Lifetime of dynamic heterogeneities in a binary Lennard-Jones mixture

Elijah Flenner and Grzegorz Szamel
Department of Chemistry, Colorado State University, Fort Collins, CO 80525
(Dated: March 23, 2022)

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 sub-ensemble and analyzes its dynamics after some waiting time. The lifetime of the sub-ensemble selected by the four-time correlation function is calculated, and compared to the lifetimes of slow sub-ensembles selected using two different definitions of mobility, and to the α relaxation time.

PACS numbers: 61.43.Fs,64.70.Pf

The origin of the non-exponential relaxation found in supercooled liquids has been studied extensively in the last ten years. Two possibilities exist [1][2]. Either all the particles undergo non-exponential 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][4][5][6][7][8][9][10][11] and experiments [12][13][14][15][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 \( \Delta t_{12} \) 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 sub-ensemble remains slow, but for large enough \( t_w \), the relaxation of the slow sub-ensemble 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 sub-ensemble 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 \( T_g = 243 \text{ K} \). Using a pulse sequence they selected a set of particles which did not rotate appreciably over a time interval \( \Delta t_{12} \), i.e. a slow sub-ensemble. The particles were then allowed to evolve during a time interval \( t_w \). Finally they measured what fraction of the slow sub-ensemble were still slow over a time interval \( \Delta t_{34} \). The characteristic time for the slow sub-ensemble 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 \( T_g + 4 \text{ K} \) the lifetime of the dynamic heterogeneities was found to be 6 times longer than the α relaxation time and at \( T_g + 1 \text{ K} \) 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 sub-ensemble, and monitor the relaxation and the lifetime of the slow subensemble. The four-time correlation function selects a sub-ensemble 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 sub-ensembles whose relaxation is similar to the sub-ensemble selected by the four-time correlation function. Finally, we measure the lifetime of these slow sub-ensembles.

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 [10]. Briefly, the potential is given by \( V_{\alpha\beta} = 4\epsilon_{\alpha\beta} \left[ (\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^{6} \right] \), where \( \alpha, \beta \in \{ A, B \} \), 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 \( \sigma_{AA} \) and \( \epsilon_{AA} \) 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 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 \[10, 24, 21\].

The details and the results of the Brownian dynamics simulation are given elsewhere [22]. In particular, we found that a relaxation times, Fig. 2, follow a power-law temperature dependence in the temperature range $0.47 \leq T \leq 0.8$ and deviate from this power-law dependence for $T < 0.47$. This is similar to earlier findings using Newtonian [10, 21] and stochastic dynamics [20].

To examine lifetime of dynamic heterogeneities we follow the procedure discussed above: we use a filtering function $f(t_1, t_2) = e^{\alpha q (r_j(t_2) - r_j(t_1))}$ where $r_j(t)$ is the position of particle $j$ at time $t$. Thus \(f(t_1, t_2)\) 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 $M^A$ and $M^B$, respectively. The four-time correlation function is defined as follows:

$$M^\alpha(q, t_1, t_2, t_3, t_4) = \frac{\langle f(t_1, t_2) f(t_3, t_4) \rangle}{\langle f(t_1, t_2) \rangle}$$

where $\alpha \in \{A, B\}$. The normalization of the correlation function is such that if $t_3 = t_4$, then $M^\alpha = 1.0$. For small $t_w = t_3 - t_2$, the relaxation of the slow sub-ensemble remains slow, but for large enough $t_w$ the relaxation of the slow sub-ensemble 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 $\tau_\alpha$ is the $\alpha$ relaxation time ($\tau_\alpha$ is defined by the usual relation $F_s(q, \tau_\alpha) = e^{-1}$). This is comparable to the longest time intervals $\Delta t_{12}$ used to select a slow sub-ensemble 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 [2, 4, 9]. The second time interval, the waiting time $t_w = t_3 - t_2$, is varied. Finally, for a given $t_w$, $M^\alpha(q, t_w, t) \equiv M^\alpha(q, 0, 3\tau_\alpha, 3\tau_\alpha + t_w, t + 3\tau_\alpha + t_w)$ is calculated as a function of time $t$ (i.e. as a function of the last time interval, $\Delta t_{34} = t_4 - t_3$). $M^\alpha(q, t_w, t)$ is shown in Fig. 3 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 sub-ensemble measures how long it takes for this convergence to occur.

![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. (Insert) $H^A(q, t_w, t)/H_{max}^A(q, 0)$ for $t_w = 0, 5, 50, 250, 500$, and $1000$ at $T = 0.45.$](image)
A relaxation time of the full ensemble. For a small enough partition time of the slow particles is longer than the average relaxation time of the whole ensemble, for smaller values of $\alpha$ the sub-ensemble behaves like the full ensemble. For the intermediate scattering function, 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. 2, $F_{\text{slow}}^\alpha(q, t_w, t)$ for $r^2_{\text{cut}} = 0.015$. This cutoff corresponds to the 0.075% slowest particles. As $t_w$ increases, the value of $r^2_{\text{cut}}$ resulting in $F_{\text{slow}}^\alpha \approx M^\alpha$ also increases. For the higher temperatures, it was not possible to find a value of $r^2_{\text{cut}}$ so that $F_{\text{slow}}^\alpha \approx M^\alpha$ for short waiting times. The characteristic lifetime of the slow particles $\tau_0$ 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 sub-ensemble is shown in Fig. 3. 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 sub-ensemble 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 $\alpha$ relaxation time to within the uncertainty of the data.

Refs. [3, 7] used the following measure of the mobility $\delta_i$ (Eq. (3)) to define the mobility $(\sigma)$, compared to the $\alpha$-relaxation time (dashed line).

\[
\sigma_i(\Delta t) = \sigma_{i}(\Delta t) = |r_i(t) - r_i(t_1)|^2, \tag{3}
\]

where the bar denotes an average over time $t \in (t_1, t_1 + \Delta t)$. A particle is defined as slow over a time interval $\Delta t$ if $\sigma_i(\Delta t)$ is less than a cutoff value $r^2_{\text{cut}}$. These are the particles which stay closest to their position at $t_1$ during the whole time interval $\Delta t$. To make a connection with the four-time correlation function study we fix $\Delta t = 3\tau_0$. Next, the incoherent intermediate scattering function, $F_{\text{slow}}^\alpha(q, t)$, is calculated for the slow particles after a waiting time $t_w$ has elapsed. $F_{\text{slow}}^\alpha$ is shown in Fig. 2 for different values of $r^2_{\text{cut}}$, and is compared to $F^\alpha$ and $M^\alpha$. Note that $F_{\text{slow}}^\alpha$ and $M^\alpha$ are calculated for the same waiting time $t_w = 0.2$. For a large cutoff $r^2_{\text{cut}}$, the sub-ensemble behaves like the full ensemble. For smaller values of $r^2_{\text{cut}}$, the average relaxation time of the slow particles is longer than the average relaxation time of the full ensemble. For a small enough cutoff, $F_{\text{slow}}^\alpha(q, t) \approx M^\alpha(q, t_w, t)$. 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. 2, $F_{\text{slow}}^\alpha(q, t) \approx M^\alpha(q, 0.2, t)$ for $r^2_{\text{cut}} = 0.015$. This cutoff corresponds to the 0.075% slowest particles. As $t_w$ increases, the value of $r^2_{\text{cut}}$ resulting in $F_{\text{slow}}^\alpha \approx M^\alpha$ also increases. For the higher temperatures, it was not possible to find a value of $r^2_{\text{cut}}$ so that $F_{\text{slow}}^\alpha \approx M^\alpha$ for short waiting times.

The characteristic lifetime of the slow particles $\tau_0$ 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 sub-ensemble is shown in Fig. 3. 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 sub-ensemble 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 $\alpha$ relaxation time to within the uncertainty of the data.

Ref. [3, 7] used the following measure of the mobility $\delta_i$ (Eq. (3)) to define the mobility $(\sigma)$, compared to the $\alpha$-relaxation time (dashed line).

\[
\sigma_i(\Delta t) = |r_i(t_2) - r_i(t_1)|^2, \tag{4}
\]

where $\Delta t = t_2 - t_1$. We defined a slow sub-ensemble as the 10% with the smallest $\delta_i(3\tau_0)$, and calculated $F_{\text{slow}}^\alpha$ for this sub-ensemble. Again, the average relaxation time of the sub-ensemble was longer than the average relaxation time of the full ensemble. The lifetime of the sub-ensemble defined using the second definition of the mobility, $\tau_3$, is equal to the $\alpha$ 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).

B Particles

FIG. 2: The characteristic lifetime found using the four-time correlation function (▲), by using $\sigma_i$ (Eq. (3)) to define the mobility (○), and by using $\delta_i$ (Eq. (4)) to define the mobility (⟨⟩), compared to the $\alpha$-relaxation time (dashed line).

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

\[ T = 0.55 \]

\[ q = 7.25 \]
selected using $\delta_i$ as the definition of mobility. Figure 4 compares $F_{s}^{\alpha}$ for $S \cap D$, $S - D$, and $D - S$ to $F_{s}^{\alpha}$ for $T = 0.55$. The relaxation of the particles which are in set $S$ but not $D$, or are in set $D$ but not $S$, 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 sub-ensemble and analyze the dynamics of the slow sub-ensemble. The lifetime of the slow sub-ensemble selected by the four-time correlation function is not longer than the $\alpha$ relaxation time. On approaching $T_c$, the lifetime increases faster with decreasing temperature than the $\alpha$ relaxation time. 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 $\alpha$ relaxation time. We also identified two other slow sub-ensembles whose average relaxation time is longer than the average relaxation time of the full ensemble using two different definitions of mobility. The essential sub-ensemble, the sub-ensemble chosen such that $F_{s}^{\alpha} \approx M^{\alpha}$, consists of the particles which stay closest to their position at $t_1$ and are still close to their position at $t_1$. This suggests that the slow sub-ensemble are the particles which are confined to their cage over the time interval $\Delta t = t_2 - t_1$, and are still close to their position at $t_1$. Thus, direct comparison of the two sets of results is impossible. The same comment applies, however, to almost all simulational studies of glassy dynamics.

This work was supported by NSF Grant CHE 0111152.

[1] M. Ediger, Annu. Rev. Phys. Chem. 51, 99 (2000).
[2] R. Richert, J. Phys. Cond. Matt. 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. Cond. Mattt. 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, 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); Phys. Rev. E 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, J.-L. Barrat et al., eds. (EDP Sciences-Springer Verlag, 2003).
[22] G. Szamel and E. Fleisher, cond-mat/0407537 (accepted for publication in Europhys. Lett.).
[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 $\alpha$ relaxation time and the lifetime of the slow sub-ensemble 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.