

## INTRODUCTION

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### 1.1 Dielectric materials and their technological importance *in* modern industry

Electrical insulator materials which will prevent the flow of current in an electrical circuit are being used since from the beginning of the science and technology of electrical phenomena. Dielectrics are insulating materials that exhibit the property of electrical polarization, thereby they modify the dielectric function of the vacuum.

The first capacitor was constructed by Cunaeus and Mussachenbroek in 1745 which was known as Leyden jar [1]. But there were no studies about the properties of insulating materials until 1837. Faraday published the first numerical measurements on these materials, which he called dielectrics [2]. *He* has found that the capacity of a condenser was dependent on the nature of the material separating the conducting surface. This discovery encouraged further empirical studies of insulating materials aiming at maximizing the amount of charge that can be stored by a capacitor. Throughout most of the 19<sup>th</sup> century, scientists searching for insulating materials for specific applications have become increasingly concerned with the detailed physical mechanism governing the behavior of these materials. In contrast *to* the insulation aspect, the dielectric phenomena have become more general and fundamental, as it has the origin with the dielectric polarization.

Mossotti [3, 4] and Clausius [5] have done a systematic investigation about the dielectric properties of materials. They attempted to correlate the specific inductive capacity, a macroscopic characteristic of the insulator introduced by Faraday [2] which is now popularly termed as dielectric constant with the microscopic structure of the material. Following Faraday in considering the dielectrics to be composed of conducting spheres in a non-conducting medium, Clausius and Mossotti succeeded in deriving a relation between the real part of the dielectric constant  $\epsilon_r$  and the volume fraction occupied by the conducting particles in the dielectric.

In the begning of 20<sup>th</sup> century, Debye [6] realized that some molecules had permanent electric dipole moments associated with them, and this molecular dipole moment is responsible for the macroscopic dielectric properties of such materials. Debye succeeded in extending the Clausius -Mossotti theory to take into account the permanent

moments of the molecules, which allowed him and others to calculate the molecular dipole moment from the measurement of dielectric constant. His theory was later extended by Onsager [7] and Kirkwood [8, 9] and is in excellent agreement with experimental results for most of the polar liquids. Debye's other major contribution to the theory of dielectrics is his application of the concept of molecular permanent dipole moment to explain the anomalous dispersion of the dielectric constant observed by Drude [10]. For an alternating field, Debye deduced that the time lag between the average orientation of moments and the field becomes noticeable when the frequency of the field is within the same order of magnitude as the reciprocal relaxation time. This way the molecular relaxation process leads to the macroscopic phenomena of dielectric relaxation, i.e., the anomalous dispersion of the dielectric constant and the accompanying absorption of electromagnetic energy over certain range of frequencies.

Debye's theory shows excellent agreement with the experiments for the polar liquids while the dielectric behaviour for solids was found to be deviating considerably. Several modifications and extensions of Debye's theory have been proposed to correct this. There are two major approaches in the extension of Debye's theory. The first approach, pioneered by Cole [11], Davidson [12] and Williams [13], interprets the non-Debye relaxation behavior of the material in terms of the superposition of an exponentially relaxing process, which then leads to a distribution of relaxation times. The second approach by Joncher [14] proposes that the relaxation behaviour at the molecular level is intrinsically non-Debye-like due to the cooperative molecular motions.

After more than eighty years of development, the theory of dielectrics is still a active area for research. Understanding the behaviour of dielectric materials with the variations of field, temperature and frequency is of particular importance for present day electronics. Modern day electronics demand dielectric materials with narrowly defined properties tailored for particular applications. The scaling of metal-oxide-semiconductor (MOS) devices for ultra large-scale integration (ULSI) applications has been placing an ever-increasing burden upon the performance of gate dielectrics [15]. Durability has become an issue as the dielectric thickness is decreased leading to a search for dielectrics with better properties than the conventional  $\text{SiO}_2$  dielectric. The gallium arsenide (GaAs) based metal - insulator- semiconductor field effect transistor (MISFET) is still largely unavailable due to the lack of a suitable dielectric material for the insulation layer [16]. Recent advances in wireless communication technologies have elevated the interest in materials with the unusual combination of properties like high dielectric constant, low

dielectric loss and low values of temperature dependence of dielectric constant [17]. The constant need for miniaturization provides a continuing driving force for the discovery and the development of increasingly sophisticated materials to perform the same or improved function with decreased size and weight. The dielectric materials mentioned above are used as the basis for resonators and filterers for the microwaves carrying the desired information [18]. These materials are presently employed as bulk ceramics in microwave communication devices. They are not integrated into the microelectronics but are being used as discrete components. The need for better dielectrics with improved properties suitable for modern integrated manufacturing needs is the motivation behind the present study.

## 1.2 Theory of dielectrics

This section presents a brief description of the atomic interpretation of the dielectric and optical properties of insulator materials on the basis of classical theory. This section is essentially concerned with the static dielectric constant, the frequency dependence of dielectric constant and dielectric losses.

### 1.2.1 Electric susceptibility and permittivity

It was Michael Faraday who first noticed that when a capacitor of value  $C_0$  under vacuum is filled with a dielectric material, its charge storage capacity (capacitance) increases to a value of  $C$ . The ratio  $\chi'$  of the increase of capacitance  $\Delta C = C - C_0$  to its initial capacitance-  $C_0$ ,

$$\chi' = \frac{C - C_0}{C_0} = \frac{\Delta C}{C_0} \quad (1.1)$$

$\chi'$  is called the electrical susceptibility of the dielectric. The most often used terminology is the dielectric permittivity or dielectric constant instead of susceptibility, which is defined as the ratio of the capacitance  $C$  of the capacitor filled with a dielectric to the value  $C_0$  of the same capacitor under vacuum.

$$\epsilon_r = \frac{C}{C_0} \quad (1.2)$$

From the above equations the relationship between the electric susceptibility and the dielectric permittivity is given as:

$$\chi' = \epsilon_r - 1 \quad (1.3)$$

Thus, by definition, the electric susceptibility and permittivity are non-dimensional real quantities. The dielectric constant or permittivity of a material is a measure of the extent to which the electric charge distribution in the material can be distorted or polarized by the application of an electric field.

### 1.2.2 Mechanism of electric polarization

At the atomic level, all matter consists ultimately of positively and negatively charged particles whose charges balance each other macroscopically in the absence of an electric field giving rise to overall charge neutrality. Once the electric field is applied, the balances of charges are perturbed by the following four basic polarization mechanisms [19].

**Electronic polarization:** It occurs in neutral atoms when an electric field displaces the nucleus with respect to the negative charge. Thus electronic polarization is an induced polarization effect.

**Atomic/ionic polarization:** It is observed when different atoms that comprise a molecule share their electrons asymmetrically, and cause the electron cloud to be shifted towards the stronger binding atom, the atoms acquire charges of opposite polarity and an external field acting on these net charges will tend to change the equilibrium positions of the atoms themselves, leading to the atomic polarization.

**Dipolar/orientational polarization:** When an ionic bond is formed between two molecules by the transfer of some valence electrons, a permanent dipole moment will originate in them. This permanent dipole moment is equal to the product of the charges of the transferred valence electrons and the inter-atomic distance between them. In the presence of an electric field  $E$ , the molecules carrying a permanent dipole moment will orient to align along the direction of the electric field  $E$ . This process is called the dipolar or orientational polarization. This occurs only in dipolar materials possessing permanent dipole moments.

**Space charge polarization:** It is present in dielectric materials which contain charge carriers that can migrate for some distance through the bulk of the material (via diffusion, fast ionic conduction or hopping, etc.) thus creating a macroscopic field distortion. Such a distortion appears to an outside observer as an increase in the capacitance of the sample and may be indistinguishable from the real rise of the dielectric permittivity. Space charge polarization is the only type of electrical polarization that is accompanied by macroscopic charge transport (and in the case when the migrating charge carriers are ions a macroscopic mass transport as well). In general, the space charge polarization can be

grouped into hopping polarization and interfacial polarization. In dielectric materials, localized charges (ions and vacancies, or electrons and holes) can hop from one site to another site, which creates the hopping polarization. Similarly the separation of the mobile positive and negative charges under an electric field can produce an interfacial polarization.

### 1.2.3 Polarization and dielectric constant

The ability of a dielectric material to store electric energy under the influence of an electric field, results from the field-induced separation and alignment of electric charges. Polarization occurs when the electric field causes a separation of the positive and negative charges in the material. The larger the dipole moment arms of this charge separation in the direction of a field and the larger the number of these dipoles, the higher the material's dielectric permittivity.

In the presence of electronic, ionic and dipolar polarization mechanisms, the average induced dipole moment per molecule  $P_{av}$  will be the sum of all the contributions in terms of the local field (effective field) acting on each individual molecule.

$$P_{av} = \alpha_e E_{loc} + \alpha_i E_{loc} + \alpha_d E_{loc} \quad (1.4)$$

Here,  $\alpha_e$ ,  $\alpha_i$ ,  $\alpha_d$  are the electronic, ionic and dipolar polarizabilities.  $E_{loc}$  is the local field or the effective field at the site of an individual molecule that causes the individual polarization. Each effect adds linearly to the net dipole moment of the molecule. Interfacial polarization cannot be simply added to the total polarization as  $\alpha_{ij} E_{loc}$  because it occurs at the interfaces and cannot be put into an average polarization per molecule in bulk. Moreover, the fields are not well defined at the interfaces.

For simple dielectrics ( eg. gases) one can take the local field to be the same as the macroscopic field. This means that  $E_{loc}=E$  the applied field and therefore the polarization is,

$$P = \chi_e \epsilon_0 E = (\epsilon_r - 1) \epsilon_0 E \quad (1.5)$$

$P = N \cdot P_{av}$  where  $N$  is the number of atoms or molecule per unit volume [20].

$$\epsilon_r = 1 + N\alpha / \epsilon_0 \quad (1.6)$$

$\alpha$  is the polarizability of the molecule.

#### 1.2.4 Clausius and Mossotti relation for dielectric permittivity

Consider a molecule of a dielectric medium situated in a uniform electric field  $E$ . The total electric field acting on this molecule  $E_{loc}$  will have three main components-  $E_1$ ,  $E_2$ , and  $E_3$ . Here  $E_1$  is the applied electric field  $E$ ,  $E_2$  is the field from the free ends of the dipole chain and  $E_3$  is the near field arising from the individual molecular interactions. In solids we have to consider the actual effective field acting on a molecule in order to estimate the dielectric permittivity. For electronic and ionic polarization, the local field for cubic crystals and isotropic liquids can be given by the Lorentz field, given by

$$E_{loc} = \frac{1}{3\epsilon_0} P \quad (1.7)$$

By assuming the near field  $E_3$  is zero, Clausius and Mossotti derived a relation for the dielectric constant of a material under electronic and ionic polarization [21].

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} (N_i \alpha_i + N_e \alpha_e) \quad (1.8)$$

Here,  $\epsilon_r$  is the relative permittivity at low frequencies,  $\alpha_i$  is the effective ionic polarizability per ion pair,  $N_i$  is the number of ions pair per unit volume,  $\alpha_e$  is the electronic polarizability and  $N_e$  is the number of ions (or atoms) per unit volume exhibiting electronic polarization. The atomic/ionic polarizability  $\alpha_i$  and the electronic polarizability  $\alpha_e$  cannot be separated at low frequencies and hence they are together represented as the induced polarizability  $\alpha_{ind}$

Hence equation 1.8 can be written as:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_0} (N_m \alpha_{ind}) \quad (1.9)$$

This is known as the clausius –Mossotti equation for non polar dielectrics.

Above the frequencies of ionic polarization relaxation, only electronic polarization will contribute to the relative permittivity, which will be lowered to  $\epsilon_{r\infty}$  (relative permittivity at optical frequencies).

$$\frac{\epsilon_{r\infty} - 1}{\epsilon_{r\infty} + 2} = \frac{N_e \alpha_e}{3\epsilon_0} \quad (1.10)$$

By using the Maxwell relation for a lossless (non-absorbing), non magnetic medium,

$$n^2 = \epsilon_{r\infty} \quad (1.11)$$



where  $n$  is the index of refraction of the material, equation (1.10) can be rewritten as:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N_e \alpha_e}{3\epsilon_0} \quad (1.12)$$

In this form, it is known as Lorentz-Lorenz equation. It can be used to approximate the static dielectric constant  $\epsilon_r$  of non polar and non magnetic materials from their optical properties. In the case of dipolar materials we cannot use the simple Lorentz field approximation and hence the Clausius–Mossotti equation cannot be used in the case of dipolar materials.

### 1.2.5 Debye theory for polar dielectrics

In addition to the induced polarization present in all dielectrics, the polar dielectrics possess an orientational polarization that exists even in the absence of an applied electric field. It should be noted that the polarizability  $\alpha_o$  corresponding to the orientational polarization is related to the orientation of the molecules which are heavier than that of atoms or electrons that are involved in induced polarization. Hence the  $\alpha_o$  contributes to the total molecular polarizability  $\alpha$  at much lower frequencies than  $\alpha_{ind}$  does. So the dielectric constant that remains after the relaxation of orientational polarization (the dielectric constant due to the induced polarization) can be designated separately and it is usually represented by  $\epsilon_\infty$  in the case of dipolar dielectrics. So the equation (1.9) can be written as:

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{N_m}{3\epsilon_0} \alpha_{ind} \quad (1.13)$$

To account for the orientational contribution to the dielectric constant, Debye [22] used classical Boltzman statistics and the Langevin function  $L(y) = \coth y - \frac{1}{y}$  from the theory of paramagnetism, to estimate the temperature dependence of permanent dipole orientation. Assuming that these dipoles do not interact with each other, Debye derived the following equation for the orientational polarizability.

$$\alpha_o = \frac{\mu^2}{3KT} \quad (1.14)$$

Using Clausius-Mosotti's internal field argument discussed above, this additional polarization contributes to the static dielectric constant according to the following formulae:

$$\frac{\epsilon^1 - 1}{\epsilon^1 + 2} = \frac{N_m}{3\epsilon_0} \alpha_{ind} + \frac{N_d}{3\epsilon_0} \alpha_o \quad (1.15)$$

Here  $N_d$  is the number of dipolar molecules per unit volume which is same as  $N_m$ .

This equation can be rewritten in the following form using equation (1.13).

$$\frac{\epsilon^1 - 1}{\epsilon^1 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{N_d \mu^2}{9\epsilon_0 KT} \quad (1.16)$$

This result, from Debye [23], has been used successfully to predict the static dielectric constant of many polar gases and polar liquids. However, when applied to the condensed state of matter, Debye's theory breaks down while predicting the infinite dielectric susceptibility (Mosotti catastrophe). The reason for this breakdown lies in the assumption that is made in the expression for the Clausius-Mosotti local field. The near field in this case is assumed to be zero. In the condensed phase, permanent dipoles tend to lose their individual freedom of orientation through association and steric hindrance. Their interaction with their surroundings has to be taken into account and the near field cannot be neglected.

### 1.2.6 Onsager theory

To avoid the Mosotti catastrophe, Onsager modified the Debye theory by introducing a cavity. In his new approach to the problem, the electric field was represented by the sum of a 'cavity field' and a 'reaction field'. If the surroundings of each molecule are considered to be a homogeneous continuum having the macroscopic properties of the substance, then the 'cavity field' is the field inside a cavity of molecular dimensions due to a uniform external field. This cavity field is the field in the cavity resulting from the polarization induced in the surrounding medium by the molecule in the cavity. This part of the field exerts no torque on the molecule. Onsager's molecular model consisted of a sphere with a permanent dipole moment and an isotropic polarizability. Based on this model he arrives at the following expression, linking the molecular dipole moment with the static dielectric constant:

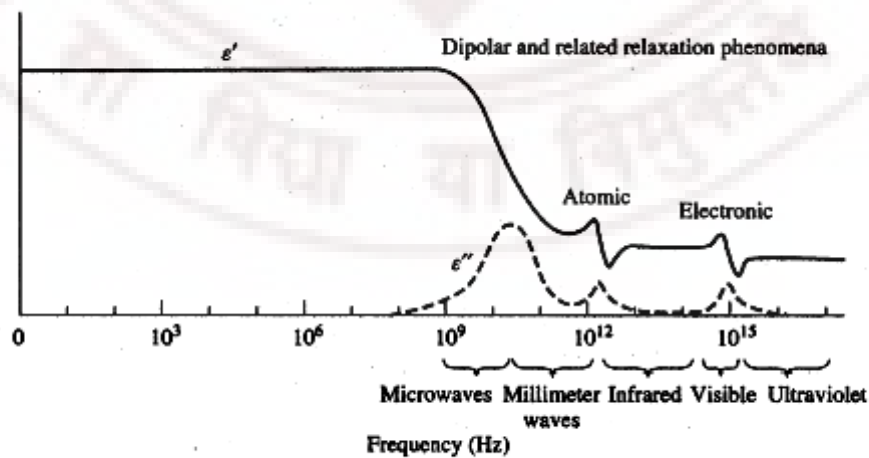
$$\frac{\epsilon^1 - 1}{\epsilon^1 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{3\epsilon^1(\epsilon_\infty + 2)}{(2\epsilon^1 + \epsilon_\infty)(\epsilon^1 + 2)} \frac{N_d \mu^2}{9\epsilon_0 KT} \quad (1.17)$$



Onsager's relation is quite well satisfied for non associated polar liquids [24, 25] and can also be applied to weakly bound Van der Waals solids. In general, most of the solid dielectrics do not obey any of the local field expressions at sufficiently low frequencies due to the charge carriers present in these materials, mostly ions, but possibly also electrons. This renders any meaningful measurement of the low frequency dielectric permittivity very difficult, making the comparison with local field theory rather doubtful.

### 1.2.7 Dielectric loss

The permittivity of a dielectric material has both real and imaginary mathematical representations. The imaginary part of permittivity is represented in mathematical equations as  $\varepsilon''$ . This imaginary part of permittivity describes the energy loss from an AC signal as it passes through the dielectric. The real part of permittivity,  $\varepsilon'$  is also called the dielectric constant and relative permittivity. The permittivity of a material describes the relationship between an AC signal's transmission speed and the dielectric material's capacitance. When the word "relative" is used in front of permittivity, the implication is that the number is reported relative to the dielectric properties of a vacuum. The imaginary part of the dielectric permittivity which is a measure of how much field is lost as heat during the polarization of a material by an applied alternating electric field is also termed as dielectric loss. The characteristic orientation of the dipoles in an electric field results in a frequency variation of dielectric constant and loss over a broad band of frequencies. The typical behavior of real and imaginary part of the permittivity as a function of frequency is show in Figure 1.1 [26].



**Figure1.1** Frequency dependence of dielectric permittivity for an ideal dielectric material.