

Spatial correlations of particle displacements in a glass-forming liquid

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Abstract

We define a generic correlation function that quantifies the spatial correlation of single-particle displacements in liquids and amorphous systems. We evaluate this function using computer simulations of an equilibrium glass-forming liquid, and show that the displacements of particles are spatially correlated over a range that grows with decreasing temperature as the glass transition is approached. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Systems containing both disorder and frustration, including simple and polymeric glass-forming liquids [1,2], foams [3], colloids [4,5], and granular materials [6], are known to exhibit complex relaxation behavior. The underlying particle dynamics responsible for this behavior is assumed to be nontrivial, and qualitatively different from the particle dynamics at high temperatures or low densities where correlation functions often relax exponentially. In all of these systems, the nature of individual particle motions, the connection between these motions and the observed complex relaxation, and the relationship between individual particle motion and local structure, are not well understood.

In the particular case of supercooled, glass-forming liquids, an open question concerns whether correlated particle motion arises, and if these correlated motions are responsible both for the stretched exponential decay of the density–density autocorrelation function, and for the increasing time scales associated with the approach to the glass transition. For example, it has been proposed that particles are at short times trapped in cages formed by their neighbors, which break up slowly and cooperatively to allow diffusion of the particles at long times. In the mode-coupling theory of Götze and Sjogren [7], this complicated dynamics is believed to be tied

to very slow, strongly coupled, density fluctuations, which conspire to produce a dynamical singularity where structural relaxation is arrested and relaxation times diverge. While experiments on supercooled liquids can readily test many of the predictions of mode-coupling theory [8], they have been unable to directly investigate phenomena associated with the motion of individual particles on long time scales.

In this regard, simulation provides a unique window into the detailed particle motion which underlies the ubiquitous slow relaxation of glass-forming liquids. Indeed, computer simulations have clearly demonstrated that the individual particle motions in glass-forming systems are highly complex [9–12], and recent work showed that at least one typical glass-former, a binary Lennard–Jones mixture, is “dynamically heterogeneous” in the sense that highly “mobile” particles, and highly “immobile” particles, are spatially correlated [13,14]. Mobile particles in particular were shown to move cooperatively, following one another along string-like paths [15,16]. An increasingly large body of experimental evidence supports the existence of some form of “dynamical heterogeneity” in supercooled liquids [17–20].

The observation of “dynamical heterogeneity” in simulated liquids has to date been carried out through the selection of a specific subset of the particles in the liquid, based on local dynamical properties. Such an approach raises the concern that the results will depend on the choice of arbitrary thresholds in the selection criteria. We show here that it is possible to address the question of the existence of spatially correlated dynamics in glass-forming liquids in a manner that does not require the selection of subsets of particles. Specifically, we construct a spatial correlation function for individual particle displacements in which the behavior of all of the particles of a liquid is incorporated. We evaluate this function using simulation data for a glass-forming Lennard–Jones liquid, and find that the growth of the “dynamically correlated” regions reported in previous work can also be identified in the present approach. A more complete description of the approach described here is given in Ref. [21].

2. Displacement–displacement correlation function

Consider a liquid consisting of N identical particles, each with no internal degrees of freedom, contained in a volume V . Let the position of each particle i as a function of time t be denoted $\mathbf{r}_i(t)$. For an isotropic liquid in equilibrium, the structure can be quantified in terms of $g(r)$, the radial distribution function [22], defined as

$$g(r) = \frac{1}{\rho N} \left\langle \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(0)) \right\rangle. \quad (1)$$

Here, $r = |\mathbf{r}|$ and $\rho = N/V$ is the density; $\langle \dots \rangle$ indicates an average over the choice of the time $t = 0$, which is equivalent to an ensemble average for a system in equilibrium.

The factor of $1/\rho$ is included so that $\lim_{r \rightarrow \infty} g(r) = 1$. The function $g(r)$ quantifies the probability to find a particle within dr of a distance r from a given particle. As such, $g(r)$ can be described as a “position–position” correlation function.

A simple way to characterize the dynamics of a particle i in a liquid is to consider its displacement u_i over some interval of time Δt , starting from a time t :

$$u_i(t, \Delta t) = |\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t)|. \quad (2)$$

The general question of whether there exist dynamically correlated regions in a glass-forming liquid can be addressed using these individual particle displacements. Specifically, we test if the values of u for two distinct particles are, on average, correlated if the two particles are initially close in space. To quantify this, we modify the definition of $g(r)$ so that the contribution of each particle to the correlation function is weighted by its subsequent displacement over a time interval Δt . That is, we define a “displacement–displacement” correlation function,

$$g^{uu}(r, \Delta t) = \frac{1}{\langle u(\Delta t) \rangle^2 \rho N} \left\langle \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N u_i(0, \Delta t) u_j(0, \Delta t) \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(0)) \right\rangle. \quad (3)$$

The quantity $\langle u(\Delta t) \rangle = \left\langle \frac{1}{N} \sum_{i=1}^N u_i(0, \Delta t) \right\rangle$ is the average displacement of particles over the time interval Δt . The factor of $1/\langle u(\Delta t) \rangle^2$ is included so that like $g(r)$, $\lim_{r \rightarrow \infty} g^{uu}(r, \Delta t) = 1$. Note that the definition used here for $g^{uu}(r, \Delta t)$ differs from that used in Ref. [21].

For a fixed choice of Δt , note that if $u_i(t, \Delta t)$ were always the same for every particle, then $g^{uu}(r, \Delta t)$ and $g(r)$ would be identical for all r . Hence, it is deviations of $g^{uu}(r, \Delta t)$ from $g(r)$ that will inform us of displacement correlations among the particles. However, the question immediately arises as to how to select the particular value of Δt . We shall see in the next section that the behavior of the liquid itself suggests a unique and physically motivated choice for Δt .

3. Computer simulation results

We demonstrate the usefulness of the displacement–displacement correlation function by presenting preliminary results for $g^{uu}(r, \Delta t)$ evaluated using data obtained [13,15] 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 [23] chosen to prevent demixing or crystallization [24]. Throughout this section, all values, including those for temperature T and pressure P , are quoted in reduced units [23]. We analyze data from nine (ρ, P, T) state points that lie on a line in the P, T plane, approaching the mode-coupling dynamical critical temperature $T_c \approx 0.435$ at a pressure $P \approx 3.03$ [24]. The highest and lowest temperature state points simulated are $(\rho = 1.09, P = 0.50, T = 0.550)$ and $(\rho = 1.19, P = 2.68,$

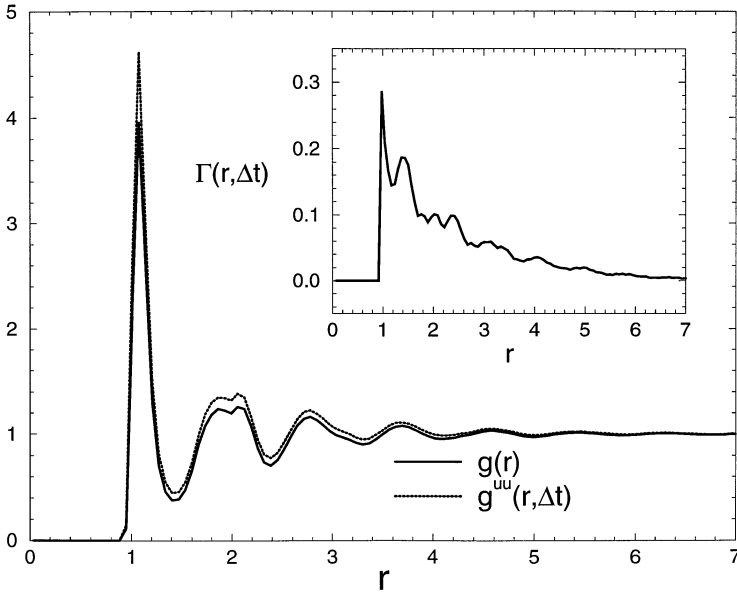


Fig. 1. For $T = 0.451$, dotted line: $g^{uu}(r, \Delta t)$ for $\Delta t = 340.062$; solid line: $g(r)$. Inset: The excess correlation given by $\Gamma(r, \Delta t)$ as defined in the text.

$T = 0.451$), respectively. At each state point, the system is equilibrated for a time longer than the typical (primary) relaxation time of the system before accumulating data on the particle displacements. Following equilibration, the simulations are carried out in the microcanonical (NVE) ensemble and the particle trajectories are stored for up to 1.2×10^4 reduced time units (25.4 ns in argon units) for the coldest T . Complete simulation details may be found in [14]. Because the sample consists of 80% A particles, in this paper we only consider correlations between these particles. All quantities calculated in this section were therefore averaged only over the 6400 A particles.

For all temperatures simulated, a plateau exists in both the mean square displacement and the self part of the intermediate scattering function $F_s(\mathbf{q}, t)$ as a function of t . The plateau separates an early time ballistic regime from a late time diffusive regime, and is thought to indicate “caging” of the particles typical of low T , high density liquids. Over the range of T studied, the primary (α) relaxation time τ_α that describes the decay of $F_s(\mathbf{q}, t)$ increases by between 2 and 3 orders of magnitude. The simulated liquid states used here to evaluate $g^{uu}(r, \Delta t)$ therefore exhibit the complex bulk relaxation behavior characteristic of a supercooled liquid approaching its glass transition.

Fig. 1 shows both $g^{uu}(r, \Delta t)$ and $g(r)$ for a cold temperature $T = 0.451$, with $\Delta t = 340.062$. For comparison, the typical “collision” time at this T is $\tau_{coll} \approx 0.09$ [25]. To quantify the difference between $g^{uu}(r, \Delta t)$ and $g(r)$, the inset shows the “excess” displacement correlation $\Gamma(r, \Delta t)$ defined as

$$\Gamma(r, \Delta t) = \frac{g^{uu}(r, \Delta t)}{g(r)} - 1. \quad (4)$$

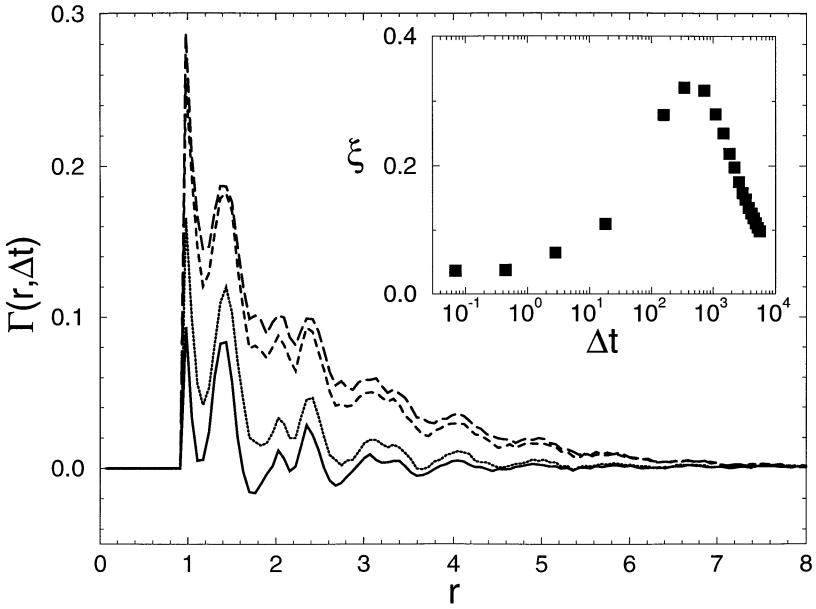


Fig. 2. $\Gamma(r, \Delta t)$ for $T = 0.451$ for $\Delta t = 0.441$ (solid curve), 19.944 (dotted curve), 155.511 (short-dashed curve), and 340.062 (long-dashed curve). Inset: Characteristic range ξ vs. Δt .

With this definition $\lim_{r \rightarrow \infty} \Gamma(r, \Delta t) = 0$. If $\Gamma(r, \Delta t) = 0$ for all r , then the displacements are totally uncorrelated. We see from the figure that the particle displacements are spatially correlated on the time scale Δt . Note that $\Gamma(r, \Delta t)$ is still appreciably different from zero out to a distance of approximately $r = 5$. This rather substantial length scale should be compared with the simulation box size divided by 2, which for $T = 0.451$ is approximately 9.4. We note that the system sizes used in this study are large relative to other simulations investigating dynamics in glass-forming liquids [9,11,24,26]. If we assume a typical molecular diameter of 0.4–0.5 nm (like in the case of orthoterphenyl or salol), we can expect to find non-zero spatial correlations in the particle displacements on length scales up to 2.5 nm at $T = 0.451$, which is of the same order of magnitude as experimental estimates of the length scale associated with spatially heterogeneous dynamics closer to T_g [27–29].

The importance of calculating correlations in non-instantaneously defined dynamical quantities like $u_i(t, \Delta t)$ is demonstrated in Fig. 2, which shows $\Gamma(r, \Delta t)$ for several choices of Δt at $T = 0.451$. The dependence on Δt of a characteristic range ξ defined by

$$\xi(\Delta t) = \int_0^\infty dr \Gamma(r, \Delta t) \tag{5}$$

is shown in the inset. The figure demonstrates four important points: (i) As $\Delta t \rightarrow 0$, the characteristic range $\xi \rightarrow 0$. Recall that in the limit $\Delta t \rightarrow 0$, $|\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t)|/\Delta t$ is equal to the magnitude of the instantaneous velocity. Thus ξ cannot be observed

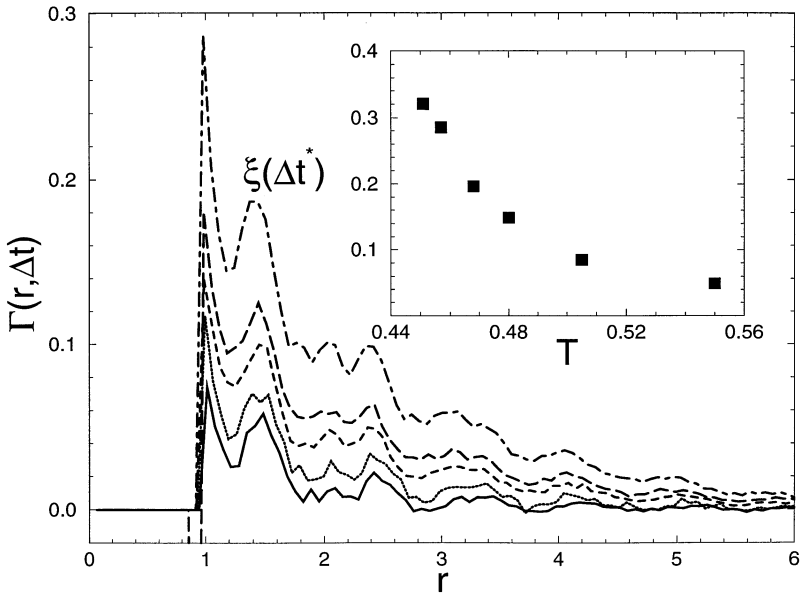


Fig. 3. $\Gamma(r, \Delta t)$ vs. r for $T=0.55$ (solid curve), 0.505 (dotted curve), 0.480 (dashed curve), 0.468 (long-dashed curve) and 0.451 (dot-dashed curve). Inset: Characteristic length $\xi(\Delta t^*)$ vs. T .

by looking at a “snapshot” of the system, that is, by measuring correlations in the velocity. (ii) Initially, as Δt increases, ξ increases. Thus the correlation of particle displacements develops over time. (iii) There is a time Δt^* where ξ is maximum. We find that Δt^* increases with decreasing T , and for all T is in the late- β /early- α relaxation regime. It appears that the T -dependence of Δt^* is the same as that of τ_α . This suggests that the strongest correlation in the particle displacements may be closely related to the long-time structural relaxation of the system governed by the breaking up of the cages mentioned in the Introduction. Hence in the following we set $\Delta t = \Delta t^*$ for each T studied, in order to ensure that we examine the system at that value of Δt for which the displacement correlations are the most prominent, as defined by the largest value of ξ . (iv) As $\Delta t \rightarrow \infty$, ξ decreases. At higher T where the simulations could be run well into the diffusive regime and where the particles act like Brownian particles, $\xi \rightarrow 0$ at long times. This is consistent with the expectation that Brownian particles are statistically independent, and thus should not exhibit correlations in their displacements.

Fig. 3 shows $\Gamma(r, \Delta t)$ at Δt^* for several different temperatures. Here Δt^* is again the time-window for which ξ is a maximum, and thus Δt^* depends on T as described above. The inset shows the T -dependence of the characteristic length $\xi(\Delta t^*)$. The data shows that $\xi(\Delta t^*)$ increases with decreasing T . It is important to note that despite careful experimental and computational investigations, no statically defined growing characteristic length associated with the correlation function $g(r)$ has been found for this, or any other (see, e.g., [30,31]) glass-forming liquid [32].

The data shown in Fig. 3 suggests a number of scenarios, all of which require further simulations to elucidate. One possibility is that $\zeta^* \equiv \zeta(\Delta t^*)$ continues to increase with decreasing T , possibly diverging at some temperature (perhaps at the mode-coupling critical temperature, or at the ideal glass transition). Another possibility is that ζ^* grows and then saturates at some T due to some inherent physical limitation in the size of the clusters [33]. However, saturation of ζ^* as a function of T might also result from finite-size effects. A finite size scaling study [34] like that done in studies of ordinary critical phenomena would help to distinguish between these contributions.

In this system, it was shown previously that the 5% most “mobile” particles in the liquid at any time form clusters which grow with decreasing T [13,14], and which rearrange cooperatively [15]. Particle mobility was defined in [13] in terms of the distance traveled by the particle after some time interval. The particles which travel farther than a certain distance r^* after a characteristic time t^* are defined as mobile, where t^* is calculated via the non-Gaussian parameter [35] and is on the order of the late- β relaxation of the intermediate scattering function. It was subsequently shown that the 5% *least* mobile particles also cluster [14]. Those results can be recovered by calculating suitably modified versions of $g^{(m)}(r, \Delta t)$ that assign, e.g., $u(r, 0, \Delta t) = 1$ to particles in the mobile subset, and $u(r, 0, \Delta t) = 0$ to the rest of the system. One important advantage of the approach outlined in the present paper and in Ref. [21] is that it allows the direct calculation of spatial correlations in the local particle motions without having to define artificial thresholds either in Δt or in the particle displacements.

4. Discussion

In this paper, we have defined a general 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 exhibit spatial correlations over a characteristic range ξ and time scale Δt that both grow with decreasing T as the glass transition is approached.

Experiments and simulations that have looked for a growing correlation length associated with the static density–density correlation function $g(r)$ have found no evidence for such a length [30,31]. Nevertheless, it has often been speculated that a growing length might be associated with the increasingly slow dynamics observed near the glass transition. Recently, experiments investigating the effect of confinement on the glass transition have extracted length scales over which molecular motion is cooperative [28,29], and several recent simulations have found evidence for growing correlation lengths as the glass transition is approached [12,13,15,36]. In this paper, we have shown that it is possible to define a *dynamical* correlation length that grows as T_g (and the T_c of mode-coupling theory) is approached from above. Whether the correlation length measured here will diverge at lower T cannot be determined from the present data. However, such a divergence would raise the possibility that the glass

transition could be understood in a way similar to that used to describe static critical phenomenon.

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