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Ergodic convergence properties of supercooled liquids and glasses

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The dynamical properties of two measures to probe ergodic behavior in Hamiltonian systems with a large number of degrees of freedom are investigated. The measures, namely, the energy metric $d(t)$ and the fluctuation metric $\Omega(t)$ are both based on the time-averaged energies of the individual particles comprising the system. The energy metric $d(t)$ is obtained by following the dynamics of the system using two *independent* configurations, whereas $\Omega(t)$ is expressed in terms of the properties of a single trajectory. Both measures obey a dynamical scaling law for long but finite times. The scaling law for $d(t)$, which was previously established numerically, and for $\Omega(t)$ is derived for systems that are effectively ergodic. The scaling function suggests that the configuration space is explored by a "diffusive" process in the space of the variables used to construct $d(t)$ and $\Omega(t)$. Furthermore, a single parameter, namely D_E and D_Ω, characterizes the time scales needed for effective ergodicity to be obtained. These ideas are used to study the behavior of supercooled and glassy states of soft-sphere binary alloys using microcanonical molecular dynamics. The scaling forms for $d(t)$ and $\Omega(t)$ are explicitly demonstrated. The temperature dependence of the numerically computed diffusion constants (D_E and D_Ω) reveals that the nature of phase-space exploration changes both near the fluid-solid transition and near the liquid-to-glass transition. The changes in D_E and D_Ω with temperature are well described by a Vogel-Fulcher equation close to the glass transition temperature. In addition, the distribution of the time-averaged individual particle energies $P(e;t)$, moments of which are related to $\Omega(t)$, is shown to be broad in the glassy state. We argue that the time dependence of $P(e;t)$ can be used to probe local structural relaxations in glasses.

I. INTRODUCTION

Recently we showed that one can assess the time intervals needed for effective ergodicity to be established by following the dynamics of Hamiltonian systems using two distinct initial conditions.[1] The essence of our idea is to note that for ergodic systems any two dynamical trajectories lying on the same energy shell with different initial conditions would become equivalent, in the sense of sampling phase space, in some finite observational time interval $\mathcal{T}$.[2] As a consequence numerical values of any observable computed from using either of the two trajectories for the interval $\mathcal{T}$ would be identical and the trajectories would be statistically equivalent. This is the situation in the equilibrium liquid state. On the other hand, it is generally accepted that structural glasses are nonergodic systems on the time scale for observations.[3] In statistical-mechanical language, the motion of a nonergodic system is confined to only a part of the energy surface in phase space.[4] This is to be contrasted with the trajectories of effective ergodic systems which uniformly cover the entire energy surface. The widespread use of computer simulations for accurately predicting various thermodynamic properties of liquids (provided the interatomic or intermolecular potentials are adequately known) is an indication of the acceptance by the physics and chemistry communities of the general validity of the ergodic hypothesis.[5] However, given an N-particle Hamiltonian system with N very large, the time interval for approaching equilibrium (if it exists on the experimental time scale) is still an open problem.

It is therefore of great interest to examine the conditions for which ergodicity is obtained in simulations of dense systems. In a recent paper[1] (to be referred to as I) we introduced a quantity called the energy metric which could be used to estimate an approximate time for a dynamical trajectory to uniformly cover the allowed phase space. Furthermore, if ergodicity is broken, the long-time limit of the energy metric approaches (approximately) a nonzero constant indicating that a bottleneck in phase space restricts the range of the configurations explored by the individual trajectories. The system is thus prevented from sampling overlapping parts of phase space. In this way the energy metric is a measure of the degree of statistical equivalence of the two trajectories.

Consider what happens in undercooled liquids and in glasses where two initial configurations lie in two separate local metastable minima of the free-energy hypersurface of the system. The rate at which equivalent configurations are sampled will depend on the free-energy barrier separating the two minima and often the time required for a transition from one minimum to another can be very long. It will take a correspondingly long time for the energy metric to approach zero. The sampling of equivalent configurations is necessary for the development of the statistical equivalence of the trajectories. Physically the process of moving from one minima to another involves the structural rearrangement of several particles, at least on a local scale.

In I we showed that the energy metric could be used to verify some of these ideas, and that it was especially useful in assessing whether or not a system was effectively ergodic. Explicit results demonstrating this were obtained for a binary, glass forming system of soft spheres.[1] In this paper we elaborate on the properties of the energy metric for this system. The temperature and composition dependence of the rate of decay of the energy metric to zero for long times is determined for a wide range of liquid and supercooled liquid states. Also, we introduce a computationally simpler quantity, called the fluctuation metric, and examine the temperature and composition dependence of it for supercooled liquids. This quantity, which is determined from a single trajectory in phase space, also provides a measure of ergodicity. An explicit demonstration of this statement is provided. A preliminary application of the fluctuation metric to probe the time scales for ergodic behavior in several liquids, including liquid water, has been presented elsewhere.[6]

II. PROBES OF EFFECTIVE ERGODIC CONVERGENCE

The ergodic hypothesis of statistical mechanics states that time averages and ensemble averages are identical for a system in thermodynamic equilibrium.[7] Thus, if one waits long enough, the dynamical trajectory would fill the phase space according to a well-defined measure, independent of the initial conditions. To illustrate this statement, suppose that $g(t)$ is a phase-space function whose time average represents a physically observable quantity. The ergodic hypothesis asserts that for $\mathcal{T}\rightarrow\infty$,

$$\langle g\rangle=\frac{1}{\mathcal{T}}\int_0^{\mathcal{T}}dt\,g(t)\ , \tag{2.1}$$

where the $\langle\ \rangle$ indicates an ensemble average. The appropriate ensemble for molecular-dynamics simulations, where the energy and the volume of the system are held constant, is the microcanonical ensemble. Thus for a system with total energy E_0 and Hamiltonian $\mathcal{H}$,

$$\langle g\rangle=\int d\Gamma\,g(\Gamma)\delta(\mathcal{H}(\Gamma)-E_0)\bigg/\int d\Gamma\,\delta(\mathcal{H}(\Gamma)-E_0)\ , \tag{2.2}$$

where the integration is over the phase space Γ of the system. The δ function determines the allowed set of configurations, Γ, for a given value of E_0.

In practice, the appropriate value of $\mathcal{T}$ is determined by requiring that the average value of g obtained using Eq. (2.1) is not sensitive to the value of $\mathcal{T}$. Averages over that interval are assumed to satisfy the condition, Eq. (2.1), and effective ergodic convergence is said to have been obtained in the interval $\mathcal{T}$.[8]

The necessary and sufficient conditions for the ergodic hypothesis to be satisfied are not known for most physically interesting systems. A sufficient condition for obtaining global stochastic motion is that two trajectories in phase space, which are initially close, diverge as time advances. This instability condition is satisfied if the maximal Lyapunov exponent is positive.[9] While this approach has proven useful for systems with a few degrees of freedom, it is computationally much more demanding for systems of several hundred particles than is the solution of the equations of motion.[10,11] An alternative approach to the determination of effective ergodic behavior is desirable and the energy metric $d(t)$ was introduced to address this need.

The energy metric $d(t)$, which is straightforward to compute numerically, is an especially useful probe of the approximate time scale for effective ergodicity to be obtained in systems with a large number of degrees of freedom. By effective ergodicity we mean that the trajectory adequately samples all of the allowed parts of the phase space. The allowed phase space, which in the microcanonical ensemble is a surface of constant total energy of the system, is imagined to be coarse grained into small subregions. If the density of points accessed by the trajectory in every subregion is relatively uniform then the system is effectively ergodic. Although our use of ergodicity is analogous to the concept of mixing in describing stochasticity,[12] we have refrained from using the terminology "mixing" because a numerical test of mixing in principle should involve the computation of the density of phase points in a finite volume of phase space.

The probes of stochasticity that we have constructed should be viewed as a possible alternative for the information that can be obtained (in principle) from Lyapunov exponents. The scaling properties of the measures we introduced seem to be the same as that obtained for the finite-time properties of the maximal Lyapunov exponent for billiard systems.[13,14] In the case of the two-dimensional billiard systems the finite-time scaling property of the maximal Lyapunov exponent could be described in terms of a Markov process. An analogous argument was suggested for the behavior of $d(t)$.[1] For measure preserving systems with large numbers of degrees of freedom, the energy metric provides a reduced description that seems general enough to be applied to both liquids as well as highly supercooled states of matter.

In what follows, we define two measures for probing effective ergodicity in N-body Hamiltonian systems. We also prove the scaling property of the two measures for ergodic systems. Consequently any deviation from the expected scaling of the probes is an indication that ergodicity is broken at least on the observational time scale. For simplicity we assume that the systems consist of a single component. The generalization of the equations to multicomponent systems is given in the Appendix.

A. Fluctuation metric $\Omega(t)$

The energy metric $d(t)$ can be used to probe the time scale for mixing of two independent trajectories in the phase space of the system. This measure provides a natural means of determining if the underlying topography of the free-energy surface has a multivalley structure. The existence of multiple valleys is a characteristic of undercooled liquids and glasses. However, for a high-temperature fluid, the free energy is dominated by a single valley and the system quickly reaches the minimum in that valley (or basin) independent of the initial conditions. Under these circumstances the property of a single dynamical trajectory can be used to determine effective ergodic behavior. This approach has the advantage of removing the need for the computation of two separate trajectories. The basic concept behind this approach to probing ergodicity is the statistical equivalence of the atoms or molecules which make up a fluid in thermal equilibrium. This measure, to be referred to as the fluctuation metric and to be denoted by $\Omega(t)$, is also useful when the free-energy profile has multiple minima provided the observation time scale is less than the time required for activated transitions from one metastable well (or basin) to another. This is discussed further in Sec. IV.

The fluctuation metric is defined in terms of time averages of the energies of individual particles. Let $e_{ja}(t)$ be the time-averaged energy of particle j over the trajectory a,

$$e_{ja}(t)=\frac{1}{t}\int_0^t ds\, E_j(s;a)\ , \tag{2.3}$$

where $E_j(s;a)$ is the energy of particle j at time s on trajectory a. If the total potential energy is pairwise additive then $E_j(s;a)$ is the sum of the kinetic energy and one-half of the potential-energy terms involving particle j. The parameter a indicates that the time evolution of the system is obtained starting from a trajectory labeled a. Such a label is not needed for ergodic systems because in that case, $e_{ja}(t)$ tends to a well-defined value for long times regardless of the initial conditions. This limiting value, $\overline{e_a(t)}$, is an average over all particles of the system,

$$\overline{e_a(t)}=\frac{1}{N}\sum_{j=1}^{N} e_{ja}(t)\ . \tag{2.4a}$$

In analyzing experimental results on macroscopic systems using statistical mechanics it is normally assumed that the properties of a single large system do not differ from that computed using a configurational average over an ensemble of systems. Thus the results of an experiment done on a single sample are expected to coincide with theoretical calculations in which an average over an ensemble is performed. Properties which obey this criterion are said to be self-averaging. Therefore Eq. (2.4) is equivalent to an ensemble average provided energy of the individual particles is self-averaging, i.e.,

$$\lim_{t\to\infty}\overline{e_a(t)}=\lim_{N\gg 1}\frac{1}{N}\sum_{j=1}^{N} e_{ja}(t)\equiv\langle e\rangle \tag{2.4b}$$

where $\langle\ \rangle$ denotes an ensemble average.

The fluctuation metric is defined as

$$\Omega_a(t)=\frac{1}{N}\sum_{j=1}^{N}[e_{ja}(t)-\overline{e_a(t)}]^2\ . \tag{2.5}$$

If the system is effectively ergodic then it is easy to show, using the law of large numbers, that $\Omega_a(0)$ is $\langle\varepsilon^2\rangle-\langle\varepsilon\rangle^2$ is the energy per particle. Thus $\Omega_a(0)$ gives the equilibrium fluctuations in the energy of a particle. For ergodic systems, where the subscript a is unnecessary, the asymptotic scaling behavior of $\Omega(t)$ can be computed by noting that Eq. (2.5) can be rewritten as

$$\Omega(t)=\frac{1}{t^2}\int_0^t ds_1\int_0^t ds_2\frac{1}{N}\sum_{j=1}^{N}\delta E_j(s_1)\delta E_j(s_2) \tag{2.6a}$$

where

$$\delta E_j(s)=E_j(s)-\overline{E(s)} \tag{2.6b}$$

and $\overline{E(s)}$ is the average energy per particle at time s. If we make use of the weak law of large numbers and replace the sum over the individual particles by an ensemble average we can write Eq. (2.6a) as

$$\Omega(t)/\Omega(0)=\frac{1}{t^2}\int_0^t ds_1\int_0^t ds_2 C_e(s_1,s_2)/C_e(0,0) \tag{2.7a}$$

where

$$C_e(s_1,s_2)=\frac{1}{N}\sum_{j=1}^{N}\delta E_j(s_1)\delta E_j(s_2)\ . \tag{2.7b}$$

If the property $\delta E_j(t)$ is self-averaging, which is expected to be the case for ergodic systems, then $C_e(s_1,s_2)$ can be identified as an equilibrium time correlation function. For equilibrium correlation functions there is no preferred origin of time and thus $C_e(s_1,s_2)$ can only depend on $|s_1-s_2|$. Under these circumstances, $\Omega(t)$ for long times becomes[15]

$$\Omega(t)/\Omega(0)\approx 1/D_\Omega t \tag{2.8a}$$

where

$$D_\Omega=\lim_{t\to\infty}1\Big/\left[2\int_0^t ds\, C_e(s)/C_e(0)\right]\ . \tag{2.8b}$$

Notice that the notion of self-averaging has been repeatedly used to obtain Eq. (2.8b).

We wish to emphasize that $\Omega(t)$ can be viewed as a measure of whether or not the energy is self-averaging on the time scale of the simulation. To make the point in general let us consider at time s, an arbitrary physical observable $O_j(s)$ associated with particle j. The time-averaged value of $O_j(s)$ is

$$\overline{O_j(t)}=\frac{1}{t}\int_0^t ds\, O_j(s)\ . \tag{2.9}$$

The fluctuation metric associated with O can be constructed as

$$\Omega_0(t)=\frac{1}{N}\sum_{j=1}^{N}[O_j(t)-\overline{O(t)}]^2 \tag{2.10a}$$

with

$$\overline{O(t)}=\frac{1}{N}\sum_{j=1}^{N}\overline{O_j(t)}\ . \tag{2.10b}$$

Thus the value of $O(t)$ for large enough N is expected to differ negligibly from an average over an ensemble of systems provided self-averaging occurs. The assumption that $\overline{O(t)}$ for large t is identical to an ensemble average of course holds only for ergodic systems. Thus if $\Omega_0(t)$ is nonzero for times comparable to the observation time, that is an indication of the lack of self-averaging for the observable O.

B. Energy metric $d(t)$

The energy metric $d(t)$ is also defined in terms of time averages of energies of individual particles and is constructed as follows. Two independent initial states of the system are chosen, and these are labeled a and b. The time average energy of particle j is computed using Eq. (2.3) for both trajectories a and b. Let these energies be $e_{ja}(t)$ and $e_{jb}(t)$ corresponding to the two independent trajectories a and b, respectively. The trajectories labeled a and b differ because they originate from two distinct initial conditions. The time needed for them to become "equivalent" is roughly the mixing time. The energy metric $d(t)$, which is related to a Euclidian norm in the space of the variables $e_{ja}(t)$ and $e_{jb}(t)$, is given by the square of the energy difference between the energy averages of the particles over the two trajectories, namely,

$$d(t)=\frac{1}{N}\sum_{j=1}^{N}[e_{ja}(t)-e_{jb}(t)]^2 , \tag{2.11}$$

where the sum runs over all the N particles of the system. For ergodic systems, it is easy to show that $d(0)=2(\langle \varepsilon^2\rangle-\langle \varepsilon\rangle^2)$, i.e., $d(0)$ is twice the value of the fluctuation metric. If the system is ergodic, both trajectories, a and b effectively cover (in the coarse-grained sense) the entire energy surface in phase space over a sufficiently long-time interval and therefore the time-averaged energies of the particles approach the same values for long times. Therefore for an ergodic system we expect

$$\lim_{t\to\mathcal{T}}[e_{ja}(t)-e_{jb}(t)]=0 \tag{2.12}$$

for each particle j. This is because the time averages for the system reach their equilibrium values in a time $\mathcal{T}$ independent of any initial condition and $e_{ja}(\mathcal{T})=e_{jb}(\mathcal{T})$ is then the time-averaged value of the energy of particle j. Our experience indicates that an acceptable estimate for $\mathcal{T}$ is obtained by determining when $d(\mathcal{T})/d(0)=0.01$ is satisfied. For a fluid, a stronger statement can be made, namely, that the average energies of all particles of a given species become identical in the limit of $t\to\mathcal{T}$. This is not the case for a glass where structural relaxation takes place extremely slowly. In this case the long-time limiting values for a particular species are distributed broadly about an average value and the distribution depends on which trajectory in phase space is followed. This is discussed further in Sec. IV.

In I we showed that the functional form describing the time dependence of $d(t)$ is identical for various thermodynamic states. The short-time value of $d(t)$ decreases rapidly and we have not attempted to determine the precise functional form. The behavior of $d(t)$ for times greater than a transient time t_I is characterized by a single parameter, namely, a "diffusion constant" D_E associated with the exploration of phase space. The decay of $d(t)$ for $t>t_I$ was shown to obey the dynamical scaling form

$$d(t)=d(0)f(tD_E) , \tag{2.13a}$$

where

$$f(x)=\begin{cases}1, & x\to 0\\ 1/x, & x\gg 1 .\end{cases} \tag{2.13b}$$

The characteristic time t_I depends on the nature of the interaction potential and on the thermodynamic state. The reciprocal of D_E is roughly the time required for effective ergodicity to be obtained. We emphasize that this "diffusion coefficient" refers to motion in the space of the set of $e_j(t)$'s and not to the configurational diffusion of the particles in the fluid. The diffusion process is more analogous to the familiar Arnold diffusion involving the excursion of the action along resonance layers.[4] One of the objectives of the present investigations is to examine the temperature and composition dependence of D_E for a mixture of soft spheres, the system used to illustrate the properties of supercooled liquid and glassy states in our earlier studies.[16]

We now derive the scaling relation given in Eq. (2.13) which had been previously established by us numerically.[1] This derivation is valid only for ergodic systems. In order to derive Eq. (2.13) it is useful to establish a relationship between $d(t)$ and $\Omega(t)$, and this can be done provided the system is effectively ergodic. For such a system, we add and subtract

$$\overline{e_a(t)}=\frac{1}{N}\sum_{j=1}^{N}e_{ja}(t)=\frac{1}{N}\sum_{j=1}^{N}e_{jb}(t) \tag{2.14}$$

to $d(t)$. Now the energy metric can be written as

$$d(t)=\Omega_a(t)+\Omega_b(t)-\frac{2}{N}\sum_{j=1}^{N}[e_{ja}(t)-\overline{e_a(t)}][e_{jb}(t)-\overline{e_b(t)}] \tag{2.15}$$

where $\Omega_a(t)=\Omega_b(t)$ is given by Eq. (2.5). Notice that Eqs. (2.14) and (2.15) are strictly valid only for ergodic systems. In systems in which the free-energy surface has multiple minima, $\overline{e_j(t)}$, $\Omega_a(t)$, and $\Omega_b(t)$ will depend on the trajectory labels for times less than that required for activated processes to take place. This is expected to be the case in glassy states. The last term of Eq. (2.15), which is the cross term between the two trajectories, becomes

$$X_{ab}(t)=-\frac{2}{t^2}\int_0^t ds_1\int_0^t ds_2\frac{1}{N}\sum_{j=1}^{N}\delta E_{ja}(s_1)\delta E_{jb}(s_2) . \tag{2.16}$$

For ergodic systems one can view Eq. (2.16) as an integral involving an unusual equilibrium time correlation function whose argument is expected to depend on s_1-s_2.

For ergodic systems the distribution of individual particle time-averaged energies, $e_{ja}(t)$, is expected to be symmetrically distributed around the thermodynamic mean value per particle, $\overline{e_a(t)}$.[1] The mean energy per particle for a given species is rapidly approached by the $e_{ja}(t)$ assuming that the individual particle energies are self-averaging. The cross term then can be rewritten by replacing the sum over j by an ensemble average, i.e.,

$$X_{ab}(t)=-\frac{2}{t^2}\int_0^t ds_1\int_0^t ds_2\langle \delta E_{ja}(s_1)\delta E_{jb}(s_2)\rangle \ . \tag{2.17}$$

The ensemble average $\langle \delta E_{ja}(s_1)\delta E_{jb}(s_2)\rangle$ becomes

$$\langle \delta E_{ja}(s_1)\delta E_{jb}(s_2)\rangle=\langle \delta E_{ja}(s_1)\rangle\langle \delta E_{jb}(s_2)\rangle=0 \ . \tag{2.18}$$

The validity of Eq. (2.18) follows from the fact that this average represents an ensemble average of quantities which are independent and have zero mean. Thus for ergodic systems under the assumption of self-averaging, it follows that $X_{ab}(t)=0$. This leads us to conclude

$$d(t)=2\Omega(t) \ . \tag{2.19}$$

The scaling property displayed in Eq. (2.13) follows from Eqs. (2.19) and (2.8a), i.e.,

$$d(t)/d(0)=\Omega(t)/\Omega(0) \ . \tag{2.20}$$

The right-hand side of Eq. (2.20) obeys the characteristic $1/t$ behavior for long times. Therefore it follows that $d(t)$ should be described by our previously postulated scaling behavior for ergodic systems. Interestingly it follows from Eq. (2.20) that $D_\Omega \cong D_E$ for systems which are expected to be effectively ergodic on the time scale $\mathcal{T}$. It is not surprising because for this case one has only a single valley structure (a liquid for example) and consequently the rate of exploration of phase space can be described by a single parameter.

For glassy systems for which one has a multivalley structure in phase space the fluctuation metric manifestly depends on the initial conditions, i.e., the Ω's depend on the trajectory labels. In this case $d(t)$ will differ from $\Omega(t)$ for times less than that needed for the two trajectories to become equivalent. So when the phase space exhibits a multivalley structure, $d(t)$ and $\Omega(t)$ probe entirely different aspects of the dynamical approach to equilibrium. The energy metric can be used to investigate the rare activated processes connecting the set of configurations belonging to two distinct free-energy minima. On the other hand, $\Omega(t)$ is a measure of relaxation processes that occur on a single trajectory. The combination of the two metrics offers the prospect of exploring the distinction between processes involving movement between free-energy minima and those occurring within a specified free-energy minimum.

III. COMPUTATIONS

The details of the model and the computational methods used are discussed elsewhere[16] so only a summary is provided here. The binary model alloy used here for illustration of the ideas given in the preceding section has been recently studied extensively.[16–20] The model consists of a set of $N_1+N_2=N$ particles interacting via a softly repulsive potential of the form

$$\phi_{AB}(r_{ij})=\varepsilon(\sigma_{AB}/r_{ij})^{12} \ , \tag{3.1}$$

where $A,B=1,2$ and r_{ij} is the distance between particle i of type A and particle j of type B. The size of the type-1 particle is given by $\sigma_{11}=1$. Two different values for the size of the type-2 particles are considered, namely, $\sigma_{22}=1.1$ and 1.3. The value of the cross diameter is taken to be $\sigma_{12}(\sigma_{11}+\sigma_{22})/2$. The mass of the type-1 particles, m_1, is taken as the unit of mass and the mass of type-2 particles is $2m_1$. The unit of time is

$$\tau=(m_1\sigma_{11}^2/\varepsilon)^{1/2} \ . \tag{3.2}$$

All times are reported in these units. The composition of a mixture is specified by $X=N_1/N$ and for the results reported here, $N=500$. Finally, for the soft-sphere mixtures, it has been found empirically that it is possible to specify the thermodynamic state of the system in terms of an effective reduced density or coupling constant which is[16,17]

$$\Gamma_{\text{eff}}=n^*(\sigma_{\text{eff}}/\sigma_{11})^3/(T^*)^{1/4} \ . \tag{3.3}$$

Here $n^*=N\sigma_{11}^3/V$ is the reduced number density (V is the volume of the system), $T^*=k_BT/\varepsilon$ is the reduced temperature, and σ_{eff} is the one-fluid van der Waals equivalent diameter.[21] The compressibility factor PV/Nk_BT, for example, depends only on this natural coupling parameter Γ_{eff} for the soft-sphere mixture. For this model, the equilibrium liquid states have values of $\Gamma_{\text{eff}}\le 1.15$ and glassy states have satisfying $\Gamma_{\text{eff}}>1.5$.[16–19] A state is termed glassy if the single-particle self-diffusion coefficient is vanishingly small and if the pair correlation function displays no crystallization signature.

The calculation of $d(t)$ and $\Omega(t)$ for a fluid state with a given total energy was performed in the following way. First, a configuration with the desired E_0 was constructed, usually by scaling the velocities of the N particles. Next, this configuration was allowed to evolve at the constant total energy E_0 for a time interval of 40τ to 80τ to ensure that it was in "equilibrium." The resulting configuration is called α. Next, starting with α, a 200τ run was made and $\Omega(t)$ was determined. The final configuration is called β. A second 200τ run was made starting from β and a second realization of $\Omega(t)$ was obtained. The final configuration of that run is γ. The next step was to perform a two-trajectory simulation using β and γ as starting points. The energy metric $d(t)$ is constructed during the two-trajectory run which is of 100τ duration. While in principle β and γ are on the same trajectory, the configurations for both β and γ are recorded with five significant figures and this truncation of the configuration ensures that the two trajectories are in fact distinct. It should be added that we reached similar conclusions for the fluid states by constructing $d(t)$ using two clearly distinct trajectories, i.e., trajectories whose initial points are manifestly different.

While the above procedure for obtaining the metrics is valid for examining the dynamical relaxations in the liquid, care should be taken to ensure that the trajectories are truly distinct when one is concerned with the glassy states. This is in general true if the free-energy hypersurface has several minima into which the system may be locked for long times. Under this condition, if a and b are two initial configurations belonging to two separate valleys, then for times less than that required for the mixing of a and b [which is roughly equal to $\exp(\Delta F/k_B T)$ with ΔF being the free-energy barrier separating the minima] $d(t)$ should be different from $\Omega(t)$.

In order to observe the difference between $\Omega(t)$ and $d(t)$ care must be taken to ensure that the starting configurations belong to separate minima so that the two trajectories are indeed distinct. In our simulations we used the following procedure when examining $d(t)$ and $\Omega(t)$ for glassy states for the $\sigma_{22}=1.1\sigma_{11}$ case. A total of three distinct glassy states with $\Gamma_{\text{eff}}\cong 1.7$ and $X=0.5$ were generated by quenching initially liquid states, $\Gamma_{\text{eff}}<0.95$, at three different rates until the desired glassy state was reached. The quenches were performed by rescaling the particle momenta at each time step by a factor of 0.9, 0.999, and 0.9999, respectively. These quench rates are fast enough to avoid crystallization of the sample while the $1.4<\Gamma_{\text{eff}}<1.5$ range was traversed. The resulting configurations were then used to construct $d(t)$ and $\Omega(t)$.

To ensure that truly independent initial configurations were being prepared, we followed yet another procedure for the glassy states for the system with the diameter ratio $\sigma_{22}/\sigma_{11}=1.3$. Four separate dynamical trajectories for the state with $\Gamma_{\text{eff}}=1.6$ were analyzed. The initial configuration for one of the trajectories was obtained by directly quenching a well-equilibrated fluid state at $\Gamma_{\text{eff}}=1.0$ to $\Gamma_{\text{eff}}=1.6$ by rescaling the momentum of each particle by 0.999 at each step until the desired state was reached. The other glassy state trajectories were obtained from the liquid state with $\Gamma_{\text{eff}}=1.0$ by first moving away from the energy shell to a different fluid state with either higher or lower energy and allowing the system to evolve for some time. Next the system was returned to the state with $\Gamma_{\text{eff}}=1.0$ and allowed to equilibrate. Then the system was quenched to the $\Gamma_{\text{eff}}=1.6$ glassy state. This procedure ensures that the four glassy trajectories were independent.

IV. RESULTS AND INTERPRETATION

We illustrate the dynamical properties of $d(t)$ and $\Omega(t)$ using the soft-sphere mixture as a model. The properties of these metrics discussed in Sec. II are established numerically. It should be emphasized that these ideas can be used for other systems as well.[6,22] In fact the general scaling properties derived in Sec. II are universal and only depend on the notions of ergodicity and self-averaging. This has been established already in applications to liquids consisting of Lennard-Jones mixtures and liquid water.[6,22]

A. Time dependence of $d(t)$ and $\Omega(t)$

The energy metric for a slightly supercooled state, $\Gamma_{\text{eff}}=1.22$ with $\sigma_{22}=1.1\sigma_{11}$, is displayed in Fig. 1. The fact that the long-time limit of $d(t)$ is 0 indicates that this system is effectively ergodic. The fluctuation metrics $\Omega_a(t)$ and $\Omega_b(t)$, and the cross-trajectory term $X_{ab}(t)$ [Eq. (2.16)] are also displayed. The two curves for $\Omega_a(t)$ and $\Omega_b(t)$ are superimposable and this suggests that the system is effectively ergodic for $\Gamma_{\text{eff}}=1.22$. It is noteworthy that for this state the cross terms rapidly vanish. This is in accord with the argument that for this value of Γ_{eff} the variables $e_{jb}(t)$ are self-averaging and $e_{jb}(t)$ should tend to $\overline{e_b(t)}$ which equals $\overline{e_a(t)}$. Thus one expects the set of average values, $\{e_{jb}(t)\}$, to be sharply distributed about $\overline{e_b(t)}$ and this leads to a rapid cancellation of the cross term. Notice that because we are dealing with a binary mixture, the distribution of the time-averaged values of the individual particle energies has two peaks, one for the smaller particles and one for the larger particles.[1] For this state the system has effectively one valley in the free-energy surface, and the dynamical trajectory uniformly samples the allowed configurations on the time scale of the simulation. This is independent of the initial conditions. The scaling behavior of Eq. (2.8a) is illustrated in Fig. 2. There $d(0)/d(t)$, the reciprocal of the energy metric, and the corresponding quantities for the Ω's are shown as functions of the time for $\Gamma_{\text{eff}}=1.22$. It is evident that both $d(t)$ and $\Omega(t)$ ex-

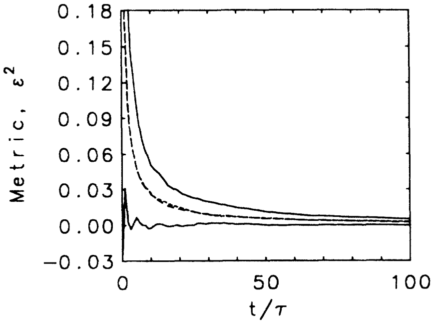

FIG. 1. The energy metric $d(t)$ (solid line), the fluctuation metrics $\Omega(t)$ (dashed lines), and the cross-trajectory term $X(t)$ (solid line fluctuating about zero), are shown for the slightly supercooled state with $\Gamma_{\text{eff}}=1.22$.

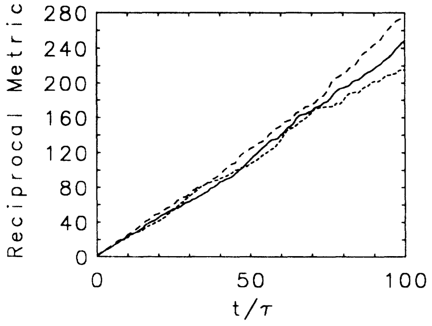

FIG. 2. The reciprocals, normalized to unity at $t=0$, of the energy metric (solid line) and of the fluctuation metrics (dashed lines) for the $\Gamma_{\text{eff}}=1.22$ state are shown as functions of the time. The approximately linear behavior of these quantities illustrates the universal form of these functions. The energy-space diffusion coefficients were obtained from the slope of such plots.

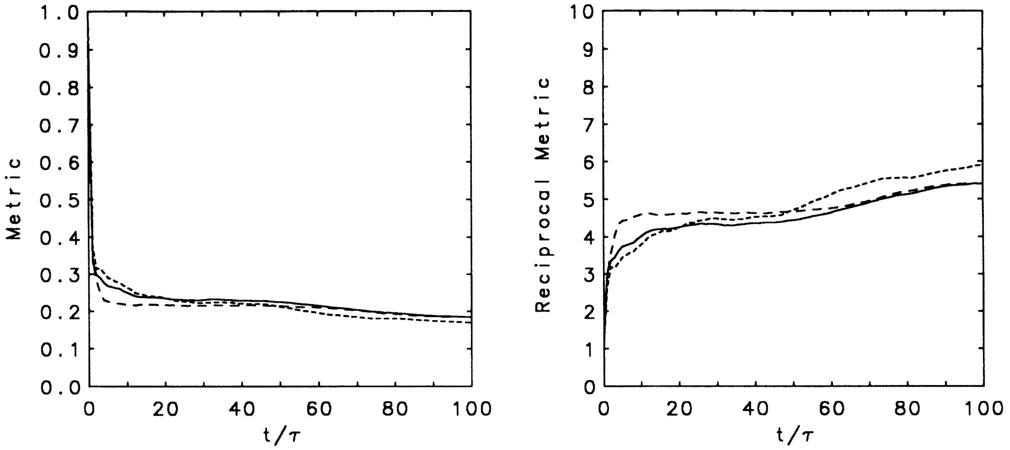

FIG. 3. The energy metric $d(t)/d(0)$ (solid line), the fluctuation metrics $\Omega(t)/\Omega(0)$ (dashed lines), and the reciprocals of these metrics are shown for the glassy state with $\Gamma_{\text{eff}}=1.6$ of the system with $\sigma_{22}/\sigma_{11}=1.3$. The trajectories labeled a and b were used here.

hibit the characteristic $1/t$ decay predicted for ergodic systems.

We now consider the case of $\sigma_{22}=1.3\sigma_{11}$. The value of 1.3 for the ratio of the particle sizes was chosen so that we could examine $d(t)$ in the range of coupling constant values, $1.4<\Gamma_{\text{eff}}<1.5$. In this range for the 1.1 size ratio case, crystallization occurs during the time required to determine the long-time value of the metric but it does not for the larger size ratio. The metrics in the liquid state for the larger size ratio case behave qualitatively in the same manner as for the case with $\Gamma_{\text{eff}}=1.22$ shown in Figs. 1 and 2. In order to illustrate the behavior of the metrics in the glassy state, four independent trajectories, labeled a, b, c, and d were computed for the value of the coupled constant $\Gamma_{\text{eff}}=1.6$. The details of the generation of the trajectories are discussed in Sec. III.

In Figs. 3–6, plots of both $d(t)/d(0)$ (solid line) and $\Omega(t)/\Omega(0)$ (dashed lines) and their reciprocals are shown as functions of t for various trajectories given in the figure captions. Although all the curves roughly yield the characteristic scaling behavior there are some significant differences. The long-time values for $d(t)$ and $\Omega(t)$ are critically dependent on the trajectory labels. This is a clear indication that in glassy systems the initial conditions are important for the dynamics. Thus the properties of the glassy states can be computed only by averaging over an ensemble of initial conditions.[23] In all these figures, the long-time limit of the metrics is not zero, implying that the system is not effectively ergodic on this time scale. The nonzero value of $\Omega(t)$ implies that the associated property, namely the energy per particle, may not be self-averaging in the glassy systems. This implies that one could see variation from sample to sample. We wish to caution the reader that this conclusion is really based on a long- but certainly finite-time simulation and this may not even hold on experimental time scales. It appears that these metrics rapidly drop to about $\frac{1}{3}$ of their initial value within about 10τ and slowly decrease to about a value of 0.15–0.25 for $t\cong 100\tau$. The rate of decay at long times (and hence the associated diffusion con-

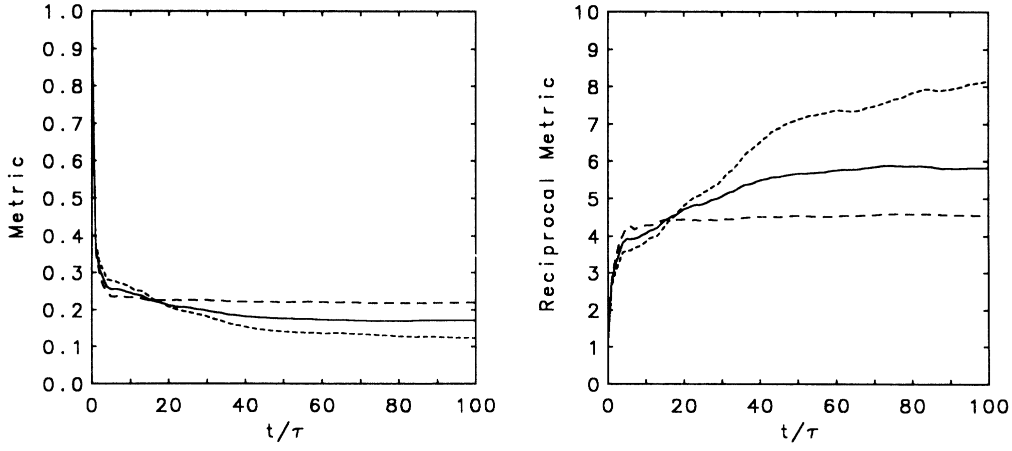

FIG. 4. Same as Fig. 3 except that trajectories a and c were used.

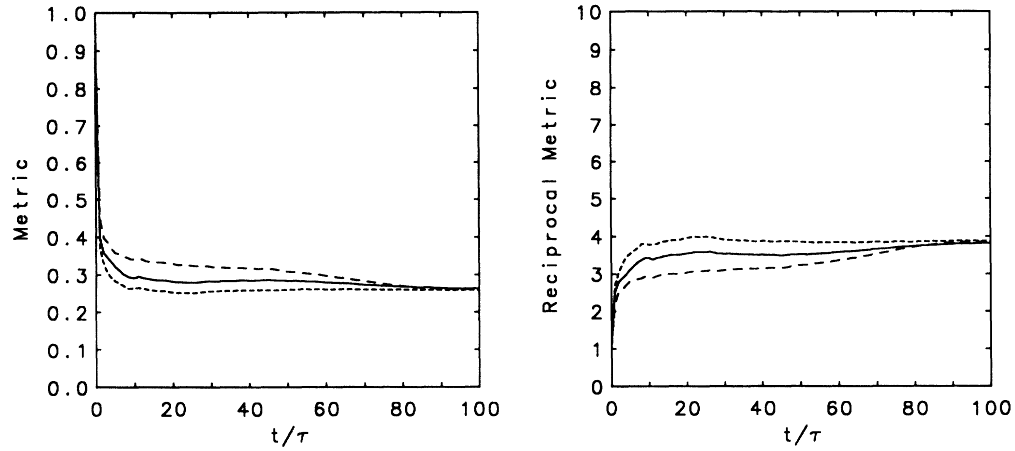

FIG. 5. Same as Fig. 3 except that trajectories *a* and *d* were used.

stants) also depends on the trajectory labels.[24] Hence there is a distribution of the diffusion constants and the exploration of the configuration space in glasses is dependent on the preparation history.

To further illustrate the dependence of the long-time values of the energy metrics and the associated diffusion constants D_E and D_Ω on the history of the state preparation we performed the following computations. The dynamical trajectories *a*, *b*, *c*, and *d* were calculated for long times and the metrics were computed using different segments of the trajectory. If the systems were ergodic then averages over two different long and independent segments would yield results that differ negligibly from each other. In Figs. 7 and 8 we show the results for $d(t)$ and $\Omega(t)$ (for the trajectories labeled *a* and *b*) computed using different segments. It is obvious that the values of the scaling parameters D_E and D_Ω as well as the long-time limiting values are dependent on the trajectory labels. The results shown in Fig. 8 were obtained by continuing the trajectories *a* and *b* for an interval of 100τ beyond that needed to compute the metrics displayed in Fig. 7. Thus one would expect some annealing in the system. The rearrangement of particles would then be expected to lead to the monotonic decrease of $d(t)$ and $\Omega(t)$. However, a comparison of Figs. 7 and 8 indicates that the metrics over different segments do not decrease monotonically. The changes in the long-time values are indicative of structural rearrangements and possible transitions from one minimum to another. The difference in diffusion constants inferred from Figs. 7 and 8 implies that when structural rearrangements occur, the systems may have made a transition to a region in which the bottlenecks for mixing of two configurations are different. Thus in the glassy systems one could have a wide range in the distribution of free-energy barriers—a notion that has certainly been advanced in the past.[3] The analysis done here may be a way of probing these properties.

B. Diffusion coefficients D_E and D_Ω

The analogy between the dynamical scaling obeyed by the probes of ergodicity, $d(t)$ and $\Omega(t)$, and the finite-

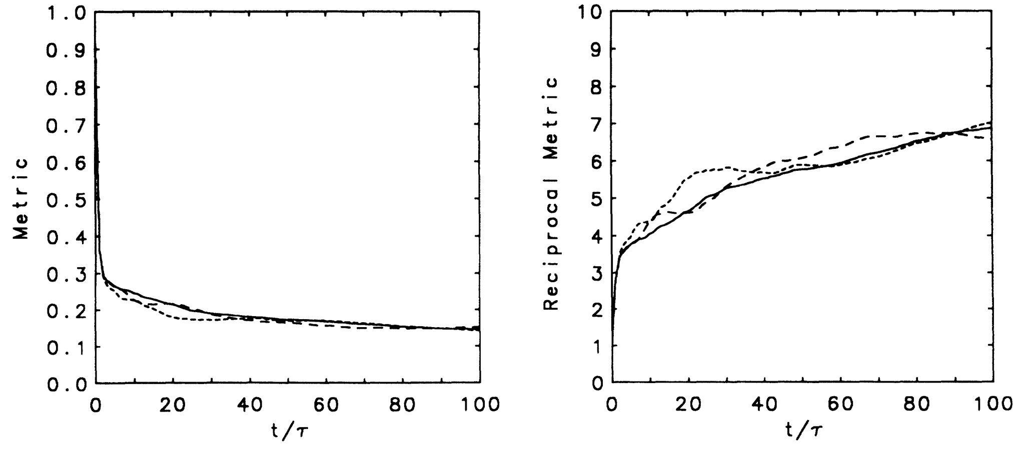

FIG. 6. Same as Fig. 3 except that trajectories *b* and *d* were used.

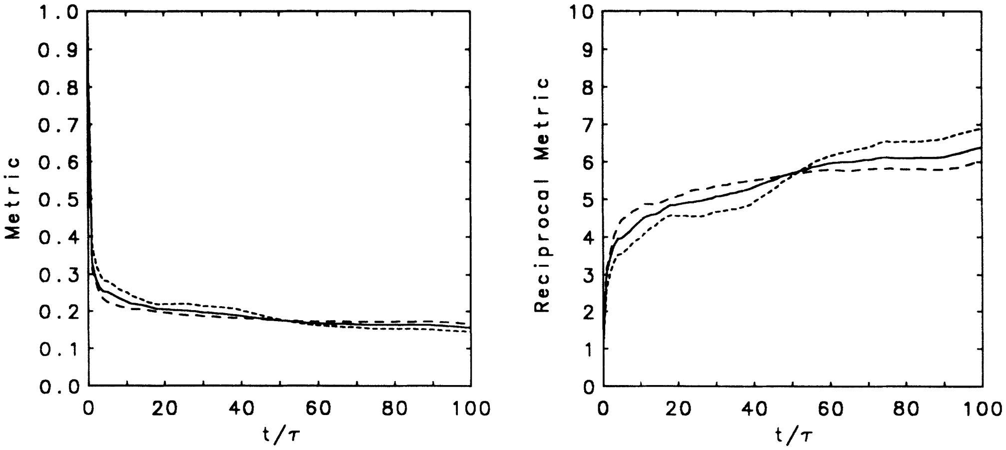

FIG. 7. An extension of the trajectories of Fig. 3 for an additional 100τ.

time scaling behavior found for the maximal Lyapunov exponent for mixing systems[13,14] leads us to suggest that the characteristic parameters D_E and D_Ω essentially determine the rate of exploration of the accessible configuration space. Specifically it is found that for billiard systems[13,14] the time-dependent maximal Lyapunov exponent

$$\gamma(t)=\langle \ln \| Df^t(x_0)\cdot\hat{e}\| \rangle \ , \tag{4.1}$$

where $Df^t(x_0)$ is the Jacobian matrix associated with the flow f^t, $\hat{e}$ is a unit vector, and $\langle\ \rangle$ is an average over x_0, obeys the scaling form[13,14]

$$\gamma(t)/\gamma_\infty = 1 - A/\gamma_\infty t \ . \tag{4.2}$$

Here γ_∞ is the maximal Lyapunov exponent. The analogy with Eq. (2.8a) suggests that the diffusion coefficient D_E (or D_Ω) plays the role of the maximal Lyapunov exponent γ_∞. This suggest that $\tau_E \approx 1/D_E$ is the characteristic time required for the mixing of two distinct configurations. The parameter D_E is physically analogous to the rate of Arnold diffusion in action space.[1] In the glassy state τ_E gives an indication of the barrier separating the two different metastable minima. The approximate magnitude of the bottleneck, ΔF, separating the two minma may be obtained by writing D_E as

$$D_E^{-1} \approx \tau \exp(\Delta F/k_B T) \ . \tag{4.3}$$

For times less than that required for activated processes to become important (which grows rapidly below the glass transition temperature), $\tau_\Omega \approx 1/D_\Omega$ would describe the time needed for effectively sampling the configurational space within a specified minimum. In addition the possible differences between D_Ω and D_E can provide information about the underlying free-energy surface. In light of the importance of these parameters we have attempted to obtain the dependence of D_E and D_Ω on the composition and on the temperature of the mixture. We wish to emphasize that D_E and D_Ω have nothing to do with the single-particle self-diffusion coefficient.[25] The correlation function appearing in $\Omega(t)$ is truly a multiparticle dynamical function. The results for D_E and D_Ω for the two choices of particle diameter

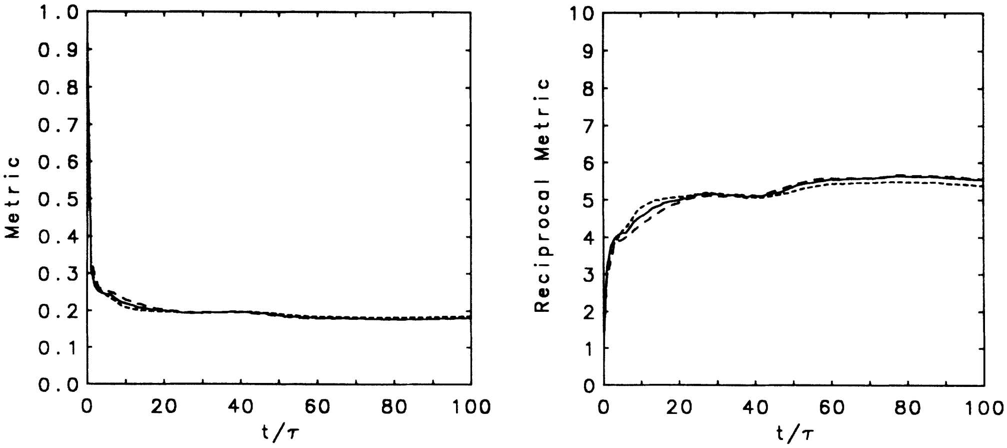

FIG. 8. An extension of the trajectories of Fig. 7 for an additional 100τ.

TABLE I. The states examined and the resulting energy-space diffusion coefficients.

X	T^*	Γ_{eff}	D_Ω	D_E
		$\sigma_{22}=1.1\sigma_{11}$		
0.2	1.01	0.90	4.5	4.5
	0.253	1.27	1.6	1.4
0.5	0.593	1.12	3.1	3.3
	0.429	1.22	2.2	2.1
	0.396	1.24	1.9	2.2
	0.372	1.26	1.8	1.9
	0.331	1.30	1.2	1.2
	0.303	1.33	1.2	0.9
	0.286	1.35	0.9	0.7
	0.273	1.37	0.7	0.6
	0.258	1.38	0.7	0.6
0.8	0.707	0.95	2.8	3.0
	0.313	1.16	1.8	1.7
		$\sigma_{22}=1.3\sigma_{11}$		
0.5	1.41	1.22	4.1	4.1
	1.09	1.30	2.0	1.9
	0.79	1.40	0.5	0.6
	0.75	1.43	0.08	0.08

are presented below.

The scaling behavior of $d(t)$ and $\Omega(t)$ [cf. Eqs. (2.8a), (2.13)] was used to numerically obtain D_E and D_Ω for several different temperatures and compositions for the soft-sphere mixture. The states examined and the values of D_E and of D_Ω are shown in Table I. Most of the effort was devoted to the equimolar mixture ($X=0.5$). A check was made on composition dependence by examining a few states with $X=0.2$ and with $X=0.8$ for the $\sigma_{22}=1.1\sigma_{11}$ case. For the case with $\sigma_{22}=1.1\sigma_{11}$ we found that the system invariably crystallized[20,26] when the system was annealed in the interval $1.4\leq\Gamma_{\text{eff}}\leq 1.5$. This prevented us from obtaining meaningful values of D_E and D_Ω close to the glassy state for this size ratio. In order to probe the behavior of these characteristic coefficients for Γ_{eff} near the glassy region we considered the larger size ratio. In this case crystallization is easily avoided (on the time scale of our simulation) and the behavior of D_E and D_Ω close to and below T_g can be examined.

The energy-space diffusion coefficients D_E and D_Ω are displayed in Fig. 9 as functions of Γ_{eff}^4. From Eq. (3.3) it follows that Γ_{eff}^4 is proportional to $1/T$. Several features of this plot are worth noting. We see that these quantities have composition dependence not contained in Γ_{eff}. Unlike the thermodynamic properties which only depend on Γ_{eff} the characteristic coefficients D_E and D_Ω exhibit departures from the corresponding scaling. Figure 9 also shows that D_E and D_Ω depend on the size ratio. The approximate equality of D_E and D_Ω for a given condition confirms the analysis of Sec. II where it was shown that for the systems considered here, ergodic convergence information can be obtained from single-trajectory studies as well as from the two-trajectory calculations.

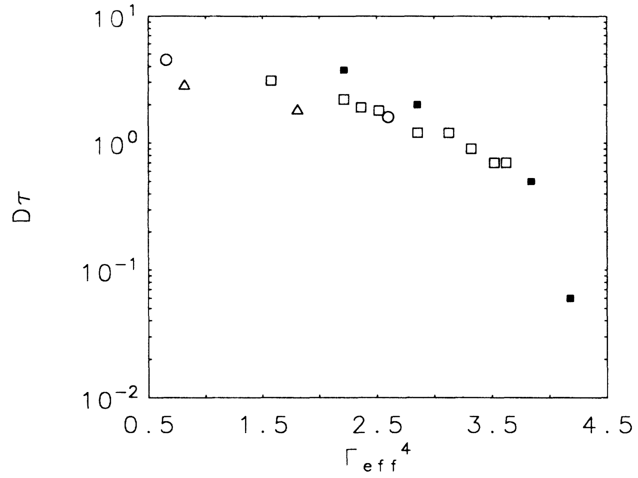

FIG. 9. An Arrhenius plot of the characteristic coefficients D. The abcissa, Γ_{eff}^4, is proportional to $1/T$. The open symbols are for the $\sigma_{22}/\sigma_{11}=1.1$ case with $X=0.2$ (○), $X=0.5$ (□), and $X=0.8$ (△) and the solid squares are for the $\sigma_{22}/\sigma_{11}=1.3$ case with $X=0.5$.

The most dramatic observation is the striking temperature dependence of the diffusion coefficients. While it is not possible to make strong arguments based on this plot, the pattern of the points suggests that the nature of the exploration of phase space changes character at two places. The first change occurs at about the fluid-solid transition ($\Gamma_{\text{eff}}^4\approx 2$) where the slope of the plots appears to change. The second change occurs in the strongly supercooled region where the slope again increases. The apparent activation energy for mixing increases at these two points. It is clear from Fig. 9 that for $\sigma_{22}/\sigma_{11}=1.3$ the characteristic coefficients D_E and D_Ω exhibit non-Arrhenius behavior when the temperature is close to the glass transition temperature. For this case the logical choice describing the temperature of D_E (or D_Ω) is the Vogel-Fulcher law, i.e.,

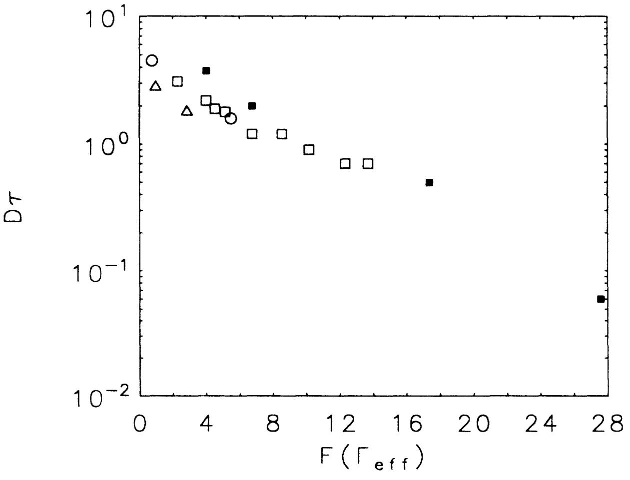

FIG. 10 A Vogel-Fulcher plot of the characteristic coefficients D. The abcissa, $F(\Gamma_{\text{eff}})$ defined in Eq. (4.5), has $\bar{\Gamma}=1.49$.

$$D_\alpha = A \exp[-B/(T-\bar{T})] \quad (\alpha = E \text{ or } \Omega) \tag{4.4}$$

where $\bar{T}$ is related to the apparent glass transition temperature and A and B are constants. A Vogel-Fulcher plot of the D's is shown in Fig. 10. There D versus $F(\Gamma_{\text{eff}})$, where

$$F(\Gamma_{\text{eff}}) = \Gamma_{\text{eff}}^4 / [1-(\Gamma_{\text{eff}}/\bar{\Gamma})^4] , \tag{4.5}$$

is the appropriate combination of Γ's for a $1/(T-\bar{T})$ plot, is displayed. A value $\bar{\Gamma} = 1.49$ produces a linear plot. From this analysis it is not possible to unambiguously identify the temperature at which one obtains an essential singularity in Eq. (4.4) as the ideal glass transition temperature. A more natural interpretation based on the entropy crisis is given below.

It appears that for the case with $\sigma_{22} = 1.1\sigma_{11}$ the behavior of the D's seems to be consistent with a simple Arrhenius behavior in the highly supercooled region (see Fig. 9). However, we believe that the general form of the temperature dependence of D_E and D_Ω is the Vogel-Fulcher behavior given in Eq. (4.4). The reason this behavior is not seen in the case of the smaller particle diameter ratio is as follows. In the region with $1.4 \leq \Gamma_{\text{eff}} < 1.5$, the system crystallizes upon annealing. The geometrical rearrangements needed for crystallization are possible because of the similarity in the size ratio of the particles. Thus the system locates the narrow pathway leading to crystallization on the annealing time scale and consequently the metastable glassy states are not probed. Thus the entropy crisis is avoided and consequently Vogel-Fulcher law behavior cannot be observed for this case.

The behavior of D given in Eq. (4.4) allows for a transparent interpretation of the Kauzmann paradox.[27,28] It is generally believed that upon vitrification there is a loss in the so-called configurational entropy and the temperature at which the entropy of the glass equals that of the crystal is denoted as the Kauzman temperature T_K.[29-30] Since D_E^{-1} is roughly the mixing time for configurations belonging to two different metastable valleys it follows that the loss in configurational entropy is a consequence of the breakdown of effective ergodicity. It is tempting to suggest that the characteristic temperature T_0 at which the shear viscosity of fragile glass forming substances diverges is precisely the temperature where the mixing time becomes infinite, i.e., $T_0 = \bar{T}$. Notice that at this temperature there is no reason to expect the configurational entropy to be strictly zero, which means T_0 is not necessarily equal to T_K.[31]

C. Distribution of energies of individual particles

In I it was shown that the distribution of time-averaged energies $P(e;t)$ provides some clear-cut differences between the equilibrium states of a liquid and nonequilibrium glassy states. Notice that the sum over the energies of all the particles is indeed a constant. However, the distribution of the individual energies can exhibit considerable dispersion. The fluctuation metric is in fact related to the moments of the distribution function $P(e;t)$. It has been previously shown that in the liquid state $P(e;t)$ becomes very sharply peaked about the two mean energies of the particles in a binary mixture. There is no overlap between the two peaks for long times. For glassy states with $\sigma_{22}/\sigma_{11} = 1.1$ there is considerable overlap between the two peaks, just as there is for an equilibrium liquid mixture for short times. By analyzing the dispersion of $P(e;t)$ we suggested that statistical equivalence of particles is lost when the liquid-to-glass transition takes place. This implies that permuting particles in the glassy state can lead to large dispersion in the distribution $P(e;t)$. This is to be contrasted with the situation in the liquid state in which the effect of particle permutation is completely lost on a short transient time scale. Thus the discrete permutation symmetry is broken when the transition from the liquid to glass takes place. This point is discussed further elsewhere.[1,32]

We focus here on the distribution $P(e;100\tau)$ for the glassy state with $\Gamma_{\text{eff}} = 1.6$ for the $\sigma_{22} = 1.3\sigma_{11}$ equimolar soft-sphere mixture. Several distribution functions were generated using the dynamical trajectories a, b, c, and d. A typical plot of $P(e;100\tau)$ as a function of e is shown in Fig. 11. An analysis of several such plots suggests the following. (i) The mean energies for each component approach the thermodynamic value quite rapidly. This observation is based on examining the behavior of both the fluid and glassy states for the $\sigma_{22} = 1.1\sigma_{11}$ case. We expect this to hold true for the $\sigma_{22} = 1.3\sigma_{11}$ case as well. (ii) The distribution functions for glassy states appear to be a superposition of two broad, nonoverlapping Gaussians. The energy ranges from 4ε to 7ε for the small spheres and from 7ε to 10ε for the larger spheres. This behavior is to be contrasted with that obtained for the glassy states for the $\sigma_{22} = 1.1\sigma_{11}$ case in which the distribution functions for the different sized spheres showed considerable overlap. (iii) When $P(e;100\tau)$ was constructed from independent segments of a long trajectory, "fine structure" is observed in the distribution functions. This "fine structure" appears to have a width of about 0.5ε. The location of such fine structure moves from sequence to sequence. An example of such a distribution function is shown in Fig. 12. The difference between Fig. 11 and Fig. 12 lies

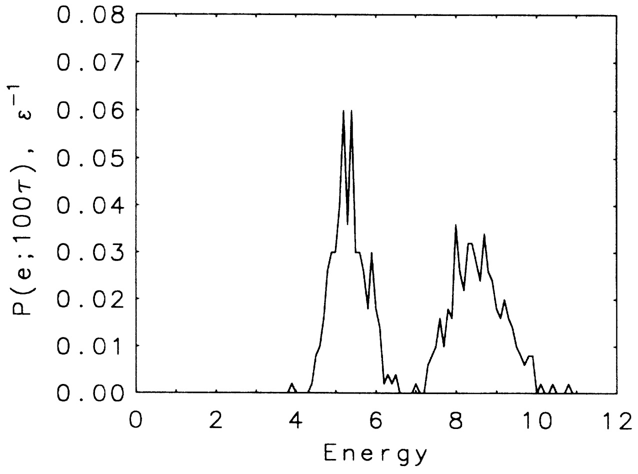

FIG. 11. The distribution of average energies at 100τ for a glassy state with $\sigma_{22} = 1.3\sigma_{11}$ and $\Gamma_{\text{eff}} = 1.6$.

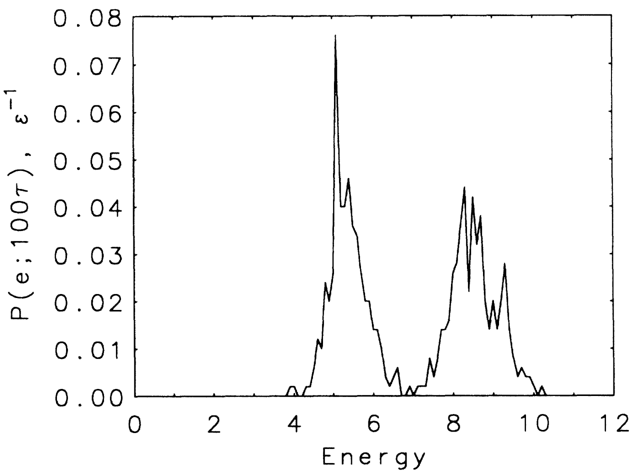

FIG. 12. The distribution of average energies at 100τ for a second glassy state with $\sigma_{22}=1.3\sigma_{11}$ and $\Gamma_{\text{eff}}=1.6$.

principally in the enhancement of peaks for energies between 5ε and 6ε and between 8ε and 9ε. An amplitude value of 0.05 in $P(e;t)$ involves about 12 particles. These changes in peak heights imply a redistribution of energies among several (typically 10–20) particles, a process that surely leads to local structural changes.[33] Thus the presence and movement of these spikes in $P(e;100\tau)$ is indicative that several particles are involved in the structural relaxation. These ideas are also in accord with recent studies of soft-sphere mixtures in which correlated jump motions involving 3–4 particles were explicitly monitored.[19] (iv) The metrics are related to the moments of the distribution function $P(e;t)$. Thus the metrics become sensitive to the details of the distributions for large differences from the means for each species. For example, a decrease in value of $\Omega(t)/\Omega(0)$ at 100τ from 0.25 to 0.15 correlates closely with the contraction of the wings of the peaks. Thus the decay of $d(t)$ and the ease with which structural relaxation proceeds is closely related to the tails of the distribution function. In the glassy state transport appears to be associated with the rearrangement of particles in the tail of $P(e;t)$, i.e., if there is sufficient amplitude in the tail of $P(e;t)$ one would expect structural relaxation in the system. In fact using this sort of idea one can argue that the average structural relaxation time scales as $\tau\approx\exp[(T_0/T)^2]$,[34,35] a form that has been used to fit viscosity data in certain glasses.[36]

V. CONCLUSIONS

In this paper we have suggested means of probing effective ergodic convergence in supercooled liquids and in glasses. Two measures, namely the energy metric $d(t)$ and the fluctuation metric $\Omega(t)$, were used to assess the approach to equilibrium in systems with very large numbers of degrees of freedom. Both metrics obey a universal dynamical scaling law for long but finite times for ergodic systems. The explicit form of the scaling function obtained analytically has also been verified numerically. The argument of the scaling function contains a parameter, namely, a characteristic constant D_E or D_Ω whose reciprocals are indicative of the time required for effective ergodic convergence to be obtained. Let us conclude by stressing several implications raised by the present study as well as other related investigations.[1,6,32]

A direct consequence of the scaling behavior established for effective ergodic systems is also of practical interest. The scaling behavior leads to a quantitative criterion for deciding on the time interval $\mathcal{T}$ that is needed to establish ergodic convergence. A useful estimate for $\mathcal{T}$ can be obtained as the value of t for which $d(t)$ or $\Omega(t)$ is one one-hundredth of its initial value. From this it follows that $\mathcal{T}=100/D_\alpha$ ($\alpha=E$ or Ω). Using the information we have gained from examining many such plots for the soft-sphere alloys, we find that times of 25τ or so are adequate for normal liquids, but that times on the order of 100τ or longer are required for strongly subcooled liquids. Notice that in order to use this sort of criterion to obtain $\mathcal{T}$ one need not numerically integrate the equations of motion for very long times. The characteristic $1/t$ behavior is obtained after a small transient time and this allows one to determine D rather quickly.[37]

The universal scaling behavior has been shown to hold only for systems that are effectively ergodic. Conversely if these metrics do not display the scaling behavior it follows that the system is not expected to be ergodic, at least on the time scale of observation.[36] Thus these measures are useful diagnostics of the approach to equilibrium in systems with a large number of degrees of freedom.

Although the present study has only dealt with measures associated with the time-averaged energies of individual particles, it is clear that one can perform calculations using other phase-space functions as well. In fact, these ideas can be applied to molecular liquids and other complex systems in which energy is not the natural variable to monitor.[6,22] Since the arguments used to establish the dynamical scaling behavior only depend on the concepts of ergodicity and self-averaging, it is not difficult to establish the expected $1/t$ characteristic for other systems.[32]

It is remarkable that the dependence of the characteristic coefficients D_E and D_Ω on temperature seems to be well described by a Vogel-Fulcher law. Since the D's describe the rate of exploration of the accessible configuration space, it seems natural to suggest that T_0 in the usual expression for the shear viscosity for glasses is the temperature where the ergodic diffusion coefficients D_E and D_Ω vanish. The vanishing of D_E implies that the system effectively explores one minimum (or a number of order N degenerate minima). The reduction in the "configurational entropy" is therefore associated with the inability of the system to explore all the available minima.[38] The temperature at which D_E vanishes then can be interpreted as being associated with the formation of the amorphous phase from which the system is unable to escape and could correspond to the "ideal glass state." It therefore seems logical to assert that $\bar{T}$ should be equal to the Kauzman temperature T_K. The assertion that T_K (or $\bar{T}$) should be associated with the failure of ergodicity is consistent with the recent experimental observation that the Vogel-Fulcher form from relaxation times with

$T_0 = T_K$ is valid provided the physical quantity that is monitored describes closely the ergodicity of the system.[31,39]

It is interesting that for almost all the states investigated in this paper we have found that $D_E \approx D_\Omega$ and that the cross terms $X_{ab}(t)$ [see Eq. (2.8b)] decay to zero at long times. This suggests that rapid thermal excitation is sufficient to overcome any bottleneck between the various states considered. In realistic systems it is believed that such rapid excitation between the various amphorous minima occur for fragile liquids which have a high density of such minima.[39] The soft-sphere alloys considered in this work are fragile liquids and hence the equality of D_E and D_Ω we have found is consistent with the picture of the topology of the potential-energy hypersurface envisioned by Angell[39,40] for these systems. Based on this interpretation we conjecture that pronounced differences between $d(t)$ and $\Omega(t)$ can only be seen in "strong" liquids. We also wish to add that because of large cooling rates obtained in computer simulations the states probed are probably high-energy states, which are, of course, highly degenerate. It is probably for this reason the numerical values of D_E and D_Ω are quite large.

ACKNOWLEDGMENTS

This work was supported in part by a grant from the National Science Foundation.

APPENDIX

Here we describe the natural generalization of the fluctuation metric $\Omega(t)$ to mixtures. Recall the objective is to ensure that for effective ergodic systems $\Omega(t)$ tends to zero on the time scale $\mathcal{T}$. Let N_α be the number of particles of type α so that

$$\sum_{\alpha=1}^{M} N_\alpha = N \qquad \text{(A1)}$$

where M refers to the total number of species and N is the number of particles in the system. The time-averaged value of the phase-space observable f for the particle j of type α originating from the trajectory labeled a, $f_{ja}(t;\alpha)$, is given by

$$f_{ja}^{\alpha}(t) = \frac{1}{t}\int_0^t ds\, f_{ja}(s;\alpha)\ . \qquad \text{(A2)}$$

The average of $f_{ja}^{\alpha}(t)$ over all the particles of type α is

$$\bar{f}_a^{\alpha}(t) = \frac{1}{N_\alpha}\sum_{j\in\alpha}^{N_\alpha} f_{ja}^{\alpha}(t)\ . \qquad \text{(A3)}$$

The long-time limit of $\bar{f}_a^{\alpha}(t)$ is the average per particle for the observable f. If the system is ergodic, then $\bar{f}_a^{\alpha}(t)$ is expected to be a well-defined quantity for any reasonable choice of f and clearly depends only on α and is independent of the label a. Furthermore, if f is self-averaging, then the right-hand side of Eq. (A3) can be viewed as an ensemble average provided $N_\alpha \gg 1$. The generalization of $\Omega(t)$ to a mixture is

$$\Omega_f^a(t) = \frac{1}{N}\sum_{\alpha=1}^{M}\sum_{j\in\alpha}^{N_\alpha} [f_{ja}^{\alpha}(t) - \bar{f}_a^{\alpha}(t)]^2\ . \qquad \text{(A4)}$$

The above equation has all the properties of the metric found for one-component systems. In particular $\Omega_f^a(t) \to 0$ if the system is ergodic. This follows from the discussion following Eq. (A3). The scaling property of $\Omega_f^a(t)$ given by Eq. (A4) for ergodic systems follows directly from Eqs. (2.6)–(2.8) and is explicitly given by

$$\Omega_f^a(t) \approx 1/D_\Omega t \qquad \text{(A5)}$$

where

$$D_\Omega = \lim_{t\to\infty} 1 \Bigg/ \left[2\sum_{\alpha=1}^{M}\int_0^t ds\, C_f^{\alpha}(s)/C_f^{\alpha}(0) \right] \qquad \text{(A6)}$$

with

$$C_f^{\alpha}(|s_1 - s_2|) = \frac{1}{N_\alpha}\sum_{j\in\alpha} \delta f_{j\alpha}(s_1)\delta f_{j\alpha}(s_2) \qquad \text{(A7)}$$

and

$$d f_{j\alpha}(s) = f_{j\alpha}(s) - \bar{f}_\alpha(s)\ . \qquad \text{(A8)}$$

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[1] D. Thirumalai, R. D. Mountain, and T. R. Kirkpatrick, Phys. Rev. A **39**, 3563 (1989).

[2] Throughout this paper the subspace over which we expect the N-particle systems to be ergodic is the constant-energy surface. This is the relevant surface for the microcanonical ensemble. The usual sense in which ergodicity is used is far too strict to be of practical utility. Strictly speaking the time needed for a dynamical trajectory to pass arbitrarily close to all the allowed points scales as $\exp(N)$ for N-body systems. Thus the question of practical significance is if the system is effectively ergodic in a finite time $\mathcal{T}$. If this is the case we expect the density of phase-space points in a finite volume of the allowed configurational space to be roughly uniform. This is roughly the meaning of effective ergodicity (or ergodicity) used in this paper. For a fuller discussion of the "practical" meaning of ergodicity see S. K. Ma, *Statistical Mechanics* (World Scientific, Singapore, 1989), Chap. 26.

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[15] $\Omega(t)$ for all times is given by the explicit equation

$$\Omega(t)/\Omega(0)=\frac{2}{t}\int_0^t(1-s/t)C_e(s)/C_e(0)ds \ .$$

For almost all generic N-body systems the functional form for the decay of $C_e(s)$ for small values of s is expected to be similar. Naturally the parameters of the function depend on the system and the thermodynamic conditions. Using the argument we conjecture that the form of $\Omega(t)$ for all times should be a universal function.

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[25] It has been shown (see Ref. 20) recently that the single-particle diffusion coefficients D_i for these binary soft-sphere alloys ($i=1,2$) show an Arrehenius dependence on temperature. The dramatic changes seen in the ergodicity parameters D_E and D_Ω re not reflected in the self-diffusion coefficients.

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