Dynamical Heterogeneity and Nonlinear Susceptibility in Short-Ranged Attractive Supercooled Liquids

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Recent work has demonstrated the strong qualitative differences between the dynamics near a glass transition driven by short-ranged repulsion and one governed by short-ranged attraction. Here, we study in detail the behavior of non-linear, higher-order correlation functions that measure the growth of length scales associated with dynamical heterogeneity in both types of systems. We find that this measure is qualitatively different in the repulsive and attractive cases with regards to the wave vector dependence as well as the time dependence of the standard non-linear four-point dynamical susceptibility. We discuss the implications of these results for the general understanding of dynamical heterogeneity in glass-forming liquids.

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The underlying reasons for the dramatic increase in the viscosity of glass-forming liquids are not well understood. It has become increasingly clear that simple structural measures remain short-ranged close to the glass transition, and thus a growing simple static length scale does not appear to be implicated \cite{1}. This has led to the search for a growing dynamical length scale that drives dynamical arrest \cite{2}. For simple spherical particles: that of the short-range attractive range of approximately 3\% and 4\% of $\sigma$ respectively. To prevent crystallization, a 50:50 mixture of 1 and 2 is used. Standard molecular dynamics simulations with a number of particles $N = 256$ have been performed in the microcanonical ensemble with a time step $\Delta t < 1.3 \times 10^{-3}$. Finite-size effects were tested by comparison to a $N = 2048$ system with little discernable difference found for the quantities studied here. In Fig. 1 we plot a dynamical phase diagram ($T$ vs. volume fraction $\phi$) of the system. The arrest line is determined by extrapolation of the iso-diffusion

\begin{equation}
U(r) = 4\epsilon \left[ (\frac{\sigma_{AA}}{r})^{2n} - (\frac{\sigma_{BB}}{r})^n \right],
\end{equation}

where the temperature scale $T$ is set by $\epsilon$, the length scale is set by $\sigma_{BB}$ and time $t$ is rescaled by $(\epsilon/\sigma_{AA}^2)^{1/2}$. For our study $n = 40$ and 30, yielding a potential with an attractive range of approximately 3\% and 4\% of $\sigma_{BB}$, respectively. To prevent crystallization, a 50:50 mixture with size ratio $\sigma_{AA}/\sigma_{BB} = 1.2$ and $\sigma_{AB} = \sigma_{BA} = (\sigma_{AA} + \sigma_{BB})/2$ is used. Standard molecular dynamics simulations with a number of particles $N = 256$ have been performed in the microcanonical ensemble with a time step $\Delta t < 1.3 \times 10^{-3}$. Finite-size effects were tested by comparison to a $N = 2048$ system with little discernable difference found for the quantities studied here. In Fig. 1 we plot a dynamical phase diagram ($T$ vs. volume fraction $\phi$) of the system. The arrest line is determined by extrapolation of the iso-diffusion
Simple two-point dynamical correlation functions have already been extensively characterized in these systems [24]. The two-point function $f_s(k, t)$ displays drastically different decay characteristics at the three selected state points, ranging from standard two-step relaxation with associated power-law relaxation at point $A$ to intermediate-time logarithmic decay spanning several time decades at point $B$. Here we characterize the fluctuations of two-point dynamical quantities that are directly relevant for understanding dynamical heterogeneity. In particular, we focus on the normalized $\chi_4(k, t)$ susceptibility defined as

$$\chi_4(k, t) = \frac{\langle f_s(k, t)^2 \rangle - \langle f_s(k, t) \rangle^2}{N^{-1} \sum_i \langle (f_s^i(k, t))^2 - (f_s^i(k, t))^2 \rangle},$$

(2)

where $f_s(q, t) = N^{-1} \sum_i \cos \{k \cdot [r_i(t) - r_i(0)]\} \equiv N^{-1} \sum_i f_s^i(k, t)$. This quantity measures the size of fluctuations in self-density correlations at a particular wave vector; its growth is related to the increase of a cooperative dynamical length scale. Here, unlike in some earlier work, we explicitly label the wave vector dependence of this susceptibility, which indicates that the fluctuations associated with dynamical heterogeneity may be large or small depending on the intrinsic length scale that is probed. Indeed, as discussed by Chandler et al. [13] (see also Ref. [27]), the $k$-dependence of $\chi_4(k, t)$ is a useful way to probe the various length scales associated with dynamical heterogeneity. The $k$-dependence of $\chi_4(k, t)$ should not be confused with that of $S_4(k, t)$, which provides a four-point analog to the static structure factor, and allows for the direct extraction of a length scale associated with cooperative heterogeneous motion. On the other hand, it is expected that $\max_k \{\chi_4(k, t)\} \sim \xi(t)^{2-\eta}$, where $\xi(t)$ is the same dynamical heterogeneity length scale extracted from $S_4(k, t)$ [28] and $\eta$ is the susceptibility exponent. Thus, as long as $\eta$ does not vary for the region of interest in the dynamical phase diagram, one may infer some information concerning the growth and absolute size of $\xi(t)$ [29]. Lastly, it should be noted that the definition of $\chi_4(k, t)$ given above slightly differs from the standard definition, due to the normalization factor in the denominator. This normalization is used to attempt an unbiased comparison of peak amplitudes. We have checked that the conclusions drawn from the results presented below are not altered if the standard, unnormalized definition is used.

We start with a comparison between the $k$-dependence of the maximal values of $\chi_4(k, t)$ for state points $A$ and $C$. As shown in Fig. 2 a striking qualitative distinction exists between the size of dynamical fluctuations in the cases where glassy behavior is driven by strong, short-ranged bonding compared to the hard-sphere limit, where crowding drives vitrification. In particular, dynamical fluctuations are maximized for wave vectors below that of the main diffraction peak of $S(k)$ in the hard-sphere limit, while in the attraction-driven case the maximal

curves to the limit of zero diffusivity [24]. Three ($T, \phi, n$) state points in the supercooled-liquid regime are considered: $A = (4.4, 0.605, 30)$, $B = (0.36, 0.59, 30)$, and $C = (0.34, 0.6, 40)$. Point $A$ lies close to the hard-sphere limit, while point $C$ lies close to the attraction-driven arrest line, but away from the putative ($A_4$) dynamical singularity predicted by mode-coupling theory (MCT) [28]. Point $B$ lies close to the arrest line in the “reentrant pocket”, near the location of the higher-order ($A_4$) singularity predicted by MCT. In all cases, state points have been chosen not only to reflect potentially distinct physics, but so that the $\alpha$-relaxation time $\tau_\alpha$ and the bulk diffusion constants are similar as well [26]. This allows for comparison of the potentially different physics at points $A-C$ for comparable degrees of absolute sluggishness.
fluctuations occur for wave vectors in excess of the first-neighbor peak of $S(k)$. This finding makes clear the fact that, while in the hard-sphere case dynamical heterogeneity fluctuations are most sensitive to collective events on scales larger than the particle size, in the case of strong short-ranged attractions it is bonding fluctuations that trigger the emergence of dynamical heterogeneity (potentially associated with large length scales), as measured in $\chi_4(k, t)$.

It is instructive to compare this result with the recent calculations of Greenall et al. [30]. In this work, the sensitivity of the $k$-dependent plateau height to changes in the structure, as computed by MCT, was measured for both the hard-sphere and the attractive glass-forming limits. For the hard-sphere system, it was found that sensitivity is most pronounced for changes in structure just beyond the first shell of neighbors. Greenall et al. deemed this the “caged-cage” effect. On the other hand, it was found that the plateau for systems near the attraction-driven arrest line is most sensitive to changes of structure that occur at high wave vectors associated with short-ranged bonding – i.e. at $k$ values much in excess of an inverse particle size.

A strong qualitative similarity is thus seen between the $k$-dependence of the plateau sensitivity, as computed by MCT, and the $k$-dependence in the peak height of $\chi_4(k, t)$ as measured directly via MD simulation. To interpret this we first remark that, at least in the $\beta$-relaxation regime, $\chi_4(k, t)$ is an indicator of the spatial fluctuations of the plateau height, which has been shown to be spatially heterogeneous even at these short time scales in recent numerical simulations [31]. Clearly the MCT calculations of Greenall et al. measure the sensitivity of the plateau of a uniform system to uniform changes in structure, while at any instant in a real liquid the local structure varies from site to site. However, it is reasonable to assume that these spatial fluctuations will mirror the very same sensitivity to local structure as the global plateau does to a global change in structure. Thus, our dynamical results for the $k$-dependence of the peak height of fluctuations associated with dynamical heterogeneity provides a deep connection with the static MCT calculations of Greenall et al. This interpretation is in harmony with recent calculations and speculations concerning the nature and interpretation of dynamical heterogeneity within MCT [32, 33].

We now turn to the full time dependence of $\chi_4(k, t)$. In Fig. 3 we show $\chi_4(k, t)$ for $k$-values above and below the peak of $S(k)$ for the three different state points. Clearly the temporal shape of $\chi_4(k, t)$ is qualitatively different at the three points. The time-dependent growth of $\chi_4(k, t)$ to its peak in the repulsion-driven limit of point $A$ may be fit to a power-law form, as shown in the log-log inset of Fig. 3(top). This behavior is similar to that observed in many other systems, such as mixtures of soft-sphere or Lennard-Jones particles [34]. This is in contrast to the case of point $B$, which lies closest to a putative MCT higher-order singularity. Here, as shown in Fig. 3(middle) the amplitude of $\chi_4(k, t)$ in the $\beta$ regime is extremely small, while the peak heights in the $\alpha$ regime are sizable and actually exceed those calculated in the hard-sphere case. Thus, the $\beta$ regime at this state point is local in its physics, displaying none of the hallmarks of cooperativity that have already set in at short times in the hard-sphere case. Further, the dramatic change in temporal behavior of $\chi_4(k, t)$ from intermediate to long times suggests the possibility of different length scales governing the $\beta$ and $\alpha$ regimes, respectively, in contrast to what is usually observed in typical glassy systems [34, 35]. Lastly, at state point $C$, where attractions dominate relaxation but far from the location of the reentrant elbow of the arrest line, a behavior with mixed properties is seen. In particular, the growth of $\chi_4(k, t)$ does not display the drastic differ-

![FIG. 3: (Color online) Time evolution of $\chi_4(k, t)$ for wave vector $k = 6.6$ (squares), 11.2 (diamonds), 18.7 (circles), and 22.5 (triangles) at state points $A$, $B$, and $C$, from top to bottom. Insets: thick black lines show approximate power-law growth at intermediate times in hard-sphere limit (top) and logarithmic growth at state point $B$ (middle). Dashed lines are guides for the eye.](image-url)
gence between the $\beta$ and $\alpha$ regimes, although the growth is quite slow, and peak values reach only modest amplitudes.

A close inspection of the behavior of $\chi_4(k,t)$ at state point $B$ indicates that it grows in the $\beta$ regime not as a power law, but essentially logarithmically in time (see linear-log inset of Fig. 3(middle)). While the decay of the two-point function $F_s(k,t)$ is known to be nearly logarithmic in this regime [24], it is not at all obvious that this should also be true for its fluctuations. It has recently been argued that the susceptibility $\chi_T(k,t) \sim \frac{dF_s(k,t)}{d\log t}$ may serve as a mimic of $\chi_4(k,t)$ [14, 34, 35]. By considering $F_s(k,t)$, it is clear that the growth of $\chi_4(k,t)$ to its peak should be a power law for standard repulsive systems. On the other hand, the same considerations are not informative for the attractive regime, where the leading term of $\chi_T(k,t)$ in the $\beta$ regime is not dependent on time at all. Indeed, argumentation based on the susceptibility $\chi_T(k,t)$ would suggest that $\chi_4(k,t)$ grows logarithmically in time only if subleading terms in the expansion of the two-point function is a power series in the logarithm, as suggested from MCT analysis near higher-order singularities [25]. Indeed, the result presented here for $\chi_4(k,t)$ may be taken as indirect evidence for the reality of these subleading terms.

In conclusion we have systematically studied how the dynamical heterogeneity indicator $\chi_4(k,t)$ varies along the arrest line in attractive colloidal systems. The behavior of $\chi_4(k,t)$ in the attraction-dominated limit markedly differs from that previously observed in standard repulsion-dominated systems. First, the scale of fluctuations is maximized for intrinsic length scales significantly smaller than a particle diameter, as opposed to the hard-sphere case where fluctuations are maximized at length scales in excess of the particle size. This result suggests that short-ranged bonding fluctuations trigger dynamical heterogeneity in attractive systems, while intrinsic dynamics at scales larger than the cage scale couple most strongly to dynamical heterogeneity in repulsive systems. In addition, the time dependence of $\chi_4(k,t)$ varies dramatically from one limit to the other. These suggest marked differences in the degree of cooperativity seen in attractive and repulsive cases. In particular, the amplitude of $\chi_4(k,t)$ is much smaller in the $\beta$ regime in the attractive case, and the growth of $\chi_4(k,t)$ is logarithmically slow near the onset of reentrance, as opposed to the more common power-law behavior. These results deepen our understanding of the physics of dynamical heterogeneity as well as provide testable targets for theoretical approaches. In particular, it would be interesting to apply the recent extension of MCT of Ref. [32], which has successfully predicted the behavior of $\chi_4(k,t)$ and the growth of the dynamical length scale in standard systems to the case of attractive glass-forming systems.

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The relaxation time $\tau_\alpha$ is defined as the time at which the self-intermediate scattering function $F_s(k, t) = \left\langle N^{-1} \sum_i e^{i k \cdot (r_i(t) - r_i(0))} \right\rangle$ has decayed to $e^{-1}$ at the peak of the structure factor $S(k) = \left\langle N^{-1} \sum_{ij} e^{i k \cdot (r_j - r_i)} \right\rangle$, where $r_i$ is the position of particle $i$ and $k$ is the magnitude of the wave vector probed.

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