

Relaxation and flow mechanisms in "fragile" glass-forming liquids

Frank H. Stillinger

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 12 July 1988; accepted 11 August 1988)

Fragile glass-forming liquids are characterized by strongly non-Arrhenius temperature dependence of shear viscosity, and by unusually high heat capacity in the supercooled liquid above the glass transition. Using the inherent structure formalism, a theoretical model is developed to explain these characteristics. The vitrifying liquid is viewed as a dynamic patchwork of relatively strongly bonded (but amorphous) molecular domains that are separated by irregular walls of weakened bonds. Mean domain diameter ξ rises as temperature declines to minimize wall free energy, but the process is self-limiting due to intradomain frustration energy. Shear flow occurs by a "tear and repair" mechanism involving elemental wall areas of mean size ξ^2 . The relation of the present model to the tiling models for glass formation is explored, and helps to establish the presence of anomalous heat capacity in the supercooled liquid. The analysis suggests in strongly supercooled fragile liquids that the Stokes-Einstein formula may underestimate self-diffusion constants, and that the Adam-Gibbs relation for mean relaxation time in terms of calorimetric entropy may display systematic errors.

I. INTRODUCTION

Thermodynamic and relaxational properties of glass-forming substances offer phenomena in bewildering variety. These phenomena fail to support the idea of an underlying "universality" for molecular glass transitions analogous to that which describes critical phenomena.¹ Instead, glass behavior in certain key respects appears to be rather material specific, and Angell's classification of glass formers along a scale between "strong" and "fragile" extremes^{2,3} is both useful and illustrative of the nonuniversality. As a consequence of this situation, theory is challenged to produce explanations that are both comprehensive in applicability and cognizant of the specific molecular details which distinguish various classes of glass formers. The present paper is intended as a small step in that direction.

In large measure the following analysis is directed at the shear viscosity $\eta(T)$ for glass-forming liquids near Angell's fragile extreme. Notable examples of this class are *o*-terphenyl, propylene carbonate, and the molten salt mixture $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$. As Fig. 1 illustrates, their defining characteristic is a vividly non-Arrhenius behavior for $\eta(T)$. By contrast, glass formers such as SiO_2 at the strong extreme exhibit nearly perfect Arrhenius behavior over the accessible liquid range.

A concomitant characteristic of fragile liquids is the tendency for their heat capacity substantially to exceed that of the corresponding crystal phase, with a discrepancy that magnifies with increasing extent of undercooling. This is indicated schematically in Fig. 2(a). Kauzmann pointed out many years ago⁴ that such a calorimetric scenario seemed logically to produce a paradox. Entropy curves resulting from such heat capacities (and the measured latent heat of melting at the thermodynamic melting point T_m) appeared headed for an intersection at $T_K > 0$, as shown in Fig. 2(b). Only intercession of dynamical arrest at the glass transition temperature T_g , always slightly in excess of T_K , seemed to prevent direct observation of this encounter. The Kauzmann

paradox consisted in the presumption, first, that dynamical arrest in principle could be defeated either by sufficiently slow cooling or by some catalytic agent to speed rate of equilibration, and second, that the result would be creation of a manifestly disordered ideal glass with (as the crystal at T_K) a substantially vanishing configurational entropy. Interest in this possibility was amplified some years after Kauzmann's publication when Gibbs and DiMarzio produced a statistical mechanical theory of polymer melts^{5,6} with an ideal glass transition of second order just as illustrated by Fig. 2(b).

Viscosities measured for glass formers have often been fitted to an expression of the Vogel-Tammann-Fulcher (VTF) form⁷⁻⁹:

$$\eta(T) \cong \eta_0 \exp[A/(T - T_0)],$$
$$\eta_0, A > 0,$$
$$T_0 \geq 0. \quad (1.1)$$

The strong-liquid limit corresponds to vanishing T_0 . The positive T_0 values required to fit the non-Arrhenius behavior of fragile liquids usually correspond closely to the apparent calorimetric Kauzmann temperature T_K , suggesting perhaps that if an amorphous ideal glass state were to exist its shear viscosity would be infinite.

Careful examination of $\eta(T)$ data for the very fragile glass formers seems to show systematic deviations from VTF behavior as T_g is approached. Instead of continuing to rise without bound, the Arrhenius plot slopes appear to have reached a constant value. The corresponding activation energies are large, in some instances at least five times the vaporization energy.¹⁰ This strongly implies that whatever might be the mechanism for viscous flow near T_g it probably involves concerted motion of a large number of molecules. In this connection we might recall Donth's estimates¹¹ that 10^2 to 10^3 molecules cooperate in flow and relaxation processes near T_g .

A basic analytical tool employed in the following is the

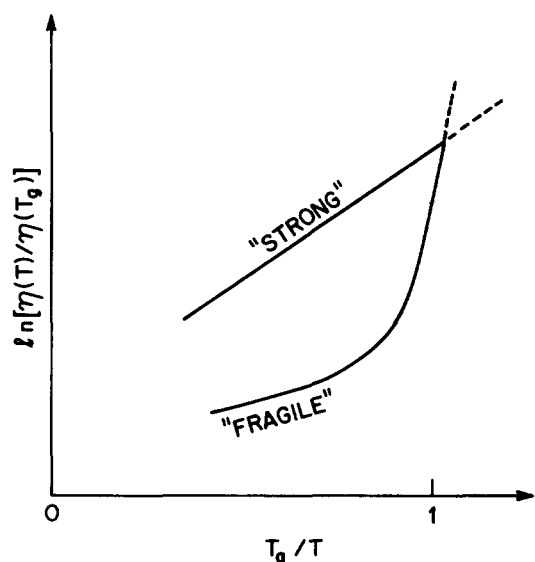
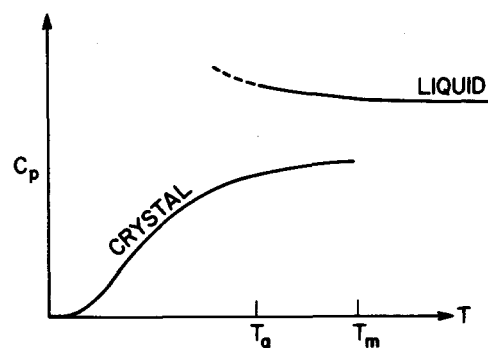
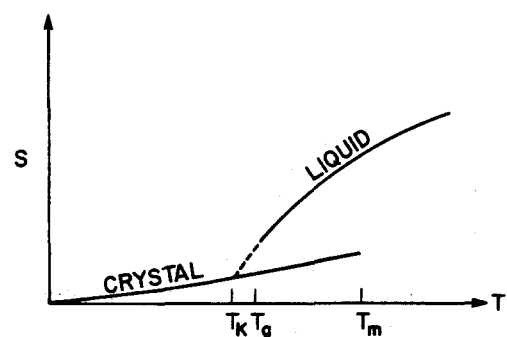


FIG. 1. Contrasting behaviors of shear viscosity η for strong and for fragile glass-forming liquids. These Arrhenius plots have been normalized by the respective glass transition temperatures T_g (suitably defined).

“inherent structure” formalism, a multidimensional basin description of the multiparticle potential energy function Φ . This tool was first developed to study the inherent structure in liquids,¹²⁻¹⁴ and has been used to identify two-level sys-



(a) FRAGILE GLASS-FORMER HEAT CAPACITY



(b) ENTROPY CURVES FOR (a) ABOVE

FIG. 2. (a) Heat capacities (C_p) for liquid and crystal phases of the fragile glass formers; (b) corresponding entropy curves with an extrapolated apparent intersection at the Kauzmann temperature T_K .

tems in amorphous solids,^{15,16} and to extend the Lindemann melting criterion to include a complementary freezing criterion.¹⁷ Section II provides a comprehensive description of this basin formalism. Section III reviews the fundamental statistical mechanical expressions for $\eta(T)$, and interprets them in terms of the dynamics of interbasin transitions.

Section IV proposes a mechanism for flow and relaxation in fragile liquids near T_g , the “tear and repair” mechanism. This picture involves identification of a fluctuating pattern of well-bonded amorphous domains separated by walls of weakened bonds. Relaxation and flow processes then are associated with “domain tectonics” in microscopic analogy to geologic processes. The mean linear dimension $\xi(T)$ of the well-bonded domains is an important parameter for describing temperature variation of viscosity and relaxation, and so Sec. V is devoted to identifying what determines this characteristic length.

The domain view of fragile liquids near T_g has been previously advocated in simplified form in study of the family of “tiling models.”¹⁸⁻²⁰ The relationship to the present work is explored in Sec. VI. Tiling models utilize a rigid background lattice with unit spacing and for that reason have no capacity to represent hydrodynamic flow. Nevertheless their thermal relaxation properties resemble those seen in real glass formers, including nonexponential relaxation functions, nonlinear relaxations that are asymmetric in the sign of temperature jumps, and hysteresis effects. At least in their simple versions the tiling models possess ideal glass transitions of *first* order with a substantial latent heat. In fact it has been demonstrated that ideal glass transitions cannot exist for substances with bounded molecular weight and reasonable interactions between the constituent particles.²¹ The material in Sec. VI includes a simple but significant generalization of the tiling models which frustrates their tendency to exhibit ideal glass transitions, yielding instead a temperature range of enhanced heat capacity. By analogy we expect the present domain theory for fragile glass formers also to produce an enhanced heat capacity, as indeed experiment demonstrates to be the case for real substances [Fig. 2(a)].

Some implications of the present theory are explored in the final Sec. VII. These include the status of the Stokes-Einstein and Adam-Gibbs relations, the bifurcation of “ α ” and “ β ” relaxations, and the spatial distribution of two-level systems in the low-temperature glass.

II. POTENTIAL ENERGY HYPERSURFACE

The potential energy function governing interactions in the glass-forming system will be denoted by $\Phi(\mathbf{R})$. Configuration variables are comprised in the vector \mathbf{R} , and will include three Cartesian coordinates for each of the N atoms present. If constant volume (V) conditions apply only these $3N$ components of \mathbf{R} are required. However, if the experimentally more conventional constant pressure (p) conditions apply, a $(3N + 1)$ st component must be appended to \mathbf{R} to specify the fluctuating volume; this can simply be the position x_0 of a spring-loaded piston that transmits hydrostatic pressure to the material system of interest, and Φ will then

include a term $pV(x_0)$ in addition to the usual molecular interactions.

With the possible exception of atomic overlap configurations that might cause divergence to $+\infty$, $\Phi(\mathbf{R})$ will be bounded and differentiable in all \mathbf{R} components. Furthermore, this function will possess some number Ω of local minima, each of which represents a mechanically stable arrangement of the N atoms. In the large system limit it is easy to establish that Ω has the following asymptotic form¹²:

$$\begin{aligned} \ln \Omega &\sim \nu N + \sum_i \ln(N_i!), \\ \nu &> 0, \\ \sum_i N_i &= N, \end{aligned} \quad (2.1)$$

where the N_i are the numbers of atoms of each of the distinct species present. The factorials in Eq. (2.1) have a trivial permutational origin, while the νN enumerates the fundamentally distinct Φ minima. The quantity ν depends on atomic composition of the system, as well as V (or p), and normally is $O(1)$.

The existence of discrete Φ minima leads to a natural subdivision of the $3N$ (or $3N + 1$)-dimensional configuration space into "basins," one surrounding each minimum configuration \mathbf{R}_α ($\alpha = 1 \cdots \Omega$). Each basin B_α is defined to be the set of configurations \mathbf{R} which are connected to \mathbf{R}_α by a solution of the mass-weighted gradient descent equation¹⁶:

$$\mathbf{m} \frac{d\mathbf{R}(u)}{du} = -\nabla\Phi[\mathbf{R}(u)] \quad (u \geq 0). \quad (2.2)$$

Here \mathbf{m} is the vector comprising atomic masses, with the first three components equal to the mass of atom 1, etc. In the event that constant pressure is involved, the $(3N + 1)$ st component of \mathbf{m} would be a macroscopic mass M_0 for the piston motion. The union of all basins exhausts the multidimensional configuration space available to the system.

Basins can be classified by depth. On a per-atom basis the corresponding order parameter is

$$\phi = \Phi(\mathbf{R}_\alpha)/N. \quad (2.3)$$

The enormous number Ω of minima and basins for macroscopic systems legitimizes introducing a continuous distribution, and in view of Eq. (2.1) the number of basins with ϕ values in the range $\phi \pm \frac{1}{2}d\phi$ can be written¹²

$$\begin{aligned} \exp[\sigma(\phi)N] d\phi, \\ \sigma(\phi) \geq 0. \end{aligned} \quad (2.4)$$

Intrabasin vibrational partition functions can next be defined in an obvious way. For the specific basin B_α the corresponding constant- V classical canonical partition function is

$$\begin{aligned} Z_\alpha(\beta) &= \left(\prod_i \lambda_i^{-3N_i} \right) \int_{B_\alpha} \exp[-\beta\Delta_\alpha(\mathbf{R})] d\mathbf{R}, \\ \Delta_\alpha(\mathbf{R}) &= \Phi(\mathbf{R}) - \Phi(\mathbf{R}_\alpha), \end{aligned} \quad (2.5)$$

where the λ_i are mean thermal deBroglie wavelengths. The integration in Eq. (2.5) spans the entire $3N$ -dimensional region B_α , and generally includes very anharmonic configurations far from the minimum. The constant- p version con-

tains an additional integration over piston variable x_0 , and for dimensional reasons must also be multiplied by the inverse of a piston mean deBroglie wavelength λ_0^{-1} .

It is useful to introduce a mean vibrational free energy per atom, f_v , for all basins with depth ϕ . To be precise,

$$\beta f_v(\beta, \phi) = - \lim_{\epsilon \rightarrow 0} \lim_{N \rightarrow \infty} N^{-1} \ln [\langle Z_\alpha(\beta) \rangle_{\phi \pm \epsilon}], \quad (2.6)$$

where the average $\langle \cdots \rangle_{\phi \pm \epsilon}$ covers all basins lying within the cited depth range.

Having introduced the intensive functions σ and f_v , an exact free energy expression immediately becomes available for the large system limit:

$$\beta F/N \sim \max_{(\phi)} [\beta f_v(\beta, \phi) + \beta\phi - \sigma(\phi)]. \quad (2.7)$$

This is the Helmholtz free energy for constant- V conditions, or the Gibbs free energy for constant- p conditions. The value $\phi_m(\beta)$ that maximizes the linear combination in Eq. (2.7) over ϕ identifies the depth of the basins within which the system is virtually certain to be found at the given temperature.

An equally precise quantum version of the above can be developed.²² However, there is no compelling reason to believe that the glass phenomena to which this paper is devoted are intrinsically quantum mechanical. The classical description will be used for simplicity.

As derived, free energy expression (2.7) strictly pertains to thermodynamic equilibrium states. Formation of most glasses, however, demands entering the metastable regime of liquid supercooling. Fortunately, a straightforward modification accommodates that necessity.²¹ One removes from consideration all basins whose stable packings (the structures at the minima) display significant crystalline portions. Then $\sigma(\phi)$ and $f_v(\beta, \phi)$ are evaluated just for the remaining set of amorphous basins. The resulting free energy from Eq. (2.7) is the appropriate metastable extension of the stable liquid branch, and can be used to describe properties of fully relaxed supercooled liquids, i.e., those that have substantially equilibrated over the amorphous basin subset.

Contiguous pairs of basins will have at least one transition state (simple saddle point of Φ) embedded in their shared boundary hypersurface. The standard reaction pathway connecting the pair of Φ minima through this transition state consists of two branches that emanate in either direction from that transition state, and are solutions to the descent equation (2.2) in the respective basins.^{16,23}

Computer simulations on a variety of model systems^{15,16,24} reveal that the fundamental dynamical transitions between contiguous basins (at least those transitions with modest barriers) involve rearrangement only of an $O(1)$ subset of all N atoms. That is, the basic dynamical transitions are strongly localized. This has two important consequences for the geometry of basins. The first is that such transitions will only cause a change in absolute basin depth by $O(1)$, or equivalently that ϕ will change by a small amount of $O(N^{-1})$. The second is that each basin will have in its boundary $O(N)$ transition states to neighboring basins, due to the fact that localized rearrangements are possible

anywhere within the macroscopic system. It should be appreciated that in spite of this high "mean coordination number" for basins, the transition states are quite inhomogeneously distributed in direction about each minimum: because the fundamental transitions involve localized rearrangements the directions are strongly concentrated along low-dimensional subspaces containing axes for just a few neighboring particles.

Even after projecting out the crystallite-containing basins, the span of basin depths (the difference between deepest basins and highest-lying basins) is $O(N)$. Since individual transitions only change $\Phi(\mathbf{R}_\alpha)$ by $O(1)$, a sequence of at least $O(N)$ transitions would be required to rearrange the system from the bottom of the distribution described by $\sigma(\phi)$ to the top.

Topographic details of the multidimensional Φ hypersurface obviously depend in a sensitive way on the substance involved. In the case of fragile glass formers a key question concerns whether the statistical topography of those basins identified by $\phi_m(\beta)$ changes significantly as the system is cooled to the glass transition range. The distinctly non-Arrhenius behavior illustrated in Fig. 1 could be explained this way, if reaction pathways between deep amorphous minima (those populated at low temperature) require surmounting much higher intervening barriers than is the case for the higher-lying basins populated at high temperature.²¹

Questions concerning ergodic behavior are especially pertinent for glasses and amorphous solids, not only regarding relaxation kinetics within these states, but also regarding nucleation and subsequent growth of the crystalline phase. It is important to realize that kinematically the latter is always possible at any positive temperature in a large system. The potential energy barrier that must be surmounted to create a critical nucleus is $O(1)$, whereas the available energy is proportional to $Nk_B T$. The time scale for such a possible event is the decisive feature, however, and for good glass formers may stretch well beyond any available time for observation.

Even apart from kinetic sluggishness associated with the glass state, the Φ basin description provides an instructive insight into the ergodic character of many-body systems. It is easy to compute a lower bound on the amount of time t_0 required to visit one of each of the distinct basin species, numbering $\exp(\nu N)$ according to Eq. (2.1). The line of reasoning is illustrated by Fig. 3. One imagines the optimal scenario in which (a) all basins are identical hypercubes arranged in a regular multidimensional array, and (b) the system dynamics manages to thread all hypercubes ballistically, one after the other, without any returns to previously visited hypercubes until all have been threaded. Given the number of basins and the overall configuration space content at constant volume it is easy to see (for a single component substance) that the edge length of the hypercubes must be

$$l = [(V/N)\exp(1 - \nu)]^{1/3}. \quad (2.8)$$

Furthermore, the ballistic motion of the configuration point occurs at an expected linear speed:

$$v = (3Nk_B T/m)^{1/2} \quad (2.9)$$

at temperature T . Consequently we arrive at the bound

$$t_0 \gg (l/v)\exp(\nu N). \quad (2.10)$$

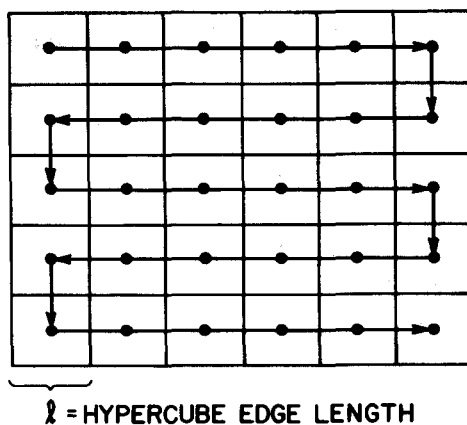


FIG. 3. Hypothetical basin-threading dynamics. The distinct basins are simplified to identical hypercubes, and a ballistic trajectory (arrows) is postulated to visit them all in turn. Potential energy minima have been symbolized as dark circles.

An approximate value of ν for liquid Ar at 1 atm is 0.2.²⁵ For 1 mol of this substance at its triple-point temperature (84 K) we obtain the following estimates:

$$\begin{aligned} l &\cong 4.4 \times 10^{-8} \text{ cm}, \\ v &\cong 1.8 \times 10^{16} \text{ cm/s}, \\ \exp(\nu N_{Av}) &\cong 10^{5 \times 10^{22}}. \end{aligned} \quad (2.11)$$

In spite of the fact that the implied residence time in each basin is extremely short,

$$l/v \cong 2.4 \times 10^{-24} \text{ s}, \quad (2.12)$$

the right-hand side of inequality (2.10) is entirely dominated by the exponential enumeration factor:

$$t_0 \gg 10^{5 \times 10^{22}} \text{ s}. \quad (2.13)$$

The implication of this result is indeed remarkable. Even under conditions where conventional standards decree that equilibrium is quickly attained (as in the liquid above T_m), the configuration space is explored extremely slowly. Evidently thermal equilibrium only requires sampling of a tiny, but representative, fraction of the basins.

Argon atoms and their interactions are too simple to permit easy formation of the vitreous state. The greater molecular complexity of good glass formers affects the foregoing estimate primarily through ν , which is expected to be significantly larger than for argon. This change simply strengthens the conclusion about representative basin sampling. Structural arrest at a glass transition evidently must result from disruption of representative sampling of the amorphous basin set.

III. MOLECULAR EXPRESSIONS FOR VISCOSITY

Linear transport coefficients quite generally can be expressed as time integrals of appropriate molecular autocorrelation functions evaluated in equilibrium ensembles.^{26,27} Application of such formulas to supercooled liquids would require restriction of the ensembles to the amorphous portion of configuration space. The previously mentioned elimi-

nation of basins for crystallite-containing packings in principle accomplishes this restriction.

The usually exhibited expression for shear viscosity η is the Green-Kubo formula²⁸

$$\eta(T) = (\rho\beta/N) \int_0^\infty dt \langle J^{xy}(0)J^{xy}(t) \rangle_{\text{eq}}, \quad (3.1)$$

where J^{xy} measures off-diagonal shear stress:

$$J^{xy} = \sum_{j=1}^N (p_{jx}p_{jy}/m_j + x_jF_{jy}). \quad (3.2)$$

Here the position, momentum, and force vectors for particle j have components x_j , p_{jx} , F_{jx} , etc. The physical content of Eq. (3.1) is quite clear. Thermal motions in the equilibrium ensemble quite naturally produce spatially varying patterns of shear stress. These shear stress fluctuations regress toward their mean (zero) at a rate proportional to η . In a normal liquid above its melting point stress decay is very rapid, but in a very viscous supercooled liquid approaching its glass transition the shear stress patterns persist for very long times. The autocorrelation time integral (3.1) represents that persistence.

A viscosity formula complementary to that in Eq. (3.1) can also be displayed, involving a time integral of a shear current autocorrelation function in the (restricted) equilibrium ensemble:

$$1/\eta(T) = \lim_{k \rightarrow 0} (2\beta k^2/N\rho) \int_0^\infty dt \langle J_{xy}(0)J_{xy}(t) \rangle_{\text{eq}}, \quad (3.3)$$

where now

$$J_{xy} = \sum_{j=1}^N \sin(ky_j)(p_{jx}/m_j). \quad (3.4)$$

Transverse currents produced by thermal fluctuations obviously will persist longer in low-viscosity media than in high-viscosity media.

The existence of complementary pairs of autocorrelation function time integrals for transport coefficients (and their inverse) is apparently quite general. At equilibrium the thermally driven molecular motions cause both thermodynamic fields and their conjugate flows to fluctuate, and each member of a complementary pair keys on just one of these attributes.

Regardless of whether Eq. (3.1) or Eq. (3.3) is employed, a positive finite $\eta(T)$ can only result from molecular motions that execute an unending and multidimensionally untrapped sequence of interbasin transitions. Indeed there have been some prior analyses of η from this general point of view,²⁹⁻³¹ though not specifically directed toward the peculiar behavior of fragile liquids near their glass transitions.

IV. TEAR AND REPAIR MECHANISM

Fragile glass formers have many geometric options in formation of low-potential-energy amorphous packings. This diversity arises from molecular asymmetry and flexibility (as in the case of *o*-terphenyl) and from feasible rearrangements of distinct particles [a possibility in $\text{K}_{0.6}\text{Ca}_{0.4}(\text{NO}_3)_{1.4}$]. The most stable packings for any substance correspond to periodic crystalline arrays, but these

have been eliminated from consideration as explained above. In the following we shall be concerned primarily with the structure and interconvertibility of the low-potential-energy amorphous packings that are expected to dominate the properties of supercooled liquids near and below T_g .

Thermal motions in strongly supercooled liquids will spontaneously rearrange molecules into relatively well-bonded arrangements, for the most part. On account of the many structural options, local particle groupings can be expected to fit together in near-optimal fashion in a variety of ways, adopting bonding lengths and angles between neighbors that produce the most advantageous cohesion. However, the geometric demands of optimal bonding in one microscopic region may be at odds with similar demands in a neighboring region, leading to a weakly bonded surface (wall) between them. The entire material sample then would consist of an irregular patchwork of well-bonded amorphous domains separated by domain walls across which the bonding is suboptimal.

Above T_g the supercooled liquid undergoes continual packing rearrangement, so the pattern of well-bonded domains will be dynamic, not static. Structural relaxation will be associated primarily with change in domain pattern. Such change can arise from motions of molecules at and across the weak walls, from elastic deformations of domains, and from creation and annihilation of domain walls ("cracks" in the otherwise well-bonded amorphous medium). The mean spatial extent of a domain is expected to vary with temperature at and above T_g , and will be denoted by $\xi(T)$ in the following.

If a shear stress is applied to the liquid the fluctuating domain pattern would preferentially respond in a way that creates shear flow. The predominant process permitting shear flow must be slippage across domain walls. This is illustrated schematically in Fig. 4. Steady state flow obviously requires a sequence of such slippage events, and that will be enhanced by spontaneous creation of new walls at appropriate positions and times.

The basic events in the domain tectonics just described entail free energy (likewise energy and entropy) changes proportional to domain wall area, namely $\xi^2(T)$ in order of magnitude. This is true whether slippage across a preexisting

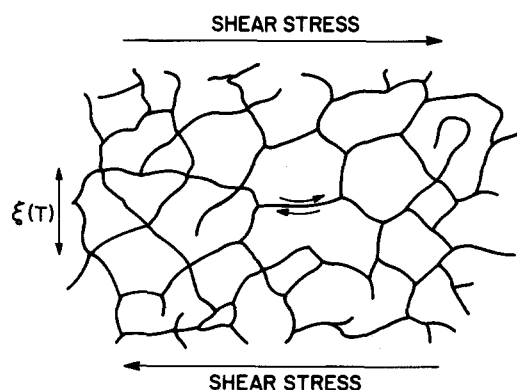


FIG. 4. Domain wall slippage (antiparallel arrows at center) induced in the fluctuating domain pattern by applied shear stress.

wall is involved, or whether a new element of wall area must be created by fracturing a domain. Typical sequences of multidimensional Φ basins that would have to be traversed schematically should produce a Φ profile that appears as shown in Fig. 5. On the rising portion of the contour the bonds across the affected area element are weakening or breaking ("tearing"), while on the descending portion they are reforming ("repairing").

Exactly the same tear and repair processes occur in the absence of external stress, as a result of thermal fluctuations. These processes are involved in production and in eventual regression of internal stresses and flows. The equilibrium autocorrelation function expressions (3.1) and (3.3) for $\eta(T)$ emerge as a result of the presence of these fluctuations.

V. MEAN DOMAIN SIZE

The considerations of Sec. IV indicate that the activation energy for viscous flow should be proportional to $\xi^2(T)$, since this measures the mean height of those composite barriers (Fig. 5) over which the system configuration point must move. Consequently the shear viscosity would have approximately the form

$$\eta(T) \cong \eta_1 \exp[B\xi^2(T)/k_B T], \quad (5.1)$$

where η_1 and B are positive constants. The strongly non-Arrhenius behavior of $\eta(T)$ for fragile liquids which the VTF equation (1.1) is designed to fit thus arises from the temperature dependence of $\xi(T)$. The next step in the analysis is identification of those features which determine $\xi(T)$.

It is clear that the presence of wall interface between well-bonded domains on average will cost some potential energy per unit area, say λ . Such an interface also should be able to adopt a variety of shapes that are rough at the length scale of individual molecules, and therefore possesses an entropy per unit area $\sigma_0(T)$. The wall free energy per unit area then is

$$\gamma(T) = \lambda - k_B T \sigma_0(T) > 0. \quad (5.2)$$

If this were the only important feature, reduction in temperature (provided equilibration remained possible) would

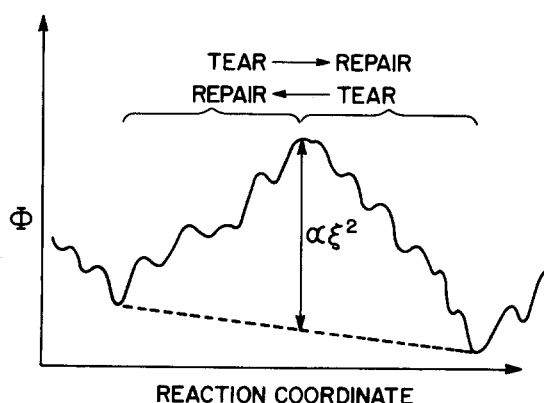


FIG. 5. Typical potential energy contour through the basin sequence involved in a basic tear and repair event that leads to shear stress relaxation. As indicated, the net barrier height will be proportional to mean area of domain walls, i.e., proportional to $\xi^2(T)$.

produce continual expulsion of the domain walls that are costly in free energy. The result would be that $\xi(T)$ grows without bound as temperature declines, and through Eq. (5.1) the activation energy for viscous flow would also grow without bound.

It is an experimental fact that activation energies for fragile liquid viscosities appear to be limited, though indeed they become quite large.¹⁰ Evidently another feature is present to prevent domains from growing to infinite size. Since particles composing any domain are packed together in an irregular amorphous manner, the concept of geometric frustration seems inevitably to be germane. A particle-by-particle construction of a compact amorphous domain should at first proceed with several options available for each particle placement. But as this process continues fewer and fewer options should present themselves for adding the next particle in a strongly bonded arrangement, considering the positions of already placed particles. Eventually, the only bonds possible are weak ones, and this heralds the presence of a wall around the domain.

An analogous situation has been studied in connection with supercooled noble-gas liquids, where small stable clusters have icosahedral form.³² It has been pointed out³³ that outward growth of such icosahedral clusters leads to a self-limiting geometric frustration in three-dimensional space; addition of successive shells of particles around an interior seed cluster generates intrinsic strain which counteracts the prior stability.

While the particles comprising a fragile glass former need not display icosahedrally packed domains (due to molecular asymmetry, flexibility, etc.), the general concept of geometric frustration in the relevant amorphous domains is still applicable. A corresponding positive frustration energy should therefore be included in the present analysis.

If V denotes the system volume, then the expected number of domains is $V\xi^{-3}$, suppressing unimportant factors of order unity. Similarly the total domain wall area is essentially $V\xi^{-1}$. For each typical domain of linear dimension ξ it will be supposed that the internal frustration energy varies as $\theta\xi^p$, where multiplier θ and exponent p are both positive. Consequently, the potential energy in a typical packing for which the mean domain size is ξ will be given by the expression

$$\Phi \cong \Phi^{(0)} + V(\lambda\xi^{-1} + \theta\xi^{p-3}). \quad (5.3)$$

Here $\Phi^{(0)}$ is the hypothetical (but unattainable) potential energy of an amorphous single-domain packing that spans the entire system but is immune to frustration. The frustration energy, the last term in Eq. (5.3), will impose a limit on domain size if its exponent is positive, i.e.,

$$p > 3. \quad (5.4)$$

Then the minimum value with respect to ξ for Eq. (5.3) is achieved for

$$\xi(0) = [\lambda/\theta(p-3)]^{1/(p-2)}, \quad (5.5)$$

corresponding to a lowest amorphous structure potential energy:

$$\Phi_{\min} \cong \Phi^{(0)} + V\lambda \left(\frac{p-2}{p-3}\right) \left[\frac{\theta(p-3)}{\lambda}\right]^{1/(p-2)}. \quad (5.6)$$

Unfortunately there is no *a priori* way to determine the key parameters λ , θ , and p in this expression; at least the first two are expected to be substance specific.

If the viewpoint advocated has merit, one would expect that low-potential structural excitations should exist out of the minimum- Φ structure(s) represented by Eq. (5.6). In particular it should be possible to displace small sets of particles at or near the walls of weak bonds. The number of such excitation possibilities is proportional to the total wall area present, and thus to V itself. This is a situation which detailed analysis shows to be inconsistent with the existence of a second order ideal glass transition.²¹

When the temperature is positive the criterion for determining mean domain size requires minimizing the combination

$$\gamma(T)\xi^{-1} + \theta\xi^{p-3}, \quad (5.7)$$

where $\gamma(T)$ was shown in Eq. (5.2) above. Consequently we find the following generalization of Eq. (5.5):

$$\xi(T) = \left[\frac{\lambda - k_B T \sigma_0(T)}{\theta(p-3)} \right]^{1/(p-2)}, \quad (5.8)$$

and it is clear that entropy effects reduce the mean domain size below that at $T=0$. The temperature variation of $\xi(T)$, and therefore of the total amount of domain wall, produces a contribution to the configurational heat capacity in the supercooled regime, which for fragile substances is substantially larger than in the crystal phase.

Formally it would appear from Eq. (5.8) that $\xi(T)$ might vanish at a temperature for which

$$k_B T \sigma_0(T) = \lambda, \quad (5.9)$$

and indeed this might even occur below the melting point. However, it should be obvious that it becomes difficult if not impossible to identify well-bonded domains when T rises enough to reduce $\xi(T)$ to, say, two molecular diameters. Above such a temperature the domain picture simply becomes inapplicable, and an alternative description of local order and kinetic processes becomes necessary. It is tempting to speculate that this "crossover" should be identified with the point at which the mode-coupling theory³⁴⁻³⁶ and its algebraically singular viscosity expression that fits high temperature measurements well,³⁷

$$\eta(T) \cong \eta_2(T - T_0)^{-\zeta}, \quad (5.10)$$

begins to apply.

VI. RELATION TO TILING MODELS

The description of glasses in terms of well-bonded amorphous domains has been explored previously in simplified form with the so-called tiling models.¹⁸⁻²⁰ These models postulate a D -dimensional lattice with unit spacing, and suppose that it is covered without gaps (tiled) by D -dimensional cubes with integer side lengths. The states permitted by the model are all possible distinguishable tilings of this kind. The potential energy for any configuration is taken to be proportional to the total boundary "area" shared by contiguous tiles:

$$\Phi_t = D\lambda \sum_{j=1}^{\infty} j^{D-1} n_j. \quad (6.1)$$

Here λ represents (as in the preceding) an energy cost per unit area. The numbers of tiles of linear dimension $j = 1, 2, 3, \dots$ have been denoted by n_j . Two distinct kinds of transitions between tiling configurations have been considered^{19,20} which in principle permit ergodic behavior, but which in practice lead to kinetic arrest and glass-transition behavior as temperature declines.

It should be noted in passing that expression (6.1) could be augmented with a term that induces nucleation and crystallization behavior, if study of those phenomena were of interest.¹⁸

It is known that the tiling models possess a *first* order "ideal glass transition" at a positive temperature T_c , provided $D \geq 2$. This is a point at which the high-temperature pattern of relatively small tiles becomes unstable with respect to replacement of a single system-spanning tile. In the two-dimensional version this transition occurs at

$$k_B T_c \cong 3.73 \lambda \quad (D=2), \quad (6.2)$$

and the resulting drop (to zero) of the potential energy per unit area in the system is

$$\Delta\Phi_t/N \cong 0.988 \lambda, \quad (6.3)$$

where N is the number of lattice sites in the system.¹⁹

It has been argued that ideal glass transitions are not to be expected, even in principle, in systems composed only of finite-molecular-weight substances.²¹ In the light of Sec. V it is desirable to inhibit the phase transition in the tiling models by including in the potential a domain frustration energy:

$$\Phi_t = D \sum_{j=1}^{\infty} (\lambda j^{D-1} + \theta j^p) n_j, \quad (6.4)$$

$$\theta > 0, \quad p > D.$$

When θ is very small this will cause little change in the tiling model properties for $T > T_c$. However, below T_c the coarsening of the tile texture would proceed only to sizes of order:

$$\langle j \rangle \cong [\lambda / \theta(p-D)]^{1/(\rho-D+1)}. \quad (6.5)$$

The latent heat of transition that exists when $\theta = 0$ becomes spread over a narrow temperature range near T_c , thereby creating a significant heat capacity rise in the amorphous state. This is the tiling-model version of the enhanced heat capacity in supercooled fragile liquids identified in Sec. V.

VII. DISCUSSION

The Stokes-Einstein formula³⁸ relates the diffusion constant D and hydrodynamic radius a for a particle undergoing Brownian motion in a fluid medium, to the shear viscosity η and temperature T of that medium:

$$D = k_B T / C \eta a. \quad (7.1)$$

The numerical constant C depends on hydrodynamic boundary conditions at the surface of the Brownian particle:

$$C = 6\pi \quad (\text{stick})$$

$$= 4\pi \quad (\text{slip}). \quad (7.2)$$

In particular the Stokes-Einstein formula can be applied to self-diffusion in pure fluids with surprisingly good results,³⁹

considering the continuum approximation on which it is based.

There may be good reason to question the validity of the Stokes–Einstein formula for strongly supercooled fragile liquids. If the characteristic length ξ substantially exceeds radius a , the continuum hydrodynamic flow model must be inappropriate. Shear flow would be retarded by the log-jam effect of large well-bonded domains, while self-diffusion might still proceed at a less inhibited rate due to molecular motions within the weakly bonded walls. A reasonable inference is that Eq. (7.1), using the hydrodynamic radius obtained at high temperature, should underestimate the self-diffusion constant D for a fragile glass former near T_g . Admittedly it will be difficult to measure accurately the small D values expected near T_g , but the insights that could result should provide strong impetus to surmounting experimental problems.

Dielectric, ultrasonic, and light scattering measurements on many molecular glass formers often reveal a separation of relaxation times into two groups as temperature declines toward T_g .⁴⁰ These are, respectively, designated as primary (or “ α ”) relaxations, and secondary (or “ β ”) relaxations for the slower and the faster groups. The present picture of domains and weakly bonded walls offers an explanation at least in part.⁴¹ Molecules at or near the domain walls should remain relatively mobile even at T_g , and their contribution to relaxation should be concentrated mostly in the β portion of the spectrum. In contrast, the slower appearance and disappearance processes for domains and domain walls should be concentrated in the α portion of the spectrum. Clearly the latter should exhibit the greater sensitivity to temperature change. It would be informative to see whether the viscosity crossover from algebraic form (5.10) to VTF form (1.1), which we have tentatively associated with appearance of identifiable domains, occurs near the temperature of relaxation spectrum bifurcation.

Adam and Gibbs have proposed a relationship between mean relaxation time $\langle\tau\rangle$ in a glass-forming substance, and its configurational entropy S_c :

$$\langle\tau\rangle \cong \tau_0 \exp[K/TS_c(T)]. \quad (7.3)$$

Here τ_0 is an appropriate molecular-scale time, and $K > 0$. The literature contains several tests of Eq. (7.3), claiming that it successfully accounts for the behavior of at least some substances⁴² and models.⁴³ The presence of distinguishable primary and secondary relaxations may complicate application of the Adam–Gibbs relation, but presumably it is just the former which Eq. (7.3) is intended to describe.

The Adam–Gibbs analysis postulates activation volumes whose (essentially independent) rearrangements control relaxation. Each such elementary volume is capable of adopting a fixed number of alternative configurations, and the free energy of activation for rearrangement is proportional to the size of the elementary volume.

The present view of flow in cold fragile liquids differs from that of Adam and Gibbs primarily in that the rearranging unit is an elementary wall *area*, rather than a compact *volume*. If the intradomain frustration effect discussed in Sec. V is sufficiently weak to allow ξ to become large, this

geometrical distinction can become important. In the limit of very large ξ the dimensional change from volume to area would cause Eq. (7.3) to be replaced by

$$\langle\tau\rangle \cong \tau_0 \exp[K'/TS_c^{2/3}(T)]. \quad (7.4)$$

In deriving this alternative we have supposed that activation free energy is proportional to ξ^2 , but that each well-bonded domain of approximate size ξ^3 has a fixed number of internal configurational options.

The frustration effect will prevent the form (7.4) from ever being strictly exhibited. However, for fragile liquids it may be possible to detect quantitative errors in the conventional Adam–Gibbs formula (7.3) in the direction indicated by Eq. (7.4).

It is worth stressing that the low-barrier two-level systems, which dominate low-temperature properties of virtually all amorphous solids,^{44,45} are likely to be concentrated spatially at weakly bonded domain walls in fragile glass formers.

Finally, it should be mentioned that Hoare has extensively studied self-limiting (frustrated) amorphous clusters of simple particles and has conveniently summarized the relation of his “amorphon” results to prior speculations about the nature of the glass state.⁴⁶

¹S.-K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, MA, 1976).

²C. A. Angell, in *Relaxation in Complex Systems (Proceedings of the Workshop on Relaxation Processes, Blacksburg, VA, July 1983)*, edited by K. Ngai and G. B. Smith (National Technical Information Service, U.S. Dept. of Commerce, Washington, D.C., 1985), p. 3.

³C. A. Angell, *J. Non-Cryst. Solids* **73**, 1 (1985).

⁴W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).

⁵J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.* **28**, 373 (1958).

⁶E. A. DiMarzio and J. H. Gibbs, *J. Chem. Phys.* **28**, 807 (1958).

⁷H. Vogel, *Phys. Z.* **22**, 645 (1921).

⁸G. Tammann and G. Hesse, *Z. Anorg. Allg. Chem.* **156**, 245 (1926).

⁹G. S. Fulcher, *J. Am. Chem. Soc.* **8**, 339 (1925).

¹⁰C. A. Angell, *J. Phys. Chem. Solids* **49**, 863 (1988).

¹¹E. Donth, *J. Non-Cryst. Solids* **53**, 325 (1982).

¹²F. H. Stillinger and T. A. Weber, *Phys. Rev. A* **25**, 978 (1982).

¹³F. H. Stillinger and T. A. Weber, *J. Phys. Chem.* **87**, 2833 (1983).

¹⁴R. A. LaViolette and F. H. Stillinger, *J. Chem. Phys.* **82**, 3335 (1985).

¹⁵F. H. Stillinger and T. A. Weber, *Phys. Rev. A* **28**, 2408 (1983).

¹⁶T. A. Weber and F. H. Stillinger, *Phys. Rev. B* **32**, 5402 (1985).

¹⁷R. A. LaViolette and F. H. Stillinger, *J. Chem. Phys.* **83**, 4079 (1985).

¹⁸F. H. Stillinger and T. A. Weber, *Annals N.Y. Acad. Sci.* **484**, 1 (1986).

¹⁹T. A. Weber, G. H. Fredrickson, and F. H. Stillinger, *Phys. Rev. B* **34**, 7641 (1986).

²⁰T. A. Weber and F. H. Stillinger, *Phys. Rev. B* **36**, 7043 (1987).

²¹F. H. Stillinger, *J. Chem. Phys.* **88**, 7818 (1988).

²²F. H. Stillinger, *J. Chem. Phys.* **89**, 4180 (1988).

²³F. H. Stillinger (to be published).

²⁴F. H. Stillinger and T. A. Weber, *Phys. Rev. B* **31**, 5262 (1985); **33**, 1451(E) (1986).

²⁵T. A. Weber and F. H. Stillinger, *J. Chem. Phys.* **80**, 2742 (1984).

²⁶R. Zwanzig, *Annu. Rev. Phys. Chem.* **16**, 67 (1965).

²⁷J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, New York, 1976), Chap. 8.

²⁸M. S. Green, *J. Chem. Phys.* **22**, 398 (1954).

²⁹M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969).

³⁰R. Zwanzig, *J. Chem. Phys.* **79**, 4507 (1983).

³¹U. Mohanty, *Phys. Rev. A* **32**, 3055 (1985).

³²O. Eicht, K. Sattler, and E. Recknagel, *Phys. Rev. Lett.* **47**, 1121 (1981).

³³D. R. Nelson, *Phys. Rev. B* **28**, 5515 (1983).

³⁴T. Geszti, *J. Phys. C* **101A**, 477 (1980).

- ³⁵E. Leutheusser, *Phys. Rev. A* **29**, 2765 (1984).
- ³⁶U. Bengtzelius, W. Götze, and A. Sjölander, *J. Phys. C* **17**, 5915 (1984).
- ³⁷P. Taborek, R. N. Kleiman, and D. J. Bishop, *Phys. Rev. B* **34**, 1835 (1986).
- ³⁸Reference 27, p. 278.
- ³⁹H. J. Parkhurst and J. Jonas, *J. Chem. Phys.* **63**, 2705 (1975).
- ⁴⁰T. G. Parker, in *Polymer Science*, edited by A. D. Jenkins (North-Holland, Amsterdam, 1972), Vol. 2, pp. 1317–1326.
- ⁴¹I am indebted to Professor C. A. Angell for pointing out this connection.
- ⁴²C. A. Angell and D. L. Smith, *J. Phys. Chem.* **86**, 3845 (1982).
- ⁴³G. H. Fredrickson, *Ann. N.Y. Acad. Sci.* **484**, 185 (1986).
- ⁴⁴P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972).
- ⁴⁵*Amorphous Solids: Low-Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981).
- ⁴⁶M. Hoare, *Ann. N.Y. Acad. Sci.* **279**, 186 (1976).