Universal Features of Dynamic Heterogeneity in Supercooled Liquids

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A few years ago it was shown that *some* systems that have very similar local structure, as quantified by the pair correlation function, exhibit vastly different slowing down upon supercooling. Recently, a more subtle structural quantity, the so-called "point-to-set" length, was found to reliably correlate with the average dynamics. Here we use computer simulations to examine the behavior of fluctuations around the average dynamics, i.e., dynamic heterogeneity. We study five model glass-forming liquids: three model liquids used in previous works and two additional model liquids with finite range interactions. Some of these systems have very similar local structure but vastly different dynamics. We show that for all these systems the spatial extent and the anisotropy of dynamic heterogeneity have the same correlation with the average dynamics. This result complements a recent experimental finding of a universal correlation between the number of correlated particles and the apparent activation enthalpy.

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Upon supercooling, universal phenomena are observed in seemingly unrelated glass-forming systems. Similarly, glass transition theories predict universal relationships between different static and dynamic quantities. Some of the relationships predicted by the theories are difficult to verify experimentally but they can be tested in computer simulations. These tests can help to differentiate between different theories. Because of the large computational resources required, simulations often examine one relatively simple model system. However, this does not establish that the relationships between different static or dynamic quantities are truly universal. Here, we examine universal features of dynamic heterogeneity, i.e., fluctuations around the average dynamics.

Our study is inspired by a reevaluation of the van der Waals picture [1] of the liquid state in the context of supercooled liquids' dynamics. Within this picture the liquid's local structure, as quantified by the pair correlation function, is primarily determined by the repulsive part of the interparticle potential. Importantly, it was believed (with somewhat limited simulational [2,3] and theoretical [4] support) that the local structure, and thus the repulsive part of the potential, also determines the liquid's dynamics. Therefore, it was surprising when Berthier and Tarjus [5] showed that two standard model liquids, which differ only by the presence of the attractive part of the potential and have very similar local structure, exhibit vastly different viscous slowing down upon approaching the glass transition. Subsequently, Pedersen *et al.* [6] complicated the picture by finding a system with a purely repulsive potential, the same local structure, and the same dynamics as the model liquid with both repulsive and attractive interactions.

More recently, Hocky *et al.* [7] investigated a different, more subtle, static quantity, the so-called "point-to-set" length [8] in the systems considered by Berthier and Tarjus, and Pedersen *et al.* Hocky *et al.* found that this length can have different values for systems with very similar local structure, but it correlates very well with the average dynamics and shows universal features for all the systems studied.

We present results of an extensive computer simulation study that tests the universality of fluctuations around the average dynamics, i.e., dynamic heterogeneity. First, we investigate two standard quantities used to characterize dynamic heterogeneity, the four-point susceptibility, which measures the overall strength of the heterogeneity, and the dynamic correlation length, which measures the spatial extent of the heterogeneity. In addition, we calculate quantities that are sensitive to the anisotropy of dynamic heterogeneity. Investigation of the latter quantities has been prompted by recent experiments of Zhang *et al.* [9], who studied two glassy colloidal systems that differed by the presence of an attractive part of the effective colloid-colloid potential. They found profound dependence of the shape of the clusters of fast particles on the presence of the attractions.

For large enough supercooling, we find that all quantitative characteristics of dynamic heterogeneity for all systems investigated have the same dependence on the relaxation time that characterizes the average dynamics.

We divide the systems we studied into two groups. The systems in the first group (which were also studied by Hocky *et al.*) are derived from the Kob-Andersen binary Lennard-Jones mixture [10–12]. We simulated the standard Kob-Andersen (KA) mixture, the Weeks-Chandler-Andersen (WCA) truncation [13,14] of the standard mixture, and a system with an inverse power law (IPL) potential [6]. All three systems have similar pair-correlation functions at the same temperature. However, only the KA and IPL mixtures exhibit the same temperature dependence of the relaxation time [5,6]. We studied dynamic properties of these systems as a function of temperature at a fixed volume using Newtonian dynamics [15].

The second group consists of two 50:50 mixtures of spherical particles with the same size ratio. The first system is a hard sphere (HARD) system, where the particle positions are updated using Monte Carlo dynamics with local moves [16,17]. The second system is a repulsive harmonic sphere (HARM) system [18], which we studied using Newtonian and Brownian dynamics. The control parameter for the HARD system is the volume fraction, while it is the temperature for the HARM system [15].

To find a correlation between dynamic heterogeneity and the average dynamics in systems with different potentials, control parameters, and underlying microscopic dynamics, we define a rescaled relaxation time. To this end we use a hallmark property of supercooled liquids: violation of the Stokes-Einstein relation. In the normal liquid state the Stokes-Einstein relation holds and the self-diffusion coefficient is inversely proportional to the relaxation time, $D \sim \tau_\alpha^{-1}$. The violation of this relation in supercooled liquids is frequently associated with the appearance of dynamic heterogeneity [19,20]. We define a rescaled relaxation time in such a way that all systems we study deviate from the Stokes-Einstein relation at the same rescaled relaxation time [21].

To rescale the relaxation time, we used the HARM system as a reference. For the remaining systems, we rescaled the relaxation time τ_α by a constant τ_0 so that these systems deviate from the Stokes-Einstein relation at the same τ_α/τ_0. This procedure results in $\tau_0 \approx 1/15$ for the KA, WCA, and IPL systems [22], and $\tau_0 \approx 70$ for the hard-sphere system. By adjusting τ_0 and examining the scaling, we estimate an approximate 20% uncertainty in τ_0. Unexpectedly, we found that by plotting $Dk_0^2\tau_0$ as a function of τ_α/τ_0 we obtain a reasonable collapse of all the data, see Fig. 1.

We note that a crossover time scale (defined by the crossing point of two power-law relations showed in Fig. 1) is approximately equal to $\tau_\alpha^s = 303\tau_0 \pm 65\tau_0$. This time scale corresponds to a temperature T_s (or volume fraction ϕ_s) located between the onset of glassy dynamics and the mode-coupling transition temperature [23].

To obtain the four-point susceptibility and the dynamic correlation length we examine a four-point structure factor defined in terms of overlap functions pertaining to individual particles,

$$S_4^{\mathrm{ov}}(q;t) = \frac{1}{N}\left\langle \sum_{n,m} w_n(a;t) w_m(a;t) e^{i\mathbf{q}\cdot[\mathbf{r}_n(0)-\mathbf{r}_m(0)]} \right\rangle. \quad (1)$$

Here the overlap function $w_n(a;t) = \Theta[a - |\mathbf{r}_n(t) - \mathbf{r}_n(0)|]$, where $\Theta(x)$ is Heaviside's step function. $S_4^{\mathrm{ov}}(q;t)$ is the structure factor of the particles that move less than a distance a over a time t, and it is used to characterize the size of clusters of slow particles. We calculate this structure factor at time $\tau_\alpha^{\mathrm{ov}}$, which is defined in terms of the average overlap function [24]. We use the previously described procedure [16,25] to calculate the four-point susceptibility χ_4^{ov} and the dynamic correlation length ξ_4^{ov}.

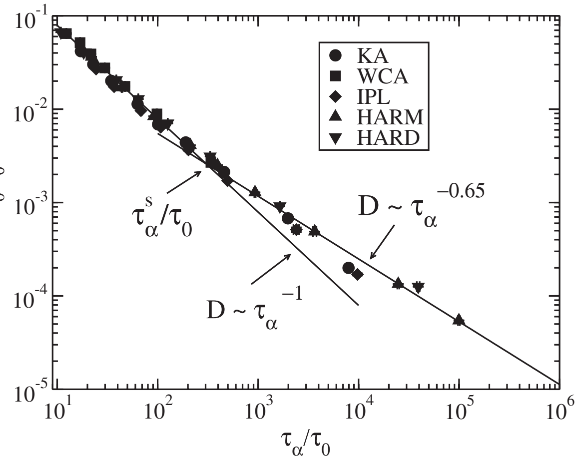

FIG. 1. Rescaled self-diffusion coefficient $Dk_0^2\tau_0$ versus rescaled relaxation time τ_α/τ_0. The lines are fits of the HARM data to $D \sim \tau_\alpha^{-1}$ for $T \geq 12$ and to a fractional Stokes-Einstein relation $D \sim \tau_\alpha^{-\lambda}$ for $T \leq 7$. These fits are equal at τ_α^s/τ_0.

First, we investigate the relationship between these two quantities. In Fig. 2 we show χ_4^{ov}/K plotted versus ξ_4^{ov}. Here K is a system dependent scaling constant. For $\xi_4^{\mathrm{ov}} > 2.6$ we find that χ_4^{ov} grows as $(\xi_4^{\mathrm{ov}})^3$ for all systems investigated. We note that $\xi_4^{\mathrm{ov}} = 2.6$ when the system's relaxation time is τ_α^s, Fig. 3. We recall that the random-first-order transition (RFOT) approach predicts compact dynamically correlated regions for temperatures below the mode-coupling transition temperature [26]. We find $\chi_4^{\mathrm{ov}} \propto (\xi_4^{\mathrm{ov}})^3$, which

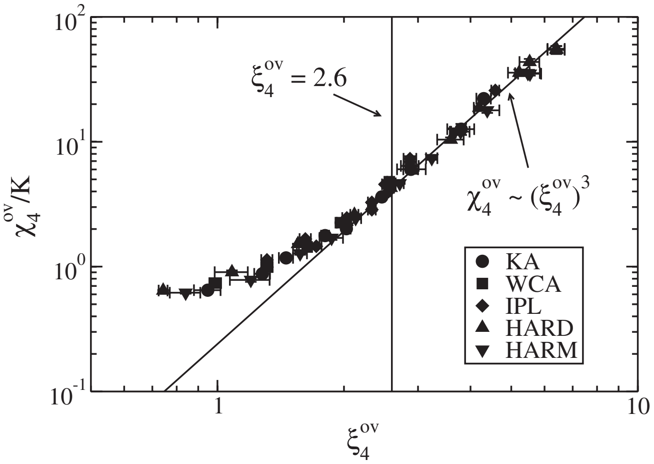

FIG. 2. A rescaled susceptibility χ_4^{ov}/K versus ξ_4^{ov}. $K = 1.55$ for the KA, WCA, and IPL systems, $K = 0.83$ for the HARD system, and $K = 1$ for the HARM system.

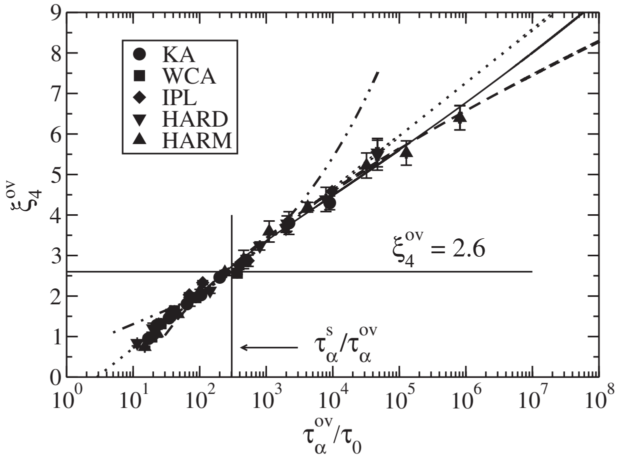

FIG. 3. The correlation length ξ_4^{ov} versus $\tau_\alpha^{\mathrm{ov}}/\tau_0$. The dash-dotted line is a mode-coupling-like fit $\xi_4^{\mathrm{ov}} \sim (\tau_\alpha^{\mathrm{ov}})^{1/z}$ where $z = 4.8$. The dotted line is a fit to $\xi_4^{\mathrm{ov}} \sim \ln(\tau_\alpha^{\mathrm{ov}})$. For longer relaxation times the data are better described by $\xi_4^{\mathrm{ov}} \sim \ln(\tau_\alpha^{\mathrm{ov}})^{3/2}$ which is shown as the dashed line. The solid line is a fit to the facilitation prediction of $\ln(\xi_4^{\mathrm{ov}}) = A\sqrt{\ln(B\tau_\alpha^{\mathrm{ov}})} + C$. The solid vertical line indicates the relaxation time where the Stokes-Einstein violation begins and the solid horizontal line shows the correlation length where the relationship $\chi_4^{\mathrm{ov}} \sim (\xi_4^{\mathrm{ov}})^3$ begins.

indicates compact clusters of slow particles, starting from the crossover temperature T_s (or volume fraction ϕ_s) [27].

We now examine the correlation between the dynamic correlation length ξ_4^{ov} calculated at $\tau_\alpha^{\mathrm{ov}}$ and $\tau_\alpha^{\mathrm{ov}}/\tau_0$. Note that to define a rescaled time scale we use the values of τ_0 which were determined before by analyzing the relation between D and τ_α. This is justified since the temperature (or volume fraction) dependence of $\tau_\alpha^{\mathrm{ov}}$ and τ_α is very similar. We note that the results for all systems investigated collapse onto the same curve when plotted as ξ_4^{ov} versus $\tau_\alpha^{\mathrm{ov}}/\tau_0$, Fig. 3. While we anticipated having to rescale ξ_4^{ov}, this does not seem necessary for these systems. This collapse is similar to the observation of Fragiadakis *et al.* [28], who used an approximation for χ_4 proposed by Berthier *et al.* [29], to show that the number of dynamically correlated molecules only depends on the relaxation time. We conclude that the spatial extent of dynamic heterogeneity correlates very well with the average dynamics when the average dynamics is rescaled relative to the point at which the Stokes-Einstein relation is violated.

We compare our results to three theoretical scenarios. The relationships between the dynamic correlation length and the relaxation time obtained from these scenarios are showed as lines in Fig. 3. We find that a power law relationship between ξ_4^{ov} and $\tau_\alpha^{\mathrm{ov}}$ (dash-dotted line) obtained from a mode-coupling-like approach [30–32] is a poor description of the data for more than about a decade of slowing down. Next, we find that a logarithmic relationship $\xi_4^{\mathrm{ov}} \sim \ln(\tau_\alpha^{\mathrm{ov}})^{1/\zeta}$, inspired by an Adam-Gibbs–like [33] or a RFOT theory [34,35], describes well the initial slowing down with $\zeta = 1$ (dotted line) but at longer relaxation times $\zeta = 2/3$ (dashed line) provides a better fit. Finally, the relation inspired by the facilitation picture, $\ln(\xi_4) = A\sqrt{\ln(B\tau_\alpha^{\mathrm{ov}}/\tau_0)} + C$ (solid line) [36], is also compatible with the data. In principle, a more detailed analysis of the existing data may be able to distinguish between the latter two approaches. We note that the theoretical scenarios are nearly indistinguishable over a large range of ξ_4 versus $\tau_\alpha^{\mathrm{ov}}/\tau_0$. The most direct comparison would be enabled by extending the range of relaxation times by some 2 orders of magnitude.

Figure 2 indicates a change in the spatial organization of dynamic heterogeneity. This fact, together with the experimental finding of Zhang *et al.* [9], prompted us to examine in some detail the shape of dynamic heterogeneity. To this end we study a four-point structure factor defined in terms of microscopic self-intermediate scattering functions pertaining to different particles,

$$S_4(\mathbf{k},\mathbf{q};t) = \frac{1}{N}\left\langle \sum_{n,m} \hat{F}_n(\mathbf{k};t)\hat{F}_m(\mathbf{k};t)e^{i\mathbf{q}\cdot[\mathbf{r}_n(0)-\mathbf{r}_m(0)]}\right\rangle. \tag{2}$$

Here $\hat{F}_n(\mathbf{k},t) = \cos\{\mathbf{k}\cdot[\mathbf{r}_n(t)-\mathbf{r}_n(0)]\}$ is the microscopic self-intermediate scattering function. Its ensemble average is the self-intermediate scattering function. A similar four-point structure factor was examined in Ref. [37].

The four-point structure factor $S_4(\mathbf{k},\mathbf{q};t)$ is sensitive to dynamics along the wave vector $\mathbf{k}$. A slow spatial decay of correlations of the dynamics along $\mathbf{k}$ would be revealed in the small q values of $S_4(\mathbf{k},\mathbf{q};t)$. The spatial decay of correlations of the dynamics along (perpendicular to) the direction of the initial separation vector $\Delta\mathbf{r}_{nm}(0) = \mathbf{r}_n(0) - \mathbf{r}_m(0)$ is measured by examination of $S_4(\mathbf{k},\mathbf{q};t)$ where $\mathbf{k}$ and $\mathbf{q}$ are parallel (perpendicular). We calculate $S_4(\mathbf{k},\mathbf{q};t)$ at a fixed angle θ between $\mathbf{k}$ and $\mathbf{q}$. We determine ξ_4^θ by fitting $S_4(\mathbf{k},\mathbf{q};t)$ using the same procedure described in Refs. [16,25,38].

Shown in Fig. 4 is ξ_4^θ for $\theta = 0$ and $\theta = \pi/2$ as a function of τ_α/τ_0 [39]. The results for all the systems follow the same trend. For the first 1.5 decades of slowing down correlations along the particles separation vector grow faster than correlations perpendicular to the separation vector, and there is a small dynamics dependence in the growth of ξ_4^θ, but there is no dependence on the specifics of the interactions for this set of glass formers. The similarity between the KA, WCA, and IPL systems indicates that there is no change in the shape of dynamically heterogeneous regions due to the presence of attractive interactions for this range of relaxation times. This is qualitatively different from the results of Zhang *et al.* [9]. We note that in the latter study clusters of fast particles in *glasses* were monitored whereas we examine correlations of slow particles in equilibrium *liquids* approaching the glass transition.

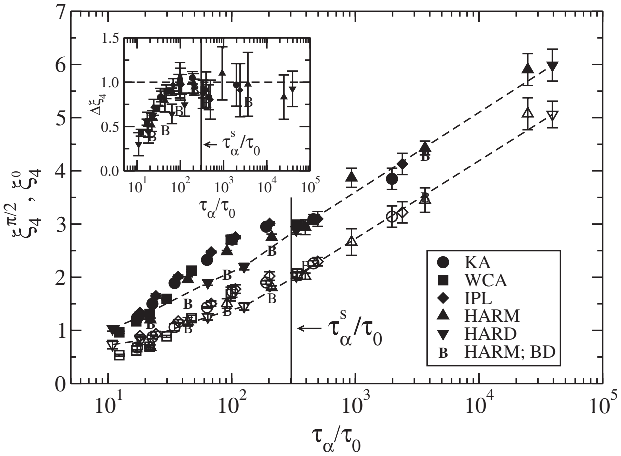

FIG. 4. The dynamic correlation lengths ξ_4^0 and $\xi_4^{\pi/2}$ versus τ_α/τ_0. The dashed lines connect the data for the hard-sphere system. The points for the HARM system with Brownian dynamics are marked with a B, and their error bars, which are about the size of the points, are omitted for clarity. The inset shows $\Delta\xi_4 = \xi_4^0 - \xi_4^{\pi/2}$ versus τ_α/τ_0. The dashed line is $\Delta\xi_4 = 1.0$.

For all systems the initial growth of ξ_4^0 is faster than the initial growth of $\xi_4^{\pi/2}$, see inset to Fig. 4 where we show $\Delta\xi_4 = \xi_4^0 - \xi_4^{\pi/2}$. The correlation length ξ_4^0 grows faster than $\xi_4^{\pi/2}$ until the difference between the two is around one particle diameter, then they grow at statistically the same rate as a function of τ_α/τ_0. The initial growth of $\Delta\xi_4$ depends slightly on the microscopic dynamics, but is independent of the system. For times exceeding τ_α^s, $\Delta\xi_4$ is around one particle diameter and it is independent of the dynamics or the details of the interactions.

Having a larger ξ_4^0 than $\xi_4^{\pi/2}$ is suggestive of the string-like motion reported in previous work [40,41]. However, our work examines the slow particles, while the string-like motion is observed for the fast particles. We leave a more detailed study of a possible connection for future work.

In summary, we demonstrated universal behavior of the size and shape of dynamic heterogeneity for temperatures below T_s (or volume fractions above ϕ_s), i.e., below the temperature (above the volume fraction) where Stokes-Einstein violation begins. We note that T_s is below the onset temperature of supercooling, T_o, thus below the temperature where dynamic heterogeneity emerges [23]. Thus, there is an intermediate temperature (volume fraction) regime where the spatial extent of the dynamic heterogeneity is universal but its shape is dynamics dependent. We compared our results to predictions of different theories of glassy dynamics. In order to clearly differentiate between the RFOT theory and the facilitation approach we would need to extend the range of relaxation times by approximately two decades.

We note that our universal correlation between the dynamic correlation length and the relaxation time parallels the correlation between the static point-to-set length and the relaxation time found by Hocky *et al.* Combining our results and those of Ref. [7] we could claim a correlation between the dynamic length and the static length. However, there are two cautionary notes regarding this possible relationship. First, we examined a significantly bigger range of slowing down whereas Hocky *et al.* were restricted by the well-known difficulty of equilibrating systems in confinement. Second, Hocky *et al.*'s lengths were determined using the so-called spherical geometry [42]. Charbonneau and Tarjus [43] used an alternative way to obtain the point-to-set lengths, the so-called random pinning geometry, and obtained static lengths that seem to be uncorrelated with dynamic lengths. It is unclear whether the fundamental difference between Refs. [7] and [43], originates from different geometry and/or the different systems used in these two studies. However, we note that Hocky *et al.*'s spherical geometry point-to-set length was recently found to be proportional to a length scale associated to where the lowest eigenvalue of the Hessian matrix becomes sensitive to disorder [44]. The latter length is easier to evaluate at low temperatures and this may allow a closer investigation of the relation between dynamic and static lengths. Future work should also explore a possible connection between the universality found here and quasiuniversality found in so-called Roskilde-simple liquids [45].

Finally, our simulational verification of a universal behavior of dynamic heterogeneity complements a recent experimental finding [46] of a universal correlation between the number of correlated molecules and the apparent activation enthalpy. We note that Bauer *et al.* were able to examine much more supercooled liquids than is feasible in simulations and a direct, quantitative comparison of their finding and our results is difficult.

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[22] Since it has been observed previously that for the KA, WCA, and IPL systems the static length has the same correlation with the relaxation time [7], we scaled these systems by the same τ_0.

[23] See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.112.097801 for more details on the definition and location of T_s (ϕ_s), the onset of glassy dynamics T_o (ϕ_o), and the mode-coupling temperature T_c (mode-coupling volume fraction ϕ_c).

[24] $\tau_\alpha^{\mathrm{ov}}$ is close to the relaxation time τ_α. See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.112.097801 for the definition of $\tau_\alpha^{\mathrm{ov}}$.

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