Chapter 1

Introduction

The main aim of this thesis is to introduce the phenomena of glass transition in Orientationally disordered plastic crystals. Although many different techniques are currently in use to study glass transition, the most used of these techniques the dielectric spectroscopy. Dielectric spectroscopy data are the most abundant, because dielectric measurements are easy to perform with a high accuracy over a large frequency range. For the convenience of discussion, in part A, the phenomena of glass transition has been introduced and in part B the basic principles of dielectric relaxation are given.

A: Phenomena of Glass Transition

A.1 Classification of Solids

There are mainly two kinds of solids, which exist in the universe.\(^1\) First is the crystalline solids and second the amorphous solids. Crystalline solids are arranged in fixed geometric patterns or lattices. Examples of crystalline solids are ice and sodium chloride. They have an ordered arrangement of units maximizing the space they occupy, and are practically incompressible. Amorphous solids have a random arrangement of molecules/atoms. Examples of amorphous solids are ordinary silica glass and glassy polymers like polyvinylacetate etc., which are extended super-cooled liquids where the molecules are arranged in a random manner as in a
Crystalline structure is formed by repeating a three-dimensional pattern of atoms, ions or molecules. Repetition of the structural units of the substance over long atomic distances is referred to as long-range order. Liquids and amorphous solids (e.g., glass) do not have long range order, but have a limited, localized order proximate to their structural units. The physical properties of liquids and amorphous solids are identical in all directions along any axis. These are referred to as isotropic properties. Optical, electrical and mechanical properties of crystals relate to orientation and are dependent on the crystal’s axes. These are referred to as anisotropic properties.

Another difference between solids in a crystalline versus amorphous state is their behavior when they are heated. Crystals become liquids at a specific temperature, $T_m$ (the melting point). At this temperature physical properties of the crystalline solids like enthalpy, specific heat and specific volume etc. changes sharply and that of amorphous solid changes gradually as shown in Figure 1.1. There tends to be a relatively wide temperature range for the melting point, a zone between the solid and the liquid state where physical properties of the substance change gradually.

![Figure 1.1: Specific volume vs. Temperature curve: (a) crystalline solid and (b) amorphous solid](image-url)
Figure 1.2: Classification of solids

The crystalline state is relatively more stable state than the amorphous state. The Gibbs free energy, $\Delta G$, of a substance in the amorphous state is always higher than the Gibbs free
energy of that same substance in its crystalline state. This accounts for the transformation of an amorphous solid into its crystalline state. The reverse, transformation from the crystalline state to the amorphous state, does not occur because it is energetically unfavored ($\Delta G > 0$). However, the energy difference between the amorphous and crystalline state is relatively small, so the amorphous solid is quite stable. Figure 1.2 shows various types of solids which include a wide variety of substances.

A.2 Introduction to glass science

When, where, or how human beings discovered how to make glass is not known. Very small dark-colored beads of glass have been dated back to 4000 BC. By 2500 BC small pieces of true synthetic glass appeared in areas such as Mesopotamia, but an actual glass industry did not appear until about 1500 BC in Egypt.² By this time various small vases, cosmetic jars, and jewelry items made of glass had begun to appear.

All the ancient glasses were based on silica (sand), modified with considerable amounts of various metal oxides, mainly soda ($Na_2O$) and lime ($CaO$). This is still the most common glass being used today. It is known as soda lime glass. It was first produced by accidental fusion inside furnaces. Typical compositions of the ancient glass are 68.5% $SiO_2$ + 16.5% $Na_2O/K_2O$ + 7.5% $Al_2O_3$ + colouring agents such as some oxides of $Cu$, $Pb$, $Fe$ etc. Here glass is understood as the solidified form of (liquid) silica. Actual planned research on these glasses started around the years 1890 and the research publications started appearing in scientific journals dealing with the temperature variation of viscosity.³ So according to the earlier point of view, glass was understood as supercooled form of the liquid where the viscosity is $10^{13}$ Poise (Figure 1.3). It was thought⁴,⁵ that the large increase of viscosity on lowering the temperature was due to some kind of 'networking' of the molecules. However, in the early 20th century, the same phenomenon was observed in organic liquids too. The phenomenon was then attributed to 'clustering' of molecules. Around the same time, it was
observed that glass transition phenomena also shows-up as a step like change in specific heat with respect to temperature. These measurements have encouraged the researchers to calculate the excess entropy of the liquid over the corresponding crystalline state, based on which a suggestion was made that glass is perhaps a fourth state of matter. However, by 1949, Huffman et al. observed the same kind of behaviour in the specific heat measurement of some plastically crystalline materials, where the phenomenon of glass-like transition occurs in a crystalline medium (of infinite viscosity). This necessitated redefinition of glass. In the 1950s, synthetic polymers also showed similar phenomenon. In these materials, the glass transition is due to the obvious difficulty associated with the packing of the large molecules into crystalline lattice. From new techniques like dielectric spectroscopy and mechanical relaxation spectroscopy measurements, it was realized that the 'glassy polymer' is not a completely dead state. During the same period, a lot of work was carried out on
a number of monomeric liquids using dielectric spectroscopy. In these liquids the relaxation was found to be very much different from that of the 'Debye type' but very similar to that occurring in polymers. Among the new techniques, dielectric spectroscopy is also widely used to study the dynamics of 'water' in its liquid and solution state. Based on dielectric study (where water shows a strong dispersion in the GHz region, which is nearly Debye in nature) as well as the detailed study of the configurational entropy of both the solid and liquid form of water, the supercooled water (SCW) predicted to be a strong liquid. The same technique is also popular to study the behaviour of ferrites, which shows that relaxation process found (in the radio frequency region) in these materials often identified as Maxwell-Wagner polarization which was attributed to their heterogeneous structure.

Another, turning point came in 1970's, when it was found that some rigid molecular liquids were also capable of exhibiting some amount of freedom even below the glass transition temperature. This gave rise to a fresh speculation that the glass might contain some 'liquid-like' regions in an otherwise rigid matrix. An alternate proposal was also made that the same molecule could go through 'small' and 'large' angle rotational mobility, where the kinetic freezing of the relaxation corresponding to the large angle rotations is the one that causes the main glass transition event. The recent observation of 'multiple glass transitions' in the same material and wide frequency dielectric measurements have given a fresh approach to the 'glass problem'. More recent techniques such as the 'specific heat spectroscopy' have clearly proved that the glass transition is due to 'structural relaxation'.

In addition to all the above types, the glass transition event has been found in many other materials consisting of different disorders, e.g. ices and ice clathrates, dipolar glasses and liquid crystal glasses. There is also a recent belief that the 'non-Debye' type of relaxation and 'distribution of relaxation times' should be viewed as two different phenomena that could be used to differentiate glasses from non-glasses.
A.3 Salient features of glass transition

If a liquid is cooled slow enough below its melting temperature $T_m$, it usually transforms into the solid crystalline phase which is thermodynamically favourable phenomena. However, in order for the liquid to undergo a phase transition to the crystalline state a two-step process must take place: (i) nucleation (ii) further growth. As the liquid is cooled below $T_m$, the nucleation of crystals starts and its rate increases with decreasing temperature.

![Diagram](image)

Figure 1.4: Variation of crystal growth rate ($G$) with temperature in panel (a). The diagrams show the different relation between nucleation rate and crystal growth in a crystallization system in panel (b) and glass forming system in panel (c). $\eta$ is the viscosity of melt.

The second stage of the phase transition is the growth of these crystals which is a thermally activated process which means its rate is also dependent on temperature. For crystals to nucleate and grow, fluctuations must occur, and these will occur more slowly if the system is more viscous. Hence, with decreasing temperature of liquid, a competition between the two factors to control the growth of crystals will take place. However, if the liquid is cooled fast enough, the increasing viscosity will dominate and will hamper the
growth of nuclei of crystals and crystallization can be avoided. Such a liquid is called 'supercooled liquid'. Hence crystallization → nucleation and growth and absence of nuclei or no growth → glass formation as can be seen in Figure 1.4. As the temperature decreases further with a certain rate, the constituent atoms or molecules in the liquid move more and more slowly until, at some temperature $T_g$, the time scales of molecular rearrangements become long compared to the typical laboratory time scales of, say, 200 secs. At this temperature, supercooled liquid behaves like a solid for all practical purposes and is called 'glass'; this temperature is called the glass transition temperature $T_g$. Typically, the $T_g$ is defined as the temperature at which the viscosity of a supercooled liquid reaches the typical value of $10^{13}$ poise (Figure 1.3 and 1.4). The crystallization is a first order phase transition and is characterized by a discontinuous change in those thermodynamical parameters which are the first derivatives of the free energy. Figure 1.5 shows how the enthalpy of a liquid held at a constant pressure changes with temperature under cooling from the stable liquid state. If liquid is cooled fast enough so that increasing viscosity of the liquid is able to hamper the

![Figure 1.5: Effect of temperature on the enthalpy ($H$) of glass forming melt.](image)

8
increase in number of crystallites (or nuclei) then even below melting temperature, liquid will exhibit liquid-like properties and will be called as 'supercooled liquid'.

The glass forming ability is influenced by many factors; one of the most important factors is the molecular structure of the material\textsuperscript{6,65} and difficulty in packing of the molecules into lattices as in polymers.\textsuperscript{66} Besides, free energy diagram corresponding to various possible states exhibited by material, predicts the glass forming ability of the substance. The ability of a substance to vitrify is determined in the crystalline state, not in liquid state. The probability of glass formation in non-glass forming liquids can sometimes be enhanced by adding a second component (Figure 1.6). This results in depression of the freezing temperature which in turn makes liquid more viscous at the point where thermodynamic instability is reached, hence slowing down the crystallization.\textsuperscript{68} The freezing point depresses according to the following well known equation.\textsuperscript{67}

\[
\ln(x) = -\frac{\Delta H_f}{R} \left( \frac{1}{T_{liq}} - \frac{1}{T_m} \right)
\]  

(1.1)
where \( x \) is the weight fraction or mole fraction of the second component, \( T_m \) is the melting temperature, \( \Delta H_f \) is the enthalpy of melting and \( T_{\text{liq}} \) (or \( T_{\text{liquidus}} \)) is the freezing (liquidus) temperature. The various physical parameters of such homogeneous mixtures are found to follow the well known mixture rule \(^{67,69,70}\):

\[
y_{\text{mix}} = y_1(1-x) + y_2x + k\cdot x(1-x)
\]

(1.2)

Or well known Gordon-Taylor equation,\(^{71}\)

\[
y_{\text{mix}} = \frac{y_2x + y_1k(1-x)}{x + k(1-x)}
\]

(1.3)

where \( y_1 \) and \( y_2 \) are the properties of the components and \( x \) is the weight fraction of the 2\(^{nd} \) component and \( k \) is the interaction parameter. Both rules are found to be valid for substances those do not form complexes,\(^ {64,67,69,72,73} \) simple binary system\(^ {9,10,28,67,69,70} \) and also for many polymer-plasticizer systems. The above equations can be used in estimating the glass transition temperature of the materials which do not form glass easily.

A.4 Thermodynamics of Glass

The thermodynamic state of glass has always been a point of debate among researchers. The temperature at which the glass transition takes place can vary according to how slowly the material cools. If it is cooled slowly it has longer time to relax and hence the transition occurs at a lower temperature and the glass formed is more dense. There is a minimum limit to the glass transition temperature for infinite slow cooling rate. Hence the glass transition temperature \( T_g \) is not unique like thermodynamic melting temperature \( T_m \) because if the cooling rate of material is changed, \( T_g \) of the material will also change (Figure 1.7).

In order to study thermodynamic state of glass, specific heat measurements have been made and the entropies corresponding to the liquid and glassy state are calculated.\(^ {54-57,74} \) It has been found that glass shows some extra and non-zero entropy even at absolute zero.
Figure 1.7: $T-$ variation of various physical properties with cooling rates where $q_1 > q_2 > q_3$. In the middle diagram $\tau$ is the structural relaxation.
temperature. This at one time appeared to be the violation of third law of thermodynamics. Later, it was explained on the basis that the entropy differences do not necessarily disappear between all conceivable states at absolute zero, but only between those which are in internal equilibrium. The discussion of the entropy of glass also led to what is known as Kauzmann paradox.\textsuperscript{42-45,7,75,76} According to Kauzmann,\textsuperscript{42} the excess entropy of a supercooled liquid (Figure 1.8) over the corresponding crystalline state would vanish at a temperature $T_k$ located a few degrees below $T_g$, if the liquid is allowed to be in internal equilibrium.

\[ S_{\text{excess}} = S_{\text{melting}} + \int_{T_k}^{T_m} \left( \frac{C_c - C_l}{T} \right) dT \]  

(1.4)

where $C_c$, $C_l$ correspond to crystallization and liquid values. Subsequently, the temperature was identified with the temperature where the corresponding viscosity becomes infinite and hence, led to the speculation of an underlying second order transition\textsuperscript{12,42-45} at $T_k$. This has also been a topic of investigation and recent findings\textsuperscript{73} show that if internal equilibrium is allowed, the supercooled liquid would approach a temperature somewhere in between $T_g$ and
Hence, Kauzmann temperature $T_k$ need not be identified with the so-called ideal glass transition.

Adam and Gibbs\textsuperscript{77} suggested that for densely packed liquids the conventional transition state theory of liquids, based on the notion of single molecule passing over energy barriers established by their neighbours is not adequate. They proposed that instead, viscous flow occurs by increasingly cooperative rearrangements of groups of particles. Each such group was thought to be acting independently of other such groups in the system. However, the minimum size of such a group was to be determined by the temperature. This led to an expression for the relaxation time which contains the excess configurational entropy $S_c$ of the Kauzmann paradox in the exponent denominator as:

$$\tau = \tau_0 \exp \left( \frac{G'(\Delta \mu)}{TS_c} \right)$$

where $\Delta \mu$ is the conventional free energy barrier to rearrangements and $G'$ is a constant. The familiar departure from Arrhenius behaviour comes from the temperature dependence of $S_c$ which itself depends on the value of the configurational heat capacity. A frequently used, though not direct, test of the Adam Gibbs equation is to develop Vogel-Fulcher-Tammanns (VFT) type equation, which is often used to describe the temperature dependence of relaxation rates in glassy systems. In their original treatment, Adam and Gibbs made the simplest assumption for the excess heat capacity, which determines the configurational entropy temperature dependence, viz that it is a constant. This yields,

$$S_c = \Delta C_p \ln \left( \frac{T}{T_k} \right)$$

Substitution into eq. 1.5 then yields the VFT equation as an approximation, valid near $T_k$. However, $\Delta C_p$ is a constant, does not describe many molecular systems. More accurate relationship\textsuperscript{78–80} is given by $\Delta C_p = K/T$, from which,

$$\Delta S(T) = \frac{K(T - T_k)}{T_k T}$$
which leads to the famous VFT equation as an identity.

$$\tau = \tau_0 \exp \left( \frac{D (T_0 - T)}{(T - T_0)} \right)$$

(1.8)

where D is related to the fragility of the liquids\textsuperscript{81}.

**A.5 Structural relaxation**

The structural relaxation is the slow co-operative dynamic process attempting to restore thermodynamic equilibrium in a glass. Such a process is of fundamental importance on both the experimental and theoretical point of view being strictly related to the glass transition phenomenon. Structural relaxation occurring in the glassy state can be characterized by differential scanning calorimetry (DSC), mechanical response and can be realized as volume relaxation or enthalpy relaxation.

**A.5.1 Volume relaxation**

Volume relaxation is usually assessed by dilatometry. The observed response of the volume V to a sudden jump in P at a given T (see Figure 1.9) is an example of volume relaxation which can be written as:\textsuperscript{82}

$$V = V_1 + (V_2 - V_1).(1 - e^{-t/\tau}) = V_1 + (V_2 - V_1).(1 - \phi(t))$$

(1.9)

where \(\tau\) is called the structural relaxation and \(\phi(t)\) is the dissipative response. The same behavior in the frequency domain can be recognized as

$$\frac{K^*(\omega) - K_\infty}{K_0 - K_\infty} = \int_0^\infty -\phi(t).e^{i\omega t}.dt$$

(1.10)

where \(K^* = K' - iK''\)

$$\frac{K'(\omega) - K_\infty}{K_0 - K_\infty} = \int_0^\infty \phi(t) \cos(\omega t)dt$$

(1.11)

$$\frac{K''(\omega) - K_\infty}{K_0 - K_\infty} = \int_0^\infty \phi(t) \sin(\omega t)dt$$

(1.12)
Where $K'$ and $K''$ are the real and imaginary parts of volume (bulk) modulus respectively. In case of dielectric $K^*(\omega)$ is $\epsilon^*(\omega)$. For non ideal cases $\phi(t) \propto e^{(-t/\tau)^\theta}$, which is William-Watts function.\textsuperscript{11,25}
A.5.2 Enthalpy relaxation

Enthalpy relaxation usually observed from differential scanning calorimeter (DSC) or adiabatic calorimeter (AC). In the context of DSC, a sample and a reference material are heated at a constant rate, the difference in the electrical power needed for each is calculated, and the specific heat is given as a function of temperature. The enthalpy recovery (or enthalpy relaxation) is obtained by integrating the DSC scan. In case of adiabatic calorimeter, the
temperature of a sample is kept constant for thermal equilibration. If any spontaneous temperature changes are observed during the equilibration periods, this is a clear indication that the sample is undergoing structural relaxation. The spontaneous change of calorimetric temperature is well represented by the following equation:

\[
\frac{dT}{dt} = a + b t + \exp[-(t/\tau)\beta]
\]  

Here a small correction term “bt” due to residual heat leakage was taken into account. This equation is simply derived by assuming that the enthalpy \(H = H_{\text{vib}} + H_c\) remains constant under adiabatic conditions and that the rate of enthalpy relaxation is described by the Kohlrausch Williams Watts (KWW) equation:

\[
\Delta H_c(t) = \Delta H_c(0) \exp[-(t/\tau)\beta]
\]  

where \(\Delta H_c\) is the configurational enthalpy to be relaxed, \(\tau\) the average relaxation time, and \(\beta\) the non-exponential parameter representing a distribution of the relaxation times. Figure 1.10 depicts (upper panel) the enthalpy of a glassy solid and (lower panel) the rate of spontaneous change in calorimetric temperature \(dT/dt\) near its \(T_g\). The oblique segment in the upper panel represents the temperature rise due to a Joule heating and the slope corresponds to the quasi-equilibrium heat capacity. The horizontal segment shows a spontaneous temperature change arising from the enthalpy relaxation.

**A.6 Strong and fragile nature of liquids**

The ‘fragility’ is a qualitative concept related to the rapidity with which a liquid structure, which is arrested at the glass transition during cooling, becomes disrupted on reheating. The disruption is monitored by the structural relaxation time of the liquid which decreases from the value at \(T_g\) (\(=10^2\) sec.) toward the picoseconds values characteristic of highly fluid system. One often finds in the scientific literature a distinction is made between glass formers
based on the different temperature dependence of the viscosity. That is, the glass formers those show a behavior close to an Arrhenius one (i.e. a straight line in the representation of Figure 1.11) are called 'strong' glass formers while those departing from this behavior are called 'fragile'. A quantitative description of 'fragility' can be done by calculating the fragility index \( (m) \) defined as\(^{78-81}\)

\[
m = \frac{d(\log \tau)}{d(T_g/T)} \bigg|_{T=T_g} \tag{1.15}
\]

where \( \tau \) is the structural relaxation time. Angell\(^{78-81}\) has categorized all liquids into 'strong' and 'fragile' liquids. The 'strong' liquids are those which have self-reinforcing tetrahedral
network structure as they exhibit strong resistance to structural degradation and show a very small change in specific heat at $T_g$ whereas 'fragile' liquids are those which lack such directional bonds and show a large change in specific heat measurements at $T_g$ (see Figure 1.11). However, this classification fails when applied to hydrogen bonded systems as they are intermediate in their fragile character which exhibit a large change in specific heat at $T_g$ than the fragile liquids. The famous stretched exponential form has been proposed which gives a measure of the fragility of liquids:

$$\tau = \tau_0 \exp \left[-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right]$$

(1.16)

where $\beta$ lies between 0 and 1. This non-exponentiality parameter $\beta$ has been correlated with the fragility parameter to give a measure of the fragility. An interesting correlation between the William Watts parameter $\beta_{KWW}$ and fragility index $m$ is given by Böhmer et al. as:

$$m = 250 \pm 30 - 320\beta_{KWW}$$

(1.17)

Experimental evidences show that the above equation is fairly valid for liquid glass formers.

A.7 Secondary Relaxation Processes in Glassy Matrix

It should also be pointed out that, in glass forming liquids, while most of the non-vibrational heat capacity is lost at the glass transition, a part remains and only lost at much lower temperatures. This is usually a weak component associated with a faster process (or processes) which is less cooperative than the principle relaxation process and has different dynamic character. These faster processes are called secondary relaxations ($\beta-$, $\gamma-$ relaxations etc.) to distinguish them from the primary ($\alpha-$) relaxation which carries most of the thermodynamic strength (see Figure 1.12). They have been well known in the field of polymers where the secondary relaxations are usually associated with the side chain motion of the molecule but their general occurrences in the simple glasses was not expected until Goldstein pre-
Figure 1.12: $T-$variation of dielectric loss at a test frequency $f$, or $T-$variation of the specific heat ($C_p$) in glass forming liquids.
dicted them as a necessary consequence of his landscape picture\textsuperscript{84} of glass forming systems. However, their origin in simple glass formers is a topic of debate as several origins have been put forward. In many cases, they have been shown as the continuation of the high temperature relaxation process before any cooperative processes set in.\textsuperscript{85} It appears that the origin of these processes is very vital to the understanding of the glass. Their calorimetric characterization is comparatively a recent development\textsuperscript{54–57,65,86}.

**A.8 Mode Coupling Theory**

The increasing viscosity of the system as it approaches its glass transition temperature means that the rearrangements of the atoms become slower and slower. These rearrangements are directly related with the fluctuations in the local density of the liquid. The information about the structural changes is therefore contained in the density-density correlation function. Mode Coupling Theories\textsuperscript{87–89} (MCT) are based on such correlation functions. These correlation functions have been obtained from generalized hydrodynamic equations. MCT is an effective medium theory in which simultaneous treatment of relaxation and vibration effectively places molecules in 'cages' formed by surrounding molecules. This leads to high frequency motion based on a frequency dependent 'deformability' of the cages and a gradual transition to diffusive motion at low frequencies. Frequency dependent relaxation effects are generated through frequency dependent friction terms arising from the interactions with the neighbouring molecules. Here, we summarize some of the important predictions of MCT:

i) Temperature independent structure of primary relaxation peak (time-temperature superposition) at higher temperature is obtained.

ii) A secondary relaxation peak is found which is wider and more symmetric than the primary relaxation peak and has different dynamic characteristics.

iii) A convergence of the time of primary and secondary relaxations at high temperature.

iv) An ergodic to non-ergodic transition at temperature $T_c$ where viscosity rises roughly five
orders of magnitude over its high temperature value.

v) A power law divergence in the hydrodynamic viscosity at $T_e$.

However, recent results$^{80,90-94}$ show incompetence of MCT in describing the experimental results. It has also been shown that MCT is more like a theory for liquids rather than for supercooled liquids. The identification of $\beta$-process of MCT with the one occurring in glass forming liquids is also a topic of debate.

**A.9 Various types of glass**

From what has been discussed in the previous section, a glass is a general way can be defined as the system which on cooling, has a relaxation time corresponding to a mode that is comparable to the experimental time scale. With this definition one can see there is a large variety of glasses as shown in Figure 1.13, in which the structural glass is only one example.
A.10 Orientationally disordered Crystals

'Orientationally disordered' solids have been predicted as far back as early thirties when Pauling\textsuperscript{95} and Frenkel\textsuperscript{96} indicated the possibility of a phase in which molecular crystals could be rotationally disordered. Substances forming orientationally disordered crystals freeze from a liquid into a solid in which the centers of mass of the molecules are ordered on a lattice (equivalently, translationally ordered), but the molecules retain their orientational degrees of freedom (Figure 1.14). On further cooling, molecular orientations will get ordered and the crystal will attain ground state. However, transition from this disordered phase to an ordered phase can in principle be bypassed by supercooling of the crystal. The supercooled orientationally disordered crystals exhibit a glass-like transition near a temperature $T_g$. Below glass transition, material is often referred as 'glassy crystal'\textsuperscript{54–57} or 'orientational glass'. These crystals are mostly formed of molecules that are globular in shape and offer little steric hindrance for the molecular reorientational processes. This often causes a high plasticity, a property that led to the term 'plastic crystal'\textsuperscript{96,97}. Due to their translational symmetry, plastic crystals are much simpler to treat in theoretical and simulation approaches of the glass transition and therefore, these materials are considered as model systems for structural glass formers. Although the OD phase was observed in dielectric measurements by White et al.\textsuperscript{102,103} in the year 1940, it was not categorized as glass-like phenomena until the work of Huffman et al.\textsuperscript{8} in 1949 where it became apparent in specific heat measurements as a step-like change. After that dielectric spectroscopy has proved to be an important tool for the investigation of the relaxational response in plastic crystals as the electric field directly couples with orientational degrees of freedom, provided the molecule has permanent dipole moment. Apart from the primary relaxation process, a variety of faster dynamic processes are also exhibited by plastic crystals below the $T_g$. Unfortunately, this so called $\beta$—relaxation or excess wing in plastic crystals is not being well understood and has been discussed contro-
versally in the past\textsuperscript{30,32}. Besides, transition temperatures of plastic crystals are found to be very sensitive to the amount of impurity\textsuperscript{77} present in the material because of their tendency to exhibit various conformers. In addition, often plastic crystals are found to exhibit more than one plastic crystalline phases\textsuperscript{54–57,96–101}; such crystals can exhibit more than one glass transition event.\textsuperscript{28,58,93} These topics have been of prime concerned in our study of plastic crystals as discussed in this thesis.
B: Basic Principle of Dielectrics

B.1 Definition of polarization

Non polar molecules do not have intrinsic dipole moments, since the "centre of mass" of the positive and negative charges in them coincide. Hence if a dielectric material placed in an electric field, the field will induce in each a tiny dipole moment, pointing in the same direction as the field for the substance consist of neutral atoms. If the material is made up of polar molecules, each permanent dipole will experience a torque, tending to line it up along the field direction and hence as a result the materials become polarized. This phenomena is called polarization. Hence polarization is nothing but the dipole moment per unit volume.\(^{104,105}\)

\[
P = \sum_i N_i \mu_i
\]

(1.18)

where \(N\) is the number of dipoles per unit volume and \(\mu\) is the dipole moment relating two opposite charge (\(\pm q\)) separated by a distance \(d\) by \(\mu = qd\). The displacement vector \(D\), which is a measure of the sum of current flow from the shifting charge, can be related\(^{104,105}\) to the electric field through the permittivity of the material \(\varepsilon\) by

\[
D = \varepsilon E = \varepsilon_0 E + P
\]

(1.19)

where \(P\) is the resultant polarization or surface charge density of the material caused by the bound charges and \(\varepsilon_0\) is the dielectric constant of vacuum. Thus polarization can equivalently designate either the bound-charge density or the dipole moment per unit volume. Figure 1.15 schematically represents the dielectric polarization by dipole chains and bound charges of the dielectric material.

B.2 Mechanism of polarization

The local dipole moment \((\mu)\) can be related to the local electric field strength \(E'\) by,

\[
\mu = \alpha E'
\]

(1.20)
The proportionality factor $\alpha$, known as polarizability, measures the electrical pliability of the particle, that is, the dipole moment per unit field strength. The locally acting field $E'$ will differ from the applied field $E$, due to the polarization of the surrounding dielectric medium. It is important to understand the various polarization phenomena that generate the sum of contributions to the polarization of a dielectric material:

(a) Electronic polarizability ($\alpha_e$) is due to the displacement of the negatively charged electrons with respect to the positively charged nuclei in response to an external electric field; induced dipole moments result and cause the so-called electronic polarization of materials.\textsuperscript{104,106}

(b) Ionic polarizability ($\alpha_i$) is the result of asymmetric sharing of electrons from atoms of different types form molecules as the electron clouds will be displaced eccentrically toward the stronger binding atoms.

(c) Dipole polarizability ($\alpha_d$) or orientation polarizability is related to the asymmetric charge distribution between the unlike partners of a molecule giving rise to permanent dipole mo-
ments which exist also in the absence of an external field. Such moments experience a torque in an applied field that tends to orient them in the field direction.

(d) charge polarizability (\(\alpha_s\)) is due to the mobile charges which are present because they are impeded by interfaces, because they are not supplied or discharged at the electrodes. Space charges resulting from these phenomena appear as an increase in capacitance as far as the exterior circuit is concerned.

The total polarizability of the dielectric can be represented as the sum of all these:

\[
\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s
\]  

(1.21)

It is the response of these polarization mechanisms to periodic fields that determine the frequency dependence of the dielectric properties of solid. For each polarization mechanism, there exists some sufficiently high frequency such that the particular mechanism will not be able to follow the applied alternating field and thus will cease the contribution to the polarization and dielectric properties which consequently will lead to a frequency dispersion of dielectric properties (Figure 1.16). In an ideal capacitor the electric charge adjusts itself instantaneously to any change in voltage. In practice, however, there is an inertia to movement of charge that shows up as a relaxation time (for charge transport). The electronic polarization is the only process sufficiently rapid to follow alternative fields in the visible part of the spectrum. Ionic polarization process is also able to follow an applied high-frequency field and contribute to the dielectric constant at frequencies up to the infrared region of the spectrum.

**B.3 Non-Polar Dielectrics: Clausius Mossotti and Lorentz-Lorenz eq.**

In the static and low frequency fields that we shall be considering, the electronic polarizability \(\alpha_e\) cannot be separated from the ionic (atomic) polarizability \(\alpha_i\). We will therefore only be interested in the induced polarizability, \(\alpha_{ind} = \alpha_e + \alpha_i\) as a high frequency background
Figure 1.16: Schematic representation of various dielectric process of the low frequency dielectric behaviour. In case of non-polar materials, the induced polarization is the only polarization. A calculation based on the model given by Clausius and Mossotti\textsuperscript{20-24,104} relates the dielectric susceptibility $\chi'$ and dielectric constant of a dielectric material $\varepsilon_{\infty}$ as:

$$\frac{\chi'}{\chi' + 3} = \frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} = \frac{N_m}{3\varepsilon_v}\alpha_{\text{ind}}$$  \hspace{1cm} (1.22)
This equation is known as Clausius-Mossotti equation and interprets the static (low frequency) dielectric constant \( \varepsilon_{\infty} \) of a medium (a macroscopic quantity) in terms of the polarizability \( \alpha_{\text{ind}} \) of the contributing molecules (a microscopic quantity).

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

\[
n_D^2 = \varepsilon_{\infty} \tag{1.23}
\]

where \( n_D \) is the index of refraction of the material. Using eq. 1.23, eq. 1.22 can be rewritten as,

\[
\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{N_m}{3\varepsilon_v} \alpha_{\text{ind}} \tag{1.24}
\]

This equation is known as Lorentz-Lorenz equation.104

### B.4 Polar Dielectrics: The Debye eq. and Mossotti catastrophe

In addition to the electronic polarizability, \( \alpha_{\text{ind}} \), present in all dielectric materials, polar dielectrics possess orientational polarizability \( \alpha_d \) that exists even in the absence of an electric field. Because \( \alpha_d \) has to do with reorientation of molecules, which are much heavier objects than either atoms or electrons responsible for the \( \alpha_{\text{ind}} \) does. For this reason, it is customary to designate the dielectric constant due to \( \alpha_{\text{ind}} \) as \( \varepsilon_{\infty} \). To account for orientational contribution, Debye used classical Boltzmann statistics and the Langevin function from paramagnetism theory to estimate the temperature dependence of permanent dipole orientation. Assuming that these dipoles, do not interact with each other, Debye derived the following expression for orientational polarizability:21,23,104—106

\[
\alpha_d = \frac{\mu^2}{3kT} \tag{1.25}
\]

If we use the 'internal field' argument of Clausius-Mossotti, we can write the dielectric constant of the materials as:

\[
\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{\varepsilon_{\infty} - 1}{\varepsilon_{\infty} + 2} = \frac{N_d \mu^2}{9\varepsilon_v kT} \tag{1.26}
\]
This result due to Debye, predicts successfully the dielectric constant of many polar gases and many polar liquids but failed when applied to the condensed state of matter predicting infinite dielectric susceptibility (Mossotti Catastrophe). The reason for this breakdown lies in one of the assumptions used in Clausius-Mossotti local field that the field arising from the individual contributions of the molecules is zero. However, in condensed phases, permanent dipoles tend to lose their individual freedom of orientation through association and steric hindrance. Their interaction with surroundings has to be taken into account.

B.5 Onsager’s equation and Kirkwood-Frohlich equation

To avoid Mossotti catastrophe, Onsager modified Debye’s theory by introducing a different kind of cavity, with the following distinct properties:

i) While the Clausius-Mossotti cavity is a mathematical entity, the Onsager’s cavity is real, thus causing the electric field lines to be bent. ii) While the Clausius-Mossotti cavity contains a large number of molecules, the Onsager cavity encloses only a single dipole molecule. iii) The center of the Onsager’s cavity is marked by a point dipole which polarizes the surrounding medium. This polarization, acting back on the dipole in the cavity, creates the reaction field. Based on the above assumptions, Onsager’s theory arrives at the following expression linking the molecular dipole moment of the static dielectric constant:

\[
\frac{\varepsilon_0 - \varepsilon_\infty}{2\varepsilon_0 + \varepsilon_\infty} = \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty} \left( \frac{\varepsilon_\infty + 2}{3} \right)^2 \frac{4\pi \mu^2 N_d}{3kT}
\]

(1.27)

where \( N_d \) is number of dipolar molecules per unit volume. Onsager’s relation is quite well fulfilled for the non-associated polar liquids and can also be applied to weakly bound van-derwaals solids. However, in derivation of Onsager’s eq., short range interactions between dipoles were neglected. A modified calculation was done by Kirkwood taking into account the short range interaction, arrived at the following expression:\textsuperscript{20,21,23}

\[
\frac{\varepsilon_0 - \varepsilon_\infty}{2\varepsilon_0 + \varepsilon_\infty} = \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon_\infty} \left( \frac{\varepsilon_\infty + 2}{3} \right)^2 \frac{4\pi \mu^2 N_d}{3kT} (1 + z \cos \gamma)
\]

(1.28)
where $z$ is the average number of nearest neighbours and $\cos \gamma$ is the average of the cosine of the angle between neighbouring dipoles. This eq. is known as Kirkwood-Frohlich eq. The difference between Onsager's eq. and Kirkwood-Frohlich eq. is the additional term $(1 + \cos \gamma)$ which is usually refer as Kirkwood correlation factor "$g$". This quantity $g > 1$ for parallel alignment and $g < 1$ for antiparallel alignment. In general, however, most solid dielectrics do not obey any of the local field expressions at sufficiently low frequencies due to the charge carriers present in these materials in their ions or electrons. This renders any meaningful measurement of the low frequency permittivity very difficult, making the comparison with local field theory rather doubtful.

**B.6 Dielectric Relaxation**

Before understanding the concept of dielectric relaxation, let us first define the term "Relaxation". In general sense, relaxation is a concept, that applies to a linear systems where a response and the stimulus are proportional to one another in equilibrium or we can say, it is a delayed response to a changing stimulus in such a system.

**B.6.1 Relaxation Phenomena**

Dielectric relaxation occurs in dielectrics which have a permanent dipole moment. The Stimulus is almost always an electric field and the response is a polarization. The concept of dielectric loss arises when a dielectric material is placed in an a. c. field. The dielectric loss relates the polarization and current in an alternating field. The time required for the polarization is reflected as a phase retardation of the charging current. Instead of being $90^\circ$ advanced to the voltage, the current is advanced by some angle $90-\delta$, with difference generally referred to as the loss angle ($\delta$). Consider the most general periodic field:

$$E = E_0 \cos(\omega t) \quad (1.29)$$

31
then,

\[ D = D_0 \cos(\omega t - \delta) = D_1 \cos(\omega t) + D_2 \sin(\omega t) \]  

(1.30)

where,

\[ D_1 = D_0 \cos(\delta) \quad \text{and} \quad D_2 = D_0 \sin(\delta) \]  

(1.31)

For most dielectrics, \( D_0 \) will be proportional to \( E_0 \), but the ratio \( D_0/E_0 \) usually depends on frequency. Therefore, two different dielectric constants, \( \epsilon'(\omega) \) and \( \epsilon''(\omega) \), both frequency dependent, can be introduced by:

\[ D_1 = \epsilon' E_0 \quad \text{and} \quad D_2 = \epsilon'' E_0 \]  

(1.32)

From eq. 1.31 and 1.32,

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

(1.33)

The \( \epsilon'' \) is also known as the loss factor because the energy loss per second \( W \) in the dielectric per unit volume is directly proportional to \( \epsilon'' \) as,

\[ W = (\omega/8\pi) E_0^2 \epsilon'' \]  

(1.34)

It is convenient to introduce a complex dielectric permittivity constant \( \epsilon^* \) having \( \epsilon' \) as real component and \( \epsilon'' \) as imaginary component as:

\[ \epsilon^*(\omega) = \epsilon'(\omega) - i \epsilon''(\omega) \]  

(1.35)

where \( \omega = 2\pi f \) is the angular frequency; \( f \) is the angular frequency (Hz) of the oscillating field. The real component \( \epsilon' \) (in phase with the field) and the imaginary component \( \epsilon'' \) (component in quadrature) of the complex permittivity are dependent on each other as shown by the Kramer-Kronig relations:

\[ \epsilon'(\omega) - \epsilon_{\infty} = 2/\pi \int_0^\infty \epsilon^*(\omega') \frac{\omega'}{\omega'^2 - \omega^2} \, d\omega' \]  

(1.36)
\[ \epsilon''(\omega) = 2\pi \int_{0}^{\infty} (\epsilon'(\omega') - \epsilon_{\infty}) \frac{\omega}{\omega'^2 - \omega^2} \, d\omega' \]  

(1.37)

where \( \epsilon_{\infty} \) is the usual high frequency dielectric constant. Such relations evidence the correlation between dispersion (variation of \( \epsilon' \) as a function of frequency) and absorption (non-zero value of \( \epsilon'' \)): any dielectric dispersion is accomplished by an absorption peak. \( \epsilon' \) is correlated with the polarization of the system, while \( \epsilon'' \) with the energy losses in dielectric materials.

**B.6.2 Relaxation with a Single Relaxation Time**

At low frequencies the field changes slowly enough to allow dipoles to reach equilibrium before the field has measurably changed. For frequencies at which dipole orientations cannot follow the applied field due to the thermal agitation of the medium, absorption of the field's energy leads to energy dissipation. The mechanism of dipolar relaxation is also called dielectric relaxation and for ideal dipoles it is described by classical Debye relaxation. According to Debye, when the molecules are placed in an external electric field, the alignment of molecular dipoles takes place. This is because the dipoles are rigidly attached to the relatively large molecules in a viscous medium, the orientation process can be characterized by a relaxation time \( \tau_d \). In terms of the dielectric constant \( \epsilon_{\infty} \) to the instantaneous polarization \( P_{\infty} \) (the dielectric constant at frequencies much higher than the inverse of characteristic time \( \tau_d \)), the complex dielectric constant may be expressed as,

\[ \epsilon^*(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau_d} \]  

(1.38)

Dividing into real and imaginary parts gives,

\[ \epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{(1 + \omega^2\tau_d^2)} \]  

(1.39)

\[ \epsilon'' = \frac{\epsilon_0 - \epsilon_{\infty}}{(1 + \omega^2\tau_d^2)} \omega \tau_d \]  

(1.40)

where \( \tau_d \) is the relaxation time, \( \epsilon_0 \) is the permittivity at low frequency (\( f << 1/2\pi\tau_d \)) and \( \epsilon_{\infty} \) is the one at high frequency (\( f >> 1/2\pi\tau_d \)). The Debye curves for dielectric dispersion \( \epsilon' \)
Figure 1.17: Frequency dependence of real and imaginary parts of complex permittivity

and absorption $\varepsilon''$ are symmetric about $\omega \tau_d = 1$. $\varepsilon'$ decreases to $\varepsilon_\infty$ with increasing frequency and $\varepsilon''$ is maximum at the frequency $\omega = 1/\tau_d$ (Figure 1.17). The Debye equations are based on the assumption that the transient polarization can be represented by a simple exponential with a single relaxation time. Hence any model which predicts a simple exponential rise of polarization on applying a field within an ac field lead to dielectric dispersion and absorption curves of the form given by eqs. 1.39 and 1.40. For most materials, however, the experimental data are not well described by the Debye equations. Rather, the dispersion of the dielectric constant occurs over a wider range of frequency, and the absorption curves are much broader and flatter than shown in Figure 1.17 for Debye case. The value of relaxation time $\tau_d$ in the Debye equation is correlated to the energy barrier $E$ separating the two minima corresponding to the two equivalent positions of the non-interacting dipoles in a double-well potential (viscous interaction between the dipole and the environment). Sometimes $E$ is called the apparent activation energy. The variation of the relaxation time with temperature may be expressed as a thermally activated process through the Arrhenius relationship:\textsuperscript{20,21,23}

$$\tau = \tau_0 \exp \left( \frac{E}{RT} \right)$$  \hspace{1cm} (1.41)
where \( \tau \) is the time constant of the relaxation mechanisms (or the reciprocal of the measurement frequency in angular unit); \( \tau_0 \) is the pre-exponential factor (and is related to the nature of mechanism responsible for relaxation phenomenon); \( E \) is the activation energy of the relaxation mechanism; \( R \) is gas constant. The last eq. can be transformed to frequency domain as follows:

\[
 f_m = f_0 e^{\frac{E}{RT}} 
\]

where \( f_m \) is the peak loss frequency at temperature \( T \) and is related with characteristic time \( \tau \) as: \( f_m = 1/2\pi\tau \).

**B.6.3 Distribution of Relaxation Times Approach**

The actual dispersion behavior observed in most dielectric solids is usually quite different than that is predicted by the Debye equations. The \( \epsilon''(\omega) \) peaks are broader and do not reach the expected magnitude, and the dispersion of \( \epsilon'(\omega) \) occurs over a wider frequency range than expected. These differences from single-relaxation-time behavior are generally associated with the fact that in condensed phases the environments of different ions are not all identical. Even in crystals, the magnitudes of the interactions between ions and the thermal fluctuations are not identical throughout the medium at all times. Hence it seems reasonable that a distribution of relaxation times, \( G(\tau) \), distributed about the most probable relaxation time, is observed in experiments. This broader distribution can be characterized in terms of the superposition of Debye-like relaxation processes:

\[
\frac{\epsilon^*(\omega) - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \int_{-\infty}^{\infty} \frac{G(\tau/\tau_d)}{1 + i\omega\tau_d} d\ln(\tau/\tau_d) \]

where a normalized form \( G(\tau/\tau_d) \) is used for the distribution of relaxation times. This eq. may be represented graphically by the construction shown in Figure 1.18. It is evident that, within very wide limits, any sufficiently slowly varying function of frequency \( \epsilon^*(\omega) \) can be represented by eq. 1.43.
B.7 Empirical relationships to describe the complex permittivity

The evaluation of experimental data is much facilitated by certain graphical methods of display, which permit the derivation of parameters by geometrical construction. The earliest and most used of these methods consists of plotting \( \varepsilon''(\omega) \) for a certain frequency against \( \varepsilon'(\omega) \) at the same frequency, in cartesian coordinates or in the complex plane for the entire frequency range. It is often called Cole-Cole (CC) diagram. The CC plot provides an elegant method of finding out whether a system has a single relaxation time. This plot is also useful for the characterization of different types of distribution function, and is widely applied.

For a dielectric with a single relaxation time the CC plot is a semi-circle as shown in Figure 1.19. Cole and Cole\textsuperscript{107} also observed that the locus of experimental data often formed the arc of a circle having a center depressed below the \( \varepsilon''=0 \) axis and proposed that the data of this kind could be described empirically by a modified Debye equation.

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{(1-\alpha_\infty)}} \tag{1.44}
\]

where \( \alpha_\infty \) is a distribution parameter that characterizes the breadth of the relaxation time distribution and lies between 0 (infinitely broad distribution) and 1 (Debye’s single relaxation limit). This eq. is known as Cole-Cole (CC) equation.\textsuperscript{107} The plots of real and imaginary
parts of complex permittivity are symmetric about an angular frequency $\omega = 1/\tau$ (Figure 1.17). The corresponding functional form of the distribution of relaxation times is also found to be symmetric and centered about the value $\omega=1/\tau$.

Another empirical relationship describing some experimental dielectric relaxations was proposed by Cole and Davidson\textsuperscript{108} and is usually referred to as CD eq:

$$\epsilon^*(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \frac{1}{(1 + i\omega\tau)\beta_{CD}}$$ (1.45)

where $\beta_{CD}$ is asymmetric parameter and lies between 0 and 1. This eq. reduces to Debye eq. for $\beta=1$. The graphs of $\epsilon'$ and $\epsilon''$ are found to be asymmetric when plotted against $\ln \omega$. The maximum of $\epsilon''$ is now found for a value of $\omega$ larger than $1/\tau$ (Figure 1.17). The CC plot is also asymmetric (Figure 1.19) and is therefore often called a skewed arc.

Havriliak and Negami,\textsuperscript{109} gave the most general empirical relationship by combining the two above empirical relationships, which is now called Havriliak-Negami (HN) equation.

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \frac{1}{[1 + (i\omega\tau_0)^{1-\alpha_{HN}}\beta_{HN}]}$$ (1.46)

This eq. reduces to CC eq. and CD eq. depending on parameters $\alpha$ and $\beta$. The graphs of real and imaginary parts for HN equation are found to be asymmetric and broader than the corresponding Debye curves (Figure 1.17).
B.8 Universal Power Laws and Suggested Universalities

As discussed above, the dielectric loss for a Debye process shows a peak at \( \omega = \omega_p = 1/\tau \). The width of this peak at half height in the logarithmic presentation is found to be 1.144 decades in frequency. Such logarithmic plots for various empirical relationships are shown in Figures 1.20-1.23. The most noticeable feature of these diagrams is the demonstration of so-called universal power laws with fractional exponents\(^{106,110}\) (Table 1.1). It has been proposed that the dielectric response of all materials, both in frequency and time domain, is characterized by certain universal power laws. For the understanding of proposed universal laws, it is convenient to introduce two new parameters \( m \) and \( n \) which are related with the HN empirical parameters \( \alpha_{HN} \) and \( \beta_{HN} \) as follows:\(^{106}\)

\[
\begin{array}{c|c|c|c|c}
\text{Process} & \text{Functional form (frequency domain)} & \text{Functional form (time domain)} & \omega < \omega_p & \omega >> \omega_p \\
\hline
\text{Debye} & (1 + i \omega/\omega_p)^{-1} & e^{-\ell/\tau} & 2.0 & 1.0 \\
\text{Cole - Cole} & [1 + (i \omega/\omega_p)^{1-H}]^{-1} & (1-\alpha_{cc}) & 1.0 \\
\text{Cole-Davidson} & (1 + i \omega/\omega_p)^{B_{cd}} & & -2.0 & -1.0 \\
\text{Havriliak-Negami} & [1 + (i \omega/\omega_p)^{1-H}]^{B_{HN}} & (1-\alpha_{HN}) & 2.0 \\
\text{William Watts} & \sum_{n=1}^{\infty} \left[ \frac{[\Delta_n]}{(n-1)!} \left( \frac{\exp(-\Delta n/\tau)}{\omega^{\alpha_n}} \right)^n \right] & [\exp(-\Delta \tau)^{\beta}] & 2.0 & 1.0 \\
\end{array}
\]

\[
m = 1 - \alpha_{HN} \quad \text{and} \quad n = 1 - \beta_{HN}(1 - \alpha_{HN}) \quad (1.47)
\]

In these notations, HN equation can be rewritten as:

\[
\epsilon^* - \epsilon_{\infty} = (\epsilon_0 - \epsilon_{\infty}) [1 + (i \omega \tau)^m]^{(n-1)/m} \quad (1.48)
\]

with \( 0 < m, n < 1 \). In these notations, the Debye equation is seen as a limiting case of above equation for \( m=1 \) (\( \alpha_{HN} = 0 \)) and \( n=0 \) (\( \beta_{HN} = 1 \)). It can be shown easily that at sufficiently
Figure 1.20: For Debye equation (eq. 1.38) (a) typical plots of real and imaginary parts and (b) corresponding double logarithmic plots 1: log $\varepsilon''$ vs log $\omega$; 2: log ($\varepsilon' - \varepsilon_{\infty}$) vs log $\omega$ and 3: log ($\varepsilon_{0} - \varepsilon'$) vs log $\omega$. Note that slopes at limiting frequencies have different frequency dependence.

Figure 1.21: For Cole-Cole equation (eq. 1.44) (a) typical plots of real and imaginary parts and (b) corresponding double logarithmic plots 1: log $\varepsilon''$ vs log $\omega$; 2: log ($\varepsilon' - \varepsilon_{\infty}$) vs log $\omega$ and 3: log ($\varepsilon_{0} - \varepsilon'$) vs log $\omega$. 

39
Figure 1.22: For Cole-Davidson equation (eq. 1.45) (a) typical plots of real and imaginary parts and (b) corresponding double logarithmic plots 1: \( \log \varepsilon'' \) vs \( \log \omega \); 2: \( \log (\varepsilon' - \varepsilon_\infty) \) vs \( \log \omega \) and 3: \( \log (\varepsilon_0 - \varepsilon') \) vs \( \log \omega \).

Figure 1.23: For Havriliak-Negami equation (eq. 1.46) (a) typical plots of real and imaginary parts and (b) corresponding double logarithmic plots 1: \( \log \varepsilon'' \) vs \( \log \omega \); 2: \( \log (\varepsilon' - \varepsilon_\infty) \) vs \( \log \omega \) and 3: \( \log (\varepsilon_0 - \varepsilon') \) vs \( \log \omega \).
high frequencies, $\omega >> 1/\tau$, the above equation may be written as:

$$
\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty) [\sin(n\pi/2) - i\cos(n\pi/2)]\omega^{n-1}
$$

(1.49)

This equation suggests that at high frequencies $\varepsilon' - \varepsilon_\infty$ and $\varepsilon''$ have same frequency dependence, so that their ratio

$$
\frac{\varepsilon''}{\varepsilon' - \varepsilon_\infty} = \cot(n\pi/2)
$$

(1.50)

is independent of frequency. This can be seen clearly in Figures 1.21-1.23. It can also be noted from Figure 1.20 that this ratio is not frequency independent in the case of Debye as this ratio turns out to be $\omega \tau$ (eqs. 1.39 and 1.40). This is consistent as the Debye process corresponds to 'viscous' behaviour in which loss is always proportional to the angular velocity.

The low frequency behaviour for $\omega << 1/\tau$ is obtained from eq. 1.48 for small values of $\omega \tau$:

$$
\varepsilon_0 - \varepsilon' = ((\varepsilon_0 - \varepsilon_\infty)/m) (1 - n) \cos(m\pi/2)\omega^m
$$

(1.51)

and,

$$
\varepsilon'' = ((\varepsilon_0 - \varepsilon_\infty)/m) (1 - n) \sin(m\pi/2)\omega^m
$$

(1.52)

from which follows the relationship:

$$
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon} = \tan(m\pi/2)
$$

(1.53)

At this juncture, it is important to recall the property of the Fourier transform of fractional power laws which are as follows\textsuperscript{106}:

$$
\omega^m \rightarrow t^{-(1+m)} \quad \text{for } \omega << 1/\tau
$$

(1.54)

and,

$$
\omega^{n-1} \rightarrow t^{-n} \quad \text{for } \omega >> 1/\tau
$$

(1.55)
Figure 1.24: The demonstration of universal power laws in time domain (ref. 106). Note that at short times a logarithmic slope smaller than -1 is exhibited while at long times a steeper power law is obeyed. The exponential Debye response is also shown for comparison purpose.

Clearly, the above written power laws in frequency can be transformed to time domain using inverse Fourier transform as:

\[ I(t) \propto t^{-(1+m)} \quad \text{for } t \gg 1/\omega_p \]  

(1.56)

and,

\[ I(t) \propto t^{-n} \quad \text{for } t \ll 1/\omega_p \]  

(1.57)

so that these power laws determine the time-domain response of dipolar systems in which a loss peak is seen in the frequency domain. These power laws in time domain are shown in Figure 1.24. Similar universal laws in frequency and time domain have been proposed for the so-called low frequency dispersion where there is no loss peak but a continuously rising loss toward low frequencies is observed. This kind of loss is usually attributed to
slowly mobile ionic or electronic charges. It has also been proposed that similar power laws can also be applied to describe mechanical relaxation data and even to magnetic relaxation data for which much less experimental evidence is available. Most important characteristic of these power laws is that they are found to be relatively insensitive to the details of the structure and composition of the materials in question. However, the concept of 'universality' is not free from controversies and a few questions have been raised on its validity and any conclusions derived based on it.

**B.9 The Temperature Dependence of $\epsilon'$, $\epsilon''$ and $f_m$**

The dielectric permittivity is a complex function of at least two parameters namely frequency and temperature. The temperature dependence of dielectric loss for the Debye case can be obtained if we substitute eq. 1.41 into eq. 1.40, which if plotted against temperature for a particular frequency will show a peak. However, as we have discussed before most materials tend to deviate from Debye behaviour and the typical temperature dependence of real and imaginary parts of complex permittivity at a particular frequency can be seen in Figure 1.25. It is noticeable from Figure 1.25 that dielectric loss at a particular frequency shows peaks corresponding to different processes including secondary processes. Often the loss peaks corresponding to secondary processes are found to be broader than the corresponding primary peak showing large distribution of relaxation times. In another dielectric data representation, one plots the peak loss frequency $f_m$ ($f_m=1/(2\pi T)$) against inverse of temperature. In such a plot, single relaxation data is quite easily characterized by a linear curve as suggested by eq. 1.42. This kind of temperature dependence is usually called Arrhenius temperature dependence. However, as discussed above, most materials tend to deviate from Arrhenius temperature dependence. Vogel, Fulcher and Tammanns proposed the following relationship
to describe such non-Arrhenius temperature dependence.\textsuperscript{6,82}

\[ f_m = f_0 \exp \left( -\frac{B}{T - T_0} \right) \]  

(1.58)

This equation is called Vogel-Fulcher-Tammanns (VFT) equation. This equation can be obtained as an identity from the Adam-Gibbs theory which is based on a modification of conventional transition state theory to accommodate the notion that, in viscous liquid, the rearrangements over energy barriers must be cooperative. In VFT equation, the pre-
exponential factor is usually identified with the lattice vibrational frequency and the parameter $B$ is related with apparent activation energy $E$ of the process as $B = E/R$, where $R$ is gas constant. In VFT eq., $T_0$ is zero relaxation frequency temperature or equivalently the limiting glass transition temperature. However, there has always been a lot of dispute concerning the validity of VFT eq. Researchers have shown that particularly for fragile liquids there is a region at relatively high temperatures where VFT fits well but yields a $T_0$ that is considerably higher than $T_K$ and often is also larger than $T_g$ (which is physically meaningless).

Another popular empirical relationship to describe the temperature dependence of $f_m$ is given by\textsuperscript{66,80,93,94}:

$$f_m = A \left( \frac{T - T_g'}{T_g'} \right)^r$$

(1.59)

where $r$ is dynamic exponent while $T_g'$ is the limiting glass transition temperature. This equation is known as Power Law (PL) equation. The physical significance of parameter $r$ is still in debate but this equation is found to describe temperature dependence of $f_m$ for various systems very well.

C: REFERENCES


