The Glass Transition: Salient Facts and Models*

By R. Parthasarathy, K. J. Rao, and C. N. R. Rao†
SOLID STATE AND STRUCTURAL CHEMISTRY UNIT, INDIAN INSTITUTE OF SCIENCE, BANGALORE-560012, INDIA

1 Introduction

Glasses constitute a class of amorphous solids prepared by melt-quenching and are distinguished by the unique transition, the so-called glass transition, that they exhibit. The glass transition is marked by more or less discontinuous changes from solid-like to liquid-like values in the second derivatives of the Gibbs free energy (*e.g.* the specific heat, C_p) around a temperature, T_g, called the glass transition temperature; the first derivatives (*e.g.* volume, entropy) change continuously through T_g. Many models have been proposed to explain the glass transition but a clear picture of the nature of the transition has not yet emerged. An early review on the phenomenon of the glass transition by Kauzmann[1] appeared in 1948. Since then, a large body of valuable experimental data has become available in the literature in respect of this transition. We have been investigating the glass transition by employing various spectroscopic and other techniques for some time. In this article, we shall discuss the important experimental results on the glass transition including the results from computer simulation studies, an aspect reviewed by Cohen and Grest[2] in relation to a modified version of the free volume model. We shall then critically examine the different theoretical models for the glass transition.

It would be particularly instructive if the phenomenological similarity between various disordered solids could be correlated with the existence of a structural motif common to these solids. We shall attempt to show in this article how the concept of clusters could provide such a unifying element. Disordered solids may be visualized as conglomerates of islands of more ordered material (density fluctuations) or clusters dispersed in a less ordered matrix or 'connective tissue'.[3] In the most general case, clusters may be differentiated from the tissue by a higher degree of correlation in position, orientation, or some other appropriate degree of freedom. In the context of glasses, the cluster-tissue material theme has had its genesis in the microcrystallite model, earlier workers having used terms such as 'vitrons'[4] or 'amorphons'[5] to identify the ordered regions. It seems that the use of

---

*Contribution No. 211 from the Solid State and Structural Chemistry Unit.
†To whom all correspondence should be addressed.

[1] W. Kauzmann, *Chem. Rev.*, 1948, **3**, 219.

[2] M. H. Cohen and G. S. Grest, *Adv. Chem. Phys.*, 1981, **48**, 455.

[3] M. R. Hoare and J. Baker, in 'The Structure of Non-Crystalline Materials', ed. P. H. Gaskell, Taylor and Francis, London, 1976; M. R. Hoare, *Ann. N.Y. Acad. Sci.*, 1976, **279**, 186.

[4] L. W. Tilton, *J. Res. Nat. Bur. Stand., U.S.A.*, 1957, **59**, 139.

[5] R. Grigorovici, *J. Non-Cryst. Solids*, 1969, **1**, 371.

the cluster-tissue formalism may be useful in interpreting experimental data related to the glass transition.

Recent studies have demonstrated that phenomena such as the glass transition, β-relaxations and so on, ascribed to solids with long-range positional disorder, are also found in solids that are characterized by disorder in other degrees of freedom.[6,7] This implies that any model of the glass transition as it occurs in the usual glasses, should be applicable to other disordered solids as well. A logical corollary is that such a model should not be restricted by the assumption of long-range positional disorder. We shall briefly discuss orientational glasses (or glassy crystals) obtained by quenching orientationally disordered (plastic) crystals towards the end of the article alongwith the so-called dipolar glasses.

2 The Glass Transition

The glass transition, unlike other phase transitions,[8] exhibits unusual changes in the derivatives of the Gibbs free energy, G, around the transition temperature. In Figure 1(a), we show the variation of entropy, S, or volume, V, of a substance with temperature; a plot for the second derivatives of G (the heat capacity, C_p, expansivity, α, or compressibility, β) is given in Figure 1(b). It is evident that the supercooled liquid departs from the equilibrium line (broken) at a *'fictive'* temperature, T_f, which depends upon the cooling rate. T_g is usually estimated as the temperature at which the specific heat increases steeply, and is generally quite close to T_f.

The response of a system to a perturbation from equilibrium is governed by a spectrum of relaxation times, τ_i, which define the times at which the equilibrium response to the perturbation will have decayed to 1/e of its initial value.[9] At low temperatures or at high frequencies of the applied field, the system cannot respond to the field within the time scale of the experiment. The shortest relaxation time of the system then exceeds the experimental time scale and the parameter associated with that relaxation time remains constant during the experiment.[10] The liquid, at this point (T_g or T_f), is said to have fallen out of equilibrium or to display 'solid-like behaviour'; τ_i itself shows an exponential temperature dependence. Considering that a glass can be described as a snapshot picture of a liquid, the glass transition can be defined as that event wherein the translational degrees of freedom (capable of inducing liquid-like configurational rearrangements) are activated. However, it is evident that the glass transition temperature observed in a given experiment is a function of the time scale employed[11] — the shorter the time scale, the higher is the T_g; it is therefore not obvious that the glass transition is a thermodynamic phenomenon. Empirically, T_g is generally around 0.67 T_F, where T_F is the temperature of fusion.[12]

---

[6] H. Suga and S. Seki, *Faraday Discuss. Chem. Soc.*, 1980, **69**; *J. Non-Cryst. Solids*, 1974, **16**, 171.

[7] G. P. Johari, *Phil. Mag., B*, 1980, **41**, 41; *Ann. N.Y. Acad. Sci.*, 1980, **279**, 117.

[8] C. N. R. Rao and K. J. Rao, 'Phase Transitions in Solids', McGraw Hill, London, 1978.

[9] R. O. Davies and G. O. Jones, *Adv. Phys.*, 1953, **2**, 370.

[10] C. A. Angell and W. Sichina, *Ann. N.Y. Acad. Sci.*, 1976, **279**, 53.

[11] C. A. Angell, *Ann. N.Y. Acad. Sci.*, 1980, **282**, 123.

[12] S. Sakka and J. D. Mackenzie, *J. Non-Cryst. Solids*, 1971, **6**, 145.

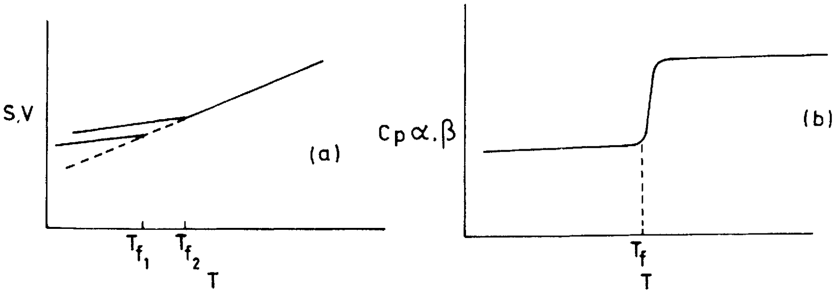

Figure 1 *Schematic variation with temperature of (a) entropy, S, volume, V, and (b) heat capacity,* C_p*, expansivity,* α*, and compressibility,* β*, for a typical glass-forming liquid. The* T_f *represent fictive temperatures with the lower one representing the slower cooling rate*

The decrease in heat capacity as the liquid vitrifies is interesting. If the transition at T_g were purely relaxational, would a sufficiently slow cooling rate obviate the transition? Figure 2(a) shows the temperature dependence of the normalized entropy difference between the solid and liquid.[1] Should no transition intervene, the entropy of the liquid would equal that of the solid well above absolute zero. This is unphysical in that it implies that a supercooled liquid has an entropy equal to that of an ordered solid. This problem, first studied by Kauzmann,[1] has been circumvented by postulating the existence of a transition at a temperature T_0 which limits the decrease in entropy — the so-called 'thermodynamic' glass transition.[9, 13—16] T_0 is obtained using the construction[16] shown in Figure 2(b). The

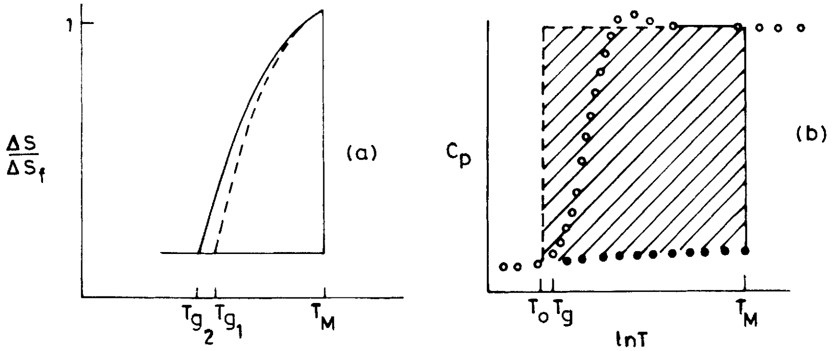

Figure 2 *(a) Schematic dependence on temperature of the normalized difference in entropy between glass and crystal for a typical glass-former.* S_f *= entropy of fusion. (b) A schematic Kauzmann plot of* C_p *versus* ln T *for a glass (○) and crystal (●). The hatched area is equal to the entropy of fusion*

---

[13] M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, 1959, **31**, 1164.
[14] J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.*, 1958, **28**, 373.
[15] M. H. Cohen and G. S. Grest, *Phys. Rev. B.* 1980, **20**, 1077.
[16] C. A. Angell, *J. Chem. Educ.*, 1970, **47**, 583.

hatched area represents melt entropy, which at T_0 must equal the entropy of fusion. The line joining the points represents an experimental trace.

The self-conflicting situation that would arise for $T < T_0$, in the absence of a transition at T_0, is often called the Kauzmann paradox. There has been extensive debate about the existence of a transition at T_0. The justification given for extending the free energy curve on both sides of a second-order transition has been questioned.[17] Kauzmann[1] himself resolved the paradox by stating that the glass would crystallize at a temperature greater than T_0. According to him, this would be possible if the barrier to homogeneous nucleation decreases with temperature while that impeding molecular motion (and hence the maintenance of equilibrium) increases. A cross-over temperature, T_K, where the two are equal may be expected and Kauzmann suggests that $T_K > T_0$. Assuming the existence of a Kauzmann limit, Angell[18] has developed the concept of an 'ideal' glass, wherein a glass is reckoned to be the more ideal, the closer T_g is to T_0. Ideality of a glass is thus a measure of the entropy frozen in at T_g (this should be zero if T_g equals T_0) and present indications are that ionic glasses may be amongst the most ideal.[19]

The temperature dependence of dynamic properties such as viscosity, η, fluidity, ϕ, and ionic conductivity, Λ, is described by the empirical Vogel–Tammann–Fulcher[20] (VTF) equation,

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

where ψ_0, B, and T_0 are constants (ψ_0 is weakly temperature dependent) evaluated by a least-squares fit to the data. Setting T_0 equal to zero reduces the VTF equation to the Arrhenius equation. It is significant that T_0 so determined is often equal to the T_0 obtained from calorimetric data.[21] This finding has been taken to support the notion that T_0 may mark the occurrence of a transition. The value of η at T_0 is formally infinite so that T_0 is said to be the lower limit of the liquid regime. T_g is also defined as that temperature at which η is equal to 10^{13} P, the 'isoviscous' definition of the glass transition.

3 Experimental Studies of the Glass Transition

Viscosities of many glass-forming melts, both organic and inorganic, have been measured as functions of temperature.[2,22] For $T > T_g$, η shows an Arrhenius dependence while at temperatures close to T_g, the dependence is often non-Arrhenius. In some cases,[23,24] reversion to Arrhenius behaviour is noted close to

---

[17] L. V. Woodcock, in 'The Structure of Non-Crystalline Materials', ed. P. H. Gaskell, Taylor and Francis, London, 1976.

[18] C. A. Angell, *J. Am. Ceram. Soc.*, 1968, **51**, 117.

[19] K. J. Rao in 'Preparation and Characterization of Materials', ed. J. M. Honig and C. N. R. Rao, Academic, New York, 1981.

[20] H. Vogel, *Physik. Z.*, 1921, **22**, 645; G. Tammann and W. Hesse, *Z. Anorg. Allg. Chem.*, 1976, **56**, 245; G. S. Fulcher, *J. Am. Ceram. Soc.*, 1925, **77**, 3701.

[21] A. J. Easteal and C. A. Angell, *J. Chem. Phys.*, 1972, **56**, 4231; H. Tweer, H. Laberge, and P. B. Macedo, *J. Am. Ceram. Soc.*, 1971, **54**, 121; C. T. Moynihan, L. R. Smalley, C. A. Angell, and E. J. Sare, *J. Phys. Chem.*, 1969, **73**, 2287.

[22] A. Bondi, 'Physical Properties of Molecular Crystals and Glasses', Wiley, New York, 1968.

[23] R. Weiler, S. Blaser, and P. B. Macedo, *J. Phys. Chem.*, 1969, **73**, 4147; P. B. Macedo and A. Napolitano, *J. Chem. Phys.*, 1968, **49**, 1887.

[24] A. C. Ling and J. E. Willard, *J. Phys. Chem.*, 1968, **72**, 1918.

T_g. Heat capacity measurements indicate that T_g is greater than the Debye temperature since the value of C_p at T_g is nearly always of the order of the Dulong–Petit value of $3NR$, where N is the number of independently vibrating particles.[18] An interesting correlation has been found between the temperature dependence of η and of ΔC_p of some glasses; strong network glasses such as SiO_2 and GeO_2 show a small change in C_p at T_g and their viscosities show an Arrhenius behaviour over large ranges of η.[10] Ionic glasses such as acetate,[10] nitrate,[10] and sulphate[25] glasses show pronounced changes in C_p at T_g and marked non-Arrhenius variation of viscosity (for the first two) around T_g. Glassy $ZnCl_2$, which is of intermediate character, shows only a moderate change in C_p and a small deviation from Arrhenius behaviour.

A. Relaxation Methods.—If the glass transition is indeed relaxational, relaxation spectroscopy would be particularly useful for studying the phenomenon.[26] Goldstein and co-workers[27] have found sub-T_g dielectric loss peaks (β-relaxations) in several glasses. Since β-relaxations are present both in glasses containing rigid molecules as well as flexible ones, they may be regarded as a consequence of amorphous packing. Recent work[28–30] has shown that β-relaxations exist in 'glasses' formed by supercooling liquid crystals and plastic crystals. The presence of these relaxations therefore seems to be less dependent on the nature of long-range disorder than supposed earlier. In covalent network inorganic glasses, dispersions in dielectric constant and dielectric loss are observed near T_g where large scale reorganization of the glassy matrix occurs.[31]

Mechanical relaxations under low frequency (10^{-3} to $1\,\mathrm{rad\,s^{-1}}$) alternating stress fields have been studied in multi-component commercial glasses.[32] A loss peak appears at $T > T_g$ in all the systems so far studied.[32] The systems studied to date are thermorheologically simple and the relaxation function shifts along the time axis with temperature, but shows no change in shape.[33] In silicate glasses,[34] a single mechanism seems to be responsible for both flow and relaxation at $T > T_g$. Perez *et al.*[35] have, however, found the existence of a double relaxation for $T < T_g$; the α- and β-relaxations appear to correspond to viscous flow and delayed elasticity respectively.

Ultrasonic relaxation phenomena of glass-forming melts can be divided into

---

[25] K. J. Rao, *Bull. Mat. Sci.*, 1980, **2**, 357.

[26] J. Wong and C. A. Angell, 'Glass: Structure by Spectroscopy', Marcel Dekker, New York, 1976.

[27] G. P. Johari and M. Goldstein, *J. Chem. Phys.*, 1971, **55**, 4245; L. Hayler and M. Goldstein, *J. Chem. Phys.*, 1977, **66**, 4736; J. Haddad and M. Goldstein, *J. Non-Cryst. Solids*, 1978, **30**, 1.

[28] G. P. Johari and J. W. Goodby, *J. Chem. Phys.*, 1982, **77**, 5165; G. P. Johari, *J. Chem. Phys.*, 1982, **77**, 4619.

[29] H. R. Zeller, *Phys. Rev. Lett.*, 1982, **44**, 583.

[30] R. Parthasarathy, K. J. Rao, and C. N. R. Rao, *J. Phys. Chem.*, 1983, in press.

[31] J. M. Stevels, 'Handbook der Physik', Vol. 20, Springer, Berlin, 1957.

[32] A. Zdaniewski, G. E. Rindone, and D. E. Day, *J. Mater. Sci.*, 1979, **14**, 763.

[33] S. M. Rekhson, *J. Non-Cryst. Solids*, 1980, **38**, 457 and 1980, **39**, 457; C. R. Kurkjion, *Phys. Chem. Glasses*, 1963, **4**, 128.

[34] J. J. Mills, *J. Non-Cryst. Solids*, 1974, **14**, 255.

[35] J. Perez, D. Duperray, and D. Lefevre, *J. Non-Cryst. Solids*, 1981, **44**, 113.

three categories.[36] In organic liquids, the real, K', and the imaginary, K'', components of the bulk modulus, K, do not in general, fit single relaxation time formulations and the relaxation time distribution function is not a symmetric function of $\ln \tau$. In molten oxides, the single relaxation time behaviour at $T > T_g$ broadens into a distribution symmetric in $\ln \tau$ as the temperature is lowered through T_g. In molten salts, however, the departure from single relaxation time behaviour occurs well above T_g.[36] The relation between the dielectric relaxation time, τ_D, and the shear relaxation time, τ_S, has been explored.[37] The ratio of $\langle \tau_\sigma \rangle$, the conductivity relaxation time (which is more appropriate for conducting materials than τ_D), to $\langle \tau_S \rangle$ in ionic salts varies from near unity well above T_g to about 10—15 just above T_g.[37] In covalent materials the ratio is 10^4—10^5 at low temperatures and could be as high as 10^{10} in fast ion conducting glasses.[38] The divergence of the ratio through T_g indicates that fundamentally different processes are likely to be involved in the two cases in the glassy state.

B. Spectroscopic Methods.—Resonance spectroscopy yields valuable information about structure as well as particle dynamics.[26] The latter feature has, however, found little application in glasses since the static broadening due to site distributions, for example, often obscures the more subtle dynamical effects. Molecular shapes of glass formers are also often asymmetric, rendering model-based interpretation difficult. It is recognized that resonance spectroscopy is ideally suited to probe changes in local site symmetry and hence valuable in investigating the glass transition. A Raman study[39] of a $Ca(NO_3)_2$–KNO_3 glass has shown that bandwidths change through T_g, with the depolarized bandwidth increasing more rapidly than that of the polarized line at $T > T_g$. Raman bandshape analyses of glassy methyl salicylate carried out in this laboratory show that the vibrational correlation time, τ_V, is practically constant through T_g, while the reorientational correlation time, τ_R, decreases sharply in this region. It is possible that the glass transition is associated with the activation of roto-diffusional modes.

An early variable temperature n.m.r. study on *o*-terphenyl has shown[40] that there is a marked increase in the relaxation and correlation times as the supercooled liquid vitrifies. The times do not reach values characteristic of a rigid lattice until $T > T_g$. This may be due to the arrest at T_g of the long range diffusion and rotation characteristic of the supercooled liquid; local relaxation in statistically distributed regions of lower density may, however, continue to lower temperatures.[40] A recent n.m.r. hole-burning experiment with glycerol has shown that relaxation around T_g occurs through large angle (~45°) steps and not through continuous diffusion.[41] ^{11}B n.m.r. studies of glassy B_2O_3 and B_2S_3 has indicated

---

[36] C. A. Angell and L. M. Torell, *J. Chem. Phys.*, 1983, **78**, 937.

[37] F. S. Howell, R. A. Bose, P. B. Macedo, and C. T. Moynihan, *J. Phys. Chem.*, 1974, **68**, 739; C. T. Moynihan, N. Balitactac, L. Boone, and T. A. Litovitz, *J. Chem. Phys.*, 1970, **55**, 3013.

[38] S. I. Smedley and C. A. Angell, *Solid State Commun.*, 1978, **27**, 1; *Mat. Res. Bull.*, 1980, **15**, 421.

[39] C. A. Angell 'Vibrational Spectroscopy of Molecular Liquids and Solids' ed. S. Bratos and R. M. Pick, Plenum, New York, 1980; J. H. R. Clarke and S. Miller, *Chem. Phys. Lett.*, 1972, **13**, 97.

[40] D. W. McCall, *J. Chem. Phys.*, 1973, **47**, 530.

[41] P. L. Kuhns and M. S. Conradi, *J. Chem. Phys.*, 1982, **77**, 1771.

that a narrow line emerges for $T > T_g$ in B_2O_3, corresponding to the motionally narrowed powder pattern.[42] In B_2S_3, this line overlaps the powder pattern, a feature that the authors have explained using a cluster model of glass. Due to the low T_g ($\sim 380\,K$), the B_2S_3 molecular units in the less dense tissue material are expected to rotate readily giving rise to the motionally narrowed line.[42] A rise in temperature would increase the fraction of such units and, hence, the intensity of the spectral line. Another possible explanation for the simultaneous presence of both patterns would be in terms of an equilibrium between three- and four-coordinated boron atoms.[43] E.s.r. studies have shown that there is motional narrowing and change in lineshape as the glass transforms into a liquid.[44] The available relaxation theories are rather difficult to apply to glasses so that the few studies reported in this area have employed lineshape simulation to explain the experimental observations.

In their e.s.r. study of glycerol–water mixture using the 'spin-probe' peroxylamine disulphonate (PADS) Antsiferova *et al.*[45] reported that the relation between the correlation time τ_c, and η/T deviated from linearity in the region of slow tumbling. The activation barrier to tumbling was found to be *ca.* 50 kJ mol^{-1}. In a study of *o*-terphenyl glass using vanadyl(IV) chelates as probes, Matsunaga[46] found a sudden decrease in the average value of the tumbling angle for $T > T_g$. Molecular motion appears to be anisotropic and the results seem to substantiate the presence of interlocked clusters in the melt ('the cogwheel effect') around T_g. A spin-probe e.s.r. study on some glass-forming liquids carried out in this laboratory[47] showed a marked decrease in the spin correlation time, τ_c, at a temperature, T_k, $T_k \gtrsim T_g$, as the glass was warmed (Figure 3). This seems to indicate that the spin probe is immobilized within clusters in the glass; these clusters would dissolve at T_k. The difference between T_g and T_k depends on the liquid and seems to be related to the intermolecular forces present. An analogous study by Spielberg and Gelerinter[48] shows similar features and these authors suggest that translational, but not rotational diffusion is inhibited as the temperature is lowered through T_g.

E.s.r. studies of Mn^{2+} and Fe^{3+} in silicate glasses show that resonance intensity decreases with temperature.[49] There seems to be no change in the linewidth even for $T > T_g$. The rate of the decrease appears to be larger than what might be expected from the Boltzmann term alone. It has been suggested[49] that the observed decrease in the intensity of the Fe^{3+} ($g = 4.3$) resonance may be due to the disappearance of the orthorhombic distortion associated with this signal; the intensity of the isotropic $g = 2.0$ resonance remains nearly constant. We have carried out

---

[42] M. Rubinstein, *Phys. Rev. B*, 1976, **14**, 2778.

[43] J. R. Hendrickson and S. G. Bishop, *Solid State Commun.*, 1975, **17**, 301.

[44] 'Electron Spin Relaxation in Liquids', ed. L. D. Muus and P. W. Atkins, Plenum, New York, 1972.

[45] L. I. Antsiferova, N. N. Korst, V. B. Strynkov, A. N. Ivanova, N. S. Nazemets, and N. V. Rabin'kina, *Mol. Phys.*, 1978, **25**, 909.

[46] Y. Matsunaga, *Bull. Chem. Soc., Jpn.*, 1977, **51**, 422.

[47] R. Parthasarathy, K. J. Rao, and C. N. R. Rao, *J. Phys. Chem.*, 1981, **85**, 3085.

[48] J. I. Spielberg and E. Gelerinter, *J. Chem. Phys.*, 1982, **77**, 2159.

[49] F. Momo, G. A. Ranieri, and A. Sotgui, *J. Non-Cryst. Solids*, 1981, **46**, 115; E. Baiocchi, A.

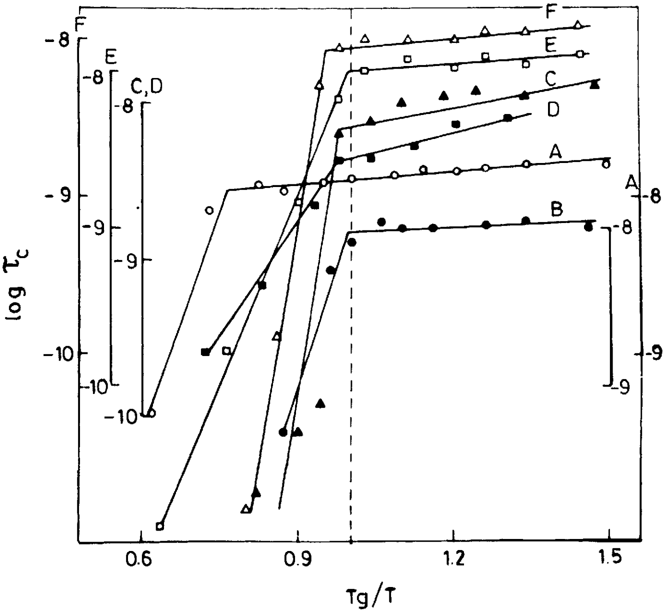

Figure 3 *Plot of log* τ_c *against* T_g/T *for (A) glycerol; (B) o-toluidine; (C) methyl salicylate; (D) propylene carbonate; (E) dimethyl phthalate and (F) p-anisaldehyde. The broken line indicates* T_g
(After R. Parthasarathy, K. J. Rao, and C. N. R. Rao, 1981, *Ref.* 47)

e.s.r. spectroscopic studies of ionic and covalent glasses containing Fe^{3+} and Mn^{2+} through the glass transition temperature.[50] We find that the anomalous decrease in signal intensity at $T > T_g$ can be related to the marked decrease in configurational entropy expected at T_g. Changes in the dielectric constant may also affect e.s.r. resonance intensity,[51] particularly at the glass transition.

Mössbauer spectroscopic studies (using ^{57}Fe nuclei) have been conducted as a function of temperature in some glasses, both organic[52,53] and inorganic.[54,55] The main experimental finding from these studies, particularly those on organic glasses, is that the Lamb Mössbauer factor (the recoil-free fraction) decreases sharply (along with a change in the quadrupole splitting) near T_g. Diffusion appears to be significant only at temperatures greater than T_g.[53] ^{57}Fe Mössbauer studies of inorganic glasses carried out in this laboratory[55] show that a decrease in the

---

[50] R. Parthasarathy, K. J. Rao, and C. N. R. Rao, *Chem. Phys.*, 1982, **68**, 393.

[51] F. J. Owens, C. P. Poole, and H. A. Farach, 'Magnetic Resonance in Phase Transitions', Academic, New York, 1979.

[52] P. A. Flinn, B. J. Zabransky, and S. L. Ruby, *J. Phys. (Paris)*, *C6*, 1976, **37**, 739; S. L. Ruby, B. J. Zabransky, and P. A. Flinn, *J. Phys. (Paris)*, *C6*, 1976, **37**, 745; A. Vasquez and P. A. Flinn, *J. Chem. Phys.*, 1980, **72**, 1958, J. A. Eliott, H. E. Hall, and D. St. P. Bunbury, *Proc. Phys. Soc.*, 1966, **89**, 595.

[53] D. C. Champeney, *Rep. Prog. Phys.*, 1980, **42**, 1017.

[54] J. P. Gosselin, U. Shimony, L. Grodzins, and A. R. Cooper, *Phys. Chem. Glasses*, 1968, **8**, 56.

[55] S. Bharati, R. Parthasarathy, K. J. Rao, and C. N. R. Rao, *Solid State Commun.*, 1983, **46**, 457.

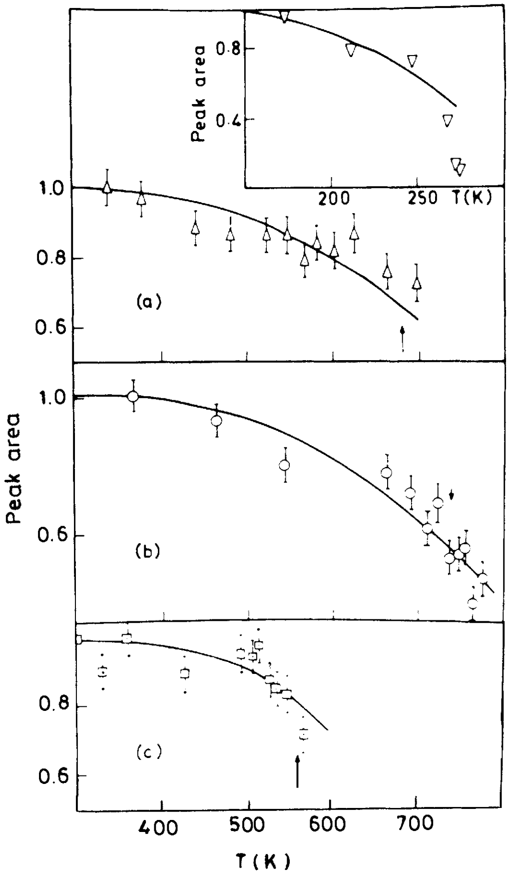

Figure 4 *Variation of the normalized area under resonance with temperature in a* ^{57}Fe *Mössbauer study of (a) borate (b) borosilicate and (c) vanadate glasses. Inset: A similar plot for glassy glycerol* $FeCl_3$ *(data from Elliott et al., Ref.* 52*). Points are experimental data while the lines are theoretical fits obtained using the cluster model of the glass transition (Section* 5*) The arrows denote* T_g
(After Seeta Bharati *et al.*, 1983, *Ref.* 55)

recoil-free fraction is generally found around T_g (Figure 4). Such a behaviour may be due to the onset of librational motion or of diffusional motion and can be explained, using the cluster model of the glass transition in terms of mode softening at T_g. It may be noted that the concept of soft modes has been most useful in understanding phase transitions in crystalline substances.[8]

Extended *X*-ray Absorption Fine Structure[56] (EXAFS) has been used[57] to study

---

[56] R. Parthasarathy, P. R. Sarode, K. J. Rao, and C. N. R. Rao, *Proc. Indian Nat. Sci. Acad., Sect. A*, 1982, **48**, 119.

[57] J. Wong and F. W. Lytle, *J. Non-Cryst. Solids*, 1980, **37**, 273.

the glass transition in GeO_2 and $ZnCl_2$ in order to observe the possible evolution of disorder. An increase in the vibrational disorder of $ZnCl_2$ was noticed at the T_g. $ZnCl_2$ is known to be a weak structural analogue of GeO_2 and hence shows more disorder, even at lower temperatures.

The experimental results presented hitherto suggest that the glass transition can be associated with the emergence of degrees of freedom in the supercooled liquid that are inactive in the glass. The manner in which these motional modes are activated is not very clear but a probable mechanism may be described in terms of a cluster model. There is some evidence that local motion in the connective tissue is frozen out only at $T < T_g$; upon reheating the glass, these are the modes which would be excited first, leading, in suitable cases, to the simultaneous presence of both 'cluster' and 'tissue' contributions to the spectrum.

Glasses are known to possess anomalous properties at low temperatures. Some of these are:[58] (a) an excess specific heat proportional to T, (b) thermal conductivity that increases as T^2, and (c) ultrasonic velocity proportional to ln T. The model used to explain these phenomena suggests that these are due to the presence of some structural entity of the glass in a double-well potential in which tunnelling takes place.[59] The number of such particles appears[60] to be proportional to $(T_g)^{-1}$ or $(T_f)^{-1}$. There are as yet no data available on the dependence of such states upon the thermal history of the sample,[61] and the identity of the tunnelling particles has not been established. Nevertheless, the dependence of T_g on the number of such particles is taken to reflect the structure frozen in at T_g.[58,60,61]

4 Ideality of Glasses

An issue central to the study of the glassy state has been that of defining the thermodynamic state of a glass — in particular, the so-called amorphous ground state. We noted earlier that an ideal glass can be described in Kauzmann's terms as a glass whose T_g is equal to T_0, *i.e.*, one which contains no frozen-in configurational entropy.[1] Such a glass may also be said to be in the 'amorphous ground state' and one may then ask if a distinction can be drawn between such an amorphous ground state and the crystalline state. It has been suggested by Kauzmann that T_K is usually greater than T_0 so that there cannot be a distinct amorphous ground state. The alternative is to consider $T_K < T_0$which can lead to such a state. The work of Donnella and Angell[62] hints at the possibility of such a situation which one may also expect to encounter in atactic polymers. The problem essentially reduces to one of deciding which alternative is physically more plausible: a distinct amorphous ground state ($T_K < T_0$) or a liquid-to-crystal transition at T_K, $T_K \ll T_F$, which is implied by the condition, $T_K > T_0$.

It is interesting to regard the existence of a unique temperature, T_0, as a consequence as much of geometric, as of energetic considerations.[18] In that case, T_0

---

[58] M. H. Cohen and G. S. Grest, *Solid State Commun.*, 1981, **39**, 145.

[59] P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.*, 1972, **25**, 1; W. A. Phillips, *J. Low Temp. Phys.*, 1972, **7**, 351.

[60] A. K. Raychaudhuri and R. O. Pohl, *Solid State Commun.*, 1981, **37**, 105.

[61] C. L. Reynolds, *J. Non-Cryst. Solids*, 1980, **37**, 125.

[62] J. Donnella and C. A. Angell, *J. Chem. Phys.*, 1977, **67**, 4560.

would be that temperature at which the close-packing limit is reached. This high density limit was first described by Bernal[63] in his experiments with mechanical assemblies, but computer simulation experiments have recently been shown to produce amorphous packings of marginally higher density.[64] T_0 would then be that temperature at which the excess volume disappears, but volume does not appear to be a significant parameter in determining the occurrence of the glass transition (see Section 7).

An answer to the question of the possible existence and nature of the amorphous ground state may be expected from computer simulation studies. These may also answer the more general question of whether a glass can exist in a definite thermodynamic state, or whether it is merely trapped, metastably, in a local potential minimum. The former would imply the possibility of phase transitions from one glassy state to another at well-defined temperatures, but there is no evidence to date for such phenomena. In a later section we shall examine the implications of the cluster model in this regard.

5 Computer Simulation Studies

Simulation of local structures of liquids has had its genesis in the classic work of Bernal[63] who used mechanical assemblies to this end. Studies by Tilton,[4] Grigorovici,[5] and Hoare[3] have shown the importance of non-space filling symmetries such as the pentagonal and the icosahedral to the 'ordered' aggregates in the amorphous state (Figure 5). Such aggregates can indeed be far larger than originally considered.[3] The glass transition from this viewpoint is regarded as the interlocking or 'congelation' of such clusters followed by the gradual freezing out of the tissue material.[3]

The role that dynamic simulation can play in describing the glass transition has been recognized recently.[65,66] The use of high quenching rates and (often) of small sample sizes limit the applicability of the results. Nonetheless, these studies yield useful information on the prototype glass transition in simple liquids, particularly because the transition at T_g is known to be a non-equilibrium transition that is closely related to the cooling rates employed. The diffuse nature of the simulated glass transition requires the definition of 'upper' and 'lower' glass transition temperatures, but more often, T_g in these studies is quite simply defined as the intersection point of glassy and liquid density-temperature plots.[65] The high fictive temperatures of the simulated glasses, however, imply high diffusion rates.

Both hard and soft spheres can be compacted into amorphous assemblies but the typical discontinuity in C_p is absent in these cases.[65] The C_p jump is apparent with the Lennard–Jones (LJ) potential and the attractive component of the potential appears to be responsible for this feature.[67] This also leads one to expect that the

---

[63] J. D. Bernal, *Nature*, 1960, **185**, 68, *Proc. R. Soc. London, Ser. A*, 1964, **280**, 299.

[64] L. V. Woodcock and C. A. Angell, *Phys. Rev. Lett.*, 1980, **47**, 1129.

[65] C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, *Adv. Chem. Phys.*, 1981, **48**, 397.

[66] D. Frenkel and J. P. McTague, *Ann. Rev. Phys. Chem.*, 1980, **31**, 49.

[67] J. H. R. Clarke, *J. Chem. Soc., Faraday Trans. 2*, 1979, **75**, 1371.

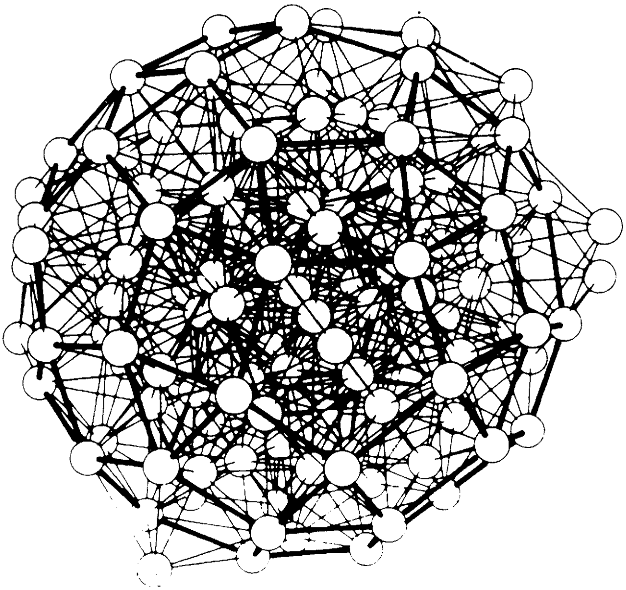

Figure 5 *Cluster obtained spontaneously on cooling a simulated Lennard–Jones liquid drop of 129 atoms in a molecular dynamics study. The heavy lines indicate elements of pentagonal symmetry*
(After M. R. Hoare and J. Barker, 1976, *Ref.* 3)

C_p anomaly would be difficult to observe under pressure as is, in fact, the case.[68] In a system of soft spheres, diffusivity, D, is proportional to a reduced volume at higher temperatures, consistent with the variation in the heat capacity.[65] At lower temperatures though, a recent study using a hard sphere ensemble shows that D does not vary linearly with free volume.[64] Experimentally, the variation of D with volume is exponentially dependent upon the free volume, or fluidity as described by the Doolittle equation,[69]

$$\phi = A\exp[-B/(V - V_0^{\mathrm{D}})] \tag{2}$$

where V_0^{D} and A are constants with the dimensions of volume. Woodcock and Angell[64] have found that V_0^{D} is the Bernal dense random packing of hard spheres limit. These workers were able to produce liquids of higher density and the significance of the Bernal limit is not entirely clear.

Radial or pair distribution functions have also been used to characterise T_g, at which point the ratio of the intensity of the first peak to the first trough is found to show a change in slope.[70] This is probably due to the change in density (which determines the height of the first peak) and to the commencement of diffusion (to

---

[68] T. Atake and C. A. Angell, *J. Phys. Chem.*, 1977, **81**, 232.

[69] A. K. Doolittle, *J. Appl. Phys.*, 1951, **22**, 1471.

[70] H. R. Wendt and F. F. Abraham, *Phys. Rev. Lett.*, 1978, **41**, 1244.

which the depth of the first trough is related). The well known splitting of the second peak in the radial distribution function appears as a liquid is compacted, though it has not been observed with soft interaction potentials. The distant component of the split peak is more intense, probably due to the effect of diffusion. An intriguing result is the discovery of bond orientational fluctuations above T_g suggesting a broken icosahedral symmetry in a molecular dynamics study of a Lennard–Jones fluid by Steinhardt et al.[71]

Inspite of such simulation studies, some important questions yet remain unanswered. First, it is not clear whether an underlying phase transition does exist. Secondly, properties of the system at temperatures close to T_g have not been explored in detail. Finally, the heating run of a glass remains to be simulated — the existence of the C_p overshoot, the hallmark of the laboratory glass transition, has not yet been demonstrated in simulated glasses.[65]

6 Models for the Glass Transition

A. Free Volume Model.—This model was first developed for liquids and was thereafter used to describe the glass transition in polymers by Fox and Flory.[72] Turnbull and Cohen[13,73] proposed a generalization of this model to glass transitions in other materials. Essentially, the model rests on the following assumptions: (a) it is possible to associate a free volume v with each particle; (b) when v exceeds some value v_c, the excess may be regarded as free; (c) transport occurs only when voids of volume greater than some v^* ($v^* \sim v_m$) form by redistribution of free volume and (d) no local free energy is required for the redistribution of free volume.[13]

The model concludes that a liquid can be vitrified only if it can be sufficiently undercooled without crystallization. It relates dynamic quantities, *e.g.* diffusivity, to the free volume, v_f, so that these vanish at T_0 where v_f is zero. Since $v_f \propto (T - T_0)$ in this approach, the VTF equation (equation 1) is easily derived.

Cohen and Grest[2,15,58] have refined this model further in order to evaluate thermodynamic properties. In this refinement, individual cells are described as being either liquid-like or solid-like, depending on whether or not their volume exceeds a certain volume v_c. Only liquid-like cells have free volume, and the change in free energy associated with redistribution of free volume arises from the change in entropy due to such redistribution. It is crucial to note that exchange of free volume is possible only between liquid-like cells. A further restraint on such exchange is that a given liquid-like cell must have at least a certain number of near neighbour liquid-like cells so that the volume of neighbouring solid-like cells is not constrained to change simultaneously. This defines the underlying percolation problem. The fraction of liquid-like cells is,

$$p = \int_{v_c} p(v)\mathrm{d}v \qquad (3)$$

---

[71] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, *Phys. Rev. Lett.*, 1981, **47**, 1297.

[72] T. G. Fox and P. J. Flory, *J. Polym. Sci.*, 1954, **14**, 315.

[73] D. Turnbull and M. H. Cohen, *J. Chem. Phys.*, 1961, **34**, 1120; *J. Chem. Phys.*, 1970, **52**, 3038.

For $p \neq 0$ there are clusters of liquid-like cells each one of which has at least z liquid-like neighbours. For p larger than a value p_{cz}, an infinite cluster exists. With this model, Cohen and Grest[2] view the thermodynamic glass transition as a first order transition at which p changes discontinuously from $p_l > p_{cz}$ to $p_g < p_{cz}$. Nevertheless, molecular dynamics studies have shown that the percolation transition need not be first order, but this finding could be an artefact of the non-equilibrium ensembles, inevitably found in simulated glasses.[74] The equilibrium transition is associated with the decrease in p with temperature. Such a decrease demands an activated exchange of volume between solid-like and liquid-like cells. This is progressively frozen out as $T \rightarrow T_g$ at a value that depends on the cooling rate, so that below the glass transition, p does not attain its equilibrium value but remains at p_{froz}. The presence of liquid-like cells in the glass even for $T < T_g$ makes it possible to discuss sub-glassy relaxations in terms of this model.

B. Configurational Entropy Model.—This model was first developed by Gibbs and DiMarzio[14,75] in the context of glass transitions in polymers. These authors relate the configurational entropy, S_c, to the number of configurations available to the system. In polymers, S_c can be calculated by considering the entropy due to the mixing of holes and links on a model lattice. The major conclusion of this approach is that a solution of the Kauzmann Paradox requires a transition at a temperature T_0 where the configurational entropy vanishes. First, a region of z particles is rigorously defined as that region that can undergo a transition to a new configuration without requiring a simultaneous change on or outside its boundary. Transport properties can then be calculated, assuming the existence of these small co-operatively rearranging regions; the dependence of z on temperature yields the temperature dependence of the property itself.[76] At T_0, z is of the order of a macroscopic portion of the sample itself, and the dearth of configurations at this temperature is responsible for the observed sluggishness of mass transport. Dynamic properties can be shown to be related to the configurational entropy as[76]

$$\phi(T) = A \exp[B/TS_c] \tag{4}$$

where A and B are constants. It is evident that the size of the co-operatively rearranging regions is determined by configurational restrictions related to melt entropy.

C. Cluster Model.—The notion that glass may consist of ordered aggregates has been prevalent since Tammann.[77] Recent studies by Hoare and co-workers[3] suggest the possibility that these clusters may be embedded in a more ordered, less dense, 'tissue material'. The cluster model of the glass transition proposed from this laboratory[78] suggests that the size of the clusters decreases with increasing

[74] Y. Hiwatari, *J. Chem. Phys.*, 1982, **76**, 5502.

[75] J. H. Gibbs, 'Modern Aspects of the Vitreous State', ed. J. D. Mackenzie, Butterworths, London, 1963.

[76] G. Adams and J. H. Gibbs, *J. Chem. Phys.*, 1965, **43**, 139.

[77] G. Tammann, 'Der Glaszustand', Leopold Voss, Berlin, 1933.

[78] K. J. Rao and C. N. R. Rao, *Mater. Res. Bull.*, 1982, **13**, 1337.

temperature due to the surfacial melting of the clusters. The relative size, r/r_0 of the clusters is used as an order parameter, ξ; the cluster model is the first model to describe the glass transition in terms of an order parameter. Cluster melting would increase the tissue fraction and, at T_g, the clusters would be about the size of critical nuclei (or 'flickering' clusters) which would spontaneously dissolve. The variation in the configurational properties arises from particle motion in the tissue material which is supposed to consist of extremely anharmonic potential wells as in Figure 6. With this qualitative picture in mind, we proceed to analyse the cluster model in some detail.

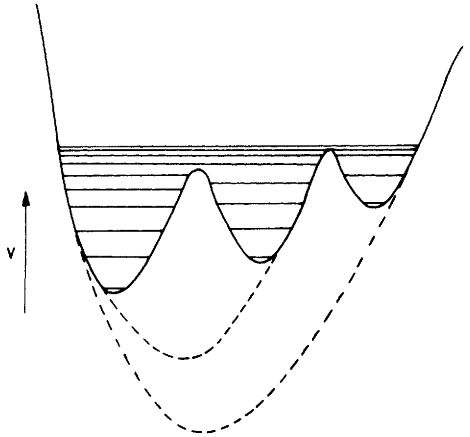

Figure 6 *Schematic diagram of 3-connected potential wells. Broken lines indicate the anharmonic pseudo-wells. V is the potential energy*

The total volume of the glass is given by,

$$V_g = V_{\text{cluster}} + V_{\text{tissue}} \tag{5}$$

Now, the particles on the cluster surfaces are regarded as vibrating in highly anharmonic potential wells where the well depth, V, is given by

$$V = \tfrac{1}{2}kx^2 - \tfrac{1}{3}ckx^3 \tag{6}$$

where k is the vibrational force constant, x is the displacement co-ordinate and c is the anharmonicity constant. With increase in temperature, a particle in a given well is excited to a higher vibrational state. Owing to the anharmonicity of the potential, the wells get connected. A modified pseudo-well, caused by the coalescing of two anharmonic wells, is described by

$$V' = \tfrac{1}{2}k'(x + x')^2 - \tfrac{1}{3}c'k'(x + x')^3; c' \ll c \tag{7}$$

At still higher temperatures, motion in the tissue material is even more anharmonic, but now the surfaces of the clusters begin to 'melt'. The dislodged particles fall into the ground vibrational state. It is assumed for simplicity that the ground state population does not vary with temperature till the clusters dissolve completely. In other words, if N_t is the total number of particles and f_0 is the fraction in the ground state,

$$\frac{\mathrm{d}(N_t f_0)}{\mathrm{d}T} = 0 \text{ or } \frac{\mathrm{d}N_t}{\mathrm{d}T} = -\frac{\mathrm{d}f_0}{\mathrm{d}T} \tag{8}$$

This is the key assumption in our simple mathematical treatment (and not of the model), A canonical partition function, z, may now be written for the ensemble of particles:

$$z = \sum_{i=1}^{n} \exp(-\Delta E_i/kT) \tag{9}$$

so that the population in the ith level is given by,

$$f_i = \exp(-\Delta E_i/kT) \tag{10}$$

We use a heuristic scheme for calculating the E_i,

$$\Delta E_i = \Delta E_1 \sum_i 1/i \tag{11}$$

where ΔE_1 is the separation between the ground state and the first excited state; it is apparent that the separation between levels progressively decreases with increasing i. The normalized variation with temperature of the order parameter is given by,

$$\xi = (r/r_0) = a^{1/3}\left[1 - \left(\frac{a-1}{a}\right)z\right]^{1/3} \tag{12}$$

where r is the radius of the cluster, r_0 is its initial radius and a is the initial ratio of V_g, the total volume, to V_c ($a = 1$ for an ideal glass in this model). The variation of the order parameter with respect to $kT/\Delta E_1$ is shown in Figure 7. Clearly, the temperature at which the rate of descent is steepest is a function of both a and i, the number of levels used in the calculation. It is also clear that r_c, the critical cluster size, tends to zero in first order fashion.

It is clear from the above discussion that particles in the higher vibrational states execute large amplitude oscillations. If there is a simultaneous change in the co-ordinates of the environment, memory of the initial position of the particle is lost and the particle will essentially have undergone diffusive motion. Because of such a close correspondence between the vibrational state of a particle and its dynamics, it is possible to calculate configurational properties based on the populations in the different states. Writing the total enthalpy involved in the excitation, ΔH_t, as,

$$\Delta H_t = V_t/V_g \sum_i E_i f_i \tag{13}$$

We differentiate ΔH_t with respect to T to obtain C_p. Subtracting the specific heat

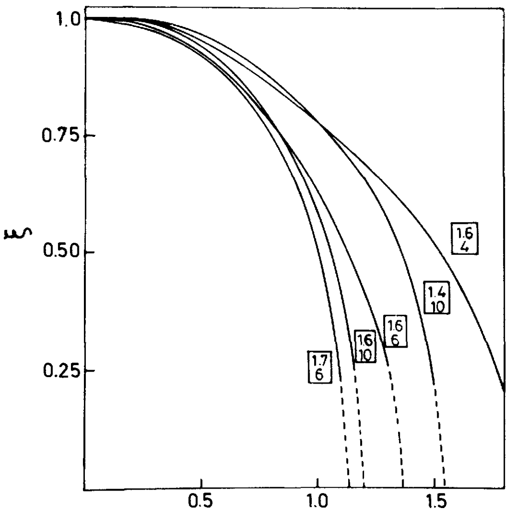

Figure 7 *The variation of the normalized cluster radius, ζ, with temperature. The upper value in each rectangle is a, and the lower, the number of levels used in the calculation*
(After K. J. Rao and C. N. R. Rao, 1982, *Ref.* 78)

due to excitation to the first excited state, δC_p, from C_p, we obtain the configurational heat capacity,

$$C_p^{\text{conf}} = C_p - \delta C_p \tag{14}$$

A plot of C_p^{conf} *versus* temperature is shown in Figure 8 for various values of the input parameters. Configurational entropy, S_c, is given by

$$S_c = (V_t/V_g) \sum_{i=1}^{n} R f_i \ln f_i \tag{15}$$

so that using equation (4), dynamic parameters may be determined.

The dimensionless parameter, ξ, describes the radius of an ordered aggregate and may thus be used as an order parameter. It also defines a region in which there is positional correlation, permitting phonon propagation. It is thus analogous to a correlation length and can be used in Landau's expansion of the free energy to show that the cluster model belongs to the class of mean free models.

The salient aspects of this model are (a) the order parameter, ξ, shows the expected behaviour, tending to zero as $T \to T_g$. (b) When the cluster radius reaches a critical value, V_c, the clusters dissolve spontaneously or $\xi_c = (r_c/r) \to 0$ in first order fashion, a feature that has been considered to be quite realistic.[2,15,58] (c) A distribution of cluster sizes will not vitiate the conclusions given here which were drawn assuming a uniform cluster size.

A distinctive type of mode softening is indicated in the cluster model, described as follows. It is known that the vibrational frequency ω_i is related to the force

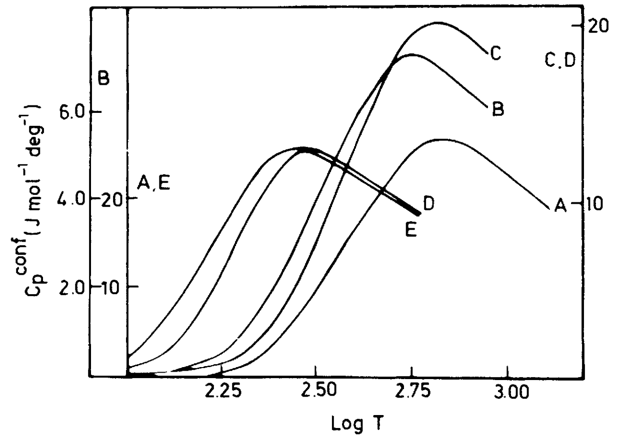

Figure 8 *Plot of* C_p^{conf} *versus log temperature. The parameters used in the calculation are a,* ΔE_1(kJ mol^{-1}), i = 1.8, 4200, 10(A); 1.8, 4200, 4(B); 1.8, 4200, 8(C); 1.8, 2100, 6(D); 1.8, 2100, 4(E)

constant, k_i, of the bond as $\omega_i \propto \sqrt{k_i}$. Considering the two-well case shown in Figure 6,

$$\tfrac{1}{2}k_2(x + x')^2 \sim \tfrac{1}{2}k_2 4x^2 = 2k_2x^2 = \tfrac{1}{2}kx^2 - \tfrac{1}{3}ckx^3 \tag{16}$$

Then,

$$\frac{k_2}{k} = \tfrac{1}{4}(1 - \tfrac{2}{3}cx) \sim \tfrac{1}{4};\, cx \ll 1 \tag{17}$$

For the n-well case,

$$(k_n/k) = (1/n^2) \tag{18}$$

This implies that the soft mode does not steeply decrease at the glass transition, but that it decreases in discrete steps. This is an important difference between the glassy 'soft mode' and the soft mode in crystals. Another difference between the two is the absence, for the glass transition, of a restoring mode in the transformed phase, the liquid.

D. Other Approaches to the Glass Transition.—The 'bond-lattice' model of Angell and Rao[79] was one of the first models to study the glass transition as a solid state phase transition. These authors consider a glass as a lattice of bonds each of which may be 'on' or 'off'. Configurational heat capacities were calculated using this model and it was found that experimental C_p *versus* T plots could be matched

---

[79] C. A. Angell and K. J. Rao, *J. Chem. Phys.*, 1972, **52**, 470; K. J. Rao and C. A. Angell, 'Amorphous Materials', ed. R. W. Douglas and B. E. Ellis, Wiley, New York, 1971.

theoretically without requiring the existence of a transition at T_0. The significance of T_0 in this treatment is of an operationally defined quantity which is related to a simple temperature dependence of excess thermodynamic quantities.

In the 'potential barrier' model, Goldstein[80] regards glass as a system trapped kinetically in a potential energy well of depth, U, accessible to the equilibrium liquid at T_g. The number of such wells, $\Omega\ (U)$, increases with U so that the transition from deeper to shallower wells as T_g is approached is favoured by entropic considerations. The softening of vibrational modes and the concomitant gain in the amplitude of the β-relaxations also favour the transition between wells. The model is qualitative so that comparisons with experimental results are not easily made. It is worth noting that by assuming that the energy well has a 'corrugated' bottom, the potential barrier model can account for the existence of β-relaxations.

Eyring and co-workers[81] have approached the glass transition through a theory of viscosity. In their 'significant structures' theory, the partition function of a glass is regarded as a product of solid-like and gas-like contributions. Only the former is assumed to contribute to viscosity which, for a system of hard spheres is given by,

$$\eta = AT^{1/2}/(V - V_s)\exp(\varepsilon^{\neq}/kT) \tag{19}$$

where A is a constant related to the distance between nearest neighbours, particle mass, and a constant transmission coefficient, and V and V_s are total and solid-like volumes respectively; $\varepsilon^{\neq}$ is the activation barrier to particle motion. T_g in this model, is evaluated using the isoviscous criterion.

The glass transition has been the focus of much interest recently. Kanno[82] regards configurational entropy as a sum of communal and positional entropy. Communal entropy is defined, after Kirkwood,[83] as the entropy due to the sharing of the available volume in the liquid by all the particles. Since positional entropy is always greater than zero, Kanno concludes that the glass transition is due to the vanishing of communal entropy. Thus the uniqueness of T_0 as a limit of T_g disappears. Phillips[84] uses the cluster formalism to describe the temperature dependence of viscosity which can also be used to understand the glass transition. Other workers have regarded glass as a crystal with a high density of dislocations and have proceeded to discuss its properties from this point of view.[85] An analogy with spin glasses has also been described using a model of entangled rod-like polymers.[86] Most of these notions are as yet in preliminary states of development and their validity remains to be proven.

---

[80] M. Goldstein, *J. Chem. Phys.*, 1969, **51**, 3728; *J. Chem. Phys.*, 1976, **64**, 4767; *J. Chem. Phys.*, 1977, **67**, 2246.

[81] L. Faerber, S. W. Kim, and H. Eyring, *J. Phys. Chem.*, 1970, **74**, 3510.

[82] H. Kanno, *J. Non-Cryst. Solids*, 1980, **37**, 203.

[83] J. G. Kirkwood, *J. Chem. Phys.*, 1950, **18**, 380.

[84] J. C. Phillips, *J. Non-Cryst. Solids*, 1981, **44**, 17.

[85] S. F. Edwards and M. Warner, *Philos. Mag. A*, 1971, **40**, 257.

[86] S. F. Edwards and K. E. Evans, *J. Chem., Soc., Faraday Trans. 2*, 1982, **78**, 113.

7 Pressure as a Variable in the Glass Transition

Studies of the glass transition as a function of applied pressure are rather small in number and the data available are scanty. These studies are nonetheless essential if one is to determine the merits of the various models of the glass transition. Simulation studies have shown that an amorphous packing may be produced by the application of pressure alone but these need to be further explored.[65]

If the thermodynamic excess quantities, volume, V_e ($V_{\text{liquid}} - V_{\text{glass}}$) and entropy, S_e, are functions of a single parameter, $Z(P, T)$, we mean that P and T may simultaneously be changed so that Z remains constant.[87] If $V_e = V_e(Z)$ and, $S_e = S_e(Z)$ and T_g is determined by a single ordering parameter, it can be shown that[87]

$$\left(\frac{dT_g}{dP}\right)_{V_e} = \Delta\beta/\Delta\alpha,\ dV_e = 0 \tag{20}$$

or

$$\left(\frac{dT_g}{dP}\right)_{S_e} = T_g V_g \Delta\alpha/\Delta C_p,\ dS_e = 0 \tag{21}$$

where V_g is the volume of the glass and $\Delta\alpha$ and $\Delta\beta$ are changes in expansivity and compressibility, respectively, at T_g.

Should dS_e and dV_e vanish simultaneously at T_g,[9,87]

$$\Delta\beta/\Delta\alpha = \frac{T_g V_g \Delta\alpha}{\Delta C_p} \text{ or } \frac{T_g V_g (\Delta\alpha)^2}{\Delta C_p \Delta\beta} = \Pi = 1 \tag{22}$$

where Π is the Prigogine–Defay ratio.[88]

To date, it appears that Π is always greater than unity and equation (21) rather than equation (20) is found to be experimentally valid. However, equation (21) also fails for $ZnCl_2$ glass where dT_g/dP is less than $T_g V_g \Delta\alpha/\Delta C_p$.[89] If T_g is taken to be that temperature at which a relaxation time, τ, is constant,[89]

$$(\partial S/\partial P)_\tau = \frac{\Delta C_p}{T_g}\left(\frac{\partial T_g}{\partial P}\right)_\tau - V_g\Delta\alpha \tag{23}$$

or

$$(\partial T_g/\partial P) = (\partial S_e/\partial P)_\tau (T_g/\Delta C_p) + V_g T_g \Delta\alpha/\Delta C_p \tag{24}$$

In glassy $ZnCl_2$, $(\partial S/\partial P)_\tau$ appears to be negative indicating a possible route to the ideal glass.[89] From the standpoint of the cluster model, increase of pressure should increase the cluster fraction which is just what the notion of ideality entails. In any event, the validity of equation (21), noted in many experiments, is strange since it suggests that τ is a function of S_c alone, while $\tau = \tau(TS_c)$ in the configurational entropy model.

In summary, a single ordering parameter appears to be insufficient to describe the glass transition.[9,87] The configurational entropy model seems to describe the

---

[87] M. Goldstein, *J. Chem. Phys.*, 1963, **39**, 3369.

[88] I. Prigogine and R. Defay, 'Chemical Thermodynamics', Longmans Green, London, 1954.

[89] C. A. Angell, E. Williams, K. J. Rao, and J. C. Tucker, *J. Phys. Chem.*, 1977, **81**, 238.

variation of T_g with pressure more accurately than the free volume theory.[87] Further constraints on the ordering parameters have also been extensively discussed.[90]

8 Concluding Remarks

It is clear that the experimental transition at T_g occurs when a relaxation time, τ, attains a constant value on the time scale of the experiment.[9,89] A thermodynamic transition has been proposed at a temperature $T_0(\lesssim T_g)$ but this transition has not so far been (can never be!) observed, since relaxation times are too long below T_g. The configurational entropy model is unable to describe the change in viscosity with temperature accurately.[91] Its description of the variation of T_g with pressure is in error in the case of $ZnCl_2$.[89] Further, its extension to non-polymeric glasses is not obvious. Most importantly, perhaps, the entropy model requires the value of S_c as input data to yield the values of other parameters.

The free volume model has no means of accounting for transitions with negative expansivity.[92] Its prediction of dT_g/dP is usually seriously in error.[87,89,93] In the Cohen–Grest modification of the original theory, the distinction between solid-like and liquid-like cells is rather arbitrary and interconversion of one into the other at sub-T_g temperatures is ignored. In this form, though, the theory can account for an entropy catastrophe. However, both the free volume and the configurational entropy model are able to account for the observed identity of T_0 values obtained from various experiments.

With respect to the order of the transition at T_0, the free volume theory predicts that it is of first order,[2] but so far there has been no evidence for such a transition.[94] The bond lattice model does not require the existence of a transition at T_0 in order to match the variation of C_p; in this respect this model is unique. The cluster model predicts that the transition at T_g itself is of second order with a first order component where the clusters dissolve spontaneously. Experimentally, relaxation effects are likely to preclude verification of this prediction. The cluster model, in particular, does not distinguish between an ideal glass and the corresponding crystal, at least in a restricted class of glass formers; even though proof to the contrary is scarce,[62] this appears to be a singular conclusion. As with Goldstein's potential barrier approach,[80] change in lattice frequencies, increasing anharmonicity, and an increase in the number of particles participating in secondary relaxations (the last two are closely linked) are the factors governing the approach to T_g in the cluster model.

The free volume model does not explicitly consider configurational entropy, and the configurational entropy model does not consider communal entropy. The

---

[90] P. K. Gupta and C. T. Moynihan, *J. Non-Cryst. Solids*, 1978, **29**, 143; J. Kovacs, *J. Phys. Chem.*, 1981, **85**, 2060.

[91] W. T. Laughlin and D. R. Uhlmann, *J. Phys. Chem.*, 1972, **76**, 2317; R. J. Greet and D. Turnbull, *J. Chem. Phys.*, 1967, **46**, 243.

[92] E. Williams and C. A. Angell, *J. Polym. Sci., Polym. Lett.*, 1973, **11**, 382.

[93] E. Williams and C. A. Angell, *J. Phys. Chem.*, 1977, **81**, 232.

[94] L. Boehm, M. D. Ingram, and C. A. Angell, *J. Non-Cryst. Solids*, 1981, **44**, 305.

distinction between the two due to Kanno, is however, likely to be only of heuristic interest, since the apportioning of this quantity between.these two components is rather arbitrary. Further, it has also been stated that Kanno's approach neglects the observed dependence of T_g on cooling/heating rates, and is therefore unrealistic.[19] To the extent that T_g is not determined by a single excess parameter, ($\Pi > 1$ for most of the systems studied) there may be little to choose between the free volume and configurational entropy models. It is worth noting here that the free volume model in its current form resembles the configurational entropy model rather closely. The free volume model appears to describe the 'cells' of the Gibbs–DiMarzio approach in physical terms that are applicable to glasses other than polymeric ones.

The cluster model is successful in many respects. Primarily, there is visual proof that clusters exist. High resolution electron microscopy (HREM) work has revealed the existence of positionally correlated regions ~ 50 Å across in a number of glasses.[95] Interestingly, if r_c is taken to be 5—10 Å (in the steeply decreasing region in Figure 7), then the cluster radius in the glass may be estimated to be around 25—50 Å. Simulation studies have shown that these are of pentagonal or related symmetry so that they cannot be space filling.[3] The observation of an anomalous temperature dependence of viscosity (equation 1) at temperatures just greater than T_g can be explained by the formation of clusters (and therefore, increased co-operativity) at $T > T_g$.[96] The observation of β-relaxations in glasses consisting of rigid molecules suggests that these relaxations are features characteristic of amorphous packing.[22] It has also been shown that decreasing the fictive temperature reduces the amplitude of these relaxations but not their frequency,[27,28] so that it is appealing to consider that β-relaxations originate in the tissue material. Mechanical relaxation studies have also used the cluster model to identify the α- and β-relaxations with viscous flow and delayed elasticity respectively.[35] N.m.r. studies have detected sub-glassy relaxations and these have been attributed to particle motion in regions of lower density.[41] In certain cases, it is indeed possible to study both cluster and tissue contributions to the spectrum simultaneously.[43] Spin probe e.s.r. studies[47,48] indicate that cluster dissolution takes place only at $T_k \gtrsim T_g$. Current indications are that the low-temperature anomalies in glasses arise in the tissue material.

Current theoretical work has tended to study the relaxation phenomena characteristic of the glass transition using concepts developed for other solid state phase transitions.[97] It is well-known that the non-Arrhenius dependence of dynamic variables near T_g is indeed due to co-operative processes. Primarily, there appears to be a rapid increase in the correlation length in this temperature regime.[98] This

---

[95] P. H. Gaskell, D. J. Smith, C. J. D. Catto, and J. R. A. Cleaver, *Nature*, 1979, **881**, 465; L. A. Bursill, J. M. Thomas, and K. J. Rao, *Nature*, 1981, **289**, 157.

[96] E. McLaughlin and A. R. Ubbelohde, *Trans. Faraday Soc.*, 1958, **54**, 804; A. J. Matheson, J. H. Magill, and A. R. Ubbelohde, *Trans. Faraday Soc.*, 1958, **54**, 1811.

[97] P. W. Anderson, 'Ill Condensed Matter', ed. R. Balian, R. Maynard, and R. Toulouse, North-Holland, Amsterdam 1979.

[98] B. I. Halperin and P. C. Hohenberg, *Rev. Mod. Phys.*, 1977, **49**, 435.

is very easily rationalized using the cluster model, in which an increase in the correlation length would imply cluster growth. Thus, T_0 no longer marks merely the termination of the liquid state, *i.e.* a point at which viscosity is infinite. It is, theoretically, a temperature at which the correlation length would be infinite in crystals.[97] In glasses, it represents a temperature at which the correlation length is large enough to suppress relaxations even on the longest practicable time scales.[99] The major advantage in using the cluster model to explain glass transition phenomena lies in the close relation that it builds between the structure of a glass and its behaviour at T_g. The term 'structure' need not connote only translational disorder — the cluster model assumes the existence merely of correlationally differentiated regions. This flexibility makes it possible for one to discuss glass-like transitions in plastic crystals, using the cluster model, for which conventional glass transition models that rely on positional disorder are not easily employed. Furthermore, the cluster model regards the glass transition as an aspect of solid state phenomenology and not primarily as an event that marks the end of the liquid regime. This enables one to explain the glass transition in terms of well-understood concepts developed for solid state phase transitions (*e.g.* soft modes).

The possible existence of soft modes in glasses has been indicated by spectroscopic studies.[52,53,55,100] These can be accounted for by the cluster model, where excitation of particles to higher states naturally leads to the weakening of vibrational force constants. In contrast to soft modes in crystals, however, the 'soft' modes in glasses are likely to soften continuously.

Orientational and Dipolar Glasses.—We have seen earlier that disorder in other degrees of freedom may be frozen-in to yield glass-like solids which are akin to *bona fide* (positionally disordered) glasses. In particular, it has been shown that orientational disorder found in plastic crystals may be quenched in to yield 'glassy crystals'. Calorimetric studies[6] have demonstrated the existence of glass-like transitions in these solids at a temperature, T_g'. Dispersions in dielectric loss and dielectric constant are seen[30,101] both at and below T_g' (Figure 9). E.s.r. spin probe spectroscopic studies indicate that there is a marked decrease in the correlation time around T_g' as the glassy crystal is warmed.[30] Raman and i.r. band shape studies on glassy crystalline cyclohexanol carried out in this laboratory also show the onset of molecular motion around T_g'. Dielectric studies on glasses formed by supercooling liquid crystals yield results very similar to these.[28,29]

Disorder in dipole interactions may be frozen-in to yield dipole glasses, substances which have features similar to those of spin glasses. A typical case is that of KBr doped with CN^- in which relaxation has been discerned by dielectric studies[102,103] (Figure 10). Yet another kind of dipole glass is exemplified by

---

[99] M. Shablakh, R. M. Hill, and L. A. Dissado, *J. Chem. Soc., Faraday Trans. 2*, 1982, **78**, 625.

[100] G. J. Exarhos, P. J. Miller, and W. M. Risen, *J. Chem. Phys.*, 1974, **60**, 4145.

[101] K. Adachi, H. Suga, S. Seki, S. Kubota, S. Yamaguchi, D. Yano. and Y. Wada, *Mol. Cryst. Liq. Cryst.*, 1972, **18**, 345.

[102] S. Bhattacharya, S. R. Nagel, L. Fleishman, and S. Susman, *Phys. Rev. Lett.*, 1982, **46**, 1267.

[103] A. Loidl, R. Feile, and K. Knorr, *Phys. Rev. Lett.*, 1982, **48**, 1263.

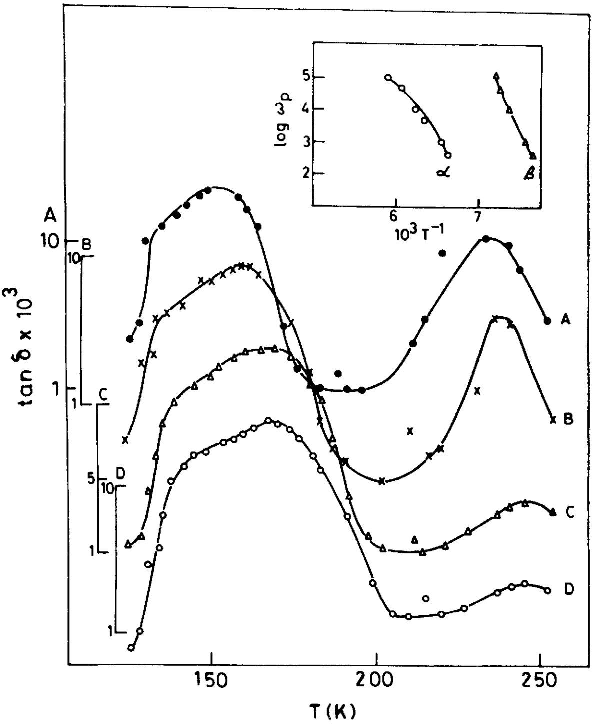

Figure 9 *A semi-log plot of* tan δ *against temperature for camphor at the following frequencies in* kHZ: *(A)* 1; *(B)* 10; *(C)* 50; *(D)* 100. *Inset: Plots of* ω_p *against* T^{-1} *for the low temperature,* β-, *and high temperature,* α-, *relaxations*
(After R. Parthasarathy, K. J. Rao, and C. N. R. Rao, 1983, *Ref.* 30)

Li^+-doped $KTaO_3$ studied by Höchli *et al.*[104] The off-centre impurity seems to stabilize locally polarized clusters in the matrix and the distributions of relaxation times at various dopant concentrations appear to reflect cluster interactions. We have reported dielectric studies on dilute solutions of ferroelectrics in antiferroelectrics in which we found that tan δ goes through a minimum and dielectric constant through a maximum around 5% solute concentration.[105] This anomalous variation of dielectric parameters could reflect the presence of locally polarized clusters in these transitional phases.

Thus the glassy state seems to include long range disorder of many types while the glass transition, in very general terms, manifests itself when relaxational and experimental time scales intersect. Nevertheless, the existence of an ideal glass transition temperature in glassy crystals as well as in glasses hints at the possibility

---

[104] U. T. Höchli, H. E. Weibel, and L. A. Boatner, *J. Phys. C; Solid State Phys.*, 1979, **12**, L563.
[105] R. Parthasarathy, K. J. Rao, and C. N. R. Rao, *J. Mater. Sci.*, 1981, **16**, 1424.

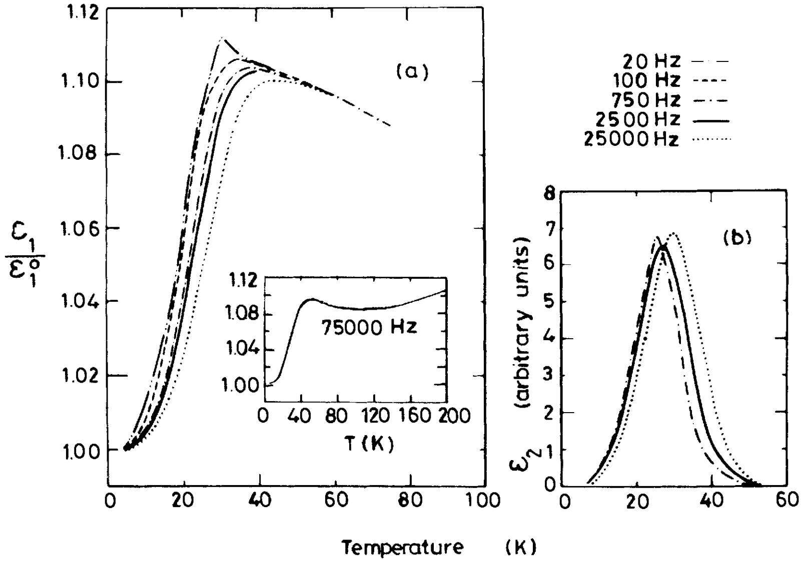

Figure 10 *(a) The normalized dielectric constant versus temperature at various frequencies, of* $(\mathrm{KBr})_{0.5}(\mathrm{KCN})_{0.5}$. *Inset:* 75KHz *data up to* 200K. *(b) Dielectric loss versus temperature for several frequencies*
(After Bhattacharya *et al.*, 1982, *Ref.* 102)

that the glassy state is a thermodynamic entity and not a kinetic accident. Furthermore, the evolution of excess entropy with temperature in these materials is known to parallel that in glasses.[7] It is clear, therefore, that a theory proposed for glasses and the glass transition should be extensible even to those glasses that are not positionally disordered.