Growing spatial correlations of particle displacements in a simulated liquid on cooling toward the glass transition

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We define a correlation function that quantifies the spatial correlation of single-particle displacements in liquids and amorphous materials. We show for an equilibrium liquid that this function is related to fluctuations in a bulk dynamical variable. We evaluate this function using computer simulations of an equilibrium glass-forming liquid, and show that long range spatial correlations of displacements emerge and grow on cooling toward the mode coupling critical temperature.

\[ g(r) = \frac{1}{\langle n \rangle \langle N \rangle} \left( \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r + r_j - r_i) \right). \]  (1)

The Fourier transform of \( G(r) \) gives the static structure factor \( S(q) = \langle N^{-1} \sum_{i=1}^{N} \sum_{j=1}^{N} \exp[-iq \cdot (r_i - r_j)] \rangle \).

To determine the behavior of \( G(r) \) for large \( r \), it is useful to evaluate the fluctuations of \( N \), which are related to the volume integral of \( G(r) \), and also related to a thermodynamic response function, the isothermal compressibility \( \kappa \)

\[ \langle [N - \langle N \rangle]^2 \rangle = \int d^3r G(r) = \langle n \rangle \langle N \rangle kT \kappa, \]  (2)

where \( k \) is Boltzmann’s constant. The convergence or divergence of the volume integral of \( G(r) \) depends on how rapidly \( G(r) \) decays to zero as \( r \to \infty \). If the integral converges, \( G(r) \) is “short ranged”; if it diverges, \( G(r) \) is “long ranged”. Near a conventional critical point, \( \kappa \) diverges, macroscopic density fluctuations occur, and the behavior of \( G(r) \) approaches that of a long ranged function.

To develop a simple spatial correlation function for a local dynamical property in a liquid, we consider for a particle \( i \) its displacement \( \mu_i(t, \Delta t) = |r_i(t + \Delta t) - r_i(t)| \) over some interval of time \( \Delta t \), starting from a reference time \( t \). We examine the spatial correlations of these displacements by modifying the definition of \( G(r) \) so that the contribution of a particle \( i \) to the correlation function is weighted by \( \mu_i \). That is, we define a “displacement-displacement” correlation function

\[ G_u(r, \Delta t) = \int d^3r' \left[ u(r' + r, \Delta t) - \langle u \rangle \right] \left[ u(r', t, \Delta t) - \langle u \rangle \right], \]  (3)

where

\[ u(r, t, \Delta t) = \sum_{i=1}^{N} \mu_i(t, \Delta t) \delta(r - r_i(t)). \]  (4)
$G_u(r, \Delta t)$ measures correlations in fluctuations of local displacements away from their average value. We are considering an equilibrium liquid and so $G_u$ does not depend on the choice of the reference time $t$. Similarly, $\langle u \rangle \equiv \langle u(r, t, \Delta t) \rangle$ does not depend on $t$; for a homogeneous liquid, it also does not depend on $r$. In analogy to the relation between $\langle n \rangle$ and $\langle N \rangle$, we define the “total displacement” $U(t, \Delta t) = \int dr u(r, t, \Delta t)$ and its ensemble average $\langle U \rangle \equiv \langle U(t, \Delta t) \rangle$. In a constant-$N$ ensemble, both $\langle u \rangle$ and $\langle U \rangle$ are readily evaluated from the mean displacement $\overline{\mu} \equiv \langle N^{-1} \sum_{i=1}^{N} \mu_i(t, \Delta t) \rangle$: $\langle u \rangle = \overline{\mu}(n)$ and $\langle U \rangle = \overline{\mu}(N)$. In equilibrium, $\langle u \rangle$, $\langle U \rangle$ and $\overline{\mu}$ do not depend on $t$, but they retain a dependence on $\Delta t$.

$G_u(r, \Delta t)$ can be written so as to identify a spatial correlation function $g_u(r, \Delta t)$ analogous to $g(r)$:

$$G_u(r, \Delta t) = \langle N \rangle \overline{\mu}^2 \delta(r) + \langle u \rangle \langle U \rangle [g_u(r, \Delta t) - 1],$$

where

$$g_u(r, \Delta t) = \frac{1}{\langle u \rangle \langle U \rangle} \left( \sum_{i=1}^{N} \sum_{j=i}^{N} \mu_i(t, \Delta t) \mu_j(t, \Delta t) \delta(r + r_j(t) - r_i(t)) \right).$$

The mean squared displacement $\overline{\mu}^2 \equiv \langle N^{-1} \sum_{i=1}^{N} \mu_i^2(t, \Delta t) \rangle$, and also depends on $\Delta t$. The Fourier transform of $G_u(r, \Delta t)$ gives a “structure factor” $S_u(q, \Delta t)$ for the particle displacements: $S_u(q, \Delta t) = \langle (N\overline{\mu}^2)^{-1} \sum_{i=1}^{N} \sum_{j=1}^{N} \mu_i(t, \Delta t) \mu_j(t, \Delta t) \exp[-iq \cdot (r_i(t) - r_j(t)) \rangle \rangle$.

In analogy to Eq. 3 the fluctuations of $U$ are related to the volume integral of $G_u(r, \Delta t)$:

$$\langle [U - \langle U \rangle]^2 \rangle = \int dr G_u(r, \Delta t) \equiv \langle u \rangle \langle U \rangle kT \kappa_u.$$

We have defined the quantity $\kappa_u$ in analogy to $\kappa$. Hence, as for $G(r)$, we can determine the large $r$ behavior of $g_u(r, \Delta t)$ from the fluctuations of a bulk quantity, $U$.

To evaluate these quantities we use data obtained from a molecular dynamics simulation of a model Lennard-Jones glass-former. The system is a three-dimensional binary mixture (80:20) of 8000 particles interacting via Lennard-Jones interaction parameters [15]. We analyze data from seven $(\rho, P, T)$ state points on a line in the $P, T$ plane approaching $T_c \approx 0.435$ at a pressure $P \approx 3.03$ [15]. (In the remainder of this paper, all values are quoted in reduced units [13]). The highest and lowest $T$ state points simulated are $(\rho = 1.09, P = 0.50, T = 0.550)$ and $(\rho = 1.19, P = 2.68, T = 0.451)$. Following equilibration at each state point, the particle trajectories are monitored in the $NVE$ ensemble ($E$ is the total energy) for up to $1.2 \times 10^5$ Lennard-Jones time units (25.4 ns in argon units) for the coldest $T$. Complete simulation details may be found in [15]. All quantities presented here are calculated using all 8000 particles in the liquid. The results presented here do not change when the minority particles are excluded [15].

For all seven state points, a “plateau” exists in both $\overline{\mu}^2$ and the self part of the intermediate scattering function $F_a(q, t)$ as a function of $t$ [8]. The plateau separates an early time ballistic regime from a late time diffusive regime, and indicates “caging” of the particles typical of low $T$, high $\rho$ liquids. The $\alpha$-relaxation time $\tau_\alpha$ describes the decay of $F_a(q, t)$ to zero at the value of $q$ corresponding to the first peak in the static structure factor $S(q)$. Over the range of $T$ studied, $\tau_\alpha$ increases by 2.4 orders of magnitude, and follows a power law $\tau_\alpha \sim (T - T_c)^{\gamma}$, with $T_c = 0.435$ and $\gamma \approx 2.8$. The diffusion coefficient $D$ follows a power law $D \sim (T - T_c)^{2}$, with $T_c = 0.435$ and $\gamma \approx 2.13$, and thus diffusion and structural relaxation are “decoupled” [21]. The simulated liquid states analyzed here therefore exhibit the complex bulk relaxation behavior characteristic of a supercooled liquid approaching its glass transition. Both $g(r)$ and $S(q)$ for this liquid have been calculated previously [8,18], and it has been shown that as $T$ decreases, no long range structural correlations due to density or composition fluctuations occur.

![FIG. 1. $g_u(r, \Delta t)$ and $g(r)$ versus $r$ at $T = 0.451$. $\Delta t$ is chosen on the order of $\tau_\alpha$. Inset: $\Gamma(r, \Delta t)$ versus $r$.](image)
However, the question arises as to how to select the value of $\Delta t$. We find that the behavior of the liquid itself suggests a unique choice for $\Delta t$. To demonstrate this, we show in Fig. 2 the total excess correlation $A \equiv \int dr \Gamma(r, \Delta t)$ as a function of $\Delta t$. We find that there is a value of $\Delta t = \Delta t^*$ at which $A$ is a maximum and that both the maximum value of $A$ and $\Delta t^*$ increase with decreasing $T$. Hence for each $T$ the spatial correlation of particle displacements is most prominent at $\Delta t^*$. Moreover, all curves for $T \leq 0.525$ collapse onto a single master curve when $t$ is scaled by $\Delta t^*$ and $A$ is scaled by $A(\Delta t^*)$, suggesting that $\Delta t^*$ is a characteristic time for this liquid. In the remainder of this Letter, all quantities are therefore evaluated for $\Delta t = \Delta t^*$. Fig. 2 shows that $\Delta t^*$ follows a power law with $T$: an excellent fit $[21]$ to the form $\Delta t^* \sim (T - T_c)^{-\gamma}$ is obtained when $T_c = 0.435$, and yields $\gamma = 2.3 \pm 0.2$. This value for $\gamma$ is different from the exponent found for $\tau_u$ (within our numerical uncertainty) cannot be distinguished from the exponent governing the apparent vanishing of $D$ at $T_c$.

If $A$ is largest at $\Delta t^*$, then we might also expect $\kappa_u$ to be largest at $\Delta t^*$, since by Eq. $[22]$ $\kappa_u$ quantifies the total magnitude (integrated over space) of the displacement correlations quantified by $G_u(r, \Delta t)$. We evaluate $\kappa_u$ from the fluctuations of $U$ according to Eq. $[23]$ (Fig. 2b) and confirm $\kappa_u$ exhibits the same behavior as $A$: $\kappa_u$ goes to zero at short and long times, and has a maximum at a $T$-dependent $\Delta t^*$.

![Figure 2](image1.png)  
**FIG. 2.** (a) $A$ versus $\Delta t$ for different $T$. (b) $\kappa_u$ as a function of $\Delta t$ for the same $T$ as in (a).

In Fig. 3 we show the $T$-dependence of $\kappa_u$ for $\Delta t = \Delta t^*$. We find that $\kappa_u(\Delta t^*)$ grows monotonically with decreasing $T$, indicating that the range of the correlation measured by $G_u(r, \Delta t^*)$ is growing with decreasing $T$. We find that a power law $\kappa_u(\Delta t^*) \sim (T - T_c)^{-\gamma}$ fits well to the data when $T_c = 0.435$, and gives $\gamma = 0.84$. Thus $\kappa_u$ exhibits an apparent divergence at a $T$ that is within numerical error of $T_c$, demonstrating that $G_u(r, \Delta t^*)$ is becoming increasingly long-ranged as $T \to T_c$.

![Figure 3](image2.png)  
**FIG. 3.** $\Delta t^*$ plotted versus $T$. The solid curve is a power-law fit to the data. INSET: Log-log plot of $\Delta t^*$ versus $T - T_c$, and the power-law fit to the data. $T_c = 0.435$.

To estimate a correlation length associated with these displacement correlations, we evaluate $S_u(q, \Delta t^*)$ for different $T$ (Fig. 4). For intermediate and large $q$, $S_u(q, \Delta t^*)$ coincides with $S(q)$. However, for $q \to 0$ a peak develops and grows with decreasing $T$, again demonstrating the presence of long range dynamical correlations. No growing peak at $q = 0$ appears in the static structure factor $S(q)$ (Fig. 5, inset). To quantify the correlation length, we attempted to fit $S_u(q, \Delta t^*)$ using an Ornstein-Zernike form, $S_u(q) \propto 1/(1 + \xi^2 q^2)$, where $\xi$ is the correlation length. Although this form fits well to
the data at the highest $T$, it fails at lower $T$, making the interpretation of the fitted $\xi$ values ambiguous.

Nevertheless, it was shown previously for this system that highly “mobile” particles move cooperatively [22] and form clusters [3] whose mean size diverges at $T_c$. These clusters contribute to the growing range of $G_u(r, \Delta t^*)$, and thus they can be used to give a rough estimate of the length scale over which particle motions are correlated. At $T = 0.451$, this average length scale exceeds 3 particle diameters, and the largest cluster has a length scale that exceeds the size of our simulation box (approximately 19 particle diameters on a side.)

In summary, we have defined a correlation function that quantifies the spatial correlation of single-particle displacements in a liquid. Using this function, we have shown in computer simulations of an equilibrium liquid that the displacements of particles are spatially correlated over a range and time scale that both grow with decreasing $T$ as the mode coupling temperature is approached. While MCT makes no predictions concerning a growing dynamical correlation length [22,23], calculation of the vector displacement-displacement correlation function may be tractable within the mode coupling framework. We have also identified a bulk dynamical variable $U$ whose fluctuations appear to diverge at $T_c$. Hence, $U$ is behaving much like a static order parameter on approaching a second-order phase transition. Our analysis therefore suggests that an extension to dynamically-defined quantities of the framework of ordinary critical phenomena may be useful for understanding the nature of supercooled, glass-forming liquids.

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\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig5.pdf}
\caption{\label{fig5} $S_u(q, \Delta t^*)$ versus $q$ for different $T$. The values at $q = 0$ are obtained from the fluctuations in $U$ via the relation $S_u(q = 0, \Delta t^*) = \rho T \kappa_u(\Delta t^*)$. INSET: Static structure factor $S(q)$ for four different $T$.}
\end{figure}
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