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N. Lacevic

Francis W. Starr
Wesleyan University

T. B. Schröder

V. N. Novikov

S. C. Glotzer

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

N. Lačević, 1,2,3 F. W. Starr, 2 T. B. Schröder, 2,4 V. N. Novikov, 2,6 and S. C. Glotzer 1,2

1Departments of Chemical Engineering and Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109
2Center for Theoretical and Computational Materials Science and Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899
3Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21210
4IMFUF A, Roskilde University, DK-4000 Roskilde, Denmark

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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 characteristic 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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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 \( T_{MCT} \) [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 \( \rho(r,t) = \sum_{i=1}^{N} \delta(r - r_i(t)) \). 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 \([11,12,14]\):

\[
Q(t) = \int dr_1 dr_2 \rho(r_1,0) \rho(r_2,t) w(|r_1 - r_2|)
= \sum_{i=1}^{N} \sum_{j=1}^{N} w(|r_i(t) - r_j(t)|). \tag{1}
\]

Here, \( r_i \) in the second equality refers to the position of particle \( i \), and \( w(|r_i - r_j|) \) is an “overlap” function which is unity for \(|r_i - r_j| \leq a\) 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

\[
\chi_4(t) = \frac{\beta V}{N^2} \langle \langle Q^2(t) \rangle - \langle Q(t) \rangle^2 \rangle. \tag{2}
\]
where $\beta = 1/k_B T$, $k_B$ is Boltzmann’s constant, and $(\cdots)$ 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

$$\chi_4(t) = \beta V \int d\mathbf{r}_1d\mathbf{r}_2d\mathbf{r}_3d\mathbf{r}_4 G_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, t),$$

where

$$G_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, t) = \langle \rho(\mathbf{r}_1, 0)\rho(\mathbf{r}_2, t)w(|\mathbf{r}_1 - \mathbf{r}_2|) \rangle_{\rho(t)}$$

$$\times \langle \rho(\mathbf{r}_3, 0)\rho(\mathbf{r}_4, t)w(|\mathbf{r}_3 - \mathbf{r}_4|) \rangle_{\rho(t)}$$

$$\times \langle \rho(\mathbf{r}_1, 0)\rho(\mathbf{r}_1, t)w(|\mathbf{r}_1 - \mathbf{r}_2|) \rangle_{\rho(t)}.$$  

As written, $G_4$ is a function of four spatial and two temporal coordinates, constrained in a particular way by the overlap functions. To investigate the behavior of $G_4$, we consider a function $g_4(r, t)$ such that $\chi_4(t) = \beta \int d\mathbf{r} g_4(\mathbf{r}, t)$. We integrate first over $\mathbf{r}_2$ and $\mathbf{r}_4$ in Eq. (3), define $\mathbf{r}_3 = \mathbf{r}_1 - \mathbf{r}_1$, and then integrate over $\mathbf{r}_3$ to obtain

$$g_4(r, t) = \left\{ \frac{1}{N\rho} \sum_{i,j,l} \delta(\mathbf{r} - \mathbf{r}_i(0) + \mathbf{r}_j(0))w(|\mathbf{r}_i(0) - \mathbf{r}_j(0)|) \right\} \times \langle Q(t) \rangle \frac{2}{N} - 1.$$  

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

$$g_4(r, t) = g_4^0(r, t) - \left\{ \frac{Q(t)}{N} \right\} \frac{2}{N} g_4^0(r, t) \left[ \frac{Q(t)}{N} \right] \frac{2}{N} - 1.$$  

Since $\langle Q(t) \rangle / N$ is a function of time only, information about spatial correlations is contained in $g_4^0(r, t)$, which we investigate in the rest of the paper. In comparing $g_4(r, t)$ with other correlation functions used to study glass-forming liquids, we note that neutron scattering studies, such as those by Colmenero and Richter and co-workers on polymer systems [18], measure at most two-point spatiotemporal density correlation functions. 4-D NMR methods used to probe dynamical heterogeneity measure multiple time correlation functions [19]. In contrast to those, $g_4(r, t)$ contains additional, higher order spatiotemporal information.

To evaluate $g_4^0(r, t)$, we perform MD simulations of a model LJ glass-forming liquid. The system is a three-dimensional (50:50) binary mixture of 8000 particles interacting via LJ interaction parameters [12,20]. We simulate eight state points in the microcanonical ensemble at fixed density $\rho = 1.29$, in a temperature range $0.59 - 2.0$; we estimate $T_{\text{MCT}} = 0.57 \pm 0.02$ and the Vogel-Fulcher temperature $T_0 = 0.48 \pm 0.02$. The error bars are confidence intervals obtained as a result of fitting $\tau_\alpha(T)$ to a power law and exponential form, respectively. The onset of caging and non-exponential relaxation of the intermediate scattering function occur at $T_{\text{cage}} \approx 1.0$. Our simulations thus span a range that includes the onset of caging and the initial slowing down of the liquid approaching $T_{\text{MCT}}$. The isochore along which the simulations are performed was chosen to reproduce simulations of a smaller system size performed earlier, which showed (i) that this model exhibits spatially heterogeneous dynamics [12], and (ii) that transitions between inherent structures close to $T_{\text{MCT}}$ occur through the collective, quasi-one-dimensional motion of strings of particles [21]. All data evaluated in the present work are in thermodynamic equilibrium above the glass transition temperature.

We plot $g_4^0(r, t)$ for several $t$ at our second coldest temperature $T = 0.60$ in Figs. 1(a) and 1(b). The positions of the peaks in $g_4^0(r, t)$ are identical to the positions of the peaks in $g(r)$ (not shown). We confirm that $g_4^0(r, t) = g(r) - 1$ in the ballistic and diffusive regime. Note that in the diffusive regime $g_4^0(r, t)$ is the pair correlation function of the random overlaps normalized by $\langle Q(t) \rangle / N^2$ to yield $g(r)$. We plot $\chi_4(t)$ and $\langle Q(t) \rangle / N$ at $T = 0.60$ in Fig. 1(c); as found in Refs. [11,12], $\chi_4(t)$ has a maximum at an intermediate time $t_*^\chi$. References [11,12] showed that this maximum increases and shifts to longer time as $T$ decreases toward $T_{\text{MCT}}$, and we further find that $t_*^\chi$ is in the $\alpha$-relaxation regime. At each $T$, $g_4^0(r, t)$ deviates from $g(r) - 1$ when $\langle Q(t) \rangle / N$ deviates from unity and $\chi_4(t)$ becomes nonzero [22]. The amplitude and range of $g_4^0(r, t)$ increase with increasing $t$ until a time $t_*^g$. At $t_*^g$, $g_4^0(r, t_*^g)$ [indicated by the solid curve in Figs. 1(a),1(b)] exhibits a long tail which decreases slowly to zero with increasing distance. For $t$ greater than $t_*^g$, the amplitude and range of $g_4^0(r, t)$ decrease, and $g_4^0(r, t) = g(r) - 1$ when $\chi_4(t)$ decays to zero (not shown). The positions of the peaks in $g_4^0(r, t)$ do not appear to change with decreasing $T$.

Figure 2 shows the $T$ dependence of $g_4^0(r, t)$ at the peak characteristic time $t_*^g$ when the correlations at each $T$ are most pronounced, as measured by $\chi_4(t)$. The inset of Fig. 2 shows the “four-point” structure factor $S_4^g(q, t_*^g) = \rho \int d\mathbf{r} g_4^0(\mathbf{r}, t_*^g) \sin(q \mathbf{r}) / q^2$ and static structure factor $S(q) = -1 = \rho \int d\mathbf{r} \langle g(r) - 1 \rangle \sin(q \mathbf{r}) / q^2$. We find that while $S(q)$ shows no change at small $q$, $S_4^g(q, t_*^2)$ develops a peak at small $q$ that grows with decreasing $T$, indicating a growing range of correlations.
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, $\xi_4(t)$ begins to grow larger than $\xi$; over the limited $T$ range of our simulations, we find that $\xi_4(t)$ increases from $0.8 \pm 0.1$ particle diameters above $T_{\text{cage}}$ to $1.5 \pm 0.1$ particle diameters within $5\%$ of...
$T_{\text{MCT}}$ (Fig. 4 inset). In contrast, we find that $\xi$, which is coincident with $\xi_i(t)$ at short times when $Q(t)/N = 1$, changes less, from $0.8 \pm 0.6$ lower no tendency for slowing down of its growth, unlike the small. The behavior of $\xi_i(t)$ below $T_{\text{MCT}}$, if extrapolated to lower $T$, appears consistent with measured length scales of dynamical heterogeneity of several nanometers close to $T_g$ [1,2].

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 $B$-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 $\xi_i(t)$ 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.

[20] The LJ interaction parameters $\epsilon_{ab}$ and $\sigma_{ab}$ are given by $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{BB} = 1$, $\sigma_{AA} = 1$, $\sigma_{ab} = (\sigma_{AA} + \sigma_{BB})/2$. Lengths are defined in units of $\sigma_{AA}$, temperature $T$ in units of $\epsilon_{AA}/k_B$, and time in units of $(m\sigma_{AA}^3/48\epsilon_{AA})^{1/2}$.
[22] Strictly speaking, a simulation in the grand canonical ensemble would instead yield a small but nonzero $\chi(t)$ value at early times.