Fragilities of liquids predicted from the random first order transition theory of glasses

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A microscopically motivated theory of glassy dynamics based on an underlying random first order transition is developed to explain the magnitude of free energy barriers for glassy relaxation. A variety of empirical correlations embodied in the concept of liquid "fragility" are shown to be quantitatively explained by such a model. The near universality of a Lindemann ratio characterizing the maximal amplitude of thermal vibrations within an amorphous minimum explains the variation of fragility with a liquid's configurational heat capacity density. Furthermore, the numerical prefactor of this correlation is well approximated by the microscopic calculation. The size of heterogeneous reconfiguring regions in a viscous liquid is inferred and the correlation of nonexponentiality of relaxation with fragility is qualitatively explained. Thus the wide variety of kinetic behavior in liquids of quite disparate chemical nature reflects quantitative rather than qualitative differences in their energy landscapes.

It is believed that all classical fluids could form glasses if cooled sufficiently fast so as to avoid crystallization. Central to glass formation is a dramatic slowing of molecular motions on cooling the liquid. The existence of a universal description of glass transitions is suggested by empirical observations connecting deviations from the Arrhenius law for the slowing of rates, nonexponential relaxations in the super cooled liquid state, and the behavior of thermodynamic properties on cooling (1). Quantitative differences in behavior of different substances sometimes obscure this universality. This has led to a classification of liquids into "fragile" ones like o-terphenyl, having the most dramatic deviations from the Arrhenius law, and into "strong" ones like pure SiO_2 where the Arrhenius equation works well (1). In this paper, we show how the fragile versus strong behavior of liquids can be understood within a microscopically motivated theory based on the idea that glassy dynamics is caused by an underlying thermodynamic, ideal "random first order" transition (2–7).

The notion that a random first order transition lies at the heart of glass formation received its early theoretical support from the remarkable confluence of approximate microscopic theories of the liquid glass transition (8–10) and the behavior of a large class of exactly solvable statistical mechanical models of spin glasses with quenched disorder (11). Two closely connected theories of the liquid glass transition suggest features similar to first order transitions. One of these, the so-called mode–mode coupling theory (8, 12), focuses on the feedback between the slow fluctuations of fluid density in a molecule's environment on the motion of that molecule. This theory predicts a sharp transition in the dynamics as well as a characteristic behavior of the time correlation functions near the predicted transition. Mössbauer effect (13) and neutron scattering (14) are roughly consistent with these precursor phenomena. At temperatures below the transition, mode coupling theory predicts the freezing of the liquid's configuration near to a given random configuration; i.e., there is broken ergodicity. Another approach to the glass transition directly addresses broken ergodicity by investigating the stability of a frozen density wave using either self-consistent phonon theory (9) or the density functional theory of liquids, applying them to aperiodic structures (10, 15). The mode coupling, self-consistent phonon and density functional approaches all predict that there is a Lindemann criterion for the stability of an aperiodic density wave: just as for a periodic crystalline solid, thermal vibrations cannot yield a root mean square displacement of particles from their fiducial location exceeding roughly one-tenth of the interparticle spacing. The precise value of the Lindemann ratio only weakly depends on the detailed intermolecular forces. The predicted Lindemann ratio corresponds well to the experimentally measured magnitude of the intermediate time plateau in the structure function measured by neutron scattering (14). A finite Lindemann ratio would be consistent with a first order phase transition, but glass transitions in the laboratory do not show a latent heat as ordinary first order transitions do. This lack of latent heat is explained by the existence of the large number of aperiodic structures that may be frozen in at a glass transition in contrast to the unique periodic structure formed in ordinary crystallization. Many exactly solvable models of disordered magnetic systems have been shown to exhibit freezing into many structures (11, 16, 17). The major class of these also show a first order jump in a locally defined order parameter without any latent heat. This defines what has been called a "random first order" transition. Unlike Ising spin glasses, these models possess no symmetry between local states but have long range, quenched random interactions. Such systems include Potts spin glasses (11), p-spin glasses (17), and the elegantly solved Random Energy Model (16). There are further parallels between these systems and the phenomenology of glass forming liquids, most notably both glass forming liquids and these models exhibit a Kauzmann entropy crisis, i.e., the configurational entropy vanishes at a finite temperature above absolute zero (18). This crisis would define an underlying ideal glass transition. Whether the crisis for liquids would be avoided in some way at lower temperature than measurements have been made is controversial and is of limited relevance to describing the observed behavior using the analogy. In the exactly solvable statistical mechanical models, a dynamic transition occurs at a high temperature T_A coincident with mode coupling and stability analyses, but the thermodynamic transition does not occur until at a lower temperature, T_K the configurational entropy of different frozen solutions vanishes (4). The idea then is that the glassy dynamics in the measured temperature range is governed by the approach to an ideal glass transition described like that shown in the exactly solved models. There are two seeming differences between the exactly solved models and the situation for the liquid–glass transition. First, in liquids there is no quenched randomness; it must be self-generated. Second, while the models have infinite range forces, interactions in liquids are of finite range. The absence of quenched randomness has been addressed by exhibiting several mean field models without quenched randomness that do generate randomness internally (19–21). Also the formal statistical mechanical tools used for quenched random Hamiltonians, e.g., the replica technique,

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have been shown to be applicable to atomic fluid systems with self-generated randomness (7). Furthermore, computer simulations of fluid glass transitions show replica symmetry breaking like a random first order transition (22). The consequences of finite range interactions are more important. The finite range causes the dynamic transition at T_A, like a spinodal of an ordinary first order transition to be smeared out. It becomes a crossover to activated dynamics. Below T_A, motions in the finite range system that involve the rearrangement of large regions of the liquid can still occur. The transition to such collective activated events in liquids has been confirmed in simulations (23, 24). The events are driven by the configurational entropy. For finite range systems approaching a random first order transition, an "entropic droplet" scaling argument for the activation barriers naturally explains the non-Arrhenius transport behavior and leads to the Vogel–Fulcher law (4, 5). The idea that configurational entropy is needed for motions in glasses predates the random first order transition theory and was described by Adam and Gibbs (25). The older argument is quite different, however, from the random first order transition theory, because it provides no explanation for how a rearranging unit's activation energy is related to the microscopic forces. Here we show how the near universality of the Lindemann ratio explains the connection between barrier heights and thermodynamics for liquids of varying fragility.

The naive density functional approach used to obtain the Lindemann criterion for vitrification allows an estimate for the free energy of dynamic rearrangements. The density functional (10, 26) assesses the cost of forming any density wave by breaking the free energy into an entropic localization penalty and an interaction term.

$$F = \int f(\rho(\mathbf{r})) d^3\mathbf{r} = k_B T \int d^3\mathbf{r} \rho(\mathbf{r})[\ln \rho(\mathbf{r}) - 1]$$
$$+ \int\int d^3\mathbf{r} d^3\mathbf{r}'(\rho(\mathbf{r}) - \rho_0)c(\mathbf{r} - \mathbf{r}')(\rho(\mathbf{r}') - \rho_0), \quad [1]$$

where ρ_0 is the mean density. The localization cost is the same as for a perfect gas while the interaction term involves the direct correlation function of the liquid, a renormalized form of the bare interaction potential. The direct correlation function is determined by the condition that the functional gives small fluctuations in density reproducing the static liquid structure factor. Higher order terms in the density can also be included. In the frozen aperiodic state, the density wave is decomposed into a sum of Gaussians centered around random lattice sites, $\rho(\mathbf{r}) = \sum_i (\frac{\pi}{\alpha})^{3/2} \exp(-\alpha(\mathbf{r} - \mathbf{r}_i)^2)$, where α represents the effective local spring constant that determines the rms displacement from the fiducial lattice site. The localization sites are $\{\mathbf{r}_i\}$. For large α, the densities around different sites overlap weakly giving

$$\frac{F}{N} = k_B T \left[\frac{3}{2} \ln\left(\frac{\alpha r_0^2}{\pi}\right) - \frac{5}{2}\right]$$
$$+ \frac{1}{N} \int\int d^3\mathbf{r} d^3\mathbf{r}'(\rho(\mathbf{r}) - \rho_0)c(\mathbf{r} - \mathbf{r}')(\rho(\mathbf{r}') - \rho_0), \quad [2]$$

where N is the total number of particles and r_0 is the mean lattice spacing. We can take $\rho_0 r_0^3 = 1$. For small α, F/N reduces to the perfect gas value.

A similar free energy expression is obtained from self-contained phonon theory where the direct correlation function is replaced by the Mayer function $f = e^{-\beta u(r)} - 1$ for hard potentials (10) or by the potential itself (7). The free energy varies with the particular arrangement of sites $\{\mathbf{r}_i\}$, but assuming α is the constant, the mean free energy of aperiodic structures is plotted in Fig. 1A. The lowest value of α for which a secondary minimum occurs is given by the Lindemann value α_L.
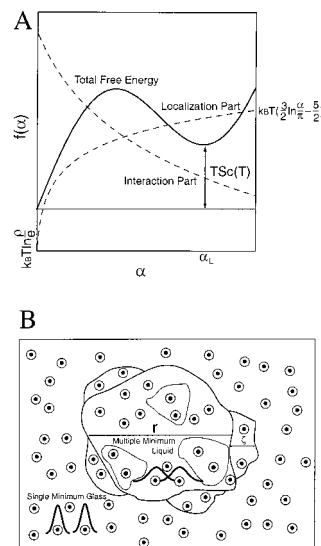

Fig. 1. (A) Free energy as a function of order parameter α. Right below T_A, a second minimum emerges around $\alpha \approx \alpha_L$, which corresponds to a glassy state. The free energy difference between the liquid and glass state is $TS_c(T)$, which approaches zero at the Kauzmann temperature T_K. (B) An illustration of a liquid-like (multiconfiguration) droplet inside a glassy region corresponding to a single mean field minimum free energy configuration. The interface is wetted by suitable configurations to lower the surface energy. One considers an inhomogeneous situation with single minimum given by the density functional theory abutting another minimum as in a naive droplet solution with a radius of curvature r. Upon this surface, one erects a smaller droplet of one of the other solutions of the density functional theory as shown in the figure. The free energy of interpolating this wetting phase is given by $\Delta F = \sigma(r) r^{d-1}(\frac{\xi}{r})^2 - T\sqrt{k_B \Delta C_p} r^{d/2}(\frac{\xi}{r})^{1/2}$. This additional free energy cost depends on the surface tension at the scale r, $\sigma(r)$ and on the fluctuations in driving force for forming this smaller wetting droplet. In the Ising model, the fluctuations in driving force for these droplets arise from the random part of the magnetic field. For a random first order transition, the field fluctuation's role in the disordered magnet is played by the fluctuations of configurational entropy density. The magnitude of these fluctuations should be given by the usual Landau expression $\Delta S_c^2 = k_B \Delta C_p$, where ΔC_p is the configurational heat capacity of a region. The contribution to the free energy from the interpolating wetting droplet yields a change with size of the surface tension at size r, $d\sigma$ (Eq. **4**).

This minimum representing the frozen wave is higher in free energy than the $\alpha = 0$ fluid phase. For the exactly solvable random first order transitions the excess free energy of the frozen solution is known to equal the configurational entropy of possible mean field solutions, TS_c. For the fluid system in addition to the $\alpha = 0$ and $\alpha \approx \alpha_L$ uniform stationary solutions of the variational equation $\delta F = 0$, there are saddle points representing droplet configurations in which a region of low $\alpha \approx 0$ forms in the midst of a given large α solution (See Fig. 1B). This saddle point is a transition state for reconfiguring the frozen density wave. Within the melted region there is a multiplicity of states corresponding to other aperiodic arrangements of the atoms. Much below T_A, the interface should be quite sharp, that is, in a single atomic layer α changes from a value near α_L to near zero. Close to T_A the transition should be smoother with α slowly varying over many atomic layers. In both cases, there will arise a surface tension σ reflecting the deviation of α in the layers from the α for bulk free energy minima. The density functional expression for the droplet free energy then is given as a function of the radius of the droplet much as in conventional nucleation,

$$F(r) = -\frac{4}{3}\pi T s_c r^3 + 4\pi\sigma r^2. \quad [3]$$

Here s_c is the configurational entropy density.

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The maximum of $F(r)$ gives a reconfiguration barrier $\Delta F^{\ddagger} = \frac{16}{3}\pi\sigma^3/(Ts_c)^2$. A detailed calculation of this barrier for a specific glassy system, the random heteropolymer has been given by Takada and Wolynes (27). This naive droplet result (4, 28) differs from the Adam Gibbs suggestion $\Delta F^{\ddagger} = s_c^*\Delta\mu/s_c$ (25), where $\Delta\mu$ is a bulk "activation energy" per particle and s_c^* is the "critical configurational entropy" taken to be usually $k_B\ln 2$. The AG formula is not the result of a self-contained microscopic calculation but assumes the free energy cost of dynamically reconfiguring a region is independently given from the free energies that determine the low energy structures themselves. There is no apparent reason to assume $\Delta\mu$ a constant for different substances. On the other hand, the modern random first order transition theory does suggest universality for σ based on the universality of the Lindemann ratio $\alpha_L^{-1/2}/r_0$. We see this in the following way: assuming a sharp interface between the localized and delocalized regions, the energy associated with the interface should be one-half of the interaction part of the free energy in the bulk stable phase. Therefore,

$$\sigma = \frac{T}{2}r_0\left[\frac{3}{2}nk_B\ln\left(\frac{\alpha r_0^2}{\pi e}\right) - s_c(T)\right],$$

where n is the density of particles. Because the localization part of the free energy depends only logarithmically on α, we can replace α by its minimum value α_L which achieves at T_A. Near T_K, on the other hand, we can neglect the configurational entropy part of the expression. For temperatures between T_A and T_K, the errors of making these two approximations largely cancel. This gives

$$\sigma = \frac{3}{4}nr_0k_BT\ln\left(\frac{\alpha_L r_0^2}{\pi e}\right) = \sigma_0$$

as an approximation for temperatures much below T_A. The universality of the Lindemann ratio $\alpha_L^{-1/2}/r_0$ means σ/nr_0k_BT is nearly universal and therefore that $\Delta F^{\ddagger}$ increases more rapidly with cooling for substances with a large configurational heat capacity. This explains the empirical correlation that strong liquids with nearly Arrhenius rate slowing have small excess heat capacities contrasting with fragile liquids having large excess heat capacity with dramatically non-Arrhenius slowing. Near T_A the interface broadens and the sharp interface approximation breaks down. A gradient expansion of the free energy as a function of α yields a surface energy vanishing near T_A. The universal value of σ_0 is only approximate. For a given substance, the remaining temperature dependence of σ from the broadening of the interface implies that the apparent fragility of liquids measured at high temperature should be larger than that measured at low temperature, as noted by Angell in his detailed survey of viscosity data (29). Similarly we note that σ depends on the density and therefore the pressure. Thus although a kinetic glass transition defined by a specific numerical barrier height or fiducial relaxation time will be largely a function of the configurational entropy density there will be another explicit but weak thermodynamic dependence on pressure too. Consistent with Nieuwenhuizen's recent analysis of the dynamic effects on glass transitions caused by pressure and temperature change (30), this could explain the mild deviation of the Prigogine–deFay ratio from 1.

While the simple density functional calculation explains qualitatively the fragility/heat capacity density correlation, viscosity data are more consistent with an s_c^{-1} scaling for the free energy of activation [like that suggested by Adam and Gibbs (25)] rather than the s_c^{-2} behavior predicted from the simple density functional theory. The scaling theory of the entropic droplet formulation already accounts for this observation (5). The modification comes from the complexity of the interface between aperiodic crystalline minima (5). Correct scaling near T_K is restored by the wetting of droplets corresponding with one particular density wave, by a surface coating corresponding to a different aperiodic arrangement. This acts to lower the surface energy much like what happens in the random field Ising model (31). Wetting for a random system gives a surface tension that depends on the radius of the drop. This r dependent surface tension yields s_c^{-1} scaling when the thermodynamic critical exponents for the random first order transition are used. We now reprise this argument based on a similar one for the random field Ising magnet (31) in Fig. 1B.

The wetting argument leads to a differential renormalization group equation for $\sigma(r)$,

$$\sigma^{1/3}d\sigma = -(4^{-1/3} - 4^{-4/3})\left(T\sqrt{k_B\Delta\tilde{c}_p}\right)^{4/3}r^{-5/3}dr, \quad [4]$$

where $\Delta\tilde{c}_p$ is the heat capacity jump per unit volume. This renormalization group equation is integrated outward from r_0 where the short range value is set by the naive density functional theory without wetting discussed earlier, σ_0. Between T_K and T_A, $\sigma(r)$ vanishes at large distance and is only finite below T_K. By using this boundary condition, the solution of the renormalization equation for $\sigma(r)$ at T_K is then

$$\sigma(r) = \sigma_0\left(\frac{r_0}{r}\right)^{1/2}. \quad [5]$$

When this is substituted into the expression for $F(r)$, one finds that the maximum gives a barrier, $\Delta F^{\ddagger}$ which now varies inversely to the first power of the configurational entropy density: i.e., the Vogel–Fulcher scaling. We find a simple expression for the activation barrier:

$$\Delta F^{\ddagger} = \frac{3\pi\sigma_0^2r_0}{Ts_c} = \frac{3\pi\sigma_0^2r_0}{T\Delta\tilde{c}_p}\frac{T_K}{T - T_K} = k_BTD\frac{T_K}{T - T_K}. \quad [6]$$

The coefficient D in this expression has been called the liquid's fragility, which has the expression

$$D = \frac{27}{16}\pi\frac{nk_B}{\Delta\tilde{c}_p}\ln^2\frac{\alpha_L r_0^2}{\pi e}. \quad [7]$$

Based on the Lindemann ratio universality, the root mean square displacement, $\alpha_L^{-1/2}$ is taken as $0.1r_0$, the hard sphere value, so that D can be expressed in terms of the heat capacity jump per mole, Δc_p,

$$D = 32R/\Delta c_p, \quad [8]$$

where $R = 8.31$ J mole^{-1} K^{-1}. The value of D depends on the heat capacity jump per mole, which varies greatly from substance to substance and is far from being universal. In Fig. 2 we plot the D predicted from this theory versus the inverse of the configurational heat capacity for several glass forming liquids. The straight line is given by Eq. 8. Superimposed on the plot are the experimental values of the D. The agreement is excellent. We see that the magnitude of the activation barriers for rearrangement of the viscous liquid depends on the difference in temperature from T_K, on universal microscopic parameters connected with the Lindemann ratio and on the excess heat capacity connected with configurational excitations.

A hallmark of the random first order transition theory of glass dynamics is the dynamic heterogeneity required to explain the growing barriers upon cooling. After combining Eqs. 3 and 5 with our expression of σ_0, a little algebra shows the
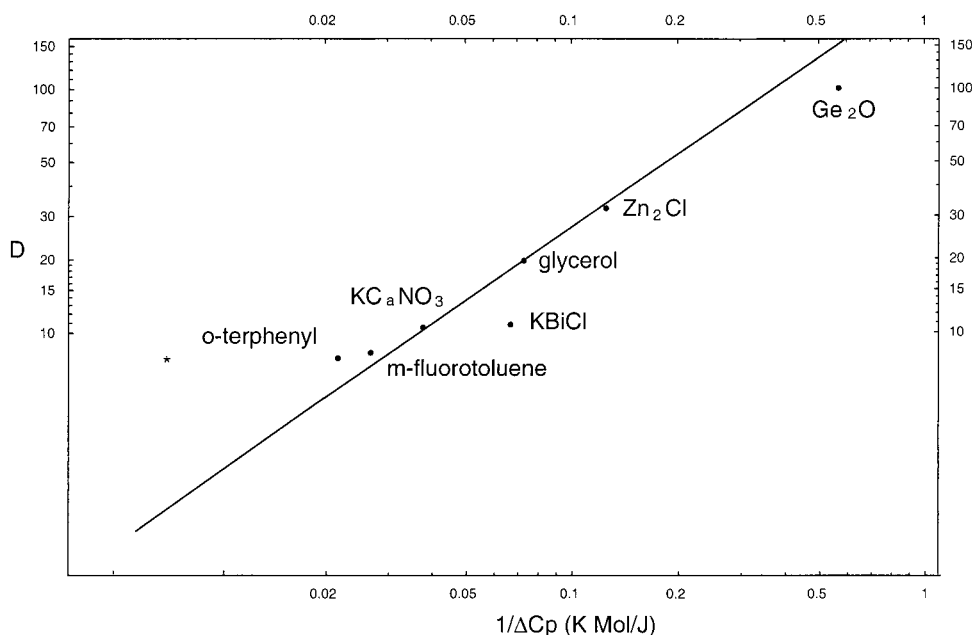
Fig. 2. The fragility parameter D as a function of the inverse heat capacity jump per mole. The glass formers chosen are those shown in Angell's review article (35). The solid line in the graph is calculated with random first order transition model (Eqs. **7** and **8**) based on the universality of the Lindemann ratio and the points are from experiments. Data for fragility parameter D are found in refs. 35–37 and references therein; for specific heat jump, see refs. 38–40. The heat capacity jump is given as per mole "beads" (38, 41) or "mobile units" (42). Generally speaking, "beads" are "rearrangeble elements in a relaxing liquid" (38). We have used the bead count of previous workers (41). The number of beads for GeO$_2$ and ZnCl$_2$ is 3 (38), 6 for glycerol (38), 10 for KCl·2BiCl$_3$ (40), 12 for 3KNO$_3$·2Ca(NO$_3$)$_2$ (39), 2 for m-fluorotoluene (41, 43), and 3 for o-terphenyl (43). The "bead" count is a crude way of accounting for internal flexibility of the molecules (because the free energy functional is essentially that for a monatomic fluid). To illustrate the robustness of the correlation we indicate also the values of o-terphenyl as shown by a star (∗) if its internal flexibility is ignored and it is assigned a bead count of one.

characteristic size of a rearranging region is

$$\frac{\xi}{r_0} = 2 \left(\frac{2}{3\pi \ln(\alpha_L r_0^2/\pi e)} \right)^{2/3} \left(\frac{DT_K}{T - T_K} \right)^{2/3}.$$

This can be expressed as a universal function of the relaxation time

$$\frac{\xi}{r_0} = 2 \left(\frac{2}{3\pi \ln(\alpha_L r_0^2/\pi e)} \right)^{2/3} \left(\ln \frac{\tau}{\tau_0} \right)^{2/3},$$

because

$$\tau = \tau_0 \exp\left(\frac{DT_k}{T - T_k} \right)$$

according to the Vogel–Fulcher law. This is plotted in Fig. 3.

The kinetic laboratory glass transition occurs when molecular slowing gives relaxations in the hours range, i.e., $\frac{\tau}{\tau_0} = 10^{17}$. Thus at T$_g$, $(\frac{\xi}{r_0}) \approx 4.5$, a rather modest size. We also note the universality of σ_0 suggests that s_c is nearly the same for all substances at the laboratory glass transition. Roughly 90 molecules are involved in a rearranging unit according to the random first order transition theory at the conventionally defined glass transition temperature. The rearranging unit according to the Adam–Gibbs argument is a region just capable of having two states; therefore, $(\frac{\xi_{AG}}{r_0}) = (\frac{R\ln 2}{s_c})^{1/3}$. ξ_{AG} grows slowly as T$_K$ is approached in contrast to the random first order

transition theory. The Adam–Gibbs argument gives rearranging units with at most 10 molecules near T$_g$ for the most fragile substances. It is clearly very ambiguous to have such small "cooperative" units. Recent observations of structural heterogeneities are inconsistent with units of the small size predicted by Adam–Gibbs but are in harmony with the estimates of the random first order transition entropic droplet picture (32). A single size does not characterize the viscous liquid completely.
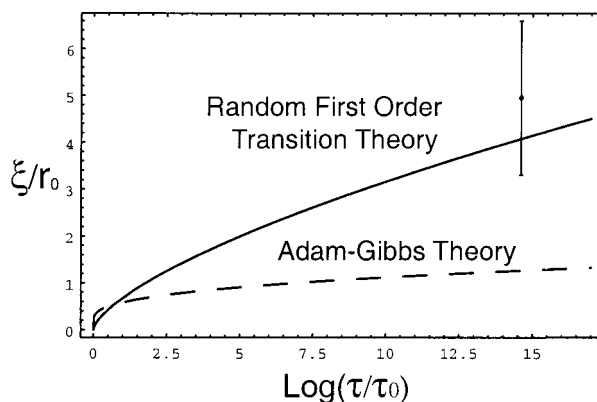

Fig. 3. The correlation length ξ (in the unit of lattice spacing r_0) is shown as a function of relaxation time. The solid line is that predicted by random first order transition theory, and the dashed line is the result of Adam–Gibbs theory (25) assuming $\Delta c_p = 51.8$ J mole^{-1} K^{-1}, the value for PVAC (polyvinyl acetate) (25). The Adam–Gibbs result weakly depends on fragility. The point (and its error bar) gives the only "direct" measurement by Spiess et al. on PVAC (32). Results of many "indirect" measurements on different glass formers around the glass transition temperature also fall in the range of the Spiess experiment (32).

The random first order transition entropic droplet picture actually leads to a "mosaic" structure of the supercooled liquid (33) with cooperative regions only somewhat larger than the critical droplet size ξ. These regions fluctuate in size and therefore have different flipping rates because of the configurational entropy fluctuations whose magnitude depends on the configurational heat capacity density jump $\Delta \tilde{c}_p$ and the volume of the rearranging region, $\Delta S_c = \sqrt{k_B \Delta \tilde{c}_p \xi^3}$. At T_g both strong and fragile liquids have roughly the same size scale for their mosaic structures, i.e., ξ/r_0 is nearly universal at the laboratory glass temperature. It follows that the range of activation barriers is smaller for strong than for fragile liquids because of their smaller $\Delta \tilde{c}_p$. This is in accord with the observed correlation between growing non-exponentiality of relaxation with growing fragility (34).

We conclude that the wide variety of kinetic behavior seen in liquids reflects quantitative rather than qualitative differences in their energy landscape. Furthermore, the random first order transition approach coupled with microscopic considerations about the stability of aperiodic structures can account semi–quantitatively for these differences.

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