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Growing correlation length on cooling below the onset of caging in a simulated glass-forming liquid

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We present a calculation of a fourth-order, time-dependent density correlation function that measures higher-order spatiotemporal correlations of the density of a liquid. From molecular dynamics simulations of a glass-forming Lennard-Jones liquid, we find that the characteristic length scale of this function has a maximum as a function of time which increases steadily beyond the correlation length of the static pair correlation function \(g(r)\) in the temperature range approaching the mode coupling temperature from above. This length scale provides a measure of the spatially heterogeneous nature of the dynamics of the liquid in the alpha-relaxation regime.

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Relaxation in liquids near their glass transition involves the correlated motion of groups of neighboring particles [1–3]. This correlated motion results in spatially heterogeneous dynamics, which becomes increasingly heterogeneous as the liquid is cooled. Much remains to be understood regarding the nature of this heterogeneity, and how to best measure and quantify it. The traditional two-point, time-dependent, van Hove density correlation function \(G(r, t)\), provides information about the transient “caging” of particles upon cooling [4], but does not provide local information about correlated motion and dynamical heterogeneity. In particular, the static correlation length associated with two-point density fluctuations remains relatively constant upon cooling [5,6]. Instead, other correlation functions, which involve, e.g., spatial correlations of the displacements of particles in the liquid, and other measures of correlated motion, have been used to demonstrate the heterogeneous nature of the liquid dynamics in molecular dynamics (MD) simulations [7,8]. These “measures” are readily accessible in colloidal suspensions, where microscopy provides detailed information on particle trajectories similar to the information obtained from MD simulations. Indeed, such experiments have confirmed simulation predictions of increasingly heterogeneous dynamics near the glass transition [9].

In this paper, we evaluate a fourth-order, time-dependent density correlation function \(g_4(r, t)\) that is more sensitive to spatially heterogeneous dynamics than \(G(r, t)\). This four-point function was first investigated in supercooled liquids by Dasgupta et al. [10], but they did not detect a growing correlation length in their simulations. Recently, it was shown [11,12] that it is possible to define a generalized, time-dependent susceptibility \(\chi_4(t)\) which (i) is proportional to the volume integral of \(g_4(r, t)\) in the same way that the isothermal compressibility is related to the volume integral of the static pair correlation function [13], (ii) is nonzero in the caging regime, and (iii) increases with decreasing \(T\).

While this indirectly suggests the presence of a growing correlation length, neither \(g_4(r, t)\) nor its range \(\xi_4(t)\) was calculated in those works. Here we calculate \(g_4(r, t)\) in a simulation of 8000 Lennard-Jones (LJ) particles, and show that \(\xi_4(t)\) grows slowly but steadily beyond the correlation length \(\xi\) of the static pair correlation function \(g(r)\) as temperature \(T\) is decreased from the onset of caging towards the mode coupling temperature \(T_{\text{MCT}}\) [4].

We first briefly review the general theoretical framework, some of which was previously discussed in Refs. [11,12,14], and extend it to obtain a form for \(g_4(r, t)\) suitable for calculation in our simulations. Consider a liquid of \(N\) particles occupying a volume \(V\), with density \(\rho(r, t) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t))\). Extending an idea originally proposed for spin glasses [15], one may construct a time-dependent “order parameter” that compares the liquid configuration at two different times [11,12,14],

\[
Q(i) = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \rho(\mathbf{r}_1, 0) \rho(\mathbf{r}_2, t) w(|\mathbf{r}_1 - \mathbf{r}_2|)
= \sum_{i=1}^{N} \sum_{j=1}^{N} w(|\mathbf{r}_i(t) - \mathbf{r}_j(t)|).
\]

Here, \(\mathbf{r}_i\) in the second equality refers to the position of particle \(i\), and \(w(|\mathbf{r}_i - \mathbf{r}_j|)\) is an “overlap” function which is unity for \(|\mathbf{r}_i - \mathbf{r}_j| = a\) and zero otherwise, where the parameter \(a\) is associated with the typical vibrational amplitude of the particles [11,12]. For the present work, we take \(a = 0.3\) particle diameters as in Refs. [11,12], since this value maximizes the effect studied here [16]. As defined, \(Q(t)\) is the number of “overlapping” particles when configurations of the system at \(t = 0\) and at a later time \(t\) are compared; that is, \(Q(t)\) counts the number of particles that either remain within a distance \(a\) of their original position, or are replaced (within a distance \(a\)) by another particle in an interval \(t\).

The fluctuations in \(Q(t)\) are described by a generalized susceptibility

\[
\chi_4(t) = \frac{\beta V}{N^2} \langle (Q^2(t)) - (Q(t))^2 \rangle.
\]
where $\beta = 1/k_B T$, $k_B$ is Boltzmann’s constant, and $\langle \cdots \rangle$ indicates an ensemble average as in Ref. [12]. Note that at very early times, when $Q(t) = N$ because no particle has yet moved beyond a distance $a$, $\chi_4(t)$ is identical to the isothermal compressibility $\kappa_T$ [17]. Substituting Eq. (1) into Eq. (2), we obtain

$$\chi_4(t) = \frac{\beta V}{N^2} \int \, dr_1 dr_2 dr_3 dr_4 G_4(r_1, r_2, r_3, r_4, t),$$

where

$$G_4(r_1, r_2, r_3, r_4, t) = \langle \rho(r_1, 0) \rho(r_2, t) \rho(r_3, t) \rho(r_4, t) \rangle$$

and

$$\langle \rho(r_1, 0) \rho(r_2, t) \rangle = \langle \rho(r_1, 0) \rho(r_2, t) \rangle = \langle \rho(r_1, 0) \rangle \langle \rho(r_2, t) \rangle.$$

We integrate first over $r_2$ and $r_4$ in Eq. (3), define $r := r_3 - r_1$, and then integrate over $r_3$ to obtain

$$g_4(r, t) = \left( \frac{1}{N^2} \sum_{i,j} \delta(r-r_0, r_i(0)) w(r_i(0) - r_j(t)) \right) - \frac{Q(t)}{N}.$$

We investigate the behavior of $g_4(r, t)$, which is the angular averaged function of a single variable $r$. With the above choice of integration variables, $g_4(r, t)$ describes spatial correlations between overlapping particles at the initial time (using information at time $t$ to label the overlapping particles). The first term in $g_4(r, t)$ is a pair correlation function restricted to the subset of overlapping particles, $g_4^0(r, t)$. The second term represents the “bulk” probability of any two particles overlapping. We can rewrite $g_4(r, t)$ as

$$g_4(r, t) = g_4^0(r, t) - \frac{Q(t)}{N}.$$
Figure 3 provides a closeup of the behavior of $g^*_{4}(r,t_4^*)$ for $1.7 < r < 7$, for several values of $T$. To extract a value for $j_4(t)$, we fit peaks of $g^*_{4}(r,t)$ in the range shown to the exponential function $y(r) = a \exp[-r/j_4(t)]$. We refer to this method as an “envelope fit.” The time dependence of $j_4(t)$ obtained from this fit is plotted for several state points in Fig. 4. We see that the qualitative behavior of $j_4(t)$ is similar to that of $\chi_4(t)$: $j_4(t)$ has a maximum in time, and as $T$ decreases, the amplitude and time of this maximum increase.

The length scale $j_4(t)$ characterizes the typical distance over which “overlapping” particles are spatially correlated, and includes contributions from the static two-point density correlations. At temperatures above the onset of caging, where the dynamics is everywhere homogeneous, $j_4(t)$ and $\xi$ coincide. Below the onset of caging, $\xi(\xi^*)$ begins to grow larger than $\xi$; over the limited $T$ range of our simulations, we find that $\xi(t)$ increases from $0.8 \pm 0.1$ particle diameters above $T_{cage}$ to $1.5 \pm 0.1$ particle diameters within 5% of
The relatively small but growing correlation length calculated here from the four-point spatiotemporal density correlation function should be contrasted with that characterizing the size of highly mobile regions within the fluid [7]. That length was shown to grow much more rapidly on cooling, approaching the size of the simulation box close to \( T_{\text{MCT}} \). Interestingly, whereas the correlation length of highly mobile regions was found to be largest on a time scale in the \( \beta \)-relaxation regime, the length calculated in the present paper is largest in the \( \alpha \) regime. We note that \( g_4(r, t) \) is dominated by “caged” particles, and thus \( \xi_4(t) \) may be related to length scales calculated in Ref. [23]. The relationship of the different length scales characterizing dynamical heterogeneity will be explored in a subsequent publication.