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 that for an equilibrium liquid 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. [S0031-9007(99)09452-1]

Liquids cooled toward their glass transition exhibit remarkable dynamical behavior [1]. The initial slowing of transport processes for liquids at temperatures T well above their glass transition temperature T_g is described by the mode coupling theory (MCT) [2], which predicts diverging relaxation times at a dynamical critical temperature T_c (in real and simulated liquids, this divergence is only apparent). The dynamical singularity of MCT occurs without a corresponding growing static correlation length associated with density or composition fluctuations [3]. Yet recent studies show that in the range of T described by MCT, simulated glass-forming liquids exhibit spatially heterogeneous dynamics [4–6]. In this Letter, we define a correlation function that quantifies the spatial correlation of particle displacements and evaluate this function for a Lennard-Jones liquid. We find that spatial correlations of displacement arise and become long ranged on cooling toward T_c.

First, we briefly review the conventional static correlation function that describes the average microscopic structure of a liquid. We use a definition that will facilitate an extension to a new correlation function for particle displacements. Consider a liquid in the grand canonical ensemble confined to a volume V, consisting of identical particles, each with no internal degrees of freedom. Let the position of each particle i be denoted $\mathbf{r}_i$. In equilibrium, the structure of a homogeneous liquid can be quantified by the "density-density" correlation function [7] $G(\mathbf{r}) = \int d\mathbf{r}' \langle [n(\mathbf{r}' + \mathbf{r}) - \langle n \rangle][n(\mathbf{r}') - \langle n \rangle] \rangle$. Here, $n(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$, and $\langle \ldots \rangle$ indicates an ensemble average. $N = \int d\mathbf{r}\, n(\mathbf{r})$ is the number of particles in a given configuration. For a homogeneous liquid the density $\rho = \langle n \rangle = \langle N \rangle / V$. If the liquid is isotropic, $G(\mathbf{r})$ further reduces to $G(r)$, where $r = |\mathbf{r}|$. $G(\mathbf{r})$ measures the spatial correlations of fluctuations of local density away from the average value. The pair correlation function $g(\mathbf{r})$ conventionally presented to characterize the structure of a liquid is related to $G(\mathbf{r})$ via $G(\mathbf{r}) = \langle N \rangle \delta(\mathbf{r}) + \langle n \rangle \langle N \rangle [g(\mathbf{r}) - 1]$. $g(\mathbf{r})$ can be written as $g(\mathbf{r}) = \frac{1}{\langle n \rangle \langle N \rangle} \langle \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \delta(\mathbf{r} + \mathbf{r}_j - \mathbf{r}_i) \rangle$. The Fourier transform of $G(\mathbf{r})$ gives the static structure factor $S(\mathbf{q}) = \langle N^{-1} \sum_{i=1}^N \sum_{j=1}^N \exp[-\iota \mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)] \rangle$.

To determine the behavior of $G(\mathbf{r})$ for large r, it is useful to evaluate the fluctuations of N, which are related to the volume integral of $G(\mathbf{r})$ and to a thermodynamic response function, the isothermal compressibility κ [7]: $\langle [N - \langle N \rangle]^2 \rangle = \int d\mathbf{r}\, G(\mathbf{r}) = \langle n \rangle \langle N \rangle kT\kappa$, where k is Boltzmann's constant. The convergence or divergence of $\int d\mathbf{r}\, G(\mathbf{r})$ depends on how rapidly $G(\mathbf{r})$ decays to zero as $r \to \infty$. If the integral converges, $G(\mathbf{r})$ is "short ranged"; if it diverges, $G(\mathbf{r})$ is "long ranged." Near a conventional critical point, κ diverges, macroscopic density fluctuations occur, and the behavior of $G(\mathbf{r})$ approaches that of a long ranged function.

To develop a simple spatial correlation function for a local *dynamical* quantity in a liquid, we consider for a particle i its (scalar) displacement $\mu_i(t, \Delta t) = |\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t)|$ over some interval of time Δt, starting from a reference time t. We examine the spatial correlations of these displacements by modifying the definition of $G(\mathbf{r})$ so that the contribution of a particle i to the correlation function is weighted by μ_i. That is, we define a "displacement-displacement" correlation function [8,9],

$$G_u(\mathbf{r}, \Delta t) = \int d\mathbf{r}' \langle [u(\mathbf{r}' + \mathbf{r}, t, \Delta t) - \langle u \rangle]$$
$$\times [u(\mathbf{r}', t, \Delta t) - \langle u \rangle] \rangle, \qquad (1)$$

where $u(\mathbf{r}, t, \Delta t) = \sum_{i=1}^N \mu_i(t, \Delta t)\, \delta(\mathbf{r} - \mathbf{r}_i(t))$. $G_u(\mathbf{r}, \Delta t)$ 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, $\langle u \rangle \equiv \langle u(\mathbf{r}, t, \Delta t) \rangle$ does not depend on t; for a homogeneous liquid, it also does not depend on $\mathbf{r}$. In analogy to the relation between $\langle n \rangle$ and $\langle N \rangle$, we define the "total displacement" $U(t, \Delta t) = \int d\mathbf{r}\, u(\mathbf{r}, t, \Delta t)$ 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 $\overline{\mu} \equiv \langle N^{-1} \sum_{i=1}^{N} \mu_i(t, \Delta t)\rangle$: $\langle u \rangle = \overline{\mu}\langle n \rangle$ and $\langle U \rangle = \overline{\mu}\langle N \rangle$. In equilibrium, $\langle u \rangle$, $\langle U \rangle$, and $\overline{\mu}$ do not depend on t, but they retain a dependence on Δt.

$G_u(\mathbf{r}, \Delta t)$ can be written so as to identify a spatial correlation function $g_u(\mathbf{r}, \Delta t)$ analogous to $g(\mathbf{r})$: $G_u(\mathbf{r}, \Delta t) = \langle N \rangle \overline{\mu^2} \delta(\mathbf{r}) + \langle u \rangle \langle U \rangle [g_u(\mathbf{r}, \Delta t) - 1]$, where

$$g_u(\mathbf{r}, \Delta t) = \frac{1}{\langle u \rangle \langle U \rangle} \left\langle \sum_{i=1}^{N} \sum_{\substack{j=1 \\ j \neq i}}^{N} \mu_i(t, \Delta t) \, \mu_j(t, \Delta t) \right.$$
$$\left. \times \, \delta[\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t)] \right\rangle. \quad (2)$$

The mean squared displacement $\overline{\mu^2}$ is defined as $\overline{\mu^2} \equiv \langle N^{-1} \sum_{i=1}^{N} \mu_i^2(t, \Delta t)\rangle$, and also depends on Δt. The Fourier transform of $G_u(\mathbf{r}, \Delta t)$ gives a "structure factor"

$$S_u(\mathbf{q}, \Delta t) = \left\langle (N\overline{\mu^2})^{-1} \sum_{i=1}^{N} \sum_{j=1}^{N} \mu_i(t, \Delta t)\mu_j(t, \Delta t) \right.$$
$$\left. \times \exp\{-\imath \mathbf{q} \cdot [\mathbf{r}_i(t) - \mathbf{r}_j(t)]\} \right\rangle. \quad (3)$$

In analogy to the fluctuations of N, the fluctuations of U are related to the volume integral of $G_u(\mathbf{r}, \Delta t)$ via

$$\langle [U - \langle U \rangle]^2 \rangle = \int d\mathbf{r} \, G_u(\mathbf{r}, \Delta t) \equiv \langle u \rangle \langle U \rangle kT \kappa_u. \quad (4)$$

We have defined the generalized, time-dependent susceptibility κ_u in analogy to κ. Hence, as for $G(\mathbf{r})$, we can determine the large r behavior of $G_u(\mathbf{r}, \Delta t)$ from the fluctuations of a bulk quantity, U.

To evaluate these quantities we use data obtained [4] 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 [10]. We analyze data from seven (ρ, P, T) state points on a line in the P, T plane approaching $T_c \approx 0.435$ at a pressure $P \approx 3.03$ [11]. (In the remainder of this paper, all values are quoted in reduced units [10].) 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 1.2×10^4 Lennard-Jones time units (25.4 ns in argon units) for the coldest T. Complete simulation details may be found in [4]. All quantities presented here are calculated using all 8000 particles in the liquid. Our results do not change when the minority particles are excluded [12].

For all seven state points, a "plateau" exists in both $\overline{\mu^2}$ and the intermediate scattering function $F(q, t)$ as a function of t [11]. 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 ρ liquids. The α-relaxation time τ_α describes the decay of the self part $F_s(q, t)$ to zero at the value of q corresponding to the first peak in $S(q)$. Over the

range of T studied, τ_α and the self-diffusion coefficient D follow power laws with $(T - T_c)$, with $T_c = 0.435$, but with different exponents [11] ($\gamma_\tau \approx 2.8$, $\gamma_D \approx 2.13$ [13]). The simulated liquid states analyzed here thus 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 [11], and it has been shown that as T decreases, no long range structural correlations due to density or composition fluctuations occur.

In Fig. 1 we show $g_u(r, \Delta t)$ as a function of r for $T = 0.451$, and with Δt chosen to be on the order of τ_α. $g(r)$ for the same T is also shown. For a fixed choice of Δt, note that if the displacement were always the same for every particle, then $g_u(r, \Delta t)$ and $g(r)$ would be identical for all r. Hence, it is deviations of $g_u(r, \Delta t)$ from $g(r)$ that will inform us of spatial displacement correlations in excess of those that would be expected based on a knowledge of $g(r)$ alone. We find that for this choice of Δt, $g_u(r, \Delta t)$ is appreciably higher than $g(r)$ for values of r up to several interparticle distances. This excess correlation is made clearer in the inset of Fig. 1, where we show the function $\Gamma(r, \Delta t) \equiv [g_u(r, \Delta t)/g(r)] - 1$.

However, the question arises as to how to select the value of Δt. We find that the behavior of the liquid itself suggests a unique choice for Δt. To demonstrate this, we show in Fig. 2 the total excess correlation $A \equiv \int dr \, \Gamma(r, \Delta t)$ as a function of Δt. We find that there is a value of $\Delta t = \Delta t^*$ at which A is a maximum and that both the maximum values of A and Δt^* increase with decreasing T. Hence for each T the spatial correlation of particle displacements is most prominent at Δt^*. Moreover, all curves for $T \leq 0.525$ collapse onto a single master curve when t is scaled by Δt^* and A is scaled by $A(\Delta t^*)$,
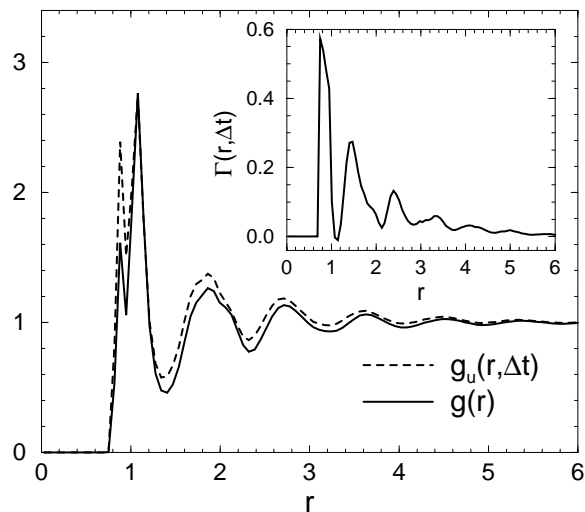

FIG. 1. $g_u(r, \Delta t)$ and $g(r)$ versus r at $T = 0.451$. Δt is chosen on the order of τ_α. Inset: $\Gamma(r, \Delta t)$ versus r. The error in our evaluation of $g_u(r, \Delta t)$ and $g(r)$ is of the order of the line thickness.
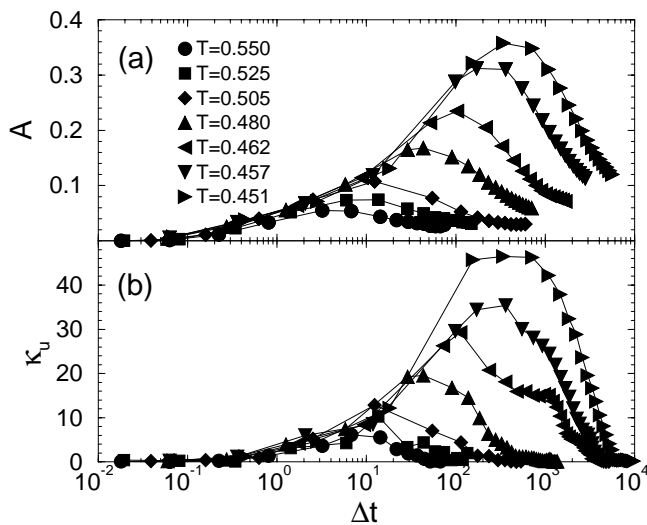
FIG. 2. (a) A versus Δt for different T. (b) κ_u as a function of Δt for the same T as in (a).

suggesting that Δt^* is a characteristic time for this liquid. In the remainder of this Letter, all quantities are therefore evaluated for $\Delta t = \Delta t^*$. Figure 3 shows that Δt^* follows a power law with T: an excellent fit [14] 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 γ is different from the exponent found for τ_α, but (within our numerical uncertainty) cannot be distinguished from the exponent governing the apparent vanishing of D at T_c. In any case, the proposal of a power law divergence is preliminary, until the data are extended over several decades of $T - T_c$.

If A is largest at Δt^*, then we might also expect κ_u to be largest at Δt^*, since κ_u quantifies the total magnitude (integrated over space) of the displacement correlations quantified by $G_u(\mathbf{r}, \Delta t)$. We evaluate κ_u from
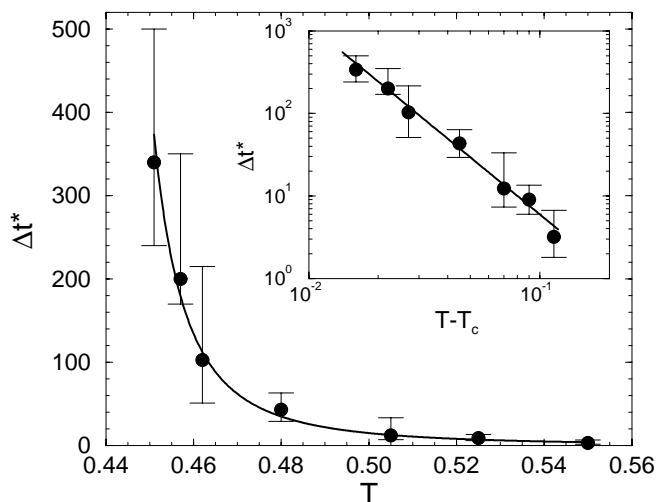
the fluctuations of U (Fig. 2b) and confirm κ_u exhibits the same behavior as A: κ_u goes to zero at short and long times, and has a maximum at a T-dependent Δt^* [15].

In Fig. 4 we show the T dependence of κ_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 $\gamma = 0.84$, although as for Fig. 3, to firmly establish a power law divergence requires further data. Thus κ_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 $T \to T_c$. We note that on closer approach to T_c, beyond the range of the present simulations, this divergence may be shifted to lower T, like that of other quantities associated with MCT.

To estimate a correlation length associated with these displacement correlations, we evaluate $S_u(q, \Delta t^*)$ for different T (Fig. 5). 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 extract the correlation length, we attempted to fit $S_u(q, \Delta t^*)$ using an Orstein-Zernike form, $S_u(q) \propto 1/(1 + \xi^2 q^2)$, where ξ 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 ξ values ambiguous.

Nevertheless, it was shown previously for this system that highly "mobile" particles form clusters whose mean size diverges at T_c [4]. These clusters contribute to the growing range of $G_u(r, \Delta t^*)$, and thus give an estimate of the length scale ξ over which particle motions are

FIG. 3. Δt^* plotted versus T. The solid curve is a power law fit to the data. Inset: Log-log plot of Δt^* versus $T - T_c$, and the power law fit to the data. $T_c = 0.435$.
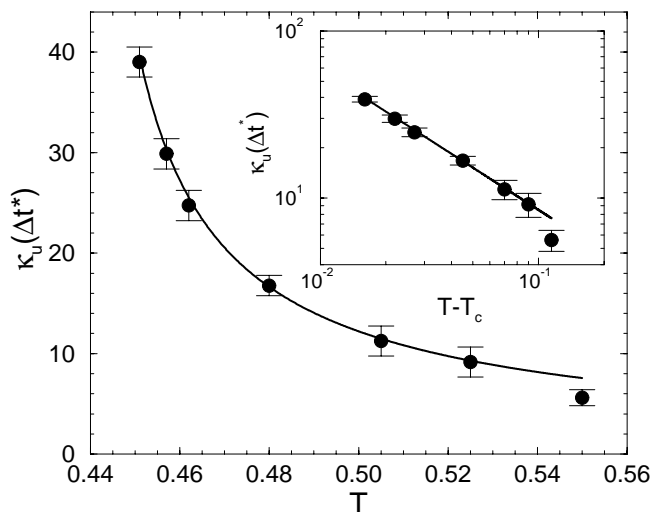

FIG. 4. $\kappa_u(\Delta t^*)$ plotted versus T. The solid curve is a power law fit to the data. Inset: Log-log plot of $\kappa_u(\Delta t^*)$ versus $T - T_c$, and the power law fit to the data. $T_c = 0.435$.
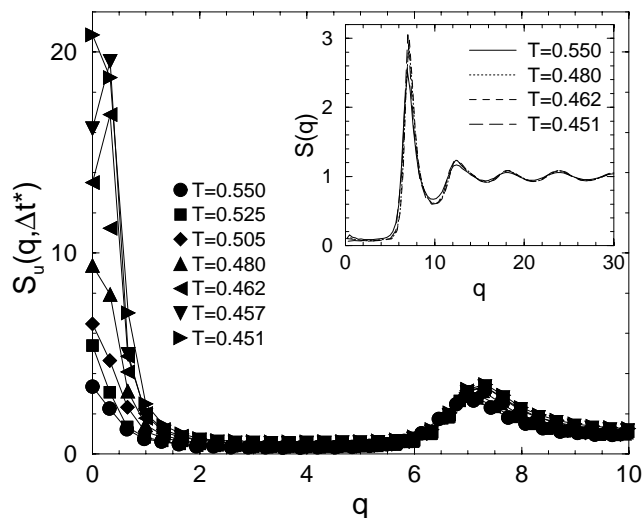
FIG. 5. $S_u(q, \Delta t^*)$ versus q for different T. The values at $q = 0$ are obtained from the fluctuations in U via the relation $S_u(q = 0, \Delta t^*) = \overline{\mu}^2 \rho T \kappa_u(\Delta t^*)/\overline{\mu^2}$. Inset: Static structure factor $S(q)$ for four different T's.

correlated. At $T = 0.451$, ξ exceeds 3 particle diameters, and the largest cluster exceeds the size of our simulation box (≈ 19 particle diameters on a side.)

We emphasize that the growing length scale identified here is dynamic rather than static as in conventional critical phenomena. We note that a growing dynamical correlation length may also be calculated within Maxwell's viscoelastic theory [17,18]. It may be possible to calculate the displacement-displacement correlation function within the mode coupling framework, allowing the relationship of these two dynamical lengths to be explored. Experimentally, the measurement of the new quantities defined here presents a challenge [19]. One possibility is to calculate them for a glass-forming colloidal suspension, in which particle trajectories may be directly followed using confocal microscopy [20]. However, more analysis is required to connect them to quantities readily measured for atomic and molecular liquids. In this paper, 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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