Time-dependent, four-point density correlation function description of dynamical heterogeneity and decoupling in supercooled liquids

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Dynamical heterogeneity and the decoupling of diffusion and relaxation in a supercooled liquid is investigated via a time-dependent, four-point density correlation function. We show that the main contribution to the corresponding generalized susceptibility \( \chi_4(t) \) in a molecular dynamics simulation of a Lennard-Jones liquid arises from spatial correlations between temporarily localized (“caged”) particles. By comparing \( \chi_4(t) \) with a generalized susceptibility \( \chi_M(t) \) related to a correlation function for the squared particle displacements, we demonstrate a connection between dynamical heterogeneity and the decoupling of relaxation and diffusion.

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Spatially heterogeneous dynamics (“dynamical heterogeneity”) in otherwise homogeneous supercooled, glass-forming liquids is now well established in experiments close to the glass transition temperature \( T_g \), and this heterogeneity is even apparent at higher temperatures \( T > T_g \) far above the mode coupling temperature \( T_c \) in simulations. For example, recent studies of the dynamics of supercooled, glass-forming polymeric and binary simple liquids in terms of the correlations of monomer or particle displacements revealed the dynamical heterogeneity of these liquids and a rapidly growing range of correlated motion on cooling towards \( T_c \). At the same time, the decoupling of translational diffusion and relaxation as well as translational and rotational diffusion in these fluids is also well known, and simulations show that this decoupling begins well above \( T_c \) where dynamical heterogeneity first appears. Several authors have argued that the decoupling of diffusion and relaxation is a direct result of dynamical heterogeneity, with the slowest particles dominating structural relaxation and the fastest particles dominating diffusion.

In this Letter we use a four-point time correlation function of the density to probe dynamical heterogeneity in a glass-forming liquid, and elucidate the connection between this heterogeneity and the decoupling of bulk transport processes. This four-point function was first investigated in a supercooled liquid by Dasgupta, et al. and recently Donati, et al. have demonstrated analytically and computationally the interesting behavior of the related generalized four-point susceptibility \( \chi_4(t) \) (defined below). As shown in Ref. \( \chi_4(t) \) can be represented in terms of the fluctuations of an "order parameter" that is a bilinear, time-dependent product of densities. Here we show that the self-part of \( \chi_4(t) \) is directly related to spatial correlations between temporarily localized particles, while the distinct part is related to the correlated motion of particles into positions previously occupied by neighboring particles. We evaluate these quantities for a cold Lennard-Jones (LJ) liquid, and show that in this system \( \chi_4(t) \) is dominated by growing spatial correlations between localized particles. We then compare the behavior of \( \chi_4(t) \) with a generalized time-dependent susceptibility related to a correlation function of squared particle displacements. From these two quantities we find two different characteristic time scales: the time scale on which temporarily localized particles are most spatially correlated scales with temperature like the structural relaxation time, while the time scale on which the correlation between squared particle displacements is strongest scales like the inverse diffusion coefficient. In this way, we demonstrate that the decoupling of diffusion and relaxation in this model liquid arises from dynamical heterogeneity.

Consider a liquid of \( N \) particles in a volume \( V \), with density \( \rho(\mathbf{r}, t) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)) \). The simplest density correlation function that contains information on correlated particle motion is fourth order. We write this function in terms of the deviations of \( \rho(\mathbf{r}, t) \) from its average value, \( \Delta \rho(\mathbf{r}, t) = \rho(\mathbf{r}, t) - \rho_0 \), where \( \rho_0 = \langle \rho \rangle = N/V \), and \( \langle \ldots \rangle \) denotes an ensemble average:

\[
\mathcal{F}_4(\mathbf{r}_1, \mathbf{r}_2, t) = \langle \Delta \rho(\mathbf{r}_1, 0) \Delta \rho(\mathbf{r}_1, t) \Delta \rho(\mathbf{r}_2, 0) \Delta \rho(\mathbf{r}_2, t) \rangle - \langle \Delta \rho(\mathbf{r}_1, 0) \Delta \rho(\mathbf{r}_1, t) \rangle \langle \Delta \rho(\mathbf{r}_2, 0) \Delta \rho(\mathbf{r}_2, t) \rangle. \tag{1}
\]

Terms involving one position only are subtracted in Eq. (1) since they contain no information on spatial correlations of particle motions. \( \mathcal{F}_4(\mathbf{r}_1, \mathbf{r}_2, t) \) can be written,

\[
\mathcal{F}_4(\mathbf{r}_1, \mathbf{r}_2, t) = \mathcal{G}_4(\mathbf{r}_1, \mathbf{r}_2, t) + \Delta \mathcal{F}_4(\mathbf{r}_1, \mathbf{r}_2, t),
\]

where the two-point, two-time, fourth-order correlation function of densities \( \mathcal{G}_4 \) is defined as

\[
\mathcal{G}_4(\mathbf{r}_1, \mathbf{r}_2, t) \equiv \langle \rho(\mathbf{r}_1, 0) \rho(\mathbf{r}_1, t) \rho(\mathbf{r}_2, 0) \rho(\mathbf{r}_2, t) \rangle - \langle \rho(\mathbf{r}_1, 0) \rho(\mathbf{r}_1, t) \rangle \langle \rho(\mathbf{r}_2, 0) \rho(\mathbf{r}_2, t) \rangle.
\]

\( \Delta \mathcal{F}_4(\mathbf{r}_1, \mathbf{r}_2, t) \) consists of second- and third-order correlation functions of density. A straightforward calculation...
shows that \( \int dr_1 dr_2 \Delta F_4(r_1, r_2, t) \) vanishes by symmetry, and as a result, the volume integrals of \( F_4(r_1, r_2, t) \) and \( G_4(r_1, r_2, t) \) are equal to each other and correspond to the same generalized susceptibility \( \chi_4^0(t) \),
\[
\chi_4^0(t) = \frac{\beta V}{N^2} \int dr_1 dr_2 G_4(r_1, r_2, t).
\]
It is straightforward to show that \( \chi_4^0(t) \) can be written as
\[
\chi_4^0(t) = \frac{\beta V}{N^2} \langle Q_0^2(t) \rangle - \langle Q_0(t) \rangle \langle Q_0(t) \rangle,
\]
where \( \beta = 1/k_B T \), and the time-dependent “order parameter” \( Q_0(t) \) equals
\[
Q_0(t) = \int dr \rho(r, 0) \rho(r, t) = \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r_i(0) - r_j(t)).
\]
In a simulation, \( Q_0(t) \) is numerically ill-defined (for a finite system) since the probability that particle \( j \) exactly replaces particle \( i \) is infinitely small. Following Parisi, we therefore modify \( Q_0(t) \) by an “overlap” function \( w(r) \) that is unity inside a region of size \( a \) and zero otherwise, where \( a \) is taken on the order of a particle diameter. This leads to an \( a \)-dependent counterpart to \( Q_0(t) \),
\[
Q(t) = \int dr_1 dr_2 \rho(r_1, 0) \rho(r_2, t) w(|r_1 - r_2|).
\]
where \( r_{ij} \equiv r_i(0) - r_j(0) \) and \( \bar{\mu}_i \equiv r_i(t) - r_i(0) \) is the displacement of particle \( i \) during the time interval from zero to \( t \). We choose \( a = 0.3 \sigma_{AA} \) as in Ref.\textsuperscript{13}
Replacing \( Q_0(t) \) in Eq. (3) by \( Q(t) \) yields
\[
\chi_4(t) = \frac{\beta V}{N^2} \langle Q^2(t) \rangle - \langle Q(t) \rangle \langle Q(t) \rangle,
\]
which gives the following expression for \( \chi_4(t) \) in terms of the four-point correlation function \( G_4(r_1, r_2, r_3, r_4, t) \):
\[
\chi_4(t) = \frac{\beta V}{N^2} \int dr_1 dr_2 dr_3 dr_4 w(|r_1 - r_2|) w(|r_3 - r_4|)
\times G_4(r_1, r_2, r_3, r_4, t)
\]
where
\[
G_4(r_1, r_2, r_3, r_4, t) = \langle \rho(r_1, 0) \rho(r_2, t) \rho(r_3, 0) \rho(r_4, t) \rangle
- \langle \rho(r_1, 0) \rho(r_2, t) \rangle \langle \rho(r_3, 0) \rho(r_4, t) \rangle.
\]
We can write \( Q \) in terms of its self and distinct parts, \( Q = Q_S + Q_D \). The self part \( Q_S \) corresponds to terms with \( i = j \) in Eq. (4):
\[
Q_S(t) = \sum_{i=1}^{N} \int dr w(r) \delta(r + r_i(0) - r_i(t)) = \sum_{i=1}^{N} w(\bar{\mu}_i).
\]
where \( \bar{\mu}_i \) is the magnitude of \( \bar{\mu}_i \). The distinct part \( Q_D \) is equal to
\[
Q_D(t) = \sum_{i=1}^{N} \sum_{j=1, j \neq i}^{N} w(|r_{ij} - \bar{\mu}_j|).
\]
Then \( \chi_4(t) \) can be decomposed into self \( (\chi_{SS}) \), distinct \( (\chi_{DD}) \), and interference \( (\chi_{SD}) \) parts: \( \chi = \chi_{SS} + \chi_{DD} + \chi_{SD} \). From Eq. (5), \( \chi_{SS} \) and \( \chi_{DD} \) describe the fluctuations of \( Q_S \) and \( Q_D \), respectively, and \( \chi_{SD} \) describes the cross fluctuations: \( \chi_{SS} \propto \langle Q_S^2 \rangle - \langle Q_S \rangle^2 \), \( \chi_{DD} \propto \langle Q_D^2 \rangle - \langle Q_D \rangle^2 \), and \( \chi_{SD} \propto \langle Q_S Q_D \rangle - \langle Q_S \rangle \langle Q_D \rangle \). According to Eq. (8), \( Q_S(t) \) contains only contributions from small displacements, \( \bar{\mu}_i < a \), since \( w(\bar{\mu}_i) = 0 \) for \( \bar{\mu}_i > a \), and thus \( \chi_{SS}(t) \) is the susceptibility of localized particles, those which during a time interval \([0, t]\) move less than a distance \( a \). In contrast, \( Q_D(t) \) contains contributions from particles for which \( |r_{ij} - \bar{\mu}_j| < a \); that is, particles that replace neighboring particles in a time interval \([0, t]\).
In Ref.\textsuperscript{14} a different generalized susceptibility \( \chi_U(t) \) was defined in terms of the fluctuations in an “order parameter” given by the total particle displacement in a time interval \( t \), \( U(t) = \sum_{i=1}^{N} \mu_i(t) = \int dr u(r, t) \), where the displacement density field \( u(r, t) = \sum_{i=1}^{N} \mu_i(t) \delta(r - r_i(0)) \). In a similar fashion, Eq. (8) can be rewritten as
\[
Q_S(t) = \int dr q_S(r, t)\delta(r - r_i(0)))
\]
where \( q_S(r, t) \) is the localization density field \( q_S(r, t) = \sum_{i=1}^{N} w(\bar{\mu}_i) \delta(r - r_i(0)) \). Here we compare \( \chi_4(t) \) with \( \chi_M(t) \), defined as
\[
\chi_M(t) = \frac{\beta V}{\langle M(t) \rangle^2} \langle M^2(t) \rangle - \langle M(t) \rangle^2
\]
where \( M(t) \equiv \sum_{i=1}^{N} \mu_i^2(t) \) (i.e. \( M(t) \) is the sum of the squared displacements for one system in a time interval \([0, t]\)). Like \( \chi_U(t) \), \( \chi_M(t) \) is proportional to the volume integral of a correlation function of (in this case squared) particle displacements.\textsuperscript{15} Note that both the displacement density field \( u(r, t) \) and squared-displacement density field \( m(r, t) \) are dominated by delocalized, or mobile particles, while the localization density field \( q_S(r, t) \) is dominated by localized, or immobile particles.
To evaluate these quantities we use data obtained from a molecular dynamics simulation of a model LJ glass former. The system is a three-dimensional binary mixture (50:50) of 500 particles interacting via LJ interaction parameters.\textsuperscript{16} We analyze data from state points at seven different temperatures \( T \) approaching \( T_c \approx 0.592 \) from above\textsuperscript{17} at a constant density \( \rho \approx 1.3 \). (In the remainder of this paper, all values are quoted in reduced units.\textsuperscript{17}) All quantities presented here are evaluated in the \( NVE \) ensemble following equilibration of the system at each state point. Further simulation details may be found in Ref.\textsuperscript{16}
In Fig. 1a the susceptibility $\chi(t)$ calculated via Eq. (1) is shown as a function of time for different values of $T$. As found for a different LJ mixture in Ref. [20], for all $T$, $\chi(t)$ is zero at short time and attains a small constant value at large time, and has a maximum at some intermediate time $t^*_\chi$. Both $t^*_\chi$ and the amplitude of the peak, $\chi(t^*_\chi)$, increase strongly with decreasing $T$. At the lowest value of $T$, the amplitude of $\chi(t)$ decreases, possibly due to finite size effects or to the change in dynamics near $T_c$. The inset shows the self, distinct and cross terms of $\chi(t)$ for one value of $T$, and we see that $\chi_{SS}$ is indeed the dominant term. Thus, $\chi(t)$ is dominated by the growing range of spatial correlations between localized particles in this fluid, and $t^*_\chi$ is the time when this correlation is strongest. In fact, several authors have reported evidence of a growing length scale associated with solid-like behavior in dense fluids.

![FIG. 1. (a) Time dependence of the susceptibility $\chi(t)$ at various temperatures, as indicated in (b). Inset: Self, distinct and cross terms of $\chi(t)$ at $T = 0.62$. (b) Time dependence of the “squared-displacement” susceptibility $\chi_M(t)$ at the same values of $T$ as in (a).](image)

As shown in Fig. 2, both $\chi(t)$ and $\chi_M(t)$ increase strongly with decreasing $T$ (with the exception of $\chi(t)$ at the lowest temperature). Over the limited temperature range of our simulations, both functions may be reasonably fitted by power-law functions $(T - T_c)^{\gamma}$ with $T_c = 0.592$, with the apparent exponents $\gamma = 0.80 \pm 0.07$ and $\gamma_M = 0.87 \pm 0.05$, as shown in the figure. (In fitting the power law, $T_c$ is held fixed to the value $T_c = 0.592$ determined in previous work.) Of course, precise determination of the functional form requires simulations at lower temperatures, and larger simulations to reduce any possible finite size effects expected due to the growing range of correlated particle motion and localization driving the growth of $\chi_M(t)$ and $\chi(t)$, respectively.

![FIG. 2. Temperature dependence of $\chi(t)$ and $\chi_M(t)$ at different temperatures. The solid and dashed lines are power law fits to the data as indicated (excluding the lowest temperature). The error bars are estimated from deviations between three independent samples, where for each sample, $\chi(t)$ and $\chi_M(t)$ are calculated by averaging over 128 independent time origins.](image)
attributed to the emergence of dynamical heterogeneity, as argued by, e.g., Sillescu and coworkers, Ediger and coworkers, Stillinger, and Douglas.\footnote{On leave from Institute of Automation \& Electrometry, Russian Academy of Sciences, Novosibirsk, 630090, Russia.}

We note that it should be possible to determine the 4-point functions studied here in colloidal suspensions using particle tracking methods.

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Our results demonstrate the importance of time-dependent higher order density correlation functions in the characterization of dynamical heterogeneity in supercooled liquids, and the ramifications of this heterogeneity for the bulk dynamics. In particular, the increasing amplitude of the generalized time-dependent susceptibility $\chi_4(t)$ with decreasing $T$, as shown also in Ref.\footnote{R. Böhm, Curr. Opin. Sol. State Mater. Sci. 3, 378 (1998) and references therein.}, demonstrates an essential difference between two- and four-point density correlation functions in these fluids. For a glass-forming LJ liquid, we have shown that $\chi_4(t)$ is dominated by growing spatial correlations between temporally localized particles. Finally, we have demonstrated that the decoupling of diffusion and structural relaxation observed in supercooled liquids follows naturally from dynamical heterogeneity, as discussed by Sillescu, Ediger, Stillinger and Douglas: the time scale for spatial correlations of localized particles to develop governs structural relaxation, while the (different) time scale for the development of spatial correlations of squared particle displacements, which is dominated by mobile particles, governs diffusion. We note that it should be possible to

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FIG. 3. (a) Temperature dependence of $\tau_\alpha$ and the time $t_4^*$ at which $\chi_4(t)$ exhibits a maximum. (b) Temperature dependence of the inverse self-diffusion coefficient $D$ and the time $t_M^*$ at which $\chi_M(t)$ exhibits a maximum. The solid lines are power law fits to $t_4$ and $D^{-1}$ respectively (excluding the lowest temperature), with $T_c$ fixed. Insets: Comparison of $t_4^*$ and $t_M^*$ with both $D^{-1}$ and $\tau_\alpha$. As plotted, a line of zero slope (dashed line) indicates proportionality.

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The LJ interaction parameters are $\sigma_{BB}/\sigma_{AA} = 5/6$, $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$, and $\epsilon_{AA} = \epsilon_{AB} = \epsilon_{BB}$. The masses are given by $m_B/m_A = 1/2$. The length of the sample is $L = 7.28\sigma_{AA}$ and the potential was cut and shifted at $2.5\sigma_{\alpha\beta}$. All quantities are reported in reduced units: $T$ in units of $\epsilon_{AA}$, lengths in units of $\sigma_{AA}$ and time in units of $\tau \equiv (m_B\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$. Adopting Argon parameters for the A particles gives $\tau = 3 \times 10^{-13}$ s.