charges is constant in space and time [35].

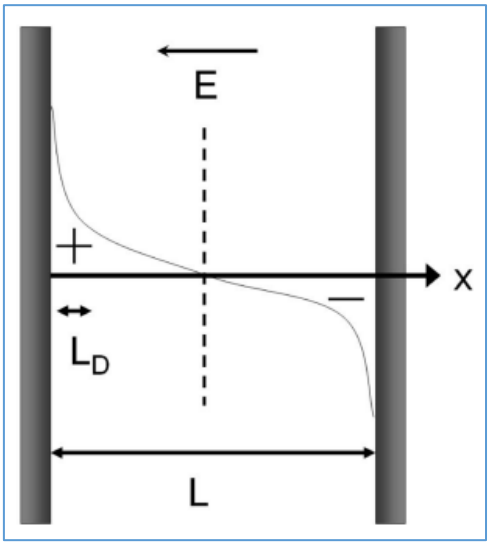

Fig. 2.15 Graphical of charge density distribution under a dc parallel plate field.

Figure 2.15 illustrates the schematic diagram of the physical situation involving two parallel plates of equal area separated by a distance L[35]. The spatial dimension of interest in this context is X, which is bounded at X=0 and X=L by blocking and non-injecting electrodes. When an electric field is applied, free cations accumulate near the negative electrodes, resulting in the creation of a positive charge near the negative electrode and an uncompensated negative charge near the negative interface. When a

stable state is achieved, the distribution of statistical space charges resembles that depicted in Figure 2.16, and the system essentially behaves as a macroscopic dipole.

The Einstein and Poisson relations are employed to derive expressions relating the diffusion relaxation time (τ) to the medium dielectric constant (ε) and the conductivity (σ_0). For comprehensive derivations and detailed explanations, Coelho [36] and Macdonald [33] provide thorough treatments of these relationships.

The dielectric constant of the medium (ε) can be expressed as the product of the low-frequency dielectric constant with no electrode polarization (ε_R) and the vacuum permittivity (ε_{vacum}). The Debye length, which represents the characteristic length scale of the electrostatic double layer in the presence of an applied electric field with angular frequency ω, is given by the following formula.

$$\mathbf{L_D} = \frac{1}{q}\left[\frac{\varepsilon_R E_{Vacuum} KT}{P_0}\right]^{\frac{1}{2}} \tag{2.100}$$

Relaxation time (τ) is defined by

$$\boldsymbol{\tau} = \frac{\varepsilon}{\sigma_0} = \left(\frac{\varepsilon_R E_{Vacuum}}{P_0 q \mu}\right) \tag{2.101}$$

Where, p_0 is equilibrium number density of free positive charge carriers, σ_0 represent DC conductivity, q is charge of cation, k indicate Boltzmann's constant T is temperature and μ is ion mobility.

Here, M is defined as the ratio of the thickness to twice of the Debye length (L_D).

$$\mathbf{M} = \frac{L}{2L_D} = \frac{qL}{2}\left[\frac{P_0}{\varepsilon_R E_{Vacuum} KT}\right]^{\frac{1}{2}} \tag{2.102}$$

In the Coelho model, electric polarization (EP) is described by simple Debye relaxation [34].

$$\boldsymbol{\varepsilon^*_{EP}} = E_R + \frac{\Delta\varepsilon_{EP}}{1+j\omega\tau_{EP}} \tag{2.103}$$

The low frequency dielectric constant in the present of EP is

$$E_{R,}EP = M\varepsilon_R \tag{2.104}$$

The relaxation time (τ) for electrode polarization is typically given by the formula:

$$\boldsymbol{\tau_{EP}} = M\tau = \frac{L}{2\mu}\left[\frac{\varepsilon_R E_{Vacuum}}{P_0 KT}\right]^{\frac{1}{2}} \tag{2.105}$$

In equation (2.103), the real and imaginary parts are typically represented as follows:

$$\boldsymbol{\varepsilon'_{EP}} = E_R + \frac{\Delta\varepsilon_{EP}}{1+\omega^2\tau^2_{EP}} \tag{2.106}$$

$$\boldsymbol{\varepsilon''_{EP}} = \frac{\Delta\varepsilon_{EP}\tau_{EP}}{1+\omega^2\tau^2_{EP}} \tag{2.107}$$

Real part and imaginary part of the complex permittivity spectra can be fitted to experimental data to give values for τ, M, and ε_R.

Ion mobility (μ) is determined by calculations outlined in equations (2.101) and (2.105).

$$\boldsymbol{\mu} = \left(\frac{qL^2}{4M\tau_{EP}KT}\right) \tag{2.108}$$

The mobile ion concentration is determined using the equation $\sigma_0 = p_0 q\mu$, where σ_0 is the DC conductivity, p_0 is the charge carrier density, q is the elementary charge, and μ is the ion mobility.

$$\boldsymbol{p_0} = \left(\frac{\sigma_0}{q\mu}\right) \tag{2.109}$$

The above equation assumes a cation transference number of unity, and it is applicable to the case where anions are relatively immobile.

The ion diffusivity (D) can be determined from the mobility (μ) using the Einstein relation.

$$\boldsymbol{D} = \left(\frac{\mu KT}{q}\right) = \frac{\mu TR}{F} \tag{2.110}$$

In the Einstein relation, the constants involved are the ideal gas constant (R) and Faraday's constant (F).

2.10.1 Electrode Polarization is Fitted within Tan δ Spectra.

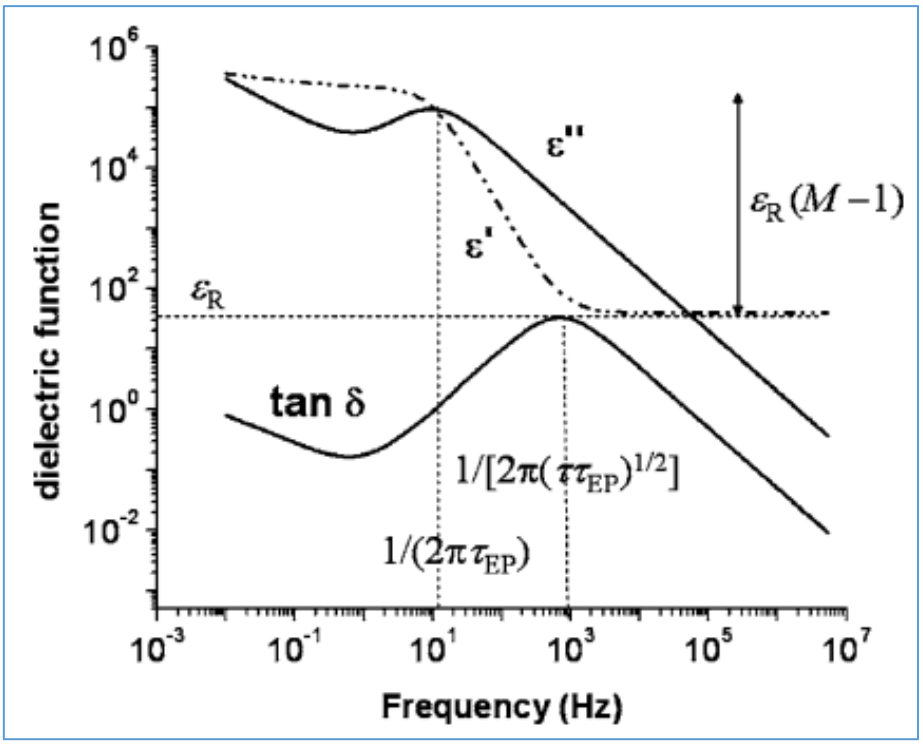

Fig. 2.16 Schematic plot of the EP relaxation in ε′, ε" and tan δ for a conductive system, with peak frequencies, dielectric relaxation strength and ε_R denoted.

Converting real (ε′) and imaginary parts (ε′′) of complex permittivity spectra into a loss tangent (tan δ) is useful because it suppresses conductivity effects, shifts the peak maximum to higher frequencies, and eliminates the dielectric constant with no relaxation process (ε_R) from the fitting procedure. Schematic plot of the electrode polarization (EP) relaxation in real (ε') , imaginary (ε") and tangent (tan δ) for a conductive system with peak frequencies is shown in Fig. 2.16.[35]. The loss tangent (tan δ) after neglecting the conductivity term and simplifying is given by the following equation:

$$\mathbf{tan\delta} = \frac{\varepsilon''}{\varepsilon'} = \frac{\omega\tau_{EP}}{1+\omega^2\frac{\tau^2_{EP}}{M}} \tag{2.111}$$

The peak in the loss tangent (tan δ) is shifted by $M^{\frac{1}{2}}$.[37]

$$\boldsymbol{\omega^{tan\delta}_{max}} = \left(\frac{M^{\frac{1}{2}}}{\tau_{EP}}\right) = \frac{1}{(\tau\tau_{EP})^{\frac{1}{2}}} \tag{2.112}$$

2.10.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) serves as a valuable analytical quality control method, offering insights into both fundamental electrochemical and electronic processes. Experimental impedance results can be correlated with a multitude of practically useful variables spanning chemical, physical, mechanical, and electrical domains. With the current availability of ever evolving automated impedance equipment covering broad frequency and potential ranges, EIS studies have become increasingly popular as more and more electrochemists, material scientists and engineers understand the theoretical basis for impedance spectroscopy and acquire skills in data analysis impedance. The impedance spectroscopy technique is extensively employed to obtain valuable information about the dielectric properties of a medium.[38] It is very important to study different relaxation processes in the liquids. The Nyquist and Bode plots are the most used impedance spectroscopy data plots. Such plots are representations of calculated data.

2.10.3 Nyquist and Bode Plots Represent Complex Impedance Data for Ideal Electrical Circuits.

Most real-life situations, systems deviate from idealized models and are better represented by circuits combining both resistive and capacitive elements. Figure 2.17 shows a typical R-C circuit featuring a parallel combination of a resistor and a capacitor. The impedance of two parallel branches is composed of a constant resistance R and $\frac{-j}{\omega C}$,

where j represents the imaginary unit and ω is the angular frequency. According to Kirchhoff's law for a parallel circuit, the potential across both circuit elements is equal, while the total current is the sum of the currents flowing through the resistor and capacitor branches.

$$\mathbf{I(t)} = V(t)\left(\frac{1}{R} - \frac{\omega C}{j}\right) = V(t)\left[\frac{1+(\omega RC)^2}{R-j\omega R^2 C}\right] \quad (2.113)$$

From the above equation (2.113), the expression for the resulting impedance is given by the following formula:

$$\mathbf{Z}^* = \frac{\mathrm{R}}{1+(\omega \mathrm{RC})^2} - \mathrm{j}\frac{\omega \mathrm{R}^2 \mathrm{C}}{1+(\omega \mathrm{RC})^2}$$

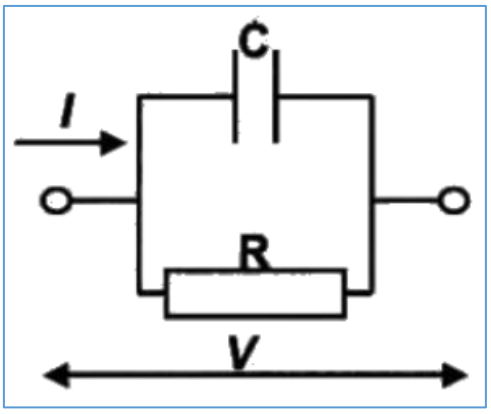

Fig. 2.17 Parallel R-C Circuit.

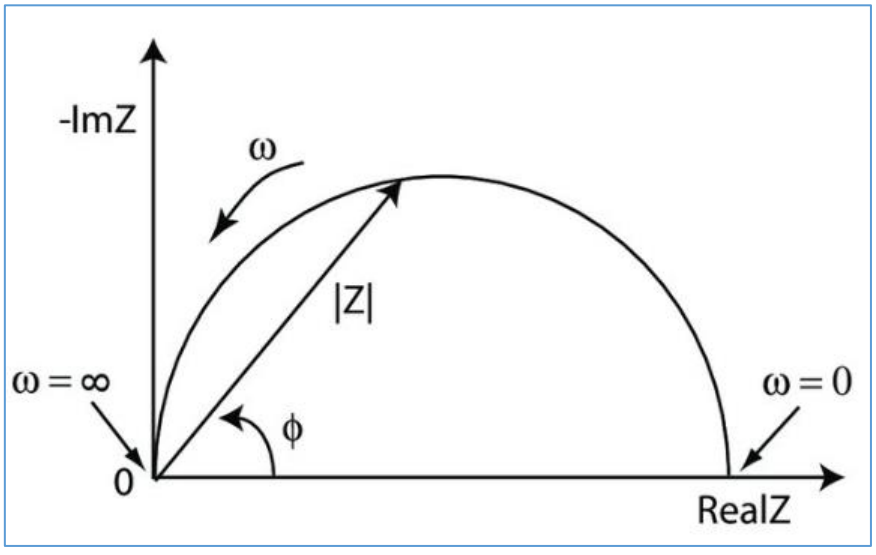

Fig. 2.18 Nyquist impedance plot.

The plot of the real part of impedance on the X-axis against the imaginary part of impedance on the Y-axis is commonly indicated to as the Nyquist plot. As depicted in Figure 2.18, the Nyquist plot often exhibits a semi-circular shape. Now Y-axis is select

as negative notation and that both point on the Nyquist plot is the impedance at single frequency [39]. From the graphical representation, it's apparent that lower frequency data points are located to the right side of the plot, while higher frequency data points are positioned towards the left. In the Nyquist plot, the impedance can be visualized as a vector with a length represented by |Z|. The angle between this vector and the X-axis is ϕ, or phase angle which also has a negative notation [40].

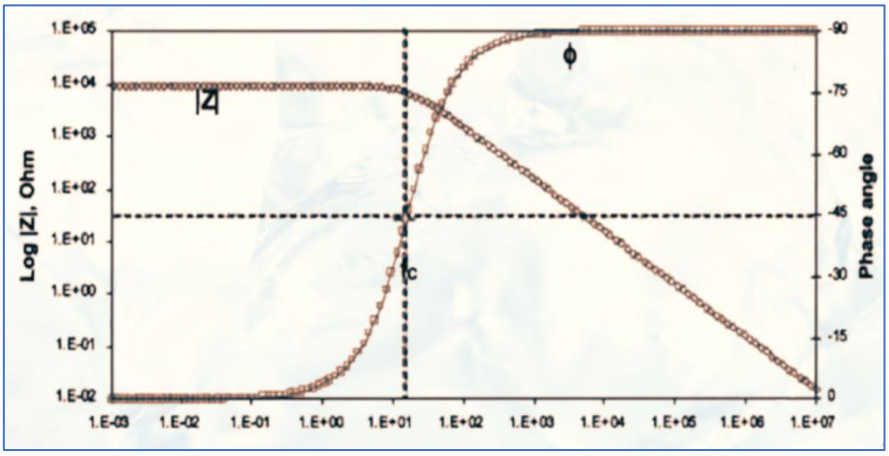

Fig. 2.19 Bode Plot with Impedance Vector.

The "Bode plot" provides an alternative representation of the data, depicting the phase angle and the logarithm of impedance magnitude as functions of the logarithm of frequency. The Bode plot is illustrated in Figure 2.19. Unlike the Nyquist plot, the Bode plot clearly exhibits frequency information and reveals an important low impedance behaviour seen at high frequencies.[38]

2.10.4 Different Circuit Models & Elements

Impedance analysis seeks to elucidate complex phenomena by interpreting the intricate interplay of chemical, physical, electrical, and mechanical components in terms of electrical properties. Impedance data are commonly fitted using an equivalent circuit composed of circuit elements that correspond to the physical processes within the system under investigation.[38] Various circuits comprising two, three, four, or more elements are used in impedance analysis to model and understand the complex behavior of systems. In several cases, ideal circuit elements such as resistors can be applied for the analysis purpose. In addition to this some types of inductors are also applied. Particularly, in addition to the ideal circuit elements, distributed circuit elements are required to sufficiently describe the impedance response of real systems. Indeed, elements such as the constant phase element (CPE) and Warburg diffusion impedance are frequently utilized to model and analyze the impedance response of real

systems[41]. Various circuit models showing elements used in circuits are depicted in Figure 2.20, with corresponding details provided in Table 2.2.

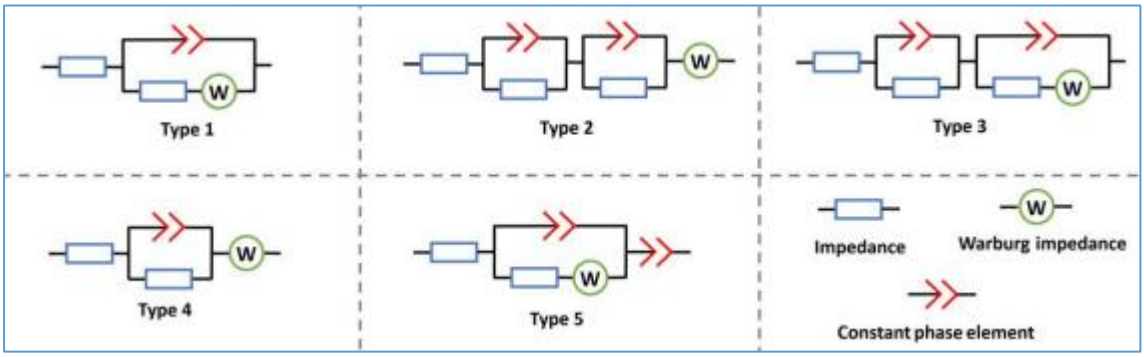

Fig. 2.20 Different equivalent circuit models.

Table 2.2 Ideal circuit elements used in different models.

Components	Current vs. Voltage	Impedance
Resistor (R) (Ω)	$V = IR$	R
Capacitor (C) (F)	$I = C\left(\frac{dV}{dt}\right)$	$\frac{1}{j\omega C}$
Inductor (L) (H)	$V = L\left(\frac{dI}{dt}\right)$	$j\omega L$
Constant phase element (CPE) Q (Ω^{-1} s^{α})	----	$\frac{1}{Q(j\omega)^{\alpha}}$

Indeed, elements like the constant phase element (CPE) and Warburg diffusion impedance are commonly employed in circuit models to accurately represent and analyze the impedance behavior of real systems. In EIS experiments, many capacitors, especially the double-layer capacitor (CDL), often deviate from ideal behavior due to current distribution and the presence of electro active species. These capacitors frequently demonstrate behavior resembling that of a constant phase element (CPE) rather than ideal capacitors. As a result, CPEs have become a common choice for modeling impedance data in various applications [42]. The term "constant phase element" originates from the fact that the phase angle of the circuit portion represented by this element remains independent of the AC frequency [43]. The Warburg diffusion element (ZW) behaves as a constant phase element (CPE) with a fixed phase angle of

45°, which remains independent of frequency. Its magnitude is inversely proportional to the square root of the frequency [43].

2.11 Physico-Chemical Properties

The physico-chemical properties of liquid mixtures reflect the intermolecular forces and microscopic structure inherent within the liquids. Understanding physico-chemical properties such as density, viscosity, and ultrasonic velocity, FTIR is crucial for comprehending the interactions between different molecules within liquid solutions.

2.11.1 Density

Density, also referred to as specific gravity, is an intensive property of matter, defined as the mass of a substance per unit volume. The relative density is determined by multiplying the density of water by the ratio of the weight of a given volume of the substance to the weight of an equal volume of water at the same temperature. Density quantifies the compactness of a substance, indicating the extent to which its atoms or molecules are closely packed together. A comprehensive investigation of density provides valuable insights into microscopic interactions and the inherent strength of materials. It provides an experimental background to develop, test and then modify theories for liquid mixtures and their transport properties [44].

2.11.2 Ultrasonic velocity

The ultrasonic velocity method has been widely used to study the physico– chemical manners and molecular interactions in liquid mixtures in the last two–three decades [45]. The mechanical longitudinal waves generated by the crystal propagate through various mediums such as solids, liquids, or gases. These waves can be categorized into different classes based on their frequency:

- Infrasonic waves, which have frequencies below 20 Hz.
- Audible waves, which fall within the frequency range of 20 Hz to 20 kHz.
- Ultrasonic waves, which have frequencies higher than 20 kHz.

The term ‘Ultrasonic’ defines as vibrating waves with frequencies higher than what humans can hear, typically above 20 kHz. It covers all frequencies above this range [46]. Ultrasonic waves can be produced using various methods, which largely depend on the desired frequency range and power output. The simplest and most popular method for generating high-frequency ultrasonic waves is through piezoelectric crystal transducers. The piezoelectric method arises from the coupling between the mechanical and electrical properties of a material. It is a phenomenon exhibited by certain crystals that deform in shape when subjected to electric stresses in specific directions.

Commonly used crystals for generating ultrasonic waves include Rochelle salt, quartz, potassium dihydrogen phosphate, lithium sulfate, dipotassium tartrate, and ammonium dihydrogen phosphate. Indeed, Magnetostrictive transducers can also be utilized for generating ultrasonic waves. When an alternating magnetic field is applied parallel to a ferromagnetic rod such as iron or nickel, the rod experiences contraction and expansion at the same frequency as the applied magnetic field. This phenomenon generates ultrasonic waves.

The application of ultrasonics has not only simplified the evaluation of physicochemical properties of mixtures and solutions but has also enhanced the reliability of interpreting molecular interactions. Due to low cost, easy operational procedure and spontaneous results, the molecular interaction studies through ultrasonic have gained importance all over the world.

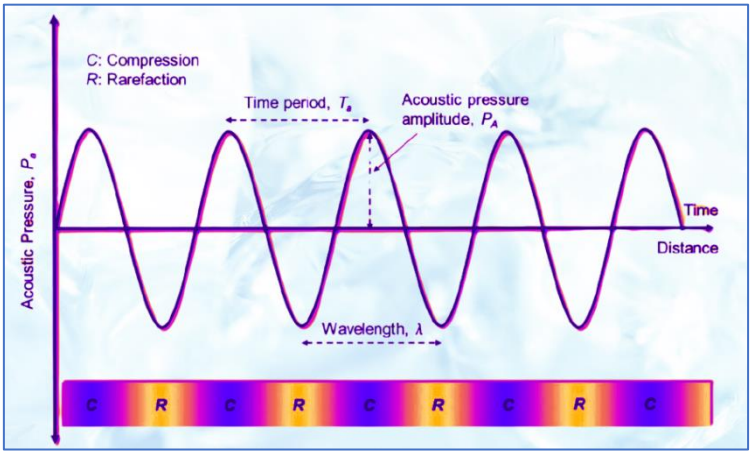

Fig. 2.21 Schematic of ultrasonic waves and properties.

The schematic of ultrasonic waves is depicted in Figure 2.21. When an ultrasonic wave propagates through a medium, the molecules in that medium vibrate over very short distances in a direction parallel to the longitudinal wave. During this vibration, momentum is transferred among molecules, allowing the wave to propagate through the medium.

2.11.3 Viscosity

Viscosity is a transport property typically defined as the resistance to flow under applied shear stress. Fluids are classified into two categories: Newtonian and non-Newtonian fluids. Newtonian fluids adhere to Newton's law of viscosity. In Newtonian fluids, viscosity remains constant regardless of the shear rate. Non-Newtonian fluids do not conform to Newton's law, meaning their viscosity (the ratio of shear stress to shear rate)

is not constant and varies depending on the shear rate [47]. Viscosity is expressed in two distinct forms: (I) dynamic viscosity and (II) kinematic viscosity [48].

The absolute viscosity is the proportionality constant in an equation provided by Newton's law of viscosity, which relates shear stress to shear rate or velocity gradient [48].

$$\boldsymbol{\sigma_S} = \eta\left(\frac{dv}{dx}\right) \tag{2.115}$$

In this equation, σ_s represents shear stress, which is the force applied to the fluid per unit area, and dv/dx represents the velocity gradient, which measures the shearing experienced by the liquid, known as shear strain (γ). η is a constant for a given material and is known as viscosity. Therefore, dynamic viscosity can be defined mathematically as

$$\boldsymbol{\eta} = \frac{\sigma_S}{\gamma} = \frac{\text{Shear Stress}}{\text{Shear Strain}} \tag{2.116}$$

Kinematic viscosity (υ) requires knowledge of the density of the liquid (ρ) at a specific temperature and pressure. It is the measure of the resistive flow of a fluid under the weight of gravity, and it is defined as: [47,48]

$$\boldsymbol{v} = \frac{\eta}{\rho} \tag{2.117}$$

The viscosity of pure compounds and liquid mixtures has garnered significant attention from researchers in recent years. More accurate and precise viscosity data, particularly for liquid mixtures, are essential for understanding the structure of liquids and liquid mixtures. Accurate viscosity data is also crucial for designing most fluid flow equipment. The pharmaceutical industry relies on viscosity measurements to assess the flow behavior of materials for various applications.

2.12 FTIR

The Fourier Transform Infrared Spectrometer (FTIR) is an analytical technique used to identify the functional groups present in both inorganic and organic compounds. A standard FTIR spectrometer includes components such as a source, interferometer, sample compartment, detector, amplifier, A/D converter, and a computer for data analysis[49]. A spectrophotometer is a device that analyzes and shows the absorption spectrum of a compound. The specific absorption bands identified by a spectrophotometer aid in confirming the specifications of a compound and detecting the presence of impurities. Molecules contain definite frequencies of internal vibrations. When a material is subjected to a beam of infrared (IR) radiation, it absorbs

radiation at frequencies that match its molecular vibration frequencies, while allowing the transmission of other frequencies. The IR spectrometer identifies the frequencies of radiation absorbed, and the resulting plot of absorbed energy versus frequency is referred to as the IR spectrum of the material. Specific materials possess specific vibrations that results into distinct IR spectra and it makes identification of a substance possible. The frequencies of absorption aid in detecting the presence or absence of various chemical groups within a chemical structure. The interferometer produces a specialized signal for rapid signal detection, usually completing within a few seconds.

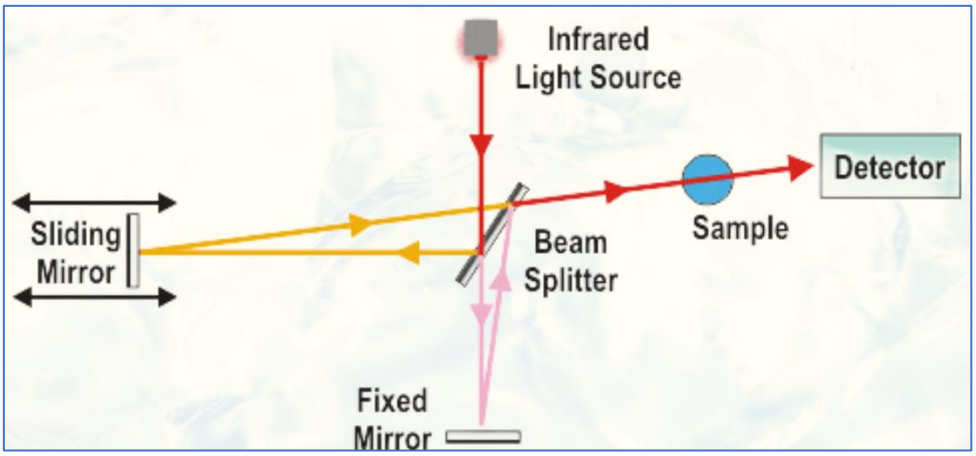

Fig.2.22 Schematic diagram of an FTIR spectrometer

The Michelson interferometer, central to FTIR spectrometers, divides a single beam of light into two, creating beams with different paths. Infrared radiation emitted by a broad-band source is then split into two beams of equal intensity. These beams, one of which may pass through a sample, are then recombined. Depending on the relative displacement of a movable mirror, the beams are recombined either constructively or destructively, producing an interference pattern. This pattern, known as the interferogram, varies with the optical path difference. The interferogram is converted into a plot of absorption versus wave number through Fourier transformation, utilizing a computer integrated into the instrument (Fig.2.22). [50,51]

The FTIR technique is used to analyze gas, liquid, and solid samples across different frequency ranges: near-IR (14000-4000 cm^{-1}), mid-IR (4000-400 cm^{-1}), and far-IR (400-10 cm^{-1}). Most inorganic and organic materials exhibit absorption in the mid-infrared region.

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