PART II
CHAPTER I

INTRODUCTION

1. GENERAL

The term "Glass" describes a distinct state of matter, glassy or vitreous substances being defined by certain characteristic properties. They are included among amorphous materials, which is a general classification embracing all solids lacking the regular internal lattice structure characteristic of crystals. The regular arrangement of the particles (atoms or molecules) from which crystals are formed is indicated by the way in which x-rays are diffracted in sharply defined lines or spots by crystalline material. In contrast, the amorphous nature of glass is indicated by the scattering of x-rays in diffuse bands quite similar to the bands observed in liquids.

Besides the amorphous structure, both inorganic and organic glasses exhibit another characteristic property, the transformation (glass transition). Transformation of glass may be demonstrated on the diagram of temperature dependence of some physical property, for instance, specific volume [1]. When proceeding from the liquid state (Fig.1.1), with most substances one encounters solidification and crystallization at the melting point. Simultaneously the volume decreases abruptly, and becomes temperature-dependent according to a relationship which differs from that of the liquid state. A liquid capable of readily forming glass does not undergo any such abrupt change at the melting point. Below this temperature, it behaves as an undercooled liquid and its specific volume then decreases continuously (the metastable equilibrium range). After attaining a viscosity of the order of $10^{14}$ poise there appears a distinct deflection on the temperature-volume curve. Till this point, the given substance can be considered as a metastable undercooled liquid. At lower temperatures the substance is regarded as being in glassy or vitreous state, which is a non-equilibrium state. The transition from the undercooled liquid to the vitreous state is called transformation and the corresponding temperature is designated as
Figure 1.1: Dependence of specific volume on temperature for liquid, crystal and glass.
the transformation temperature. However, the temperature pertaining to the deflection mentioned above depends on the rate of cooling as indicated by Fig. 1: The lower the rate of cooling, the lower the temperature, and vice versa. For this reason, preference is given to the term transformation range within which the substance being cooled begins to exhibit properties characteristic of the solid state. Having chosen a certain standard rate of cooling, for instance 10°/min, one obtains the transformation point, designated as \( T_g \) in the literature.

The interpretation of this phenomenon is based on the assumption that the volume change of a glass on heating and cooling is the result of two independent phenomena. At temperatures below \( T_g \), i.e., as long as the glass is rigid, change of volume with temperature is considered to be a purely physical phenomenon comparable with the reversible thermal expansion of a crystal. At temperatures above \( T_g \), other "chemical" processes such as the dissociation of molecules or aggregates are superimposed over the "physical" process of expansion. In contrast to the physical part of the thermal expansion, which is an instantaneous process, the expansion resulting from chemical changes is time consuming. Chemical changes involve the inertia of masses, their diffusion and rearrangement in space. Consequently they require some time and can be "frozen in" by cooling the melt rapidly.

Most of the discussion on the structure of glassy materials is in terms of data from diffraction experiments using x-rays, electrons, neutrons or a combination of radiations. There are sophisticated techniques such as EXAFS (Extended X-ray Absorption Fine Structure), Electron Microscopy etc. in which one can probe the short-range structure of the glassy state directly. While it is necessary to know the structure of a glass, it is equally important to understand the nature of transformation from the liquid to glassy state, which has many implications on the properties of materials. The various diffraction experiments enable one to probe the structure of dynamically frozen (glassy) matter, but they do not provide any direct or indirect information on the molecular motion of a substance as it passes through the transformation regime. Glass forming systems, including viscous molecular, inorganic and amorphous liquids, exhibit relaxation and scattering phenomena in the transformation regime (glass transition region) which arise from the motion of molecules. Such phenomena are observed in a
variety of experiments including volume, enthalpy and specific heat relaxation, mechanical, dielectric and NMR relaxation, and light scattering. The experiments are performed in the time or frequency domains, yielding time relaxation functions or spectral lineshapes respectively.

2. THERMODYNAMIC STATE OF GLASS

A lot of studies have been made to verify the thermodynamic state of glass. For this purpose, the specific heat $C_p$ of the supercooled liquid and the corresponding crystal are measured [2-5], from which the corresponding entropies are calculated. It was noticed [2] that the glass had some extra entropy even at absolute zero temperature, which at one time appeared to be a violation of the third law of thermodynamics. This had led to a clarification [2] of the third law of thermodynamics. We know 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 the suggestion of a solution to what is now known as the Kauzmann paradox [6] which states that the excess entropy of a liquid would vanish at a temperature $T_k$ located at a few degrees below $T_g$ if the liquid is allowed to be in internal equilibrium. Subsequently, the temperature was identified with the temperature where the corresponding viscosity becomes infinite (very large) and hence, led to the speculation of an underlying second order transition at $T_k$ [7-10]. It has also been observed that systems which are more fragile have an imminent Kauzmann entropy paradox [8]. However, recent experiments [11] suggest that the supercooled liquid would approach a temperature somewhere between $T_g$ and $T_k$ if internal equilibrium is allowed. Hence $T_k$ need not be identified with an ideal glass transition temperature.

Adam and Gibbs [12] 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 inadequate. They proposed that instead, viscous flow occurs by increasingly cooperative rearrangements of groups of particles. Each rearrangeable group was conceived of as acting independently of other such groups in the system. But it was supposed that the minimum size of such an independent group would depend on the temperature. By evaluating the relationship between the minimum sized group
and the total configurational entropy of the liquid, Adam and Gibbs arrived at the relationship

\[ \tau = \tau_0 \exp \left[ \frac{\Delta h}{T S_c} \right] \]  

(1.2.1)

where \( S_c \) is the configurational component of the total entropy and \( \Delta h \) is the free energy barrier to be crossed by the rearranging group. It is clear that as long as the configurational entropy remains constant, Eq.(1.2.1) is just another form of the Arrhenius law. The importance of the equation lies in the fact that due to the increase of heat capacity at the glass transition, the configurational component of the total entropy will increase with temperature. This adds an additional temperature dependence to the exponential law. The next step is to determine the temperature dependence of \( S_c \). Formally, this is given by

\[ S_c = \int_{T_2}^{T} \frac{\Delta C_p}{T} dT \]  

(1.2.2)

where \( \Delta C_p \) is the configurational heat capacity and \( T_2 \) is identified with the Kauzmann temperature. For the temperature dependence of \( \Delta C_p(T) \), it is common to equate it with the difference between the liquid and glass heat capacities, on the assumption that this is totally configurational. This assumption has been challenged by Goldstein [13] who suggested that \( \Delta C_p \) has vibrational components and possible contributions from secondary relaxation. The temperature dependence of \( \Delta C_p \) is also uncertain as it is obtained by extrapolation. It is convenient to use the approximate hyperbolic form (such a term is the best simple description of the experimental behavior of \( \Delta C_p \) for many systems [14]):

\[ \Delta C_p = \frac{K}{T} \]  

(1.2.3)

where \( K \) is a constant. Inserting \( \Delta C_p \) in Eq.(1.2.2) and \( S_c \) in Eq.(1.2.1) one obtains an equation identical to that of the empirical Vogel–Tammann–Fulcher (VTF) equation i.e.,
\[
\tau_0 \exp \left[ \text{(constant)} \left( \Delta h/K \right) \frac{T_2}{(T - T_2)} \right] = \tau_0 \exp \left[ D \frac{T_2}{(T - T_2)} \right] \tag{1.2.4}
\]

The parameter D in Eq.(1.2.4) has been related to the fragility of liquids [15]. The term fragility was introduced by Angell in his classification of liquids [15], which is based on the stability of short-range and medium-range order against the temperature-induced degradation. He classified all the liquids as either strong or fragile. 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 \( T_g \). By contrast, 'fragile' liquids are those which lack such directional bonds and show a large change in the specific heat at \( T_g \). This classification becomes invalid for the hydrogen bonded systems as they are intermediate in their fragile character and exhibit a larger change in the specific heat at \( T_g \) than the fragile liquids. For the classification of liquids Angell used the modified Vogel-Tammann-Fulcher equation (Eq.1.2.4) in which viscosity data of various liquids (strong-fragile) could be fitted qualitatively well just by the variation of a single parameter (D). He argued that this parameter determines the fragility of liquids. It is interesting to note that the fragility is also related to the parameter \( \beta \) in Kohlrausch Williams Watts (KWW) function [16,17].

3. LINEAR RESPONSE REGIME

Since the approach to the glassy state is relaxational in nature a wide variety of relaxational techniques have been used to verify the molecular motion. Significant among them are dielectric relaxation [18-21], mechanical relaxation [18,19] and nuclear magnetic resonance (NMR) [18,19,22]. Due to inherent difficulties with mechanical relaxation measurements, this technique is mainly confined to polymers [18,19]. Recently, specific heat spectroscopy has also joined this group of techniques [23], though it is not sensitive enough to probe minor relaxations observed below \( T_g \). It has another drawback that its application is confined to lower frequencies. However, its strength is that it directly probes the structural (enthalpy) relaxation which has direct relevance to thermodynamics.
All the above techniques suggest a secondary relaxation (β-process) below \(T_g\) of a much smaller magnitude, in addition to the \(\alpha\)-relaxation above \(T_g\) (the kinetic freezing of which leads to glass transition phenomena at \(T_g\)) [24,25]. The β-process is observed in a wide variety of glasses leading to the speculation that it is connected to amorphous packing. In addition to this some other processes are observed at much lower temperatures [26,27]. All these processes resemble the multiple relaxations observed in polymers [18,19]. It appears that the origin of these processes is very vital to the understanding of the glass. Since the dielectric relaxation technique is used very widely, the technique is discussed in detail below.

The phenomenon of dielectric dispersion in materials containing polar molecules, and its nature was first demonstrated by Debye [28]. When an isotropic polar material is subjected to a static electric field the permittivity of the material which depends on dipole moment \((\mu)\) and their distortion polarizability \((\alpha)\) is called the static permeability (or static dielectric constant) and is denoted by \(\varepsilon_0\). Debye calculated an expression for dipolar polarizability, using Langevin's method to find the mean dipole moment parallel to an applied field of gas molecules having permanent dipole moments. Assumptions made in the derivation of this equation limits its applicability to gases or very dilute solutions of polar molecules. Onsagar [29] avoided one of the assumption made by Debye and found a relation between permittivity and dipole moment which could be applied to liquids.

Both Debye's theory and Onsager's might be considered semi-statistical in nature. They use a statistical argument in the calculation of dipolar polarizability, but use macroscopic arguments, based on a particular model of the dielectric, to obtain expressions for the local field. Kirkwood [30] and later Frohlich [31] obtained rigorous expressions for the static permittivity, using statistical methods throughout. They avoided the neglect of local forces which limits the validity of Debye's and Onsager's theories to fluids. Cole has also devised a theory of static permittivity [32], which is similar in many respects to the theories of Kirkwood and Frohlich, but differs from these in the treatment of distortion polarization.
In the above theories permittivity has been calculated for the case where the applied field is static. Much of the interest in the dielectric properties of materials is concerned with the frequency region where dispersion occurs. Debye gave a diffusive theory of dispersion [28] based on Einstein's theory of Brownian motion. He supposed that the rotation of a molecule due to an applied field is constantly interrupted by collisions with the neighbours, and that the effect of these collisions may be described by a resistive couple proportional to the angular velocity of the molecule. He also assumed that in the absence of an applied field the molecules must follow a diffusive law. With the assumption due to Lorentz for the local field, he derived the following expression for permittivity:

\[
\frac{\varepsilon^*-n^2}{\varepsilon_0-n^2} = \frac{1}{1 + \omega \tau}
\]

(1.3.1)

where,

\[
\tau = \frac{\varepsilon_0 + 2}{n^2 + 2}
\]

(1.3.2)

where \( n \), \( \varepsilon_0 \), \( \tau' \) and \( \tau \) are refractive index, static permittivity, microscopic relaxation time (relaxation time associated with an individual molecule) and macroscopic relaxation time (average relaxation time of the system) respectively. As is clear from Eqs.(1.3.1) and (1.3.2) the macroscopic relaxation time is in all cases longer than the microscopic relaxation time. This theory was later modified by Onsagar in which he avoided the assumption of the Lorentz field and derived an expression for permittivity \( (\varepsilon^*) \) which did not give the simple dependence of \( \varepsilon^* \) on \( \omega \) given by the Debye theory.

Among rate process theories of dielectric relaxation, Eyring's theory [33] has been quoted very widely. In his theory dipole rotation is treated by analogy with chemical rate processes. He begins by considering a chemical reaction of the type \( A + B \rightarrow C \). He assumes that for this reaction to take place \( A \) and \( B \) must first form an activated complex \( AB \) - for example, they might have to approach within a certain minimum distance of one another. To form this activated complex they must acquire a certain amount of energy and when it is formed they will react to form \( C \). When this model is applied to dipole rotation, it has to be
interpreted in the following way: The reaction co-ordinate is interpreted as an angular co-ordinate, the two states 'A+B' and 'C' as two different equilibrium orientations of the dipole, and the activated state AB as the state in which the dipole has sufficient energy to pass from one equilibrium position to the other over a potential barrier. Using the concepts of reaction rate Eyring derives an expression for microscopic relaxation time $\tau$ as

$$\tau = \frac{(h/kT) \exp(\Delta G^*/RT)}{1}$$

where $\Delta G^*$ is the free energy of activation. A more generalized rate theory was presented by Bauer [34] which is analogous to Eyring's reaction rate theory but refers explicitly to dipole rotation throughout. His results are quite similar to that of Eyring's reaction rate theory.

Many materials, particularly long-chain molecules and polymers, show a broader dispersion curve and lower maximum loss than would be expected from the Debye relationship. In such cases the $\varepsilon''$ versus $\varepsilon'$ curve falls inside the Debye semicircle. Cole and Cole [35] suggested that in these cases the permittivity might follow the empirical equation

$$\frac{\varepsilon^* - n^2}{\varepsilon_o - n^2} = \frac{1}{1 + (\omega \tau)^{1-\alpha}}$$

where $n$ is the refractive index and $\alpha$ is a constant, $0 \leq \alpha < 1$. The variation of the shape of Cole-Cole arc (this is a plot of $\varepsilon''$ versus $\varepsilon'$, where $\varepsilon''$ and $\varepsilon'$ are imaginary and real part of the complex dielectric constant) with $\alpha$ is shown in Fig.(1.2a). The value of $\alpha$ found experimentally show a tendency to increase with increasing number of internal degrees of freedom in the molecule, and with decreasing temperature. The Cole-Cole arc is symmetric about a line through the centre and parallel to $\varepsilon''$ axis. Cole and Davidson [36] found that the experimental results for certain materials do not have this symmetry and the $\varepsilon''$ versus $\varepsilon'$ plot (Cole-Cole plot) is a skewed arc. They suggested that behavior of this kind could be represented by an empirical equation.
Figure 1.2: (a) Cole-Cole diagram corresponding to Eq.(I.3.4) for $\alpha=0$ (Debye semi-circle) and $\alpha \neq 0$; and (b) Cole-Cole diagram corresponding to Davidson-Cole equation (Eq.I.3.5) for $\beta=1$ (Debye semi-circle) and $\beta \neq 1$. 
where $\beta$ is a constant, $0 < \beta \leq 1$. Fig.(1.2b) shows the Cole-Cole plot of Eq.(1.3.5). This equation has been very successful in representing the behavior of liquids at low temperatures. For, $\beta \rightarrow 1$, it reduces to the Debye equation. The Cole-Cole and Cole-Davidson types of behavior can be understood as arising from the existence of a continuous spread of relaxation times, each of which alone would give rise to a Debye type of behavior. The depressed Cole-Cole arc would arise from a symmetrical distribution of relaxation times, while the Cole-Davidson arc would be obtained from a series of relaxation mechanisms of decreasing importance extending to the high frequency side of the main disperson.

Havriliak and Negami [37] found a number of polymeric systems whose data could not be fitted to either Cole-Cole equation or Davidson-Cole equation. They suggested a very general empirical relation for the permittivity which incorporates both the equations. This equation is used to analyse the data and will be discussed in detail in subsequent chapters.

Recently, Ngai and co-workers [38] have developed a coupling scheme based on Adam Gibb’s theory for relaxation in complex systems in which they use a master equation of the type

$$\frac{d\phi(t)}{dt} = - \omega(t) \phi(t)$$

(1.3.6)

where $\phi(t)$ is relaxation function which is unity at $t=0$ and goes to zero monotonically for $t=\infty$. Such an equation with $\omega(t) = bt^{-\beta}$ was first used by Kohlrausch [39] and later Williams and Watts [40,41] used the same equation in frequency domain. In the integrated form it reduces to

$$\phi(t) = \exp - (t/\tau_0)^\beta$$

(1.3.7)

By taking a different kind of time dependence of parameter $\omega(t)$ in Eq.(1.3.6) Ngai et.al. derived a very general relation for $\phi(t)$ of which Eq.(1.3.7) is a special case. In addition, there are also suggestions of a power law in the

\[
\frac{\varepsilon^* - n^2}{\varepsilon_0 - n^2} = \frac{1}{(1 + i\omega\tau)^\beta}
\]
asymptotic regimes [41] and scaling behavior [42].

3. MODE COUPLING THEORIES (MCT)

As a system approaches glass transition temperature its viscosity and corresponding structural relaxation time increase very rapidly implying that the rearrangements of the atoms among various configurations become slower and slower. These rearrangements are directly related to fluctuations in the local density of the system. The detailed information about the time dependence of structural rearrangements is therefore contained in the density-density correlation function or relaxation function. Mode coupling theories (MCT) [44-46] are based on various correlation functions which are obtained from generalized hydrodynamic equations. It is an effective-medium theory in which simultaneous treatment of relaxation and vibration effectively places molecules in 'cages' formed by the surrounding molecules. This leads to high frequency motion based on a frequency-dependent 'deformability' of the cages, and a gradual transition to diffusional motion at low frequencies. Frequency dependent relaxation effects are generated through frequency dependent friction terms arising from the interactions with the neighbouring molecules. Mathematically, one can consider a density-density correlation function. The fluctuations in the correlation function relax through a current-current correlation function, which is itself dependent on the density correlation function through a relaxation kernel. Thus, a closed set of non-linear equations is obtained. They are then solved under various assumptions for the relaxation kernels which are expressed in terms of correlators. Some important predictions of the mode coupling theories can be summarized as follows:

(a). Temperature independent structure of the primary relaxation peak (also known as α-process) (time-temperature-superposition) at higher temperature is obtained.

(b). A secondary relaxation peak (also known as β-process) is found which is wider and more symmetric than the primary relaxation peak and has general physical origin in a different time scale.

(c). A convergence of the time of α- and β- peaks at high temperature.

(d). An ergodic to non-ergodic transition at $T_c$ where viscosity has risen roughly five orders of magnitude over its high temperature value.

(e). A power law divergence in the hydrodynamic viscosity at $T_c$, which is masked if hopping processes are included.
A specific scaling in the region between $\alpha$- and $\beta$-relaxation peaks.

However, recent measurements [47,48] suggest that the MCT is more a theory for liquids than for supercooled liquids. The $\beta$-relaxation quoted in the MCT does not appear to be the same $\beta$-process talked about in dielectrics [49].

The difficulty in understanding the diverse relaxation phenomena in molecular terms is that the different experiments probe different aspects of molecular motion, and different probes are involved in those experiments. The theory of molecular relaxation leading to diffusion, orientational relaxation and light scattering has been described in terms of molecular time-correlation functions [50,51]. The mathematical relationships between measured quantities such as volume, specific heat, complex dielectric permittivity and the molecular time correlation functions for the translational and reorientational motions of molecules are extremely complicated and may involve several auto-correlation and cross-correlation functions for a given experimental method [50]. Thus it is difficult to obtain information on the dynamics of individual molecules, side groups or chain segments because there are usually too many unknown quantities. Therefore, it is desirable to study model systems where the molecular probe is well defined and where the basic mechanism which leads to the behavior of the measured quantity is known. Dielectric relaxation spectroscopy is one such technique in which rotation of polar molecules or group or segment is probed by measuring the complex dielectric permittivity and has been used extensively by physicists and chemists for more than a hundred years. The aim of this part of the thesis is to study the various relaxations occurring in glass forming liquids both above and below glass transition, using dielectric and calorimetric techniques.
REFERENCES