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Relaxation in liquids, polymers and plastic crystals – strong/fragile patterns and problems

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An overview of relaxational phenomenology is given in a manner intended to highlight a number of the important problems which, notwithstanding much recent sophisticated investigation, continue to confront the field. The rapidly lengthening timescale for diffusional and/or reorientational motion, which provokes the glass transition, is examined within the framework of the 'strong' and 'fragile' classification of both liquids and plastic crystals. The behavior patterns observed are related to the topological features of the potential energy hypersurfaces which may characterize each extreme. In view of the implication that the observed glass transition is the kinetically obscured reflection of an underlying higher order thermodynamic transition which could be associated with a diverging length scale (at least for fragile systems), the problem of the basic diffusional length scale at the glass transition, using a probe molecule approach, is considered. Then, details of the kinetics of relaxation under isothermal conditions are reviewed to decide on the range of deviations from Debye behavior which may be encountered. A correlation with fragility is strongly indicated. The phenomena of serial decoupling of relaxational modes from the main structural relaxation as T_g is approached is outlined and, finally, the additional phenomena that may be encountered in experiments that explore the state-dependence (or non-linearity) of relaxation are briefly examined.

1. Introduction

As an introduction to this broad field, this paper must necessarily remain general and hence (to an extent I will try to minimize) somewhat superficial. Its purpose will be (i) to outline some broad patterns of behavior which may be perceived among relaxing systems, and some unexpected or little recognized phenomena to which they lead, (ii) to point out apparently important relationships for which adequate explanations do not yet exist, and therefore (iii) to suggest some key questions which need to be answered. Since there appears to be an increasing number of researchers becoming interested in this field and its challenges, it will also be appropriate to point out the extent to which earlier observations become rediscovered, and earlier errors get repeated.

In pure liquids and many plastic crystals, the exploration of the viscous liquid (or cooperative relaxation) region invariably depends on the system being kinetically inhibited from attaining a lower free energy crystalline state [1]. As is emphasized below, this fact is of special value in placing limits on the range of temperature over which liquid-like behavior is possible for the metastable phase. For many solutions [2] and polymers [3], however, the amorphous state would appear to be the actual ground state, as indeed is the case for quadrupolar glasses of the KBr–KCN type [4] which are often treated as a separate case (probably unnecessarily). Within each of these classes of systems with slow relaxation and consequent ergodic-state-to-nonergodic-state transitions, there appears to be a range of behavior with recurring features suggestive of underlying universalities. The pattern is most simply exhibited by reduced plots of some appropriate time-dependent property. For liquids, the most commonly studied property is the shear viscosity and it has become quite well known that a wide variety of viscosity data can be organized in a useful way by plotting in Arrhenius-form using the dimensionless temperature scale T^*/T, where T^* is the temperature at which the viscosity reaches some large value, usually 10^{12} Pa s [5], the value commonly associated with the glass transition. The pattern shown in fig. 1 using data for a variety of liquid types is effectively unchanged if the scaling temperature is changed to the temperature at which the viscosity has some other value, e.g., 10^{11} Pa s which is more characteristic of molecular liquids and aqueous solutions at their glass transition temperatures. This diagram has become the basis of a classification of liquids [5] to which further reference will be made below. For the moment we only note (inset (a) in fig. 1) that the pattern can be reproduced by variation of a single parameter D in the modified Vogel–Tammann–Fulcher equation

$$\eta = \eta_0 \exp[DT_0/(T - T_0)], \tag{1}$$

(η_0, D, T_0 constants), and (inset (b)) liquids showing only small deviations from Arrhenius-behavior tend to exhibit only small changes of heat capacity as the liquid-like degrees of freedom are lost/gained at the glass transition.

The above scaling has the advantage of forcing all systems to share a common point at low temperatures but it is not necessarily the most informative way of contrasting the behavior of different liquids. Since our principal interest is in correlating the *timescales* on which perturbed liquids recover their equilibrium states in relation to temperature above the glass transition, a more appropriate scaling would be by the temperature at which the shear *relaxation time*, τ_s, reaches a common large value, e.g., 10^2 s. (Here $\tau_s = \eta/G_\infty$, where G_∞ is the relevant, solid-like elastic property of the system, namely the shear modulus measured at high frequency.) However, there is a problem with this scaling in that there are relatively few data available on G_∞, particularly for its variation with temperature in the liquid state, so neither the scaling temperature nor the relaxation times themselves are generally available. A compromise which has some particular advantages is to plot the widely available viscosity data using, as reducing parameter, the temperature at which the relaxation time for the fundamental *enthalpy relaxation* process reaches some fixed value [6], e.g., 10^2 s. Fortunately this latter temperature is generally available since, within narrow limits, it is the temperature of the glass transition, T_g, obtained

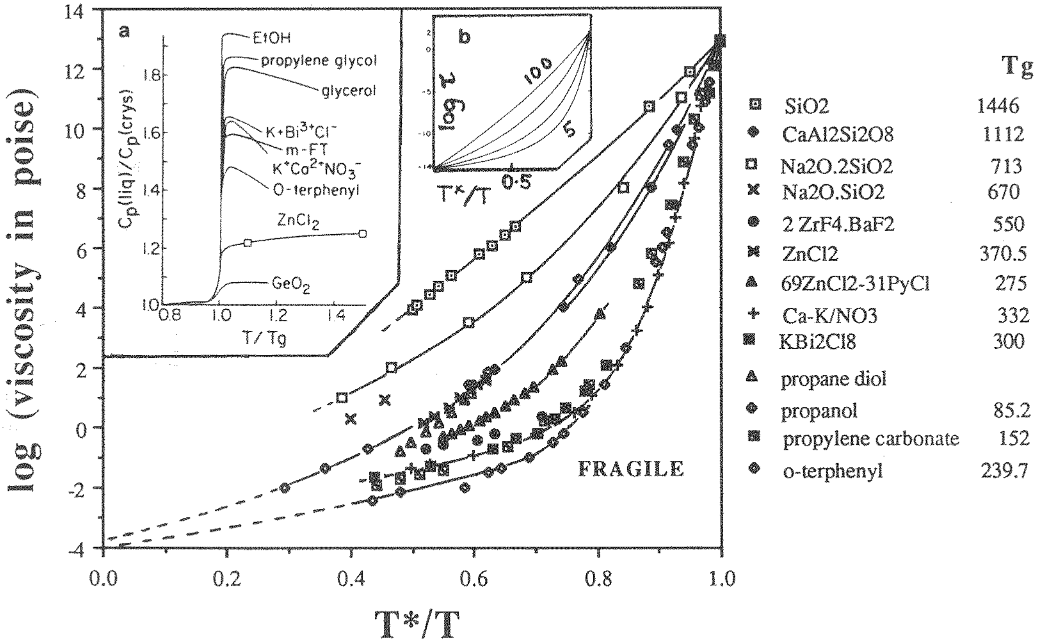

Fig. 1. Strong → fragile behavior in glass-forming liquids as shown by T^*-scaled Arrhenius plots of viscosity. Here T^* is the temperature at which the shear viscosity reaches 10^{12} Pa s. Inset (a) shows how this pattern is reproduced by normalized Vogel–Tammann–Fulcher equation, eq. (1), by variation of the parameter D. Inset (b) shows the corresponding configurational components of the heat capacity introduced at T_g by ratioing the liquid (and glass) data to the crystal values at each temperature.

from standard scanning measurements [7]. Specifically, it is the temperature at which the heat capacity jump characteristic of the glass transition (when the sample temperature is raised at 10 K/min) commences, provided the sample has been cooled into the glassy state at about the same rate and then immediately reheated. Glass transition temperatures are widely available and easily measured, and different laboratories usually report values agreeing within 2 K even when no special attention is given to defining conditions of measurement other than the heating rate. Examples may be seen in refs. [8] and [9] for common molecular liquids.

When viscosity data are scaled by the calorimetric glass transition (see fig. 2) [6], it becomes clear that the traditional idea of the glass transition as an isoviscous phenomenon is not wholly correct. While the majority of strong and intermediate liquids indeed have viscosities near 10^{12} Pa s (10^{13} P) at the calorimetric T_g, a variety of molecular liquids (mostly fragile in character) evidently have viscosities as low as 10^{10} P at T_g. Evidently in some cases the response to a shear stress can be significantly decoupled from the response to a thermodynamic stress [10]. (We discuss serial decoupling in fragile liquids in more detail below.)

The general pattern of liquid behavior seen in fig. 1 is not much changed by the choice of scaling temperature. The pattern raises the question of the structural origin of such wide differences in viscosity–temperature relations. The notion that the observed behavior reflects in some way the stability of the short- and medium-range order against temperature-induced degradation has suggested [5] the terms 'strong' and 'fragile' for the extremes of the behavior pattern seen in figs. 1 and 2. The 'strong' liquids are observed to be those with self-reinforcing tetrahedral network structures, which also manifest their resistance to structural degradation by small changes in heat capacity at T_g ($C_{p(\mathrm{liq.})}/C_{p(\mathrm{glass})} \approx 1.1$) (see fig. 1 inset (b)). By contrast, the 'fragile' cases, which always have large increases in heat capacity (60–80%) at T_g, are usually liquids without directional bonds and

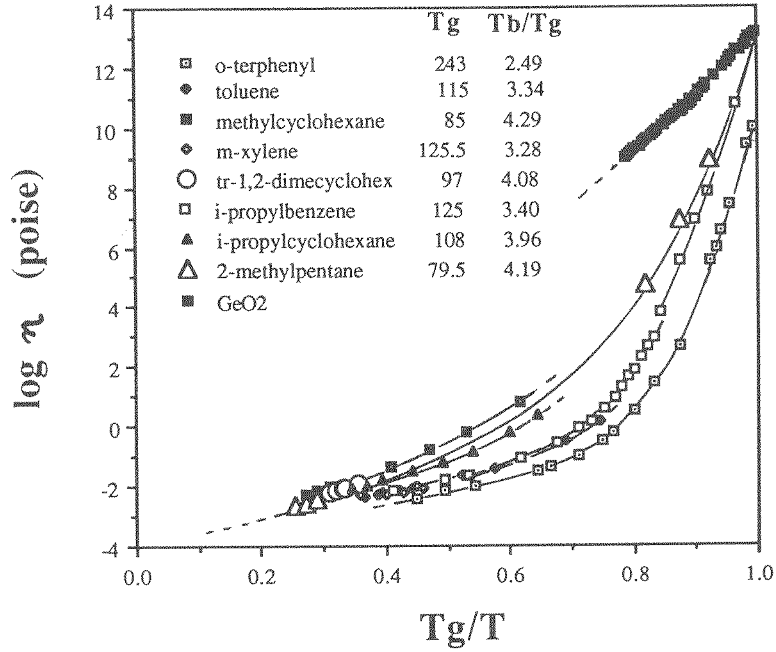

Fig. 2. Alternative representation of viscosity data (here all for cyclic hydrocarbons) obtained by scaling temperature by the calorimetric glass transition temperature, T_g, at which the enthalpy relaxation has a constant value. Note correlation of fragility with 'liquid range' indicated by the ratio of boiling point to glass transition temperature. Many examples in the gap between o-terphenyl and the remainder, with viscosity at $T_g/T = 1$ less than 10^{13} P, are known (see, for example, ref. [66]) but are omitted for clarity.

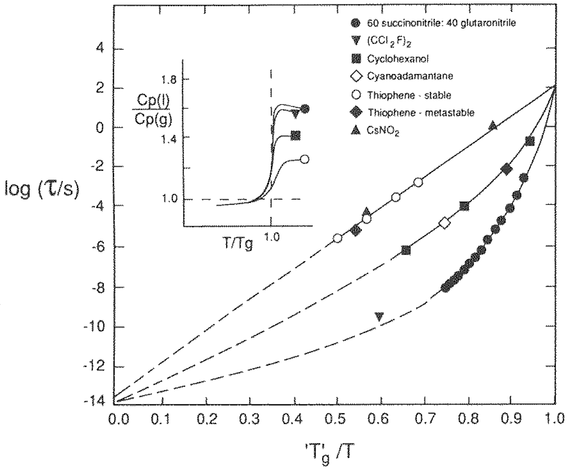

Fig. 3. Strong–fragile behavior of orientationally disordered crystal phases. Inset shows heat capacity of the plastic crystal normalized to that of glass at T_g (since crystal data are not available in all cases).

often with ionic or aromatic character. However, no reliable predictions of fragility from structural character, seem possible at this time. For example, simply hydrocarbon liquids such as 2-methylpentane and methylcyclohexane find themselves in the center of the pattern (see fig. 2), while chain polymers, examined [11] in a similar classification for polymers based on a T_g-scaled Arrhenius representation of *segmental* relaxation times (see below), may appear at the extreme fragile edge. Note also that for the alcohols, which fall at intermediate fragilities, the change in heat capacity at T_g is even larger than for the fragile liquids. Evidently some peculiarities associated with hydrogen bonding (which is very common among glass-forming liquids) need special explanation. We deal with this, albeit briefly, in section 3 below.

Before further consideration of fig. 2 and its implications, it is useful to realize that a similar pattern of behavior is characteristic of systems that are intrinsically simpler to interpret than are liquids or polymers. We refer here to the substances known as 'rotator phases' or 'plastic crystals' in which the molecules are free to reorient around one or more molecular axes, while the centers of mass remain ordered. While the majority of such substances lose their orientational freedom on cooling at a first order phase transition to an orientationally ordered phase, a number of them behave like glass-forming liquids and supercool to an orientationally arrested or 'glassy crystal' [12] state. If data on reorientation times for such substances are plotted in an Arrhenius form using the temperature at which the relaxation time reaches some fixed value (e.g., 10^2 s) as scaling parameter, then a pattern very similar to that of fig. 1 is obtained [13] (see fig. 3). Now, however, it is no longer necessary to turn, as in liquids, to covalent networks for examples of strong behavior. They are found in simple planar molecular compounds such as thiophene [14] and ionic crystals such as $TlNO_2$ [15] in which the molecules/ions cause minimal disturbance to their lattices as they reorient.

Despite the very different structural character of the 'strong' examples of the liquid and plastic crystal families, the other thermodynamic and relaxational characteristics of 'strong' behavior seen in liquids are maintained. For example, the 'strong' plastic crystals exhibit very weak thermal manifestations of the ergodic–non-ergodic (i.e., 'glass') transition ($C_{p,l}/C_{p,g} < 1.1$) [14b,15] and the relaxation spectrum is essentially Lorentzian [14c], i.e., the relaxation is essentially exponential, $e^{-t/\tau}$, as Macedo and colleagues [16,17] showed long ago was the case for liquids such as GeO_2 and a borosilicate which find themselves at the strong end of the fig. 1 pattern. It seems likely that a proper interpretation of the liquid–glass transition will be greatly assisted by, and perhaps preceded by, the development of theories for the full range of behavior of plastic crystal systems.

It may be appropriate to suggest here the use of the distinguishing terms (and abbreviations) center-of-mass disordered (CMD) glasses and orientationally disordered (OD) glasses. Within the latter, the subsets quadrupole disordered (QD) and dipole disordered (DD) systems could be distinguished. The ergodic state of the OD glass would then be the OD plastic crystal. This terminology avoids a certain awkwardness in the term 'glassy crystal' (suggested by Seki et al. [12] in their first systematic study of the phenomenon) and in particular avoids the implied companion term 'glassy liquid' which we see as a contradiction in terms.

Before leaving this section, we should note that in the case of chain polymers, the fig. 3-type diagram contains no example stronger than cyclohexanol, although increased strength could be induced by dense cross-linking.

2. The Kauzmann limit

Before further consideration of the relaxation processes themselves, it is necessary to consider the state towards which these systems are moving when they become arrested at T_g. To assist this aim, we should recognize that figs. 1–3 are only partial representations of a more extended 'picture' which would be obtained if data from much longer timescale experiments were to be included in the figures. Our reference temperature, T^*, in other words, is just a crossing point for each liquid viscosity as it moves at different rates towards the divergence at T_0 implied by eq. (1). At the crossing point, T^*, the ratio T^*/T_0 will differ according to the value of D in eq. (1). It is worth noting a couple of characteristic T^*/T_0 values for comparison with analogous quantities to be derived shortly from purely thermodynamic data. First, for the alcohols ethanol and glycerol, for each of which the D value of 13 in eq. (1) is appropriate according to fig. 1, the value of T_g/T_0 is 1.35 [18,19] [§]. Second, for the two most fragile liquids so far studied, molecular propylene carbonate [20] and ionic $La_2O \cdot 3B_2O_3$ [21], the D value of 3.2 best accounts for the whole range of data (although in each case the viscosity is tending to return to Arrhenius behavior at the lowest temperatures because of viscosity decoupling) [10]. For this value of D, we expect T_g/T_0 to be 1.12. Third, for the well-studied covalent glassformer As_2Se_3, the viscosity [22,23] is best described by $D = 33$, for which $T_g/T_0 = 1.86$.

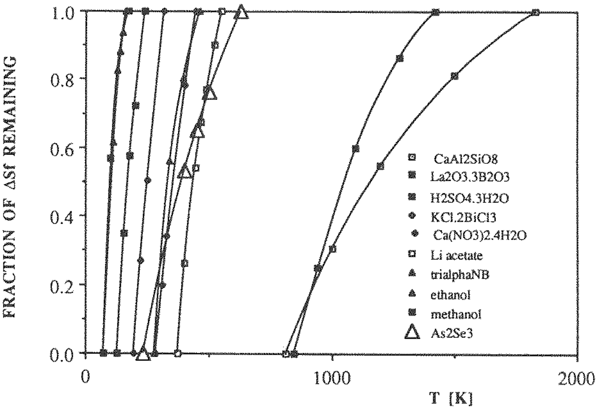

Fig. 4. Variation of excess entropy of liquid over crystal normalized by the value at the melting point (ΔS_f) showing the approach to Kauzmann's liquid/crystal isoentropy condition (at temperature T_K) at temperatures as high as 800 K depending on substance. Note the different rates at which T_K is approached by $La_2O \cdot 3B_2O_3$ (fragile) [21], $CaAl_2Si_2O_8$ (intermediate [21,34]. $NaAlSi_3O_8$ (strong) [34] (not shown) has a smaller slope than any shown, and an uncertain extrapolation to zero (at ~ 350 K). The last point above zero in each case is the T_g.

Now we ask whether the viscosity divergence temperature T_0 can be identified with any other physically meaningful quantity, and accordingly recall Kauzmann's famous review paper of 1948 [24] in which he identified an impending thermodynamic crisis for supercooling liquids. Kauzmann showed, using thermodynamic data for several molecular glassformers, that because of the large heat capacity of the liquid relative to crystal, the extra entropy, ΔS_f, introduced on fusion would be completely lost from the supercooling liquid not far below the observed glass transition temperature. This implied that at a temperature now called the Kauzmann temperature, T_K, the liquid and crystal would have the same entropy if the liquid were cooled slowly enough without crystallization to avoid the ergodicity-breaking which occurs at T_g on normal cooling. The heat capacity and entropy of fusion data necessary to evaluate the Kauzmann temperature are available for the three substances mentioned above, and are used in fig. 4 to show in each case how the excess entropy is vanishing with decreasing temperature below the fusion point. Note that in the case of $La_2O \cdot 3B_2O_3$ the isoentropy condition is approaching very rapidly at $T_g = 1013$ K. If the kinetic glass transition were not to intervene, then the isoentropy condition would arrive at 904 K (and the *total*

[§] We note that eq. (1) requires T_g/T_0 to be linearly related to D ($T_g/T_0 = 1 + 0.0255\ D$ if $\eta_0 = 10^{-5}$ Pa s and $\eta_{T_g} = 10^{12}$ Pa s).

entropy would become negative at ~850 K). Clearly the partition function descriptive of such a liquid must be of a form that predicts, as an equilibrium feature, a rather sudden heat capacity decrease in order to avoid these absurdities. We note that such a feature, which was present in the disputed [25] Gibbs–Dimarzio theory for polymers [26], is found in the spin-glass random energy model of Derrida [27], and also in the scaling model of Souletie [28] for certain exponent values.

For the moment, though, our concern is with the relation between the T_g/T_K values for these liquids of very different fragilities, and the T_g/T_0 values expected from eq. (1) for these fragilities. The agreement is quite impressive and, we believe, is too good to be coincidental. For As_2Se_3 we find $T_K = 236$ K [23,29], so $T_g/T_K = 1.93$ compared with $D = 33$, $T_g/T_0 = 1.86$. For glycerol we confirm earlier findings $T_K = 134$ K, $T_g/T_k = 1.37$ compared with $D = 13$, $T_g/T_0 = 1.34$ [18]. Note that for ethanol, whose position in fig. 1 requires $D = 13$, and therefore $T_g/T_0 = 1.34$ (as for glycerol), T_K was found by Seki et al. [30] to be 71 K; hence $T_g/T_K = 1.34$. Finally for $La_2O \cdot 2B_2O_3$ we have [21] $T_K = 845$ K, $T_g/T_K = 1.11$, compared with $D = 3.2$ and $T_g/T_0 = 1.083$. We should note here the even more convincing correspondence of T_K with T_0 for several fragile molecular liquids for the cases in which T_0 was extracted from the eq. (1) fit to the most fundamental relaxation time of all, namely, that for enthalpy, as derived from ac heat capacity measurements [31,32]. We should also mention other examples of demonstrated coincidences of T_K and T_0, e.g., in the geochemical liquids albite and anorthite (Na and Ca aluminosilicates [33,34]).

Taken all together, these correlations provide compelling evidence that, irrespective of recorded failures of eq. (1) to provide a precise fit of a given set of viscosity data over the entire available range [35,36], the broad picture of viscous liquid behavior is well interpreted in terms of a Vogel–Fulcher law with T_0 of special *thermodynamic* significance, namely the configurational ground state temperature $T_0 \equiv T_K$. The fact that T_K is an inaccessible temperature because of the ever-increasing timescale for equilibration does not decrease its significance any more than does the inaccessibility of the absolute zero of temperature. It is for theory to decide whether T_K corresponds to an actual phase transition or just an extrapolated representation of a short regime of very rapid change of C_p with temperature.

Three theories referred to above [26–28] are consistent with the phase transition interpretation of T_K. In this case, the question of diverging length scales as the transition is approached must be raised. Clearly this will be a more pressing question for systems of the higher fragility in which T_g/T_K is smaller. Indications of system-size-dependent properties have in fact been found for spin-glass systems, which we have not discussed but which show non-exponential relaxation and Arrhenius relaxation times analogous to those we have discussed but which seem to be intrinsically more fragile than CMD or OD glasses [37]. We return below to the matter of length scales after a brief consideration of the connection between our observations to date and the topological features of the $3N+1$-dimensional potential energy hypersurface descriptive of the configuration space energetics of glass-forming systems.

3. Potential energy hypersurface and the Adam–Gibbs theory

For discussion purposes, it is common to represent the unimaginably complex higher dimensional potential energy hypersurface of an N-particle system in terms of a two-dimensional diagram of chemical potential versus some collective coordinate Z (see fig. 5). When the system has thermal energy, kT, it can be imagined as having access to all the minima of energy lower than kT provided time is not a consideration. The settling of the system into a configuration ground state of zero excess entropy at the Kauzmann temperature then corresponds to the system finding its way to the lowest minimum on the potential energy surface. As Gibbs pointed out long ago [3], it is reasonable to suppose that the smaller the number of minima available to the system, the more difficulty the system will experience in finding them. From this can be understood [3] the relationship between the diverging relaxation time (or viscos-

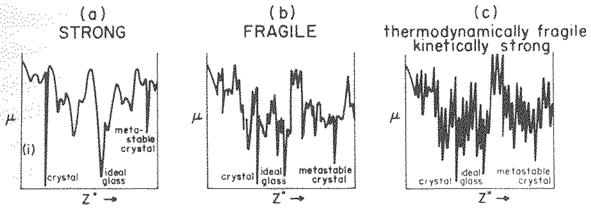

Fig. 5. Sections of the potential energy hypersurfaces suggested as characteristic of (a) strong liquids, (b) fragile liquids, (c) alcohols. The last have large heat capacity changes at T_g; hence they have a high density of minima on the potential energy but are still relatively strong according to fig. 1, probably because of a larger $\Delta\mu$ contribution to D (eq. (4)) due to the need to break H-bonds during particle rearrangements.

ity) and the vanishing excess entropy implied by the Kauzmann paradox (see eq. (2) below).

We have proposed [38] that the connection between fragility and the topology of the potential energy surface is directly related to the density of minima on the surface characteristic of systems of different bonding character. For the strong liquids which, structurally, have a well-defined tetrahedral network coordination, the restrictions on placing particles in space associated with the specific bonding scheme implies that the number of distinct minima on the surface will be small relative to that for liquids which lack such network bonding schemes. Accordingly, the number of minima at any temperature above the ground state energy will be relatively small; hence the entropy of the liquid will increase slowly with reduced temperature T/T_g. According to the Adam–Gibbs theory for viscosity [39] (which we discuss below), this hypersurface feature would imply a more Arrhenius behavior of the viscosity than would be found in a system with a high density of minima. A system that may lend itself to simpler theoretical treatment is the Ge–As–Se system in which bonds of comparable energy and bond angle constrains can be introduced or removed by composition changes, thus decreasing the number of minima on the potential energy surface as the coordination number changes from the value 2.0, characteristic of the chain polymer component Se, to 2.4 which is the value of the mean-field percolation threshold of the Phillips–Thorpe theory. That ΔC_p reaches a minimum at this average coordination number has recently been demonstrated [23].

Our depiction of these characteristics of the hypersurface is given in figs. 5 (a) and (b). Part (c), which is drawn so as to have the same number of minima as part (b), but to have higher energy barriers separating the minima, is intended to depict the situation for the alcohols for which the exceptional characteristic of intermediate fragility but high ΔC_p was mentioned above. The reason is given at the end of this section. These depictions are highly qualitative. A good start on the very difficult task of quantifying the description has been made recently by Stillinger [40,41], who manages to link the nature of the hypersurface to the non-exponential character of the process (relaxation) by which the surface is explored (see section 5).

In 1965, Adam and Gibbs [39] suggested that for densely packed liquids the conventional transition state theory for liquids, which is based on the notion of single molecules passing over energy barriers established by their neighbors, must be inadequate. They proposed that, instead, viscous flow occurs by increasingly cooperative rearrangements of groups of particles. Each rearrangeable group was conceived of as acting independently of other such groups in the system but it was supposed that the minimum size of such an independent group would depend on the temperature.

By evaluating the relationship between the minimum sized group and the total configurational entropy of the liquid, Adam and Gibbs arrived at the relationship

$$\tau = \tau_0 \exp C/TS_c, \tag{2}$$

where S_c is the configurational component of the total entropy and C is a constant containing a term $\Delta\mu$, which is the free energy barrier which must be crossed by the rearranging group. It is clear that, so long as the configurational entropy remains constant, eq. (2) is just another form of the Arrhenius law.

What makes the equation unique and useful is the fact that, due to the increase of heat capacity at the glass transition, the configurational component of the total entropy will increase with temperature. This adds an additional temperature dependence to the exponential law. Finally if, according to Kauzmann, the configurational entropy tends to vanish at some finite temperature, then all the features needed to relate the theory to the empirical Vogel–Tammann–Fulcher (VTF) equation are present. In fact. eq. (2) can be converted identically to eq. (1) if the S_c is expressed in the integrated form,

$$S_c = \int_{T_K}^{T} \Delta C_p/T \, dT, \tag{3}$$

and the quantity ΔC_p is given a hyperbolic temperature dependence $\Delta C_p = K/T$. (That such a form is the best simple description of the experimental behavior of ΔC_p for many systems has been demonstrated elsewhere [16,42].) The result is

$$\begin{aligned} \tau &= \tau_0 \exp[(\text{constants})(\Delta\mu/K)T_0/(T-T_0)] \\ &= \tau_0 \exp[DT_0/(T-T_0)]. \end{aligned} \tag{4}$$

From this development the quantity D, which determines the fragility of the liquid according to eq. (1), can be seen to contain, in addition to constants, two parameters, one of which (K of the hyperbolic relationship) can be related to the density of minima on the potential energy surface, while the second, $\Delta\mu$, can be identified with the barrier heights separating the minima. Therefore an alternative way in which an observed low fragility can be interpreted, even when there is evidence (e.g., large ΔC_p) that the potential energy surface for the system has a high density of minima (tending to give fragile behavior), is to suppose that there are high barriers separating the minima. Such high barriers could be understood if the rearrangement of the molecules in the stress-relaxing process involves the rupture of some sort of specific bond. The exceptional behavior of the alcohols (low fragility despite large ΔC_p – see fig. 1) is probably to be interpreted in these terms [43] since the rearrangement of molecules will involve, in addition to the work of locally expanding the liquid to give a favorable density fluctuation, the energy to rupture one or more hydrogen bonds between the molecular units.

4. Length scales at the glass transition

The time necessary to relax some perturbation of the (configurational) equilibrium state of a molecular system of given diffusivity will depend on the distance over which the molecules must diffuse. For instance, the mean diameter of droplets in a microemulsion stops changing (i.e., the system becomes non-ergodic) at a temperature well above the glass transition temperature of the medium in which they are suspended [44] because the distance over which the molecules must diffuse to change the droplet size is of nanometer dimensions (this is the interdroplet separation). By contrast, the distance moved by the average molecule during structural equilibration in a pure supercooling liquid is only of the order of one or two molecular diameters according to both molecular dynamics studies [45], and the Stokes–Einstein relation. To use the latter, we assume that t in the Einstein equation

$$D = \bar{l}^2/t \tag{5}$$

can be replaced with a relaxation time τ, that $\bar{l}$ is the mean distance moved in the time τ, and finally that the friction coefficient, ξ, in a second Einstein relation

$$D = kT/\xi, \tag{6}$$

can be written as a Stokes-law viscous friction

$$\xi = 6\pi\eta r, \tag{7}$$

where η is the viscosity and r is the molecular radius. This leads to

$$\bar{l} = \left(\frac{1.48 \times 10^{-11}}{6\pi r} \frac{\tau}{\eta} \right)^{1/2}. \tag{8}$$

At T_g, τ is ~ 200 s [7], so $\bar{l} \approx 0.2$ Å if $r = 1$ Å and if the viscosity at T_g is taken to be 10^{12} Pa s as for strong liquids. For molecular liquids, η tends to be lower at T_g, ~ 10^{10} Pa s, raising $\bar{l}$ to the order of the molecular diameter. Since τ is assumed to go as η, this length scale will not change much with T. Since relaxation is non-exponential in most viscous liquids, the liquid will require diffusion over distances of some 10 × the above distance to fully relax a perturbation, i.e., over distances of the order of one to several molecular diameters depending on the viscosity at T_g.

The assumption eq. (7) in the above argument is particularly open to question at high viscosities [46,47] (and is clearly wrong by up to 14 orders of magnitude for some ionic species in the liquid state of superionic glasses [48]) so the basis for our assessment of the relaxation length scale is shaky, and clearly in need of independent support.

The diffusion length scale in relaxation is an important quantity since it provides the lower bound on characteristic lengths which could in principle diverge as $T \to T_K$, and which may pos-

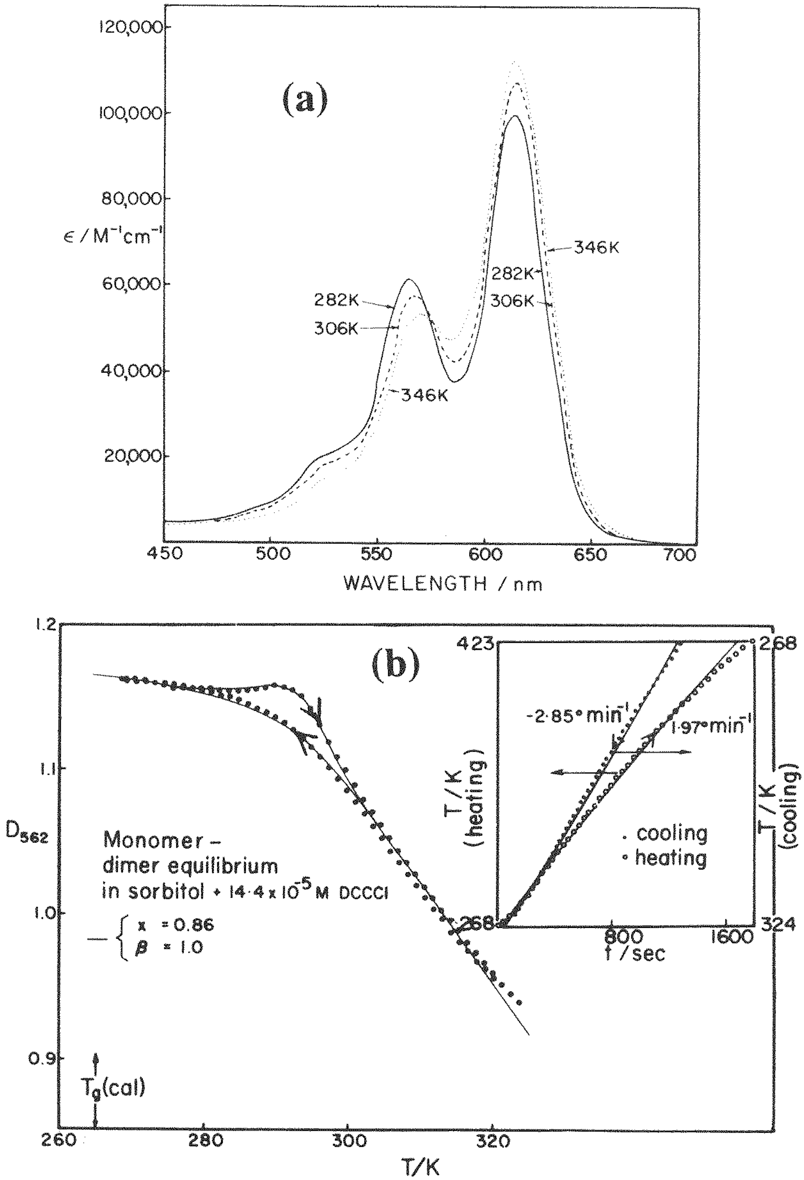

Fig. 6. (a) Absorption spectra of the dyestuff pinnacyanol dissolved in sorbitol at two temperatures. Relaxation is observed by monitoring the absorption at either peak during cool/heat cycles. (b) Absorption at 562 nm during cool/heat cycle. Because we are monitoring the band that is being favored by decrease in temperature, we see the equivalent of the *density* versus temperature behavior in normal liquid–glass transition phenomenology. Note the peak absorbance at 297 K in the heating run, characteristic of the behavior of systems with exponential relaxation (single relaxation time). Inset shows heating and cooling rate.

sibly be observed incipiently to do so if sufficiently fragile systems can be identified. Therefore, we outline briefly some measurements that give rather direct information on this problem by allowing us to determine a 'T_g' for a diffusion-controlled process that, like the freezing of the microemulsion droplet size referred to above, occurs within a matrix of known T_g. In the measurements, we will consider [49,50] we have the special advantage that the diffusion length scale is (within limits) under experimental control.

We refer here to measurements, by optical probe spectroscopy, of the ergodic-non-ergodic crossover for some systems comprised of two species engaged in a chemical association–dissociation equilibrium. Initially Barkatt [49], and more recently Arzimanoglou [50], have observed glass-like 'transitions', with the kinetic signatures of exponential relaxations, in steady heat/cool scans of the dyestuff systems pinnacyanol and methyl orange, in various solvent media ((i) sorbitol ($T_g = -7\,°\text{C}$), (ii) 46 mol% glycerol + 54 mol% sorbitol ($T_g = -29\,°\text{C}$), and (iii) glycerol +45 mol% LiCl ($T_g = -26\,°\text{C}$).

In each case the equilibrium can only be maintained by diffusion together either of two monomers (the case of pinnacyanol) or of a dyestuff anion and a proton (the case of methyl orange). Both equilibria

$$M + M \rightleftarrows D \tag{9}$$

(where M is the monomer pinnacyanol molecule, and D is the dimer) and

$$H^+In^- \rightleftarrows HIn \tag{10}$$

(where HIn = methyl orange) are chosen for their pronounced temperature dependences in order that the freezing of the equilibrium (when the time for diffusion together exceeds the scanning timescale) can be observed spectroscopically as a change in the temperature dependence of the absorption intensity (for reactant or product). The behavior observed in a cool/heat cycle, which is shown in fig. 6, is to be compared with the behavior of the enthalpy or volume, rather than with the usual heat capacity or expansivity signatures of the glass transition. The temperature at which the glass transition is observed, for a constant scan rate, depends on the dyestuff concentration (provided the reactant is randomly distributed throughout the solution to ensure that the characteristic diffusion length varies with concentration – see fig. 7(a) and approaches the glass transition of the solvent as the diffusion length approaches that for the pure solvent glass transition (fig. 7(b)). It is of course, the determination of this latter quantity which is the object of this experiment.

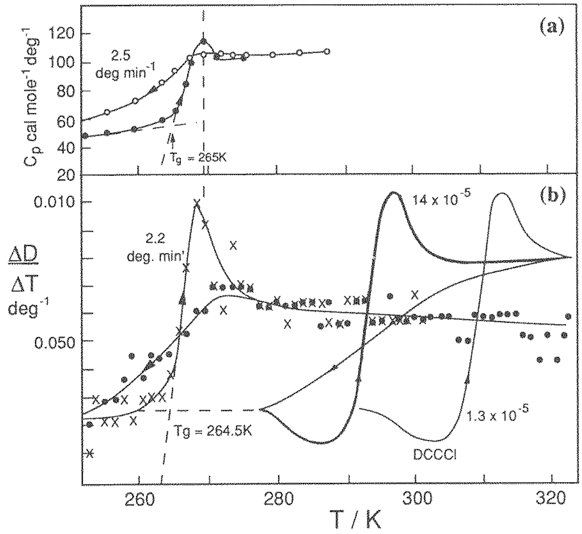

Fig. 7. (a) Calorimetric glass transition for pure sorbitol. (b) Temperature derivative of the absorbance observed during scanning at 2.5 K/min for DCCl solutions in sorbitol at different DCCCl molar concentrations (the one from fig. 6(b) is shown as a thick line), compared with the equivalent derivative spectrum of the solvent obtained by monitoring the absorbance at the –OH vibrational overtone frequency which directly reflects the solvent glass transitions, and agrees almost quantitatively with the DSC scan (see ref. [49]).

Unfortunately, experimental problems at high dyestuff concentrations prevent the observation of spectroscopic T_g at reactant separations less than ~ 50 Å, although the large difference between the reaction (dyestuff) T_g and the solvent (calorimetric) T_g even at this small separation unambiguously establishes that the solvent characteristic diffusion length at the glass transition is truly microscopic ($\ll$ 50 Å). This is also shown by the observation that if the solution conditions (low dielectric constant, low ionic strength) promote ion pairing, i.e., sub-nm H^+–In^- separations, then

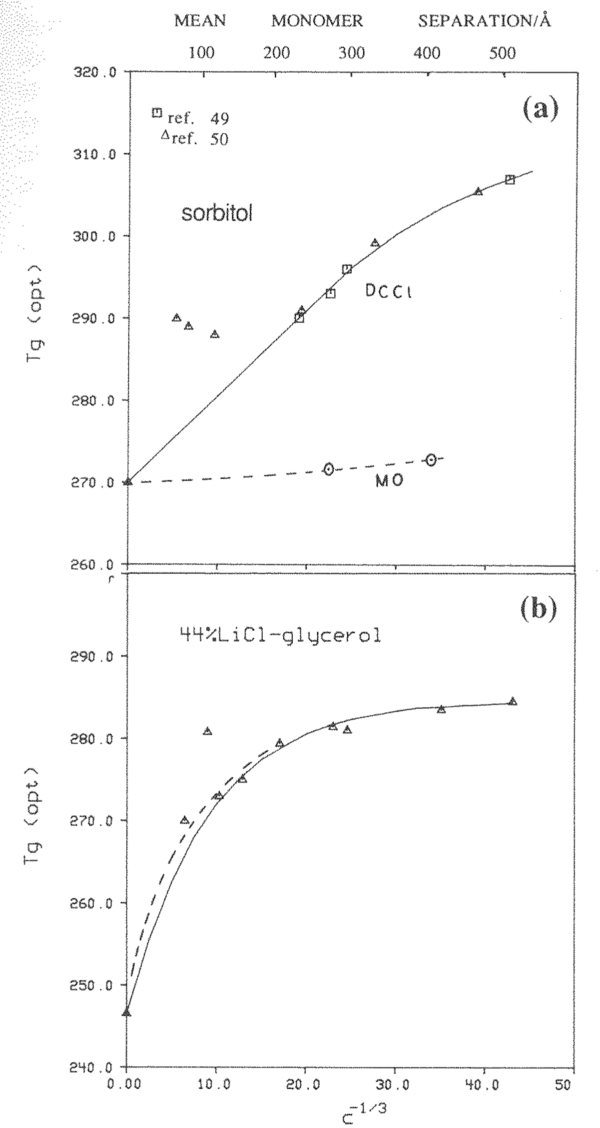

Fig. 8. (a) Variation of T_g (spectroscopic) with distance of monomer separation ($C^{-1/3}$) in units of $(M/Li)^{-1/3}$ and also in Å, assuming complete dissociation (random distribution). Dyestuffs are DCCCl and methyl orange (MO) in sorbitol solutions (adapted from ref. [50a]). The methyl orange probe is clearly not well dissociated since it exhibits the solvent T_g. (b) Variation of spectroscopic T_g for methyl orange solutions in solvent LiCl (44 mol%) in glycerol (56 mol%) with indicator ion separation (shown in units of both molarity$^{-1/3}$ and in Å). Comparison is made with the DSC scan for the solvent (from ref. [49]).

the spectroscopic T_g is the same as the calorimetric T_g of the solvent [50] (see MO fig. 8(a)).

To be more quantitative, it is necessary to understand the functional form of the T_g–concentration relationship of fig. 7(b). This is considered in more detail elsewhere [49] and we give here only the result, in the form of a dashed line extrapolation of $T_{g(spec)}$ to high concentrations, which indicates that the diffusion lengths at T_g are ~ 5–10 Å (i.e., indeed of molecular dimensions). This accords with estimates made by Donth [51] using a quite different and perhaps less direct approach, and is consistent with the finding that, in systems of nanoscopic dimensions (200 Å dia.) but bulk chemical potential (as in microemulsions), T_g is the same as in bulk samples [44]. Sample size effects may be found in smaller systems (see Jackson and McKenna [96]) and this should become an important issue in future work.

The other important point to be extracted from this study is a qualitative one related to an aspect of relaxation phenomenology which we discuss in the next section of this article. Although it is not seen reproducibly enough in the present study to be analyzed quantitatively, it is clear that there is a change-over from exponential to non-exponential relaxation as the concentration of dyestuff increases. This is indicated by the disappearance of a dip in absorbance which is seen just before the onset of the glass transition in the *dilute* solutions (fig. 6(b)). The dip is predicted for single relaxation time (exponential) processes [52,53] and is ‘filled in’ as soon as the shorter time elements of a non-exponential process are introduced. The quantification of the relation between concentration of relaxing units and loss of exponentially should be one aim of future work.

5. Non-exponential relaxation

Although the empirical base is still rather weak at this time, it seems there may be some correlation between the position of a given liquid in the fragility spectrum (fig. 1) and the extent to which the kinetics of the relaxation process depart from simple exponential decay. Since the phenomenon of non-Debye relaxation provides the central theme of this conference, we outline some key observations without going into great detail.

The existence of a correlation of fragility and non-exponentially was conjectured in our original discussion of the strong/fragile classification scheme [5] mainly on the basis of the early studies of this subject area by Litovitz. Macedo and coworkers [16,17,54,55]. Above T_g, these workers observed non-exponential relaxation in ultrasonic studies of viscous liquid oxide melts [55] but exponential relaxation in pure GeO_2 [54], and associated the non-Arrhenius relaxation with the presence of cooperative behavior causing a distribution of relaxation times. They also observed crossovers from Arrhenius to non-Arrhenius behavior with decreasing temperature [17,54], the crossover being at higher viscosities (longer relaxation times) for the stronger liquids. They associated this behavior with the existence of a Gaussian distribution of activation energies for the relaxation process. An alternative explanation within the framework of the coupling model [56] has been outlined by Ngai [57], in a treatment which associated fragility with the strength of correlation between the relaxing species in the liquid (rather than with the topology of the potential hypersurface for the system). Since their work, the case for a correlation of non-exponential decay with fragility has been strengthened considerably by the findings of Torell and colleagues [58] for a range of inorganic liquids systems, from B_2O_3 (rather strong) to $2Ca(NO_3)_2 \cdot 4KNO_3$, and $Ca(NO_3)_2 \cdot 8H_2O$ (very fragile), studied by Brillouin spectroscopy. The behavior of organic liquids has, however, remained uncertain.

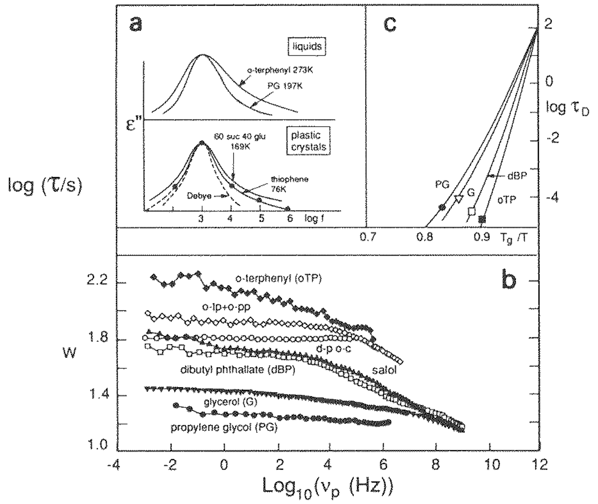

Fig. 9. (a) Some loss spectra for liquids and plastic crystals. (b) Variation of the width of the dielectric relaxation loss peak normalized by the Debye width (1.14 decades) for several organic liquids of varying fragility (adapted from ref. [59], fig. 9). (c) This shows that the order of increasing half width is also the order of increasing fragility as defined by the slope of the T^*-scaled Arrhenius plot at T_g (here $T^* = T_{\tau=10^2\ \mathrm{s}}$, as in fig. 2).

Very recently a series of wide frequency range (12 decades) dielectric studies by Nagel and coworkers [31,59] of organic liquids of varying fragility has added at least qualitative strength to the correlation. Their primary data are illustrated in fig. 9. Figure 9 shows also how, in all cases except one, the departure from exponentiality is temperature-dependent and tends to vanish at the high-temperature limit set by the quasi-lattice libration frequency. Such behavior had earlier been suggested by Ngai and colleagues [60,61] both from their coupling model [56] and from their extensive data analyses on polymer melts and other liquids which, however, were usually only studied over relatively small frequency ranges.

The detailed shapes of the Dixon–Nagel spectra conform closely to the Fourier transform of the stretched exponential relaxation function championed by Ngai [61]

$$\theta(t) = \exp\left(-[t/\tau]^{\beta}\right), \quad 0 < \beta < 1, \tag{11}$$

for the lower four orders of magnitude in frequency but depart systematically from this form at higher frequencies. A new scaling function reminiscent of multifractal scaling was introduced to reduce all data to a single masterplot although the physical basis for this form remains unknown [§].

We reproduce some of the Dixon–Nagel findings in fig. 9. Figure 9(c) shows the initial slopes of the T^*-scaled Arrhenius plots for these liquids, the scaling parameter T^* in each case being the temperature at which the relaxation time reaches 100 s. Dixon and Nagel have pointed out that, in several cases where the data are extensive enough to extrapolate, the half-width tends to diverge

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[§] An equally good scaling has been shown by Chamberlin [62] to result from equations developed for a percolation model of non-exponential relaxation in spin-glasses [63] although the parameter values are unexpected from simple percolation theory.

near but below the T_0 of the Vogel–Fulcher law. The greater spectral width w (w = width/Debye width) found in the more fragile liquids near T_g would in this case reflect their closer proximity to T_0 ($\equiv T_K$) (which does not depend on whether the D value of eq. (5) for the liquid is dominated by barrier heights, $\Delta\mu$, or density of minima, K).

While this may seem a simple correlation, the full story is more complicated because the spectral widths for *enthalpy* relaxation in the same liquids (obtained from specific heat spectroscopy [64]) are not always the same as for dielectric relaxation [65]. Further, they may show different temperature dependences and tend to diverge at the Kauzmann temperature [65]. This may reflect the greater influence exerted by secondary processes in the case of dielectric relaxation since it is known that these can be dielectrically quite strong whereas the heat capacity change on freezing out of the secondary processes is known to be very small [66]. It is clear that the development of a full account of the subtleties of relaxation kinetics will require a much broader empirical base. Again it is reasonable to anticipate some clarification to be provided by increased study of plastic crystal cases. For instance, examination of the dielectric relaxation data for constant frequency, varying temperature, scans of refs. [14c] and [15] for the strong extremes, thiophene and $TlNO_2$, shows that at tem-

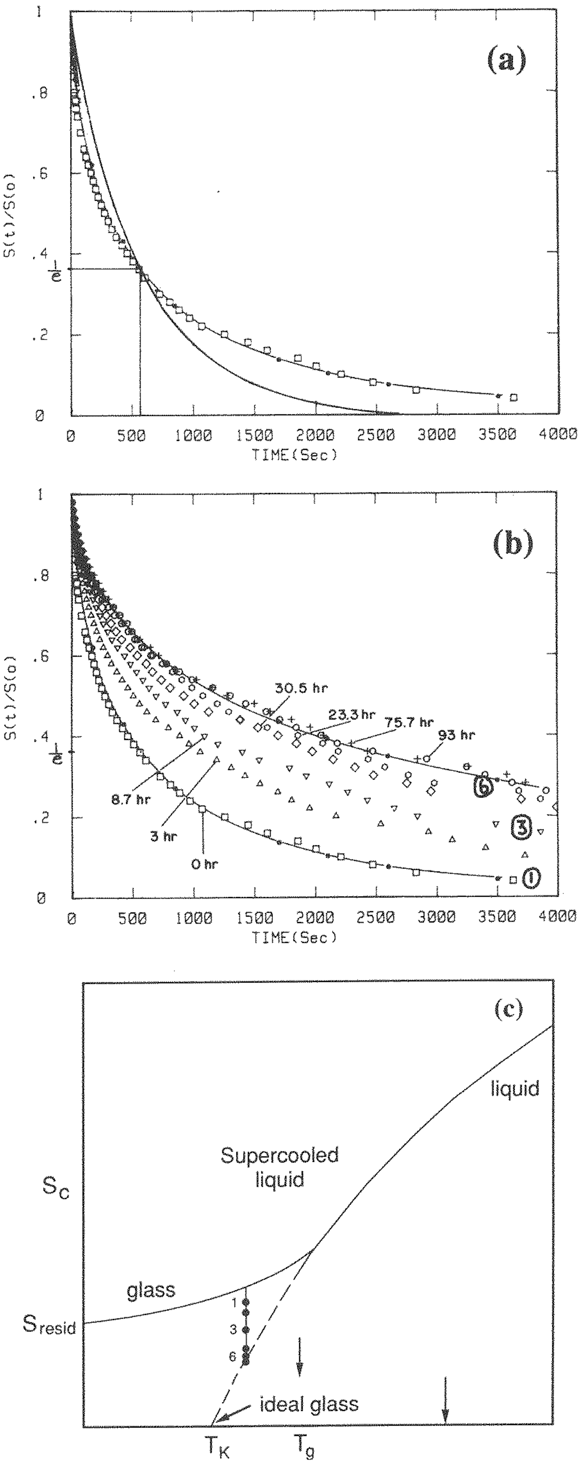

Fig. 10. (a) Decay of stress generated by instantaneous application of strain on a $40AgI \cdot 60AgPO_3$ glass rod near T_g [71] compared with exponential decay curve. (b) Results of repeat experiments after different waiting times at the same temperature, showing effects of changing fictive temperature, at constant actual temperature, on stress decay rate. Upper data plots show that, after sufficient time, the sample reaches equilibrium (i.e., ergodicity is restored, or kinetic and potential energy are fully repartitioned) and stress decay function becomes constant and reproducible. □, curve 1, 0 h; △, curve 2, 3 h; ▽, curve 3, 8.7 h, ◇, curve 4, 30.5 h; ◯, curve 5, 23.3 h; +, curve 6, 75.7 h; ○, curve 7, 93 h. * indicates values calculated using eq. (11); solid curves delineate initial and final run. (c) Illustration of the way the fictive temperature effect seen in (b) can be related to the time dependence of the configurational component of the entropy, i.e., relating the non-linear aspect of relaxation to the Adam–Gibbs equation (eq. (2)). S_c values at points marked 1, 3, 6 are appropriate to decay curves 1, 3, 6 in part (b).

peratures approaching T_g the relaxation is essentially exponential, e.g., 1.17 Debye widths at 120 K for $TlNO_2$, $T_g = 65$ K, while at the fragile extreme represented by the succinonitrile–glutaronitrile mixture in fig. 3 (which is only intermediate by liquid standards), it is rather less exponential (1.4 Debye widths [67]) and temperature-dependent – as seen in fig. 9 for liquids of comparable fragility.

While the dielectric and enthalpy relaxation techniques for study of glasses approaching their Kauzmann temperatures are now quite refined, mechanical relaxation studies in this low-frequency range have remained fairly primitive. The most sensitive techniques suffer from very limited frequency ranges.

Some progress is currently being made with enhanced frequency range forced oscillation spectrometers [68] (which have so far been applied mainly to the study of sub-T_g processes), and with time domain stress-relaxation techniques [69] which are now being enhanced by computer control-and-analysis methods. An example of the latter is given in the proceedings of this meeting where data covering some four orders of magnitude in time are presented and analyzed [70]. An example from the pre-automation literature [71] is given in figs. 10(a) and (b) to illustrate the two key features of relaxation kinetics in fragile liquids.

Figure 10 shows the decay of stress generated by imposition at $t = 0$ of a sudden bending strain, for a case (a fast ion conducting glass $40AgI \cdot 60AgPO_3$) in which the temperature of the sample has been quickly lowered below T_g such that the stress-relaxation time falls at a convenient value for the technique ($\langle\tau\rangle \approx 10^3$ s). The decay is compared with a simple exponential function to display the characteristic 'stretching' of the response seen in glassy systems. The curve passing through the points is the best-fit Kohlrausch relaxation function. The fit is clearly very good although the time range of data is relatively small. Figure 10(b) redisplays the latter result as curve 1 and shows also the decay function observed for the same sample at the same temperature when re-run several hours later, as curve 2. The much slower decay observed in the later run is the consequence of performing a measurement on a non-ergodic system under conditions in which ergodicity is being restored on a timescale not much longer than that of the observations. The stress decay experiment, in other words, is serving as a probe for the thermodynamic state of the glass as it slowly recovers the state of interval equilibrium characterizing the supercooled liquid. The result can be taken as a further demonstration of the usefulness of the Adam–Gibbs equation for the relaxation time, since what we see in fig. 10(b) is simply the consequence of the quantity S_c of eq. (2) changing (with time) at constant temperature. Finally in fig. 10(b), curves 3 and 4 show how, when the equilibrium state is achieved, the stress-relaxation function becomes reproducible. Figure 10(c) relates these results to the values of S_c at the different stages of the investigation. Although it seems probable that no single order parameter can describe the state of a relaxing system [72], the fact that the excess entropy is involved systematically in so many aspects of the relaxation phenomenology implies that it may be the closest we will get to a quantifiable order parameter in this type of study.

Before leaving this section, we should note that reversal of the above procedure, so that S_c *increases* as equilibrium is approached, will produce the opposite result, i.e., τ will decrease with increasing time until the equilibrium state is reached. Unless the displacement in temperature is very small, however, the results of an up and a down T-jump experiment will not be equivalent since the linear response regime for temperature and pressure perturbations (unlike electrical and magnetic perturbations) is very narrow. The importance of non-linear effects is discussed in section 7.

6. Serial decoupling of modes of motion on cooling

The very fact that it is possible to perform the last-described measurement means that, at least near the glass transition, the stress relaxation process occurs on a shorter timescale than does the process that produces the equilibrium structure. The recognition that shear relaxation occurs more rapidly than enthalpy or volume relaxation, at least in a number of systems, is a long-standing one, and the differences were documented for a variety of systems in 1976 [7]. On the other hand, for at least one case ($Ca(NO_3)$–KNO_3 [73]) that is decoupled near T_g [7], shear and volume relaxation times studied at higher frequencies (hence at higher temperatures), are essentially the same, suggesting that the separation of timescales may occur only near T_g. On the other hand, it is known for the same system that the electrical conductivity relaxation occurs on a shorter timescale than does the shear or volume at temperatures where the latter are the same within uncertainty. The timescale separation, quantified by the 'decoupling ratio' [74] or 'decoupling index' [75] τ_s/τ_σ, increases with decreasing temperature. Finally, it has recently been shown from light scattering studies on this system [76] that some short time relaxation mode (arguably, the nitrate anion rotation) splits off from the conductivity relaxation at even higher temperatures. This process apparently retains a very short relaxation time even in the glassy state.

Thus, there would appear to be a series of decouplings which occurs on decreasing temperature, those requiring the least disturbance of the quasi-lattice (having the smallest $\Delta\mu$ of eq. (4)) being the first to 'cut free' of the increasingly slow structural rearrangement modes that eventually give rise to the glass transition. The hierarchy is illustrated in the sequence of curves for different relaxation processes in $40Ca(NO_3)_2 \cdot 60KNO_3$ given by Torell and Grimsditch [58,76] in fig. 11. More data are urgently needed to decide if this represents the general case. Figure 11 resembles a 'relaxation map' for a polymeric material [77].

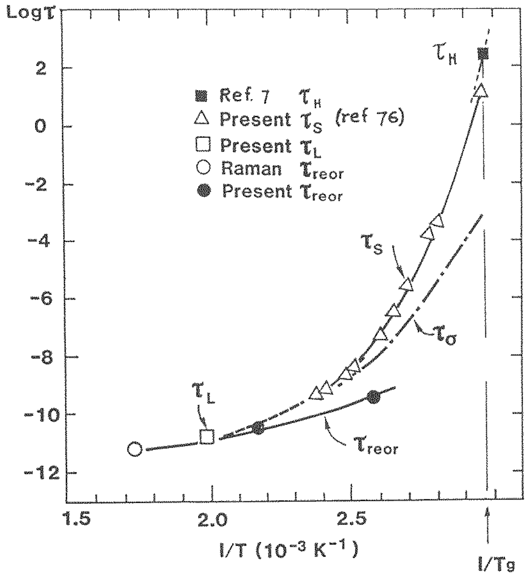

Fig. 11. Variation with temperature, approaching T_g, of the relaxation times for several distinguishable relaxation processes in $40(Ca(NO_3)_2 \cdot 60KNO_3$ supercooled liquid (τ_H, enthalpy relaxation; τ_s, shear relaxation time; τ_σ, conductivity relaxation time; τ_{reor}, reorientation relaxation time), showing decoupling of simpler processes from main relaxation process at different temperatures (adapted from ref. [58], fig. 5; see also fig. 2 in ref. [76] and fig. 9, ref. [10]).

7. Non-linear relaxation

The fact that the linear response regime for temperature and pressure perturbations from equilibrium is so narrow, means that any attempt to describe the thermal or volumetric behavior of a glass-forming system as it is heated or cooled (or compressed or decompressed [78]) through its glass transition, must take non-linear relaxation into account. This can be done either by dividing the temperature dependence of the relaxation time into pure temperature- and structural state (fictive-temperature)-dependent components, as in the Tool [79] – Narayanaswamy [80] – Moynihan [52] approach [7,94], or by using S_c of the Adam–Gibbs equation, as a guide to the non-linear relaxation as in the Scherer–Hodge approach [81,82]. The near equivalence of the two approaches has been demonstrated by Hodge [83]. The Scherer–Hodge approach is the more appealing since behavior in the non-linear regime can be predicted from the results of measurements performed at equilibrium, and since it remains valid even when relaxation near T_g is strongly non-Arrhenius (whereas the Narayanaswamy approach assumes Arrhenius behavior of the relaxation time). Application of the Adam–Gibbs analysis to enthalpy relaxation has also been demonstrated for isothermal relaxation near and far from equilibrium by Oguni et al. [84] and Scherer [85], respectively.

For details of these analysis, the reader is referred to the original articles and to the most recent developments described in the present volume *. We will only point out some of the interesting consequences of the non-linear behavior which may cause confusion to the uninformed investigator as indeed they have in the present author's laboratory in the recent past.

In strong liquids, in which ΔC_p is small so that S_c varies only slowly with temperature, the structural state dependence of the relaxation time is minimized and the linear regime is extended. The glass transition may, however, be difficult to study in such cases because of the small value of ΔC_p itself and because of the spreading out of the C_p rise at T_g due to the small temperature dependence of the relaxation time relative to T_g (see fig. 1).

In fragile liquids, on the other hand, the relaxation times are very state-dependent, as seen in fig. 10. In this case, the shape of the glass transition observed during reheating depends strongly on the previous thermal history. If the glass is cooled more slowly than it is heated, or if it is annealed below T_g before reheating, then the extra entropy lost during the anneal can be recovered rapidly near T_g during reheating and lead to a strong overshoot in the apparent heat capacity. When annealed far below T_g the overshoot can be so large that the glass transition takes on the appearance of a first order transition [87]. Comparable behavior can now be observed in isothermal studies by appropriate variations in pressure [78].

In the case in which the relaxation is highly non-exponential, annealing well below T_g can have an unexpected and easily misleading effect. In this case, as can now be predicted using the approaches discussed above, the entropy lost on annealing is mainly due to the short-time elements of the relaxation spectra. This entropy is then recovered during heating in a manner which, at first sight, looks like the result of a second (lower temperature) glass transition, which would imply

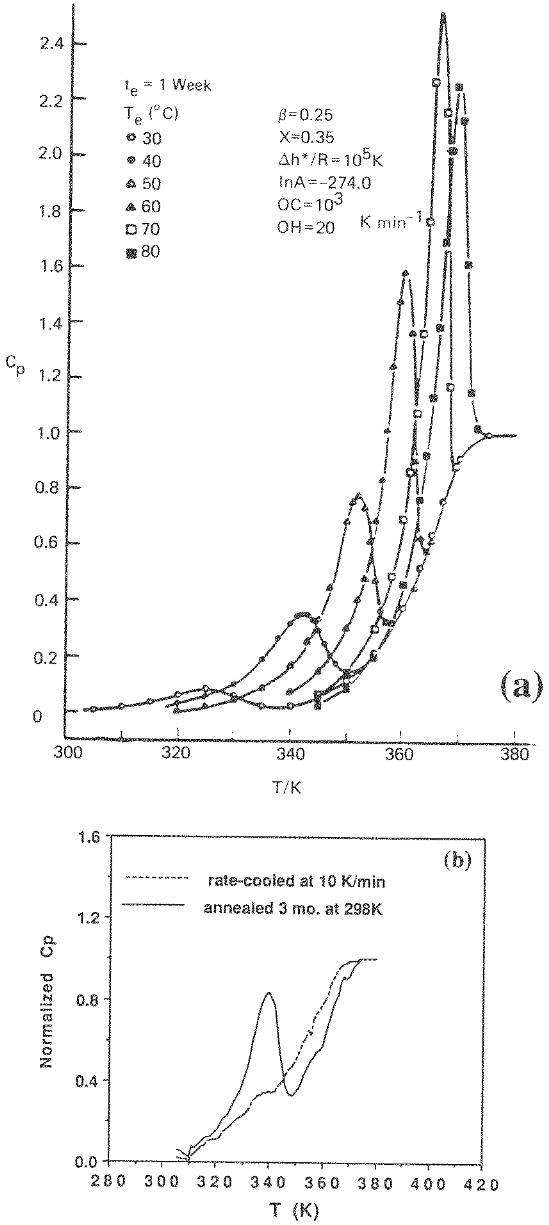

Fig. 12. (a) Phenomenological model predictions of effect of annealing heat treatments at different temperatures below T_g on the calorimetric glass transition (from ref. [88]). Note the development of a distinct endothermic pre-peak for cases of annealing far below T_g. (b) Example of annealing pre-peak in the case of annealed highly non-exponentially relaxing mixed $XO_4^{=}$ anion glass $AgI-Ag_2SO_4-Ag_2WO_4$, compared with subsequent scan of rate-cooled and rate heated sample (from ref. [89]).

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* It appears, by using data from the linear regime studies of Nagel and co-workers [64] to fix parameters in the non-linear model equations, that neither the T–N–M or S–H treatments are handling the non-linear effect properly [95]. An alternative approach [86] worked out in the context of the Ngai–Rendell coupling model [56,57] but not yet evaluated for modelling the glass transition itself, may have advantages.

that separation occurred during annealing into two distinct amorphous phases. However, as studies on single component polymers like polyvinyl chloride have shown [88], this endothermic anomaly can arise purely as a consequence of non-linear non-exponential relaxation effects. The actual observation, and the modelling prediction [88], is that on long anneals (particularly after an initial fast quench) the enthalpy (entropy) regain occurs as a relatively sharp endotherm *preceding* the glass transition which then deprives the glass transition of the overshoot usually expected from an annealing treatment. To illustrate the findings we show, in fig. 12, the modelling predictions for polyvinyl chloride, and the observations for an interesting new ternary glass-forming molten salt mixture which is extremely non-exponential without being extremely fragile, due apparently to the mixing of isovalent isosymmetric anions of different effective radii. In the example illustrated [89], the oxyanion mixture was of sulfate and tungsten ions, but the same phenomenon has been seen in other mixed $XO_4^=$ glasses [90]. Systems of this type will be very interesting to study using optically active probes by means of which different elements of the overall structure relaxation can be singled out for study.

Experiments such as the above show that a significant part of the excess entropy in a glass can be lost while the system remains thoroughly 'stuck' (in the sense that the annealing time is much less than the average relaxation time) in one minimum of the potential energy surface illustrated in fig. 5. This suggests that something important is missing from our conceptualization of this surface and its relation to the macroscopic entropy. As pointed out by Goldstein long ago [91], considerable entropy must reside in the interior degrees of freedom, i.e., in substructure within each minimum. It might be hoped that clever use of the thermal history variable will throw more light on some of these complexities.

8. Concluding remarks

While our remarks in the preceding pages address the main problem areas in the study of non-polymeric relaxing liquids, it is obvious that they represent only a scratch on the surface of the overall problem of understanding relaxation in complex liquids. The deeper view will be obtained from the many specialized articles to follow in these Proceedings. It is appropriate to point out here though, that most of what has been learned so far has come from studies of systems in the vicinity of their global potential minima, i.e., at pressures near zero. It is currently becoming possible to perform detailed dynamic studies on systems very far from this global minimum by means of diamond anvil high pressure techniques (see for instance the work of Nelson et al. [92,93] and of Oliver et al. [94] in the present volumes. At very high pressures, many of the features of the potential which give rise to the differences between liquids seen in fig. 1 should become subservient to the repulsive potential, and all liquids should begin to resemble the hard sphere fluid. While glasses are certainly observed at ~ 100 kbar, it is not clear at this time whether the viscous liquid state on which our attention is focussed here will kinetically survive at ultrahigh pressures ($\geq$ 500 kbar, 50 GPa) because of the decreasing gap in configuration space between liquid and crystal, and the consequent increase in crystallization kinetics. However, the common trends should at least be seen, perhaps enough to define a canonical glass structure and canonical relaxation behavior. Whether or not this state will be more or less fragile than the extremes we now know, will be interesting to learn, as will be the existence or otherwise of secondary relaxations and other subtleties of the normal pressure observations. In any case, it would seem that in many respects the field is still at an early stage of its development and a vigorous and challenging future may be expected.

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