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The phenomenon of glass transition*

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Abstract. Principal features of glass transition phenomenon are summarised. Various theoretical approaches such as free volume, entropy, energy surface, etc., have been briefly discussed.

1. Introduction

Many materials when cooled from their molten state do not crystallise to their parent crystalline phases at the thermodynamic melting temperatures. Such melts easily supercool to much lower temperatures than T_m, the melting temperature and congeal to solids without any attendant discontinuous changes in volume or entropy. These solids which are isotropic in all their physical properties are known as glasses. While some melts like those of SiO_2, B_2O_3, etc., become glasses even on slow cooling, melts of mixed nitrates of potassium and calcium, mixed sulphates of potassium and zinc, As_2Te_3, etc., require rapid cooling from their normal melting temperatures in order to form glasses. Melts of metals like iron and cobalt (with upto 20% silicon or phosphorus) require very much higher ($\sim 10^6$ deg sec^{-1}) quenching rates in order to form glasses (Owen 1973). Now it appears that almost any melt can be quenched into a glass at sufficiently fast rates of quenching (Turnbull 1969).

Glasses as a class are forerunners of amorphous solids. They are x-ray amorphous (Warren 1937) and give rise to haloes in Laue photographs and are structurally similar to other amorphous solids such as thin films, gels and amorphous deposits from shock and shear amorphised solids. However glasses are distinct in that they exhibit a pseudo-second order transition at a temperature known as glass transition temperature, T_g (MAB 1968). When heated sufficiently slowly, most glasses crystallise between T_g and T_m and the crystallisation temperature is often designated as T_{cr}. Both T_g and T_{cr} are easily characterised in a sensitive differential thermal analysis (DTA) experiment. A thermogram is shown schematically in figure 1.

In this brief review some salient features of glass transition are first presented followed by brief discussion of various theoretical approaches reported in the lite-

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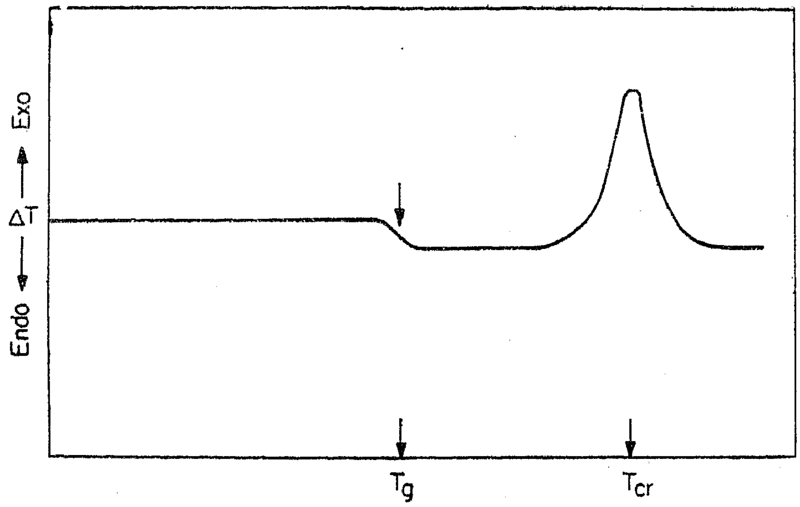

Figure 1. Differential thermogram of a typical glass (schematic).

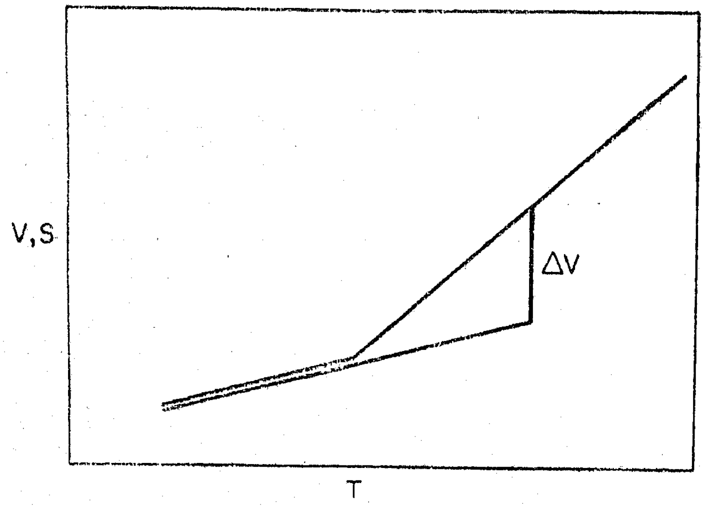

Figure 2. Variation of volume and entropy of a glass with temperature (schematic).

rature. Many details in each of these approaches have been left out since they may not substantiate the principal features of the theory. It is likely that the emphasis given in this review and that expressed in the source literature are not the same. But it may be noted that summaries of this nature often reflect author's preferences.

2. General features of glass transition

When a glass forming melt is cooled, the volume and entropy of the materials change in a manner schematically shown in figure 2. A similar plot is given in figure 3 depicting the nature of variations of heat capacity, C_p, thermal expansivity, a and compressibility, β. While S and V vary continuously there is a more or less sudden change in C_p, a and β, indicating that the glass transition is probably a second order transition in the Ehrenfest (1933) sense (Rao and Rao 1978).

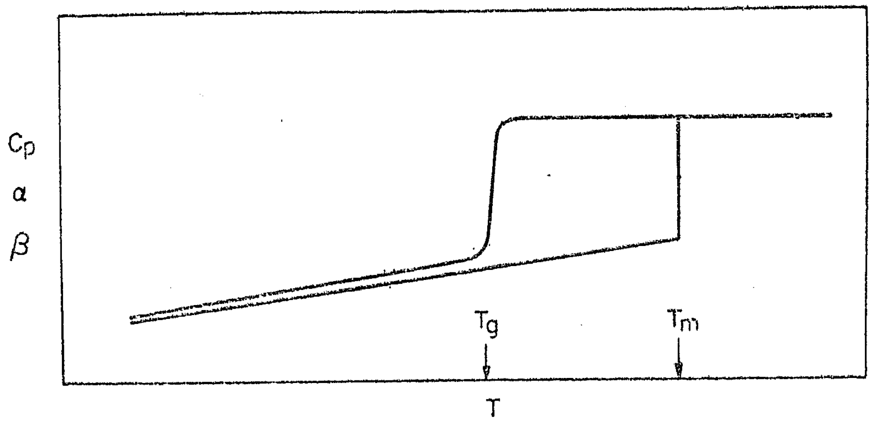

Figure 3. Variation of heat capacity, thermal expansivity and compressibility of a glass as a function of temperature (schematic).

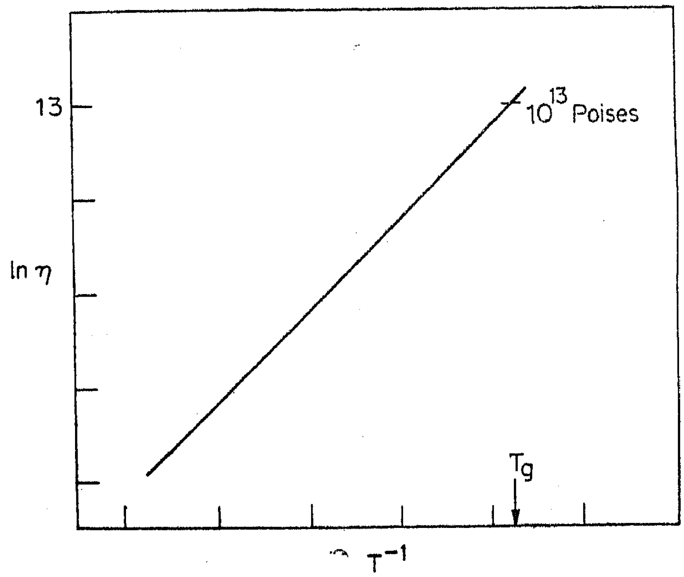

Figure 4. Variation of logarithm of viscosity of a glass forming melt as a function of inverse temperature (schematic). T_g corresponds to η of approximately 10^{13} poises.

The glass transition temperature is sensitive to the cooling rate particularly in the transition region. In figure 4, the variations of volume at different cooling rates have been shown for typical glass forming materials. The viscosities for such melts vary with temperature as shown in figure 5. Since close to the glass transition temperature, the viscosities are very high, the relaxation times also become very high. Therefore the melt takes more time to readjust its volume to its new equilibrium value. (It may be noted that in the supercooled region, the melt is really in metastable equilibrium.) With fast quenching rates, they fall out of equilibrium. Since viscosities of the order of 10^{13} poises correspond to relaxation times of the order of minutes $(\eta = G\tau)$ for reasonable values of shear moduli, the viscous (supercooled) liquid behaves like a solid for all practical purposes. Such a solid is known as glass. Hence it appears that the transition to a glass is essentially a

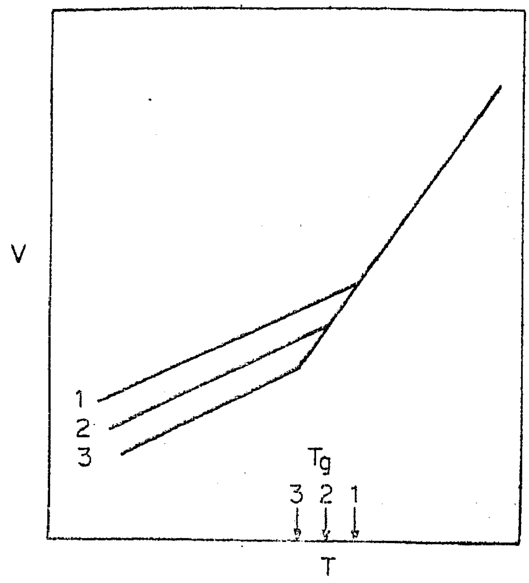

Figure 5. Effect of cooling rate on volume of the glass and hence on T_g, cooling rates for 1, 2, 3 are in decreasing order. Thus $T_g(1) > T_g(2) > T_g(3)$.

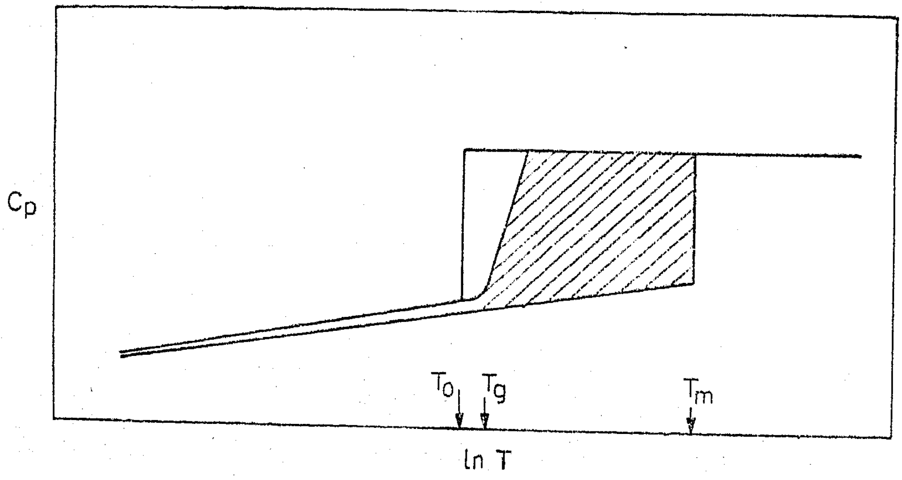

Figure 6. Variation of C_p as a function of ln T. The shaded area corresponds to the configurational entropy lost on cooling down to T_g. The unhatched area corresponds to the frozen entropy.

relaxational phenomenon and that the glass is an aberration for the supercooled melt which has fallen out of equilibrium.

The above picture of glass transition changes when we carefully examine the behaviour of heat capacity and entropy of such systems. A plot of C_p vs ln T is given in figure 6. The shaded area in the figure corresponds to the total entropy loss when the melt is cooled. Slower and slower cooling shifts the T_g to lower and lower values, increasing the area of the shaded portion. However the total shaded area cannot exceed the value of entropy gained by the system at its melting temperature. That is, as shown in figure 7, the extrapolated entropy line of the liquid cannot cross the entropy line corresponding to the crystal, because it amounts

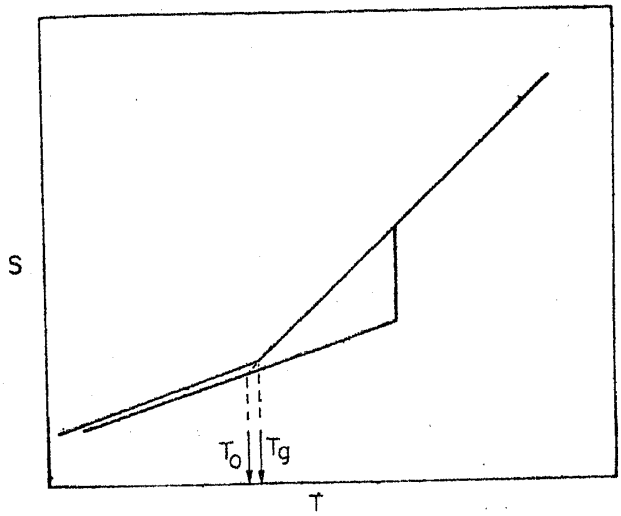

Figure 7. The limiting T_g value based on thermodynamic considerations (S vs T) is T_0 at which the extrapolated entropy line of the melt intersects the entropy line of the crystal (schematic).

to having a supercooled disordered arrangement of particles with a lower entropy than the corresponding ordered crystalline arrangement. Hence it was argued by Kauzmann (1948) that the nature averts it by a transition to a solid which is glass (the self-contradictory situation that would arise below the limiting T_g is also referred to as Kauzmann Paradox). Therefore there is a limiting T_g at which the supercooled melt undergoes a glass transition.

Supporting the thermodynamic viewpoint is the fact that in a very large number of systems involving different bonding types and molecular complexity, T_g scales as T_m or T_l (the liquidus temperature in the case of mixed melts) with constant ratio, $T_g/T_m \sim 0{\cdot}66$ (Sakka and Mackenzie 1971). Evidence to the fact that there is a limiting temperature below which liquid-like properties do not exist comes from various transport property measurements. Viscosities (η), diffusion coefficients (D) and (ionic) electrical conductivities (Λ) of many ionic melts exhibit departures from Arrhenius behaviour and their temperature variations are more appropriately described as (Angell and Moynihan 1969; Angell 1968)

$$\psi = \psi_0 \exp\ [-E/(T - T_0)], \tag{1}$$

where ψ is ϕ ($= 1/\eta$), D or Λ and ψ_0 is their infinite temperature values (ψ_0 is mildly temperature dependent as expressed above). Therefore T_0 is appropriately the temperature corresponding to the termination of liquid regime. It is close to and always less than T_g. Hence a limiting T_g corresponding to the lower bound to liquid state is likely to exist and has a thermodynamic origin.

It may be pointed out that the non-Arrhenius viscosities have often been analysed using the well-known Vogel-Tammann-Fulcher, VTF, equation (Vogel 1921; Tammann and Hesse 1926; Fulcher 1925) and the Doolittle (1951) equation which have the following form :

$$\text{VTF :} \qquad \eta = A\ \exp\ [a/(T - T_0)], \tag{2}$$

$$\text{Doolittle :} \qquad \eta = A\ \exp\ [V/v_f], \tag{3}$$

where a is a constant with units of temperature, v_f is free volume and V is constant in units of volume, Williams *et al* (1955) employed a modified expression based on equation (2) and established its correspondence to equation (3). Equation (1) is only a more general form of (2). Further, Angell and coworkers (Angell and Moynihan 1969; Easteal and Angell 1970, 1972; Angell and Helphrey 1971; Moynihan *et al* 1969) have shown that T_0 of eq. (1) and the limiting T_g found from figure 6 type of plots (Kauzmann plots) are in very good agreement, supporting the view that T_0 is a thermodynamic feature of the liquid state.

Hence, any theory of glass transition has to account for the thermodynamic character of T_g and still be able to rationalise the relaxational nature of it. Several of the theoretical approaches to glass transition have thus been theories or models for liquid viscosity involving thermodynamic quantities.

3. Theories of glass transition

3.1. *Free volume theory*

The transport properties of liquids have long been successfully discussed in terms of free volume (Doolittle 1951; Williams *et al* 1955). But the most successful development of the free volume theory has been due to Cohen and Turnbull (1959) and Turnbull and Cohen (1961, 1970). In this model which was originally developed for dense hard sphere fluids, particles are assumed to be oscillating in their own cages corresponding to their Voronoi polyhedra. Increased temperature has the effect of increasing the cage volume and as a result, the oscillatory motions of particles become diffusive (the diffusive motion having gas kinetic velocities). The additional volume of the cage permitting the diffusive motion is free volume. The total free volume of an ensemble of particles is randomly distributed over the cages. The diffusive motion is responsible for the event of transport. It is assumed that there exists a minimum free volume v for the transport to occur. The size distribution function $[P(v)]$ for the free volume is shown to be

$$P(v) = \gamma/v_f \cdot \exp\ (-\gamma v/v_f), \tag{4}$$

where γ is a free volume overlap correction constant, with a numerical value between 1/2 and 1 and v_f is the total free volume. The diffusion coefficient D may be derived as

$$D = gu \int_{v^*}^{\infty} a(v)\, P(v)\, dv, \tag{5}$$

where g is geometrical factor, u is the gas kinetic velocity in the direction of the jump, $a(v)$ characteristic jump distance and v^* is the minimum size of the void (distributed free volume) which permits the diffusive motion. Since D is related η by the relation

$$D = (k/3\pi a_0) \cdot T/\eta, \tag{6}$$

where a_0 is the molecular diameter, one can combine (4), (5) and (6) to obtain,

$$\eta = (kT/3\pi a_0 a^* gu) \cdot \exp\ [\gamma v^*/v_f]. \tag{7}$$

Equation (7) suggests that as v_f decreases the viscosity increases exponentially and the transport is severely curtailed. The diffusive nature of particle motion becomes more and more oscillatory. The empirical Doolittle and VTF equations (2) and (3) may be recovered from (7) by substituting for v_f. One plausible assumption is that $v_f \cong v_l - v_g \simeq \triangle a (T - T_g)$ where v_l is the volume of the melt at the temperature T and v_g that of the glass at T_g. However theoretical evaluations were carried out with v_f taken as the difference between the total volume and the dense random close packing volume.

The essential simplicity of the approach has lent free volume theory an undiminishing attraction. Many features of glass transition where a complete quantitative agreement is not needed are easily understood in terms of free volume theory. The use of v_{DRP} has been found to fit shear viscosities of liquids only at higher temperatures and leads to considerable discrepancies at lower temperatures. Further, high pressure studies of both viscosities and transition temperatures indicate that free volume model has been far from being correct (Goldstein 1963; O'Reilly 1962; Sperry and Mackenzie 1968; Macedo and Napolitano 1968). In cases like acetate glasses (Williams and Angell 1973) where $\triangle a$ is negative close to the transition temperature, free volume concept itself suffers a major setback.

3.2. *Entropy theory*

One important feature of the molten state is its large entropy, a large part of which is acquired discontinuously at its melting point. This acquired entropy is likely to be mostly configurational. In the entropy theory, transport is conceived to be a local cooperative rearrangement of particles into different configurations which contribute to the configurational entropy (Gibbs and DiMarzio 1958; Gibbs 1964; Adam and Gibbs 1965). As the temperature of the melt is lowered, the configurational entropy decreases and larger number of particles in the system are involved in cooperatively achieving configurational changes thus enabling a transport event to occur. At a sufficiently low temperature, the configurational entropy becomes zero leading to a second order transition to an ideal glass. However in real situations the intervention of kinetic solidification leads to glass transition at which part of the configurational entropy is frozen in.

For a group of z molecules which allows a configurational rearrangement, the transition probability $\omega(T)$ is given by (Adam and Gibbs 1965)

$$\omega(T) = A \exp\,[- z \triangle\mu/kT], \tag{8}$$

where $\triangle\mu$ is essentially the potential energy hindering rearrangement. In order that at least one rearrangement is possible there must be some minimum size of the rearranging unit which may be designated as z^*. Considering all such clusters which can yield nonzero transition probabilities, the average transition probability may be obtained as,

$$\bar{\omega}(T) = \bar{A} \exp\,(- z^* \triangle\mu/kT). \tag{9}$$

In the theory z^* is now related to the total configurational entropy S_c as $z^* = Ns_c^*/S_c$, where s_c^* is the entropy of the minimum or critical size z^* (it cannot be less than $k \ln 2$). Using the known relation between τ and $\bar{\omega}(T)$ and η and τ, Adam and Gibbs derive the expression for η as

$$\eta = A' \exp\,[B/TS_c], \tag{10}$$

where $B = (Ns_c^* \triangle \mu/k)$. Equation (10) has an important implication in that it leads to a definition of a glass with zero configurational entropy. It corresponds to an ideal glass with a defined ground state. At $T = T_0$ where $S_c = 0$, a second order transition, in the Ehrenfest sense, takes place. However, as pointed out earlier, the available configurations decrease rapidly close to T_0 and a kinetic freezing takes place leading to the glass transition and the resulting glass retains a part of the configurational entropy as frozen entropy. Once again the VTF equation (2) may be derived from (10) making the assumption,

$$S_c = \int_{T_0 \sim T_g}^{T} \triangle C_p \, d \ln T$$

where $\triangle C_p = C_p$ (liquid) $- C_p$ (glass/crystal) $\approx$ a constant.

The success of the entropy theory has been its ability to account for the pressure dependence of the glass transition temperature (Goldstein 1963, O'Reilly 1962) and to account for the second order nature of the transition. But it may be noted that whenever the configurational entropy is a simple function of the free volume only, both the free volume and entropy theories should be expected to give same results. Experimentally one observes that a certain fraction of the free volume is frozen in and so is a certain portion of configurational entropy. We may call these frozen quantities as (minimum) excess free volume V_e and (minimum) excess entropy S_e.

If the occurrence of the experimental glass transition is determined by either V_e or S_e, it is possible to evaluate the merits of the two theories as follows (Goldstein 1963). Since V_e and S_e are fixed at T_g, we have $dV_e = dS_e = 0$ and both V_e and S_e can be treated as functions of pressure and temperature. When dV_e is zero, it is possible to show that

$$dT_g/dP = \triangle\beta/\triangle\alpha \tag{11}$$

and when $dS_e = 0$, we obtain similarly,

$$dT_g/dP = VT_g \triangle\alpha/\triangle C_p. \tag{12}$$

Since (11) and (12) involve all experimental quantities only, they can be used to evaluate the two theories. If they are equivalent, then

$$VT_g \, \triangle\alpha^2/\triangle\beta \, \triangle C_p = 1, \tag{13}$$

which is the well-known Prigogine-Defay ratio (Prigogine and Defay 1954). The experimental data (O'Reilly 1962) on various substances like polyvinyl acetate, rubber, glycerol, propanol, selenium, B_2O_3 and various other materials indicate that equation (12) holds better than (11) suggesting that the entropy theory is more accurate. But in the case of $ZnCl_2$ glass it has been found that (12) also leads to large and unacceptable discrepancy (Angell *et al* 1977b).

3.3. *Significant structures approach*

Another attempt to understand glass transition phenomenon from a theory of viscosity has been made by Eyring and coworkers (Ree *et al* 1962; Faerber *et al* 1970). In their significant structures approach, the total partition function of the liquid is taken as a product of solid-like and gas-like contributions. Then the viscosity is obtained from the activated complex theory and the contribution to viscosity from gas-like part is ignored. The final working expression for the viscosity of a system of rigid spheres is of the form

$$\eta = AT^{1/2}/(V - V_s) \cdot \exp\,[\epsilon^{\ddagger}/kT], \tag{14}$$

where A is a constant involving the free distance between nearest neighbours, mass of the particle and a constant transmission coefficient. V and V_s are the total volume and the solid-like part of the liquid volume. $\epsilon^{\ddagger}$ is the activation energy for jump of a molecule. Using the isoviscosity (rheological) criterion for glass transition, namely, that at T_g the value of $\eta \sim 10^{13}\,P$, the values of T_g have been evaluated. In the homologous series of substituted benzenes, the T_g evaluations were found to be good. Considering that T_g is initially used to evaluate V_g, the glass volume, and that it involves many other assumptions, this approach is both weak and its success is only moderate. Further, the approach inherits all the limitations of free volume theory in so far as it relates the viscosity to excess volume and incorporates the concept isofree volume at glass transition.

3.4. *Bond-Lattice model*

Since glasses are disordered solids, it should be of interest to view glass transition as a feature of the amorphous solid state. Such an approach has been made in the bond-lattice model (Angell and Rao 1972). Most glasses have a local order akin to the order in respective crystalline phases. The constituent particles may be looked upon as connected to the nearest neighbours but not ordered over long range. Therefore, it should be possible to abstract a lattice of bonds from such arrangement. These bonds may be of any description (covalent, etc.) including secondary bonds. (The long range interactions do not enter the description specifically.) This abstracted lattice of bonds is similar to Polk Turnbull (Polk 1971; Turnbull and Polk 1972) lattice of amorphous germanium. When the glass is heated the thermal energy excites these bonds and are said to be broken. The quantum of energy changes in the excitation process is $\triangle E$/mole. The excitation is associated with slight rearrangement and change in volume, $\triangle V$/mole, and also with vibrational frequency changes causing entropy change, $\triangle S$/mole, of broken bonds. The excitation is assumed to be random. For this simple case of one excited state, the fraction of bonds broken (f) and the corresponding configurational heat capacity ($\triangle C_p$) are given by

$$\begin{aligned} f &= [1 + \exp \triangle G/RT]^{-1}, \\ \triangle C_p &= (\triangle H^2/RT^2) f(1 - f). \end{aligned} \tag{15}$$

Variation of $\triangle C_p$ with temperature does not exhibit any singularity but shows an asymmetrical hump-like rise in heat capacity. The value of $\triangle C_p$ is dependent on $\triangle S$ while the peak temperature (the T_g in this approach) is determined by $\triangle H$. The two-state model does not however give rise to sufficiently steep rise of $\triangle C_p$. The authors have improved on this by (i) considering a large number of excited states and (ii) by allowing a part of the excitation enthalpy, $\triangle H$, to vanish co-operatively as a function of temperature. Introduction of n excited states leads to a configurational heat capacity, $\triangle C_p\,(n)$

$$\triangle C_p\,(n) = \sum_{i=1}^{n} \triangle H_i^2/RT^2\, f_i(1 - f_i) - 1/RT^2 \sum_{i,j=1}^{n}{}' \triangle H_i \triangle H_j f_i f_j$$

where $f_i = \exp(-\triangle G_i/RT)\,[1 + \sum_{i=1}^{n} \exp(-\triangle G_i/RT)]^{-1}$. (16)

The *n* state model does sharpen the heat capacity increases but is not sufficient to simulate the real transition behaviour. Alternatively $\triangle H$ may be considered as a sum of two parts, $\triangle H = \triangle H_1 + \triangle H_2$. Further $\triangle H_2$ may be treated as a co-operatively vanishing term with the following heuristically chosen functional form

$$\triangle H_2 = \triangle H_2^0/\{1 + \exp[(T - T_r)/D]\}. \quad (17)$$

Then $\triangle C_p$ may be given any arbitrary sharpness so as to very closely simulate the experimental glass transition. In the above expression $\triangle H_2^0$ refers to the maximum value of this enthalpy (at 0 K) ; T_r and D are adjustable parameters. The idea of cooperativity used here is unconventional. It is understandable however that as temperature increases, a few secondary bonds get broken (such as H-bonds in glassy water), the strains in primary bonds (responsible for cohesion and not necessarily regidity) relax and strengthen while the energies of the remaining secondary bonds decrease to a new constant value. But there has been no direct evidence to this effect. The concept of cooperativity in glass transition has been questioned (Goldstein 1973) and alternate methods of attaining arbitrarily sharp rise in $\triangle C_p$ has been suggested (Goldstein 1972). Use of two adjustable parameters in the exponent of (17) makes the approach weak. Further, many categories of amorphous materials such as thin films, amorphous deposits, etc., for which this theory should be applicable do not exhibit glass transition. The model has however been employed with a degree of success for water and $ZnCl_2$ (Angell 1971; Angell and Rao 1972). But it may be recognised that solid state approach to glass transition phenomenon is beset with many conceptual difficulties regarding both the nature of the bonds of relevance (Rao and Mohan 1979) and their mutual interactions. The bond lattice model, however, emphasises the fact that the glass transition may not be a second-order transition at all in the Ehrenfest sense.

3.5. *Theory of potential energy surfaces*

Goldstein, whose contribution towards critical assessment of glass transition theories is monumental has himself proposed a model for viscous liquids (Goldstein 1969). In this model the $(3N + 1)$ dimensional energy surface of N particles possesses a number of minima; the system moves among these minima in time. At lower temperatures the system is restricted to explore the deeper minima which are fewer in number and hence a lower configurational entropy. The glass transition apparently corresponds to the system being trapped into one of these deep minima. In this theory, most importantly, the activation energy is temperature-dependent. The theory predicts that below the glass transition temperature there must be frozen 'islands of mobility' which are responsible for secondary relaxations (subglassy relaxations), which are now known experimentally to be almost a universal feature of glassy state (Johari and Goldstein 1971; Goldstein 1976, 1977). But such relaxations could possibly be accounted for from other models also (such as frozen regions of broken bonds, etc.). The theory does not permit quantitative evaluation in any manner.

4. Computer experiments and glass transition

Some of the most fascinating and crucial results have been obtained from computer simulation experiments. Both types of investigations namely—Monte-Carlo (MC) (Lee *et al* 1973) and Molecular Dynamics (MD) (Briant and Burton 1975; Rahaman *et al* 1976; Woodcock *et al* 1976) simulations have been performed on model systems of particles interacting with diverse types of model potentials (hard spheres, Lennard–Jones, Born–Mayer, etc.). One of the limitations of the approach is that even when very advanced computers and liberal research funding are available, one cannot cool the system at a rate lower than 10^{10} deg K/sec ! (Woodcock *et al* 1976; Angell *et al* 1977a). This rate of quenching is orders of magnitude greater than the fastest quenching known in the laboratory. The quenched systems in the computer experiments clearly indicate a glass transition. The T_g is anywhere from $0 \cdot 3\ T_m$ to $0 \cdot 7\ T_m$. In spite of such fast quenching the radial distribution functions obtained from the MD experiments are remarkably close to the experimental radial distribution functions (from scattering studies).

Using the data of Rahaman *et al* (1976), Gordon *et al* (1976) came to the conclusion that for the hard sphere and Lennard-Jones glasses, the configurational entropy does not tend to zero at the glass transition, a conclusion quite different from that of entropy theory discussed earlier.

Computer experiments with soft potentials have revealed (Hoare 1976; Hoare and Barker 1977) that stable amorphous packings with a central symmetry are formed which are quite large when compared to icosahedral (Frank 1952; Hoare and Pal 1972) or pentkidodecahedral (Tilton 1957) units. The importance of pentagonal symmetry in liquid structural models has been known through earlier classic work of Bernal (1960, 1964). But large enough units with an internal (short range) order which allows for a distinct 'connective tissue' are required for glass structures. They had only been postulated with such descriptions as 'amorphon' (Grigorovici 1969), 'Vitron' (Tilton 1957), etc., to account for the structure of viscous liquids. From the above computer experimental results, Hoare and Barker (1977) have supported a model for glass transition originally suggested by Tammann (1933). In this model large rigid clusters with inherent, self-limiting, pentagonal symmetries are formed in the liquid and grow randomly in the supercooled region. The glass transition corresponds to a 'congelation' and locking together of these clusters into a rigid structure. Sharply differentiated regions with limiting sizes lead to sharp glass transition. In the heating cycle the transition manifests because of the surfacial melting of these clusters.

Invoking clusters, or rigid and ordered but small structural units, has been a phenomenological input in the development of many a model for the glass structure. Computer experiments have confirmed that such clusters of substantial sizes and with inherent pentagonal symmetries are spontaneously generated. The connective tissue which is therefore a common feature of glasses can also be the source of weak secondary relaxations observed in many glasses (Goldstein 1977).

5. Epilogue

Glass transition is now recognised as a sufficiently well-defined phenomenon (Hoare and Barker 1977) exhibited by a wide variety of glass formers. However none of the models discussed above constitutes a theory of glass transition in the real sense of the term. Many important and useful glasses are much more complex in their chemistry and nature of bonding. Glass structural models will have to give due importance to the chemistry and structure of the parent crystalline materials. Polymorphism associated with parent crystalline phases (Goodman 1975) may play an important role in the structure and stability of the clusters. It has been pointed out (Ramaseshan 1978) that silica glass exhibits optical anomalies around 840 K at which temperature the parent crystalline (quartz) phase has a well-known transformation.

Hence the first important step in understanding glass transition is development of suitable structural model for glasses which is as general as possible from which their temperature behaviour may be hopefully derived. A complete understanding of glass transition phenomenon may therefore remain elusive till such times.

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