# The glass transition
# C Austen Angell

Key advances in the area of the glass transition include various experimental detections of the onset of microscopic inhomogeneity near $T_g$, and the calorimetric characterization of a $\beta$-glass transition well below $T_g$. Theoretical advances include development of master equation approaches, alternative formulations of the mode coupling equations, and microheterogeneity-based interpretations of the origin of strong and fragile liquid characteristics.

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**Abbreviations**

| | |
|---|---|
| EB | ergodicity-breaking |
| EM | ergodicity-making |
| MCT | mode coupling theory |
| $T_g$ | glass transition temperature |
| $T_K$ | Kauzmann temperature |
| VTF | Vogel–Tammann–Fulcher |

## Introduction

Glass is popularly thought of as the solid product of cooling a noncrystallizing liquid. Then, what is the glass transition? Not only can one not get an explanation of the glass transition, but one cannot even get a consistent answer to what is meant by the question, that is, how the glass transition is defined. For many physicists who might respond to the question, the liquid state would not even be involved. This is because the term 'glass transition' has become generalized to cover any system which passes from an internally equilibrated state to one in which the particle motions are so sluggish that a time-independent state can no longer can be reached. Consequently, the phenomenon of general interest is 'ergodicity-breaking' (i.e. the falling-out of equilibrium), and the challenge lies in finding the common features among the many examples of the phenomenon. For this review, I will concentrate on the liquid $\leftrightarrow$ glass transition. A Nobel laureate considers this probably "the deepest and most interesting unsolved problem in solid state theory" [1].

For this restricted case, that which is clear and agreed-upon is that over some finite temperature interval (which depends on cooling rate and the nature of the liquid under study and also on the test rate) any liquid with sluggish crystallization kinetics will become structurally arrested, hence glass-like. This usually, but not always, happens in association with distinct changes in the magnitude of thermodynamic response constants, constant pressure heat capacity $C_p$, expansivity $\alpha$, etc. This means the glass will crack rather than flow when sufficient stress is applied.

I review current thinking about the glass transition phenomenon, selecting the ordinary liquid $\leftrightarrow$ glass transition, amongst all the known examples of ergodicity-breaking phenomena, for special attention. After discussing how to define a transition temperature, key unsolved problems and new observations are outlined, and approaches to their solution, both from the liquid state and solid state viewpoint, are reviewed.

The transition from solid-like to liquid-like behavior was originally characterized by the temperature $T_g$ at which the viscosity reaches the (high) value of $10^{13}$ poise [2]. Later the definition was moved, by common usage, to the temperature at which the heat capacity, measured in a differential scanning calorimetry (DSC) or differential thermal analysis (DTA) scan at a $10\,K\,min^{-1}$ heating rate, abruptly starts to increase [3]. This corresponds to the temperature where common molecular liquids have viscosities of $\sim 10^{11}$ poise (for high polymers, the viscosity criterion is irrelevant). Others [4] use the '$C_p$ midpoint temperature', where the viscosity is $\sim 10^{10}$ poise. All of these temperatures depend on the precise manner in which the system under study is prepared. This is due to the sensitivity of the heat capacity evolution during heating to the initial enthalpy of the nonergodic state being heated [5,6].

The only unambiguous definitions of the glass transition temperature are those which depend only on the cooling rate, for example, the volume crossover on cooling, advocated by Plazek et al. [6,7] and the ergodicity-breaking (EB) point, defined in Figure 1 from heat capacity data during steady cooling. The fictive temperature defined by Moynihan and co-workers [8] from heating scans does not depend on heating rate but does depend on annealing history after an initial EB on cooling. This EB point is illustrated for the model glass-former system $Ca^{2+}/K^{+}/NO_3^{-}$ (CKN) [7] in Figure 1. For a cooling rate of $10\,K\,min^{-1}$, the $T_{g,EB}$ of Figure 1 falls at a relaxation time of $10^2\,s$, the normal $10\,K\,min^{-1}$ $C_p$ onset (or ergodicity-making, EM) temperature. The fictive temperature, from equal $10\,K\,min^{-1}$ cooling and heating rates, lies close to the latter. As scanning instruments can now be calibrated during cooling, using liquid crystal mesophase transitions which have negligible hysteresis (Q Lu, CA Angell, unpublished data), the only disadvantage of defining $T_g$ in the manner of Figure 1 is that, for liquids with weak glass transitions, $T_g$ is difficult to detect. As most of the interest in the glass transition problem is currently with 'fragile' glass-formers which tend to have strong $C_p$ manifestations [9,10], this problem is not too

**Figure 1**

Scaled Arrhenius plot of structural relaxation times, using $T_g$ defined from heating scan $(T_{g,EM})$ as scaling parameter, for a fragile liquid, o-terphenyl, and a strong liquid, $B_2O_3$. Dashed line at $\tau=10^{-1}$ s shows approximately how the glass transition temperature $T_{g,EB}$, defined by ergodicity-breaking on cooling, relates to $T_{g,EM}$ in each case. Insert shows how $T_{g,EM}$ and $T_{g,EB}$ are defined as onset temperatures from heat capacity upscan and downscans, respectively. Based on original data from [8] and including estimated a.c. heat capacity dispersion curve at constant frequency of 10 Hz from [111]. Note that the 'dispersion range' in an a.c. experiment is not the same as the 'transformation range' observed in a cooling experiment in which the final state is a glass (i.e. a nonergodic state).
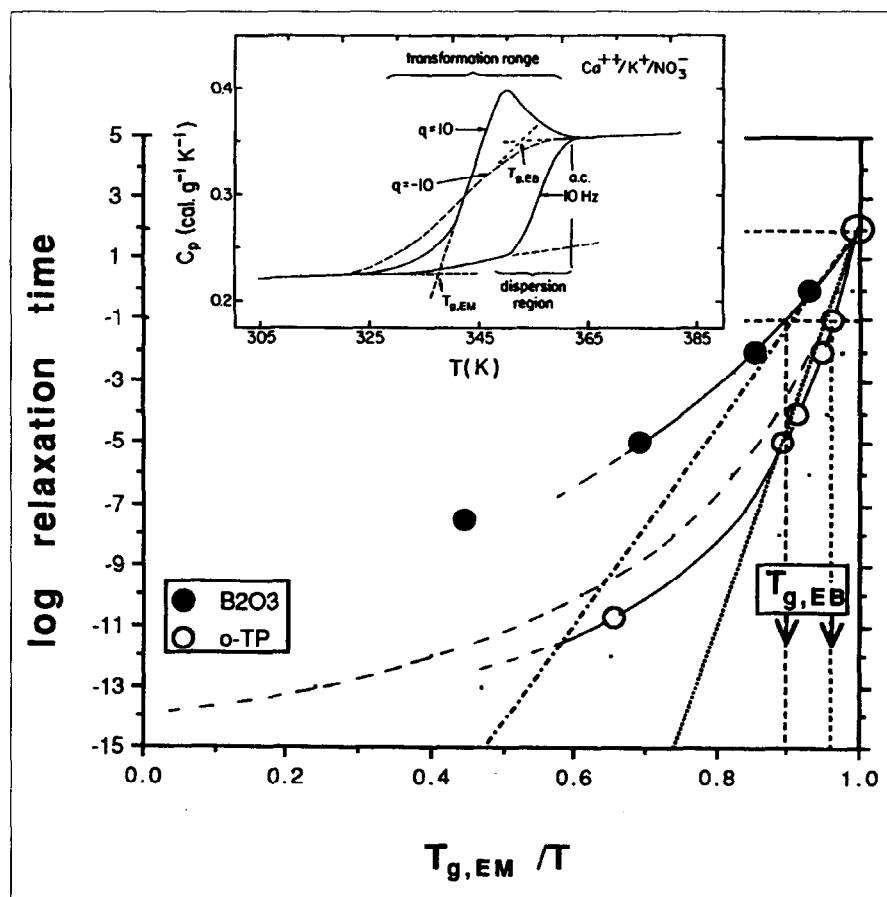


important. For fragile liquids, the two glass transition temperatures $T_{g,EB}$ and $T_{g,EM}$ (defined in Fig. 1) will be quite similar—$T_{g,EB}/T_{g,EM} = 1.05$ as seen in Figure 1. However, for strong liquids, or highly nonlinear polymeric liquids including biopolymers [11–13], Figure 1 shows they will be far apart. In fact, for proteins, $T_{g,EB}$ is not a useful definition because it would fall *above* the denaturation temperature [13], that is, it is inaccessible.

Any definition based on heat capacity behavior is useless for the majority of EB transitions currently under study because there is no detectable $C_p$ anomaly associated with the arrest of the active units. This is the case with spin glasses [14–16], vortex glasses [17], dipole glasses [18] and quadrupole glasses [19,20], and a variety of other orientational glasses [21] for which the theoretically fruitful concept of frustration [22] is most easily applied. For these glasses, the definition of glass transition, made in terms of arrival at a particular relaxation time, is also often unsatisfactory because the relaxation functions are so disperse that an attempt to represent the spectrum by a single time is not very useful. At least for mean field spin glasses, the problem is resolved by defining an order parameter and showing that it goes to zero at some finite parameter and showing that it goes to zero at some finite

temperature, so that the glass transition becomes a true phase transition [23].

Between these two groups, that is, those with and those without $C_p$ manifestations, lies a collection of orientationally-disordered glasses in which the heat capacity manifestation of the glass transition varies from 'non existent' or 'just detectable' to 'pronounced'. In the latter cases, the phenomenology seems identical in all respects to that of the 'structural' glasses under consideration in this review [24,25]. In my opinion, this class of molecular system (in some cases also ionic) deserves special attention in the search for universal aspects of the glass transition.

## Phenomenology of the glass transition and its interpretation

For systems with large $C_p$ jumps, the Kauzmann entropy crisis, or paradox, arises [26]. The paradox is that an imminent thermodynamic crisis due to the rapidly decreasing liquid entropy—at $T_g$ it may be within some 20 K of falling below the crystal value (at the Kauzmann temperature $T_K$) and within 30 K of going negative—is resolved, or rather avoided, by the *kinetic* event of ergodicity breaking. The implication is that,

except for kinetics, the system would find a global free energy minimum, and a phase transition would occur. These systems, in other words, behave as if they have a nondegenerate ground state. In this respect, they can be distinguished from other EB systems which are believed (controversially) to have highly degenerate ground states [27]. In my opinion, this gives them a special measure of interest though also of complexity.

Kirkpatrick and Wolynes [28] have shown that a p-spin Potts glass with p > 2 gives a Kauzmann-like ground state and, notwithstanding its frozen-in spin site disorder, suggest its development as the most fruitful theoretical approach to interpretation of structural glass phenomenology. The Potts glass is less frustrated than the Ising spin glass [28,29]. It is argued from the same approach [28,30] that as $T \to T_K$, state lifetimes should diverge with a temperature dependence, $\exp[c/(T-T_K)^2]$, in association with a diverging correlation length $\xi \sim (T-T_K)^{-2/d}$, where d is the dimensionality — a stronger divergence than expected from the Adam–Gibbs approach (see below). A recent modification of this analysis (Wolynes PG, APS Symposium presentation, March 1996), however, prefers the original 'VTF' (Vogel–Tammann–Fulcher) form (Eqn 2 below). Arguments for a diverging linear dielectric susceptibility at the Kauzmann temperature have been given by Menon and Nagel ([31], Nagel SR, APS Symposium presentation, March 1996), though diverging susceptibilities are not expected from the Potts-glass-based theories, at least not in mean field [30].

As suggested by the above remarks, the Kauzmann paradox may be resolved by postulating a relation between the excess entropy and the relaxation time, as in the Adam–Gibbs equation [32,33,34*],

$$\tau = \tau_o \exp(C/TS_c) \tag{1}$$

where $S_c = \int_{T_K}^{T} \Delta C_p/T dT$. If the excess $C_p$ is hyperbolic in T as is a good description for many systems [35,36], then $S_c \sim (T-T_0)/T$ and Equation 1 becomes the well known VTF equation

$$\tau = \tau_o \exp[(B/(T-T_0)] \tag{2}$$

with $T_0 = T_K$. We note that a hyperbolic relation between $\Delta C_p$ and T is a specific requirement of Derrida's random energy model [37] which can be shown to be a p→∞ version of the p-spin Potts glass (DL Stein, personal communication). The linear disappearance of $S_c$ with 1/T is illustrated alongside an Arrhenius plot of the dielectric loss maximum for the fragile liquid propylene carbonate in Figure 2. The best fit Vogel temperature is 130 K [38] (10³/130 = 7.69).

This then requires a close relation between $T_K$ from thermodynamics and $T_0$ (from Eqn 2) from low temperature

Figure 2
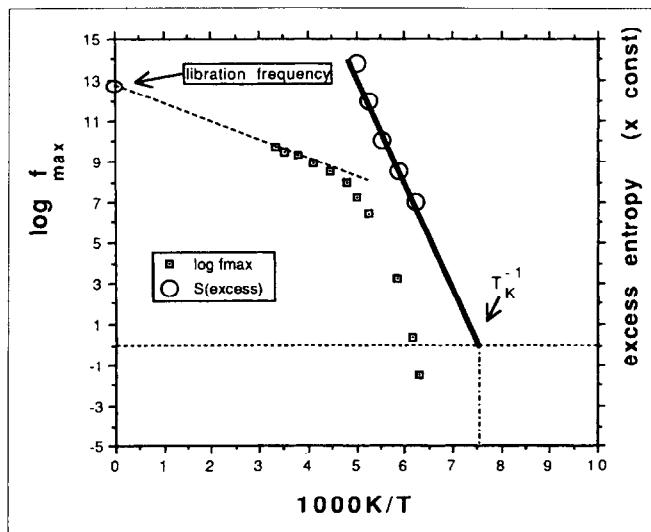


Propylene carbonate: reciprocal temperature variations of excess entropy of liquid over crystal (linear for random energy model) and the logarithm of the frequency of maximum dielectric loss ($f_{max} \cong 1/2\pi\tau$). The plot shows how relaxation time diverges as excess entropy vanishes. The VTF $T_0$ (Eqn 2) for these data is 130 K ($T_0^{-1} = 7.8 \times 10^{-3}$) in agreement with $T_{Sc \to 0} = T_K$. The far IR libration frequency which must be approached at the high temperature extreme is shown as an open circle. Data from [107] ($C_p$ and S), [38] ($f_{max}$ dielectric), and [108] (libration frequency).

relaxation measurements (Fig. 2) and is indeed found for glass-formers of all types over a temperature range of 50–1000 K (CA Angell, ACS symposium presentation, March 1996). I must, however, mention the opinion of Stickel *et al.* [39] who show that in some fragile liquids the VTF equation only fits data at $T > (T_g + 50)$, and at lower temperatures, an unambiguous value for $T_0$ cannot be extracted from the data.

There are some systems in which both the normal center-of-mass disordered (CMD) glass and the crystalline-but-orientationally-disordered (COD) glass phase exist [40]. An example of such a system is ethanol: the $T_g$ and $\Delta C_p$ values of both its CMD and COD phase are very close [40]. In other cases, the $T_g$ values of the CMD and COD phase are very different, and in such cases the $\Delta C_p$ values of these phases are also different [41].

In the Adam–Gibbs theory of relaxation, the energy barrier appears in the relaxation time–temperature dependence as part of the same exponent that contains the quantity $S_c$ responsible for the non-Arrhenius behavior (i.e. the fragility), $\exp(C'\Delta\mu/S_c)$ where $\Delta\mu$ is the energy barrier which a cooperatively rearranging group must surmount. The author [9,10,42] has attributed fragility to a combination of large $\Delta\mu$ and small $\Delta C_p$ (which determines the T dependence of $S_c$) values. On the other hand, Hodge [5,6] has argued persuasively that most of the difference between strong and fragile liquid behavior (or

the equivalent COD system behavior) is due to differences in $\Delta\mu$. That is, large $\Delta\mu$ pushes $T_g$ further from $T_K$ and thereby causes $\Delta C_p$ to *seem* smaller simply because of the $\Delta C_p$ versus T relation.

In an old interpretation of viscous liquid behavior, Macedo and Litovitz [43] introduced the notion of sequential probability conditions for relaxation. Their notion that both energy fluctuations E and volume fluctuations v* are needed leads to a form distinct from that of Equation 1:

$$\tau = \tau_o \exp(E/RT)\exp(\gamma v * /v_f) \qquad (3)$$

If the 'free' volume, $v_f$ goes as $\alpha(T-T_o)$ and if E is small, this gives VTF behavior, but if the first Arrhenius term is large, $\tau$ will exceed $10^2$ s before the second term 'tunes in'. Such liquids would be 'strong' in character. This scenario has now been shown to be a general consequence of microheterogeneity by Perera and Harrowell [44] who further show how the other canonical characteristics of fragile glass-forming liquids [9,10,45] (i.e. nonexponentiality and nonlinearity) then follow naturally.

Evidence for the validity of microheterogeneous models is being generated by an increasing number of experimental probes. Particularly persuasive are the findings of Schmidt-Rohr and Spiess [46], Cicerone and Ediger [47,48], Moynihan and Schroeder [49], and most recently Böhmer, Chamberlin and co-workers [50]. In the Perera–Harrowell approach, the first term of a generalized version of Equation 3 characterizes the kinetics of relaxation in the mobile regions; the second term relates to the volume fraction of mobile regions, and hence contains the thermodynamics. It is noteworthy that the coupling model of Ngai and Rendell [51,52] also has an Arrhenius 'primitive' relaxation as the necessary precursor of the slow process and also leads on to an explanation of other canonical glass-former characteristics. The origin of the extreme fragility attributed to spin glasses [53] (and the concomitant extreme nonexponentiality and nonlinearity) would, in these terms, be due to the barrier-free spin flipping which sets the microscopic timescale in the mobile regions. It is in accord with these ideas that the liquids in which the high-temperature viscosity is clearly Arrhenius in character but which also have Kauzmann crises, should be intermediate liquids in Figure 1 (e.g. propanol and ethanol) [54]. In fragile liquids, the residue of the primitive process can be found as a $\beta$-glass transition far below the $\alpha$-glass transition. This weak phenomenon has recently been characterized calorimetrically by Fujimori and Oguni [55], and the relation of its temperature dependence to that of the high-temperature process is interesting, as expected from Johari and Goldstein's deliberations [56] and findings [57].

Opinion is very divided over the extent to which the mode coupling theory (MCT) of the glass transition [58,59,60] has elucidated the overall glass transition problem. The MCT makes quantitative predictions about the way in which certain correlation functions behave on cooling, and in its idealized form (in which density modes dominate), it predicts a dynamical jamming at a nonzero temperature via power law relaxation time divergences. For most liquids so far tested, however, the divergence is predicted at a temperature which lies well above the experimental glass transition temperature, sometimes above the melting point. Notwithstanding this problem (which can be rectified qualitatively by adding additional mechanisms [61]), its predictions of the details of the initial slowing-down process are borne out to a remarkable extent by the most relevant molecular dynamics simulations [61,62], and also by a number of sophisticated experiments that it has inspired [63–76]. In particular, these experiments and simulations have thoroughly supported its main contention that the relaxation is a two-step process, the fast part of which is of subtle and unanticipated character. On the other hand, some of the most persuasive support for the theory has come from measurements [66–73] in which the measured quantities have proven later [75,76] to be dominated by orientational, not density, fluctuations. Thus, the structure of the theory seems to give a general description of the crossover from microscopic collective oscillatory motion (rattling or librating) to relaxation. Thus it should be equally adept at describing the early stages of slow-down of molecular rotations in orientational glass-formers [24,25]. Kirkpatrick and Wolynes [77] have argued that the MCT is formally equivalent to a density functional theory for the glass transition [78].

Although the MCT has certainly helped our understanding of the initial stages of slowdown, it has not had much to say about the lower temperature phenomenon with its unexplained development of microheterogeneities [46–49], its entropy paradox [26], and its fragility-related nonlinearities [5,6,45]. There is a body of opinion that believes these latter factors are not very important and that the difficult part of the problem has now been dealt with. Other opinion [42,79,80] holds that they are in fact the core of the problem and [80] that the MCT only describes the way a macroscopic system enters and gets trapped in a single one of the innumerable potential energy minima characterizing its configuration space, thus leaving unanswered how the plethora of minima are to be enumerated or the lower energy minima accessed. Some new support for this view is given below.

Stepping in to fill this gap are, in addition to the approaches already mentioned, the energy master equation approaches [81–88] which, for viscous liquids, trace back to Brawer [86] and find fullest expression in the paper by Dyre [87]. Although related to the random energy model [37], these equations predict neither Kauzmann crises nor Vogel–Fulcher divergencies. This is also true of the distinctive mesoscopic model of Chamberlin [88] which uniquely predicts the Dixon–Nagel susceptibility–frequency scaling relation [89].

Some reconciliation of the different views may come from new developments in the modelling of random systems. There are model spin systems, unfortunately not easily mapped onto particulate systems, which show clearly that there are two significant temperatures in the problem (G Parisi, 14th CITGES conference, 1996; see also [90–93]). The lower one is a thermodynamic temperature corresponding to the (structural glass) Kauzmann temperature and the upper one is kinetic and corresponds, like the MCT $T_c$, to the highest temperature at which trapping can occur (in accord with a view I expressed earlier [42]). Clearly, the interval between these two temperatures tells how quickly the system is excited over the full landscape (perhaps better to be regarded as a pitted plateau), and hence how fragile the liquid is. The MCT equations themselves have recently been shown to be alternatively derivable as a special case of more general nonlinear dynamics obtained from analysis of the dynamics of particles in random potentials [94].

Finally, among the liquid state approaches are two recent ideas, the avoided critical point approach of Kivelson *et al.* [95] and the local expansion modes of Dyre *et al.* [96] which explains fragility as a consequence of high temperature dependence of a solid-like property — the high frequency shear modulus. Each explains the behavior of relaxation times but neither deals with the Kauzmann problem.

Many workers believe it is better to start at the low temperature end, and ask the following question: what is it that enables the system with rising temperature to escape from its particular, mechanically stable, low energy minimum and gain access to all the other minima within kT? That is, what physics enables a system to become ergodic [97]?

Thus Buchenau and Zorn [98], monitoring the behavior of the Debye–Waller factor $<r^2>$ for liquid and glassy Se, observed a quite sudden increase in $d<r^2>/dT$ at the same $<r^2>$ value at which the crystalline form of selenium melts. As the break occurred at the temperature of the calorimetric glass transition where diffusion becomes measurable, this suggested a Lindemann law-like critical displacement criterion for the glass transition, which they then used to account for the viscosity–temperature relation [98]. The critical displacement idea is given a theoretical basis in the extended self-consistent phonon theory of Stoessel and Wolynes [99]. In the hard sphere case considered, however, this treatment seems more closely related to the stability of the glass vis-a-vis the crystal than to any glass transition phenomenon.

The anomaly in the Debye–Waller factor, which is seen even in systems of fixed configuration well before diffusion commences [45,100], has drawn attention to the behavior of the 'boson peak'. This low energy vibrational mode,

or group of modes, is observed to damp out rapidly below $T_g$ in fragile glass-formers (for which the sharpest change in the $<r^2>$ slopes is observed) [45,100], but to survive undamped to temperatures well above $T_g$ in strong glass-formers [101,102]. The localization of low frequency modes [103,104] which is thought to be associated with boson peak damping [105] may thus be the key phenomenon triggering the glass transition.

Finally, I note the importance of the pressure variable to the resolution of these problems. The apparent validity of one but not both of the Ehrenfest relations (which connect the pressure dependences of second-order transition temperatures $T_2$ to changes in thermodynamic properties, $\Delta C_p$ etc., found at $T_2$) for glasses at $T_g$ [106] provided early support for the Gibbs–Dimarzio approach to the glass transition, and should be examined in the light of the random energy model. Alba-Simionesco [107] has shown that $\Delta C_p$ of a fragile liquid decreases with increasing pressure, which means that $\Delta \alpha$ must also decrease because $dT_g/dp$ decreases at high pressure. Now Schug and King (APS presentation, March 1996) have shown definitively, from diamond anvil cell studies of viscosity, that the fragility of o-terphenyl decreases markedly with increasing pressure, consistent with Alba-Simionesco's finding through Equation 1. This suggests the possibility of a universal intermediate-like behavior for glass-formers at high pressure (Fig. 1). Although these latter fragile→intermediate conversions are continuous, analysis of experimental data [100,109], and computer simulations [96,105,106] suggest that a 'strong-to-fragile' (or to 'intermediate') transformation can occur via a weak first order-like phase transition or abrupt high-order transition. The subject of first-order polyamorphic phase transitions in isotropic liquids is, in my opinion, of the greatest importance in enhancing the general understanding of the liquid state and, in particular, in making the connection between physical and biological complexity [45].

## Conclusion

Setting aside the problem of polyamorphism, which deserves a separate discussion, I conclude that the field of viscous liquid phenomenology and the glass transition is in a state of rapid development. Highlights are the advent of microheterogeneity models which go far to rationalize fragility, and the correlation of boson peak physics with glass transition. The random energy model deserves more attention.

## Note added in proof

After this manuscript was submitted, I became aware of an additional paper recently published by Chamberlin [114].

## Acknowledgement

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