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Boson peaks and floppy modes: some relations between constraint and excitation phenomenology, and interpretation, of glasses and the glass transition

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Abstract

We make here an effort to find commonality between the athermal constraint approach to glassiness due to Phillips and Thorpe, in which composition is the key variable, and the more conventional temperature-induced softening approaches to the glass transition at constant composition. A starting point for our discussion is the parallel in behaviour of the boson peak, derived from the vibrational density of states, which is enhanced both by increasing glass fictive temperature (potential energy), and by decreasing glass coordination number (through a rigidity threshold), e.g. in chalcogenide glasses. We relate the potential energy of the glass to a topological defect concentration, and see defect formation as a means of lifting constraints, and hence promoting flow in formally overconstrained glasses. This viewpoint is supported by observations on irradiation of glasses, in which the athermal introduction of defects, or lifting of barriers, may induce flow, or relaxation/annealing. These considerations emphasize the importance of taking temperature, and fictive ('structural') temperature, considerations into account in evaluating the properties of laboratory glasses for comparison with constraint theory predictions.

1. Introduction

The study of the phenomenology of glasses, and of the glass transition which connects glasses to their liquid states, has for many years been developing along two independent parallel paths, with not much attempt to find the links between them. On the one hand, there has been the conventional approach in which the glass is studied as the non-ergodic phase generated by temperature-induced viscous slow-down of an internally equilibrated (if not strictly ergodic) phase, the supercooled liquid [1–3]. On the other hand, there has been the athermal approach, known as constraint theory [4, 5] or rigidity theory [6, 7], in which a glass is seen as the phase generated, at 0 K, by continuous increase in the number of constraints that the system's particles experience, as some composition variable is changed. In this approach, the system

is only glassy when a critical number of constraints, sufficient that ‘rigidity percolates’, have been imposed [6, 7]. Non-rigid amorphous phases are, ideally, floppy at 0 K, though the existence of van der Waals interactions imposes a finite glass transition temperature, which is low compared with the glass temperatures obtained when constraints above the percolation threshold have been added.

Both approaches lead to the expectation that the glass transition will be signalled by more or less sudden changes in the intensive properties of the system, such as compressibility or heat capacity, as the liquid, or floppy, phase becomes rigid. Because there is no temperature in the rigidity models, the changes expected formally are sharp [6] unless non-specific interactions are taken into account [6b] whereas, in the viscous slow-down models, temperature smearing causes the changes to be rounded and continuous.

Both approaches have desirable features and it is reasonable to propose that some combination of the two approaches would be better than either separately in that both temperature and composition-based effects can be simultaneously applied to the problem. Indeed, some efforts in this direction have been made. Angell [8] showed, using temperature-based extrapolations, how the ‘ideal glass temperature’, T_0 , showed a sharp reversal in composition dependence at $\langle r \rangle = 2.4$ whereas the actual glass temperature T_g showed only a blurred increase of slope. The ideal glass temperature is the transition temperature expected when the cooling process is conducted at infinitely slow cooling rates, so that the transition is no longer just a timescale crossing (ergodicity breaking) effect like the ‘normal’ T_g , but rather a true transition consequent on arrival at a configurational ground state. It relates to the ideal (ground state) transition discussed in constraint theory. Also, Roos [9] introduced temperature indirectly by focusing attention on what he described as ‘entropic rigidity’ using information from the temperature dependence of elastic constants.

The purpose of the present paper is to examine some parallels in composition and temperature effects in relevant systems. Specifically, we compare the behaviour of chalcogenide glasses undergoing composition change through the rigidity percolation zone with the behaviour of single (fixed composition) glasses undergoing structure change as the glass under consideration changes its potential energy by virtue of temperature increase. However, to avoid confusion of the important effects caused by increased vibrational amplitudes (thermal smearing), the glasses of different potential energy are examined at constant low temperature, or at 0 K in the case of computer simulations. To simplify the discussion, and also to facilitate a real space, as opposed to configuration space, interpretation, we will discuss the high potential energy glasses in terms of their higher ‘defect’ contents. Defects in glassy solids will be considered specifically in a later section.

2. Boson peaks from the vibrational density of states: (glasses of different constraint counts versus glasses of different thermal history)

Glasses of different potential energy are usually described as glasses of different fictive temperature [10], where the fictive temperature is the temperature at which the potential energy of the glass is the same as the potential energy of the liquid. When the fictive temperature is the same as the actual temperature, then the system is internally equilibrated, even if it is metastable with respect to some crystal(s). However, since there are many ways of increasing the potential energy of a glass without quenching it from liquids of different temperature, we will use the alternative term ‘structural temperature’ (equivalent to ‘effective’ temperature or ‘internal’ temperature [11]) to characterize its potential energy.

In figure 1 we reproduce from [12] the vibrational densities of states VDOS of a series of chalcogenide glasses as the composition is changed through the rigidity threshold at average

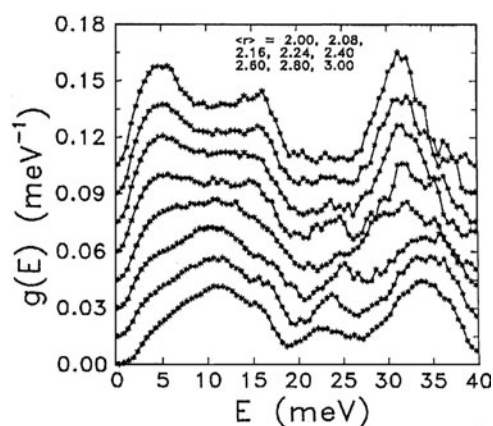


Figure 1. The VDOS for Se-As-Ge glasses obtained from neutron scattering studies. The low frequency band seen at 5 meV (40 cm^{-1}) for pure Se (upper curve) is taken as the floppy mode component of the total VDOS, and is seen to diminish in intensity with decreasing mean coordination number (see legend).

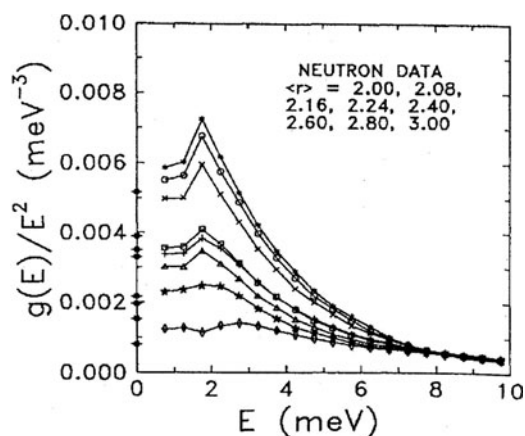


Figure 2. The second moment of the VDOS curves for the same glasses. This function [21, 25] is used to compare with the findings of light scattering studies which yield the so-called boson peak. The figure shows that this function increases in intensity with decreasing constraint count. (Figures 1 and 2 are reproduced from [12], by permission.)

coordination number $\langle r \rangle = 2.4$. In figure 2 we show (after [12]) the same data in the form of $g(E)/E^2$ so that the behaviour can be compared with the behaviour of the boson peak—an almost universal feature of glassy phases. The boson peak, elaborated upon below, is usually observed from light scattering, and the peak form is generally considered to be related to the density of states as in figure 2.

In figures 3 and 4 we show the behaviour of the boson peak in glasses of very different fictive temperature, for two types of glass. The data in figure 3 are for an ionic, disrupted silicate network, glass, studied after quenching at one million times the cooling rate of ordinary glass formation [13] and compared with data for the normal glass and the crystal of the same system. The hyperquenched glasses were studied thermally by Yue *et al* [13] and, subsequently, by means of neutron scattering [14]. Data for the lower frequency part of the total density of

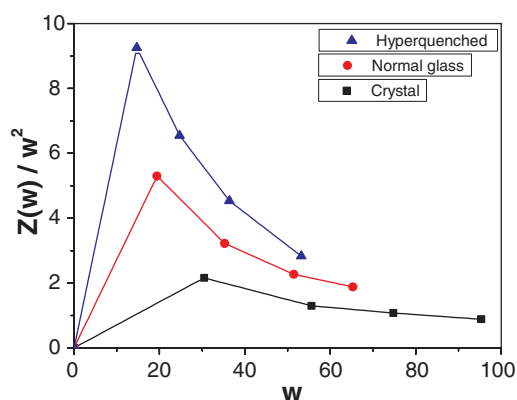


Figure 3. $Z(\omega)/\omega^2$ (related to $g(\omega)/\omega^2$) for a modified silicate, in three different potential energy states: polycrystal, normal glass, and hyperquenched glass (see the legend). The boson peak is not evident in the crystal and is most intense in the high structural temperature glass. The zero-frequency intercept should actually be finite at a value determined by the Debye theory from the sound velocity.

(This figure is in colour only in the electronic version)

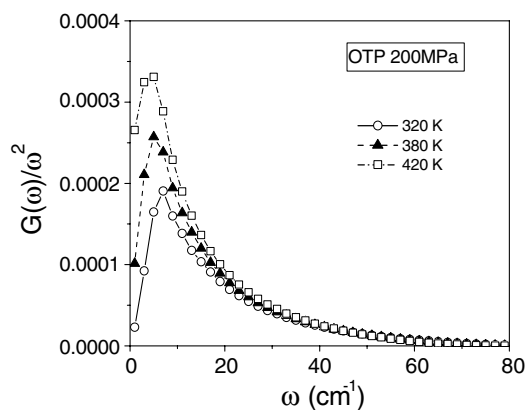


Figure 4. The second moment of the VDOS for a model molecular glass former in three different inherent structures characterized by the structural temperatures, given in the legend. The boson peak intensity increases with increasing structural temperature. (From [14b], by permission.)

states are compared, again after division by ω^2 , with data for the normal glass and the crystal in figure 3 for these three potential energy states of the same system. Behaviour comparable to that seen in figure 3 was reported long ago for As_2Se_3 glass by Kawamura *et al* [15] using light scattering methods, though over a smaller range of cooling rates.

The second glassy system for which similar boson peak behaviour with increasing disorder is seen, in figure 4, is a model molecular glass former [16], parametrized to behave like the much-studied aromatic hydrocarbon, *o*-terphenyl. In this case [16] there are none of the ambiguities that attend experimental determinations of the VDOS, fictive temperature, or uniformity of quench, so the effect of inherent liquid structure on the total VDOS is very well defined. The boson peak intensity increases with increasing structural temperature as seen in figure 4 (from [14b]), in a manner very similar to that observed for the silicate glass. If we interpret the increasing potential energy of the high structural temperature glasses as arising

from increasing concentration of defects, then the boson peak intensity would seem to be a direct indicator of defect concentration.

Before discussing the (controversial) nature of the boson peak any further we must make the principal observation of this paper. This is that, in the light of the comparison of figure 2 with figures 3 and 4, there is a suggestive similarity between the behaviour of the boson peak under composition change through a rigidity threshold, and that under temperature change through a glass transition. The suggestion is that temperature-induced structural excitations (defects) are similar in their effect on glass dynamics to ‘chemically lifted’ constraints. Both are critically involved in the ability of an amorphous structure to relax, i.e. in the fluid properties of amorphous materials. Later we review how athermal introduction of structural excitations can produce the same effects.

The boson peak is of special significance to glass former phenomenology. It occurs just at the crossover between vibration and relaxation [1], as is best seen in computer simulations of the intermediate scattering function $S(Q, t)$ for a strong liquid, e.g. SiO_2 [17, 18]. This ‘boson dip’ in $S(Q, t)$, which is exaggerated in small systems because of weak damping [17], is related to the overshoot in the mean square displacement versus time plot seen just before the onset of anomalous diffusion [1] in strong liquids. When studied in glasses produced at the same cooling rate, it is usually more prominent in ‘strong’ glass formers than in ‘fragile’ glass formers [19]. This relation can also be seen in simulations, where the ‘boson dip’ in $S(Q, t)$ for SiO_2 is greatly reduced after the liquid is converted from strong to fragile behaviour by decrease of volume [17]. The data of figures 3 and 4 suggest that this simple distinction will be reversed when glasses formed at higher cooling rates are compared in the absence of thermal smearing effects.

The boson peak is closely associated with the presence of anomalies in the low temperature specific heat, which strongly violates the Debye theory expectations [20]. The maximum in the low temperature excess specific heat is found at a temperature which corresponds to the frequency of the boson peak ($\text{IK} \equiv 0.7 \text{ cm}^{-1}$). There is general agreement that the excess vibrational modes responsible for the boson peak and the specific heat anomaly, are a consequence of disorder. On the other hand, much confusion and disagreement exists concerning the characterization of these modes as extended versus localized (random phase versus coherent phase), acoustic versus soft optic, transverse versus longitudinal, and harmonic versus anharmonic. Furthermore, there is not yet any good understanding of how these modes are generated. Their strong dependence on the potential energy of the glass (figures 3 and 4), and the manner in which the low frequency modes are generated at the expense of modes of high frequency in model glasses (figure 7 of [14a]), are new ingredients in the controversy, which we certainly do not resolve here. A number of reviews and key articles are available [21].

Before leaving this section there are two additional points about boson peaks that are to be noted. The first is that the results of light scattering and neutron scattering are not always compatible. For instance the series of light scattering-based boson peaks shown for the highly relevant Ge–Se glass series by Murase [21f] do not show the systematic development of the boson peak intensity seen in figure 2 from neutron scattering data, unless a large subtractive correction for lower frequency quasielastic scattering is first made. This could also be influenced by the effect of composition on the matrix elements of the coupling of light to the vibrational modes. The second is that the effect of temperature on the boson peak is strictly dependent on the thermodynamic conditions of the observation, particularly in fragile glass formers. In fact the behaviour described below for constant pressure systems is exactly reversed for constant volume systems. This has been discussed in detail in a recent paper [14b] and this will not be repeated here. In laboratory studies of glass formers, the natural thermodynamic condition is that of constant pressure, usually atmospheric while simulations

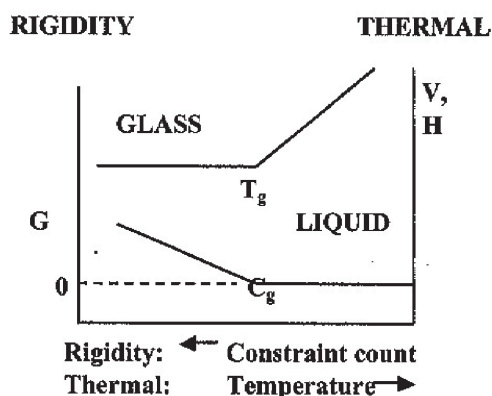


Figure 5. Comparison of the manner in which the non-rigid phase is generated in the alternative thermal and rigidity scenarios detailed in the introduction. In each case the glass is on the left side of the diagram, and the liquid on the right. In the case of the thermal scenario, the slope change is in the extensive property, volume or enthalpy, while the intensive properties, heat capacity or expansivity, execute a kinetically smeared jump. In the rigidity scenario it is an intensive property, the shear modulus, that changes slope at the onset of glassiness.

tend to be performed at constant volume. In this paper we will consider only constant pressure studies. We note, however, that the potential energy landscape that is so frequently invoked in discussions of complex systems, is only uniquely defined by the potential of interaction of the particles if the volume remains constant [22–24]. If the volume changes, the landscape changes, sometimes dramatically.

2.1. The generic glass–liquid diagram

The parallel between rigidity theory and thermal de-excitation models of vitrification may be depicted as in figure 5. Increasing constraint count has the same effect as decreasing temperature. In the former case, a system with a fixed number of constraints finds the constraints being lifted as temperature-induced excitations are introduced. As remarked in an earlier paper [8], the constraints can be treated as carrying a Boltzmann probability of being intact at any temperature. For each constraint lifted, or increase in potential energy in the case of fixed composition systems, figure 3 of this paper (and figure 7 of [14a]) show that new floppy modes appear at the expense of high frequency components of the VDOS. ‘Floppy’ implies that the new modes are generated at the low frequency end of the density of states, and hence enhance the intensity of any pre-existing boson peak. We note that the full width at half-height FWHH of the Gaussian component of the VDOS that builds up at low frequencies (at the expense of a high frequency Gaussian component) during the configurational excitation of the model OTP glass [14a] is about 20 cm^{-1} , comparable with that of the component of the VDOS attributed to floppy modes in the case of chalcogenide glasses (see figure 1).

3. Boson peaks and floppy modes in relation to thermally induced defects in glasses

Now we seek to associate the build-up in low frequency modes and the associated decrease in rigidity, with the thermal induction of defects. We do this by first presenting evidence for the existence of point defects in weak network glasses, and then relating the boson peak intensity increases observed in the higher fictive temperature glasses of figures 3 and 4 to the increases

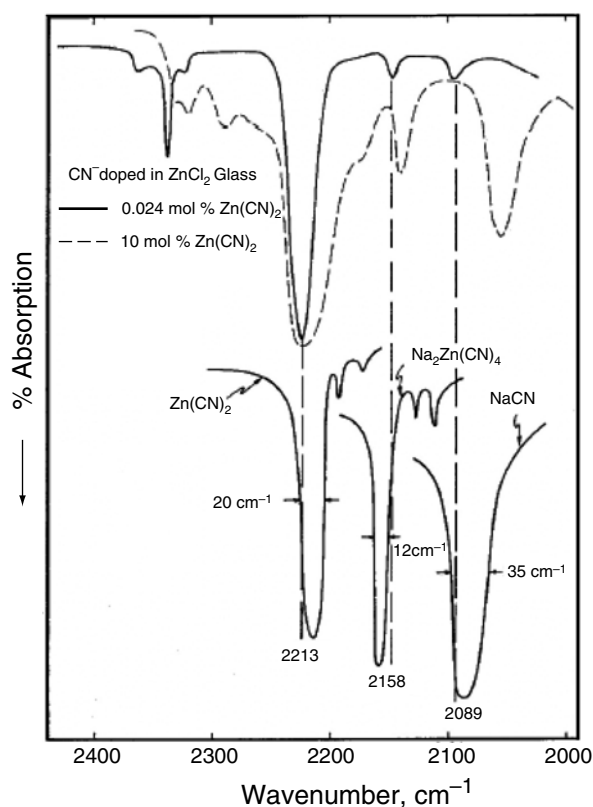


Figure 6. IR spectra of CN^- ions in ZnCl_2 glass, and three crystals, showing three distinct anion environments in the glass, two of which represent network defects. (From [25], by permission.)

in defect concentration. Later we will relate these observations to those on cold flow in glasses due to a radiation-induced defect population.

The occurrence of defects of a precise 'broken bond' nature in a network glass has been demonstrated rather clearly by using probe anions possessing vibrational signatures, as substitutes for the bridging chloride species of a zinc chloride glass. Figure 6 (taken from [25]) shows the vibrational spectra of anhydrous ZnCl_2 glasses containing small concentrations of the bridging anion CN^- (introduced as $\text{Zn}(\text{CN})_2$) that can substitute for Cl^- bridges between the tetrahedrally coordinated Zn^{2+} centres of the network structure of this substance. The electronic environment of the triple-bonded CN^- ion is signalled by its vibration frequency in the 2200 cm^{-1} region of the IR spectrum. It is clear, from figure 4, that the CN^- ion can have three distinct states in the glass. Furthermore, it is clear from comparison with the spectra of the crystalline cyanide compounds that the defects correspond to anions that are (i) bridging (as in $\text{Zn}(\text{CN})_2$), (ii) bound but not bridging (as in $\text{Na}_2\text{Zn}(\text{CN})_4$), and (iii) free CN^- (as in the sodium cyanide salt), respectively. While this system has yet to be studied by means of hyperquenching, it seems reasonable to see the distinct states, which will have Gaussian distributions, as defects in the fully bridged structure that would constitute the ground state of the glass. Network *centre* defects were studied in the same work, using $\text{Ni}(\text{II})$ probe cations. These were seen by electronic spectroscopy to occupy tetrahedral sites in the melt and in the quenched glass, but to anneal, in a simple two-site exchange manner, to octahedral sites. To the $\text{Ni}(\text{II})$ species, due to ligand field effects, the tetrahedral site is energetically an excited state, or defect. Again it is geometrically well defined, according to the spectroscopic evidence.

4. Defects and their relation to glass solidity

That well-defined topological defects, such as those described in the last section, should exist in glasses is not an accepted idea except in radiation effects circles where the necessity for point electronic defects has been made clear by decades of research on such highly structured systems as SiO₂, B₂O₃, and amorphous Si. The complex annealing kinetics of such defects is the subject of a large literature, reviewed, for example, in [27].

That defects should play a major role in the dynamics of glasses should not be difficult to accept, when it is realized how very rapidly defect-assisted diffusion occurs in crystals when compared with glasses. For instance, the diffusion coefficients of molecules in glasses have been measured directly by Ediger and co-workers [28], and the values found, $10^{-20} \text{ m}^2 \text{ s}^{-1}$, at T_g , are orders of magnitude smaller than those that had been measured in crystal state studies of even well-known substances such as ice, until very recently, comparable values now found are $10^{-20} \text{ m}^2 \text{ s}^{-1}$ at 163 K [29, 30].

The difference between the defect physics in glasses and crystals is twofold. Firstly, the amorphous phases tolerate much higher defect site fractions in their structures before changing to another phase, even if the second phase is a second liquid (polyamorphism) [1, 21c]. Secondly, the defects, rather than having a single free energy of formation, experience a distribution of energies, usually of Gaussian form. It is shown elsewhere [31] how the Gaussian distribution of defect excitation energies can remove some of the problems associated with simple defect models of the glass transition, such as the ‘bond lattice’ model in its published form [32]. Also shown elsewhere [33] is the manner in which defect models with non-random defect distributions can produce first-order phase transitions in which the coexisting phases have different excitation levels, and hence different densities (as recently seen in computer simulations of water [34, 35] and liquid silicon [36–38]).

It is clear in these models that, just as kinetic fragility and thermodynamic fragility are closely linked [39], so is the diffusive mobility of the liquid molecules closely linked to the concentration of excitations (defects).

The ‘solidity’ of a liquid [40] at any $T > T_g$, which is the quantity considered in rigidity theories, may be described in terms of its inverse viscosity η^{-1} [41] or its shear rigidity G_∞ [40]. These quantities are connected to each other through the Maxwell equation of viscoelasticity,

$$\eta = G_\infty \tau, \quad (1)$$

where τ is the average relaxation time. And since τ is related to the diffusivity by the Einstein equation, the solidity is determined by the defect concentration. Granato [42] has given reasons for expecting defects in liquids to be related to the interstitial defects of crystalline solids, which are known to have a strong depressing effect on the shear modulus.

5. Athermal constraint breaking at constant composition: radiation-induced flow and relaxation

To complete the connection of the normal temperature-induced softening to the constraint break softening of rigidity theory, we need to consider the introduction of defects at 0 K. In effect, this is achieved by low temperature irradiation of a glass, which may apparently be carried out with radiations of different character, e.g. with IR light for chalcogenide glasses [43–47] and with light or heavy ion/atom bombardment for silica and metallic glasses [48–51]. The phenomenon of radiation-induced cold flow of glasses is a direct demonstration that *isocompositional* rigidity de-percolation can be obtained by constraint breaking.

The most directly relevant case is that of sub-bandgap irradiation of chalcogenide glasses since it is the chalcogenide glasses that have been the subject of the most definitive studies

of the phenomenon of rigidity percolation by composition change [7, 52–59]. Sub-bandgap irradiation (in the tail of the band) guarantees that the whole sample is uniformly irradiated. It produces photoinduced rupture and/or switching of the chemical bonds that hold the structure in the rigid state. The process is athermal as demonstrated in both [43] and [44].

The most systematic study of this effect is the calorimetric study of the Ge–Se system by Lucas *et al* [44]. Here the dose-dependent relaxation of binary glasses of different composition, far below T_g , was quantified by irradiate-and-scan methods. Systematic effects, equivalent to annealing at much higher temperatures, were found. This means that the net effect of the irradiation was to allow defects to heal, presumably by radiatively (and temporarily) disrupting bonds that jammed the structure in the higher energy state. The converse effect is possible when a very well-annealed glass is irradiated at high dose rate and the glass is found to increase in enthalpy [44b]. In each case there should be some signal of the enthalpy change in the intensity of the boson peak, but this has yet to be studied systematically (a beginning was made in [45]). Such studies may be very helpful in sorting out the relative contributions of the thermodynamic and kinetic factors, $\Delta\mu$ (the energy barrier to rearrangements), and S_c (the configurational entropy), in the Adam–Gibbs expression [2, 44] for the relaxation time,

$$\tau = \tau_0 \exp(-C \Delta\mu / T S_c), \quad (2)$$

since, well below T_g , S_c can only decrease with time if the energy barrier $\Delta\mu$ is first decreased [44].

In the case of Tanaka’s demonstration [43] that, under irradiation, the viscosity of As_2S_3 glass is reduced to a value equivalent to that measured at T_g , one cannot tell whether the short shear relaxation time that was seen was due to a decrease in energy barrier, $\Delta\mu$, or to increase in S_c (i.e. defect generation). That near-bandgap radiation fluidizes a rigid phase by creating defects is an idea that dates back to Mott [60], and Fritsche [61], but we see now that the question is more complex. For heavy atom bombardment effects, observed in the laboratory as surface smoothing [51], diffusion, mediated by defect formation, has been directly implicated by the simulations of Mayr and co-workers [50]. The useful suggestion of the present paper is that if flow arises because constraints are lifted, e.g. by defect formation, then the evidence should be found in the co-generation of floppy modes—detectable as enhanced boson peaks. Boson peaks are certainly in evidence in the Raman studies of radiation-fluidized As_2Se_3 glass by Yannopoulos and co-workers [45, see figure 4], but correlations of the sort discussed here were not specifically researched.

In the case of the Lucas *et al* study [44], the behaviour due to $\Delta\mu$ reduction was demonstrated to correlate with the known variation in fragility with composition about the rigidity percolation threshold [53]. At the composition $\langle r \rangle = 2.4$, where the fragility goes through a minimum, the effect of radiation on the relaxation degree was minimal, which is striking. It is striking because a natural interpretation of strong liquid behaviour has been that liquids are ‘strong’ because their relaxation kinetics are dominated by a large $\Delta\mu$ term in equation (2) [62, 63]—and this would seem to be contradicted by the weakness of the irradiation-induced ageing effects at this composition. Rather, the thermodynamic effects of very small rates of entropy production with temperature increase, evidenced by the very small increase in heat capacity at T_g at this composition [53], would seem responsible, again confirming the correlation of kinetic with thermodynamic behaviour discussed elsewhere [39]. The very small heat capacity change and the correlated weak non-linearity/ageing effects [64] (called ‘reversibility’ of the kinetic glass transition, in [56]) is itself attributed [56, 65, 66] to the absence of strain at the composition where constraints just balance degrees of freedom. It will therefore be interesting to find whether the characteristics of the boson peak (localized versus collective nature [21d, 21e], anharmonicity [21h, 26], etc), show any special signatures in this

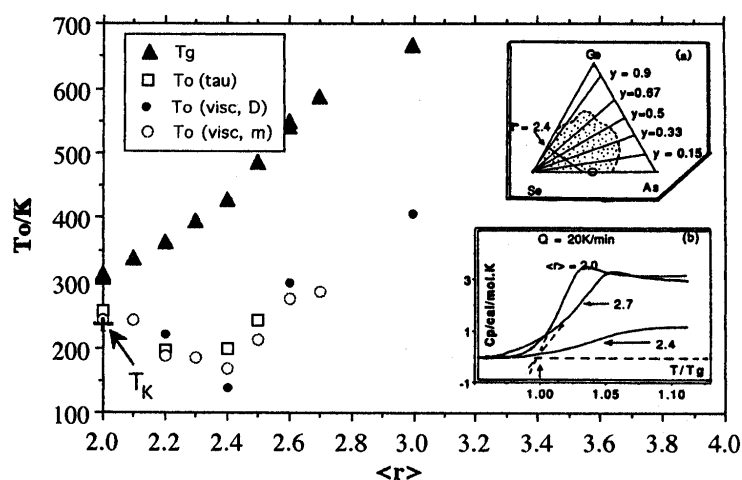


Figure 7. Glass transitions (solid triangles) and ideal glass transitions (T_0) corresponding to thermal defect-free states, for glasses in the ternary chalcogenide system, Ge–As–Se, along the $y = 0.5$ line in the inset (a). T_K is the Kauzmann temperature for pure Se derived from calorimetric data. Note the sharp change in the temperature T_0 that occurs near $\langle r \rangle = 2.4$. Within the scatter of ideal glass assessments, there could be a flat domain near 2.4 corresponding to the ‘intermediate phase’ identified by Boolchand and co-workers [56] using a finer composition grid. (From [8], by permission.)

‘intermediate phase’ of the developing constraint theory [56, 65, 66]. This theory may help interpret the origin of ‘strong’ versus ‘fragile’ behaviour in glass formers, a problem which is under intensive investigation [67].

A radiation effect on dynamics that is more difficult to interpret is that reported by Gump *et al* [46], who measured the Brillouin shift and peak width of Ge–Se glasses through the rigidity transition and found the longitudinal Brillouin peak to broaden strongly to low frequencies, such that the peak shifted by 5%, reversibly, for a threefold increase in incident power. This effect was only found in the composition range 15–25% Ge, with maximum effect close to the transition value, 20%, where the unirradiated glass structure is very insensitive to temperature change or to ageing at constant temperature below T_g [56].

It will be interesting, in view of the above, to compare the properties of irradiated glasses with those of glasses whose energies have been increased by simple mechanical damage [68].

6. Ground state properties of laboratory glasses through the rigidity threshold

The study of Lucas *et al* [44] showed that the thermodynamic state of a chalcogenide glass can be lowered towards its ideal state (free of excess entropy, or temperature-induced floppy modes) by irradiation near the bandgap (see in particular figures 3 and 4 of [44]). The glass in its ideal state—where all constraints permitted by the composition are in place—should be the state that is compared with the predictions of rigidity theory. Thus irradiation annealing tends to achieve what is usually only achieved by extrapolation, to infinite timescales, of laboratory data acquired in the ergodic regime (i.e. on laboratory timescales). It seems worthwhile in this respect to recall what the extrapolations of ergodic data predict for the glasses in the Ge–Se system. Thus we reproduce, in figure 7, the behaviour derived for the glass transition versus composition function for the ideal glasses in which there are no thermally ruptured constraints [8, 66].

Figure 5 shows that the glass transition of the ideal glass series, rather than having the very mild and continuous behaviour of the laboratory (finite timescale) quantity T_g , has a much sharper behaviour, almost singular at $\langle r \rangle = 2.4$. Of course the apparent sharpness may be a reflection of the relatively few compositions studied, and a flat ideal region corresponding to the ‘intermediate phase’ [58–60] might be revealed by use of a finer composition grid. Regardless of these details, it is clear that the defect-free behaviour is much more interesting than the ordinary glass behaviour.

Acknowledgments

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