

Molecular-dynamics study of glassy and supercooled states of a binary mixture of soft spheres

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A series of molecular-dynamics simulations of binary-fluid mixtures composed of softly repelling spheres have been made as part of an investigation of the glass-forming properties of mixtures. These mixtures are simple prototypes of glass-forming systems, as both randomness and frustration are intrinsic to them. The randomness is inherent in the fluid and frustration is due to the large, local rearrangement of atoms required for the formation of a crystal from a fluid or glassy configuration. The equation of state, pair and triplet correlation functions, single-particle velocity time autocorrelation functions, and some measures of local glassy order have been determined for a range of compositions, X , and effective reduced densities, $\Gamma_{\text{eff}} = (n^*/T^{*1/4})(\sigma_{\text{eff}}/\sigma_{11})^3$, where σ_{eff} is the one-fluid van der Waals equivalent diameter. In addition, attention has been focused on the relaxation of some anisotropic correlation functions characterizing the local environment. Attempts have been made to analyze some of these quantities using plausible phenomenological models. The changes in these quantities which occur as the fluid is supercooled and finally forms a glass are examined and the possible implication of these findings for certain dynamical theories of the glass transition are discussed. Calculations have also been performed to determine compositional conditions necessary for a supercooled liquid to crystallize and the relevance of this to recent experiments is discussed.

I. INTRODUCTION

The problem for statistical mechanics posed by the existence of glassy, nonequilibrium states of matter is one of the most challenging ones currently being studied. Although considerable progress has been made in understanding the mean-field solution to certain classes of spin-glass models,¹ the theory for the more difficult structural glass problem involving topological disorder² is not well developed. One of the main reasons for this difficulty is that, unlike in the case of mean-field spin-glass models, it has been quite difficult so far to construct a simple model³ (or a tractable field theory) that can adequately describe the abrupt increase in viscosity which is observed as a liquid nears the glass transition temperature.⁴ A way to make progress is to assume that some mode becomes frozen in (i.e., the relaxation time associated with a decay of that mode diverges or becomes extremely large) and to look for a dynamical mechanism that describes this. Indeed, Leutheusser⁵ proposed a model based on kinetic theory in which it was assumed that the density fluctuations become frozen in as the glass transition temperature, T_g , is approached.⁵⁻¹¹ The freezing in of the density fluctuations occurs because of a nonlinear feedback mechanism which inhibits structural relaxation.⁹ However, diffusion is itself determined by the ability of the particles to undergo structural rearrangements. Thus, the structural

relaxation time, τ_{st} , becomes a function of the structure-dependent viscosity, $\eta(\tau_{\text{st}})$, and the self-consistent solution for τ_{st}^{-1} leads to a power-law divergence as T_g is approached.⁵⁻⁹ However, in laboratory glasses, there appear to be several regimes where the viscosity scales differently with temperature.¹² A natural question that arises is whether there are additional parameters whose relaxation directly, or indirectly, controls the abrupt rise in the viscosity. The current dynamical theories do not predict the varied behavior of the shear viscosity, η , of laboratory glasses as a function of temperature. In particular, the crossover from a power-law behavior in η to an Arrhenius-type behavior close to T_g is not well understood. Several computer-simulation studies¹³ of simple models have been attempted in order to shed light on this issue, but many of the essential ingredients needed to postulate a dynamical model have not yet been determined. The present work is an initial attempt towards this end. In particular, the work reported here represents a preliminary step in an investigation of the formation of glassy states for two-component systems interacting via continuous potentials. It certainly is desirable to have a simple, well-characterized system to serve as a test case when developing ideas on how to describe the glassy state. One goal of this work is to provide such a well-characterized system.

We have chosen to study the binary-fluid mixture of softly repelling spheres. It is an attractive candidate for

such a test-case system because it is one of the simplest systems to form a glass readily.¹⁴ Two important features of a glass-forming system have been identified as “randomness” and “frustration.” The ease with which a “computer glass” is formed from a binary mixture is a result of the inherent randomness of the arrangement of the particles in the fluid and the frustration associated with the relatively large local displacements needed to organize the atoms in a crystalline arrangement starting with a distorted fluid configuration. A binary mixture requires interchanges of atoms whereas a one-component soft-sphere fluid only requires small displacements of atoms to form a crystal. The result is that the frustration is much weaker in the one-component fluid than in a mixture. The extent to which the system experiences topological frustration depends on the composition and the size ratio of the two components, and probably on the quenching rate. Thus it appears that frustration would be a rather difficult thing to quantify, but model free energies which capture the essence of frustration can be written down.^{15,16} It is appropriate to search for the consequences of frustration and it seems clear from the work reported here that in the structural glass-transition problem there is a finite length scale associated with frustration. Consequently, we have attempted to identify an appropriate “local” order parameter which exhibits an increasing relaxation time with decreasing temperature and which is for practical purposes frozen in at and below T_g . We report here the results of a series of molecular-dynamics simulations of the binary soft-sphere system with a view towards addressing some of the issues raised above. Another objective of this work is to develop a body of information about a typical model of glass-forming systems to serve as a resource on which to base refined studies.

We have determined equilibrium properties such as the pressure, energy, and temperature relations for mixtures of soft spheres as functions of concentration, and of the relative size of the spheres. This part of the study complements the work of Bernu *et al.*¹⁴ We also calculate the pair correlation functions and a reduced triplet function which has proved successful in characterizing the structure of fluids in other contexts.¹⁷ The latter quantity may be especially useful (and perhaps necessary) in understanding the structure in supercooled liquids where a localized, highly correlated motion is involved in the processes of structural relaxation.

One of our major objectives is to shed some light on the reasons for the large rise in the viscosity which occurs when a supercooled liquid is cooled to the glass-transition temperature. Computer-simulation studies cannot by themselves reveal the physical mechanism for properties that are dominated by events that happen with exponentially small probability. However, it is hoped that by a systematic study of several time-dependent correlation functions one will be able to propose dynamical models for relaxations in glasses and this remains one of our major purposes. Accordingly, we determine several dynamical quantities, namely, the self-diffusion coefficients and the single-particle velocity time autocorrelation functions for the mixtures. A

correlation between their behavior and the degree of supercooling is made. In addition, we also examine possible candidates for local order parameters which might help analyze relaxation near the glass-transition temperature. While we are not able to identify a specific quantity as an obvious choice of order parameter, it seems clear to us that a useful order parameter should be a local quantity. The basic reason why the order parameter characterizing the very slow structural relaxation should be a local quantity is the following. Very close to the glass-transition temperature, the viscosity is believed to be described by a Vogel-Fulcher-Tammann law¹⁸ and thus structural relaxation is expected to proceed by some type of activated process involving transitions between barriers which separate the various minima of the free-energy surface. Because liquid and glassy states do not have long-range spatial order, it is physically plausible to assume that such a barrier-crossing event should involve only a few particles and consequently the relaxation process should be described by a local order parameter. We return to this point in greater detail in Sec. IV.

The remainder of this paper is organized as follows. The details of the model and the computational procedures are described in Sec. II. In Sec. III we discuss the equilibrium properties as the binary mixture is supercooled and we also compare the results of our work with the results for dense-random-packed models. Section IV is devoted to the results of the dynamical properties including the presentation of the relaxation of several local-order parameters. An attempt is made to analyze some of these in terms of phenomenological models. In Sec. V we discuss in some detail the conditions under which binary-fluid mixtures crystallize as they are supercooled. This is corroborated with certain very simple empirical theories. The relevance of this to recent experiments involving vapor deposition of binary mixtures containing Fe is also discussed. The paper is concluded in Sec. VI with some discussion and speculation concerning the applicability of our work to the construction of dynamical models for structural glass transition.

II. MODEL AND COMPUTATIONAL DETAILS

The model for 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 σ_{22} . 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

$$\phi_{AB}(r_{ij}) = \epsilon(\sigma_{AB}/r_{ij})^{12}. \quad (1)$$

We assume that the cross-interaction diameters are additive, namely, that $\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$. Deviations from this rule lead to a variety of clustering effects which are of interest in themselves, but which are outside the scope of this investigation.¹⁷ In the simulations discussed in this paper the total number of particles, $N = N_1 + N_2$, was always 500. The concentration variable $X = N_1/N$ specifies the concentration of type-1 particles. We use σ_{11} as the unit of length, m_1 as the unit of mass, and ϵ as the unit of energy. Time is quoted in units of

TABLE I. Parameters for the soft-sphere systems studied by computer simulation.

X	σ_{22}/σ_{11}	Range of Γ_{eff}	Symbol
0.2	1.2	0.93–1.60	□
0.8	1.2	0.85–1.53	○
0.4	1.2	1.20–1.71	△
0.5	1.2	1.20–1.64	+
0.5	1.1	0.92–1.70	◇
0.8	1.1	0.83–1.71	⊠
0.2	1.1	1.02–1.67	⊞

$$\tau = (m_1 \sigma_{11}^2 / \epsilon)^{1/2}. \quad (2)$$

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 $T^* = k_B T / \epsilon$, where k_B is Boltzmann's constant, and the pressure, p , is expressed in units of ϵ/σ_{11}^3 . Bernu *et al.*¹⁴ have suggested that it is useful to introduce an effective reduced density defined as

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

The quantity σ_{eff} is the one-fluid van der Waals equivalent diameter¹⁹ and is defined by

$$\sigma_{\text{eff}}^3 = X^2 \sigma_{11}^3 + 2X(1-X)\sigma_{12}^3 + (1-X)^2 \sigma_{22}^3. \quad (4)$$

We find Γ_{eff} to be a good measure of the composition dependence of the compressibility factor, $pV/Nk_B T$.

The system parameters considered in this paper are listed in Table I along with the range of thermodynamic states examined. Given the richness of the parameter space for a binary mixture, it is not possible to be exhaustive in the coverage of the thermodynamic possibilities. Instead, choices must be made based on the motivation of the investigation. The choices represented in Table I reflect our interest in the supercooled liquid and in the glassy state.

The simulations were performed for constant energy-constant volume conditions and periodic-boundary conditions were employed. The equations of motion were integrated using the Beeman algorithm²⁰ with a time step of 0.01τ . Production runs of 10 000 time steps were made to collect results once a stable thermodynamic state had been established. The stability of the state was checked by comparing results from sequential runs.

III. EQUILIBRIUM PROPERTIES

A. Equation of state

Because of the form of the interaction, Eq. (1), the pressure p , energy E , and temperature T of the fluid are related by

$$pV/Nk_B T = 4E/Nk_B T - 5, \quad (5)$$

independent of the composition, masses, and size ratios of the components.²¹ This equation follows from the application of the virial theorem to the soft-sphere model. Bernu *et al.*¹⁴ have indicated that the compressibility

factor $pV/Nk_B T$ is a function of the effective reduced density Γ_{eff} with the form

$$pV/Nk_B T = 7 + 6.848\Gamma_{\text{eff}}^4. \quad (6)$$

Our results confirm this scaling with Γ_{eff} as is shown in Fig. 1 where $pV/Nk_B T$ values for all of the fluid states we have examined are plotted as a function of Γ_{eff} . All of the composition and size-ratio dependence of the thermodynamic properties of these mixtures is contained in their dependence on Γ_{eff} . This dependence of the compressibility factor, $pV/Nk_B T$, holds both in the liquid and in the glassy states. It is not known for how large a size ratio this result will hold, although it holds for $\sigma_{22} \leq 1.4\sigma_{11}$.¹⁴

B. Pair functions and partial three-body correlation functions

The structure of the mixture has been examined in terms of the pair functions, $g_{11}(r)$, $g_{12}(r)$, and $g_{22}(r)$. These functions are normalized so that they approach X^2 , $2X(1-X)$, and $(1-X)^2$, respectively, for large separations of the atoms. Note that this choice of normalization differs from that of Bhatia and Thornton²² by these factors. The pair functions are shown in Figs. 2–4 for $X=0.5$ and for three values of Γ_{eff} (referred to below as “the three values of Γ_{eff} ”), namely, 1.26, 1.37, and 1.7. These functions have been constructed with a spatial resolution of 0.01. The first state is a liquid, perhaps slightly supercooled, the second state is a significantly supercooled liquid and the third state is a glass. Note that for $\Gamma_{\text{eff}}=1.37$, the second peak in each of the pair functions is slightly broadened, but is not split, as is the case for $\Gamma_{\text{eff}}=1.7$. This is in contrast to the results of

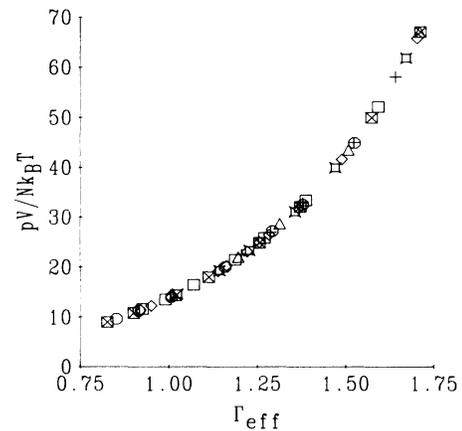


FIG. 1. Compressibility factor, $pV/Nk_B T$, is shown as a function of the reduced density Γ_{eff} for all of the fluid thermodynamic states examined in this work. Well-annealed glassy state values are slightly lower than the fluid values shown here. The plotting symbols are listed in Table I along with relevant system parameters. This clearly shows that $pV/Nk_B T$ scales with Γ_{eff} and that the concentration dependence is embodied in the reduced density.

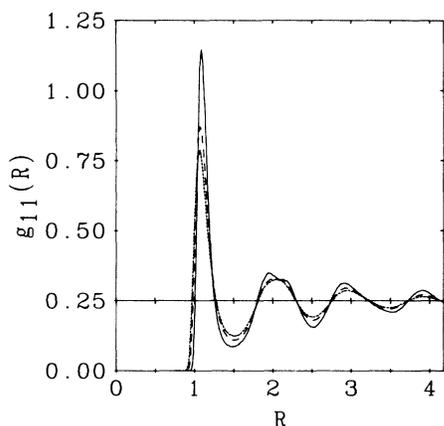


FIG. 2. Pair functions $g_{11}(r)$ for the $X=0.5$ mixture of soft spheres with $\sigma_{22}=1.1\sigma_{11}$. The solid line is for $\Gamma_{\text{eff}}=1.7$, a glass, the dashed line is for $\Gamma_{\text{eff}}=1.37$, and the dotted line is for $\Gamma_{\text{eff}}=1.26$.

Bernu *et al.*¹⁴ who report that the splitting in the second peak occurs for $\Gamma_{\text{eff}} \geq 1.3$, which is a supercooled liquid. The glassy state is reached when $\Gamma_{\text{eff}} \approx 1.5$. Probably this apparent difference in where the splitting occurs is a consequence of the different spatial resolutions used in the two simulations. (We have extended our runs for $\Gamma_{\text{eff}}=1.37$ and do not find any indication of the g_{AB} 's changing as the length of the simulation increases.) In any case, the evolution of the structure of the second peak is a gradual process suggesting that the development of the two well-defined, but slightly different, distances near $r \approx 2$ is not an abrupt event. Instead, the distance between pairs of particles becomes better defined in a continuous manner as Γ_{eff} increases. Also for the glass there is no indication of a well-defined shell of particles at the position of the second neighbors in a close-packed crystal. The same sort of structure is found for $X=0.8$ for these values of Γ_{eff} , indicating that

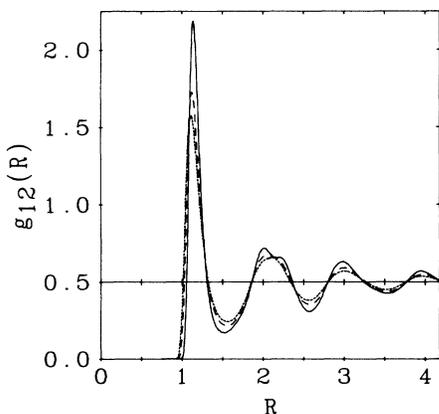


FIG. 3. Pair functions $g_{12}(r)$ for the $X=0.5$ mixture of soft spheres with $\sigma_{22}=1.1\sigma_{11}$. The solid line is for $\Gamma_{\text{eff}}=1.7$, a glass, the dashed line is for $\Gamma_{\text{eff}}=1.37$, and the dotted line is for $\Gamma_{\text{eff}}=1.26$.

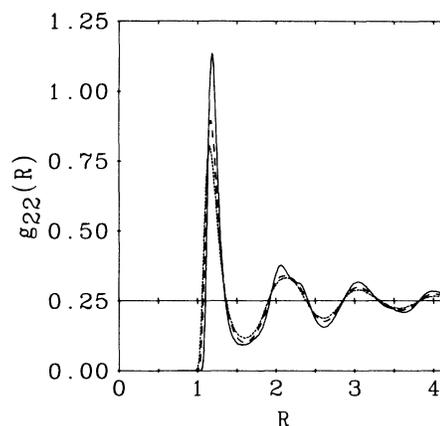


FIG. 4. Pair functions $g_{22}(r)$ for the $X=0.5$ mixture of soft spheres with $\sigma_{22}=1.1\sigma_{11}$. The solid line is for $\Gamma_{\text{eff}}=1.7$, a glass, the dashed line is for $\Gamma_{\text{eff}}=1.37$, and the dotted line is for $\Gamma_{\text{eff}}=1.26$.

the glass forming trends are not strongly dependent on the composition. The system with $X=0.2$ initially formed a glass for $\Gamma_{\text{eff}}=1.7$, but on extensive annealing at constant energy a structure with the signature of a close-packed crystal formed. This is discussed further in Sec. V.

The coordination numbers for the states displayed in Figs. 2–4 have been determined by integrating these functions to $r=1.5$, the position of the minimum in $g_{12}(r)$. The 1-1 coordination number ranges from 2.97 for $\Gamma_{\text{eff}}=1.26$ to 3.02 for $\Gamma_{\text{eff}}=1.7$. The corresponding ranges for the 1-2 and 2-2 coordination numbers are 6.19–6.21 and 3.19–3.33, respectively.

We have also examined the scaling properties of the pair distribution functions, $g_{11}(r)$, $g_{12}(r)$, and $g_{22}(r)$ by varying the composition for fixed Γ_{eff} . As is shown in Fig. 5, these functions exhibit significant departures from the form $g_{AB}(r/\sigma_{\text{eff}}, \Gamma_{\text{eff}})$. In Fig. 5 the normalization of $g_{11}(r)$ has been changed so that $g_{11}(r)$ approaches unity for large separation. This has been done in order to emphasize the departures from the scaling form as the concentration is varied. This lack of scaling in the pair functions reflects the fact that it is $pV/Nk_B T$ and not the local structure which scales with Γ_{eff} .

Pair correlations do not provide any information about how local arrangements involving three or more particles might occur. Some further insight into the structure which develops as the temperature is lowered can be obtained by examining some partial three-body correlation functions. We have generated $P(\cos\theta)$, the distribution of the cosines of the angles formed by the lines or bonds connecting two particles to a third, central particle, when the two particles are “near neighbors” of the central particle.¹⁷ Near neighbor is taken to mean that the length of the bonds is less than the position of the minimum in $g_{12}(r)$ following the principal maximum. From Fig. 3 we see that this is approximately $1.5\sigma_{11}$. (This definition of a near neighbor is used throughout this paper.) At equilibrium liquid tempera-

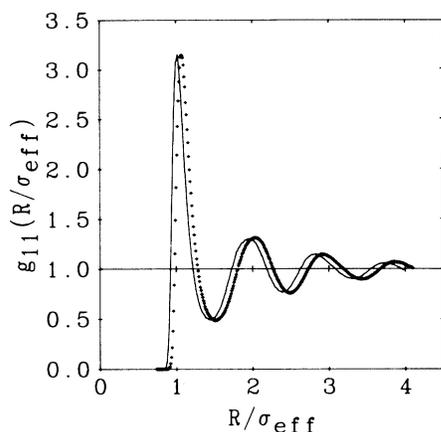


FIG. 5. The $g_{11}(r/\sigma_{\text{eff}})$ function for $\Gamma_{\text{eff}}=1.26$ with $X=0.5$ (solid line) and $X=0.8$ (+). The normalization has been changed from that of Fig. 2, so that $g_{11} \rightarrow 1$ for large separations. Similar results are obtained for the g_{12} and g_{22} functions showing that the pair functions do not scale with σ_{eff} for a given value of Γ_{eff} .

tures these distributions are peaked at about 60° with little structure for larger angles. As the temperature is lowered, additional structure develops, indicating that certain packings are favored. This type of analysis has been used to distinguish between short range fcc and bcc arrangements of particles²³ and to distinguish between crystalline and glassy configurations.²⁴ These distributions are displayed in Fig. 6 for the same states listed for Figs. 2–4. The major features, in addition to the maximum at 60° , are the secondary maxima at 110° – 120° and at 180° . These secondary maxima become more pro-

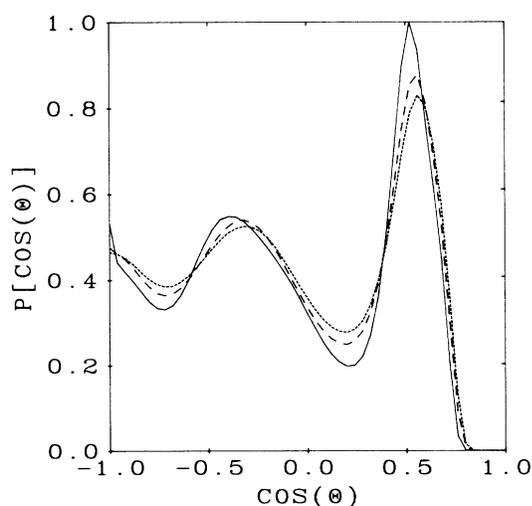


FIG. 6. Distribution of bond angles for pairs of near-neighbor particles for $X=0.5$ mixtures and $\Gamma_{\text{eff}}=1.26$ (dotted line), $\Gamma_{\text{eff}}=1.37$ (dashed line), and $\Gamma_{\text{eff}}=1.7$ (solid line). These functions have been scaled by the maximum in the $\Gamma_{\text{eff}}=1.7$ distribution.

nounced with increasing Γ_{eff} , suggesting that there is a tendency toward a locally ordered, incomplete fcc arrangement.²⁵ (A fcc structure would have spikes at 60° , 90° , 120° , and 180° for near-neighbor pairs.) However, the peaks are broad and the minima are relatively shallow when compared with a truly crystalline arrangement and the 90° feature is absent, indicating that the first shell of neighbors is not actually ordered as in a crystal. The absence of 90° feature indicates that ordering does not extend to second neighbors since the pairs with 90° bond angles are at second-neighbor distances. This information, when combined with the pair-function results, suggests that the glass consists of “units” which are locally ordered at the first-neighbor distance but are disordered for larger distances. Certainly the quasicrystalline configuration does not reach to the second-neighbor distance as evidenced by the absence of a local maximum in the pair functions at the second-neighbor distance for a fcc crystal. As noted above, the information derived from these triplet distributions is essential in determining the nature of the short-range local order present in the glass. This suggests that one should include triplet (and higher-order) correlations in an effective free energy to describe dynamical properties such as the density-density correlation function for supercooled liquids close to the glass-transition temperature.

C. Comparison with dense random packing models

There have been numerous studies of the structure of alloy glasses by generalizing the dense-random-packing (DRP) algorithm developed by Bennett.²⁶ The earliest work was due to Sadoc, Dixmier, and Guinier²⁷ and formed the basis of further investigations by Bondreaux and Greger.^{28,29} In these studies a triad consisting of three touching atoms forms the initial seed and an algorithm was developed so that the growing cluster attained the proper composition. Addition of another atom is made at random subject to the constraint of the desired composition. These authors introduced the rule that two smaller atoms (modeling the metalloid) cannot be near neighbors. The initial studies^{28(a)} indicated that close-packed structures were not obtained with this algorithm. They also discovered that the pair distribution functions were anisotropic, i.e., their values depended on the direction in which the radial distance from the center of the grown cluster is measured. These problems were circumvented by annealing by DRP cluster under a Lennard-Jones potential using the conjugate gradient method to relax the system to a local potential-energy minimum.^{28(b),29} The resulting radial distribution functions are quite similar to the results we have obtained for the soft-sphere mixtures. They also were found to reproduce experimental structures of alloy glasses. It is interesting to point out that in the DRP model of Bennett,²⁶ the second part of the split is larger than the first. This is in contrast to the simulation studies of one-component systems.³⁰ However, the relaxed DRP model of alloys also yields split second peaks of pair functions which are in accord with molecular-dynamics simulation

results. This may either be due to the relaxation of the original DRP model or due to the weak constraint prohibiting metalloid atoms to be near neighbors. It would be interesting to obtain the bond orientational order in DRP representations of metal-metalloid systems.

IV. DYNAMICAL PROPERTIES

From Sec. III it is clear that in binary mixtures, as is the case in single-component systems, the structural properties of the system change continuously as the degree of supercooling is increased. As has been pointed out in the introduction, the dynamical properties of the liquid, and in particular the shear viscosity, show an abrupt increase as T_g is approached. Although there have been experiments suggesting that in some temperature regime η scales as a power law,³¹ it seems well accepted that for T close enough to T_g (say $T/T_g \geq 0.7$), η obeys the well-known Vogel-Fulcher-Tammann law,¹⁸ $\eta \approx \exp[A/(T - T_0)]$. This can only be explained by models that involve stress-assisted thermal activation over free-energy barriers. This idea is certainly not new²² and was proposed over thirty years ago to explain cold flow in glassy polymers and plasticity properties of inorganic glasses.³³ Slow structural relaxation near T_g , which involves transitions between several local free-energy minima, appears to be consistent with the detailed numerical simulations of Stillinger and Weber.³⁴ Hall and Wolynes³⁵ have utilized the notion of the shape of inherent structure in liquids and have obtained an expression for the relaxation time for activated crossing. Using density-functional theory they were able to estimate the average barrier height in the free-energy surface in terms of the spring constant for atomic motion. Assuming that viscous relaxation is dominated by transitions between free-energy barriers, they predicted that η is proportional to $\exp[c/(V - V_0)^2]$.

Our interest in pinning down the physical mechanism leading to Vogel-Fulcher-Tammann (or similar law) behavior can be summarized as follows. By assuming that structural relaxation, and hence diffusion, in liquids near the glass transition proceeds by activated processes, it should be possible to identify an order parameter associated with this slow relaxation process. We believe that such an order parameter should be a local quantity which involves only a few particles within a specified, finite length scale. (This is in contrast to Ising spin glasses where all length scales contribute to diverging time scales near the spin-glass transition temperature.) The natural choice for this length scale seems to be the minimum in the radial-distribution function, which is approximately $1.5\sigma_{11}$. The free-energy surface (presumably) has a large number of local minima which correspond to metastable states. The various minima are separated by barriers and if the transition from one minimum to another involves rearrangement involving many particles (say hundreds) then that even is unlikely. Specifically, transitions from one metastable state to another requiring a large number of particles will either involve a large energy barrier or will have low entropy due to the coordinated motion of several particles and

thus will be a rare event. Thus activated processes enabling structural relaxation on the time scale of computer simulations, and perhaps on experimental time scales as well, can only involve clusters of a few particles. This physically reasonable assumption, which is also supported by similar findings in a previous simulation in the context of spin glasses,³⁶ has motivated us to search for relaxation of local correlation functions defined in terms of 10–15 particles. Unlike in spin-glass models, the nature of the order parameter is not obvious. Several candidates can be investigated and, in what follows, we present the results of a few of these. One of the most obvious ones that we have not investigated is associated with the decay of the local stress tensor.³⁷ We intend to pursue this topic in a future study.

A. Bond orientational order

In a series of papers Steinhardt *et al.*³⁸ have found that when a one-component Lennard-Jones liquid is undercooled about 10% below the melting temperature, a state with short-range translational order but with extended correlations in the orientation of clusters of particles results. Mountain and Brown³⁹ also observed these states for the Lennard-Jones liquid but did not observe metastable states of this type in soft-sphere one-component liquids. The orientational order of the metastable liquid was determined to be predominantly icosahedral and it was shown that the correlation length associated with the orientational order far exceeds the translational correlation length. The proliferation of icosahedral ordering in Lennard-Jones systems was rationalized using the arguments originally proposed by Frank.⁴⁰ He suggested that icosahedral clusters had lower energy compared to any microcrystalline arrangement. Nelson⁴¹ exploited this idea in a series of papers with an additional notion that frustration prevents the occurrence of infinite-range icosahedral order. This inability to form infinite-range icosahedral ordering suggests that the relaxation of the appropriate order parameter should exhibit an extremely slow decay and this has prompted us to investigate the bond orientational order parameter, Q_6 , which is defined below, as an indication of the presence of a glass.

A general parameter Q_l is defined as follows. Following Steinhardt *et al.*³⁸ we associate a bond joining an atom to its nearest neighbors. To each bond, a set of orientational order parameters Q_{lm} is defined to be the spherical harmonics associated with the orientation of the bond in the external coordinate system and $\langle Q_{lm} \rangle$ is the average over all near-neighbor bonds. The rotationally invariant quantity Q_l is then

$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^l |\langle Q_{lm} \rangle|^2 \right]^{1/2}. \quad (7)$$

The order parameter $\psi_l(t)$ is defined as an ensemble average as Q_l with itself at a later time t ,

$$\psi_l(t) = \langle Q_l(t)Q_l(0) \rangle. \quad (8)$$

Unlike in the one-component case where the average

value of Q_6 shows a strong correlation with the onset of the glassy state,^{38,39} it does not do so for a binary mixture. This has been noted earlier.⁴² Since the glass transition is inherently a kinetic effect, it is of interest to examine $\psi_6(t)$ to see if the kinetics of local order might be reflected in that quantity. Our initial work⁴² indicated that this might be the case in that the time required for the decay of $\psi_6(t)$ to its long-time value appeared to increase with decreasing temperature. This also has been found to occur in a one-component soft-sphere system.⁴³ However, as may be seen in Fig. 7, the magnitude of the time-varying part of $\psi_6(t)$ actually decreases with decreasing temperature and effectively vanishes in the glass. This indicates that the kinetics of the bond orientational parameter is not a particularly useful indicator of glass formation in binary mixtures. This is distinctly different from the one-component fluid. The bond orientational order parameter Q_6 is quite sensitive to the sizes of the particles in the fluid. Therefore, some other quantity is needed to characterize the short-range structure which leads to glass formation.

B. Relaxation of an orientational order parameter

As another probe of a local order parameter for structural relaxation, we have investigated the dynamics of the correlation function, $\varphi(t)$, which describes the possibility of a bond joining two atoms undergoing local rotation. Specifically, $\varphi(t)$ is given by⁴²

$$\varphi(t) = \frac{1}{N_A} \sum_{i,j} \langle \cos \theta_{ij}(t) \rangle, \quad (9)$$

where the average is over all central atoms, i , and all near-neighbor atoms, j , of atom i (i.e., atoms, j , that lie within a specified distance r_{\min} of the central atom), and $\theta_{ij}(t)$ is the angle between bond ij at time t and that bond at time zero. Clearly, $\varphi(t)$ is a measure of the ease with which a bond can execute local rotation in a given

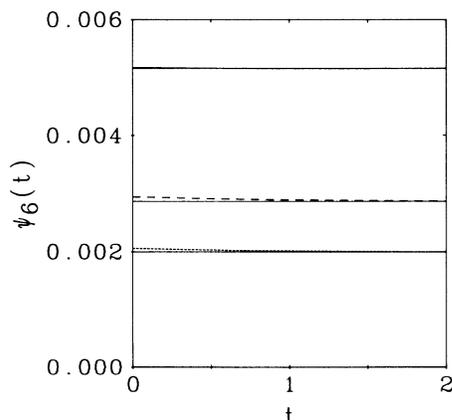


FIG. 7. Bond orientational order-parameter time correlation function $\psi_6(t)$ for $X=0.5$ mixtures and $\Gamma_{\text{eff}}=1.26$ (dotted line), $\Gamma_{\text{eff}}=1.37$ (dashed line), and $\Gamma_{\text{eff}}=1.7$ (solid line). In each case, a solid, horizontal line has been drawn so that it passes through $\psi_6(2\tau)$. This shows how the amplitude of the time variation of $\psi_6(t)$ appears to disappear in the glass.

thermodynamic state. At high temperature or low density, where the structural relaxation times are quite small, the particles rapidly diffuse away from their instantaneous local environment and thus we expect $\varphi(t)$ to decay rapidly to zero. As the liquid is supercooled, the structural relaxation time increases and the relaxation time of the order parameter, $\tau_\varphi \approx \int \varphi(t) dt$, is also expected to increase. Consequently, the decay of $\varphi(t)$, if it occurs at all, is expected to be extremely slow. In Fig. 8 a plot of $\varphi(t)$ as a function of t is given for four values of Γ_{eff} . We see that $\varphi(t)$ becomes slowly varying as the liquid is supercooled and seems to be nearly constant for the glass. A fact about time scales is worth noting. The correlation function $\varphi(t)$ is shown for 5τ while the velocity autocorrelation functions (see below) have decayed to zero in about τ , even in the glass. Thus structural relaxation, of which $\varphi(t)$ is but one measure, is a slow process in the supercooled regime and is absent in the glass. These results for $\varphi(t)$ indicate that the ‘‘orientation’’ of the local cage surrounding an atom is slowly varying and becomes frozen in for the glass.

It is tempting to speculate that $\varphi(t)$ could be a candidate quantity whose slow relaxation provides the necessary nonlinear feedback for the abrupt viscosity increase as T_g is approached. The nonvanishing of $\varphi(t)$ [$\varphi(t) \rightarrow \text{const}$ as $t \rightarrow \infty$] can then be interpreted as an analogue of the Edwards-Anderson order parameter of spin glasses.⁴⁴ It should be recognized that, unlike the spin-glass problem, no quantity which has an obvious physical interpretation has emerged whose relaxation is the slowest and is frozen in as the liquid-glass transition is reached.

We now propose a simple model that explains the reason for the continuous slowing of $\varphi(t)$ and the lack of decay of $\varphi(t)$ for $t \rightarrow \infty$ at and below the glass transition. We appeal to the well-known results in the theory of

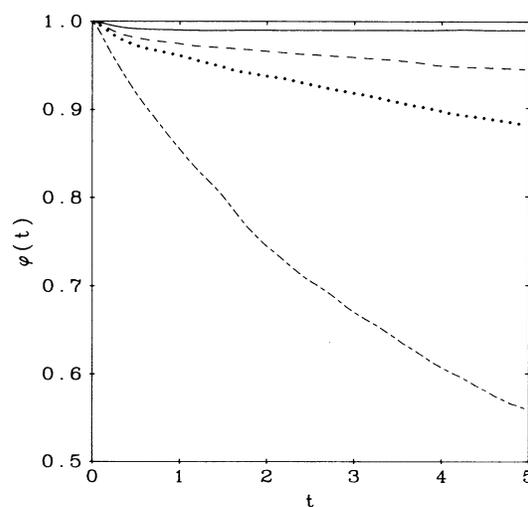


FIG. 8. The time dependence of $\varphi(t)$ for $X=0.5$ mixtures and $\Gamma_{\text{eff}}=0.95$ (dash-dot line), $\Gamma_{\text{eff}}=1.26$ (dotted line), $\Gamma_{\text{eff}}=1.37$ (dashed line), and $\Gamma_{\text{eff}}=1.7$ (solid line). The decay of $\varphi(t)$ is quite sensitive to the degree of supercooling and becomes very long for the glass.

tational Brownian motion.⁴⁵ In this discussion we view the local unit vectors as unit spheres undergoing Brownian motion in a highly viscous medium. In addition to the dissipative effects, the interaction (or entanglement) of a given unit vector with its neighbors impedes the rotational motion. But this slow structural motion itself determines the viscosity and hence a feedback mechanism emerges. Here we provide a simplified description which indicates the possibility that $\varphi(t) \rightarrow \text{const}$ for long times at $T = T_g$. For purposes of illustration, we treat the unit vector as a rotating disc and treat the interaction between it and its neighbors in a mean field sense, i.e., an effective "moment of inertia" is used. The stochastic equation describing the equation of motion of the angular velocity, ω , can be written as

$$d\omega/dt = -\Delta\omega(t) + \xi(t),$$

where the effective friction term $\Delta = 6\pi\eta a/m$, a is an effective radius associated with the unit vector, m is an effective mass, and $\xi(t)$ is the usual noise term. We also need the equation of motion for $R(t)$, the generator of rotation in two dimensions, namely,

$$dR(t)/dt = -i\sigma\omega(t)R(t),$$

where

$$\sigma = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix},$$

and

$$R(t) = \begin{pmatrix} \cos\theta(t) & \sin\theta(t) \\ -\sin\theta(t) & \cos\theta(t) \end{pmatrix}.$$

With these equations, one can obtain the correlation function of the unit vector $\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$ as⁴⁵

$$\varphi(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle = \exp\{-\gamma[t\Delta - 1 + \exp(-t\Delta)]\},$$

which, as $t \rightarrow \infty$, goes to the Debye result

$$\varphi(t) \approx \exp(-\gamma t\Delta),$$

with $\gamma = k_B T / I\Delta^2$ so that as $\eta \rightarrow \infty$, $\gamma\Delta \rightarrow 0$.

In supercooled liquids the structural relaxation time is much greater than the vibrational relaxation time and according to the self-consistent mode coupling theory,⁵⁻⁸ $\eta \approx 1/(T - T_g)^\alpha$, where $\alpha \approx 1.8$. Consequently, this phenomenology suggests that $\varphi(t) \approx \exp[-(T - T_g)^\alpha t A]$ where A is a constant greater than zero. This mechanism leads to the conclusion that $\varphi(t)$ goes to a constant as $T \rightarrow T_g^+$. In reality, the physical situation is far more complex, but this very simple model strongly indicates that as a supercooled liquid approaches the glass transition, some sort of orientational freezing should occur.

C. Self-diffusion coefficients

The self-diffusion coefficients can be calculated either from the single-particle mean square displacement or by integrating the velocity autocorrelation function. We use the mean square displacement, which is given by

$$\langle R_A^2(t) \rangle = \left\langle \frac{1}{N_A} \sum_{i=1}^{N_A} [\mathbf{r}_{iA}(t+s) - \mathbf{r}_{iA}(s)]^2 \right\rangle, \quad (10)$$

where $A = 1, 2$ and the averaging is done over several initial conditions denoted by s . (In our simulations, 1000 time origins were used.) The self-diffusion coefficients then are

$$D_A = \lim_{t \rightarrow \infty} \left[\frac{1}{6t} \langle R_A^2(t) \rangle \right]. \quad (11)$$

The self-diffusion coefficients of the two components are found to be decreasing functions of the inverse temperature, and therefore of Γ_{eff} . The vanishing of the self-diffusion coefficient is one indication of the formation of an amorphous solid or a glass. Using this criterion, it was found that the D_A were smaller than the uncertainties when $\Gamma_{\text{eff}} \approx 1.5$. This is in accord with the results of Bernu *et al.*¹⁴ These authors also noted that above the glass transition $D \sim \exp(-b\Gamma_{\text{eff}}^4)$, which is just the form of an activated process, namely, $D \approx \exp(-b'/T)$.

It should be noted that computer simulations cannot be used to distinguish between strictly zero values for D_A and exponentially small values. This point is particularly important as the glass-transition temperature is approached. The small but nonzero values observed even below the glass transition may be due to the following reason. Because of the very high quenching rate that is realized in the formation of the computer glasses, the packing fraction is lower than what would normally be found in laboratory metallic glasses. This implies that the system is quenched into a metastable state with a free energy that is still relatively high. Particles which are stuck in this state can diffuse and this may be the reason for observing very small diffusion coefficients even at $\Gamma_{\text{eff}} \approx 1.7$. Additional support for this argument comes from the work of Kristenson⁴⁶ who finds that the value of the diffusion coefficient decreases further when the atoms in a glassy state are allowed to anneal. For dense-random-packing models this problem is more severe.⁴⁷

D. Velocity time autocorrelation functions

We have already noted that the local anisotropic order that seems to develop as T_g is approached may result in long temporal correlations in certain dynamical properties. In Figs. 9-11 we present plots of the velocity time autocorrelation functions $Z_A(t)$, $A = 1, 2$, as a function of t for the three values of Γ_{eff} . These figures show that the particle undergoes discernible damped oscillatory motion with a seemingly large damping constant. The behavior is more pronounced for the bigger particle (shown as a dashed line) than for the smaller particle (shown as a solid line). Physically, this can be interpreted by observing that for times smaller than a characteristic vibration time τ_{vib} , the tagged particle is trapped in a dynamic cage formed by the neighboring particles. After about a vibrational period the cage evolves slowly (the rate of evolution decreasing drastically as $T \rightarrow T_g$) and thus $Z_A(t)$ is damped to zero. This interpretation would lead one to predict that the amplitude of the os-

cillation would become large as the temperature is lowered and the plots in Figs. 9–11 indicate that this is indeed the case.

The intuitive picture can be modeled using the exponential memory-function analysis of $Z_A(t)$ described by Berne, Boon, and Rice.⁴⁸ This formulation provides a parametrization of the velocity time correlation function of the form

$$Z_A(t) = \exp(-\frac{1}{2}\omega_2 t) [\cos(\omega t) + (\omega_2/2\omega)\sin(\omega t)], \quad (12)$$

where $\omega_2 = (m_A D_A / k_B T) \omega_v^2$, ω_v^2 is the second moment of the power spectrum of the velocity time autocorrelation function, and

$$\omega = (\omega_v^2 - \omega_2^2/4)^{1/2}.$$

In principle, this phenomenological analysis can be verified by calculating ω_v from the power spectrum of $Z_A(t)$ and then evaluating Eq. (12). Instead, we have taken the liberty of using ω_2 and ω as adjustable parameters and have obtained the best fit to $Z_1(t)$ for $\Gamma_{\text{eff}}=1.7$. The result is plotted in Fig. 11 as a dotted line. This empirical analysis provides qualitative results in satisfactory agreement with the simulation results. This provides credibility to the more intuitive analysis presented earlier and in fact the value of ω is in reasonable agreement with the value of $1/(2\pi\tau_{\text{vib}})$ obtained from both $Z_1(t)$ and the time dependence of the exponential memory function.

V. CRYSTALLIZATION OF A BINARY MIXTURE

The experience gained from the simulation of supercooled liquid states of one-component soft-sphere fluids indicates that for one-component systems the probability of forming a glassy state is small compared with that of the spontaneous formation of a crystalline state. When a second component is present, the probability of obtaining a glassy state is significantly increased. Our results for $\sigma_{22}=1.1\sigma_{11}$ indicate for $X=0.8$ and 0.5 that the glass is readily formed. However, we found for $X=0.2$

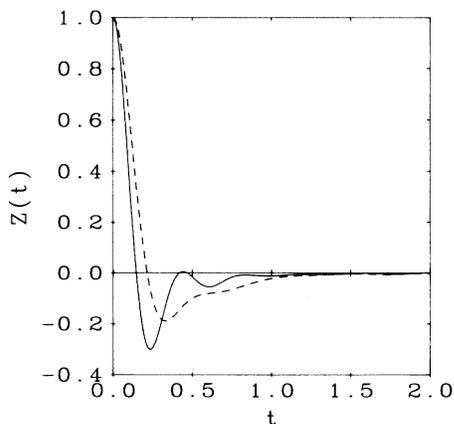


FIG. 9. Velocity time autocorrelation functions $Z(t)$ for the $X=0.5$ mixture with $\Gamma_{\text{eff}}=1.26$. The solid lines are for type-1 particles and the dashed lines are for type-2 particles.

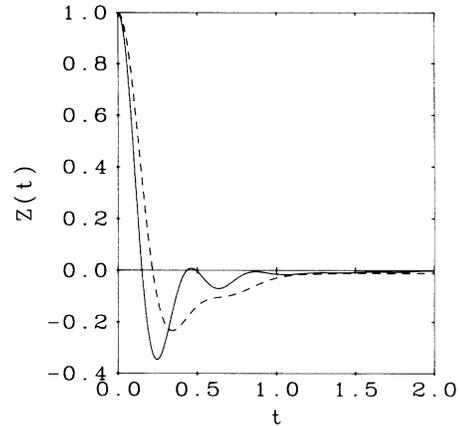


FIG. 10. Velocity time autocorrelation functions $Z(t)$ for the $X=0.5$ mixture with $\Gamma_{\text{eff}}=1.37$. The solid lines are for type-1 particles and the dashed lines are for type-2 particles.

that an initially glassy state readily transforms itself into a crystal if allowed to anneal for hundreds of time units τ . The resulting structure has the signature of a fcc crystal as the $g_{AB}(r)$'s have a sharp peak at the position of the second neighbor for a fcc structure.

The composition range over which binary amorphous solids are stable is of considerable interest and importance. Recent vapor-quenching measurements of the stability of Fe-metalloid alloys have suggested that the size ratio of the components is the major factor in determining the composition range over which the amorphous state is stable.⁴⁹ For mixtures with a size ratio of 1.14 this range is found to be $0.2 \leq X \leq 0.8$ while the theory of Egami and Waseda⁵⁰ predicts a range of

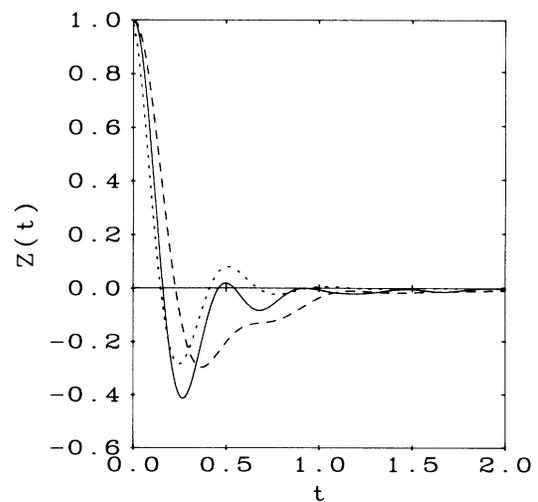


FIG. 11. Velocity time autocorrelation functions $Z(t)$ for the $X=0.5$ mixture with $\Gamma_{\text{eff}}=1.7$. The solid lines are for type-1 particles and the dashed lines are for type-2 particles. The dotted line represents Eq. (12) for type-1 particles with $\omega=8.0$ and $\omega_2=12.02$. The agreement is qualitatively satisfactory.

$0.26 < X < 0.86$. The uncertainties on these bounds is on the order of a few percent in X . We note that these measurements, when combined with this theory, suggest that the empirical rule that amorphous states are stable when the sizes differ by at least 10% should be relaxed to a difference of about 5%. Our simulation results are in good agreement with these measurements and predictions.

It is interesting to speculate on why the $X=0.2$ case, which is mostly large spheres, crystallizes more readily than the $X=0.8$, which is mostly small spheres. One possibility is that the number of densities for the cases we have examined (0.85 for $X=0.8$ and 0.69 for $X=0.2$) rather than Γ_{eff} is an important factor. This would be so if the lower density makes the nonequilibrium process of crystallization proceed more easily. Another possibility is that for a given value of Γ_{eff} the few small spheres can move more freely in a background of large spheres than can a few large spheres in a background of small spheres. If this were true, then the degree of frustration would be different in the two cases. This also would account for the simulation results. We plan to address this issue in a separate investigation as it may provide a clue to the quantification of frustration.

VI. DISCUSSION

In this paper we have reported simulation results for binary mixtures of soft spheres with a particular emphasis on identifying possible physical mechanisms that result in slow transport in supercooled liquid and glasses. It is difficult to draw definitive conclusions from computer-simulation studies involving small numbers of particles and short time scales. Nevertheless, the results indicate several interesting aspects of glass formation that can be used to construct model dynamics for viscous relaxation in glassy and supercooled states. Based on the results reported here, we are not in a position to develop a "picture" of what happens as the glassy state is formed in this binary system and to speculate on how these features should be incorporated into a theory of the glassy state. It is hoped that these results apply to most metallic glasses as well.

The most important point to be learned from these simulations is that the changes associated with the formation of the glass occur locally rather than collectively and hence there is a need for some sort of local quantity, an "order parameter," to characterize the local order. The structural results obtained from the pair and triplet correlation functions indicate that for r^{-12} soft spheres the local order develops into a smeared-out fcc arrangement of atoms in the first shell of neighbors around a given atom and that this order is sufficiently distorted that it does not extend to the second-neighbor distance in the crystal. This also provides a length, on the order of $1.5\sigma_{11}$, which characterizes the local order.

Another important feature of the glassy state is the freezing in of the local environment for each atom. The quantity $\varphi(t)$, which is a measure of the local environment, becomes long lived in the supercooled liquid and rapidly reaches a finite, asymptotic value in the glass.

This suggests that the orientation of near-neighbor bonds might be a useful means of characterizing local order. The decay of $\varphi(t)$ provides a time scale for the loss of local order. The characterization of time scales for the decay of local order has not been attempted here, but will be addressed in future studies of these systems.

In contrast to $\varphi(t)$, neither the bond orientational order parameter Q_6 , nor its time correlation function $\psi_6(t)$, is a useful indicator of the binary glass. The average of Q_6 remains small and the fluctuations about this average are small so it does not provide a convenient signal for glass formation in the two-component system. This is quite unlike the one-component case, where a striking increase in the average of Q_6 accompanies the formation of the glass. This is probably due to the differences in the way unequal-size spheres closely pack compared with like-size spheres. The closest packing of like-size spheres about a single sphere is the icosahedron. This structure would be strongly distorted when unlike-size spheres are present.

One of the major objectives of the present work is to identify possible "local modes" involving few particles and to relate the relaxation of these modes to the glass transition. The physical motivation for such a picture stems from the notion that activated processes, which dominate structural relaxation for temperatures close to the glass-transition temperature, can only involve rearrangement of particles over a small length scale. However, as has already been emphasized, the identification of such an order parameter does not appear to be unique and several candidates suggest themselves.

Among the ones we have investigated here, the most promising process is the slowing down of the relaxation of $\varphi(t)$; in fact $\varphi(t) \rightarrow \text{const}$ as $t \rightarrow \infty$ for $T \leq T_g$. The unit vector can be modeled by spins on a regular lattice where frustration is the ingredient that causes the dynamic slowing down. Nselson³ has suggested that the frustration embodied in uniformly frustrated X - Y spin systems is analogous to frustration experienced in glasses when one tries to fill space by tetrahedra. The behavior exhibited by $\varphi(t)$ is similar to that found for the Edwards-Anderson order parameter in the frustrated X - Y model in two dimensions.⁵¹ In spin language, this is described by the Hamiltonian,⁵²

$$H = - \sum_{i,j} J_{ij} s_i s_j, \quad (13)$$

with $s_i = (\cos\theta_i, \sin\theta_i)$ and $s_i^2 = 1$. The coupling constants J_{ij} are antiferromagnetic ($= -J$) on alternate columns of bonds and are ferromagnetic ($= J$) elsewhere. Thus H given by Eq. (13) can be thought of as a lattice model of interacting normals associated with the unit vector joining two atoms. In a recent numerical study⁵³ it has been shown that for a given value of J , the system freezes into a state at a temperature T_c where the Edwards-Anderson order parameter, $q_{EA} = \sum \langle s_i \rangle^2$, becomes nonzero; the brackets denote a thermodynamic average. Because s_i is very similar to the unit vector studied here, it is tempting to suggest that the frustrated Hamiltonian of Eq. (13) could be a model that can be used for the structural glass transition. If so, it would be

interesting to consider a soft spin version of the fully frustrated X - Y model and to investigate the relaxational dynamics of the model. The behavior of the spin-spin correlation function may be related to the detailed dynamics of $\varphi(t)$. We note that as a model for a Josephson-junction array in a transverse magnetic field,⁵⁴ the constraint that causes frustration can be expressed in terms of line integrals involving the vector potential across the junctions. However, as a model for structural glasses, the relation between the constraint expressed by the directed sum around the plaquette to the parameters of the supercooled state is not obvious.

In summary, we have used molecular dynamics to examine some potential order parameters for glass formation in binary mixtures. In contrast with the spin-glass problem, the task of identifying a unique order parameter that drives the "transition" to the glassy state has not been completed. Our simulation results suggest that to reach a crystalline state from a glassy state, rearrangements of particles over a finite length scale is sufficient. Consequently, a short-range order measure which is nonhydrodynamic, namely, $\varphi(t)$, has been

identified as one possible candidate for a dynamical order parameter. In order to propose a dynamical model⁵⁴ the knowledge of the free energy, $F\{\varphi\}$, affecting the relaxation of $\varphi(t)$ is required. In addition, the coupling of this order parameter to the usual hydrodynamic modes should be considered. The free-energy surface, $F\{\varphi\}$, should be general enough to account for activated processes but simple enough that the mode-coupling equations can be solved. It is hoped that such a dynamical model will predict the viscous relaxation in glasses in a more realistic way than has been achieved to date.

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- ¹K. Binder and A. P. Young, *Rev. Mod. Phys.* **58**, 801 (1986).
- ²See the articles in *Topological Disorder in Condensed Matter*, edited by F. Yonezawa and T. Ninomiya (Springer-Verlag, New York, 1983).
- ³For a review discussing this notion in detail, see D. R. Nelson in *Applications of Field Theory to Statistical Mechanics*, edited by L. Garrido (Springer-Verlag, New York, 1984), pp. 11–31.
- ⁴For a recent review, see J. Jackle, *Rep. Prog. Phys.* **49**, 171 (1986).
- ⁵E. Leutheusser, *Phys. Rev. A* **29**, 2769 (1984).
- ⁶U. Bengtzelius, W. Goetze, and A. Sjolander, *J. Phys. C* **17**, 5915 (1984); U. Bengtzelius, *Phys. Rev. A* **33**, 3433 (1986).
- ⁷T. R. Kirkpatrick, *Phys. Rev. A* **31**, 939 (1985).
- ⁸S. P. Das, G. F. Mazenko, S. Ramaswamy, and J. Toner, *Phys. Rev. Lett.* **54**, 118 (1985).
- ⁹T. Greszti, *J. Phys. C* **16**, 5805 (1983).
- ¹⁰W. Goetze, in *Amorphous and Liquid Materials*, Vol. 118 of *NATO Advanced Study Institute, Series E*, edited by E. Lüscher, G. Fritsch, and G. Jacucci (Martinus Nijhoff, Dordrecht, 1987), pp. 34–81.
- ¹¹Recently approximate connections between mode-coupling theory and density-functional theory have been established by T. R. Kirkpatrick and P. G. Wolynes, *Phys. Rev. A* **39**, 3072 (1987).
- ¹²C. A. Angell and W. Sichina, *Ann. N.Y. Acad. Sci.* **279**, 53 (1976).
- ¹³J. R. Fox and H. C. Andersen, *J. Phys. Chem.* **88**, 4019 (1984). Extensive references to earlier simulation studies are to be found here.
- ¹⁴B. Bernu, Y. Hiwatari, and J. P. Hansen, *J. Phys. C* **18**, L371 (1985); *Phys. Rev. A* (to be published).
- ¹⁵J. P. Sethna, *Phys. Rev. Lett.* **50**, 2198 (1983); *Phys. Rev. B* **31**, 6278 (1985).
- ¹⁶S. Sachdev and D. R. Nelson, *Phys. Rev. B* **32**, 1480 (1984).
- ¹⁷R. D. Mountain, *Mol. Phys.* **59**, 857 (1986). References to other uses of these triplet correlations are listed here.
- ¹⁸H. Vogel, *Phys. Z.* **22**, 645 (1921); G. S. Fulcher, *J. Am. Ceram. Soc.* **8**, 339 (1925); G. Tammann and W. Hesse, *Z. Anorg. Allgem. Chem.* **156**, 245 (1926).
- ¹⁹T. W. Leland, J. S. Rowlinson, and G. A. Sather, *Trans. Faraday Soc.* **64**, 1447 (1968).
- ²⁰D. Beeman, *J. Comput. Phys.* **20**, 130 (1976).
- ²¹W. G. Hoover, M. Ross, K. W. Johnson, D. Henderson, J. A. Barker, and B. C. Brown, *J. Chem. Phys.* **52**, 4931 (1970).
- ²²A. B. Bhatia and D. E. Thornton, *Phys. Rev. B* **2**, 3004 (1970).
- ²³A. D. J. Haymet, *Chem. Phys. Lett.* **107**, 77 (1984).
- ²⁴R. D. Mountain and P. K. Basu, *J. Chem. Phys.* **78**, 7318 (1983).
- ²⁵This is in accord with the recent work of F. H. Stillinger and R. La Violette, *Phys. Rev. B* **34**, 5136 (1986), in which they report that the inherent structures obtained from a fluid configuration tends to produce locally defective fcc crystallites. Their main observation is that the characteristic of the amorphous state is the deviation from a local twelve-fold coordination state. A detailed geometrical characterization of the inherent structure revealed that icosahedral coordination is rare.
- ²⁶C. H. Bennett, *J. Appl. Phys.* **43**, 2727 (1972).
- ²⁷J. F. Sadoc, J. Dixmier, and A. Gunier, *J. Non-Cryst. Solids* **12**, 46 (1973).
- ²⁸D. S. Boudreaux and J. M. Gregor, (a) *J. Appl. Phys.* **48**, 152 (1977); (b) **48**, 5057 (1977).
- ²⁹D. S. Boudreaux and H. J. Frost, *Phys. Rev. B* **23**, 1506 (1981).
- ³⁰See, for example, M. Kimura and F. Yonezawa, in *Topological Disorder in Condensed Matter*, edited by F. Yonezawa and T. Ninomiya (Springer-Verlag, New York, 1983).
- ³¹P. Taborek, R. N. Kleiman, and D. J. Bishop, *Phys. Rev. B* **34**, 1835 (1986).
- ³²M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969).
- ³³E. Orowan, *Creep in Metallic and Nonmetallic Materials*, Proceedings of the First National Congress of Applied

- Mechanics (American Society of Mechanical Engineers, New York, 1952), pp. 453–472.
- ³⁴F. H. Stillinger and T. A. Weber, *Science* **225**, 983 (1984).
- ³⁵R. W. Hall and P. G. Wolynes, *J. Chem. Phys.* **86**, 2943 (1987).
- ³⁶C. Dasgupta, S. K. Ma, and C. K. Hu, *Phys. Rev. B* **20**, 3837 (1979).
- ³⁷S.-P. Chen, T. Egami, and V. Vitek, *J. Non-Cryst. Solids* **75**, 449 (1985).
- ³⁸P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, *Phys. Rev. Lett.* **47**, 1297 (1981); *Phys. Rev. B* **28**, 784 (1983).
- ³⁹R. D. Mountain and A. C. Brown, *J. Chem. Phys.* **80**, 2730 (1984).
- ⁴⁰F. C. Frank, *Proc. R. Soc. London, Ser. A* **215**, 43 (1952).
- ⁴¹D. R. Nelson, *Phys. Rev. Lett.* **50**, 982 (1983); *Phys. Rev. B* **28**, 5515 (1983); D. R. Nelson and M. Widom, *Nucl. Phys. B* **240**, 113 (1984).
- ⁴²D. Thirumalai and R. D. Mountain, *J. Phys. C* **20**, L399 (1987).
- ⁴³J. G. Amar and R. D. Mountain, *J. Chem. Phys.* **86**, 2236 (1987).
- ⁴⁴S. F. Edwards and P. W. Anderson, *J. Phys. F* **12**, 965 (1975).
- ⁴⁵J. McConnell, *Rotational Brownian Motion and Dielectric Theory* (Academic, New York, 1980).
- ⁴⁶W. D. Kristensen, *J. Non-Cryst. Solids* **21**, 303 (1976).
- ⁴⁷M. R. Hoare, *Ann. N. Y. Acad. Sci.* **279**, 186 (1976); *J. Non-Cryst. Solids* **31**, 157 (1978); *Adv. Chem. Phys.* **40**, 49 (1979).
- ⁴⁸J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980), pp. 129–134; see also B. J. Berne, J. P. Boon, and S. A. Rice, *J. Chem. Phys.* **45**, 1086 (1966).
- ⁴⁹S. H. Liou and C. L. Chien, *Phys. Rev. B* **35**, 2443 (1987).
- ⁵⁰T. Egami and Y. Waseda, *J. Non-Cryst. Solids* **64**, 113 (1984).
- ⁵¹E. Fradkin, B. A. Huberman, and S. H. Shenker, *Phys. Rev. B* **18**, 4789 (1978).
- ⁵²M. Y. Choi and D. Stroud, *Phys. Rev. B* **32**, 7173 (1985); D. Stroud and S. Kivelson, *ibid.* **35**, 3478 (1987); S. Teitel and C. Jayaprakash, *ibid.* **27**, 598 (1983); T. C. Halsey, *ibid.* **31**, 5728 (1985).
- ⁵³T. C. Halsey, *Phys. Rev. Lett.* **55**, 1018 (1985).
- ⁵⁴A model similar in spirit but differing in detail was proposed and examined by S. Sachdev, *Phys. Rev. B* **33**, 6395 (1986).