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Lifetime of dynamic heterogeneities in a binary Lennard-Jones mixture

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A four-time correlation function was calculated using a computer simulation of a binary Lennard-Jones mixture. The information content of the four-time correlation function is similar to that of four-time correlation functions measured in NMR experiments. The correlation function selects a subensemble and analyzes its dynamics after some waiting time. The lifetime of the subensemble selected by the four-time correlation function is calculated, and compared to the lifetimes of slow subensembles selected using two different definitions of mobility, and to the α relaxation time.

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The origin of the nonexponential relaxation found in supercooled liquids has been studied extensively in the past ten years. Two possibilities exist [1,2]. Either all the particles undergo nonexponential relaxation (homogeneous scenario), or the relaxation of each particle is exponential and there is a large variation in the relaxation time of the particles (heterogeneous scenario). There have been many simulations [3–11] and experiments [12–16] which imply heterogeneous relaxation. The heterogeneous relaxation scenario suggests that the particles in a supercooled liquid can be categorized by their relaxation time. The particles with the shortest relaxation times are referred to as "fast" particles, and the particles with the longest relaxation times are "slow" particles. One important question is the lifetime of the dynamic heterogeneities, i.e., how long does a fast particle remain fast and a slow particle remain slow? The first part of this question was considered in one of the early simulational investigations of dynamics heterogeneities [3]: the lifetime of fast particles has been found to be much shorter than the α relaxation time. It should be noted that experiments are usually sensitive to slow particles and thus simulational investigation of the slow particles lifetime is also important; however, to the best of our knowledge, lifetime of slow particles has been studied only in two dimensions where it has been found to be comparable to the α relaxation time [17]. Here we study the lifetime of slow particles using an approach inspired by one of the experimental protocols. Our study is complementary to recent investigations of the spatial correlations of the slow particles [10,11].

The lifetime of dynamic heterogeneities has been measured in a reduced four-dimensional nuclear magnetic resonance (NMR) experiment by monitoring parts of a four-time correlation function. The general idea of the experiment has been lucidly explained by Heuer [18]: one can define a filtering function $f(t_1,t_2)$ such that $\langle f(t_1,t_2)\rangle$ selects particles which are slow over a time interval $\Delta t_{12}=t_2-t_1$. Thus, $\langle f(t_1,t_2)f(t_3,t_4)\rangle$ selects particles which are slow over time intervals Δt_{12} and $\Delta t_{34}=t_4-t_3$. The two time intervals are separated by a waiting time $t_w=t_3-t_2$. For small t_w, the relaxation of the slow subensemble remains slow, but for large enough t_w the relaxation of the slow subensemble is the same as the relaxation of the full ensemble. The lifetime of the slow ensemble is related to the minimum t_w such that the average relaxation time of the slow subensemble returns to the average relaxation time of the full ensemble. Böhmer *et al.* [12] used this idea to investigate ortho-terphenyl (OTP) at 10 K above $T_g=243$ K. Using a pulse sequence they selected a set of particles which did not rotate appreciably over a time interval Δt_{12}, i.e., a slow subensemble. The particles were then allowed to evolve during a time interval t_w. Finally they measured what fraction of the slow subensemble were still slow over a time interval Δt_{34}. The characteristic time for the slow subensemble to remain slow was found to be comparable to the average relaxation time of the full ensemble. This is in a stark contrast with results obtained for OTP by Ediger's group[13,14]: at T_g+4 K the lifetime of the dynamic heterogeneities was found to be 6 times longer than the α relaxation time and at T_g+1 K it was 100 times longer. Ediger's findings could, however, be compatible with the NMR result if strong temperature dependence of the lifetime sets in close to T_g.

The procedure used in this work to measure the lifetime of dynamic heterogeneities is closely related to the NMR approach described above. We use a four-time correlation function to select a slow subensemble, and monitor the relaxation and the lifetime of the slow subensemble. The four-time correlation function selects a subensemble without any explicit definition of mobility, thus it is not clear which particles are contributing to the four-time correlation function. To identify these particles we use different definitions of mobility to select subensembles whose relaxation is similar to the subensemble selected by the four-time correlation function. Finally, we measure the lifetime of these slow subensembles.

To investigate the lifetime of dynamic heterogeneities we use the trajectories generated by an extensive Brownian dynamics simulation study of a 80:20 mixture of a binary Lennard-Jones fluid [19]. Briefly, the potential is given by $V_{\alpha\beta}=4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12}-(\sigma_{\alpha\beta}/r)^{6}]$, where α, $\beta\in\{A,B\}$, and $\epsilon_{AA}=1.0$, $\epsilon_{AB}=1.5$, $\epsilon_{BB}=0.5$, $\sigma_{AA}=1.0$, $\sigma_{AB}=0.8$, and $\sigma_{BB}=0.88$. A total of $N=N_A+N_B=1000$ particles were simulated with a fixed cubic box length of $9.4\sigma_{AA}$. All the results are presented in reduced units where σ_{AA} and ϵ_{AA} are the units of length and energy, respectively. The system was simulated at temperatures $T=0.44$, 0.45, 0.47, 0.5, 0.55, 0.6, 0.8 and 1.0. A long equilibration run, and two to eight production runs

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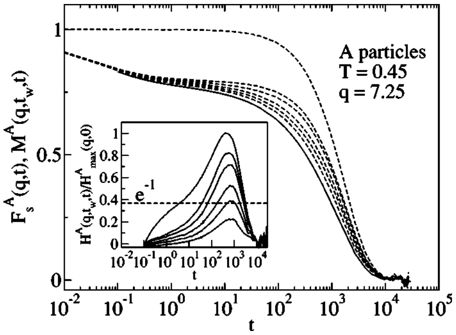

FIG. 1. $F_s^A(q,t)$ (solid line) and $M^A(q,t_w,t)$ (dashed lines) for $t_w=0$, 5, 50, 250, 500, and 1000 at $T=0.45$ listed in order from the longest relaxation time to the shortest relaxation time. (Inset) $H^A(q,t_w,t)/H^A_{max}(q,0)$ for $t_w=0$, 5, 50, 250, 500, and 1000 at $T=0.45$.

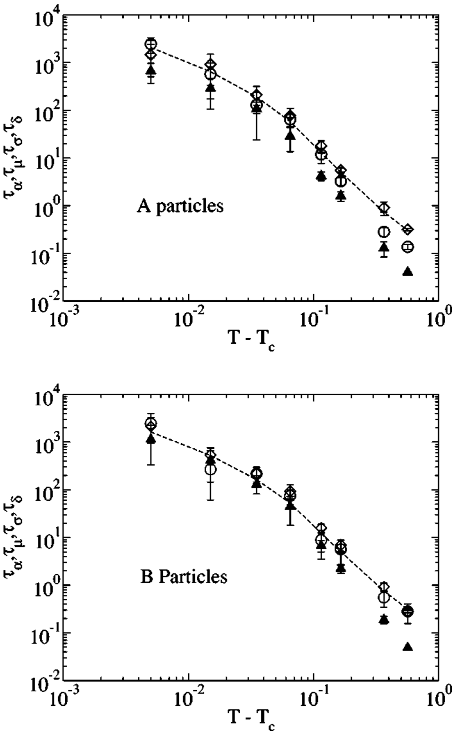

FIG. 2. The characteristic lifetime found using the four-time correlation function (▲), by using σ_i [Eq. (3)] to define the mobility (◇), and by using δ_i [Eq. (4)] to define the mobility (○), compared to the α-relaxation time (dashed line).

were performed at each temperature. The equilibration run was at least as long as the production runs. The presented results are the average of the production runs. The characteristics of this glass-forming liquid has been extensively studied [19–21]. The details and the results of the Brownian dynamics simulation are given elsewhere [22]. In particular, we found that α relaxation times, Fig. 2, follow a power-law temperature dependence in the temperature range $0.47 \leqslant T \leqslant 0.8$ and deviate from this power-law dependence for $T < 0.47$. This is similar to earlier findings using Newtonian [19,21] and stochastic dynamics [20].

To examine lifetime of dynamic heterogeneities we follow the procedure discussed above: we use a filtering function $f(t_1,t_2)=e^{i\mathbf{q}\cdot[\mathbf{r}_j(t_2)-\mathbf{r}_j(t_1)]}$, where $\mathbf{r}_j(t)$ is the position of particle j at time t. Thus $\langle f(t_1,t_2)\rangle$ is the incoherent intermediate scattering function $F_s(q;t_2-t_1)$. For all the calculations, q is set to a value around the first peak in the AA ($q=7.25$) or BB ($q=5.75$) partial structure factor for $\mathcal{M}^A$ and $\mathcal{M}^B$, respectively. The four-time correlation function is defined as follows:

$$\mathcal{M}^\alpha(q,t_1,t_2,t_3,t_4) = \frac{\langle f(t_1,t_2)f(t_3,t_4)\rangle}{\langle f(t_1,t_2)\rangle} = \frac{\left\langle \frac{1}{N_\alpha}\sum_{j=1}^{N_\alpha} e^{i\mathbf{q}\cdot(\mathbf{r}_j(t_2)-\mathbf{r}_j(t_1))}e^{i\mathbf{q}\cdot(\mathbf{r}_j(t_4)-\mathbf{r}_j(t_3))}\right\rangle}{\left\langle \frac{1}{N_\alpha}\sum_{j=1}^{N_\alpha} e^{i\mathbf{q}\cdot(\mathbf{r}_j(t_2)-\mathbf{r}_j(t_1))}\right\rangle}, \tag{1}$$

where $\alpha \in \{A,B\}$. The normalization of the correlation function is such that if $t_3=t_4$, then $\mathcal{M}^\alpha=1.0$. For small $t_w=t_3-t_2$, the relaxation of the slow subensemble remains slow, but for large enough t_w the relaxation of the slow subensemble is the same as the relaxation of the full ensemble.

We fix the first time interval, $\Delta t_{12}=t_2-t_1$, to be equal to $3\tau_\alpha$ where τ_α is the α relaxation time [τ_α is defined by the usual relation $F_s(q,\tau_\alpha)=e^{-1}$]. This is comparable to the longest time intervals Δt_{12} used to select a slow subensemble in the NMR experiment of Böhmer *et al.* Note that the time $\Delta t_{12}=3\tau_\alpha$ is well past the plateau region of the mean squared displacement, and is longer than what has been used in previous simulational investigations which examined dynamic heterogeneities [3,4,9]. The second time interval, the waiting time $t_w=t_3-t_2$, is varied. Finally, for a given t_w, $M^\alpha(q,t_w,t) \equiv \mathcal{M}^\alpha(q,0,3\tau_\alpha,3\tau_\alpha+t_w,t+3\tau_\alpha+t_w)$ is calculated as a function of time t (i.e., as a function of the last time interval, $\Delta t_{34}=t_4-t_3$). $M^A(q,t_w,t)$ is shown in Fig. 1 for several waiting times. Notice that if $t_w=0$, then $M^\alpha(q,t_w,t) = F_s^\alpha(q,3\tau_\alpha+t)/F_s^\alpha(q,3\tau_\alpha)$. Also, $M^\alpha(q,t_w,t)$ converges to $F_s^\alpha(q,t)$ as the waiting time increases. The lifetime of the subensemble measures how long it takes for this convergence to occur.

We define the lifetime of dynamic heterogeneities as the waiting time for which the difference between $M^\alpha(q,t_w,t)$ and $F_s^\alpha(q,t)$ is equal to e^{-1} of its value at short times. The exact procedure is as follows: As shown in Fig. 1, for $t_w > 0$ there is an initial decay of M^α to a plateau region, then M^α decays to zero after the plateau. This is in contrast to the $t_w=0$ case where there is no initial decay to a plateau. Since we are interested in the relaxation after the plateau, $M^\alpha(q,0,t)$ is multiplied by a temperature dependent factor $C(T)$ so that $C(T)M^\alpha(q,0,t_c)=F_s^\alpha(q,t_c)$ where t_c is at the beginning of the plateau region of F_s^α. The choice of t_c affects the results slightly, with a larger t_c leading to a somewhat longer lifetime. However, the choice of t_c does not affect any of the conclusions of this work. We calculate

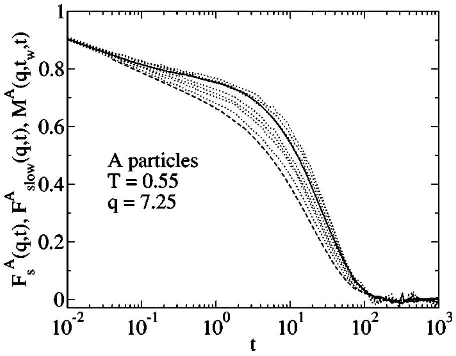

FIG. 3. $F_s^A(q,t)$ (dashed line), $F^A_{slow}(q,t_w,t)$ (dotted lines) for $r^2_{cut}=0.05$, 0.03, 0.025, 0.02, 0.015, 0.014, 0.013 listed from left to right, and $M^A(q,t_w,t)$ (solid line) for $t_w=0.2$.

$$H^\alpha(q,t_w,t)=\begin{cases} C(T)M^\alpha(q,t_w,t)-F_s^\alpha(q,t), & t_w=0, \\ M^\alpha(q,t_w,t)-F_s^\alpha(q,t), & t_w>0 \end{cases} \tag{2}$$

and determine the lifetime as the waiting time when the peak value of $H^\alpha(q,t_w,t)$, is a factor of e smaller than its $t_w=0$ value, i.e., $H^\alpha_{max}(q,\tau_\mu)/H^\alpha_{max}(q,0)=e^{-1}$, where $H^\alpha_{max}(q,t_w)$ is the maximum value of $H^\alpha(q,t_w,t)$.

Shown in Fig. 2 is the temperature dependence of the lifetime τ_μ of the slow subensemble selected by $\mathcal{M}^\alpha$ and for comparison the α relaxation time. Notice that the lifetime is not longer than the α relaxation time. The lifetime increases faster with decreasing temperature than the α relaxation time except at the lowest temperatures studied where it has the same temperature dependence as the α relaxation time.

An advantage of a computer simulation is that the trajectories of individual particles can be followed throughout the simulation. This allows us to try to identify a slow subensemble which is a major contribution to the four-time correlation function, i.e., the subensemble selected by $f(t_1,t_2)$. To this end we have defined the mobility $\sigma_i(\Delta t)$ of a particle i over a time interval Δt as

$$\sigma_i(\Delta t)\equiv\overline{|\mathbf{r}_i(t)-\mathbf{r}_i(t_1)|^2}, \tag{3}$$

where the bar denotes an average over time $t\in(t_1,t_1+\Delta t)$ [23]. A particle is defined as slow over a time interval Δt if $\sigma_i(\Delta t)$ is less than a cutoff value r^2_{cut}. These are the particles which stay closest to their position at t_1 during the whole time interval Δt.

To make a connection with the four-time correlation function study we fix $\Delta t=3\tau_\alpha$. Next, the incoherent intermediate scattering function, $F^\alpha_{slow}(q,t)$, is calculated for the slow particles after a waiting time t_w has elapsed. F^A_{slow} is shown in Fig. 3 for different values of r^2_{cut}, and is compared to F^A_s and M^A. Note that F^A_{slow} and M^A are calculated for the same waiting time $t_w=0.2$. For a large cutoff r^2_{cut}, the subensemble behaves like the full ensemble. For smaller values of r^2_{cut}, the average relaxation time of the slow particles is longer than the average relaxation time of the full ensemble. For a small enough cutoff, $F^\alpha_{slow}(q,t)\approx M^\alpha(q,t_w,t)$. The size of the cutoff needed to achieve this equality depends on t_w and the time interval used to identify the slow particles. For the temperature shown in Fig. 3 $F^A_{slow}(q,t)\approx M^A(q,0.2,t)$ for $r^2_{cut}=0.015$. This cutoff corresponds to the 0.075% slowest particles. As t_w increases, the value of r^2_{cut} resulting in $F^\alpha_{slow}\approx M^\alpha$ also increases. For the higher temperatures, it was not possible to find a value of r^2_{cut} so that $F^\alpha_{slow}\approx M^\alpha$ for short waiting times.

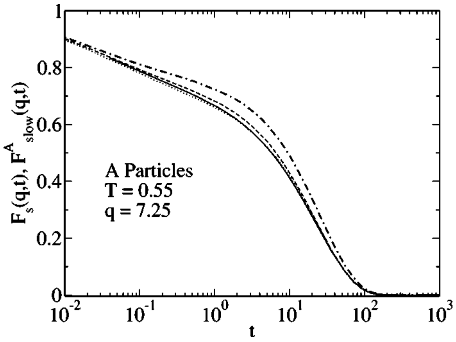

FIG. 4. F_{slow} for different subsets of particles, $\mathcal{S}\cap\mathcal{D}$ (dashed dotted), $\mathcal{S}-\mathcal{D}$ (dotted), $\mathcal{D}-\mathcal{S}$ (dashed), compared to F^A_s (solid). See text for definition of sets $\mathcal{S}$ and $\mathcal{D}$.

The characteristic lifetime of the slow particles τ_σ can be calculated using the algorithm described above [note that now we do not need the correction factor $C(T)$]. The temperature dependence of the characteristic lifetime of the slow subensemble is shown in Fig. 2. The cutoff was chosen so that on average the 10% slowest particles were used in the calculation. The choice of the cutoff has little effect on the lifetime, as long as a subensemble with a relaxation time longer than the average relaxation time of the full ensemble is identified. The lifetime calculated by identifying the slow particles is always equal to the α relaxation time to within the uncertainty of the data.

References [3,7] used the following measure of the mobility:

$$\delta_i(\Delta t)=|\mathbf{r}_i(t_2)-\mathbf{r}_i(t_1)|^2, \tag{4}$$

where $\Delta t=t_2-t_1$. We defined a slow subensemble as the 10% with the smallest $\delta_i(3\tau_\alpha)$, and calculated F^α_{slow} for this subensemble. Again, the average relaxation time of the subensemble was longer than the average relaxation time of the full ensemble. The lifetime of the subensemble defined using the second definition of the mobility, τ_δ, is equal to the α relaxation time to within the uncertainty of the data except for the A particles at the highest temperatures examined in this work (see Fig. 2).

To try to understand why both definitions give similar results, it is illustrative to examine the relaxation of different subsets of particles chosen by the two definitions of mobility. Let $\mathcal{S}$ be the set of particles selected using σ_i as the definition of mobility, and $\mathcal{D}$ be the set of particles selected using δ_i as the definition of mobility. Figure 4 compares F^A_{slow} for $\mathcal{S}\cap\mathcal{D}$, $\mathcal{S}-\mathcal{D}$, and $\mathcal{D}-\mathcal{S}$ to F^A_s for $T=0.55$. The relaxation of the particles which are in set $\mathcal{S}$ but not $\mathcal{D}$, or are in set $\mathcal{D}$ but not $\mathcal{S}$, is similar to the relaxation of the full ensemble, but the particles which are in both sets have a longer relaxation time. Thus, the two definitions of mobility give similar results since they both are able to select the particles whose average relaxation time is longer than the average relaxation time of the full ensemble.

In conclusion, we used a four-time correlation function to select a slow subensemble and analyze the dynamics of the slow subensemble. The lifetime of the slow subensemble selected by the four-time correlation function is not longer than the α relaxation time. On approaching T_c the lifetime increases faster with decreasing temperature than the α relaxation time [24]. Closer to T_c (beginning approximately at the temperature at which deviations from mode-coupling-like power laws appear) the lifetime follows the temperature dependence of the α relaxation time. We also identified two other slow subensembles whose average relaxation time is longer than the average relaxation time of the full ensemble using two different definitions of mobility. The essential subensemble, the subensemble chosen such that $F^{\alpha}_{slow} \approx M^{\alpha}$, consists of the particles which stay closest to their position at t_1 over the time interval $\Delta t = t_2 - t_1$, and are still close to their position at t_1. This suggests that the slow subensemble are the particles which are confined to their cage over the time interval Δt. The lifetime of the slow subensemble depended on the definition of mobility. If σ_i was used to define mobility, the lifetime was equal to the α relaxation time at all temperatures. If δ_i was used as the definition of mobility, the lifetime was equal to the α relaxation time except for the A particles at the highest temperature studied, in which case the lifetime was less than the α relaxation time.

Our findings qualitatively agree with NMR results of Böhmer *et al.* [12]. Note, however, that there is a significant difference in the temperature of simulations and experiments: the simulations have been performed slightly above T_c whereas the experiments were done well below T_c. Thus, direct comparison of the two sets of results is impossible. The same comment applies, however, to almost all simulational studies of glassy dynamics.

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[1] M. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).

[2] R. Richert, J. Phys.: Condens. Matter **14**, R703 (2002).

[3] W. Kob *et al.*, Phys. Rev. Lett. **79**, 2827 (1997).

[4] J. Qian and A. Heuer, Eur. Phys. J. B **18**, 501 (2000).

[5] J. Qian, R. Hentschke, and A. Heuer, J. Chem. Phys. **110**, 4514 (1999).

[6] A. Heuer and K. Okun, J. Chem. Phys. **106**, 6176 (1997).

[7] C. Donati *et al.*, Phys. Rev. Lett. **80**, 2338 (1998).

[8] B. Doliwa and A. Heuer, Phys. Rev. Lett. **80**, 4915 (1998).

[9] P.H. Poole, C. Donati, and S.C. Glotzer, Physica A **261**, 51 (1998); C. Donati *et al.*, Phys. Rev. E **60**, 3107 (1999).

[10] N. Lačević and S.C. Glotzer, J. Phys.: Condens. Matter **15**, S2437 (2003).

[11] N. Lačević *et al.*, J. Chem. Phys. **119**, 7372 (2003).

[12] R. Böhmer *et al.*, Europhys. Lett. **36**, 55 (1996); R. Böhmer *et al.*, J. Chem. Phys. **108**, 890 (1998).

[13] M.T. Cicerone and M.D. Ediger, J. Chem. Phys. **103**, 5684 (1995).

[14] C. Wang and M.D. Ediger, J. Phys. Chem. B **103**, 4177 (1999).

[15] F.R. Blackburn *et al.*, J. Non-Cryst. Solids **172–174**, 256 (1994).

[16] K. Schmidt-Rohr and H.W. Spiess, Phys. Rev. Lett. **66**, 3020 (1991).

[17] D.N. Perera, P. Harrowell, J. Chem. Phys. **111**, 5441 (1999); B. Doliwa and A. Heuer, J. Non-Cryst. Solids **307–310**, 32 (2002).

[18] A. Heuer, Phys. Rev. E **56**, 730 (1997).

[19] W. Kob and H.C. Andersen, Phys. Rev. E **51**, 4626 (1995); **52**, 4134 (1995).

[20] T. Gleim, W. Kob, and K. Binder, Phys. Rev. Lett. **81**, 4404 (1998).

[21] W. Kob, in *Slow Relaxations and Nonequilibrium Dynamics in Condensed Matter*, edited by J.-L. Barrat *et al.* (EDP Sciences–Springer-Verlag, Berlin, 2003).

[22] G. Szamel and E. Flenner, Europhys. Lett. **67**, 779 (2004).

[23] A similar definition was used *below* T_c by K. Vollmayr-Lee, W. Kob, K. Binder, and A. Zippelius, J. Chem. Phys. **116**, 5158 (2002).

[24] The α relaxation time and the lifetime of the slow subensemble were both defined by the condition that an appropriately defined function decayed to an arbitrary value of e^{-1}. If, instead of e^{-1}, 0.25, 0.35, or 0.5 were used, the same trends were observed.