Thermodynamic aspects of the glass transition in liquids and plastic crystals

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Abstract - We outline the basic phenomena characterizing the glass transition, highlighting the intimate association of thermodynamic changes and relaxation times, and the limits set by the Kauzmann entropy crises. The relation between the Kauzmann temperature and the glass transition temperature is examined in relation to the strong and fragile classification of liquids, and a consistency between the parameters of the normalized Vogel-Fulcher equation and the purely thermodynamic Kauzmann temperature is demonstrated. The separate roles of kinetic and thermodynamic factors in establishing the strong and fragile pattern are analyzed and the apparently anomalous position of the alcohols in the scheme is accounted for in these terms. Finally, the different types of excess heat capacity functions observed in different classes of glasses are reviewed, and some correlations with molecular structure are attempted.

1. INTRODUCTION

It is well recognized that the glass transition, as it is observed experimentally, is a kinetic phenomenon. It is simply the consequence of the rapidly increasing time scale for structural equilibration of the supercooling liquid crossing the time scale of the experiment being used to study the substance.[1] While the phenomenon itself is clearly under kinetic control, the thermodynamic consequences of the "falling out of equilibrium" are highly significant and are of much intrinsic interest for liquid state understanding. These changes and the analysis of their significance provide the basis for this lecture.

The most commonly studied change of thermodynamic properties consequent on the glass transition is that of the heat capacity [denoted ΔC_p (T_g)], and we will give considerable attention to this quantity and its dependence on molecular structure in this article. It must be borne in mind, though, that corresponding changes occur in the other common intensive thermodynamic properties, expansion coefficient and compressibility,[2] as well as in electric field-related properties such as the dielectric constant.

Of all the thermodynamic discontinuities observable, the heat capacity change must be considered the most important because of its relation to the Kauzmann vanishing excess entropy paradox[3] which cannot be left out of any serious discussion of the glass transition phenomenon. We refer here to the fact that, due to the great excess of heat capacity of the liquid over that of the crystal in most substances, the liquid entropy near T_g is rapidly approaching a crossover with the crystal value. This is just averted by the kinetic glass transition (at which the rate of decrease of the amorphous phase entropy changes suddenly to a value close to that of the crystal). If the glass transition, with its attendant decrease in heat capacity, were not to occur then a profound thermodynamic crisis would arise at temperatures not much further down, in fact as little as 20K in some cases.[2,3] This is illustrated in Fig. 1a.

It was the near universality of this pending entropy crossover which, in the 1960's, led Julian Gibbs and colleagues[4] to focus attention on the configurational entropy S_C as the primary extensive variable affecting the liquid viscosities. Gibbs explained the kinetic observations (eg. the viscosity divergence) as a reflection of the difficulty encountered by the molecular system in finding alternative deep potential energy minima (during its ergodic visitation of
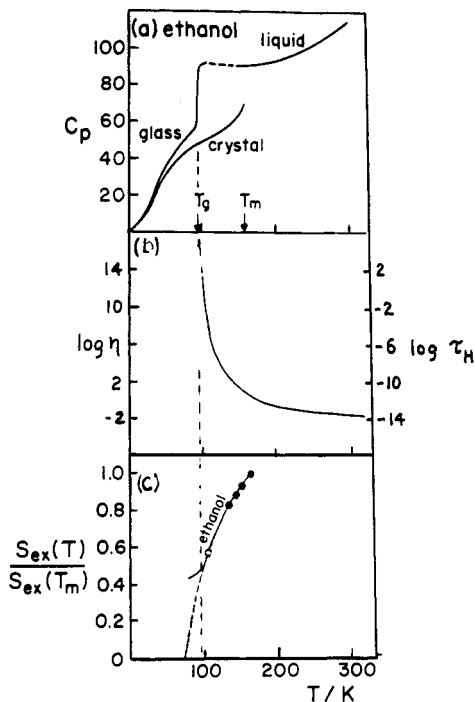
Fig. 1.

(a) Calorimetric signature of the glass transition, using the case of ethanol to show increase of heat capacity over value of crystal, occurring at T_g.

(b) Variation of log viscosity and enthalpy relaxation time associated with approach to the glass transition.

(c) Tendency of excess entropy of liquid over crystal to disappear on cooling below the glass transtion without change of heat capacity.

successive minima on the potential energy hypersurface for the system) which remain accessible at each successively lower temperature during cooling. The connection between heat capacity drop at T_g, viscosity divergence and vanishing excess entropy, is shown in Fig. 1 (a-c). Clearly the larger the change in heat capacity at T_g, relative to the entropy of fusion (which is all that distinguishes the liquid entropy from that of the crystal entropy at the one point where their chemical potential is the same viz. the melting point) the more rapidly the entropy catastrophe is approaching.

The latter observation begs the question of whether the temperature dependence of viscosity near T_g is to be correlated with the magnitude of the thermodynamic property changes observed as the liquid falls out of equilibrium. We discuss this in the next section where we give a brief theoretical review and a broad empirical correlation scheme for glass forming liquids.

2. ADAM–GIBBS THEORY AND THE STRONG/FRAGILE LIQUIDS CLASSIFICATION

Adam and Gibbs, in their 1969 theory,[5] formulated a quantitative relationship which yielded the expression

$$\eta = \eta_0 \exp C/TS_c \tag{1}$$

where C is a constant containing a free energy barrier term $\Delta\mu$. When the entropy S_c is expressed in terms of the integrated excess heat capacity $\Delta C_p = C_p(\text{liquid}) - C_p(\text{crystal})$ using the approximation[2]

$$\Delta C_p = K/T \tag{2}$$

the well known Vogel-Tammann-Fulcher Equation[3] below is obtained in a normalized form,

$$\eta = A \exp DT /(T-T_0) \tag{3}$$

in this form, the difference between all liquids obeying the VTF equation, or even approximating it, is caused by the parameter D. This is seen most readily when experimental data are plotted in the normalized form using the scaling temperature T^* as the temperature
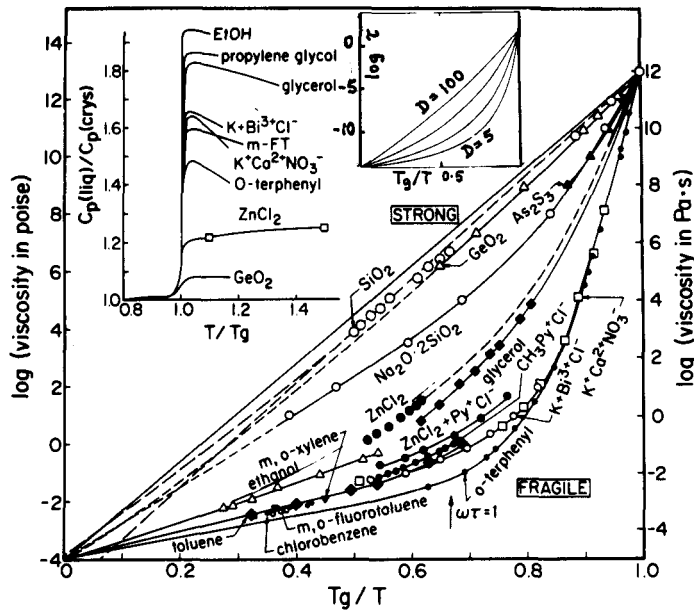
Fig. 2. T*-scaled Arrhenius plot of viscosity data for a wide variety of liquids, displaying the range of "strong" to "fragile" behavior observable in the liquid state. Here T* is the temperature at which the viscosity reaches 10^{13} poise. Inserts show variation of heat capacity through the glass transition for the same liquids, and plots of equation (3) for D values between 5 and 100.

for some fixed viscosity, e.g. $\eta = 10^{13}$ poise, or fixed relaxation time, e.g. $\tau = 10^2$ s. Fig. 2 shows viscosity data for a wide variety of liquids that are plotted in the reduced form, and establishes the "strong and fragile" pattern for liquid relaxation processes which has been discussed in several articles.[6-8] The insert to Fig. 2 shows how this pattern may be reproduced by Eq. (3) with D values falling between 3 and 50. Note that alcohols such as the much-studied glycerol and propanol fall in the middle of the diagram. Fig. 2 requires that, for the case D = 12 which is characteristic of this group, T/T_0 should have the value 1.33. It is striking that this is the average value found for the Kauzmann temperature of the series of polyalcohols [$CH_2 OH$]n where n = 1-6, studied by the author and D.L. Smith[9] (using purely thermodynamic measurements as in Fig. 1b). Furthermore, we note that this is also the ratio T_g/T_K obtained for ethanol in Fig. 1b.

We now note that, according to the Adam-Gibbs theory, the parameter D can be written

$$D = C' \Delta\mu/K \qquad (4)$$

where K of Eq. 2 is a thermodynamic quantity and $\Delta\mu$ is a kinetic quantity. We will shortly relate each of these to key features of the configuration space hypersurface for liquid systems, but first examine the data in Fig. (2) to determine which, if either, of $\Delta\mu$ and K is the dominant quantity. If K, the thermodynamic part is dominant then the order of fragilities in Fig. 2 should be the order of reduced heat capacity jumps at T_g ($C_p(liquid)/C_p(crystal)$). This quantity is shown in the insert to Fig. 2 where it is seen that for inorganic liquids the correlation indeed holds up. For aromatic molecular liquids, the same correlation is found. However, the alcohols (which are highlighted in Fig. 2) are clearly exceptional. The particularly large ΔC_p seen for the alcohols would suggest exceptional fragility with D ~ 2, while in fact the D value describing their behavior in Fig. 2 is intermediate (D ~ 12).

We suppose that the alcohols find themselves located in the middle of the diagram, Fig. 2, as a consequence of unusually large values of the term $\Delta\mu$ which is the free energy barrier to rearrangement of the critical size cooperative group. This seems reasonable, since a characteristic feature of cooperative rearrangements in H-bonded liquids must be the necessity to break a number of hydrogen bonds during passage over the energy barrier. In other words, more than just a local density fluctuation is required to permit the rearrangement.

3. INTERPRETATION IN TERMS OF THE POTENTIAL ENERGY HYPERSURFACE

We have previously[10] attempted to distinguish strong from fragile liquids in terms of the density of minima in the potential energy hypersurface in the 3N + 1 dimensional configuration space of the N particle molecular systems. In view of the above discussion, we should now distinguish the hydrogen bonded liquids from other liquids with high densities of configurational states, by the relatively large kinetic barriers between minima of different depths on the 3N + 1 dimensional hypersurface. The distinction between strong liquids and fragile liquids on the one hand, and fragile liquids with large free energy barriers between minima and the more common fragile liquids on the other, is illustrated by the schematic free energy surface cuts represented in Fig. 3.

Fig. 3 part (a) gives a two dimensional illustration of the topology of the hypersurface characteristic of strong liquids in which the requirement of tetrahedral coordination of the network centers places strong limitations on the arrangements of the other particles and thus restricts the number of distinct minima on the potential energy surface. Fig. 3 part (b) shows the situation where the coordination number restriction is lifted or where the presence of an asymmetric molecular shape leads to a proliferation of alternative distinct arrangements of about the same energy.

As discussed elsewhere the higher density of configurational states in these cases is consistent with the larger configurational entropy at a given kinetic energy kT above the energy characteristic of the deepest minimum on the surface (in which the system would reside at T_K, if time were allowed to find it). Of course, it is the larger degeneracy of the surface which drives the system to a high entropy in a short temperature interval, hence which gives the large excess liquid heat capacity characteristic of the fragile liquid. Fig. 3 part (c) shows the case where the surface is characterized by the same high density of minima as in part (b) but where the minima are separated by large free energy barriers, as in our picture of the hydrogen bonded liquids.

We show elsewhere[11] that not all alcohols are intermediate in character. The large barrier crossing term $\Delta\mu$ discussed above can evidently be reduced if the alcohol group is attached to an aromatic framework.

4. HEAT CAPACITIES OF GLASS-FORMING LIQUIDS

(a) Forms of the heat capacity

The jump in heat capacity at the glass transition reflects the access of the system to additional (configurational) degrees of freedom in the diffusive liquid state above the glass transition temperature. The overall form of the heat capacity then depends on the individual forms of the vibrational heat capacity of the amorphous phase and the configurational heat capacity of the liquid phase. Empirically it is found that the glass transition occurs in different liquids at very different states of the excitation of the vibrational degrees of freedom means that the overall form can differ greatly form liquid to liquid independent of the variations of form in the configurational heat capacity. To illustrate this point, and to show the overall range of behavior which may be observed, we present data for a variety of different liquid types in Fig. 4.

Fig. 4a shows the typical molecular hydrocarbon liquid in which, due to the high frequencies of the C-C and C-H stretching intramolecular frequencies relative to the intermolecular frequencies, the vibrational heat capacity is only partly excited at the temperature T_g where the molecular rearrangements involved in the glass transition commence. The increase in heat capacity due to the onset of the latter modes is therefore superimposed on a steeply rising background. This contrasts strongly to the behavior observed in the warm up of metallic glasses in which the glass transition occurs at temperatures where the vibrational degrees of freedom of the heavy metal atom system are almost classically excited. The glass transition therefore occurs as a spike although the difference between the liquid and glassy heat capacities i.e. the configurational heat capacity itself, is rather similar in each case. Fig. 4c shows the case of covalently bonded, chalcogenide type, glasses, in which the system is again classically excited with respect to the vibrational degrees of freedom when the glass transition
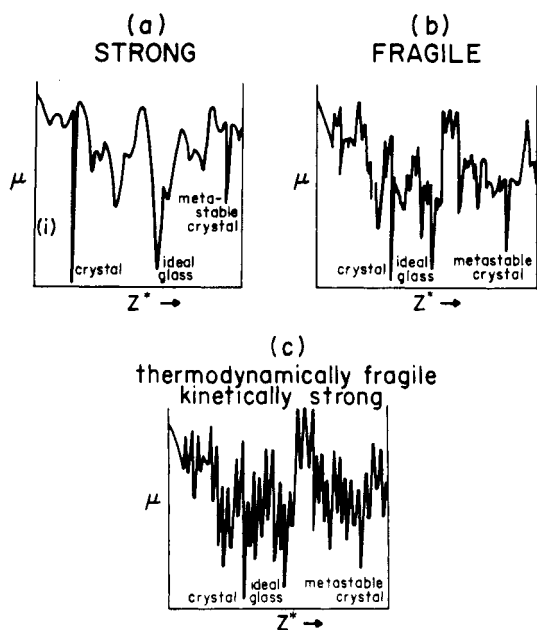
Fig. 3. Two dimensional representations of the potential energy hypersurface for (a) strong and (b) fragile liquids and (c) fragile liquids which appear strong in Figure 2 due to the existence of high energy barriers between adjacent minima on a fragile (high density of configuron states) surface.
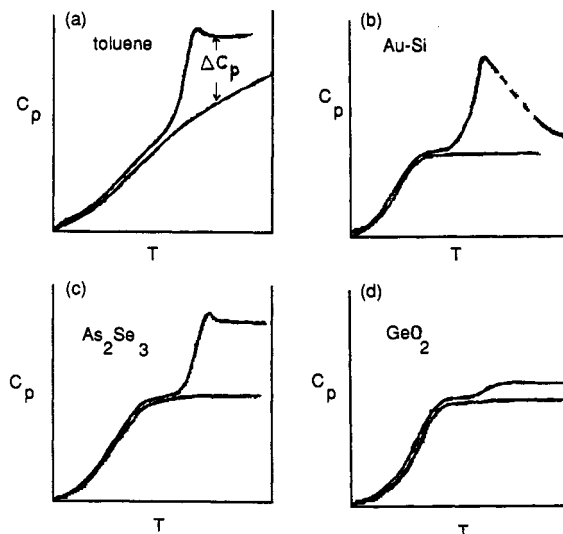

Fig. 4. Heat capacity forms for liquid and crystal phases of different types of substance (a) molecular systems like toluene[8] where the glass transition occurs in a range where the crystal heat capacity is not classical. (b) Metallic systems like Au-Si[13] where crystal and glass reach the classical regime before the glass transition occurs, (c) covalent systems like As_2Se_3[14] where the liquid heat capacity jump occurs on a classical background and ΔC_p remains large above T_g (d) open network systems like GeO_2[15] where ΔC_p is small and occurs on a classical background.

occurs. Due to a different form for the configurational heat capacity, the total form is rather different from that seen in metallic glasses. Finally we show the form for covalent or ionic network glasses where, due to the extended three dimensional bonding pattern, the jump in heat capacity at the glass transition is relatively small. Not many data for systems of this type are available. We show new data for the chalcogenide system Ge-As-Se at the "rigidity percolation" threshold, where the jump in heat capacity at T_g passes through a minimum value.

(b) Changes in heat capacity at the glass transition in relation to molecular constitution
In a recent paper considering thermodynamic aspects of the glass transition Alba et al.[8] provided data for a number of hydrocarbon liquids in which variations of the excess heat capacity of the liquid over that of the crystal obeyed the hyperbolic law given above (Eq (2)). When cast in this form it was found that the differences between the different liquids, K, were linearly related to the number of carbon atoms in the molecule. Unexpectedly, the molecules with aromatic character had larger values of K than the paraffin molecules despite the greater individual freedom of the carbon atoms in the latter. On the other hand, the larger K values are qualitatively in accord with the much greater fragility (low D values) of the aromatic substances (Fig. 2).

It is of interest to extend Alba et al's observations on the relation between the constant in the hyperbolic function and the carbon number of the molecule, to cases of large molecular weight. For this reason we introduce data on several additional compounds whose thermal characteristics have been studied previously, and one new substance, squalane. Squalane is a large (30 carbon atom) paraffin containing enough methyl groups on the backbone (three) to depress the usually rapid crystallization kinetics characteristic of straight chain paraffins, and permit glass formation. Its heat capacity change at T_g was determined by differential scanning calorimetry, using o-terphenyl as reference material.[12]

The results are shown in Fig. 5 in which the constant of the hyperbolic relation is shown as a function of carbon number (or carbon plus oxygen number, here called "bead" number) for a variety of hydrocarbons and alcohols.
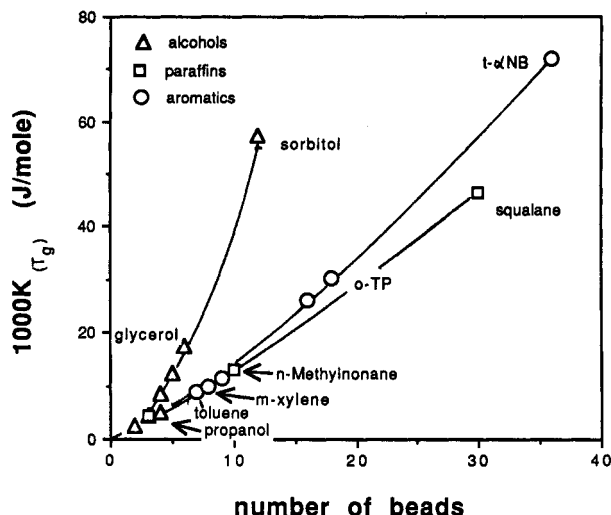
Three features are notable in Fig. 5. The first is that the normal alcohols, notwithstanding their very large changes in ΔC_p (Fig. 2), are not distinguishable from low molecular weight paraffins. However the polyalcohols, starting with propane diol, fall on a much more rapidly rising line. Other factors being equal, this would imply an exceptional fragility according to Eqs. (2) and (3). This is evidently counterbalanced by a large barrier crossing energy, $\Delta\mu$ due to the need to break H-bonds during rearrangement, since alcohols fall in the middle of Fig. 2.

The second point of note is that aromatics have larger K values than paraffins, which is consistent with their greater fragility and also with their lower boiling point to glass temperature ratio.[8]

Thirdly, we observe that all three plots are non-linear at large bead numbers which implies that the simple hyperbolic representation of ΔC_p is failing increasingly at higher temperatures. For larger molecules it should presumably be replaced with a more slowly varying function, or supplemented by a constant additive term. At the moment there is no theory for the magnitude, let alone the temperature dependence of ΔC_p, in any type of glass forming liquid. The need for theoretical developments in this area of liquid state studies is acute.

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