Long-Lived Structures in Fragile Glass-Forming Liquids

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We present molecular dynamics results for the existence of long-lived clusters near the glass transition in a two component, two-dimensional Lennard-Jones supercooled liquid. Several properties of this system are similar to a mean-field glass-forming liquid near the spinodal. This similarity suggests that the glass "transition" in the supercooled liquid is associated with an incipient thermodynamic instability. Our results also suggest that single particle properties are not relevant for characterizing the instability, but are relevant to the kinetic transition that occurs at a lower temperature than the glass transition.

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The characterization of a supercooled liquid near the glass transition is an active area of research [1]. Outstanding unsolved problems include the possible existence of an underlying thermodynamic transition [2], the history dependence of the glass, and the mechanisms responsible for the large increase in relaxation times.

The primary focus of this Letter is on our molecular dynamics (MD) simulations of a two component, two-dimensional ($d = 2$) Lennard-Jones (LJ) supercooled liquid. To help the reader understand our interpretation of the MD data and the questions we pose, we first review the behavior of a mean-field (MF) model of a structural glass transition.

We have shown [3] that the MF model has a well-defined thermodynamic glass transition associated with a spinodal. The static properties of the glass phase are dominated by localized structures (clumps). A new result is that the dynamical properties that depend directly on the clumps, e.g., the diffusion coefficient associated with their center of mass motion, go to zero at the thermodynamic glass transition. However, the transition does not affect dynamical quantities that depend on single particle motion.

In the MF model, particles interact via a repulsive, two-body potential of the form [4] $V(r) = \gamma^d \phi(\gamma r)$, where $\phi(x) = 1$ if $x \leq 1$, $\phi(x) = 0$ if $x > 1$, and r is the distance between particles. The range of the interaction is $R = \gamma^{-1}$. In the limit $R \to \infty$, the static properties of the uniform fluid are described exactly by MF theory [5]. For fixed density ρ, the system has a spinodal singularity [6] at a temperature T_s, which is defined by the condition $1 + \beta\rho\hat{\phi}(k_0) = 0$, where $\beta^{-1} = k_B T$, $\hat{\phi}(k)$ is the Fourier transform of $\phi(x)$, and k_0 is the location of the minimum of $\hat{\phi}(k)$.

The singularity is well defined only in the MF limit ($R \to \infty$). For $d = 3$ and $\rho = 1.95$, the spinodal is at $T_s = 0.705$ ($k_B = 1$). Our Monte Carlo (MC) simulations at $\rho = 1.95$ with $R = 3$ show that the measured static structure function $S(k)$ has a maximum at $k \neq 0$ that increases rapidly as T is decreased until $T \approx 0.75$, below which the peak ceases to increase as T is lowered. This behavior is characteristic of a pseudospinodal. As R increases, the pseudospinodal better approximates a true singularity and has measurable effects if R is sufficiently long.

If the system is equilibrated at $T > T_s$ and quenched to $T < T_s$ where the uniform phase is unstable [6], the particle immediately form clumps with order ρR^3 particles in each clump. The arrangement of the clumps is noncrystalline, and their number depends on the quench history [3,6]. The free energy has been calculated numerically in the MF limit and has many minima corresponding to different numbers of clumps [3,7]. These properties suggest that the MF model has a metastable glass phase for $T < T_s$. A new result is that the glassy dynamics of the MF model is associated with the *clumps*. In contrast, its single particle dynamical properties do not show the usual signature of the approach to a glass. A simple argument [8], based on the fact that all potential barriers in the MF model are finite, implies that the self-diffusion coefficient $D > 0$ for all $T > 0$. That is, the *particles* are not localized in the metastable glass phase. Hence, if the observation time is sufficiently long, the mean square displacement of the particles increases without bound.

A similar argument implies that the MF model is ergodic for all $T > 0$ if single particle properties are probed. The ergodic behavior can be characterized by several fluctuation metrics [9]. The single particle energy fluctuation metric $\Omega_e(t)$ is given by [9]

$$\Omega_e(t) = \frac{1}{N}\sum_{i=1}^{N}[\epsilon_i(t) - \overline{\epsilon(t)}]^2, \qquad (1)$$

where $\overline{\epsilon(t)} = (1/N)\sum_{i=1}^{N}\epsilon_i(t)$, and $\epsilon_i(t)$ is the mean energy of particle i over the time interval t. If the system is ergodic, $\Omega_e(t) \sim 1/t$ for t sufficiently large [9]. We find that $\Omega_e(t)$ exhibits ergodic behavior at $T = 0.4$, a value of $T < T_s$. For $T \leq 0.15$, $\Omega_e(t)$ exhibits nonergodic behavior during our longest runs, and the measured D is indistinguishable from zero at $T = 0.15$. Given our theoretical prediction that $D \neq 0$ for all $T > 0$,

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the observed nonergodic behavior implies only that the time for a particle to leave a clump is much longer than our observation time. Neither $\Omega_e(t)$ nor D show evidence of the glass-spinodal transition, and we interpret the change from ergodic to nonergodic behavior as an apparent kinetic transition.

How can we reconcile the T dependence of D and $\Omega_e(t)$ with our identification of T_s as the spinodal-glass transition? The answer lies in the dynamical properties of the *clumps*. For example, the diffusion coefficient of the center of mass of the clumps D_c is zero for $T < T_s$ in the MF limit. To understand this behavior, note that n, the mean number of particles in a clump, diverges as R^d as $R \to \infty$. In this limit, the number of clumps does not change with time, and the mean numbers of particles exiting and entering a clump are equal. From the central limit theorem, the relative fluctuations of these quantities go to zero as R and $n \to \infty$. We conclude that $D_c \leq D/\sqrt{n}$, and hence $D_c = 0$ in the MF limit. Our simulations of D_c for finite R are consistent with this prediction, and also indicate that the clumps do not see the same local environment, i.e., they have different numbers of nearest-neighbor clumps. This difference in the local environment persists as $R \to \infty$ because the clumps do not diffuse and cannot sample different local environments. Hence, the system is nonergodic on a clump (mass $\sim R^d$) scale for $T < T_s$ in the MF limit.

In summary, the clumps are long lived and localized for $T < T_s$, even though particles move from clump to clump. The time scale for the motion of the clumps diverge in the MF limit, and the spinodal-glass transition is seen dynamically only on a clump scale; single particle dynamical properties show no evidence of the underlying spinodal–metastable glass transition. However, we observe an *apparent* kinetic transition that is associated with the slow diffusion of the particles and the finite duration of our runs. The temperature of this apparent transition is less than T_s and depends on the observation time.

The well-characterized behavior of the MF model motivates us to ask if similar behavior occurs with more realistic interactions, and we consider a two component, $d = 2$ system of LJ particles of mass m. We take the LJ length parameter of the minority component to be 1.5 times larger than the length parameter σ of the majority component; the values of the energy parameter ϵ are the same for both. The role of the minority component is to inhibit nucleation [10]. We choose units such that lengths are measured in terms of σ, energies in terms of ϵ, and the time in terms of $\tau = (m\sigma^2/\epsilon)^{1/2}$. We cut off the LJ potential at $r = 3\sigma$. The MD simulations [11] are for $N = 500$ particles with 80% of the total being the majority component. The simulations are at fixed volume with the central cell size at each T chosen so that the pressure $P \approx 70$ ($\rho \sim 1$). The time step $\Delta t = 0.005\tau$, and averages are over a duration ranging from 2000τ at $T = 5.5$ to $20\,000\tau$ at $T = 2.15$. The following results are for the majority particles only.

The single particle energy and velocity fluctuation metrics show ergodic behavior for $2.15 \leq T \leq 5.5$. $D(T)$ is consistent with the Vogel-Fulcher form, $D \sim e^{-B/(T-T_0)}$ with $T_0 \approx 1.5$ (see Fig. 1). This form implies that the system loses ergodicity at $T \sim T_0$ for our runs. This behavior is similar to that of a two component, $d = 3$ LJ system [9].

If the LJ system exhibits pseudospinodal effects, we should find behavior analogous to that observed in the MF glass model [3] and in Ising models with long, but finite range interactions [12]. In these systems, $S(k)$ appears to diverge if its behavior is extrapolated from high T or small magnetic field, respectively, but the extrapolated singularity is not observed if measurements are made too close to the apparent singularity. For the LJ system we find a diffraction peak in $S(k)$ at $k = k_0 \approx 7.1$. The height of the peak $\chi(k_0, T)$ increases by a factor of ≈ 1.8 and the width $w(k_0, T)$ decreases by a factor of ≈ 1.5 as T is lowered from 5.5 to 2.15 (see Fig. 1). Because this range of T is limited, we can fit $\chi(k_0, T)$ and $w(k_0, T)$ by a variety of functional forms. If we consider the data only for $T \geq 3.1$, the most consistent fit is $\chi(k_0, T) \sim (T - 2.5)^{-0.2}$ and $w(k_0, T) \sim (T - 2.5)^{0.25}$. These fits suggest that the increase of the first peak of $S(k)$ is influenced by a weak singularity at $T = T_s \approx 2.5$. Given the limited range of T, this fit is justified only in the context of our rigorous results for $S(k)$ in the MF model [3]. If we fit the data for $2.15 \leq T \leq 5.5$, we find $\chi(k_0, T) \sim T^{-0.4}$ and $w(k_0, T) \sim T^{0.4}$, and we see no evidence of a spinodal-like singularity. This behavior is consistent with the pseudospinodal interpretation; i.e., if measurements are

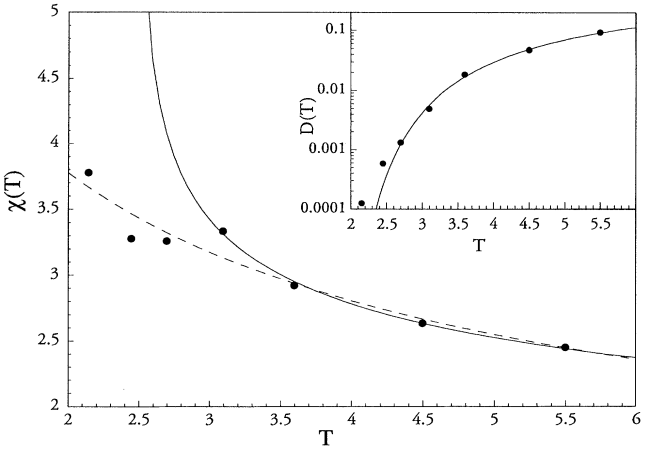

FIG. 1. The temperature dependence of $\chi(k_0, T)$, the height of the diffraction peak in the static structure function $S(k)$ at $k = k_0 \approx 7.1$. Note that $\chi(k_0, T)$ increases by approximately 1.8. The solid line represents the best fit in the range $3.1 \leq T \leq 5.5$ and has the form $(T - 2.5)^{-0.2}$; the dotted line represents the best fit in the range $2.15 \leq T \leq 5.5$ and has the form $T^{-0.4}$. The inset shows the T dependence of the self-diffusion coefficient D. The solid line represents the fit to the Vogel-Fulcher form $e^{-B/(T-T_0)}$. $T_0 = 1.5$ if we omit the two lowest values of T for which the data are limited; and $T_0 = 1.0$ if all data points are included.

made too close to the apparent singularity, its effects vanish.

For T near or below the pseudospinodal the system should show signs of an instability. We look for long-lived structures whose constituent particles remain in close proximity to each other over extended times at sufficiently low T. Because the LJ potential diverges at small interparticle separations, these structures are not identical to the clumps found in the MF model. A visual examination of the configurations shows evidence of a partial phase separation in which a significant fraction of the majority particles form clusters of hexagonal-like structures, which become better defined at T is decreased. To characterize these clusters, we determine the Voronoi structure. For each particle with six Voronoi neighbors we measure [13] $\Delta_i = (1/\langle \ell_i \rangle^2)[\langle \ell_i^2 \rangle - \ell_i \rangle^2]$, where $\langle \ell_i \rangle$ is the mean edge length of the Voronoi hexagon of particle i. If i is in an ideal crystalline environment, $\Delta_i = 0$. Such a particle belongs to a cluster if its combination of Δ and kinetic energy is sufficiently low. (The criterion assumes a linear relation, with a larger Δ implying a more stringent requirement for the kinetic energy.) Including the kinetic energy in the cluster criterion reduces the effect of thermal fluctuations. The qualitative properties of the clusters are *independent* of the cutoffs over a wide range of values.

The mean cluster lifetime is measured by dividing the system into boxes and computing the number of particles that belongs to any cluster in each box. The idea is to find if the mean number of cluster particles in each box becomes approximately the same as $t \gg 1$. If n_α, the number of cluster particles in box α, is greater than a threshold value, box α is said to be occupied; the corresponding nonzero p_α is used to compute a time-displaced cluster correlation function $G_c(t)$ and a cluster fluctuation metric $\Omega_c(t)$. (The latter is defined analogously to the energy fluctuation metric.) At $T = 5.5$, the decay of $G_c(t)$ to its equilibrium value can be fitted to an exponential function with a relaxation time $\tau_c \approx 50\tau$; similarly, Ω_c exhibits ergodic behavior. At $T = 3.1$, $G_c(t)$ does not reach its equilibrium value for $t \leq 5000\tau$, and $\Omega_c(t)$ exhibits nonergodic behavior; i.e., τ_c is much longer than our runs. At $T = 3.1$, $D > 0$ and the system appears ergodic if single particle properties are probed. This qualitatively different behavior of the clusters and the particles is analogous to the behavior of the clumps and the particles in the MF model.

The clusters also exhibit interesting static properties. Because the width of the peak of $S(k)$ decreases as $T \to 0$, we expect that the mean size of the clusters grows until they become "frustrated" by the minority component and the different cluster orientations. Our results for n_s, the number of clusters of size s, can be fit by the form (see Fig. 2)

$$n_s \sim s^{-3/2} e^{-s/m(T)}, \tag{2}$$

where $m(T)$ is a parameter that increases as T is lowered until $T \approx 3.1$; below $T \approx 3.1$ $m(T)$ does not increase. The form (2) is robust and independent of the cutoffs used to determine the clusters. Similar scaling behavior has been found near the freezing transition in a $d = 2$ LJ system using a different cluster criterion [14]. The scaling behavior of the clusters, in particular the exponent of $3/2$, is similar to the MF behavior found in other systems [15].

As noted, τ_c, the cluster lifetime, is longer than our observation time for $T \leq 3.1$. We assume $\tau_c \sim e^{-b/(T-T_{\rm cl})}$, and find that $2.5 \leq T_{\rm cl} \leq 2.9$; $T_{\rm cl}$ is the extrapolated temperature at which τ_c becomes infinite. Although our estimates for τ_c are only qualitative and the value of $T_{\rm cl}$ is the least accurate of our parameters, this value of $T_{\rm cl}$ is consistent with the value of $T_s \approx 2.5$ obtained from the extrapolation of the T dependence of the peak of $S(k)$.

To summarize our MD results, we find that there is a range of T for which $D > 0$ and τ_c is too long to estimate. (Our longest runs are for $20\,000\tau$, runs that are relatively long in comparison to most simulations of glasses.) This qualitatively different dynamical behavior of the single particle and cluster properties is analogous to the behavior of our MF model. From our extrapolations of the T dependence of the peak of $S(k)$ and τ_c, we see evidence of an incipient "transition" at $T_s \approx 2.5$. These two results provide indirect evidence for our identification of T_s with an apparent ergodic to nonergodic transition associated with the dynamics of the clusters and the presence of a pseudospinodal [16]. That is, we find evidence of an incipient thermodynamic glass "transition" at $T_s \approx 2.5$, a value of $T > T_0$ at which the single particle dynamical properties indicate an ergodic to nonergodic transition. Our extrapolation of $D(T)$ to 0 at $T_0 \approx 1.5$ suggests that T_0 can be interpreted as the kinetic transition and is distinguishable from the incipient thermodynamic transition.

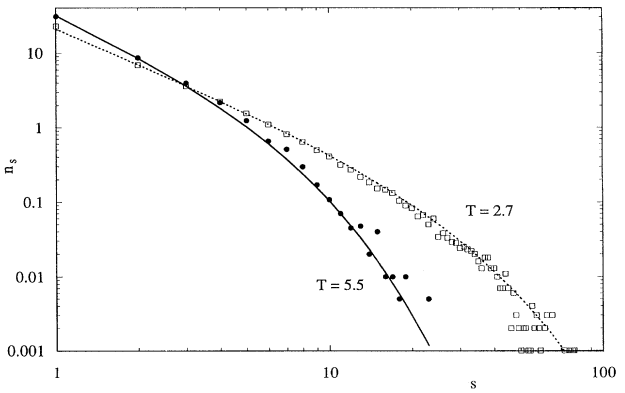

FIG. 2. The number of clusters of size s, n_s, versus s for $T = 5.5$ (filled circles) and $T = 2.7$ (open squares). The solid line is a fit at $T = 5.5$ by the scaling form (2) with $m(T = 5.5) = 4.2$; the dashed line is a fit at $T = 2.7$ to (2) with $m(T = 2.7) = 21$. These values for $m(T)$ are consistent with the mean size (mass) of the clusters that is observed directly.

The power-law scaling of n_s might be important for understanding the relaxation processes in glasses on experimental time scales. Nagel and collaborators [17] have fitted their measured dielectric susceptibility to a single scaling curve over 13 decades of frequency for a wide range of T and for many glass formers. Their results together with our simulation and theoretical results suggest that there might be a hierarchy of time and length scales and hence a hierarchy of clusters, i.e., a geometrical basis for the observed scaling.

We stress that the effects of the pseudospinodal and the incipient thermodynamic glass transition will be more or less apparent depending on the interaction range, the details of the interaction, and d [13]. We do not expect to find spinodal-like effects in all supercooled liquids. In particular, there are MF models, e.g., the MF limit of the Gaussian potential [3], which have no spinodal and hence no thermodynamic glass transition. These considerations suggest that there is a class of materials for which the observed glass transition is associated with a pseudospinodal and an incipient thermodynamic transition, and other materials for which the observed glass transition is not associated with such effects. We do not expect the behavior of the clusters we have found to be observed in all glass formers.

Based on our MC and theoretical studies of a MF model and our MD results for a $d = 2$ LJ system, we suggest that the latter is in the class of systems whose behavior can be attributed to an incipient thermodynamic instability (the pseudospinodal). We emphasize that a true thermodynamic glass transition does not exist in the LJ system, even though the pseudospinodal has measurable effects including increasing length and time scales as the pseudospinodal is approached. In addition to this glass-pseudospinodal transition, there is a temperature (for fixed density) that can be interpreted as a kinetic transition below which the diffusion coefficient is not measurable during our observation time.

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