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Relaxation behavior in atomic and molecular glasses

F. H. Stillinger
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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The time dependence of relaxation for many substances near their glass transition region is often found accurately to obey a "stretched exponential" form, $\exp[-(t/\tau)^{\alpha}]$, with the stretching exponent in the range $0<\alpha<1$. It is the objective of this paper to relate α and τ to gross topographical features of the many-particle potential-energy hypersurface. The multidimensional basin representation for the potential energy, supplied by the inherent structure theory of condensed phases, offers a convenient analytical framework. The relaxation time spectrum for stretched exponential behavior thus is related to the manner in which basins can be aggregated in the multidimensional configuration space into "metabasins," using a transition free-energy criterion. A conclusion of the analysis is that α should decline with decreasing temperature; some limited experimental and simulational support exists for this proposition. In addition, the usually found non-Arrhenius behavior for τ is connected by the study to the increasing extent of branching and tortuosity of basins inhabited as the temperature declines.

I. INTRODUCTION

The properties of glass-forming materials continue to resist comprehensive and fundamental understanding, despite intense scientific effort devoted to the subject. In particular, it remains somewhat unclear how chemical distinctions between substances influence the kinetics of relaxation processes in the glass transition region, and even how those distinctions fully control glass-forming ability itself. This study addresses some of these issues in a general way, and appears to yield a few useful insights.

It will be helpful at the outset to recall the primary experimental attributes of good glass-forming substances, i.e., those that can be readily supercooled (without nucleation) to a rather well-defined "glass transition temperature" T_g. For pure substances that melt at temperature T_m and are good glass formers, T_g occurs at about $0.7T_m$.[1] In any case T_g marks the point at which various relaxation processes have become slower than typical times of experimental observation, producing sudden shifts in the temperature dependence of most measurable properties. The heat capacity provides an important example: It usually shows a sudden drop upon cooling through T_g, becoming for the sub-T_g glass nearly equal to that for the crystal.[2,3] Naive extrapolation of the supercooled-liquid heat capacity to the regime below T_g leads to identification of the Kauzmann point $T_0<T_g$ at which an ideal glass with vanishing configurational entropy hypothetically would obtain.[4]

For temperatures in the vicinity of T_g, the relaxational behavior for most observable properties conforms to a stretched-exponential (Kohlrausch-Williams-Watts) function of time t:[5]

$$\zeta(t)=\zeta_0\exp[-(t/\tau)^{\alpha}]\ . \tag{1.1}$$

The stretching exponent α lies in the range

$$0<\alpha<1\ , \tag{1.2}$$

appears to be sensitive to the chemical nature of the material, and tends to decrease as temperature is lowered through T_g. The characteristic time scale τ of the relaxation function is strongly temperature dependent, and like the shear viscosity $\eta(T)$ it exhibits markedly non-Arrhenius behavior that can often be fitted by a Tammann-Vogel-Fulcher form in which the Kauzmann temperature T_0 (or a close approximation thereto) spontaneously reappears:[6]

$$\tau(T),\eta(T)\cong A\exp[B/(T-T_0)],\quad A,B>0\ . \tag{1.3}$$

Typically $\tau(T_g)$ will lie in the range of seconds to days, $\eta(T_g)$ in the range $10^{11}-10^{13}$ poise.

A wide variety of theoretical models have been proposed to explain glass formation and relaxation. Those that are most relevant to this analysis have stressed the highly constrained nature of atomic or molecular motions in glassy media, and have offered simplified visions of the available collective rearrangements.[7-10] An attempt will be made in the following to avoid specific modelistic assumptions. Rudimentary versions of some of the ideas used in the following were presented in an earlier paper.[11]

Section II reviews the generic properties expected for the multiparticle potential energy function Φ that describes interactions in glass formers. As often pointed out before,[11-15] it is natural and useful to describe the geometry of the Φ hypersurface in terms of its "basins," one surrounding each relative minimum of Φ. Section II therefore also considers the classification and enumeration of those basins by a relevant set of intensive order parameters. Section III examines the kinetics of interbasin transitions, and discusses the nature of history-dependent properties of low-temperature glasses. Section IV introduces a systematic procedure for aggregating basins into "metabasins" as a way to assess the hierarchical character of the Φ hypersurface topography. This procedure leads, in Sec. V, to a geometric connection with the relaxation parameters α and τ in the stretched-exponential form (1.1), the main objective of this paper. Section VI presents some comments and conclusions.

II. INTERACTION POTENTIAL

The many-particle systems of interest will contain some macroscopic numbers, $N_1, N_2, \ldots$, of distinct chemical species. If chemical reactions are involved in the formation and relaxation of the glass state (as apparently happens in liquid sulfur[16] and selenium[17]), it may be convenient to regard the different types of atoms as the elementary species. We shall denote the total numbers of particles by N:

$$N = \sum_i N_i \ . \tag{2.1}$$

The interaction potential for the system as a whole, $\Phi(\mathbf{R})$, generally will comprise intramolecular, intermolecular, and container wall interactions. It may be identified as the ground-electronic-state Born-Oppenheimer energy hypersurface for the system, with a suitable choice for the zero of energy. Experimental protocols can require either constant volume (V) or constant pressure (p) conditions. In the former case the configurational vector $\mathbf{R}$ would be composed of the position coordinates for all nuclei present in the system. In the latter case it is convenient to include a pressure-volume term pV in Φ (so it becomes a potential enthalpy), and to extend $\mathbf{R}$ to include an additional component specifying the position of a constant-force boundary piston. The following formalism accommodates both protocols.

Several generic properties can be listed for $\Phi(\mathbf{R})$.

(a) $\Phi < +\infty$ provided $\mathbf{R}$ has all atomic nuclei separated.

(b) $\Phi \geq -CN$, where the positive constant C depends on the intensive composition variables and the pressure, but is independent of N.

(c) Φ possesses full permutational symmetry under interchange of identical particles.

(d) Φ is arbitrarily many times differentiable in all its variables for all configurations $\mathbf{R}$ with separated nuclei.

(e) Absolute minima of Φ correspond to the most nearly perfect crystalline arrangement of particles that can be formed with the given composition and boundary conditions; higher-lying relative minima include imperfect crystalline and fully amorphous particle packings.

(f) An enumeration of all local Φ minima (mechanically stable particle packings) shows that their number Ω has the following asymptotic form for large system size N:

$$\ln\Omega \sim \ln\left[\prod N_i!\right] + \nu N \ , \tag{2.2}$$

where positive constant ν depends only on intensive composition variables.[12] The term containing factorials in this expression arises simply from the existence of permutation-related equivalent minima, while ν measures the exponential rise rate of the number of inequivalent particle packings.

Mass-weighted descent trajectories on the Φ hypersurface in the multidimensional configuration space can be used to define mutually exclusive and exhaustive basins surrounding each of the relative Φ minima. These trajectories are the solutions to

$$\mathbf{m}\cdot d\mathbf{R}/du = -\nabla_R \Phi \ , \tag{2.3}$$

which converge to configurations of minima as the virtual time variable $u \to +\infty$. Here $\mathbf{m}$ is the vector composed of nuclear masses (and the piston mass for the constant pressure case). The locus of all configuration-space points that lie on trajectories to a specific relative minimum at $\mathbf{R}_\mu$ defines the basin B_μ for that minimum. The solutions to Eq. (2.3) that converge to other types of extrema (saddle points, maxima) have zero measure and can be disregarded for the moment.

The pair of basins B_λ and B_μ that share a nonvanishing portion of boundary will be dynamically connected through one or more transition states (saddle points) lying in that shared boundary. The motivation for including the mass weighting in Eq. (2.3) is that the trajectories descending from the saddle point to minima λ and μ together trace out the conventionally defined reaction coordinate for the transition.[14] Variation of the masses (as by isotropic substitution) changes the shapes of the basins as already defined. However, the basin boundary hypersurfaces continue to pass through the saddle points, merely rotating the direction of their normal there, the direction of the reaction coordinate. The number of basins and their mean size remain unchanged under mass variation.

An additional attribute of the Φ hypersurface can be listed, which plays a very basic role in the subsequent analysis.

(g) Transition states, and the associated reaction coordinate paths between neighboring relative minima, involve particle rearrangements that are localized in 3-space. This is obvious for transitions leading out of the crystalline absolute minima, where localized point defects (close vacancy-interstitial pairs) are created. It is less obvious for transitions between contiguous amorphous-packing basins, but has been discovered to be the case by careful computer simulation studies on a variety of model systems,[14,18,19] and it is supported by analytical models.[20]

Several important consequences follow from property (g). The first is that the number of transition states on the boundary of any basin is expected to be $O(N)$, since the elementary localized transitions could occur anywhere throughout the macroscopic system. Furthermore the saddle point directions (i.e., normals to the basin boundary hypersurfaces at the transition states) are not isotropically distributed, but must be concentrated along directions with just a few non-negligible Cartesian components to be equivalent in fact to localized particle rearrangements. Another inference is that Φ only changes by $O(1)$ in passing from a minimum, across a saddle point, to a contiguous minimum. This contrasts with the $O(N)$ variation in Φ that the system must experience under rearrangement from a crystalline absolute minimum to one of the highest-lying amorphous relative minima; such a global rearrangement requires a sequence of elementary transitions whose number must be at least $O(N)$.

The next step involves classifying the local Φ minima, the particle packings, by a set of intensive order parameters $\{\xi_i\} \equiv \xi$. These will be chosen to be invariant to permutations of identical particles. By convention this set will always include $\phi = \Phi_\mu / N$, the depth of the minima on a per-particle basis. Other order parameters to be considered will depend on the specific application, but might include coordination number distributions, molecular conformational-state probabilities, concentrations of crystallites of various sizes, and (for constant pressure conditions) the volume per particle.

Because of (g), each ξ_i can only change by $O(N^{-1})$ as a result of an elementary interbasin transition. In the large system limit these order parameters thus can be treated as continuous functions of time, with variations that are uniquely determined by the thermal history of the system.

Even after they have been classified by ξ the number of minima (and basins) is expected to depend asymptotically on N in qualitatively the same way as exhibited in Eq. (2.2). If $\Omega(\xi)$ stands for the density of minima in order-parameter space, we can write

$$\ln\Omega(\xi) \sim \ln\left[\prod_i N_i!\right] + \sigma(\xi)N, \quad \sigma(\xi) \geq 0 , \tag{2.4}$$

and in light of Eq. (2.2) we can make the identification

$$\nu = \max\sigma(\xi) . \tag{2.5}$$

The quantity σ is k_B^{-1} times the configurational, or packing, entropy per particle in the state with given order parameters.

Intrabasin excursions away from the Φ minimum arise from vibrational motions. Large amplitude excursions can be very anharmonic and can be interrupted by a transition into a neighboring basin. In the large system limit of primary concern here, mean vibrational properties of all of the basins for a given ξ will be virtually identical. Specifically this is true for the intrabasin vibrational free energy, which on a per-particle basis will be denoted by f_v. The formal definition of this temperature-dependent property, using classical statistical mechanics, is as follows ($\beta = 1/k_B T$):

$$\begin{aligned} f_v(\xi,\beta) &= -(N\beta)^{-1}\ln\langle Z_\mu(\beta)\rangle , \\ Z_\mu(\beta) &= \left[\prod_i \lambda_i^{-3N_i}\right]\int_{B_\mu} d\mathbf{R}\exp[-\beta(\Phi-\Phi_\mu)] , \end{aligned} \tag{2.6}$$

where the λ_i are mean thermal deBroglie wavelengths for the respective species, and where the average indicated in the first line covers basins of the species denoted by the given order parameters. Though it is somewhat more cumbersome to write, a quantum version of the f_v definition could be cited.[21] As remarked in the Introduction the (vibrational) heat capacity of many glasses below T_g is similar to that of the crystalline phases, suggesting at least for those cases that f_v is relatively insensitive to variations in the ξ.

The pair of functions σ and f_v suffice to determine the thermal equilibrium state of the system at any temperature, and density or pressure. The appropriate free-energy function, Helmholtz or Gibbs for constant volume or constant pressure, respectively, is given on a per-particle basis by

$$\min_{\xi}\,[f_v(\xi,\beta) + \phi - \beta^{-1}\sigma(\xi)] . \tag{2.7}$$

Furthermore, the set of order parameters that minimizes this combination is indeed that whose basins are the occupied ones under the given conditions of temperature and pressure.

Selection of order parameters merely to describe thermal equilibrium is straightforward, at least in principle. It suffices to use just a single ξ_i, which, by convention, would be ϕ. The resulting theory would give ϕ as a function of temperature and density (or pressure). Incorporation of a larger set of ξ_i's would simply describe the same equilibrium states as before, but more fully in terms of microscopic structure. However, the requirements are more challenging in the nonequilibrium regime, where it then becomes necessary to include a sufficiently complete set of order parameters to describe at least all experimentally accessible thermal history effects.

Equation (2.7) refers to strict thermal equilibrium, and below the melting temperature it automatically accesses the crystalline phase. However, a conceptually simple modification has been advanced that permits examination of supercooled liquid and amorphous solid states.[22,23] This modification requires removal from consideration (and thus from the definitions of σ and f_v) all basins whose stable packings contain regions of crystalline order larger than a preassigned microscopic cutoff size. Projecting out of consideration such crystallite-containing packings leaves virtually unchanged the predicted thermodynamic properties of the stable liquid phase, while automatically providing a clean extrapolation of those properties into the supercooled regime.

III. INTERBASIN KINETICS

Dynamical details of intrabasin vibrational motions have little direct relevance to glass relaxational phenomena. A more coarse-grained dynamical description, which accounts only for time dependence of basin occupancy, is sufficient, and for that purpose we let $p_\mu(t)$ represent the probability that the system inhabits configuration space basin B_μ at time t. The master equation for these probabilities is:[11]

$$\frac{dp_\mu(t)}{dt} = \sum_{\nu(\neq\mu)} [K_{\nu\to\mu}(E)p_\nu(t) - K_{\mu\to\nu}(E)p_\mu(t)] . \tag{3.1}$$

The conserved energy for the system (including the piston if the constant-pressure protocol applies) has been denoted by E. The transition rates $K_{\nu\to\mu}$ and $K_{\mu\to\nu}$ obviously depend on E, and must satisfy the condition of detailed balance. If $M_\mu(E)$ is the phase-space measure of basin B_μ at energy E, then this condition requires

$$\begin{aligned} K_{\nu\to\mu}(E) &= [M_\mu(E)/M_\nu(E)]^{1/2}A_{\mu\nu}(E) , \\ K_{\mu\to\nu}(E) &= [M_\nu(E)/M_\mu(E)]^{1/2}A_{\mu\nu}(E) , \end{aligned} \tag{3.2}$$

where $A_{\mu\nu}(E) \equiv A_{\nu\mu}(E)$.

An assumption of intrabasin quasiergodicity underlies applicability of master equation (3.1). This would surely be violated at low energy (low temperature) where small amplitude, nearly harmonic, vibrations obtain. But in that regime virtually no transitions between basins would occur anyway, so violating the assumption is irrelevant. However, there is a more significant concern about Eq. (3.1) that must be kept in mind. This involves changing E by heating or cooling the system nonuniformly, specifically at its surface. In this circumstance localized transitions in the surface region would have their rates first affected, and only after thermal conduction had equilibrated temperature throughout the sample would interior localized transitions have their rates modified. We shall avoid this problem simply by assuming that on the time scale of experiment, it is possible to arrange for temperature uniformity.

Since virtually all properties of experimental interest are symmetric under exchange of identical particles, the description offered by Eq. (3.1) is still unnecessarily detailed. It suffices merely to have the probabilities that the system inhabits equivalence classes of basins. Consequently set

$$\hat{p}_\mu(t)=\sum_e p_{e(\mu)}(t)\ , \tag{3.3}$$

where the summation covers all $\prod_i N_i!$ basins related by permutations of identical particles, and henceforth index μ will label equivalence classes. The master equation for these aggregate probabilities has the following form:

$$\frac{d\hat{p}_\mu(t)}{dt}=\sum_{\nu(\neq\mu)}[L_{\nu\to\mu}(E)\hat{p}_\nu(t)-L_{\mu\to\nu}(E)\hat{p}_\mu(t)]\ , \tag{3.4}$$

in which

$$\begin{aligned} L_{\nu\to\mu}(E)&=[M_\mu(E)/M_\nu(E)]^{1/2}B_{\mu\nu}(E)\ ,\\ L_{\mu\to\nu}(E)&=[M_\nu(E)/M_\mu(E)]^{1/2}B_{\mu\nu}(E)\ , \end{aligned} \tag{3.5}$$

and the symmetric matrix $B_{\mu\nu}\equiv B_{\nu\mu}$ is composed of a sum over one or the other equivalence classes of the prior matrix elements $A_{\mu\nu}$:

$$B_{\mu\nu}=\sum_e A_{\mu e(\nu)}=\sum_e A_{e(\mu)\nu}\ . \tag{3.6}$$

Previous studies of models for various real materials indicate that direct transitions between basins belonging to the same equivalence class indeed exist, but are relatively infrequent.[13] In any case these purely permutational transitions, which switch identical particles around closed loops, do not enter into the new transition rates (3.5) and (3.6).

The order parameters $\{\xi_i\}\equiv\xi$ introduced earlier are permutation-symmetric quantities, and so they serve as appropriate classification indices for the basin equivalence classes. Time dependence of the order parameters is the central concern for understanding glass relaxation. Therefore, it is desirable to convert Eq. (3.4) explicitly to an order parameter basis, within which the probability density is given by

$$P(\xi_\mu,t)=\exp[N\sigma(\xi_\mu)]\hat{p}_\mu(t)\ . \tag{3.7}$$

Here ξ_μ represents the location of basin equivalence class μ in the order parameter space.

The configurational entropy function in ξ space will be denoted by $S(\xi,E)$. It includes both packing and vibrational contributions, and is given by

$$\exp[k_B^{-1}S(\xi,E)]=\langle M_\mu(E)\rangle\exp[N\sigma(\xi)]\ . \tag{3.8}$$

The average value indicated by $\langle\ldots\rangle$ covers equivalence classes μ in the neighborhood of location ξ. In the same spirit a suitably averaged and weighted transition matrix B can be introduced

$$B(\xi,\xi',E)=\exp\{\tfrac{1}{2}N[\sigma(\xi)+\sigma(\xi')]\}\langle\langle B_{\mu\nu}(E)\rangle\rangle\ . \tag{3.9}$$

The double average $\langle\langle\ldots\rangle\rangle$ covers equivalence classes μ at location ξ, as well as those denoted by ν at ξ'. With these definitions the master equation adopts the form

$$\frac{dP(\xi,t)}{dt}=\int d\xi' B(\xi,\xi',E)(\exp\{(2k_B)^{-1}[S(\xi,E)-S(\xi',E)]\}P(\xi',t)-\exp\{(2k_B)^{-1}[S(\xi',E)-S(\xi,E)]\}P(\xi,t))\ . \tag{3.10}$$

In the large-system limit the order parameters become continuous variables, so that the discrete ν summation in Eq. (3.4) is replaced by the ξ' integration in Eq. (3.10).

It was pointed out earlier that the fundamental interbasin transitions cause only $O(N^{-1})$ shifts in ξ. Consequently B is nearly diagonal in ξ and ξ'. To take advantage of this feature it is useful to set

$$B(\xi,\xi')=B_0(\xi+\tfrac{1}{2}\Delta\xi',\Delta\xi'),\quad \Delta\xi'=\xi'-\xi\ , \tag{3.11}$$

and to introduce the expansion

$$\begin{aligned} B_0(\xi+\tfrac{1}{2}\Delta\xi',\Delta\xi')={}&B_0(\xi,\Delta\xi')+\tfrac{1}{2}\Delta\xi'\cdot\nabla B_0(\xi,\Delta\xi')\\ &+\tfrac{1}{8}\Delta\xi'\Delta\xi':\nabla\nabla B_0(\xi,\Delta\xi')+\cdots\ . \end{aligned} \tag{3.12}$$

A corresponding expansion for P is the following:

$$\begin{aligned} P(\xi',t)={}&P(\xi,t)+\Delta\xi'\cdot\nabla P(\xi,t)\\ &+\tfrac{1}{2}\Delta\xi'\Delta\xi':\nabla\nabla P(\xi,t)+\cdots\ . \end{aligned} \tag{3.13}$$

For present purposes, it is only necessary to retain terms through quadratic order. When these expansions are inserted in the transformed master equation, Eq. (3.10), surviving terms yield a Fokker-Planck differential equation in ξ space:[24,25]

$$dP(\xi,t)/dt=-\nabla\cdot[(\boldsymbol{\mu}\cdot\mathbf{F})P]+\beta^{-1}\nabla\cdot(\boldsymbol{\mu}\cdot\nabla P) \ . \tag{3.14}$$

The quantities $\boldsymbol{\mu}$ and $\mathbf{F}$ respectively are a mobility tensor and a thermodynamic force in ξ space:

$$\boldsymbol{\mu}(\xi,E)=\tfrac{1}{2}\beta\int d\xi'\,B_0(\xi,\Delta\xi',E)\Delta\xi'\Delta\xi' \ , \tag{3.15}$$

$$\mathbf{F}(\xi,E)=(k_B\beta)^{-1}\nabla S(\xi,E) \ . \tag{3.16}$$

The temperature variable $\beta=(k_BT)^{-1}$ appearing in Eq. (3.14) has been inserted to render the result recognizable in the standard Fokker-Planck form. It is treated as a ξ-independent constant, with β and β^{-1} occurring as mutually cancelling pairs. Consequently the precise value selected is formally irrelevant, but on physically motivated grounds it is desirable for β to represent the kinetic temperature that the system would have if it were stabilized at its current ξ-space distribution by blocking further transitions.

Under thermal equilibrium conditions the distribution function P is very narrow for a macroscopically large system, in fact exhibiting a width that is $O(N^{-1/2})$. Even under nonequilibrium conditions a distribution that initially has a width that is vanishing small for $N\rightarrow\infty$ remains vanishingly small during relaxation toward equilibrium. This is true even if nucleation and phase change are involved. Clearly the basic behavior of relaxation is conveyed by the time dependence of $\bar{\xi}$, the mean of the order-parameter distribution:

$$\bar{\xi}(t)=\int d\xi\,\xi P(\xi,t) \ . \tag{3.17}$$

As mentioned at the end of Sec. II, projecting out basins whose packings contain substantial crystallites yields a formalism in which equilibrated glass states are attainable in principle. In such a circumstance the constrained equilibrium naturally corresponds to a local ξ-space maximum of $S(\xi,E)$. If the order parameter set is sufficiently complete to describe all measurable relaxation modes, then $\bar{\xi}(t)$ should exhibit simple linear relaxation behavior in the vicinity of such a maximum. Let

$$\Delta\xi=\bar{\xi}(t)-\bar{\xi}(\infty) \tag{3.18}$$

represent the deviation from equilibrium. The entropy locally may be approximated by a quadratic form in $\Delta\xi$ components:

$$\begin{aligned} k_B^{-1}\Delta S(\xi,E)&\cong-\tfrac{1}{2}\sum_{i,j}g_{ij}\Delta\xi_i\Delta\xi_j \\ &=-\tfrac{1}{2}\mathbf{g}:\Delta\xi\Delta\xi \ . \end{aligned} \tag{3.19}$$

It is straightforward to show that

$$d\Delta\xi/dt=-\beta^{-1}(\boldsymbol{\mu}\cdot\mathbf{g})\cdot\Delta\xi \ , \tag{3.20}$$

where $\boldsymbol{\mu}$ is the mobility tensor introduced earlier in Eq. (3.15). It is clear from this last expression that the relaxation spectrum is determined by the eigenvalues of the matrix $\beta^{-1}\boldsymbol{\mu}\cdot\mathbf{g}$. Understanding the physical origin of these eigenvalues in terms of the Φ hypersurface topography is the basic objective of the next Sec. IV.

While distinct measurable quantities can be expected to probe the different relaxation modes with somewhat different weights, the fact that a common functional form in the time domain, the stretched exponential of Eq. (1.1), seems to be universally applicable has unavoidable significance. With that in mind, note that the generic stretched exponential shown in Eq. (1.1) has the following spectral resolution:[11,26]

$$\zeta(t)=\zeta_0\int_0^\infty z(\lambda)\exp(-\lambda t)d\lambda \ , \tag{3.21}$$

where $z(\lambda)$ has the following behavior at small λ:

$$z(\lambda)=\exp[-A(\tau\lambda)^{-p}+o(\lambda^{-p})] \ , \tag{3.22}$$

and A and p are related to the stretching exponent α in Eq. (1.1) by

$$\begin{aligned} A&=(1-\alpha)\alpha^{\alpha/(1-\alpha)} \ , \\ p&=\alpha/(1-\alpha) \ . \end{aligned} \tag{3.23}$$

Evidently Eq. (3.22) is the intrinsic spectral density form to be expected in the long-relaxation-time limit ($\lambda\rightarrow0$) for the eigenvalues of the matrix $\beta^{-1}\boldsymbol{\mu}\cdot\mathbf{g}$ already discussed. It is thus a form we must expect to encounter in a detailed study of interbasin transitions in the following Sec. IV.

IV. BASIN AGGREGATION

The distribution of potential-energy barriers that must be surmounted controls relaxation rates in glass-forming materials. Both barrier heights and the apertures of the transition-state regions are important for the kinetics. Activation free energies F^* account for these two attributes, and so provide an appropriate description. Specifically we can employ transition-state theory[27,28] to rewrite transition rates from Eq. (3.4) as follows:

$$L_{\mu\rightarrow\nu}(E)=\omega_0(\xi)\exp[-\beta F^*(\mu\rightarrow\nu)] \ , \tag{4.1}$$

where $\omega_0(\xi)$ is a frequency factor, and β is the inverse temperature quantity appropriate for system energy E. It should be stressed that ω_0 may depend strongly on the order parameters ξ. Activation free energies $F^*(\mu\rightarrow\nu)$ and $F^*(\nu\rightarrow\mu)$ for forward and for reverse transitions generally will be unequal.

The activation free energies can now be used to formulate a criterion for basin aggregation. More precisely, equivalence classes for basins will be grouped together to form larger "metabasins." By construction, free-energy barriers within any metabasin will be low, while those between metabasins will be higher. Consequently, most motions (relaxations) within metabasins will be rapid, while those between metabasins will be slower.

Introduce a continuous free-energy cutoff variable $\eta\geq0$. For fixed η the metabasins are defined to be the largest sets of basin equivalence classes such that within each set any pair of equivalence classes is connected either directly of indirectly by a transition path along which the net rise in activation free energy does not exceed η. Notice that such net rises can consist of a sum of smaller barrier contributions, as Fig. 1 illustrates. Free energy changes along paths connecting the bottoms of distinct metabasins necessarily exceed η.

In order to make the aggregation process unique for a given η, it is necessary to proceed sequentially, starting with the equivalence class of deepest available basins (these correspond to amorphous packings, as mentioned at the end of Sec. II). After having identified the aggregate containing these basins, the same procedure is then applied to those that remain to form the second metabasin. This operation is continued until all basin equivalence classes have been exhausted. In principle, the same sequential formation method for metabasins must be followed for each new value of η.

It is obvious that the number of metabasins will be less than $\exp(\nu N)$, the original number of basin equivalence classes, and will be monotonically decreasing with η. That is, a rise in η on average creates larger metabasin aggregates that are fewer in number. The same comment applies to metabasins labelled by fixed values of intensive order parameters.

Because the barriers between metabasins by construction are at least η in activation free energy, the rates of those relaxation processes which require passage between metabasins is no faster than

$$\lambda(\eta)=\omega_\eta(\xi)\exp(-\beta\eta)\ , \tag{4.2}$$

which parallels the form utilized in Eq. (4.1). Here $\omega_\eta(\xi)$ is an appropriate frequency factor for the η-level metabasins. Processes faster than those described by Eq. (4.2) have become intra-metabasin processes.

Just as was the case before aggregation, transitions between metabasins should involve localized rearrangements of $O(1)$ particles. But now there are far fewer such transitions to be considered, as indeed there are far fewer metabasins than basins. In principle, it is possible to enumerate metabasins at aggregation level η by specifying a characteristic 3-space volume $v(\eta)$ within which, on average, a single localized transition that switches between metabasins could be expected to occur.[11] In accord with the earlier convention, we shall denote the density of metabasins in order-parameter space by $\exp[\sigma(\xi,\eta)N]$, where $\sigma(\xi,0)$ is the quantity introduced in Eq. (2.4), prior to implementing the aggregation process. This density would then have the form

$$\exp[\sigma(\xi,\eta)N]=2^{V/v(\eta)},\quad \sigma(\xi,\eta)=V\ln 2/Nv(\eta)\ , \tag{4.3}$$

where V as before denotes the volume of the entire system.

Clearly $v(\eta)$ will increase with η, though in a manner likely to be nonuniversal and sensitive to details of the particle interactions. In order to accommodate diverse glass-forming materials in the description, the following flexible form will be adopted as a reasonable representation for large η:

$$v(\eta)\cong v_0\exp\{[\omega_\eta(\xi)/\lambda(\eta)]^{q/\beta}\}\ , \tag{4.4}$$

wherein v_0 is some order-unity fixed volume that is independent of η. The quantity q, expected to be material dependent, has been introduced here to express the rate of increase of $v(\eta)$ with η. For later convenience, $\beta=1/k_BT$ has been placed in the exponent in Eq. (4.4). Notice that Eq. (4.2) transforms Eq. (4.4) to

$$\nu(\eta)\cong v_0\exp[\exp(q\eta)]\ , \tag{4.5}$$

so that the metabasin enumeration function σ may be expressed as follows:

$$\sigma(\xi,\eta)=a\exp[-\exp(q\eta)],\quad a=V\ln 2/Nv_0\ . \tag{4.6}$$

We now turn to the task of connecting the inter-metabasin kinetics to the measured relaxation functions, the stretched exponential form (1.1), for which the spectral resolution function $z(\lambda)$ was given earlier in Eq. (3.22). Note that the cumulative spectral density has the same asymptotic form as $z(\lambda)$ itself:

$$\int_0^\lambda Z(\lambda')d\lambda'=\exp[-A(\tau\lambda)^{-p}+o(\lambda^{-p})]\ , \tag{4.7}$$

where A and p were given earlier in terms of the stretching exponent α. This cumulative density involves all inter-metabasin transitions whose localized rearrangements are capable of producing a measurable change at the experimental probe. In effect this demands that probe and localized rearrangement occur within the same region of 3-space. Therefore, to within insignificant factors, the cumulative spectral density for a typical relaxation measurement will be inversely proportional to $v(\eta)$. Hence from Eqs. (4.4) and (4.7) we must have

$$[\omega_\eta(\xi)/\lambda(\eta)]^{q/\beta}\cong A(\tau\lambda)^{-p}\ . \tag{4.8}$$

The next step involves eliminating the η dependence of the left side of Eq. (4.8) in terms of rate variable λ. To do this we note first that the metabasin frequency factor $\omega_\eta(\xi)$ is expected to decline with increasing η. The reason is that the interiors of metabasins by construction exhibit rough topography, and Zwanzig has shown[29] that diffusion in rough potentials can become very slow. Furthermore, the aggregation process may produce tenuous and multiply-branched metabasins that amount to blind mazes from which the dynamical configuration

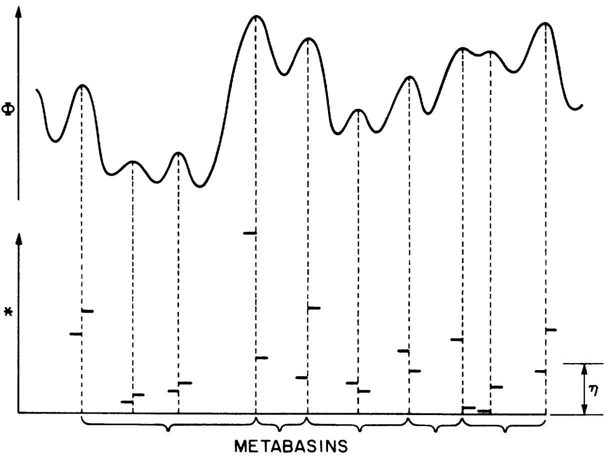

FIG. 1. Construction of metabasins using the activation-free-energy criterion.

point escapes only with difficulty. A reasonable representation of such effects should be given by the form:

$$\omega_\eta(\xi) \cong \omega_0(\xi)\exp(-\gamma\eta) \ . \tag{4.9}$$

As is the case with q, the parameter γ should vary from one glass former to another. Combining Eqs. (4.2) and (4.9), one finds

$$\omega_\eta(\xi) = [\omega_0(\xi)]^{\beta/(\beta+\gamma)}\lambda^{\gamma/(\beta+\gamma)} \ . \tag{4.10}$$

Consequently Eq. (4.8) becomes:

$$[\omega_0(\xi)/\lambda]^{q/(\beta+\gamma)} \cong A(\tau\lambda)^{-\alpha/(1-\alpha)} \ , \tag{4.11}$$

where p has been eliminated in favor of the stretching exponent α using Eq. (3.23).

As a result of these manipulations, the two principal results of this paper now emerge from Eq. (4.11). The first is that the time scale τ for relaxation is inversely proportional to ω_0:

$$\tau \propto 1/\omega_0(\xi) \ . \tag{4.12}$$

The second is that the inverse of the stretching exponent α is formally a linear function of $\beta = 1/k_BT$, and is directly related to the pair of material-specific parameters q and γ:

$$1/\alpha = 1 + (\beta+\gamma)/q \ . \tag{4.13}$$

V. DISCUSSION

It was pointed out in the Introduction that the relaxation time scale $\tau(T)$ for many glass formers has a strong temperature dependence that can often be represented by the Tammann-Vogel-Fulcher form, Eq. (1.3). Our first principal result, Eq. (4.12), states that the same must be true for $1/\omega_0(\xi)$. It is true that basins located in the region of order-parameter space accessed by well-annealed glasses are especially deep (i.e., separated by high potential barriers) compared to the basins for high-temperature liquid. But this distinction alone does not explain the strong temperature dependence of ω_0. Frequency factors for basins of simple and compact shape should vary relatively little with temperature, even though their depths may become large. Instead, the explanation seems to be that typical basins become more and more tortuous and dendritic as one proceeds along the ξ-space path from high-temperature liquid to low-temperature glass. Finding an available exit corridor in a complex glass-state basin could entail first a lengthy sequence of entrances into blocked basin corridors. It is relevant to point out that a recognizable version of this idea appears in recent modeling of glass relaxation using percolation on hypercube edge networks.[10,30]

Under the assumption that parameters q and γ are essentially constant throughout order-parameter space, Eq. (4.13) states that a plot of α^{-1} versus inverse temperature should be linear. Relatively little information is available about the temperature dependence of α over a sufficiently wide range to make effective tests of this linearity, although α does appear to decline as temperature decreases,[31–33] consistent with Eq. (4.13) and with the presumption that $q > 0$. Nevertheless we can cite two examples offered by Fredrickson.[34] The first concerns time dependence of the single-spin correlation function for the 2-spin facilitated kinetic Ising model (2SFM) on a square lattice,[8] evaluated by Monte Carlo computer simulation. Fredrickson finds that this quantity can be accurately fitted by a Kohlrausch-Williams-Watts stretched exponential at all temperatures investigated, and that the stretching exponent α has the following temperature dependence:

$$1/\alpha = 1.3 + 2.3(h/k_BT) \pm 0.1 \ . \tag{5.1}$$

Here h is an external-field coupling constant introduced in the 2SFM. Comparison between Eqs. (4.13) and (5.1) suggests that indeed q and γ may be constant for the 2SFM, and that

$$\begin{aligned} q &\cong 0.43/h \ , \\ \gamma &\cong 0.13/h \ . \end{aligned} \tag{5.2}$$

Of course the 2SFM nominally is not a continuum model as described in this paper, but procedures exist for embedding Ising-type discrete models in a continuum context,[20] to which our detailed basin aggregation procedure would apply.

The second example offered by Fredrickson is taken from Matsuoka's measurements of mechanical relaxation in polycarbonate melts and glasses.[35] Again the Kohlrausch-Williams-Watts stretched exponential adequately represents the data, and the stretching exponent α has the following temperature dependence $(0.0024 \le T^{-1} \le 0.0037)$:

$$1/\alpha = -89 + 38\,000/T \ , \tag{5.3}$$

in which T is degrees Kelvin. While this formally has the requisite linear form in $\beta = 1/k_BT$ established by Eq. (4.13), the negative constant term presents a conflict with our positive term $1+\gamma/q$. However, there may be reason to doubt whether these mechanical relaxation measurements are relevant to this context. Much of the data refers to temperatures well below T_g, and the stretching exponents are extremely small, becoming as low as 0.02 over the temperature range examined. Only a small portion of the entire relaxation is observed (on account of its slowness), and there seems to be a good possibility that the entire system is moving its state through the order-parameter space ξ while the relaxation function is under measurement. This represents a complication not encompassed in our analysis, which assumes a steady metastable state with macroscopically unchanging order parameters. While limited support seems to exist for our key result Eq. (4.13), it is clear that more systematic experiments on relaxation behavior over a wide temperature range, and including many different glass formers, would be very informative.

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