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Ten questions on glassformers, and a real space ‘excitations’ model with some answers on fragility and phase transitions

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Abstract. We formulate ten questions, covering outstanding aspects of the phenomenology of glassforming liquids, which we believe must be properly answered by any successful theory of structural glassformers. The questions range across thermodynamic, mass transport and vibrational dynamics phenomena. While these questions will only be addressed properly by a collective variables approach (many aspects of which are reported in these proceedings) a number of them can be dealt with by use of simple physical models of appropriate form. Here we discuss one such model in which the existence of elementary configurational excitations of the amorphous quasilattice is proposed. These states, which may range from broken bonds to packing defects, can be excited independently in the majority of cases, or cooperatively in others. We summarize essential results of this model. These suggest that the source of the different fragilities in liquids (and the reason that structural glasses, alone among ‘glassy’ systems, have marked heat capacity jumps at T_g) may lie largely in the way these configurational excitations couple to the vibrational modes of the system. The generation of low frequency modes in the density of *vibrational* states, as a direct consequence of the excitation of *configurational* states, explains why the quasi-elastic scattering from fragile liquids is so much stronger near and above T_g than in the case of strong liquids, and why the normal glass transition can be detected in picosecond time scale experiments.

Interactions among the ‘excitations’, or ‘defects’, are taken into account using the one component system equivalent of the binary system ‘regular solution’ model (which keeps only the first order term of the free energy of mixing expansion). We show that a liquid–liquid first order transition must occur at sufficiently strong defect–defect interactions. The highly overconstrained amorphous silicon quasilattice is a strong candidate for such a transition. We identify the ‘first order melting’ of amorphous silicon, and the sudden, reproducible, termination of supercooling in experimental liquid silicon and germanium, with the phase transition predicted by the model. Many more cases of this phase transition may be anticipated, and a corresponding range of glasses with low residual entropies—approaching the ‘perfect’ glass state—are predicted.

1. Introduction: ten questions

The behaviour of glassforming liquids is broadly recognized as being rich in phenomenology, and, as this issue shows, theorists are very actively exploring ways of accounting for both its thermodynamic and relaxational aspects. By way of providing some focus for such efforts, we start this paper by using our familiarity with many of the experimental ‘structural’ glassformer systems to formulate ten leading questions which we believe the theoretical community needs to bear in mind as questions that a successful theory should be able to answer. The questions are illustrated graphically in most cases by the panels of figure 1. Other authors working in this area would no doubt generate somewhat different lists of key questions, but many would be in common with the following. A much more detailed list, and the current ‘state of play’ with respect to observations (as seen by a panel of workers in the area), has recently become

available [1], and the following is, to a considerable extent, an extract from that overview. Both there, and here, we avoid any commentary on the adequacy, with respect to these questions, of the many available theoretical treatments. Further, we do not intend this as a review and only cite sources essential to the formulation of the questions.

The ten key questions, in the view of the present author, are:

- (1) *Why is there a pending entropy crisis for structural glassformers and not for other glass types?* By other glasses we mean spin glasses, proton glasses, vortex glasses, dipole glasses etc [2]. This question can be rephrased as: why do fragile structural glassformers generate entropy so rapidly as temperature increases above the glass transition temperature, figure 1(a, i)? This in turn means, why is the heat capacity in the *ergodic* state of fragile liquids so much greater than that of the glassy state (which has heat capacity due to phonons only, except for very weak contributions from secondary relaxations), figure 1(a, ii)? The diminutive rate at which spin glasses and quadrupole glasses generate configurational entropy above their T_g can be seen from the contrast of their heat capacity–temperature plots with those of structural glasses (see figure 1 of Angell (1990) [2]). No heat capacity jump at all is seen at ' T_g '. A detail of this question is the subsidiary problem of why the large excess heat capacity (liquid crystal) in the case of molecular liquids follows a hyperbolic temperature dependence so well (but see discussion below concerning the excitation model).
- (2) *Why do structural glasses exhibit such a range of fragilities?* Fragility can be defined both from the kinetic behaviour [3], or from the thermodynamic behaviour [3, 4] of the liquid, using the scaled plots of figure 1(b, i and ii). Very strong glassformers, like SiO_2 , show only very small departures from Arrhenius relaxation time–temperature dependence, with a phonon-like attempt frequency (pre-exponent 10^{-14} s), and exhibit only small calorimetric manifestations of the glass transition (increases of heat capacity on restoration of ergodicity). Fragile liquids by contrast show large departures from Arrhenius temperature dependence and large heat capacity jumps, see figure 1(a, i). The thermodynamic fragility can be misrepresented by looking only at the heat capacity jump, however. This is because the Adam–Gibbs equation (equation (1) below), which makes one possible connection between the two, inputs the *total* excess entropy [5]. A large molar heat capacity change only implies fragility if the frozen-in molar entropy is small, which is often not the case. This is taken care of in the recently suggested [4] thermodynamic fragility plot depicted in figure 1(b, ii). Note that the alcohols, glycerol and propanol, which seem anomalous when their large heat capacity jumps are compared with their intermediate positions in the kinetic fragility plot, are back in the middle of the pattern when the figure 1(b, ii) representation is used.

Thermodynamic and kinetic fragilities of diverse liquids will fall in the same order if the kinetic term C in the Adam–Gibbs (A–G) equation does not vary too much from system to system when correctly assessed. The A–G equation is

$$\tau = \tau_0 \exp(C/TS_c) \quad (1)$$

where τ_0 is about 10^{-14} s, C is a constant containing an energy barrier, $\Delta\mu$, per molecule, opposing the group re-arrangement, and S_c is the entropy difference between liquid and crystal. A constancy of C is hardly to be expected, especially when the re-arranging units are not the whole molecules (e.g. complex molecules and polymers, see section 2). This, and the relation between kinetic and thermodynamic fragilities, are both controversial [4, 6, 7].

A related question, specific to covalent glasses, is, why are optimally constrained glasses such as Ge–Se, or Ge–As–Se, with an average bond number per atom of 2.4 (the Phillips

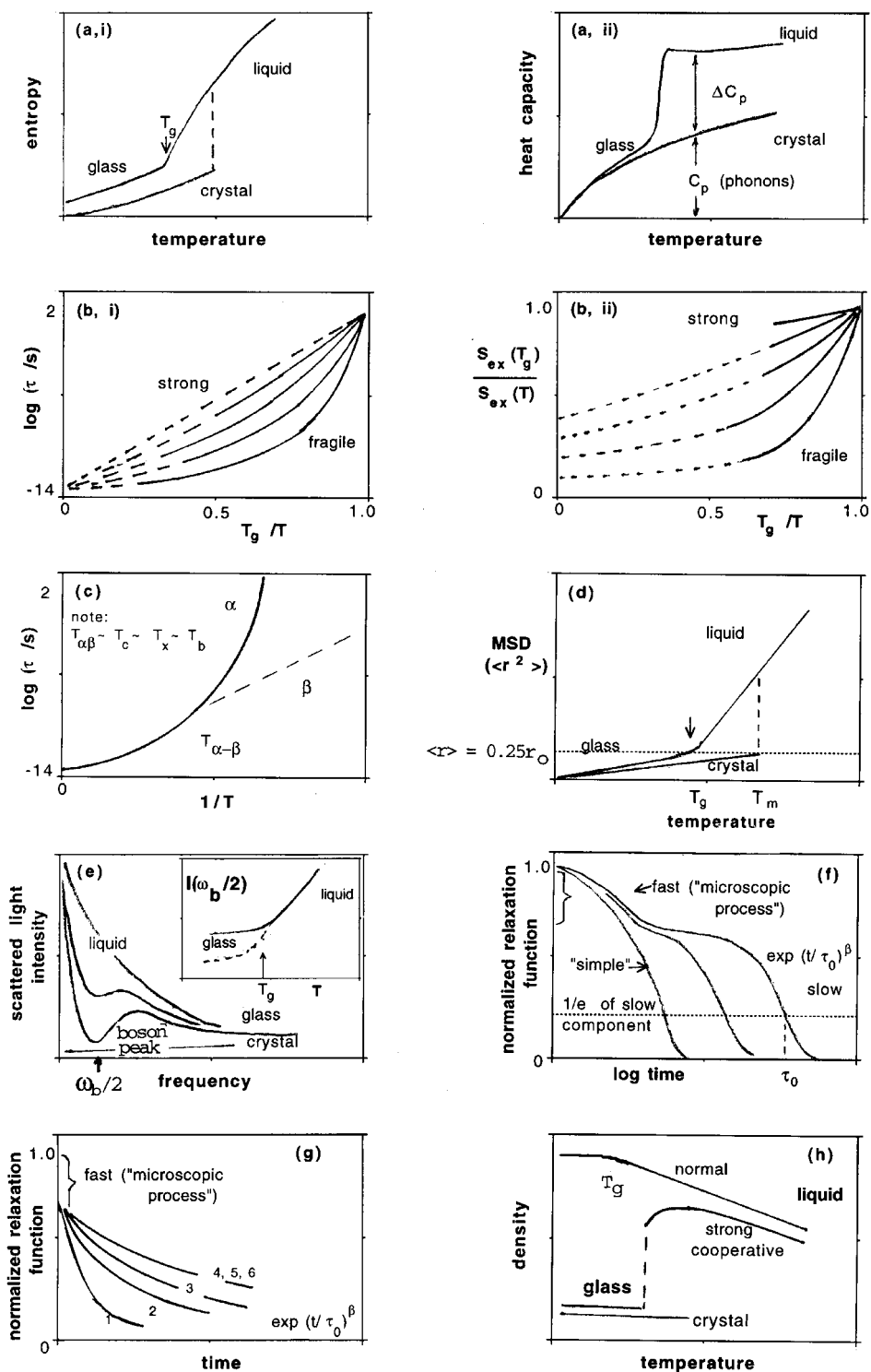


Figure 1. Key elements of the phenomenology of the viscous liquid and glassy states of matter. Details of the points being illustrated are dealt with under questions (1)–(10) in the text.

Thorpe threshold value), so non-fragile (Angell *et al* [2])? Since covalent glasses can be considered simple by virtue of the dominance of a single type of interaction and the ‘on-off’ nature of the bonds (Angell *et al* [2]), this question is non-trivial.

- (3) *Why do fragile glassformers often (but not always) show the α - β bifurcation at $T_{\alpha-\beta}$ and why does $T_{\alpha-\beta}$ correspond to T_c of the mode coupling theory?* The splitting-off of a broad, generally weak, and Arrhenius-like relaxation from the alpha relaxation as the liquid relaxation time falls below about 100 ns, (figure 1(c)) is often observed in fragile liquids [8] and can also be seen with difficulty in some intermediate liquids [9]. It has non-universal characteristics, in some cases disappearing on annealing below T_g and in other cases not [10]. Its origin is not well understood, but it seems to involve more localized motions than the α -relaxation. Its width increases as its peak strength decreases. A striking feature is that the bifurcation falls at almost the same temperature as the T_c of mode coupling theory, the crossover temperature T_x of Rössler scaling, and the T_B of the Stickel analysis of relaxation time temperature dependence [9, 11, 12]. This correspondence needs to be checked out in more detail over a wider range of systems.
- (4) *Why does the mean squared particle displacement, MSD, measured on ps time scales, show a break at or near T_g —where the alpha relaxation time is 200 s?* This phenomenon concerns motions which occur on much shorter time scales than that of the secondary or β relaxation discussed in question (3). A typical result is that seen for selenium in [13], which is reproduced schematically in figure 1(d). In a process which anticipates the glass transition, the mean squared centre of mass displacement starts to increase rapidly in the same temperature range in which the quasi-elastic scattering of neutrons or light begins its rapid increase [13, 14]. At these temperatures, the corresponding diffusional MSD should be of order 10^{-13} nm (and hence would be totally undetectable). The increase begins when the MSD determined by the low temperature harmonic oscillations reaches a value comparable with that characterizing the crystal at its melting point [13], suggesting some sort of Lindeman criterion for the α -relaxation rearrangements. Is it anharmonicity increases or non-diffusional elementary configurational excitations that are responsible?
- (5) *What is the origin of the boson peak, and the relation between the boson peak, the motions responsible for the MSD behaviour discussed in question (4), and the two-level systems responsible for the low temperature specific heat anomalies?* The boson peak is the term given to an excess in the low frequency density of states of glassy solids over the ω^2 dependence characteristic of crystalline substances. Boson peaks are seen most easily in the scattering of light from glassy solids [15] as a feature remaining after the thermal population effect has been removed (figure 1(e)). Boson peaks have seemed to be universal for glassy substances [15], though they are remarkably absent in certain cases of interest to the present paper (e.g. glassy water [16]). Low temperature anomalies in the specific heat (violations of the Debye T^3 law), which have also seemed to be ‘ubiquitous’ to glasses [17–19] have been associated with the presence of a boson peak [15]. These are also now found to be missing in the cases where no boson peak is found [20, 21].
- (6) *Why is the relaxation function non-exponential at temperatures where the relaxation time is non-Arrhenius?* It has always been assumed, in analysis of relaxation processes in glasses and viscous liquids [22, 23], that there are two principal time scales, and two sources of relaxation. The first (short time scale) step is the fast relaxation associated with vibrational degrees of freedom, which equilibrate (following some step in temperature or pressure) on such a fast time scale that glass phenomenologists have not been concerned with it—except for needing to know the magnitude of the polarization, etc, that it produces (see figure 1(f)). It is now usually referred to as ‘the microscopic process’ [24] and is an

essential component of the mode coupling theory. The second is the slower relaxation associated with the reorganization of the molecular structure to minimize the Gibbs free energy of the substance at the new T, P point. The idea is well illustrated in figure 8 of [25]. It is this latter process which is found to be non-exponential in almost all processes in viscous liquids and glasses. Exceptions associated with dominance of large length scale processes or long time processes, are discussed elsewhere [1]. In the high temperature regime ($T_m < T < T_b$), the two processes merge and the total relaxation is exponential ('simple liquid' regime figure 1(f, ii)). For any condition in which there is a two step relaxation the second step tends to be non-exponential and, at least near T_g , the departure from exponentiality increases as the temperature decreases. The behaviour depends on the interplay of α - and β - relaxations, as reviewed in [1]. The departure from exponentiality is well approximated in most cases by the stretched exponential (Kohlrausch) expression [26].

Two subsidiary questions here are: (i) why is the non-exponentiality larger and more temperature dependent for fragile glassformers [27]? (ii) what is the connection between non-exponentiality and kinetic microheterogeneity on the one hand, and structural microheterogeneity on the other? (See the next question.)

- (7) *What is the connection between microheterogeneous dynamics, seen in computer simulation studies at temperatures below the onset temperature of two-step relaxation, the microheterogeneous dynamics seen in experimental studies near T_g , and the non-exponentiality of relaxation?* Once caging (two step relaxation) has set in, computer simulation studies show that a non-Gaussian distribution of particle displacements (which is intrinsic to any two stage relaxation) sets in, accompanied by a set of especially mobile particles which seem to move in 'strings' (Donati *et al* 1998 [28]). The strings aggregate over time into clusters whose average size seems to diverge as the MCT T_c , i.e. T_x , is approached on cooling (Glotzer and Donati, Donati *et al* 1999 [28]). The average length of the strings diverges more slowly (Glotzer [28]). Comparable behaviour is now being seen in colloidal systems [29], particularly by Weeks and Weitz. On the other hand, experiments on laboratory liquids show that a dynamic heterogeneity becomes an increasingly important aspect of the structural relaxation at much lower temperatures, near T_g [30–33], and seems clearest in fragile liquids [31]. The connection to an underlying structural heterogeneity is implicit in the discussion of [32] but the structural heterogeneity connection has not yet been explicitly confirmed, and it may not be possible to detect it directly (see discussion in Ediger [36]). Annealing experiments should be very diagnostic in this respect (see question (9)). Attempts to identify directly a growing static structural length scale near T_g have so far not been successful, and the reason for this is a part of question (7). For reviews, see [34] (experiments (Böhmer) and theories (Silllescu)).
- (8) *Why does the Stokes–Einstein relation between viscosity and diffusivity in single component systems break down near and below the crossover temperature $T_X(T_c, T_B)$?* The temperature dependence of diffusivity has, surprisingly to most in the field, been found to decrease less rapidly with decreasing temperature, than the viscosity, causing violations of the Stokes–Einstein temperature which can become very large in a non-intuitive direction as T_g is approached [35, 36]. Theories and models that relate this decoupling to heterogeneity are reviewed by Silllescu [34]. Whether this applies to all molecular liquids or only to fragile liquids is not yet clear. The diffusivity of network liquids, in the strong extreme of SiO_2 at least, remains coupled to the viscosity, though only for the network centre particles (Si) [37]. The diffusivity of oxygen decouples by two orders of magnitude [38]. Decoupling of cations from anion motions is commonly

seen in ionic liquids with small alkali, or group IB cations. In some cases the decoupling ratio, $(\tau_{\text{structural}}/\tau_{\text{conductivity}})$ [25] can reach 12 orders of magnitude [39]. The situation for anions in fragile ionic liquids is not yet determined.

- (9) *Why are the kinetics of annealing (ageing, equilibration) so non-linear (structure dependent) for fragile liquids?* Sometimes called the third canonical characteristic of glassforming liquids [14, 40, 41], the dependence of the relaxation time of an equilibrating liquid on two distinct temperatures has been recognized since the early 1900s. One of these is, of course, the normal (kinetic-energy-based) temperature and the other is the (potential energy based) structural (or ‘fictive’) temperature. In liquids above T_g , the two are the same (unless a fast T -jump experiment is being performed), but below T_g where the structure has become frozen, the fictive temperature is higher. The fictive temperature is the temperature where the ergodicity of the system was broken, and it characterizes the frozen-in structure which is evolving. In strong liquids the effect of the fictive temperature is minimal. In fragile liquids it can dominate the relaxation. Then the relaxation rate depends on whether the equilibrium is being approached from above or below.

Figure 1(g) illustrates the effect of fictive temperature on the isothermal kinetics of a faster process (which could be mechanical relaxation or conductivity relaxation, for instance). The fictive temperature equals the temperature of the experiment only for runs 4, 5 and 6. An excellent review is given by Hodge [41]. How this behaviour is to be related to the non-exponentiality, hence microheterogeneity, of the earlier questions, remains to be clarified.

- (10) *Why does the excitation of the structural degrees of freedom in some overconstrained systems (e.g. Si, Ge) become first order in character, like a weak melting transition?* Here we refer to the phenomenon previously called the ‘melting’ of amorphous silicon [42, 43]. This is the sudden transition of the amorphous state to the metallic liquid predicted on the basis of thermodynamic data by Turnbull [42] and later observed by Thompson *et al* [43] by flash heating experiments. The problem in observing it is that, at the temperature of this transition, the crystallization occurs on an extremely short time scale, and hence masks it. The transition has since been studied in more leisurely fashion using computer simulation [44]. Something very similar seems to occur in supercooled water, hence the phenomenon is not simply explained by the delocalization of electrons in the high temperature phase of Si. The same phenomenon can be seen in liquid Ge and other systems with the same open network crystal structures (e.g. GaSb, AIP). A comparison with normal liquid behaviour is shown in figure 1(h).

Related questions are: what are the conditions which must be satisfied in order to generate polyamorphic transitions far below T_g , and when are these an indication of a true first order phase transition which would occur at higher temperatures except for the intervention of crystallization?

Many authors would consider some, if not all, of the above questions already to have been answered to their satisfaction. It is not our role here to adjudicate. Certainly some questions are better elucidated than others, but a comprehensive model is far from being realized. Such a theoretical framework will necessarily be very complex because of the complex many-body behaviour which must be described. While we are waiting for an appropriate collective variables’ description to be developed there will be a role for simple real-space physical models which rationalize some of the above phenomena in a manner easily understood. We feel it is worthwhile to outline here one such model. The approximate success of its ideas might be useful in guiding more rigorous treatments of the problem.

2. An ‘excitations’ model for some salient features

The model in question is one that treats each minimum in configuration space as the energetic result of a collection of individual and distinct real-space excitations of the ground state amorphous quasi-lattice. It is, for instance, obvious that the different energy minima in configuration space for a crystal represent crystals with different numbers of defects of one sort or another. What is the equivalent of the crystal defect in the amorphous system? A precise atomistic description of configurational excitations in amorphous quasi-lattices is no more available than in the case of the ‘two level systems’ which provide the accepted explanation of the ‘ubiquitous’ cryogenic anomalies in glasses, but some approximate ideas have been advanced [45–47]. In the case where the dominant interactions between particles in the quasilattice are covalent bonds, the broken bond can be taken as the excitation [45]. Spectroscopic evidence for the existence of such states was provided in an early version of the present model [48]. Where no such bonds can be invoked, the excitations can be seen as smeared-out versions of the interstitial defects of the crystalline state. This notion has been introduced and developed by Granato [46], and has been particularly influential in our own search for understanding of the origin of fragility in terms of the parameters of the ‘excitations’ model. An earlier less specific version was the ‘quasi-punctuel default’ of Perez [47].

With the bond model it is easy to turn the strongly interacting particle lattice into a weakly interacting ‘bond lattice’, so that the excitations can be treated as independent in first approximation [45]. Only the coordination numbers of the bonded particles are needed. The problem then becomes a simple ‘on–off’ model whose thermodynamic behaviour is well known. As shown in figure 2 (Angell *et al* [2]), the ‘excitation profile’ for the mixed LJ system found by Sastry *et al* [50], modelled by Kieffer [49] and extended to the Kauzmann temperature by the author (Angell *et al* [2, 49]), is reproduced quite well by the ‘bond’ model equation for the fraction of ‘off’ bonds (X_B) at temperature T , when the two disposable parameters (excitation energy ΔE^* and excitation entropy ΔS^*) are properly chosen. The similarity is modified if the effect on the simulated profile of anharmonic interactions is taken into account. Buchner *et al* [51] have shown that these cause the profile found in simulation to be lower in energy than expected from the Gaussian distribution of states which characterizes this system (a Gaussian distribution was first identified by Speedy and Debenedetti [52] for a special hard sphere system). The correction indicated by Buchner *et al* is introduced into panel (a) of figure 2 as a dotted line affecting the high temperature portion of the profile.

Associated with this profile is a heat capacity that exhibits a maximum at the inflection point of the profile. While such a maximum is observed in some cases of intermediate liquids, it is uncommon, and its absence from the data on fragile liquids was a principal factor in the present author’s long loss of interest in the excitation model after its initial development [45].

However, such a maximum has recently been seen in the simulations of the icosahedral model of Dzugutov [53] and in the hypercube model of Stillinger [54], so it is not necessarily an unacceptable feature. The model’s account of the Kauzmann entropy crisis [55] is quite impressive as demonstrated recently by Moynihan and the present author [56]. Their plot for the case of selenium is shown in figure 3. It is noted that the excess entropy is described using only two parameters, since the number of bonds per atom which best fit the data is that expected from the divalence of Se (*viz.*, 1). The simple excitation model effectively denies the existence of a Kauzmann singularity. (Note that Kauzmann himself [55] never proposed one.)

Although the account of the temperature dependence of the entropy seen in figure 3 seems quite pleasing, the absence of a C_p maximum in the experimental heat capacity of most liquids shows that the model is missing something. For instance, near T_g the parameters giving the figure 3 fit yield a heat capacity which passes through a maximum while the experiments show

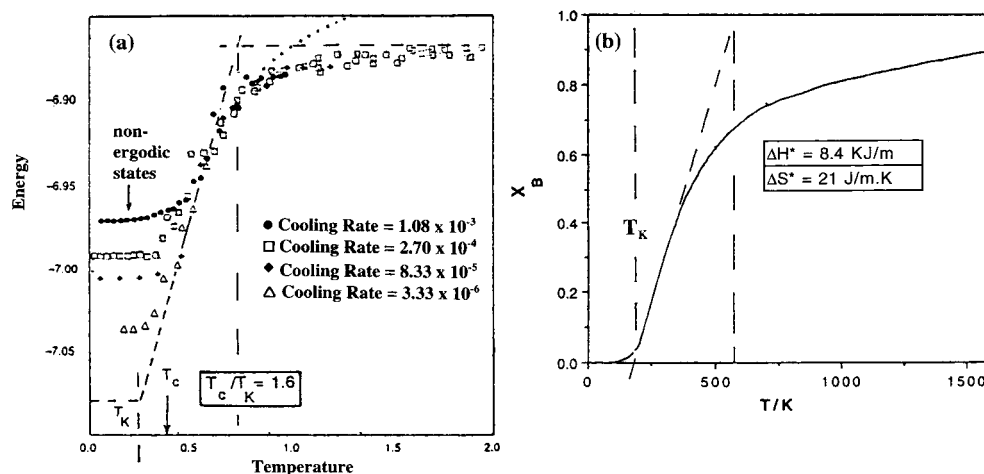


Figure 2. Comparison of the inherent structure energy–temperature profile for mixed LJ [50], with correction for high temperature anharmonicity given by Beucher *et al* [51] (dotted line) -panel (a), with prediction of the two parameter excitation model [45, 49] with parameters chosen to match the profile width (panel (b)).

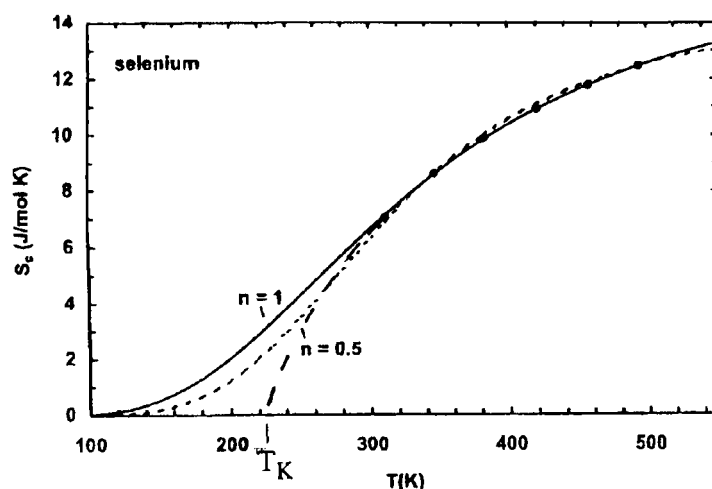


Figure 3. The excess entropy of liquid selenium over that of the crystal, showing the usual extrapolation below T_g to give the Kauzmann temperature, T_K . Full and dashed lines are the excitation model fits, assuming one mole and 1/2 mole of excitation per mole of Se, respectively. The value of ΔS^* associated with the best fit value ($n = 1$) is a little smaller than for the case of mixed LJ, implying that Se is a little less fragile than mixed LJ.

an (excess) heat capacity which continues to increase with decreasing temperature (see [56]). For molecular liquids this dependence is well fitted by a hyperbolic law. The T^{-1} variation would lead to a Kauzmann singularity at a temperature quite close to the value yielded by the linear extrapolation to zero of the steeply falling part of the excitation profile, figure 2.

This disagreement of the experimental heat capacity with that of the simple (paradox free) excitation model provides a supporting argument for the existence of a glass transition singularity under equilibrium conditions. It could be even sharper than the hyperbolic law

suggests if the conclusion of Buchner *et al* [51] for the mixed LJ system is correct. Buchner *et al* made a good case for a Gaussian distribution of inherent structure energies. For such a distribution, the constant volume heat capacity should go as T^{-2} . The singularity would then occur sharply at a higher temperature still, and one which is well above the usual Kauzmann, or VFT equation divergence, temperatures (T_K and T_0 , respectively). Furthermore, if the C_v goes as T^{-2} then the temperature at which the thermodynamic integration of [57] predicts that the system reaches the ‘top of its landscape’ will have to be revised. It will be much farther above T_c than predicted previously [57], and much closer to the value of $\sim 3 T_K$ observed in figure 2.

Before proper comparisons can be made with experiment, some assessment of the effect of the constant volume nature of the simulations (against the usual constant pressure nature of the laboratory experiments) will need to be made. Very little has been done in the way of constant volume measurements in the laboratory. The heat capacity changes at T_g will certainly be smaller if the work of expanding the structure against the attractive forces is taken out, but the effect on its temperature dependence will need to be assessed by experiment (laboratory or simulation).

So far we considered only the simplest cases, in which the number of possible excitations is the same as the number of particles (e.g. one covalent bond per Se atom in the chain, figure 3). For molecularly more complex glassformers, and polymers, it is found as expected that the number of excitable elements per molecule is more than one [45, 58]. The number proves to be in approximate correspondence with the number of conformational degrees of freedom per molecule [56, 58]. Thus it is not easy to see how the correct description of glassformer thermodynamics could be formulated in terms of distinct groupings of molecules (species) which coexist in a dynamic equilibrium of ideal mixing type, as has sometimes been argued (e.g. ‘bulky’ and ‘dense’ species in water [59, 60]). Rather, as in the case of binary solutions, any structural inhomogeneities must be thought of in terms of *collections* of the basic rearrangeable units whose interactions alone determine the thermodynamic properties. The equivalent ‘chemical species model’ of non-ideal *binary molecular solutions* was abandoned in the early 19th century.

2.1. Entropy and fragility

Of the two parameters needed to fit the selenium excess entropy data, ΔS^* is far the most interesting. This parameter controls the rapidity with which the entropy increases as temperature rises, and correspondingly the rate at which the enthalpy increases towards the value characterizing the ‘top of the landscape’. In other words it determines the thermodynamic fragility. The ΔH^* term only fixes the Kauzmann temperature, as obtained by linear extrapolation of the excitation profile of figure 2. The smaller the ΔS^* parameter is, the more extended in temperature is the excitation profile. Furthermore, the smaller the ΔS^* the smaller the energy excited at the limit of high temperature. For $\Delta S^* = 0$ only half the possible ‘bonds’ are broken. This would seem to be the case in chalcogenide systems containing Ge and Se at 20 at.% Ge where the bond density is 2.4. This is the bond density at the ‘rigidity percolation threshold’ in the Phillips–Thorpe treatment of degrees of freedom in a covalent bonded particle lattice [61]. What can the connection be?

The connection of fragility to a single model parameter is provocative and stimulates a quest for understanding of its molecular origin. Two possibilities are:

- (i) a local configurational degeneracy w associated with the excitation: in this case

$$\Delta S^* = R \ln w \quad (2a)$$

(ii) a change in lattice vibration frequency due to the bond breaking: in this case

$$\Delta S^* = -R \ln \nu_2/\nu_1. \quad (2b)$$

For the latter case the new frequencies generated should lie below the boson peak frequency in the case of fragile liquids (according to an argument given elsewhere [56]). This has stimulated a search for changes in the vibrational density of states during excitation. In his consideration of the ‘interstitialcy’ model of liquids (and melting) Granato [46] pointed out that interstitial defects in crystals produce new low frequency modes in the density of states, and that this provides a strong entropic drive to high defect populations at high temperatures. The generation of such increases in low frequency modes has been observed in neutron scattering studies of selenium liquid versus glass versus crystal [62], and quenched glass versus annealed glass [63]. We think this generation of low frequency modes (with large amplitude oscillations) may suffice to explain the sharp increases in both low frequency light scattering, and mean squared displacement, seen for fragile liquids as $T > T_g$ (compare figure 1(d) with figure 1(e)). This line of thought also predicts that these phenomena will show annealing effects, because they are measures of structural excitation, i.e. of *fictive* temperature, (potential energy), not actual temperature (kinetic energy). In effect, they are structural spectroscopy, rather than vibrational, signatures of the glass transition [23]. The role of vibrational anharmonicity in these phenomena ([14], Sokolov [15], [64]) could be subsidiary or dominant, and a relation between the two is inevitable. Very low temperature light scattering studies of high fictive temperature glasses will be needed to distinguish between them.

3. Cooperative excitations and liquid–liquid phase transitions

It remains to consider what should happen in the case in which the excitations of the basic model discussed above are permitted to become cooperative. A way of treating this case to first order is suggested by the parallel case of non-ideal interactions between molecules in binary solutions. The expression which produces the excitation profile of figure 2 results from assuming that the excitations are distributed over the quasilattice at random, which is the ideal mixing assumption of binary solutions. The non-random mixing of molecules in solutions is dealt with by expanding the free energy of mixing in a Taylor series and keeping the first term (‘regular solution’ model) and the same can be done for the mixing of bond and broken bond sites in the present model. It allows the state of excitation X_B to be obtained by solving the following equation for the Gibbs free energy, in which the only difference from the zeroth order case is the presence of the term in W , the cooperativity parameter.

$$(\partial G/\partial X_B) = \Delta H^* - T \Delta S^* + RT \ln(X_B/(1 - X_B)) + W(1 - 2X_B) = 0. \quad (3)$$

The results [56] are formally the same as those obtained by Ponyatovsky and Barkalov [65] from the two liquid model they invoked to explain the amorphous state transitions observed in InSb and related systems and Moynihan for water [66]. The results are shown in figure 4 for several values of W . It is seen how small values of W serve to increase the fragility and the (extrapolated) Kauzmann temperature, while large values lead to a liquid–liquid phase transition. This is very similar to what happens experimentally in the system Ge–Se, with increasing Ge content beyond the percolation threshold value of 20 at.% Ge [67]. In pure Ge, as in pure Si, supercooling is abruptly terminated at a temperature some 15% below the normal melting point, which in the silicon case at least, corresponds to the temperature at which the coordination number reaches 4.5 [68]. This is the value at which supercooled Stillinger–Weber silicon undergoes its first order phase transition. The first order character of this transition in the S–W model has now been established unambiguously by Sastry [69].

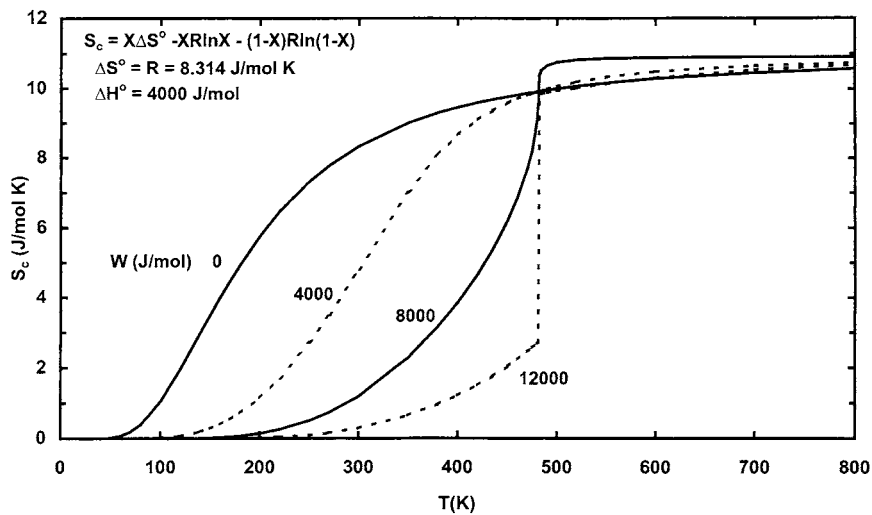


Figure 4. Excess entropy–temperature plots for the cooperative excitations model in which the cooperativity parameter W (equivalent to a binary solution's non-ideality parameter) is sequentially increased until a phase transition occurs.

These developments suggest that the extreme behaviour of Si and related systems is generically related to the same excitation scheme that is responsible for the glass transition. Now, however, the glass transition will occur, imperceptibly except by viscosity decrease, in the strong liquid phase to which the high fragility (high temperature) phase has transformed. It is significant that the low temperature phase of silicon (lightly doped with protons) and the low density phase of amorphous water [70], should be the two known cases of glasses which do not show anomalies related to the 'universal' low temperature violations of the T^3 heat capacity law. We see the sharp transition as a means of accessing a lower final entropy state than is possible by the normal continuous slowdown glassforming route. We tentatively correlate this idea with the recent findings that the two cases of amorphous solids which do not fulfil the expectation that all glassy solids have low temperature anomalies (Debye T^3 law violations etc) are Si and low density glassy water. The latter is also believed to have a sharp thermodynamic anomaly, if not an actual phase transition, in the supercooled regime [4, 71]. This revives the hope of finding a route to the 'perfect glass' state, which may in fact be closely realized by annealed low density glassy water and lightly H-doped amorphous Si. Routes other than that of liquid cooling will be needed to access this state reliably. A number of such routes exist [14].

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