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Low-temperature relaxation in glassy systems

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The stress-relaxation function $\sigma(t)$ in a stabilized glass is described by a potential-barrier model which is based on separating geometric packing considerations from thermal excitations in the dynamical evolution of a many-body system. The analysis proceeds in stages: (1) The configuration space is uniquely divided into cells, each associated with a minimum on the potential energy ϕ hypersurface. (2) "Crystal-free" particle packings are isolated. (3) Since the ϕ hypersurface in the amorphous manifold is topographically rough over a wide range of length scales, a coarse graining is carried out to suppress small-scale roughness. (4) Stress relaxation is connected with transition between cells which involve *localized* particle motions. A master equation describes the time-dependent residence probabilities in the cells. The basic physical assumption is that the slowest structural rearrangements in a dense, highly viscous supercooled fluid occur on a molecular length scale via self-diffusion. We find that $\sigma(t)=\phi_0\exp[-(t/\tau)^{\alpha}]$; for $t \ll \tau$, $\alpha=\frac{1}{3}$; for $t \sim \tau$, $\alpha=\frac{1}{2}$; for $t \gg \tau$, $\alpha=1$. The temperature dependence of τ is governed by the self-diffusion of the viscous fluid.

I. INTRODUCTION

A glass is defined as an amorphous solid which is formed by continuous solidification of a liquid. By continuous solidification one means a homogeneous process in which viscosity increases continuously with increased pressure or lowering of temperature T, from fluid to solid values. In contrast, crystallization results in a discontinuous increase in viscosity. A glass bears some resemblance to liquids and some to crystalline solids. While spatial isotropy makes glasses similar to liquids, the relaxation time of a local shear is so long that glasses behave mechanically as solids.

The recognition[1] of two time scales is essential to the understanding of the process and competition between crystallization and vitrification. The first time scale $\tau_{\text{in}}(T)$ is the time scale for relaxation within the supercooled liquid. The second time is the time needed for a chosen volume fraction of the sample to become crystalline. We will call this the escape time $\tau_{\text{out}}(T)$. Vitrification would thus be impossible if the escape time curve were to meet the internal relaxation time curve. In fact, $\tau_{\text{in}}(T)$ increases continuously as the temperature is lowered. In contrast, $\tau_{\text{out}}(T)$ does not decrease continuously with temperature but enters a regime where its value is governed by the same process which also determines the behavior of τ_{in}, i.e., the self-diffusion of the liquid.

A vast amount of experimental data[2(a),3] shows that there is a wide class of properties whose spectrum of relaxation times becomes broad near the glass transition. The Kohlrausch-Williams-Watts (KWW) correlation function has provided an accurate and convenient way to express this broad response. The correlation function has the stretched exponential form[2(b)]

$$\xi(t)=\xi_0\exp[-(t/\tau)^{\beta}] .$$

The exponent β lies in the range $0.3 < \beta \leq 1.0$ but may vary with substance, temperature, and pressure. The temperature dependence of the most probable relaxation time τ is a strong function of T and is often represented by the Vogel-Tamman-Fulcher (VTF) law[2(c)]

$$\tau=A\exp[-B/(T-T_0)],\quad A,B,T_0>0 .$$

The theoretical origins of this nonexponential relaxation of mechanical and dielectric disturbances in highly viscous supercooled liquids is a challenging problem—a problem which has recently received renewed interest.[4] It is the purpose of this paper to understand why this happens. To put the problem into perspective, the following comments are in order. First, the precise mechanism by which a system's response results in a KWW form depends on the property (e.g., stress versus dielectric relaxation) whose relaxation is being studied. Second, there are several reasons for being cautious about assigning a deep significance to the KWW distribution. (a) Since the data is usually analyzed on a log-log scale, there is a compression of data. This means that there is not much structure to the long-time relaxation curves. Many three-parameter fits would thus equally well correlate with the data. (b) There are materials in which stretched exponential is not a good fit. For example, in a composite material, the total response is a sum of responses ϕ_i. Thus if ϕ_i is of the KWW form, ϕ is not unless each ϕ_i had the same response. As a second example, photon correlation spectroscopy of the amorphous polymer [poly(di(n-butyl)itaconate)] shows that the observed[5] correlation function cannot be fitted to a single KWW function. An accurate description is obtained by fits which are sums of two such functions. As a final example, note that the relationship between complex modulus G and complex viscosity η, $G=i\omega\eta$, clearly shows that if G is of the KWW form, then η is not of the stretched exponential form and vice versa. (c) There are several cases in literature[6,7] of single-relaxation-time kinetics being observed for relaxation processes occurring in solutions near T_g. Electrical relaxation studies of charge migration in a dilute solution of NaCl in glycerol and dipole reorientation of a high moment-of-inertia dipolar species in dilute solution in *o*-terphenyl are just examples of the point.

The above arguments were intended to demonstrate the point that although nonexponential long-time relaxation is *observed* in a variety of properties near T_g, the KWW is *not* universally valid. Since there are known cases where the KWW form works well, we should inquire into the basis for its functional form.

Extensive set of data compiled by Douglas *et al.*[8] and more recently by Angell and co-workers[9] show that stress relaxation in a stabilized glass can be described by a KWW form. In particular one finds that for $t \sim \tau$, $\alpha \sim \frac{1}{2}$, and for $t \gg \tau$, α has the value of 1. There is also some evidence of a high-frequency peak not accounted for if $\alpha = \frac{1}{2}$. An analysis of the data shows that for $t \ll \tau$, α has a value of about $\frac{1}{3}$. This paper is devoted to an understanding of stress relaxation in low-temperature amorphous materials.

Stillinger and Weber[10] (SW) have recently proposed that a fruitful way to consider the many-body dynamics of a liquid is to separate the stable-packing configurations from the vibrational motions about these molecular packings which correspond to the local minima in the potential-energy hypersurface of the system. The so-called steepest-descent quench is used to map arbitrary configuration of particles onto appropriate members of the collection of potential-energy minima. The essential results obtained by Stillinger and co-workers are reviewed in Sec. II. Section III presents a potential-barrier model of glassy systems. Since our goal is to explain the stress-relaxation function in the glassy state, i.e., within a *restricted* part of the configuration space, the amorphous packings are isolated out of the full packings by a suitable projection. This is briefly described in Sec. IV. A spatial coarse graining is introduced in Sec. V which smooths out the roughness in the potential-energy hypersurface. The relevant slowly relaxing degrees of freedom are essentially unchanged by the coarse graining and they can be described by a master equation. Thus, the stress relaxation in glass is connected with probability flow in configuration space between distinct coarse grained packing of cells. In Sec. VI, the stress-relaxation function is analyzed in various regions of time scales. Concluding remarks are made in Sec. VII.

II. MAPPING ONTO POTENTIAL MINIMA

A fruitful way to consider the many-body dynamics of a liquid is to separate[10] the stable packing configurations, which correspond to the local minima in the potential-energy hypersurface of the system, from the anharmonic vibrations about these stable molecular packings. Recently, SW have implemented this idea by carrying out a so-called steepest-descent quench. One starts from any initial configuration and follows the path of steepest descent on the Φ hypersurface until a minimum is encountered. The mapping of arbitrary initial configurations to their respective minima is unique and exhaustive. The set of all configurations that quench into the same minimum α of Φ *defines* a cell $C(\alpha)$ around that minimum. In this way the configuration space is divided into distinct regions $C(\alpha)$. Note that for each Φ minimum, there are $N!$ equivalent minima which differ only by exchange. If the number of distinguishable minima occurring between ϕ (where $\phi = \Phi/N$) and $\phi + d\phi$ is $G(\phi)$, the partition function can be expressed as a simple quadrature over the potential energy:

$$Z_N = \lambda^{-3N} \int d\phi\, G(\phi) \exp[-\beta N\phi - \beta N f(\phi,\beta)] \;. \quad (1)$$

Here λ is the mean thermal de Broglie wavelength, $Nf(\phi,\beta)$ is the mean vibrational free-energy motion in those cells whose minima lie at ϕ, and $\beta = (k_B T)^{-1}$.

We now summarize the results of Stillinger and Weber.

(a) For temperatures around the melting temperature T_m, transitions between distinct "inherent structures" or packings occur frequently with returns to a previously visited value. As the temperature increases ($T \sim 3T_m$), the rate of structural transitions also increases dramatically. This means that the configurations of the system are able to probe diverse regions of the configuration space which contain many basins of diverse slope, curvature, aperture, and depth.

(b) If the fluid is moderately supercooled, the transition kinetics exhibits a pattern of *intermittency*, i.e., the state of the system gets "stuck" in the same cell for long stretches of time; exit from the cell is followed by *chaotic* bursts of changing quench ϕ-values. In other words, the system evolves through regions of the Φ hypersurface which contain intertwined "drainage ditches" that descend towards many different potential minima.

(c) The transition rate between different cells declines rapidly with temperature. If the system is supercooled into an amorphous state, then one observes transitions between *localized two*-levels. The bistable degrees of freedom are cooperative and have wide variations in barrier heights, the number of atoms involved, and the extent of curvature of the reaction pathway.

(d) Transition kinetics between cells involves *localized* particle motions with an essentially rigid host matrix; the corresponding change in Φ is of $O(1)$. Thus a small number of atoms out of the entire system participates as the system moves from, say, state A to state B. The *lower* the temperature, the more localized the particle rearrangements are between successively visited inherent structures. By contrast, the entire *span* of *depths* of minima is of order N.

(e) The radial distribution function of the quenched configuration appears to be independent of *temperature* at *constant* density, provided the *initial* state corresponds to a *fluid* state.

(f) The majority of the relative potential minima contributing to the quenched amorphous states are highly defective face-centered cubic crystalline configurations. This is true only if the substance's stable crystal form is itself face-centered cubic.

Cotterill and Madsen[11] have also analyzed the topology of the constant-potential-energy hypersurfaces of Lennard-Jones matter. These authors have obtained sections of the configuration space by probing all of the normal-mode energy profiles. For the crystal, these normal-mode profiles were single welled. In the noncrystalline states, some of the sections displayed double-well behavior; these double wells occur more frequently as the glass is warmed towards the fluid state. The occurrence of double wells in the monitored sections indicates the existence of labyrinthine and multiply connected constant-potential-energy hypersurfaces. The study reveals the probability that there are curved valleys which circumvent the barriers.

III. POTENTIAL-BARRIER MODEL

The stress-relaxation function will be studied via a potential-barrier model for glassy systems. Although the details of the model are arguable, they are, nevertheless, plausible, and are in fact supported by the findings of SW in their detailed computer simulation studies of structural transitions in liquids. The assumptions[12] of the model are as follows.

(a) A sample of glass at low temperatures is in a state which is either at or near a minimum on the potential-energy hypersurface. It is near a minimum in the sense that a sudden cooling will drop the glass into a minimum with relatively small change of most of the coordinates. In fact, the approximate equality[11] between the entropies of the glass and crystal suggests that for both these states the state point is confined to a local potential-energy valley in configuration space.

(b) The region of the potential-energy surface that represents the glassy state has a large number of minima of varying depths. This is consistent with a variety of experimental results which show that a sample of glass has finite entropy and that its state depends[13] on the rate at which the liquid has been cooled below its freezing point.

(c) At low temperatures the "inherent" structures make transition from one cell to another cell by passage across some saddle point on the Φ surface. These transitions involve localized particle motions. It is precisely these molecular rearrangements that provide a mechanism for the viscous flow and, hence, the attainment of thermodynamic equilibrium. Note that at low temperatures, even though the state point is confined to a local valley, it may go to an adjacent valley by traversing a relatively low energy barrier. This idea[14] underlies the explanation of the specific heat of glass at low temperatures.

(d) In the temperature range where thermal energies of the system become comparable to height of the potential barriers, the potential-barrier picture ceases to be applicable.

The assumption that flow involves motion in a localized region is inherent in the models of Adams and Gibbs,[15(a)] and Turnbull and Cohen.[15(b)] More recently, the computer simulation results of Helfand and Weber[16] show that molecular rearrangements of even larger polymers are thought to occur by the accumulation of rearrangements of segments of only 5—10 bond lengths.

IV. COARSE GRAINING OF POTENTIAL MINIMA IN THE AMORPHOUS MANIFOLDS

A stable liquid above the melting temperature contains a distribution of crystallites. These crystallites serve as nuclei for freezing of the liquid. A system in the supercooled regime remains in that part of the configuration space which is spanned by crystal-free particle packings. Our goal is to explain properties of the stress-relaxation function within this *restricted* configuration space. Thus, the amorphous packings are isolated, by a suitable projection, out of the full packings.

Let the amorphous manifold be characterized by $\sigma_1(\phi)$, the packing distribution by potential energy, and a mean vibrational free energy $Nf_1(\beta,\phi)$. By assumption of the potential-barrier model, the Φ hypersurface in the amorphous-packing part of the configuration space is topographically *rough* over a wide *range* of length scales.

Following Stillinger,[17] a coarse graining is carried out that suppresses small-scale roughness, while preserving the large-scale features via the following steps. First, the potential energy is separated into a repulsive part and a remainder

$$\Phi=\Phi_c+\Phi_s\ , \tag{2}$$

where Φ_s represents long-range interactions. Second, Φ_s is coarse grained over a region R:

$$\psi(\mathbf{r},l)=\int_R d\mathbf{r}'\,H(\mathbf{r},\mathbf{r}',l)\Phi_s(\mathbf{r}')\ . \tag{3}$$

R is the set of configurations without overlap. It is the physically accessible region of configuration space. The non-negative kernel satisfies

$$\begin{gathered}\lim_{l\to 0}H(\mathbf{r},\mathbf{r}',l)=\delta(\mathbf{r}-\mathbf{r}')\ ,\\ \int d\mathbf{r}'\,H(\mathbf{r},\mathbf{r}',l)=1\ ,\\ (NR)^{-1}\int d\mathbf{r}\int d\mathbf{r}'\,|\mathbf{r}-\mathbf{r}'|^2H(\mathbf{r},\mathbf{r}',l)=l^2\ .\end{gathered} \tag{4}$$

As l increases, the coarse-grained potential ψ becomes smoother since many of the minima in Φ are eliminated. Thus, the number of minima of $\psi(l)$ in the amorphous region of configuration space *decreases* with increasing l as

$$\Omega(l)\sim\Omega_p\exp[\theta(l)N]\ . \tag{5}$$

Ω_p is the number of equivalent minimum for each $\psi(l)$ minimum and $\theta(l)$ decreases monotonically with l.

Configuration mapping to minima on the coarse-grained potential ψ will lead to cells $C_\alpha(l)$ which cover the full configuration space exhaustively and without overlap. Clearly, the number of cells *decreases* as l increases.

V. DYNAMICS OF TRANSITION BETWEEN CELLS

Stress relaxation in glass is connected with probability flow in configuration space between *distinct* coarse-grained packings of cells. Denote the cells in the amorphous part of the configuration space by

$$C_\alpha(\Gamma)=\begin{cases}1 & \text{if } \Gamma \text{ is in cell } \alpha\ ,\\ 0 & \text{otherwise}\ .\end{cases} \tag{6}$$

Γ denotes the position of the system in configuration space. The cells *do not* overlap and *span* the configuration space,

$$C_\alpha(\Gamma)C_\beta(\Gamma)=\delta_{\alpha\beta}C_\alpha(\Gamma)\ ,$$
$$\sum_\alpha C_\alpha(\Gamma)=1 \text{ for all } \Gamma\ . \tag{7}$$

The probability that the amorphous state of the system lies in the cell α, at time t, is the average of the cell characteristic function $C_\alpha(\Gamma)$,

$$P_\alpha(t)=\langle C_\alpha(\Gamma);t\rangle$$
$$\equiv \int dX\, C_\alpha(X) f(X,t)\ . \tag{8}$$

Here the state of the system, i.e., a point in phase space is denoted by X and any time-dependent averages are taken with the phase-space distribution function $f(X,t)$.

By the use of Mori algorithm, one readily finds the Langevin equation[18] of motion for the set of observables $\{C_\alpha(\Gamma)\}$

$$\dot{C}_\alpha(t)=-\sum_\gamma \int_0^t dt'\, K_{\alpha\gamma}(t')C_\gamma(t-t')+F_\alpha^+(t)\ . \tag{9}$$

The "random force" and the transition memory kernel are, respectively,

$$F_\alpha^+(t)=\exp[t(1-P)L](1-P)LC_\alpha(\Gamma)\ ,$$
$$K_{\alpha\gamma}(t)=(\exp[t(1-P)L]LC_\alpha,LC_\gamma)/\langle C_\alpha(\Gamma)\rangle\ . \tag{10}$$

L is the Liouville operator, the inner product (A,B) being defined as equilibrium averages of $\langle AB\rangle$, and the projection operator P projects onto the subspace of linear combinations of the $C_\alpha(\Gamma)$. The systematic frequency term in Eq. (10) vanishes since C_α depends on coordinates only, and LC is linear in momentum.

$$f(X,0)=f_{\text{equil}}(X)T(C)\ , \tag{11}$$

where $T(C)$ is *any* function of the C's, the average of the random forces vanishes identically and the master equation for the time-dependent residence probabilities in the cell α is

$$\dot{P}_\alpha(t)=-\sum_\gamma \int_0^t dt'\, K_{\alpha\gamma}(t-t')P_\gamma(t')\ . \tag{12}$$

By conservation

$$\sum_{\alpha=1}^{M} P_\alpha(t)=1\ . \tag{13}$$

Here M is the number of distinct particle packings in the coarse-grained amorphous region of the configuration space

$$M(l)=\exp[N\theta(l)]\ . \tag{14}$$

Let us assume that the cells constructed by the steepest-descent method and after coarse graining are such that the dynamical behavior is "complex" in the sense that once the system has entered a cell, the "memory" of the initial cell has been erased. Under these circumstances, the irreversible behavior is governed by the master equation

$$\dot{P}_\alpha(t)=\sum_{\gamma\,(\neq\alpha)}[K_{\alpha\gamma}P_\gamma(t)-K_{\gamma\alpha}P_\alpha(t)]\ . \tag{15}$$

The general solution of the master equation can be expressed as

$$\sum_n A_n X_\alpha^{(n)}\exp(-\lambda_n t)\ . \tag{16}$$

$X_\alpha^{(n)}$ and λ_n are the orthonormal eigenvectors and eigenvalues of the transition operator K

$$KX^{(n)}=\lambda_n X^{(n)}\ . \tag{17}$$

The conservation Eq. (13) implies that the transition kernel must satisfy

$$\sum_\gamma K_{\gamma\alpha}=0\ . \tag{18}$$

This means that there is at *least* one *zero* eigenvalue of K, namely $\lambda_1=0$. A sufficient condition for existence of a stationary state P_β^0 is

$$\sum_{\gamma=1}^{M} K_{\alpha\gamma}P_\gamma^0=0\ . \tag{19}$$

Equations (18) and (19) lead to the condition of detailed balance

$$K_{\alpha\gamma}P_\gamma^0=K_{\gamma\alpha}P_\alpha^0\ . \tag{20}$$

Note that detailed balance condition imposes not only a sufficient restriction for the existence of a stationary solution, but it guarantees that *all* eigenvalues are *real* and *non-negative.*

The *time scale* for relaxation to equilibrium (P_α^0) depends on the *smallest* remaining eigenvalues λ_2 of $K_{\alpha\beta}$. λ_2 determines whether equilibrium can be *reached* within the time scale of physical relevance.

If *all* states are connected by a chain of *nonvanishing* elements of K, then there is only one $\lambda=0$; the stationary solution P_α^0 is unique and reached in a *finite* time if n is finite.

VI. STRESS RELAXATION

Let us choose a molecular configuration which is at a potential-energy minimum as the *reference* state and define it to be strain free. Molecular rearrangement takes the state of the system to a nearby minimum. By assumption of the potential-barrier model, changes arising from this rearrangement are localized. The displacement vector of the strain field produced by the rearrangement will give rise to deformation of the surface.

A surface force can be applied that can produce the simple macroscopic deformation. The external stress can either bias or unbias some potential-energy minima relative to others. To describe the dissipation of stored potential energy via molecular rearrangements, suppose that the stress can be assigned mean values σ_α appropriate for the interior of each of the cell equivalent classes. Then the time dependence of regression of an initial fluctuation in $\sigma(t)$ is

$$\sigma(t)=\sum_{\alpha}\sigma_\alpha P_\alpha(t)$$
$$=\sum_{n}A_n\phi_n\exp(-\lambda_n t)\ , \qquad (21)$$

where ϕ_n is given by

$$\phi_n=\sum_{\alpha}X_\alpha^{(n)}\sigma_\alpha\ . \qquad (22)$$

Since we have imposed detailed balance on the transition probabilities $K_{\alpha\beta}$, $\sigma(t)$ decays to zero at $t\rightarrow\infty$.

In deriving (21) we have made *no* assumption that stress relaxation in a glass occurs by parallel process, an assumption which necessarily means that disjoint regions of the configuration space relax independently. Rather, the expression for stress relaxation explicitly shows that it involves *coupling* of *all* degrees of freedom.

Small λ_n describes *slow* processes over large-scale topographical features and, hence, are *not* affected by the coarse-graining operation which smooths out small scale features. As l increases, $M(l)$ decreases and the few remaining effective modes of relaxation are slow. These slow modes are associated with localized repackings of particles near the test particle. In the glassy state, stress is relaxed by movement of a small subset of the system's particle positions, the motions of which are weakly coupled to the motions (the so-called α relaxation) which were frozen out at the glass transition. The basic physical assumption is that the slowest structural rearrangements in a dense, highly viscous supercooled fluid occur on molecular length scales via self-diffusion, i.e.,

$$\tau_{\mathbf{k}}^{-1}=D\mathbf{k}^2\ , \qquad (23)$$

where D is the self-diffusion coefficient and the index $\mathbf{k}$ labels the wave vector determined by boundary conditions. Sine the sum over n in Eq. (21) can be viewed as sum over the "modes" that characterize the system, we have relabelled the summation index by the wave vector $\mathbf{k}$.

There are both experimental and theoretical reasons for this assumption.

(1) In a stabilized glass, which is what we are considering, one observes experimentally[19,20] that the *same* activation energy is obtained for various relaxation processes in the transformation range. This means that each τ_n must vary with temperature in precisely the same way.

(2) The Boltzmann superposition principle is valid[20] for stabilized glass. Thus, the shear viscosity computed from the stress-relaxation function is proportional to τ^{-1}.

(3) The decay of density fluctuations in a dense fluid which occurs on a molecular scale length becomes very slow and occurs via self-diffusion; this scale length is given by $2\pi/q_0$, where q_0 is the first peak in the structure factor.

In fact, measurements of the temperature dependence of the half width of the dynamical structure factor $S(q,\omega)$ of the supercooled liquid at $q=q_0$ show that the data correlate[21] well with the slowing down of the diffusion process through which *nonpropagating* density fluctuations at any $q\leq q_0$ must decay.

(4) The detailed ion dynamics simulation for SiO_2, by Angell and co-workers,[22] over a wide range of T and density show that the particle motions by which the system explores its configuration space and finds its equilibrium state are essentially diffusive in nature.

(5) In a detailed series of experiments, Angell and coworkers[22] have used time-dependent spectroscopy of *local*-structure-sensitive optical probes for the purpose of studying relaxation processes in viscous liquids in the glass transformation range. They have found that both the average relaxation time and the form of the relaxation-time spectrum may be very different for the local structure than for the *total* structure as probed by normal thermal or mechanical methods. In other words, these experiments support the idea that the spectrum of relaxation times which is observed for a given relaxation process depends on the volume of the system subspace which must be explored to relax most of the imposed stress.

(6) Density fluctuations that are frozen in the cooling glass result in internal compression and shear strains. These strains are partially relieved by an annealing process.[23] The large value of the Landau-Placzek ratio which is due to decreasing Brillouin intensity (and not to an increase in Rayleigh scattering) has been qualitatively attributed[24] to a nonpropagating strain-relaxing mechanism.

(7) The theoretical validity of the Stokes-Einstein (SE) relation in a model of cold dense liquids based on the Stillinger-Weber construction, has recently been analyzed[25] in detail by Zwanzig and Mohanty. These authors show how the SE relation can be derived by a direct evaluation of shear viscosity and self-diffusion from the Green-Kubo formula.

(8) Experimentally there is as yet *no* conclusive evidence that the SE relation is valid in the undercooled liquid in the transformation regime. But the relation between the self-diffusion coefficient and the friction coefficient is a direct consequence of *linear-response* theory and is correct *independent* of any mechanism for the friction.

By analyzing experimental data on a variety of liquids, Zwanzig and Harrison[26] have made the suggestion that if deviations from the SE relationship are observed, and if there are no other nonviscous mechanisms, then one should look for something unusual about the interaction of the moving molecule and its environment. In this case, they suggest that the SE relation is valid in terms of an *effective* hydrodynamic radius (EHR), the EHR being a measure of the strength of this interaction.

(9) Computer simulation results of dense classical liquids have shown that the stress-tensor autocorrelation function decays as $t^{-3/2}$ for long times, where t is the time, but with an amplitude that is 500 times larger than predicted by conventional mode-coupling theory. This has recently been explained by the use of generalized hydrodynamics[27] which includes effects that occur on a molecular length scale where structural relaxation is important. The heat mode softens at liquid densities and approaches the self-diffusion mode at $q=q_0$ which corresponds to the first peak in the structure factor. At these wave numbers, there is a very slow structural relaxation due to self-diffusion. The recent molecular theories[28] of liquid-solid transition by Ramakrishnan and Yussouff, and Jones and Mohanty emphasizes and makes use of this

point.

Let us first analyze the *short*-time behavior of the stress-relaxation function. By short time we mean that the time scale of interest is much less than $\tau_s \sim \bar{\lambda}^2/D \equiv \tau_0$, where $\bar{\lambda}$ is roughly given by the short-range order in a glass. Let us consider a relaxation mode whose wavelength is λ. If the wavelength of the mode is much larger than $\bar{\lambda}$, then the mode would involve regions of the glass which are *incoherently* linked. The mode would then be *suppressed*. Hence, the probability of *exciting* a mode whose wavelength is λ is proportional to $\exp(-\lambda/\bar{\lambda})$. On introducing a continuum approximation we get

$$\sigma(t)=A^{-1}\int_{k_{\min}}^{k_{\max}} \exp(-\lambda/\bar{\lambda}-Dk^2t)\phi_{\mathbf{k}}\,d\mathbf{k}\ . \tag{24}$$

The shortest wavelength $\lambda_{\min}$ is of the order of a few angstroms and the longest wavelength $\lambda_{\max}$ is governed by the size of the sample. The wave vectors $k_{\max}$ and $k_{\min}$ are, respectively, given by $2\pi/\lambda_{\min}$ and $2\pi/\lambda_{\max}$, and the normalization factor A is bounded by $k_{\max}/\pi^2$.

The exponent in the integrand is written as

$$\begin{aligned} I&=\bar{\lambda}^{-2/3}\left[\frac{(2Dt)^{1/3}}{(k/k^*)}+\left[\frac{k}{k^*}\right]^2\left[\frac{Dt}{4}\right]^{1/3}\right] \\ &\equiv\bar{\lambda}^{-2/3}p(k/k^*)\ , \end{aligned} \tag{25}$$

where $k^*=(2Dt\bar{\lambda})^{-1/3}$. The major contribution to stress comes when I is a maximum, i.e., at $k=k^*$. Using the facts that

$$\begin{aligned} &p(1)=(\tfrac{27}{4})^{1/3}(Dt)^{1/3}\ , \\ &p''(1)=(54)^{1/3}(Dt)^{1/3}\ , \end{aligned} \tag{26}$$

we get

$$\sigma(t)=\frac{2\pi(k^*)^2}{A}\phi_{k^*}\left[\frac{\pi}{3Dt}\right]^{1/2}\exp[-(t/\tau_s)^{1/3}] \tag{27}$$

with

$$\tau_s=\tfrac{4}{27}\bar{\lambda}^2/D\ . \tag{28}$$

Note that Eq. (27) for the stress-relaxation function is valid for t much less than τ_0. However, if t is too small, then the description of stress relaxation via the master equation ceases to be applicable.

For times larger than τ_s, molecular relaxation of the various packings have occurred. Majumdar[29] has suggested a possible mechanism for stress relaxation when $t \sim \tau_0$. In this assumption, stress is effectively relaxed when mismatches between the small localized regions readjust by slipping motion along surfaces of these regions.

Let $\tilde{\sigma}$ be the activation energy per unit area for slipping motion. Since glass is isotropic, we can assume a relaxing region of radius $\lambda/2$. The probability of exciting this mode is $\exp(-\pi\tilde{\sigma}^2\lambda^2/k_BT)$. The time dependence of regression of $\sigma(t)$ is then given by

$$\sigma(t)=A^{-1}\int_{k_{\min}}^{k_{\max}} d\mathbf{k}\,\phi_{\mathbf{k}}\exp\left[-Dk^2t-\frac{\lambda^2\tilde{\sigma}^2\pi}{k_BT}\right]\ . \tag{29}$$

Define $k^*=(Dtk_BT/\pi\tilde{\sigma}^2)^{-1/4}$. Then the exponent in the integrand can be written as

$$I=\frac{\pi\tilde{\sigma}^2}{k_BT}\left[(tD)^{1/2}\left[\frac{k}{k^*}\right]^2+\frac{(Dt)^{1/2}}{(k/k^*)^2}\right]\ . \tag{30}$$

Major contribution to stress comes when I is a maximum, i.e., at $k=k^*$. Using the facts

$$\begin{aligned} &p(1)=2(Dt)^{1/2}\ , \\ &p''(1)=8(Dt)^{1/2}\ , \end{aligned} \tag{31}$$

we get

$$\sigma(t)=\frac{2\pi(k^*)^2}{A}\phi_{k^*}\left[\frac{\pi}{4Dt}\right]^{1/2}\exp[-(t/\tau_{ls})^{1/2}] \tag{32}$$

with $\tau_{ls}=k_BT/4\pi^2\tilde{\sigma}^2D$. If stress relaxation occurs by volume relaxation, one finds instead that $\beta=0.6$ in the time scale $\tau_{lv}=\tilde{\alpha}\tau_s$, where $\tilde{\alpha}$ is a constant larger than 1.

As $t\rightarrow\infty$, the system approaches equilibrium, i.e., molecular rearrangements in the glass tend to effectively relax the stress. In this case, *only* the *longest mode* contributes to $\sigma(t)$,

$$\begin{aligned} \sigma(t)&=A^{-1}\int_{k_{\min}}^{k_{\max}} \exp(-Dk^2t)\phi_{\mathbf{k}}\delta(\mathbf{k}-\mathbf{k}_{\max})d\mathbf{k} \\ &=\frac{4\pi}{A\lambda_{\max}^2}\phi_{k_{\max}}\exp(-t/\tau_\infty)\ , \end{aligned} \tag{33}$$

where $\tau_\infty=\lambda_{\max}^2/4\pi^2D$. Thus for any subspace characterized by $\lambda \gg \bar{\lambda}$ a single relaxation time should result.

For a macroscopic system, a single exponential decay is largely irrelevant since it is not observable. The longest relaxation time diverges as system size increases. The only interesting behavior is that which remains finite in the infinite-system limit. There still remains the possibility that the limiting stress-relaxation function at large time may well not be a simple exponential.

Note that since $k_BT \sim \pi\tilde{\sigma}\bar{\lambda}^2$, the observed relaxation rates τ_s, τ_{ls}, τ_∞ can all be expressed in terms of $\tau_0=\bar{\lambda}^2/D$. Hence, this model exhibits a "feedback" mechanism between the viscous liquid characteristics of nonexponential relaxation and non-Arrhenius temperature dependence of the average relaxation time.

VII. CONCLUDING REMARKS

Stress relaxation in a stabilized glass has been described by a potential-barrier model which is based on separating geometric packing considerations from thermal excitations in the dynamic evolution of a many-body system. The basic physical assumption is that the slowest structural rearrangements in a dense, highly viscous supercooled fluid occur on molecular length scales via self-diffusion. Distinct mechanisms are identified which drive the stress-relaxation function to acquire the KWW forms in a "short" time and in the "intermediate" time limit.

One also finds in agreement with Ngai's theory that the observed relaxation rates, i.e., τ_s, τ_{ls}, or τ_∞, are all related to the direct relaxation rate τ_0. The temperature dependence of τ_0 is governed by the self-diffusion of the viscous fluid.

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