Dynamic heterogeneity in a glass forming fluid: susceptibility, structure factor and correlation length

Elijah Flenner and Grzegorz Szamel
Department of Chemistry, Colorado State University, Fort Collins, CO 80523
(Dated: November 5, 2010)

We investigate the growth of dynamic heterogeneity in a glassy hard-sphere mixture for volume fractions up to and including the mode-coupling transition. We use an 80000 particle system to test a new procedure to evaluate a dynamic correlation length $\xi(t)$: we determine the ensemble independent dynamic susceptibility $\chi_4(t)$ and use it to facilitate evaluation of $\xi(t)$ from the small wave vector behavior of the four-point structure factor. We analyze relations between the $\alpha$ relaxation time $\tau_\alpha$, $\chi_4(\tau_\alpha)$, and $\xi(\tau_\alpha)$. We find that mode-coupling like power laws provide a reasonable description of the data over a restricted range of volume fractions, but the power laws’ exponents differ from those predicted by the inhomogeneous mode-coupling theory. We find $\xi(\tau_\alpha) \sim \ln^2(\tau_\alpha)$ over the full range of volume fractions studied, which is consistent with Adams-Gibbs-type relation.

PACS numbers: 61.20.Lc,61.20.Ja,64.70.P-

The search for a growing length scale associated with the dramatic slowing down of a supercooled liquid’s dynamics is an active area of research. In the last decade, a growing dynamic correlation length characterizing dynamic heterogeneity was extensively studied in simulations [1–8] and experiments [9–11], and was also investigated theoretically [12–17]. Yet there are still important and unresolved issues.

One popular way to quantify dynamic heterogeneity is to focus on the fluctuations of particles’ dynamics. Since the dynamics is determined by two-point functions, four-point quantities are introduced to characterize fluctuations of dynamics, the so-called dynamic susceptibility $\chi_4(t)$ and associated structure factor $S_4(q;t)$. Roughly speaking, $\chi_4(t)$ measures the total fluctuations of the two-point function characterizing particles’ dynamics whereas $S_4(q;t)$ is the Fourier transform of the spatially resolved fluctuations. Since the total fluctuations can formally be obtained by integrating the spatially resolved fluctuations. Since the total fluctuations are not allowed ($g(\tau)|\chi_4(t)|^2 + \chi(t)$), thus $\chi_4(t)$ measured in simulations is not equal to $\lim_{q\to 0} S_4(q;t)$. To distinguish the susceptibility determined in an ensemble with quantity $x$ fixed we henceforth use the symbol $\chi_4(t)|_x$. The difference between $\chi_4(t)|_x$ and $\lim_{q\to 0} S_4(q;t)$ makes determination of the dynamic correlation length $\xi(t)$ from the small wave vector behavior of $S_4(q;t)$ more demanding. It necessitates [3–6] using significantly larger systems than was customary in early simulations.

In a very interesting development, the difference between $\chi_4(t)$ and $\chi_4(t)|_x$ was used by Berthier et al. [9] to determine an experimentally accessible bound for $\chi_4(t)$. Specifically, by using the formalism developed in Ref. [18], they showed that $\chi_4(t) = \chi_4(t)|_x + \chi(t)$ where $\chi(t)$ is a correction term due to fluctuations suppressed in the constant $x$ ensemble. Importantly, while $\chi_4(t)|_x$ cannot be directly determined in experiments, the correction term $\chi(t)$ can. Since $\chi_4(t)|_x > 0$, $\chi(t)$ provides a lower bound to $\chi_4(t)$. Both $\chi_4(t)|_x$ and $\chi(t)$ were calculated using computer simulations [14, 19] and it was found that $\chi(t)$ becomes the dominant term close to the so-called mode-coupling transition. However, it has not been verified that the sum of these two terms agrees with the independent extrapolation of $S_4(q;t)$ to $q = 0$ and, somewhat surprisingly, the sum has not been used to facilitate the evaluation of the dynamic correlation length.

We note here two difficulties with our present understanding of dynamic heterogeneity. First, there seems to be no consensus regarding the scaling relation between the length measured at the $\alpha$ relaxation time, $\xi(\tau_\alpha)$, and the relaxation time $\tau_\alpha$, even for the range of times accessible in computer simulations. Upon approaching the mode-coupling transition almost all simulations [20] find a power law $\xi(\tau_\alpha) \sim \tau_\alpha^{1/z}$. However, the range of the scaling exponents reported is surprisingly large: $1/z$ varies from 0.43 [2] to 0.13 [21]. More importantly, it is difficult to reconcile relationships between $\xi(\tau_\alpha)$ and $\tau_\alpha$ exhibited by the simulation results with the experimentally determined dynamic correlation lengths [22]. Specifically, naive extrapolations of simulational trends result in lengths that are orders of magnitude too large for relaxation times at the glass transition temperature [23]. It has been shown [19] that the growth of the dynamic susceptibility with the relaxation time slows down near the mode-coupling transition. This suggests (but does not prove) a similar behavior of the correlation length.

In this Letter we address the issues mentioned in the preceding paragraphs. First, we calculate the ensemble independent four-point susceptibility and show explicitly that it agrees very well with the extrapolation of $S_4(q;t)$ to zero wave vector. Next, we analyze the small wave-vector behavior of $S_4(q;t)$ and determine $\xi(t)$. We demonstrate the practical advantage of using $\chi_4(t)$ for $\lim_{q\to 0} S_4(q;t)$. Finally, we analyze relations between the
\( \alpha \) relaxation time \( \tau_\alpha \), \( \chi_4(\tau_\alpha) \), and \( \xi(\tau_\alpha) \). Importantly, we find the slower-than-power law growth \( \xi(\tau_\alpha) \sim \ln(\tau_\alpha) \).

We simulated a 50:50 binary mixture of hard spheres with Monte Carlo dynamics introduced in Ref. [19]: the larger sphere’s diameter \( d_2 \) is 1.4 times larger than the smaller sphere diameter \( d_1 \), and the dynamics consists of random trial moves in a cube of length 0.1 \( d_1 \). We studied systems at fixed numbers of small and large particles \( (N_1 \text{ and } N_2, \text{ respectively}) \) or, equivalently, at constant volume fraction \( \phi = (N_1 d_1^3 + N_2 d_2^3) / (6V) \) (\( V \) is the system’s volume) and concentration \( c = N_1 / N \). We ran four trajectories with \( N = 80 \) 000 particles at \( \phi = 0.4, 0.45, 0.5, 0.52, 0.55, 0.56, 0.58, \) and 0.59, and four trajectories with \( N = 10 \) 000 particles at \( \phi = 0.54, 0.57, 0.58, \) and 0.59. We ran additional simulations to calculate derivatives with respect to \( \phi \) and \( c \). For \( \phi \leq 0.585 \) our runs are at least 100\( \tau_\alpha \) long \( (\tau_\alpha \text{ is defined later}) \) and for \( \phi = 0.59 \) we ran for 50\( \tau_\alpha \) for the 80 000 particle simulations and 85 \( \tau_\alpha \) for the 10 000 particle simulations. At each \( \phi \) at least 10\( \tau_\alpha \) were discarded for equilibration. Results are presented in reduced units: time in Monte Carlo steps (a Monte Carlo step is one attempted move per particle) and lengths in the smaller particle’s diameter. This system was shown [19] to reproduce very well the dynamics of an experimental glassy colloidal system.

To characterize the particles’ dynamics we use the overlap function \( w_n(t) = \theta(a - r_n(t) - r_o(0)) \) where \( \theta \) is the Heaviside step function, \( r_n(t) \) denotes the position of particle \( n \) at a time \( t \) and \( a = 0.3 \). The average overlap function \( F_o(t) = N^{-1} \langle \sum_n w_n(t) \rangle \) encodes similar dynamic information as the self intermediate scattering function \( F_o(k; t) = N^{-1} \langle \sum_n \exp\{-i\mathbf{k} \cdot \mathbf{r}_n(t) - r_o(0)) \} \). Here and in the following the brackets \( \langle \ldots \rangle \) denote the average over the simulational ensemble in which the volume fraction and the composition of the system are fixed. The sum in \( F_o(t) \) is taken over both the large and small particles. We define the \( \alpha \) relaxation time \( \tau_\alpha \) as the time at which \( F_o \) is equal to 1/e, \( F_o(\tau_\alpha) = 1/e \). We also evaluate the mean-square displacement of all the particles and the self-diffusion coefficient \( D \). Our results for \( \tau_\alpha \) and \( D \) are consistent with those of Brambilla et al. [19]. We find that mode-coupling theory-like power laws provide good fits to the data for 0.55 \( \leq \phi \leq 0.58 \) and the power laws’ exponents are close to those predicted by the theory. Furthermore, we observe deviations from the power law fits for \( \phi > 0.58 \). Finally, similarly to Brambilla et al., we find that our results for 0.50 \( \leq \phi \leq 0.59 \) can be well fitted by a function showing a stronger divergence at a higher volume fraction, \( \exp[A/(\phi_o - \phi)^2] \) with \( \phi_o = 0.635 \).

It should be emphasized that our simulations extend up to and include the mode-coupling transition \( \phi_c = 0.59 \) whereas previous large scale simulations [5][6] covered a temperature range where mode-coupling power law provides good fits, i.e. a temperature range starting approximately 15% above the mode-coupling temperature \( T_c \).

To characterize the heterogeneity of the system’s dynamics we examine the dynamic susceptibility \( \chi_4(\phi, c) \) and the four-point structure factor \( S_4(q; t) \),

\[
\chi_4(t|\phi, c) = N^{-1} \left( \langle |W(t)|^2 \rangle - \langle W(t) \rangle^2 \right) \tag{1}
\]

\[
S_4(q; t) = N^{-1} \left( \langle W(q, t) W(-q; t) \rangle - \langle W(q; t) \rangle^2 \right). \tag{2}
\]

In Eq. [1] the subscript \( \phi, c \) indicates that the susceptibility is calculated in the simulational ensemble with fixed volume fraction and concentration, and \( W(t) \) denotes the total overlap at time \( t \), \( W(t) = \sum_n w_n(t) \). In Eq. [2] \( W(q; t) \) is the Fourier transform of the spatially resolved overlap, \( W(q; t) = \sum_n w_n(t) \exp[-i\mathbf{q} \cdot \mathbf{r}_n(0)]. \) We expect \( \chi_4(t|\phi, c) \neq \lim_{q \to 0} S_4(q; t) \) and we define the ensemble independent dynamic susceptibility, \( \chi_4(t) \), as

\[
\chi_4(t) = \lim_{q \to 0} S_4(q; t). \tag{3}
\]

The difference between \( \chi_4(t) \) and \( \chi_4(t|\phi, c) \) originates from the fluctuations of the volume fraction and the concentration. As recognized by Berthier et al. [9] the contributions of these fluctuations to \( \chi_4(t) \) can be evaluated following Ref. [18]. We obtain

\[
\chi_4(t) \approx \chi_4(t|\phi, c) + \frac{(\rho \pi)}{6} \chi_4(\phi) \left( G_1 + \frac{(\rho \pi)}{3} \chi_4(\phi) \chi_4(c) G_2 + F_o^2(t) G_3 \right), \tag{4}
\]

where \( \rho \) is the number density and \( \chi_4(t) = \partial F_o(t)/\partial x \). There are other terms that contribute to Eq. [4], but they can be neglected for our system at every studied volume fraction. In Eq. [4], \( G_\alpha \) are functions of the partial structure factors \( S_{\alpha\beta}(q) = (N_\alpha N_\beta)^{-1/2} \langle \rho_\alpha(q) \rho_\beta(-q) \rangle \) where \( \rho_\alpha(q) \) is the Fourier transform of the microscopic density of the component \( \alpha \), and \( \alpha, \beta = 1, 2 \). Explicitly, \( G_1 = d_1^2 x_1 S_{11}(0) + 2d_1^2 d_2 \sqrt{2} S_{12}(0) + d_2^2 S_{22}(0) \) where \( x_\alpha = N_\alpha / N \), and \( S_{\alpha\beta}(0) = \lim_{q \to 0} S_{\alpha\beta}(q) \).

Shown in Fig. [1] is the volume fraction dependence of the first two terms on the right hand side of Eq. [4] and the sum of all the terms calculated at \( \tau_\alpha \). We find that the \( \chi_4^2 \) term becomes the dominant contribution to \( \chi_4(\tau_\alpha) \) as \( \phi \) increases [24].

To verify that \( \chi_4(t) \) calculated from Eq. [4] agrees with \( \lim_{q \to 0} S_4(q; t) \) and to determine \( \xi(t) \) we need to analyze the four-point structure factor. To this end we used the 80 000 particle simulations to fit Eq. [2] to several functions that are based on the following form,

\[
S_4(q; t) = \frac{A}{1 + (\xi(t)q)^2} + B^2 q^4 + \frac{C}{1 + (\xi(t)q)^2^2}. \tag{5}
\]

Specifically, we used (1) the Ornstein-Zernicke (OZ) function, i.e. we set \( B = 0 \) and \( C = 0 \); (2) a function suggested by the form of a three-point susceptibility of Ref. [14], i.e. we set \( C = 0 \); (3) a function suggested by field-theoretical considerations of Refs. [14][15][25], i.e. we set
A = \chi_4(t)|_{\phi,c} and B = 0; (4) a function utilized in Ref. 21. ln[S_4(q; t)] = ln[A] - [\xi(t)q]^2 + Dq^4. All procedures resulted in the same \lim_{q \to 0} S_4(q; t) to within error. The results for the OZ fits are shown in Fig. 1 as filled squares. They agree very well with the open squares which show the right-hand-side of Eq. (4).

Having verified the consistency of Eqs. (3) and (4), we now discuss the length \xi(\tau_\alpha). Fitting procedures (1) and (2) resulted in the same length. Procedure (4) agreed with (1) and (2) if we restricted it to wave-vectors \( q < 1/\xi(\tau_\alpha) \). As expected, procedure (3) resulted in a smaller length. This length is approximately 1.2 times smaller than the lengths obtained using other fitting procedures, independently of \( \phi \). Since we established the consistency of Eqs. (3) and (4), we redid the fits determining \( \xi(\tau_\alpha) \) by using the right-hand-side of Eq. (4) for \( \lim_{q \to 0} S_4(q; \tau_\alpha) \). This improved the quality of the fits and reduced the uncertainty in \( \xi(\tau_\alpha) \). As a final revision, since the OZ function only provided a good fit for \( \xi(\tau_\alpha)q < 1.5 \), we restricted the fits to values where \( q < 1.5/\xi(\tau_\alpha) \).

In Fig. 2, we show the results of fitting procedures (1), (2), and (4). We also show 1.2\( \xi(\tau_\alpha) \) when \( \xi \) is obtained from procedure (3). All these fits produce indistinguishable results. Finally, in Fig. 2, we show a scaling plot of \( S_4(q; t) \) shown with the OZ function (solid line). We find excellent overlap for every volume fraction and we observe deviations from the OZ form only for \( \xi > 1.5 \). We conclude that using the right-hand-side of Eq. (4) for \( \lim_{q \to 0} S_4(q; \tau_\alpha) \) allows us to reliably determine \( \xi(\tau_\alpha) \).

Having tested the procedure to calculate the dynamic correlation length we now demonstrate that it can be used to get \( \xi(\tau_\alpha) \) using a moderately large system. We find that the correlation lengths determined using 80,000 and 10,000 particles are virtually identical [see Fig. 3].

Recently, Karmakar et al. 6,8 advocated using finite size scaling to find the dynamic correlation length and showed that \( \xi(\tau_\alpha) \) obtained from this procedure are consistent with those determined from the analysis of \( S_4(q; \tau_\alpha) \) obtained from very large scale simulations (up to 351 232 particles). Finite size scaling is attractive since it does not require large simulations. However, the version used by Karmakar et al. utilizes ensemble-dependent quantities, \( \chi_4(\tau_\alpha)|_{T,n,c} (n \) is the total number density) and the fourth central moment of the total overlap \( W(t) \). Karmakar et al. found that in the temperature range investigated \( \chi_4(\tau_\alpha)/\chi_4(\tau_4)|_{T,n,c} \approx 1.4 \). We believe the temperature independence of this ratio might be necessary for the finite size scaling procedure to work. Figure 1 shows that for a range of \( \phi \)'s the ratio \( \chi_4(\tau_4)/\chi_4(\tau_4)|_{\phi,c} \) is approximately constant. However, upon approaching \( \phi_c \) it increases rapidly. Thus, Karmakar et al.'s finite size scaling procedure might not work at temperatures close to and below the mode-coupling transition \( T_c \).

Next, we examine scaling relations between \( \tau_\alpha, \chi_4(\tau_\alpha) \) and \( \xi(\tau_\alpha) \). As shown in Fig. 3, for \( \xi(\tau_\alpha) \geq 2 \) we find \( \chi_4(\tau_\alpha) \sim \xi(\tau_\alpha)^{2-\eta} \) with \( 2 - \eta \approx 2.9 \). Furthermore, as shown in Fig. 3, for the same range of volume fractions where we find good power law fits to \( \tau_\alpha \) and \( D \), we observe an approximate power law \( \xi(\tau_\alpha) \sim \tau_\alpha^{1/2} \) with \( 1/2 \approx 0.21 \). The scaling exponents disagree with the inhomogeneous mode-coupling predictions 11,12 and with Ref. 15. Interestingly, \( 1/2 \) is consistent with some of the earlier studies 3,7,8. Finally, we find that \( \xi(\tau_\alpha) \sim \ln(\tau_\alpha) \) over the whole range of volume fractions studied, thus there is a slower-than-power law increase of the dynamic correlation length with the relaxation time.

We note that Adam-Gibbs 26 and Random-First-Order-Transition 27 theories postulate an exponential dependence of the relaxation time, \( \tau \), on a length, \( \xi \),
characterizing the size of correlated regions, $\tau \sim \exp(\xi)$, and a relation between $\xi$ and the so-called configurational entropy $S_c$, $\xi \sim (1/S_c)^{1/(d-\theta)}$ [28]. A recent study [29] confirmed these relations (although somewhat indirectly) and found $\psi \approx 1$, which is consistent with our relation between $\tau_c$ and the dynamic correlation length. This suggests an intriguing connection between the length characterizing the size of correlated regions and the dynamic heterogeneity length [30] but we leave it for a future study. We also acknowledge that another dynamic length characterizing single-particle motion was also found to be a linear function of $\ln(\tau_c)$ [31].

Finally, we examine the $\phi$ dependence of the correlation length. We find that, in the same range where $\tau_c$ and $D$ are well described by power laws, $\xi(\tau_c)$ is also well described by a power law with an exponent of $\gamma_\xi = 0.46 \pm 0.03$, different from the mode-coupling exponent of 0.25. The mode-coupling-like fit breaks down at the higher volume fractions. Since we found that $\tau_\alpha \sim e^{\xi}$ and $\tau_\alpha \sim \exp(A/(\phi_0 - \phi)^2)$, we fit $\xi(\tau_\alpha) = \xi_0 + A/(\phi_0 - \phi)^2$. This function provides a good fit for the whole range of $\phi$. It results in $\phi_0 = 0.635 \pm 0.003$.

To summarize, through large scale computer simulations we verified that the procedure proposed by Berthier et al. results in $\chi_4(t)$ that agrees very well with the independent extrapolation $\lim_{q \to 0} S_6(q)$). This allowed us to propose a new, computationally easier procedure to evaluate the dynamic correlation length. Importantly, we find a slower-than-power law growth of $\xi(\tau_\alpha)$ with $\tau_\alpha$.

We thank L. Berthier for discussions and L. Berthier, G. Biroli, and D. Reichman for comments on the paper. We gratefully acknowledge the support of NSF Grant No. CHE 0909676.

[1] C. Donati et al., Phys. Rev. E 60, 3107 (1999).