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Ergodic behavior in supercooled liquids and in glasses

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Ergodic behavior in liquids, supercooled liquids, and glasses is examined with a focus on the time scale needed to obtain ergodicity. A measure, $d(t)$, which is based on the time-averaged energies of the individual particles and which is referred to as the "energy metric," is introduced to probe the approach to ergodic behavior. We suggest that $d(t)$ obeys a dynamical scaling law for long but finite times and that it can be used to characterize the degree of stochasticity in measure preserving systems with large numbers of degrees of freedom. Examination of $d(t)$ indicates that the configuration space is explored by a "diffusive" process in the space of the dynamical energy variables used in constructing the energy metric. The characteristic diffusion constant associated with this process is argued to be analogous to the well-known maximal Lyapunov exponent which is often used to characterize stochasticity in systems with few degrees of freedom. Based on the long-time behavior of $d(t)$ it is shown that ergodicity is effectively broken in the glassy state. In addition to broken ergodicity, the possibility that a subtle symmetry is broken as the liquid-to-glass transition takes place is examined. It is suggested that a "discrete" symmetry, to be referred to as the statistical symmetry, is broken in the glassy phase. This is illustrated by analyzing the distribution of the energy of the particles. Based on this, we expect long-time dynamics and structural relaxation in glasses to be dominated by fluctuations in domains of finite length within which the particles are highly correlated. This is in accord with the ideas of Adams and Gibbs. All of the above arguments are illustrated with the aid of molecular-dynamics simulations of soft-sphere mixtures.

I. INTRODUCTION

The assumption that classical many-body systems are ergodic is a central concept in equilibrium statistical mechanics.[1,2] The applicability of statistical-mechanical developments to nonergodic systems such as glasses is a topic of current interest.[3,4] In this paper we examine the approach to ergodicity in liquids and glasses and show that ergodicity is broken in the glassy phase. Our observations are based in part on molecular-dynamics simulations[5] of glassy states and a novel measure of broken ergodicity for such states. Consider a classical N-particle system confined in a box and let the phase space of the system be Ω. Any observable F is then defined as a function on the phase space Ω. The phase-space average of the observable is calculated with respect to an invariant measure, $d\mu(\omega)$, as

$$\langle F\rangle=\int_\Omega d\mu(\omega)F(\omega)\ , \tag{1.1}$$

where ω is a point in Ω. If one prescribes a dynamics such that $f^t\omega$ is the position of the phase point ω at time t, the ergodic theorem states that the time average of F is equal to the phase-space average,

$$\lim_{T\to\infty}\frac{1}{T}\int_0^T dt\,F(f^t\omega)=\langle F\rangle\ , \tag{1.2}$$

for almost all initial conditions ω with respect to the specified measure $d\mu(\omega)$.[6] The fundamental results of equilibrium statistical mechanics follow from the ergodic hypothesis.

Since we are interested in dynamical systems with a specified Hamiltonian, the ergodic theorem is explicitly written in the following form:

$$\begin{aligned}\langle F\rangle&=\lim_{T\to\infty}\frac{1}{T}\int_0^T F[f^s\mathbf{R}(0)]ds\\&=\int_\Omega F(E)\delta(E-E_0)d\Omega\Big/\int_\Omega\delta(E-E_0)d\Omega\ ,\end{aligned}\tag{1.3}$$

where $\mathbf{R}(0)$ is a set of Cartesian coordinates describing the phase point of N particles at $t=0$ and the allowed phase space Ω is determined by constraining the energy to be a constant. Thus, given infinite time, the system will visit every allowed point in the phase space Ω. The second set of integrals in Eq. (1.3) is the phase-space average evaluated in the microcanonical ensemble with energy $E=E_0$. Ergodic behavior is obtained if $t=\tau_{\mathrm{obs}}$, the averaging time or experimental observation time is sufficiently long that the surface in phase space with constant energy is adequately sampled. In practice, this does not mean that the surface is "densely" covered by the trajectory but that effectively all regions of that surface are sampled and effective ergodicity is obtained.

In the event of broken ergodicity, the measure in Eq. (1.1) can be uniquely decomposed into a union of several independent ergodic measures. The phase space Ω is then decomposable into a union of disjoint subsets Ω_i. The barrier between the various subsets becomes infinite and, consequently, if at $t=0$ the system is in a configuration ω_i belonging to the subset Ω_i, then on any relevant time scale the system will be unable to sample the configurations of other subsets Ω_j with $i \neq j$. Phase transitions are a well-known example of broken ergodicity.[3] Even in this case, the results of statistical mechanics are applicable because well-defined measures $d\mu_i(\omega)$ can be constructed using the set of configurations belonging to Ω_i and these measures can be used in Eq. (1.1) to calculate appropriate averages of observables. It should be noted that the above discussion of ergodicity is valid only when the averaging time goes to infinity. In this article we are concerned with the behavior of systems on long but finite time scales τ_{obs}. Consequently we examine only effective ergodicity of the system, i.e., the equivalence of phase-space averages and time averages with the averaging time being equal to τ_{obs}. The notion of effective ergodicity is the physically relevant concept in analyzing experiments as well. Henceforth, we will use effective ergodicity synonymously with ergodicity.

From the above discussion one concludes that the system is effectively ergodic if the trajectory adequately samples the allowed regions of phase space Ω within a time equal to τ_{obs}. A test of adequate sampling is that trajectories starting from neighboring points on the energy surface "diverge" as time advances. The rate of divergence is assessed by calculating the characteristic (or Lyapunov) exponents.[7] In dynamical systems (either dissipative or conservative) with only a few degrees of freedom, computationally managable algorithms have been devised to calculate the characteristic exponents by following the time evolution of two phase points that are infinitesimally apart at $t=0$.[8-10] The divergence or mixing property which leads to the nonvanishing of the characteristic exponents automatically implies that the system is (at least) ergodic. However, when considering dynamical system consisting of several hundred particles, these algorithms are computationally inefficient.[11] The number of characteristic exponents from such a calculation is $6N-6$, where N is the number of particles in the system. This is typically a very large number making the analysis difficult if not impossible. Thus a reduced description which leads to a tractable measure characterizing ergodicity is required.

The main purpose of the present study is to propose a useful way to characterize the ergodic behavior in supercooled liquids and in glasses. We introduce a quantity which is zero for ergodic systems and becomes essentially nonzero (decays extremely slowly) on a long-time scale when ergodicity is broken. With the aid of this measure we demonstrate that effective ergodicity is broken in the transition from supercooled liquids to glasses.

Another point we would like to address is the possibility of broken symmetry when the liquid-to-glass transition takes place. Before proceeding we wish to emphasize that notations pertaining to broken symmetry are only applicable to systems that undergo equilibrium phase transitions. In our discussions we assume that glass-forming materials have well-defined equilibrium properties which are at least in principle calculable using the laws of statistical mechanics. If there is a symmetry that is broken, it must be a subtle one because it appears that all equal-time correlation functions (like the structure factor) are continuous at the glass-transition temperature T_g.[12] In fact, it appears to be a characteristic of random systems to undergo a transition from an ergodic to a nonergodic phase in a discontinuous manner without any apparent change in the structure.[13] Thus the search for a symmetry-breaking process in the structural glass problem seems to be difficult. The motive for suggesting that some symmetry is broken is that the zero-frequency shear modulus of the glassy state is nonzero and this suggests broken symmetry.[14] It must be emphasized that this does not imply that glasses have long-range spatial order. A well-known example where the system does not possess long-range translational order but responds to external stress is the Kosterlitz-Thouless transition in two-dimensional (2D) systems.[15] To distinguish between liquids and glasses and to illustrate symmetry breaking in the structural-glass problem we introduce a distribution property based on the average energy of a particle over a period of time. The dispersion of this distribution function serves in a sense as an order parameter. We suggest, based on the behavior of this distribution, that statistical symmetry is broken when the system makes a transition from a supercooled liquid state to a glassy state. We argue that this is a (broken) discrete symmetry of the system.

These ideas are expounded by the use of molecular-dynamics (MD) simulations. It should be stressed that MD simulations cannot be used to completely characterize the consequences of broken ergodicity. However, we hope the simulations highlight the physically motivated arguments.

The remainder of the paper is organized as follows. In Sec. II the model is introduced along with a brief description of the computational details employed in the MD simulations. The measure of ergodicity is introduced in Sec. III and a few consequences of broken ergodicity are also discussed. In this section we also point to the existence of a universal dynamical scaling law that may prove useful in characterizing the approach to ergodic behavior in Hamiltonian systems with large numbers of degrees of freedom. Section IV is concerned with the distribution of energy of the individual particles and the suggestion that statistical symmetry is broken in the glassy phase. The analysis also points to the notion of cooperatively rearranging regions in the glassy state as envisioned by Adams and Gibbs.[16] In fact, we argue that dynamics and structural relaxation in the glassy state is dominated by rare fluctuations in a compact region within which the motion of particles is highly correlated.

The paper is concluded in Sec. V with several additional remarks and some speculations.

II. MODEL AND SIMULATION DETAILS

The system chosen to illustrate our arguments is a binary mixture of softly repelling spheres. It has been shown that this system can be used to generate glassy states if it is cooled sufficiently.[17,18] This is to be contrasted with the one-component soft-sphere fluid which readily forms a crystal phase when strongly supercooled.[19] The mixture consists of N_1 soft spheres of type 1 with mass m_1 and diameter σ_{11} and N_2 soft spheres of type 2 with mass $m_2=2m_1$ and diameter $\sigma_{22}=1.1\sigma_{11}$. The interaction between spheres of type AB ($A,B=1,2$), separated by a distance r_{ij}, is an inverse 12th-power repulsion of the form

$$\phi_{AB}(r_{ij})=\varepsilon(\sigma_{AB}/r_{ij})^{12} . \tag{2.1}$$

The cross-interaction diameter is additive so that $\sigma_{12}=\frac{1}{2}(\sigma_{11}+\sigma_{22})$. The total number of particles $N=N_1+N_2=500$. The composition variable $X=N_1/N$ specifies the fraction of type-1 particles in the mixture; $X=\frac{1}{2}$ for the results reported in this paper. We use σ_{11} as the unit of length, m_1 as the unit of mass, and ε as the unit of energy, so that time is quoted in units of $\tau=(m_1\sigma_{11}^2/\varepsilon)^{1/2}$. The number density is $n^*=N\sigma_{11}^3/V$, where V is the volume of the system. Finally, the temperature T is taken to be $\frac{2}{3}$ the mean kinetic energy per particle and is expressed as $T^*=k_BT/\varepsilon$, where k_B is Boltzmann's constant. The state of the system can be specified using an effective reduced density or coupling constant which is defined as

$$\Gamma_{\text{eff}}=n^*(\sigma_{\text{eff}}/\sigma_{11})^3/(T^*)^{1/4} . \tag{2.2}$$

The quantity σ_{eff} is the one-fluid van der Waals equivalent diameter and is defined by[20]

$$\sigma_{\text{eff}}^3=X^2\sigma_{11}^3+2X(1-X)\sigma_{12}^3+(1-X)^2\sigma_{22}^3 . \tag{2.3}$$

The equilibrium liquid has values of $\Gamma_{\text{eff}}\leq 1.15$ and the glass transition occurs at $\Gamma_{\text{eff}}\approx 1.5$. The reader is referred to Refs. 17 and 18 for further details on this system.

The simulations were performed for constant energy, constant volume conditions. Periodic boundary conditions were enforced to minimize surface effects. The classical equations of motion were integrated using the Beeman algorithm with a time step of 0.01τ. The initial conditions for each simulation were well-stabilized configurations generated during our earlier work on this system.

III. BROKEN ERGODICITY

The $6N$-dimensional phase-space trajectory for the system described in Sec. II is obtained by solving Hamilton's equations of motion. Since we are dealing with conservative systems, Liouville's theorem guarantees us that the volume in phase space is a constant. For a given thermodynamic state, the rate of exploration of phase space and hence the time required for ergodic behavior to obtain is unknown. Rigorous results are contained in the theorems due to Kol'mogorov, Arnol'd, and Moser (KAM)[21] and due to Sinai.[22] The KAM theorem deals with the effect of a small perturbation on an integrable system while Sinai's theorem proves that a gas of hard spheres is ergodic. However, the approach to ergodicity in systems containing a large number of degrees of freedom is still an open problem.

As stressed in the Introduction, one of the questions of interest in the context of the structural-glass problem is, what is the time scale required for ergodicity to be obtained? Alternatively, given an $6N$-dimensional trajectory $x(t_i)$ for $i=1,2,\ldots,n$, can one determine the degree of stochasticity and possibly assess if the system is ergodic on the time scale $\tau_{\text{obs}}=t_n$? One possible way to do this is to calculate the Lyapunov exponents using certain standard techniques.[8-10] These exponents not only describe the degree of stochasticity but they can be used to calculate the so-called KS entropy.[7,8] However, for the problem that we consider, the standard methods of computing Lyapunov exponents, which involve either obtaining the eigenvalues of the Jacobian matrix associated with the time evolution of two trajectories that are infinitesimally apart at $t=0$,[7] or utilizing the algorithm of Benettin *et al.*,[8] become very cumbersome. Furthermore, for liquids and glasses, the number of Lyapunov exponents that result from such calculations is $6N-6$ which in our case is 2994. Thus any practical information that can be gleaned in this way seems limited.

Since the characterization of ergodic behavior in liquids and in glasses in terms of Lyapunov exponents appears to be of limited utility, the question of practical interest is, can one devise a simplified description of phase space in terms of which the questions raised above can be answered? To address this question we propose a measure, to be called the energy metric, which is based on the energy of individual particles and which can be used to discuss the absence of ergodicity in glasses. Furthermore, one can postulate a universal dynamical scaling law for liquids and supercooled liquids based on the energy metric. This dynamical scaling law may prove useful in investigating the approach to ergodicity in Hamiltonian systems (or more generally, measure-preserving systems) with a large number of degrees of freedom. This treatment of the problem is clearly not rigorous but the computations are easily done, and the results suggest that ergodic behavior in liquids and glasses can be characterized by essentially a single parameter.

A. Energy metric, $d(t)$

Our discussion of the concept of broken ergodicity makes use of a measure constructed from a set of quantities, the time-averaged energy of individual particles, which are unconventional in classical statistical mechanics but which are well suited to examine ergodic behavior.

To define the quantities, let

$$\varepsilon_i(t)=\frac{1}{t}\int_0^t ds\, E_i(s) \tag{3.1}$$

be the average, over a time interval t, of the energy of the ith particle in a fluid. $E_i(s)$ is the value of the energy of the ith particle at time s and is the sum of the kinetic energy and one half the sum of the potential energy terms involving particle i. This is a quantity which can readily be generated in a molecular-dynamics simulation. It proves to be useful to consider the distribution of the $\varepsilon_i(t)$ as well, so we define $P(\varepsilon;t)$ to be the distribution of the energies $\varepsilon_i(t)$ of the entire set of particles of the fluid. The properties of this distribution is the subject of Sec. IV.

A well-characterized measure can be constructed based on the $\varepsilon_i(t)$ to show that ergodicity is broken in the transition from supercooled liquids to glasses. Before presenting the calculations, we sketch some essential ideas needed to interpret the present results. A detailed account exploiting the consequences of broken ergodicity with focus on certain random systems may be found elsewhere.[3,4]

To envision the breakdown of ergodicity one imagines that the allowed phase space can be partitioned into several mutually disjoint regions or components. Consequently, the physical measure, used in Eq. (1.1) to calculate averages of dynamical observables, is decomposable into a union of invariant measures. If ergodicity is broken then the phase point or configuration (which in the present problem is specified by the coordinates of all N particles) belonging to a given component will, in the process of evolution, remain in the same component for times greater than τ_{obs}. It should be stressed that the phase points belonging to different components are *energetically* accessible and, indeed, if the system were ergodic, the trajectory would fill the allowed volume in phase space (almost) uniformly. When the system is not ergodic, the trajectory will sample only those configurations belonging to a specific component. Consequently, the system can be considered to be ergodic as long as the measure is defined with respect to a given component. Thus using the invariant measure of a specified component,[23] one can calculate various correlation functions. If the equal-time correlation functions calculated using measures for two different components α and β turn out to be identical, then α and β will be called statistically similar.[24] If the number of statistically similar states is exponentially large, then the statistical mechanics using the Gibbs ensemble is inappropriate, and it has been proposed that instead the extended Gibbs formalism be used.[3,4]

Using these ideas, the theoretical demonstration of broken ergodicity in glassy states starting from a specified Hamiltonian is not an easy task. In order to show the existence of various independent components and hence demonstrate the occurrence of broken ergodicity, one must consider an ensemble of initial conditions. Furthermore, a suitable dynamical observable which can distinguish the different components must be chosen. In order to verify that the components are statistically similar, structural quantities like the pair correlation function, should be shown to be identical for the various components. It is, therefore, obvious that computer simulations cannot unequivocally demonstrate that effective ergodicity is broken. To convincingly do so one has to follow the time evolution of the system for an exponentially large number of independent starting configurations which is clearly not possible. However, numerical experiments can suggest the presence of broken ergodicity and hence certain consequences can be eludicated.

Although the various statistically similar components are expected to have identical equal-time correlation functions, the barriers separating the components are not infinite. Consequently, in supercooled liquids transport proceeds by processes that involve crossing the free-energy barriers separating the components. In general, one expects a distribution of free-energy barriers. These systems are truely ergodic[1] only if the observation time tends to infinity. In highly supercooled liquids, the time scale for such crossing events becomes longer than the typical observation times with the result that effective ergodicity is broken and the calculation of free energy should be done with care (see Sec. III C).

We use the following procedure to demonstrate broken ergodicity. Two *independent* initial states of the system are chosen and the components in which these states reside are labeled a and b. The choice of the initial states is described below. A given component consists of the set of configurations $R=\{r_1,r_2,\ldots,r_{\max}\}$, such that if the liquid is quenched starting from any configuration in the set R, then it reaches a specified (metastable) free-energy minimum a. Clearly the division of configuration space into components is useful only if there are several components separated by free-energy bottlenecks. This typically happens only in viscous liquids or in solids. A measure that distinguishes between the two components (if they exist), which we call the "energy metric," $d(t)$, is introduced as

$$d(t)=\frac{1}{N}\sum_{j=1}^{N}[\varepsilon_{aj}(t)-\varepsilon_{bj}(t)]^2 . \tag{3.2}$$

Here $\varepsilon_{aj}(t)$ is the time-average energy of particle j in state a, and $\varepsilon_{bj}(t)$ is the corresponding quantity in the state b. The sum runs over all the N particles of the system. The properties of $d(t)$ can be easily predicted. If the system is ergodic on the time scale τ_{obs}, then $d(t)$ should vanish as t approaches τ_{obs} because the system samples all of allowed phase space rapidly, and therefore $\varepsilon_{aj}(\tau_{\text{obs}})=\varepsilon_{bj}(\tau_{\text{obs}})$, implying that there is only one component.[25] For such a case the usual description of the system in terms of the familiar Gibbs ensemble in statistical mechanics is valid. This is the situation expected for the liquid state. However, when ergodicity is broken, $d(t)$ should approach a nonzero constant as t approaches τ_{obs}, suggesting that the two initial states belong to disjoint parts of phase space. The long-time behavior of $d(t)$ serves to distinguish between two components and therefore demonstrates broken effective ergodicity.

It might appear that the results for $d(t)$ can be made to vary by particle label permutations. Supercooled liquids and glasses, which are highly viscous, are ergodic if one is willing to observe them for long enough times. Consequently, the infinite-time limit of $\varepsilon_{aj}(t)$ is independent of j and a and depends only on the particle species. Thus the long-time behavior of $d(t)$ will depend on whether or not the states a and b are widely separated in phase space and on how long it takes for free-energy barrier crossings to occur.

One could also define $d(t)$ by minimizing $d(0)$ through index permutations and then computing $d(t)$ as in Eq. (3.2) with the permuted labels. The results probably would differ in detail from those reported below, but the qualitative results for $d(t)$ should be unchanged. We stress that it is the qualitative features that are significant when attempting to discuss the time scales needed for effective ergodic behavior to be obtained. We note that particle permutations will affect the results for $d(t)$ when one is considering quenched systems like spin glasses, and the definition of $d(t)$ is ambiguous in this context. Supercooled liquids and glasses do not involve quenched randomness where transport absolutely ceases, and thus $d(t)$ can be unambiguously defined.

The vanishing of $d(t)$ for long times has a further implication. If the system is ergodic, then particles of the same species sample equivalent "environments" and therefore the $\varepsilon_j(t)$ for a given species in the liquid should approach the same constant value at long times.[25] This means that all particles of a given species are statistically similar for an ergodic system. We will consider the consequences of this statistical similarity further in Sec. IV.

We have performed molecular-dynamics simulations and constructed $d(t)$ using a code which generates trajectories for a set of particles using two different initial conditions. Initial conditions for fluid states were taken as the endpoints of different simulations at a given energy. The initial conditions for the glassy state were prepared by quenching to the glassy state with $\Gamma_{\text{eff}}=1.7$ and a constant total energy $E=2.0$ at quite different cooling rates so that well-separated points on the $E=2.0$ energy surface were obtained. That this is so was confirmed by comparing the resulting single-particle energy distributions $P(\varepsilon;t)$ (see Sec. IV) and observing that they differ, indicating that their locations in phase space are distinct and are not simply related by particle permutation. For both the liquid and glassy states, the systems were carefully checked for stability in time before calculations of $d(t)$ were begun.

Our results for $d(t)$, normalized to unity for $t=0$, are displayed in Fig. 1. The solid line represents an equilibrium liquid with $\Gamma_{\text{eff}}=0.95$, the dashed line represents a supercooled liquid with $\Gamma_{\text{eff}}=1.37$, and the long-short dashed line represents a glass with $\Gamma_{\text{eff}}=1.7$. The decay of $d(t)$ reflects the expected reduction of the variance of the difference in the $\varepsilon_j(t)$ with increasing time.

These results can be analyzed in terms of the ideas presented at the beginning of this section. Let p be the probability that the system at an initial phase point in a specified component will make a transition to a different configuration belonging to other components in $t \le \tau_{\text{obs}}$. If p is smaller than some small number p_0, then initially distinct states will be confined to their respective components yielding $d(t) \cong \text{const}$ as $t \to \tau_{\text{obs}}$. This then would imply that ergodicity is broken. If p were strictly zero, which would be the case when the barriers separating the different free-energy minima are infinite, then $d(t)=\text{const}$ as $t \to \infty$.

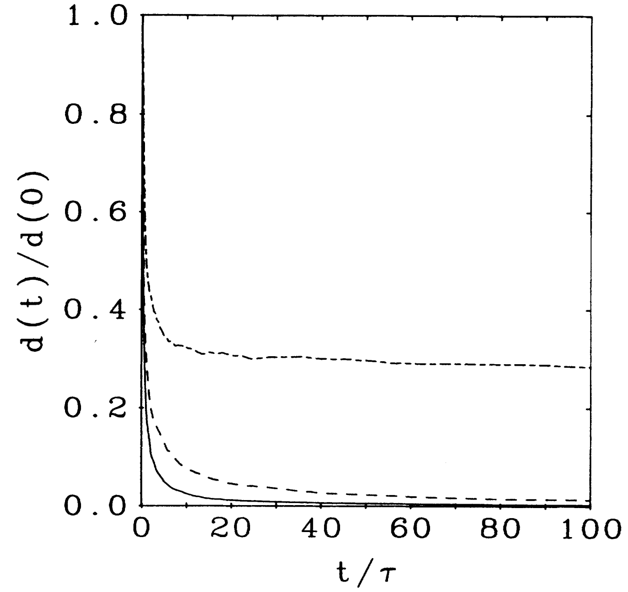

FIG. 1. The normalized energy metric $d(t)/d(0)$ as a function of averaging time is shown for an equilibrium liquid state with $\Gamma_{\text{eff}}=0.95$ (solid line), for a strongly supercooled liquid state with $\Gamma_{\text{eff}}=1.37$ (dashed line), and for a glassy state with $\Gamma_{\text{eff}}=1.7$ (long-short dashed line). The initial values $d(0)=6.6$, 0.6, and 0.2 for $\Gamma_{\text{eff}}=0.95$, 1.37, and 1.7, respectively. For the liquid, the phase-space components are identical, while they are distinct for the glass. The supercooled liquid requires a longer averaging time to demonstrate the identity of the components.

Figure 1 shows that for long times, $d(t)$ vanishes rapidly for an equilibrium liquid and more slowly for the supercooled liquid. The slow decay of $d(t)$ as $t \to \tau_{\text{obs}}$ for the supercooled state suggests that the exploration of phase space is very slow. On the other hand, for the glassy state, the long-time behavior of $d(t)$ is nearly a constant implying that the two states belong to two different components. The extremely slow decay of $d(t)$ as $t \to \tau_{\text{obs}}$ in the glassy state is indicative of the fact that there is a small (but detectable) finite probability of transitions from one component to another, i.e., $p \neq 0$. However, the nearly constant value of the long-time limit of $d(t)$ for the glassy case also suggests that these transitions are rare (perhaps exponentially rare) and hence are difficult to investigate by computer simulation studies. These observations allow us to conclude that effective ergodicity is indeed broken in the glassy states.

We have calculated $d(t)$ using other initial glassy-state points and have arrived at results similar to those shown in Fig. 1. However, the long-time limit of $d(t)$ does depend on the *initial states* considered. This implies that $d(t)$ can be used as a measure to distinguish between different components. As stressed earlier, computer simulations alone cannot be used to completely characterize these metastable components as their number should scale as $\exp(aN)$.[26] It is clear that these studies can point to the existence of broken ergodicity, and in this context $d(t)$ can serve as a useful measure. Stillinger and Weber[26(b)] have argued that at $T=0$ the number of potential-energy valleys for a system of N particles scales as $\exp(aN)$. We suggest here that a large (possibly exponential) number of *free*-energy metastable glassy states become relevant at a finite temperature. The temperature range where the typical barriers between states is greater than $k_B T$ roughly divides ergodic and nonergodic behavior.

B. Scaling of the energy metric and diffusion

The curves shown in Fig. 1 suggest that the functional form for the time dependence of $d(t)$ for the different thermodynamic states should be identical. We assume that the decay of $d(t)$ is governed by a single parameter, the "diffusion constant" D_E associated with the rate of exploration of configuration space. Consequently, we suggest that the finite-time properties pertaining to ergodicity of liquids, supercooled liquids, and glasses may be described by the following scaling form for $d(t)$:

$$d(t)=d(0)f(tD_E)\ , \tag{3.3}$$

where the scaling function $f(x)$ is unity when $x=0$ and $f(x)\to 0$ when $x \gg 1$. To determine $f(x)$ we have examined the behavior of $d(t)$ in a number of ways. The significant result is for $\sigma(t)=d(0)/d(t)$ as a function of t which is displayed in Fig. 2. It is very clear that $\sigma(t)$ grows linearly with time after a transient time and thus

$$f(x)\approx 1/x\ . \tag{3.4}$$

The diffusion constant D_E is dependent on temperature. For the systems considered in this paper it is clear that $d(t)$ approaches zero uniformly from above as $t\to\infty$. A dynamical scaling form similar to the one found here for $d(t)$ has been reported recently for the Lyapunov exponent $\gamma(t)$ for finite times for a large class of two-dimensional billiard systems.[27] For these mixing systems, the infinite time limit of $\gamma(t)$ is nonzero. It is tempting to suggest that $d(t)$ could serve a similar purpose in quantifying the degree of chaos and the time scale for ergodic behavior to obtain for systems with a very large number of degrees of freedom as does $\gamma(t)$ for few-dimensional systems. This analogy indicates that the approximate time scale needed for ergodicity to be obtained in liquids, supercooled liquids, and glasses is $\tau_E \approx 1/D_E$. A more accurate estimate of τ_E can be made by calculating the time needed for $d(t)$ to reach a small fraction of its initial value. For $t \leq \tau_E$ the system is effectively nonergodic. It is remarkable that a single parameter D_E and the scaling function $f(x)$ can be used to completely characterize ergodicity in the Hamiltonian systems that we have considered.

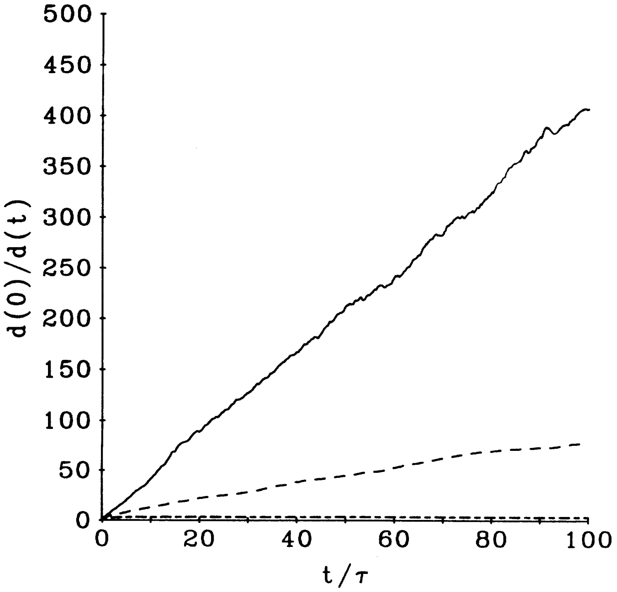

FIG. 2. The information in Fig. 1 is shown here as $d(0)/d(t)$ vs t indicating that after a relatively short-time interval, $d(t)$ decreases as $1/t$ for the equilibrium and supercooled liquids. This indicates that the differences in the mean energies are normally distributed in the statistical sense.

The result that $\sigma(t)\approx D_E t$ for times longer than some transient period suggests a very intriguing kind of diffusion process for the dynamical variable $x_i(t)=\varepsilon_{ai}(t)-\varepsilon_{bi}(t)$. The exploration of the configuration space can be described in terms of a random walk in the variables $x_i(t)$ which converges to zero for long times for an ergodic system. Because of the central role played by D_E in describing ergodic behavior, we have numerically determined it for the cases considered in Fig. 1. We find D_E to be approximately 4.1, 0.79, and 0.0032 for $\Gamma_{\text{eff}}=0.95$, 1.37, and 1.7, respectively. Using these values of D_E and assuming that effective ergodicity is reached if $d(t)/d(0)\approx 0.01$, the time scale for ergodicity to be reached turns out to be 24τ, 126τ, and $31\,000\tau$ for the three states. From this small number of points it is not possible to obtain any meaningful functional form for the temperature dependence of D_E. The dramatic decrease in D_E suggests that it may deviate considerably from any power-law behavior. A general exponential form is postulated in Sec. V based on the analogy between the behavior of $x_i(t)$ and Arnold diffusion.[7] The scaling behavior and the diffusion process seen in $x_i(t)$ suggest that a generalized central-limit theorem can be applied to $x_i(t)$.[28] The sequence of variables appears to be independent and random with the variance decreasing as $1/t$. We suggest that $x_i(t)$ is normally distributed in accord with the central-limit theorem. Deviations from the normal distribution cannot be ruled out before considering higher moments.

C. Consequences of broken ergodicity

Here we discuss three consequences of broken ergodicity which are related to this study. These are (i) the statistical similarity of phase-space components, (ii) the calculation of free energy for glassy states, and (iii) the origin of hysteresis in certain properties of glassy states.

(i) It is of interest to consider the amorphous packing of atoms in the various components. Using the set of configurations generated by starting from an initial phase point belonging to a given component, we calculated the pair correlation functions $g_{AB}(r)$, where $A,B=1,2$ indicates the two species making up the pair. The $g_{AB}(r)$ for both components a and b (and for others considered) were found to be identical. This strongly suggests that the components into which the liquid solidifies are statistically similar.[24] Because the configurations for the various components were generated by quenching the liquid at different cooling rates, these conclusions seem to depend only on the thermodynamic state of the glassy phase. However, the time scale needed to explore the set of configurations belonging to a given component is generally expected to depend on the cooling rate.

In a series of simulation studies, Stillinger and Weber[29] obtained the "quenched" pair function starting from different thermodynamic liquid states. The configurations were generated by a steepest-descent procedure where a given phase point corresponding to the high-temperature liquid converges to a relative local minimum in the potential energy. The set of configurations that comprise a specified relative minimum (called a basin by these authors and referred to as a component in this paper) are those starting points that converge to the same local minimum. The quenched pair correlation functions computed by Stillinger and Weber are for $T=0$ configurations, and so thermal vibrational motions are completely eliminated. These functions were found to be independent of the starting thermodynamic state. They referred to the structure as the inherent or underlying structure of the liquid. The identical amorphous packing found in different components allows us to conclude that the components, obtained as a consequence of quenching to $T=0$, are statistically similar. We suggest that these components can be distinguished using the dynamical observable $d(t)$ proposed here. The present results allow us to make a stronger assertion, i.e., if the liquid is quenched to a glassy state (at $T\neq 0$) starting from a liquid then the resulting components are expected to be statistically similar. It is for this reason equal-time correlation functions do not undergo any dramatic change as the glass transition takes place.

(ii) If there are an extensive number ($\sim e^{aN}$) of statistically similar free-energy states, then one is forced to calculate thermodynamic properties, such as free energy, as an average over an ensemble comprising the various components. A detailed discussion of this point has been made by Palmer.[3]

The ensemble of components that one has to consider implies that the canonical free energy

$$\beta F=-\ln Z=-\ln \mathrm{Tr}\, e^{-\beta H} \tag{3.5}$$

is not appropriate. We wish to emphasize that strictly speaking the glassy states are metastable, and hence the notion of free energy is not meaningful. However, we have argued that on the experimental time scale the glassy states are effectively ergodic as long as the set of configurations being considered is restricted to a given component, and hence a meaningful calculation of free energy is possible provided an appropriate ensemble of components is considered. For the glassy phase this leads us to the so-called component-averaged free energy,

$$\bar{F}=\sum_{\alpha} p^{\alpha} F^{\alpha} , \tag{3.6a}$$

where

$$\beta F^{\alpha}=-\ln Z^{\alpha}=-\ln \tilde{\mathrm{T}}\mathrm{r}\, e^{-\beta H} \tag{3.6b}$$

and

$$p^{\alpha}=e^{-\beta F^{\alpha}}/Z . \tag{3.6c}$$

In Eq. (3.6b) the trace operation is performed by restricting the phase space to that corresponding to a specific component α.[3] It is clear that $\bar{F}\neq F$ and in fact $\bar{F}>F$. The difference between $\bar{F}$ and F is related to the so-called complexity and is essentially the loss in configurational entropy when the liquid makes a transition to the glass.[4] With the framework established here[30] the physical meaning of configurational entropy can be made transparent. Because the glassy states are effectively nonergodic, the system does not explore all the available parts of the configurational space. The bottlenecks which restrict the system to explore only a subset of the available configurations lead to a loss in configurational entropy S_c as the liquid becomes a glass. Thus the decrease in S_c is strictly a consequence of the lack of ergodicity. This leads one to conclude that activated processes in the glassy phase should be entropically driven which was originally suggested by Adams and Gibbs.[16] The difference between $\bar{F}$ and F is only meaningful when the number of relevant random states is exponentially large as is surely the case for the structural-glass problem.[26]

(iii) It is well known that the variation of certain properties of glasses is history dependent and those properties exhibit hysteresis.[31] For example, in several glasses the enthalpy or volume show different temperature dependences depending on whether the sample is being heated or cooled. This is easily understood in terms of the division of phase space into various components with rare mixing between configurations belonging to different components. Suppose a glassy sample with initial configuration $\{r_i\}$, $i=1,2,\ldots,N$, belongs to a given component α and is heated to the liquid phase. As the temperature increases there is rapid mixing of the configurations belonging to different components. This experiment would yield a specific enthalpy versus temperature relation.[31] Now let the final liquid sample with the configuration $\{r_i'\}$ be cooled to a glassy state. In all likelihood, the configuration of this glassy state $\{r_i''\}$ would belong to a different component than the one containing $\{r_i\}$. Furthermore, the rate of exploration of configuration space will in general depend on the topography of a specific component and on the cooling rate. The lack of mixing property leads one to conclude that the result of heating and cooling experiments should yield different results resulting in hysteresis for nonergodic systems.

IV. ENERGY DISTRIBUTION

The distribution of time-averaged particle energies $P(\varepsilon;t)$ provides some further insights into the differences between equilibrium states of a liquid and nonequilibrium glassy states. Although the total energy of the system is a constant, the way the energy is distributed among the particles is difficult to predict. We have constructed the distribution $P(\varepsilon;t)$ using the time-averaged energies of the individual particles for the entire binary soft-sphere mixture. In Fig. 3 the evolution of $P(\varepsilon;t)$ with increasing averaging time for an equilibrium liquid state of an equimolar mixture of soft spheres and for a glassy, nonequilibrium state of that mixture is exhibited. First consider the distribution for the equilibrium fluid state, which is displayed on the right-hand side of the figure and is centered at $E=5.0$. The solid line joining the pluses shows this distribution at $t=10\tau$, the dashed line joining the squares shows the distribution at 50τ, and the short-long dashed line joining the triangles shows the distribution at 100τ. It is significant that an apparently short-time interval $t=10\tau$ is much greater than $t_D \cong \tau$, the time for the decay of the velocity time autocorrelation function,[18(b)] and this implies that t_D is not the relevant time for the establishment of the equivalence of time and ensemble averages.

Over short-time intervals, say 10τ, the average particle energies are broadly distributed. As time progresses, the average energies become quite well defined about two characteristic values, the lower value, which is the mean energy of the smaller particles, is approximately $E=4.7$ and the upper value, which is the mean energy of the larger particles, is approximately $E=5.3$. In fact, $P(\varepsilon;100\tau)$ can easily be represented as a sum of two sharply peaked Gaussians. For this system, 10τ is not an adequate averaging time for stationary behavior to result, but 50τ is since there is relatively little change in the distributions between 50τ and 100τ. The variances of the energies $E_j(t)$ of the individual particles are large, on the order of the width of the distribution, indicating that the particles are sampling a wide range of local environments and therefore a large region of phase space. This is consistent with the ergodicity expected for the liquid state. Essentially identical results were obtained for a strongly supercooled liquid state. The time required for a stable long-time distribution of the average particle energies to develop is one indication of the time required for ergodic behavior of time averages to apply. As we now show, a stable distribution by itself is not a measure of ergodicity.

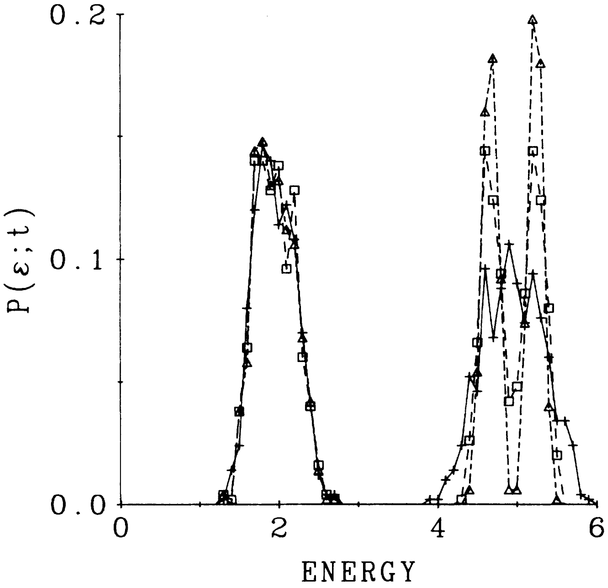

FIG. 3. The distributions of average energies of the particles in a mixture $P(\varepsilon;t)$ are shown for a fluid in thermodynamic equilibrium and for a glassy state. Energy is quoted in units of the energy parameter of Eq. (2.1). The equilibrium results are centered about an average energy of 5 and the glassy-state results are centered about an average energy of 2. The equilibrium state has an effective coupling-constant value of $\Gamma_{\mathrm{eff}}=0.95$, while the glassy state has a value of $\Gamma_{\mathrm{eff}}=1.7$. The solid line joining the pluses represents the distributions after an averaging time of 10τ, the distributions after 50τ are represented by dashed lines joining squares, and the distributions after 100τ are represented by long-short dashed lines joining triangles. In each case, the distributions were coarse grained with a resolution of 0.1 energy units. The distributions have also been obtained for a strongly supercooled state with $\Gamma_{\mathrm{eff}}=1.37$. They are quite similar to the equilibrium liquid distributions but are not shown here to avoid cluttering the figure as it is centered at $E=2.5$.

The distribution of energies for a glassy state of the binary soft-sphere fluid is displayed on the left-hand side of Fig. 3. Unlike the equilibrium liquid case, there is effectively no change with time in the distribution of the individual particle energies. Also, the variances of the individual particle energies are much smaller than the width of the distribution of energies for that species, as shown in Fig. 4, indicating that particles are effectively trapped (localized) in a fixed environment which is what is expected for a glassy state. It has been shown in the previous section that ergodicity is not preserved in the glassy phase. Thus, stability of the distribution of average particle energies in time does not insure ergodic behavior.

$P(\varepsilon;100\tau)$ is examined separately in Fig. 4. There the distributions for each species are indicated along with the total distribution. For the liquid the lower-energy peak is entirely due to type-1 particles (triangles) and the higher-energy peak is entirely due to type-2 particles (squares). This implies that all particles of a given type have identical average energies. Hence the distribution is peaked at the mean values for a given species with small dispersion. For the glass, however, the distributions for the two species are broad and there is considerable overlap of the distributions. Although the total distribution for the glass appears to be roughly a Gaussian, it should be viewed as a sum of two Gaussians, one for each species, with a large overlap between them. Note that the statistical similarity of all particles of a given type holds in the liquid but not in the glass. This suggests that the various peaks in the distribution $P(\varepsilon;\tau_{\mathrm{obs}})$ for the liquid state can be obtained by examining any arbitrary particle, whereas a similar exercise in the glassy state would lead to large errors. In this sense statistical symmetry is lost in the glassy phase.

We argue that the results for $P(\varepsilon;t)$ for liquids, supercooled liquids, and glasses point to the possibility of broken statistical symmetry. Because glasses are rigid and have nonzero shear elastic constants,[32,33] one expects that the symmetry of the system is lowered as a consequence

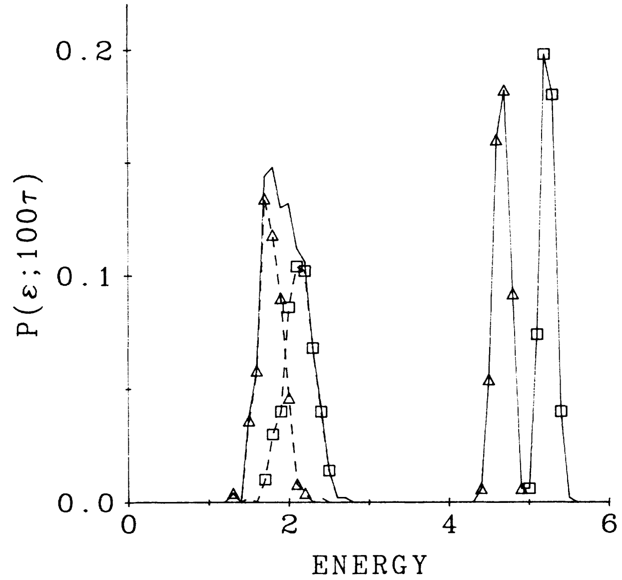

FIG. 4. $P(\varepsilon;100\tau)$ is resolved into contributions from the two species. The distribution of energies for type-1 particles are indicated by triangles connected by a dashed line, and the distribution of energies for type-2 particles are indicated by squares connected by a dashed line. The total distribution is indicated by a solid line. The dashed lines for the liquid are exactly overlaid by the solid line. The energy is in units of the energy parameter of Eq. (2.1).

of the liquid-to-glass transition, i.e., there is a broken symmetry associated with the glassy state. This statement should be treated with some caution because the connection between generalized rigidity and the presence of broken symmetry has been clearly established only for systems that undergo a genuine thermodynamic phase transitions.[14] It is well known that for glassy materials (especially polymeric glasses[34,35]) the different moduli depend on the experimental time scale. However, in many cases the changes in the elastic moduli are typically about 10% over a time range spanning several decades.[36] Thus for our arguments leading to the existence of broken symmetry, we will assume the near constancy of the elastic moduli and assume that the equations of an elastic solid are obeyed.[37] With this caveat, we present the following arguments to describe the statistical differences between the liquid and glassy states.

To illustrate the nature of this broken symmetry consider a large region of volume Ω_1 in the liquid state so that statistical measurements of the various properties [and in particular the calculation of $P(\varepsilon;t)$] become meaningful. The length implied by the choice of Ω_1 has nothing to do with the "correlation length" associated with the system. $P(\varepsilon;t|\Omega_1)$ calculated by following the dynamics of particles in Ω_1 is expected to be identical to that obtained from considering the "infinite" system. If one considers another large region of volume Ω_2 sufficiently far removed from Ω_1, then $P(\varepsilon;t|\Omega_2)$ calculated by following the dynamics of particles in Ω_2 also will be identical to $P(\varepsilon;t)$. These conclusions follow from the law of large numbers. In the liquid state there is a statistical symmetry in the sense that when a time average is performed,[38] one macroscopic region is statistically identical to another region. This is a weaker statement than the one that all particles of a given type are statistically identical.

In the glassy phase the motion of particles is cooperatively correlated within a system-specific region ξ.[16,39] Roughly speaking, there is order within a distance $r \approx \xi$ and the particles are randomly distributed for $r > \xi$. The introduction of a preferred length ξ does not imply that space is not homogeneous. In fact, for length scales larger than ξ the space is homogeneous, and there is no translational order, even when one performs a time average. For the binary mixtures we have considered here, $\xi \approx 3\sigma_{11}$, and a typical region of this size contains about 60 particles. The glassy phase can be thought of as being partitioned into a distribution of cooperatively rearranging regions (CRR) each with a correlation length of roughly ξ.[16] The distribution $P(\varepsilon;t|\Omega_i)$, Ω_i being the volume associated with the ith CRR, represents some part of the total distribution but due to the large number of distinct environments, no one $P(\varepsilon;t|\Omega_i)$ can be viewed as representative of a system, even though each CRR can contain a sufficiently large number of particles that they may be viewed as independent statistical systems. If one considers the entire sample, i.e., all the Ω_i, then the distribution has the form shown for the glass in Fig. 3. From the central-limit theorem it follows that $P(\varepsilon;t)$ for the binary soft-sphere mixture is a sum of two Gaussians. The crucial point is that the behavior of $P(\varepsilon;t)$ can only be obtained by considering the *whole sample* and any two CRR can yield results quite different from that seen in the infinite system. It is in this sense that statistical symmetry is broken in the glassy state.

In order to confirm these ideas we divided the sample (the cubic box) into eight subvolumes, each subvolume being considered to be a CRR. The distribution of energies for each of the CRR was constructed by considering only those particles residing in a given CRR. We find that the various distributions $P(\varepsilon;t|\Omega_i)$ $(i=1,8)$ are fragments of the total with considerable variation from one CRR to another, in accord with the above ideas. It should be pointed out that because of the small system being considered, the result of the simulations for this purpose should be considered as being suggestive. Nevertheless, this exercise confirms the physically motivated arguments.

The concept of statistical symmetry can also be viewed as a statement that all particles of a specific type are "equivalent." In particular, this is a statement that in the equilibrium fluid, each particle of a given type is statistically equivalent to all other particles of that type. The sharpening of $P(\varepsilon;t)$ in the liquid as time increases is a reflection of this. Conversely, the breaking of statistical symmetry in the glass is an indication that this statistical equivalence is not present. Statistical symmetry is a time-averaged quantity and cannot be inferred by examining time-independent properties of a system. More importantly, statistical symmetry cannot be examined by considering a single frozen pattern of the liquid or the glassy phase. The inference that statistical symmetry is broken in the glassy phase has been made by considering an ensemble of CRR with each CRR containing many particles. Thus in a sense this symmetry is a discrete symmetry of the system.

Due to the rigidity and the high degree of cooperativity of particles with a given CRR, the particles undergo only small-amplitude local displacements. Because the local environment varies from one CRR to another, we would predict that the density of transverse modes (excitations due to the rigidity of the glass) should be broad and structureless. This is in accord with experimental measurements on metal-metalloid systems.[40]

The dynamics in this glassy phase is expected to be dominated by rare fluctuations in CRR that lead to rearrangement of particles and hence structural relaxation.[16] Consequences of rare fluctuations of the type given here (referred to as droplet fluctuations) have been recently used to study the decay of spin-spin correlations functions in regular and random Ising systems.[41] Although there appears to be some similarity in the physics of the two problems, a more quantitative implementation of this idea, leading to precise predictions of the long-time behavior of the dynamic structure factor is difficult. However, the arguments similar to those suggested by Adams and Gibbs would immediately lead to a Vogel-Fulcher equation for the temperature dependence of the viscosity.[26(a)]

The idea that local fluctuations are important in characterizing the structure of the glassy state has also been recognized by Egami and his co-workers.[42–44] They have considered the role of local stresses and developed an elastic-energy-based model for the glassy state. They also have examined the distribution of local stresses for static situations.

V. DISCUSSION

The ergodic behavior of liquids, supercooled liquids, and glasses has been investigated in this paper. It has been shown that precise predictions about the finite-time properties and the time scale needed to obtain (effective) ergodicity can be made. This is done by the introduction of an energy metric $d(t)$, which is shown to obey a universal dynamical scaling law for long but finite times. The argument of the scaling function contains a parameter, namely a "diffusion" constant D_E, which is essentially the rate at which configuration space is sampled. Thus $1/D_E$ can be thought of as a mixing time. In the usual analysis of physical systems obeying differential equations (such as Hamilton's equations) mixing times are obtained by computing Lyapunov exponents. Although, for the conservative systems considered in this work, these characteristic exponents can be calculated in principle, in practice such computations are very difficult. Furthermore, for systems with very large numbers of degrees of freedom, the results are not easy to interpret. Here we indicate that D_E explicitly plays the role of Lyapunov exponents and thus the ergodic behavior for conservative systems (more generally measure preserving systems) with very large numbers of degrees of freedom can be inferred from a single parameter.

We have also studied the distribution of energies of the individual particles both in the liquid and in the glassy states.[45] A careful analysis of the variance of the distributions in different states has been used to argue that a discrete symmetry of the system, labeled statistical symmetry, is broken when the liquid makes the transition to a glassy state. It should be stressed once more that these arguments have been made by noting that the relevant time scale involved in the problem is the experimental or observational time scale τ_{obs}. Consequently, the lowest frequency of interest is $\omega_0 \approx 1/\tau_{\text{obs}}$. We suggest that the rigidity of the glassy phase as indicated by the nonzero shear modulus at $\omega \approx \omega_0$ is closely connected with broken statistical symmetry. These conclusions were reached by examining the time-averaged properties of the subsystems of the glass (referred to as CRR) and by noting that the statistical mechanical properties of the glassy states can only be inferred by considering the ensemble of all the subsystems. The long-time dynamics in the glassy phase is thus dominated by fluctuations in the subsystems in conformity with the ideas originally proposed by Adams and Gibbs.

The analogy between the diffusion process in the space of the time-averaged energy variables $x_i(t) = \varepsilon_{ai}(t) - \varepsilon_{bi}(t)$ suggests a similarity with the more familiar Arnold diffusion involving excursion of the actions along resonance layers.[7] The phase space is filled with the resonance layers entangled in a complicated manner leading to the Arnold web. It has been shown the time scale for Arnold diffusion goes as $\exp(1/\delta^a)$, where δ is the strength of coupling between the resonance layers and $a > 0$.[46,47] Using this diffusion analogy and noting that the diffusion constant introduced in this paper decreases dramatically as the temperature is decreased, we can infer that the effective coupling between the components decreases as the degree of supercooling increases. Thus the time scale for obtaining ergodicity increases exponentially. If this analogy is indeed correct, then this should be reflected in the motion of the particles. We have examined the local dynamics of several particles and have noted that in the glassy phase, the trajectory of a test particle appears almost "quasiperiodic" for long times. These ideas are pursued in detail elsewhere.[48]

ACKNOWLEDGMENTS

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[1] The history of the ergodic hypothesis in statistical mechanics is marked by several changes in the content of the assumptions and is not a closed subject. For our purposes, we use the term "ergodic" only to imply the equivalence of ensemble and time averages. See A. S. Wightman, in *Statistical Mechanics at the Turn of the Decade,* edited by E. G. D. Cohen (Decker, New York, 1971), pp. 1–32, for a discussion of ergodic theory.

[2] V. I. Arnold and A. Avez, *Ergodic Problems of Classical Mechanics* (Benjamin, New York, 1968).

[3] For a review, see R. G. Palmer, Adv. Phys. **31**, 669 (1982).

[4] A. C. D. van Enter and J. L. van Hemmen, Phys. Rev. A **29**, 355 (1984).

[5] The ergodic hypothesis is also central in the computer simulation technique of molecular dynamics which is a well-established method for studying condensed matter systems. The essential aspects of this technique were described by A. Rahman, Phys. Rev. **136**, A405 (1964).

[6] For a recent review see J.-P. Eckman and D. Ruelle, Rev. Mod. Phys. **57**, 617 (1985).

[7] A. J. Lichtenberg and M. A. Lieberman, *Regular and Stochastic Motion* (Springer-Verlag, New York, 1983).

[8] G. Benettin, L. Galgani, and J. M. Strelcyn, Phys. Rev. A **14**, 2338 (1976).

[9] I. Shimada and T. Nagashima, Prog. Theor. Phys. **61**, 1605 (1979).

[10] G. Benettin, L. Galgani, A. Giorgilli, and J. M. Strelcyn, Meccanica **15**, 9 (1980).

[11] Some attempts to obtain Lyapunov spectra involving 32 particles have been recently made by W. G. Hoover, H. A. Posch, and S. Bestiale, J. Chem. Phys. **87**, 6665 (1987).

[12] See, for example, C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, Adv. Chem. Phys. **48**, 397 (1981).

[13] P. W. Anderson, in *Ill Condensed Matter,* edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, Amsterdam, 1979).

[14] For a lucid discussion of the connection between rigidity and broken symmetry, see P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Benjamin, Menlo Park, CA, 1984); see also D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, Reading, MA, 1975).

[15] J. M. Kosterlitz and D. Thouless, J. Phys. C **6**, 1181 (1973). See also D. R. Nelson, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 7.

[16] G. Adam and J. M. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[17] B. Bernu, Y. Hiwatari, and J. P. Hansen, J. Phys. C **18**, L371 (1985); B. Bernu, J. P. Hansen, Y. Hiwatari, and G. Pastore, Phys. Rev. A **36**, 4891 (1987).

[18] (a) D. Thirumalai and R. D. Mountain, J. Phys. C **20**, L399 (1987); (b) R. D. Mountain and D. Thirumalai, Phys. Rev. A **36**, 3300 (1987).

[19] J. G. Amar and R. D. Mountain, J. Chem. Phys. **86**, 2236 (1987).

[20] T. W. Leland, J. S. Rowlinson, and G. A. Sather, Trans. Faraday Soc. **64**, 1447 (1968).

[21] For reviews describing the KAM theorem and its applications for dynamical systems see (a) J. Ford, in *Fundamental Problems in Statistical Mechanics,* edited by E. G. D. Cohen (North-Holland, Amsterdam, 1975) and Adv. Chem. Phys. **24**, 155 (1973); (b) K. J. Whiteman, Rep. Prog. Phys. **40**, 1033 (1977); (c) M. V. Berry, in *Topics in Nonlinear Dynamics (La Jolla Institute),* Proceeding of the Workshop on Topics in Nonlinear Dynamics, AIP Conf. Proc. No. 46, edited by S. Jorna (AIP, New York, 1978), p. 16; (d) Y. M. Treve, *ibid.*, p. 147.

[22] Y. G. Sinai, Russ. Math. Surv. **25**, 137 (1970).

[23] The invariant measure refers to the set of configurations belonging to a specified component. These configurations are the set of phase points that lead to a given local free-energy minimum in the quench process.

[24] D. A. Huse and D. S. Fisher, J. Phys. C **20**, L997 (1987).

[25] The long-time limit of $\varepsilon_{aj}(t)$ and $\varepsilon_{bj}(t)$ are well-defined quantities. There will be $1/N$ corrections to the long-time limit of the quantities which have no consequence in the thermodynamic limit. These $1/N$ corrections are not relevant in the definition of the energy metric. Thus $d(t)$ can be unambiguously defined even when N is finite.

[26] (a) It has been suggested recently [T. R. Kirkpatrick and D. Thirumalai, J. Phys. A (to be published)] that these metastable states can be viewed as saddle point solutions which minimize the free energy calculated using a coarse-grained density-functional Hamiltonian. Such a precise characterization of the metastable state is only possible because the scenario suggested above is based on a mean-field theory. (b) For a heuristic argument suggesting that the number of metastable free-energy minima should grow exponentially with N see F. H. Stillinger and T. A. Weber, Science **225**, 983 (1984).

[27] J. P. Bouchad, A. Georges, and P. Le Doussal, Europhys. Lett. **5**, 119 (1988).

[28] W. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, New York, 1950).

[29] F. H. Stilliger and T. A. Weber, Phys. Rev. A **25**, 978 (1982); **28**, 2408 (1983); T. A. Weber and F. H. Stillinger, Phys. Rev. B **32**, 5402 (1985).

[30] These ideas can be made precise using certain mean-field random Potts models. See T. R. Kirkpatrick and P. G. Wolynes, Phys. Rev. B **36**, 8552 (1987); D. Thirumalai and T. R. Kirkpatrick, *ibid.* **38**, 4881 (1988); T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. A **37**, 5342 (1988).

[31] For a recent review, see J. Jäckle, Rep. Prog. Phys. **49**, 171 (1986); C. A. Angell, J. Non-Cryst. Solids (to be published).

[32] See, for example, H.-U. Künzi, in *Glassy Metals II,* edited by H. Beck and H.-J. Güntherodt (Springer-Verlag, New York, 1983).

[33] C. P. Chou, L. A. Davis, and R. Hasegawa, J. Appl. Phys. **45**, 4126 (1974).

[34] J. R. McLoughlin and A. V. Tobolsky, J. Colloid Sci. **7**, 555 (1952).

[35] J. Murray and D. Hull, J. Poly. Sci. **8**, 1521 (1970).

[36] J. T. Krause, J. Non-Cryst. Solids **14**, 32 (1974); IEEE Trans. Sonics Ultrason. **19**, 34 (1972). In this study the change of elastic modulus was found to be a few parts per million over a period of days.

[37] L. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1986).

[38] The averaging time should be larger than any transient time in the problem.

[39] For a further discussion exploiting the concept of CRR, see E. Donth, J. Non. Cryst. Solids **53**, 325 (1982).

[40] C. G. Windsor, H. Kheyrandish, and B. C. Narasimhan, Phys. Lett. **70A**, 485 (1979); J.-B. Suck and H. Rudin, in Ref. 32.

[41] D. A. Huse and D. S. Fisher, Phys. Rev. B **35**, 6841 (1987).

[42] T. Egami and S. Srolovitz, J. Phys. F **12**, 2141 (1982).

[43] D. Srolovitz, T. Egami, and V. Vitek, Phys. Rev. B **24**, 6936 (1981).

[44] S.-P. Chen, T. Egami, and V. Vitek, Phys. Rev. B **37**, 2440 (1988).

[45] The distribution function $P(\varepsilon;t)$ can be roughly thought of as the density of single-particle states for the glass. It can be shown that variance of the distribution function is related to the Fourier transform of the dynamic energy correlation function $\langle \varepsilon(t)\varepsilon(0)\rangle$. Using the Gaussian distribution $P(\varepsilon,\tau)\approx\exp(-\varepsilon^2/2\langle\varepsilon^2\rangle)$, and by assuming that transport in the glassy phase proceeds when the energy of a single particle exceeds a typical barrier height β, an average relaxation time can be computed. This would be given by $\tau(\beta)\approx\int_{\varepsilon^*\approx kT}^{\infty}\exp(-\varepsilon^2/2\langle\varepsilon^2\rangle)\exp(\beta\varepsilon)d\varepsilon$. Evaluating this integral and taking appropriate limits, $\tau(\beta)$ can be expressed in terms of the variance. If this variance is taken to be proportional to a characteristic temperature T_0 [H. Bassler, Phys. Rev. Lett. **58**, 767 (1987)], then $\tau(\beta)\approx\exp[(T_0/T)^2]$. The variance can be related to entropy changes and this would lead to $\tau(\beta)\approx\exp[A/(T-T_K)^2]$, where T_K is the temperature where the excess configurational entropy vanishes. [J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. **28**, 573 (1959).] However, it should be pointed out that one expects structural relaxation in glasses to proceed via a correlated or cooperative mechanism involving more than one particle. A recent study [H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. **88**, 3879 (1988)] has explicitly examined such motions in the glassy state. Thus a proper account of relaxation times has to consider the distribution of energy describing such events which is more difficult to compute. Using such distributions may lead naturally to the more accepted Vogel-Fulcher form for the temperature dependence of relaxation times.

[46] V. I. Arnold, *Geometrical Methods in the Theory of Ordinary Differential Equations* (Springer-Verlag, New York, 1983), p. 163.

[47] For a numerical study of Arnold diffusion see B. B. Chirokov, J. Ford, and F. Vivaldi, in *Nonlinear Dynamics and the Beam-Beam Interaction* (Brookhaven National Laboratory, 1979), Proceedings of the Symposium on Nonlinear Dynamics and Beam-Beam Interaction, AIP Conf. Proc. No. 57, edited by M. Month and J. C. Herrea (AIP, New York, 1979), p. 323.

[48] R. D. Mountain and D. Thirumalai (unpublished).