Dynamical Heterogeneities in a Supercooled Lennard-Jones Liquid

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We present the results of a molecular dynamics computer simulation study in which we investigate whether a supercooled Lennard-Jones liquid exhibits dynamical heterogeneities. We evaluate the non-Gaussian parameter for the self part of the van Hove correlation function and use it to identify "mobile" particles. We find that these particles form clusters whose sizes grow with decreasing temperature. We also find that the relaxation time of the mobile particles is significantly shorter than that of the average particle, and that this difference increases with decreasing temperature. [S0031-9007(97)04184-7]

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An outstanding problem in the dynamics of supercooled liquids is to understand why they exhibit nonexponential relaxation of time correlation functions [1]. Two limiting microscopic scenarios have been proposed to explain this behavior [2]. In the so-called "homogeneous" scenario, all the particles relax identically by an intrinsically nonexponential statistical process, while in the "heterogeneous" case the nonexponential relaxation is due to a superposition of individual exponential contributions with different relaxation rates.

Recent NMR experiments [3], followed by optical spectroscopy, forced Rayleigh scattering, and further NMR experiments [4] has given evidence that, in the supercooled liquids studied, the relaxation is not homogeneous. However, these experiments are neither able to determine the microscopic mechanism that is responsible for these heterogeneities nor to measure their properties, such as their size or shape [5]. Moreover, no *direct* evidence of the spatial correlations which might be expected to arise between particles or regions with similar mobility has as yet been reported.

Dynamical heterogeneities have also been observed in computer simulations [6]. However, these simulations were restricted to two dimensions and because it might be expected that the dynamics of particles in two and three dimensions is significantly different, it is not clear whether the dynamical heterogeneities observed in these simulations have a counterpart in three dimensions. By analyzing the trajectories of monomers in a Monte Carlo simulation of a dense polymer melt ($d = 3$), Heuer and Okun [7] showed that in this system dynamical heterogeneities occur on short length scales, but the nature of the heterogeneities was not explored in detail. Thus despite the experimental evidence for the existence of dynamical heterogeneities, their microscopic properties are unknown and phenomenological models are used to interpret experimental results [8]. In this Letter, we study a simple, glass-forming liquid to investigate whether dynamical heterogeneities can be observed in a 3D system and, if so, to determine their properties.

We perform extensive simulations of a binary (80:20) mixture of 8000 Lennard-Jones particles consisting of two species of particles, A and B. The interaction between two particles of type $\alpha, \beta \in \{A, B\}$ is given by $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6}]$ with $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$, with a cutoff radius of $2.5\sigma_{\alpha\beta}$. Note that the AB interaction is stronger than both the AA and BB interactions, a fact which will be important in the subsequent discussion of the results. We report all quantities in reduced units, that is, length in units of σ_{AA}, temperature T in units of ϵ_{AA}/k_B, and time t in units of $\sqrt{\sigma_{AA}^2 m/\epsilon_{AA}}$, where m is the mass of either an A or B particle. We study the system at ten different values of T ranging between 0.550 and 0.451. At each temperature, the system was equilibrated for a time longer than the typical (primary) relaxation time of the system before evaluating the quantities presented below. At the lowest T, quantities were evaluated for over 4×10^6 time steps. All simulations were carried out in the microcanonical ensemble.

The dynamics of this model has been characterized in detail in previous simulations performed at different temperatures and at constant density [9]. In particular, it was found that at low T the dynamics is described well by the mode-coupling theory [10] with a critical temperature $T_c \approx 0.435$ and a critical pressure $P_c \approx 3.03$. Thus in the vicinity of the point (T_c, P_c) the relaxation of the system is very slow and the diffusion constants are small. In the present work we approach the state point (T_c, P_c) via a different path than that used in Ref. [9], on a straight line in the T-P plane along which density increases with decreasing T [11].

To detect the presence of dynamical heterogeneities, we investigate the time dependence of the self part $G_s(r, t)$ of the van Hove correlation function [12] for the A particles, where r is the distance traveled by a particle in a time t. To a first approximation $G_s(r,t)$ has a Gaussian form but deviations from this form at intermediate times have been observed in simulations of glass forming liquids [9,13,14] and are thought to reflect the presence of dynamical heterogeneities [15]. Such deviations can be characterized by the non-Gaussian parameter $\alpha_2(t) = 3\langle r^4(t)\rangle/5\langle r^2(t)\rangle^2 - 1$ [16]. Figure 1 shows the time dependence of α_2 for the A particles at three different temperatures. We find that (i) on the time scale at which the motion of the particles is ballistic, α_2 is zero; (ii) upon entering the time scale of the β relaxation, α_2 starts to increase; and (iii) on the time scale of the α relaxation, α_2 decreases to its long time limit, zero. We observe that the maximum value of α_2 increases with decreasing T, which is evidence that the dynamics of the liquid becomes more heterogeneous with decreasing T. Furthermore, we find that the time t^* at which this maximum is attained also increases with decreasing T.

To determine the reason for the strong increase of α_2 in the β-relaxation regime, we compare $G_s(r,t)$ with the distribution that is obtained from the Gaussian approximation; that is, by assuming that $G_s(r,t)$ is given by $G_s^g(r,t) = [3/2\pi\langle r^2(t)\rangle]^{3/2}\exp[-3r^2/2\langle r^2(t)\rangle]$, where $\langle r^2(t)\rangle$ is the mean squared displacement of the particles. In Fig. 2 we show $[G_s(r,t) - G_s^g(r,t)]/G_s^g(r,t)$ for $t = t^*$, where t^* depends on T (see Fig. 1). For small and intermediate values of r ($r \leq 0.6$) the relative difference between G_s^g and G_s is less than a factor of 3. However, for larger r, G_s^g underestimates G_s significantly. The discrepancy increases strongly with decreasing T in that the normalized difference becomes as large as 10^8 at the lowest T (see Fig. 2 inset). Thus we find that in the supercooled liquid there is a significant number of particles that have moved farther than would be expected from the Gaussian approximation, in agreement with the results of Ref. [13]. We define r^* as the larger of the two values of r for which $G_s(r^*,t^*) = G_s^g(r^*,t^*)$; that is, r^* is the value of r at which the normalized difference starts to become positive and very large (see Fig. 2). *We thereby define "mobile particles" as A particles that have moved farther than a distance r^* within a time t^*.* With this definition, the total number of mobile particles at any T studied is a few hundred (out of 6400 A particles), and thus constitute approximately 5% of the system. We note that the results presented below concerning the properties of the mobile particles are relatively insensitive to the details of this definition.

Snapshots of the configuration of the mobile particles show that these particles tend to form clusters; that is, they are not randomly distributed throughout the system. The spatial correlation between mobile particles is shown in Fig. 3, where we compare (cf. inset) $g_{AmAm}(r)$ and $g_{AA}(r)$, the radial distribution functions for the mobile particles and for the bulk, respectively. (In the following, "bulk" refers to all of the A particles.) We find that at short and intermediate distances ($r \leq 4$) the mobile particles are more strongly correlated than the bulk. This is demonstrated more clearly by computing the ratio $g_{AmAm}(r)/g_{AA}(r)$, which is shown in Fig. 3 for three different T. From this figure we see that with decreasing T the relative correlation between the mobile particles increases. The relative height of the first nearest neighbor peak ($r \approx 1$) increases quickly and the ratio decays more slowly as a function of r if T is decreased. At the lowest T, the size of the cluster is on the order of 3–4σ_{AA} [17]. If we assume a molecule of diameter 0.4–0.5 nm, we find that the clusters have a size of about 1 nm, which is in rough agreement with experimental expectations [4,5]. We note that at small wave vectors the partial structure factors for the bulk do not show any indication of the presence of these clusters. Thus it is perhaps not surprising that no evidence for the presence

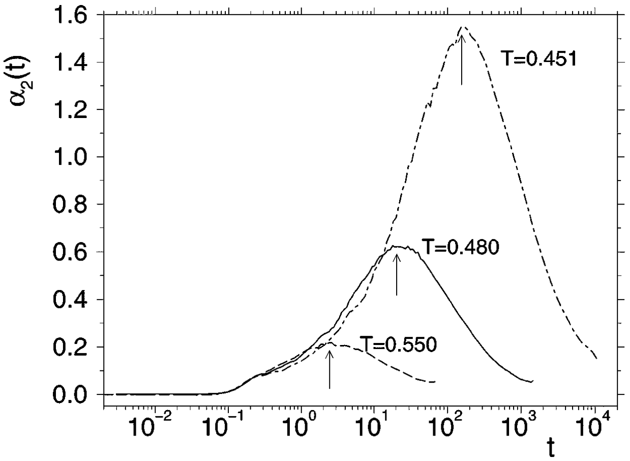

FIG. 1. Non-Guassian parameter α_2 versus time t for $T = 0.550$, $T = 0.480$, and $T = 0.451$. The arrows mark the location of the maximum, that is, of t^*.

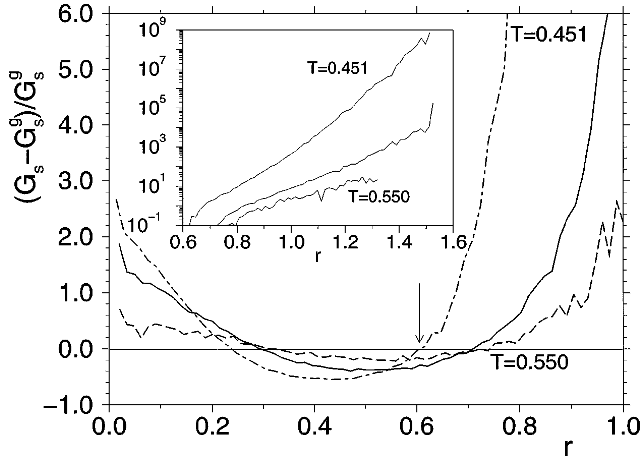

FIG. 2. $[G_s(r,t) - G_s^g(r,t)]/G_s^g(r,t)$ versus r for $t = t^*$ for $T = 0.550$, $T = 0.480$, and $T = 0.451$. The arrow marks the location of r^* for $T = 0.451$. Inset: the same quantity on a logarithmic scale.

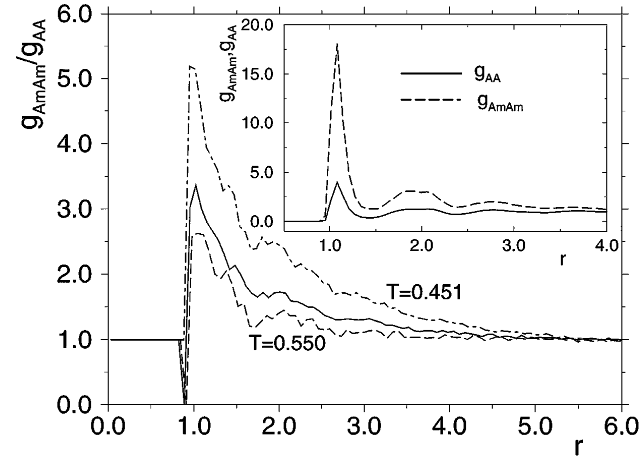

FIG. 3. Inset: radial distribution function $g_{AmAm}(r)$ and $g_{AA}(r)$ for the mobile and bulk particles, respectively, for $T = 0.451$. Main figure: Ratio between $g_{AmAm}(r)$ and $g_{AA}(r)$ for $T = 0.550$, $T = 0.480$, and $T = 0.451$.

of such clusters was found from the structure factors measured in the neutron scattering experiments of Leheny *et al.* [18].

What is the effect of these clusters of mobile particles on the bulk relaxation dynamics? To explore this question we compute the incoherent intermediate scattering function $F_s^{(Am)}(q,t)$ for the mobile particles and compare it with that for the bulk particles, $F_s^{(A)}$. These correlation functions, shown in Fig. 4 for three T, are calculated at a wave vector $q = 7.2$, which coincides with the location of the main peak in the structure factor [9]. From this figure we see that $F_s^{(Am)}$ decays faster than $F_s^{(A)}$ and that the ratio between the relaxation time of the two autocorrelation functions increases with decreasing temperature. (The relaxation time could, for example, be defined as the time it takes a correlation function to decay to e^{-1} of its initial value.) This ratio is approximately 3 for the highest T and approximately 10 for the lowest T. It is not unreasonable to extrapolate that at temperatures close to T_g the ratio between the relaxation times become as large as $10^2 - 10^4$, similar to values reported from experiments [3,4,8]. It is also interesting to note that the α-relaxation time of $F_s^{(Am)}$ is on the order of the end of the β relaxation of the bulk. This suggests that the relaxation of these clusters might be related to the β relaxation of the bulk.

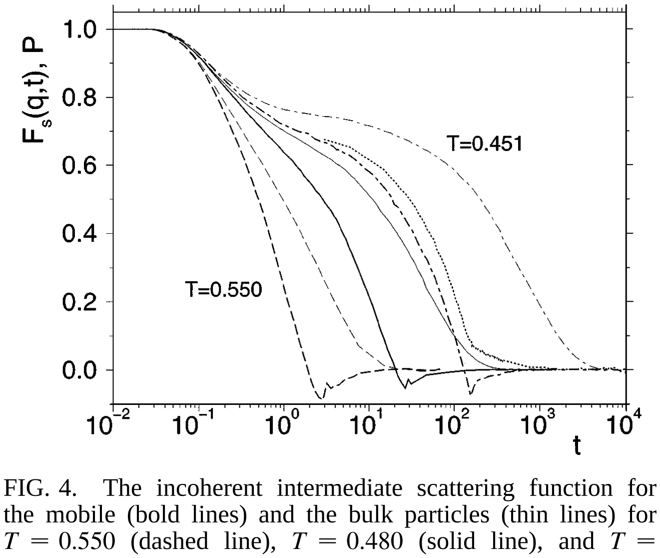

FIG. 4. The incoherent intermediate scattering function for the mobile (bold lines) and the bulk particles (thin lines) for $T = 0.550$ (dashed line), $T = 0.480$ (solid line), and $T = 0.451$ (dash-dotted line). Bold dotted line: Probability P that a particle which is mobile at time zero is also mobile at time t for $T = 0.451$.

Also shown in Fig. 4 is the probability $P(t)$ that a particle which was mobile at time zero is still mobile at time t, at the lowest T investigated (bold dotted curve). We define $P(t)$ by $\langle [N(t) - N(0)^2/N_A]/[N(0) - N(0)^2/N_A] \rangle$, where N_A is the total number of A particles and $N(t)$ is the number of particles that were mobile at time $t = 0$ and still mobile at time t. A related correlation function for the least mobile particles has been measured in experiments [3,4]. We see that P decays on the time scale of the intermediate scattering function of the mobile particles, demonstrating that the lifetime of a cluster is of the order of the relaxation time of the particles which constitute the cluster. However, the lifetime is significantly shorter than the α-relaxation time of the bulk. More details on the dynamics of the particles within the clusters will be given elsewhere [17].

We find that the existence of clusters of mobile particles is related to small, local equilibrium fluctuations in composition [19]. At all T, the pair correlation function $g_{AmB}(r)$ between the B particles and the mobile particles is smaller than the bulk quantity $g_{AB}(r)$ for $r \leq 3$. Thus mobile particles have fewer B particles in their vicinity than do generic A's. Because in this system the attractive interaction between A and B particles is stronger than either the AA or BB interaction, the presence of a B between two A's lowers the potential energy, giving rise to an effective attraction between the A's. A particles in a B-rich region can thus be expected to have a reduced mobility. A particles in a B-poor region, however, will have a reduced effective attraction between them, resulting in a higher mobility [20].

Via this mechanism we expect that this sort of dynamical heterogeneity will occur in other fragile glass-forming systems, since local equilibrium fluctuations arising in the arrangements (packing) of the molecules will always be present [21]. Energetically favorable packings will reduce the local mobility, while less favorable packings will enhance the local mobility. Such correlations have also been observed in recent spin-glass simulations [22].

In summary, we have established for the first time the existence of spatially correlated dynamical heterogeneities in a three dimensional simple glass former and characterized some of their properties. Our simulations suggest that experiments which focus only on quantities like the structure factor will be hard-pressed to observe these heterogeneities. Our findings also raise many questions; for example, does this type of dynamical heterogeneity exist also in other glass formers? Are these heterogeneities related to the localized modes found in glasses at low temperatures [23]? How are these features related to the relaxation processes predicted by the mode-coupling theory? Investigation of these questions promises to lead to a better understanding of the dynamics of glass formers from the supercooled liquid state down to the low temperature glass.

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