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 $\chi_d(t)$ in a molecular dynamics simulation of a Lennard-Jones liquid arises from spatial correlations between temporarily localized ("caged") particles. By comparing $\chi_d(t)$ 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. © 2000 American Institute of Physics.
\[ \Delta F_3(r_1, r_2, t) \text{ consists of second- and third-order correlation functions of density. A straightforward calculation shows that } \int \int d\mathbf{r}_1 d\mathbf{r}_2 \Delta F_3(r_1, r_2, t) \text{ vanishes by symmetry, and as a result, the volume integrals of } F_4(r_1, r_2, t) \text{ and } G_4(r_1, r_2, t) \text{ are equal to each other and correspond to the same generalized susceptibility } \chi_4(t). \]

\[ \chi_4^0(t) = \frac{\beta V}{N^2} \int d\mathbf{r}_1 d\mathbf{r}_2 G_4(r_1, r_2, t). \]

It is straightforward to show that \( \chi_4^0(t) \) can be written as

\[ \chi_4^0(t) = \frac{\beta V}{N^2} \langle (Q_0^2(t)) - \langle Q_0(t) \rangle^2 \rangle, \tag{2} \]

where \( \beta = 1/k_B T \), and the time-dependent “order parameter” \( Q_0(t) \) equals

\[ Q_0(t) = \int d\mathbf{r} \rho(0) \rho(t) = \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\mathbf{r}_i(0) - \mathbf{r}_j(t)). \tag{3} \]

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, \(20 \) we therefore modify \( Q_0(t) \) by an “overlap” function \( w(t) \) that is unity inside a region of size \( a \) and zero otherwise, where \( a \) is taken on the order of a particle diameter. \(19,21 \) This leads to an \( a \)-dependent counterpart to \( Q_0(t) \),

\[ Q(t) = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \rho(\mathbf{r}_1,0) \rho(\mathbf{r}_2, t) w(|\mathbf{r}_1 - \mathbf{r}_2|) \]
\[ = \sum_{i=1}^{N} \sum_{j=1}^{N} \int d\mathbf{r} w(|\mathbf{r}|) \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_j(t)) \]
\[ = \sum_{i=1}^{N} \sum_{j=1}^{N} w(|\mathbf{r}_i - \mathbf{\mu}_i|), \tag{4} \]

where \( \mathbf{r}_i = \mathbf{r}_i(0) - \mathbf{r}_i(0) \) and \( \mathbf{\mu}_i = \mathbf{r}_i(t) - \mathbf{r}_i(0) \) is the displacement of particle \( i \) during the time interval from zero to \( t \). We choose \( a = 0.3\sigma_{AA} \) as in Ref. 19.

Replacing \( Q_0(t) \) in Eq. (2) by \( Q(t) \) yields

\[ \chi_4(t) = \frac{\beta V}{N^2} \langle (Q^2(t)) - \langle Q(t) \rangle^2 \rangle, \tag{5} \]

which gives the following expression\( \tag{19} \) for \( \chi_4(t) \) in terms of the four-point correlation function \( G_4(r_1, r_2, r_3, r_4, t) \):

\[ \chi_4(t) = \frac{\beta V}{N^2} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 w(|\mathbf{r}_1 - \mathbf{r}_2|) w(|\mathbf{r}_3 - \mathbf{r}_4|) \times G_4(r_1, r_2, r_3, r_4, t), \tag{6} \]

where

\[ G_4(r_1, r_2, r_3, r_4, t) = \langle \rho(\mathbf{r}_1,0) \rho(\mathbf{r}_2, t) \rho(\mathbf{r}_3,0) \rho(\mathbf{r}_4, t) \rangle \]
\[ - \langle \rho(\mathbf{r}_1,0) \rho(\mathbf{r}_2, t) \rangle \times \langle \rho(\mathbf{r}_3,0) \rho(\mathbf{r}_4, t) \rangle. \tag{7} \]

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):

\[ Q_S(t) = \sum_{i=1}^{N} \int d\mathbf{r} v(r) \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)) = \sum_{i=1}^{N} w(\mu_i), \tag{8} \]

where \( \mu_i \) is the magnitude of \( \mathbf{\mu}_i \). The distinct part \( Q_D \) is equal to

\[ Q_D(t) = \sum_{i=1}^{N} \sum_{j \neq i}^{N} w(|\mathbf{r}_{ij} - \mathbf{\mu}_j|). \tag{9} \]

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 \( \chi_{SD} \) describe the fluctuations of \( Q_S \) and \( Q_D \), respectively, and \( \chi_{SD} \) describes the cross fluctuations: \( \chi_{SS} \langle Q_S^2 \rangle - \langle Q_S \rangle^2 \), \( \chi_{DD} \langle Q_D^2 \rangle - \langle Q_D \rangle^2 \), and \( \chi_{SD} \langle Q_S Q_D \rangle - \langle Q_S \rangle \langle Q_D \rangle \). According to Eq. (8), \( Q_S(t) \) contains only contributions from small displacements, \( \mu_i < a \), since \( w(\mu_i) \) = 0 for \( \mu_i > a \), and thus \( \chi_{SS}(t) \) is the susceptibility of localized particles, \(22 \) 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 \( |\mathbf{r}_{ij} - \mathbf{\mu}_j| < a \); that is, particles that are replaced by a neighboring particle.

In Ref. 8, a different generalized susceptibility \( \chi_M(t) \) was defined in terms of the fluctuations in an “order parameter” \( \phi \) given by the total particle displacement \( U(t) \) in a time interval \( t \):

\[ U(t) = \sum_{i=1}^{N} \mu_i(t) = \int d\mathbf{u}(\mathbf{r}, t), \]

where the displacement density field \( u(\mathbf{r}, t) = \sum_{i=1}^{N} \mu_i(t) \delta(\mathbf{r} - \mathbf{r}_i(0)) \). Here we compare \( \chi_4(t) \) with \( \chi_M(t) \), defined as

\[ \chi_M(t) = \frac{\beta V}{\langle M(t) \rangle} \langle (M^2(t)) - \langle M(t) \rangle^2 \rangle, \tag{10} \]

where \( M(t) = \sum_{i=1}^{N} \mu_i^2(t) \) (i.e., \( M(t) \) is the sum of the squared displacements for one system in a time interval \([0,t]\)). Like \( \chi_4(t) \), \( \chi_M(t) \) is proportional to the volume integral of a correlation function of (in this case squared) particle displacements. \(9,23 \) Both the displacement density field \( u(\mathbf{r}, t) \) and squared-displacement density field \( m(\mathbf{r}, t) \) are dominated by particles with large displacements.

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. \(24 \) We analyze data from state points at seven different temperatures \( T \) approaching \( T_c \approx 0.592 \) from above \(25 \) at a constant density \( \rho \approx 1.3 \). (In the remainder of this letter all values are quoted in reduced units.) \(24 \) 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 Refs. \(25,26 \).

In Fig. 1(a) the susceptibility \( \chi_4(t) \) calculated via Eq. (5) is shown as a function of time for different values of \( T \). As found for a different LJ mixture in Ref. 19, for all \( T \), \( \chi_4(t) \) is zero at short time and attains a small constant value at large
time, and has a maximum at some intermediate time $t_4^\#$. Both $t_4^\#$ and the amplitude of the peak, $\chi_4(t_4^\#)$, increase strongly with decreasing $T$. At the lowest value of $T$, the amplitude of $\chi_4(t)$ 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 $\chi_4(t)$ for one value of $T$, and we see that $\chi_{SS}$ is indeed the dominant term. Thus, $\chi_4(t)$ is dominated by the growing range of spatial correlations between localized particles in this fluid, and $t_4^\#$ 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.

Figure 1(b) shows $\chi_M(t)$ calculated from Eq. (10) as a function of time for different values of $T$. We find that $\chi_M(t)$ becomes negligible at small and large times and has a maximum at some intermediate time $t_M^\#$, where $t_{M}^\#$ is the time when this correlation is strongest. This behavior is similar to that exhibited by $\chi_U(t)$ calculated in Ref. 9.

As shown in Fig. 2, both $\chi_4(t_4^\#)$ and $\chi_M(t_M^\#)$ increase strongly with decreasing $T$ [with the exception of $\chi_4(t_4^\#)$ 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 $\gamma_4 = 0.80 \pm 0.07$ 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 $\chi_4(t)$.

Figures 3(a) and (b) show the $T$-dependence of $t_4^\#$ and $t_M^\#$, respectively, and compare them with both the inverse self-diffusion coefficient $D^{-1}$ and the structural relaxation time $\tau_a$. Here $D$ is calculated from the mean-square displacement for the $B$ (small) particles, and $\tau_a$ is calculated by fitting the $\alpha$-relaxation part of the self-intermediate scattering function at the wave vector corresponding to the first peak in

![FIG. 1. (a) Time dependence of the susceptibility $\chi_4(t)$ at various temperatures as indicated in (b). Inset: Self-, distinct, and cross-terms of $\chi_4(t)$ at $T = 0.62$. (b) Time-dependence of the “squared-displacement” susceptibility $\chi_M(t)$ at the same values of $T$ as in (a).](image1)

![FIG. 2. Temperature dependence of $\chi_4(t_4^\#)$ and $\chi_M(t_M^\#)$. 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, $\chi_4(t)$ and $\chi_M(t)$ are calculated by averaging over 128 different time origins.](image2)

![FIG. 3. (a) Temperature dependence of $\tau_a$ 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 $\tau_a$ 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 $\tau_a$. As plotted, a line of zero slope (dashed line) indicates proportionality.](image3)
the static structure factor for the A (large) particles (not shown, see Ref. 25) by a stretched exponential function. Also shown are power law fits to $D^{-1}$ and $\tau_\alpha$ excluding the lowest temperature (see Ref. 25 for details). Diffusion and relaxation are found to be “decoupled” in this cold liquid, as observed in many other real and simulated cold liquids.\(^n\) In the present system, we find that with $T_c = 0.592$, $\gamma_D = 1.11 \pm 0.03$, and $\gamma_\tau = 1.41 \pm 0.07$. Remarkably, we find\(^o\) that the $T$-dependence of $\tau_\alpha^2$ coincides within our numerical error with that of $\tau_\alpha$, while $\tau_M^2$ behaves like $D^{-1}$. That is, the time scale on which the localized particles are most spatially correlated\(^p\) scales with temperature like the structural relaxation time, and the time scale on which the correlation between squared particle displacements is strongest scales like the inverse diffusion coefficient. Thus, our data demonstrate that the “decoupling” of diffusion and relaxation (or viscosity) may be directly attributed to the emergence of dynamical heterogeneity, as argued by, e.g., Sillescu and co-workers,\(^q\) Ediger and co-workers,\(^r\) Stillinger,\(^s\) and Douglas.\(^t\)

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. 19, 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 temporarily localized particles.\(^u\) Finally, we have demonstrated that the decoupling of diffusion and structural relaxation observed in supercooled liquids follows naturally from dynamical heterogeneity, as discussed by many authors: 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 governs diffusion. We note that it should be possible to determine the four-point functions studied here in colloidal suspensions using particle tracking methods.

We thank C. Donati, J. F. Douglas, S. Franz, R. D. Mountain, G. Parisi, P. H. Poole, and F. Starr for valuable comments on the manuscript.

---

22 $\chi_{SS}$ can equivalently be said to measure correlations between (the initial positions of) particles that are not localized: substituting $1 - w$ for $w$ in Eq. (8) gives the order parameter $N - Q_{2SS}(t)$ and consequently the same susceptibility $\chi_{SS}$. $\chi_{SS}$ thus measures correlations in a subset of particles, where the subset is chosen according to whether or not the particles are localized in a time interval $[0, t]$.
24 The LJ interaction parameters are $\sigma_{bb}/\sigma_{AA} = 5/6$, $\sigma_{AB} = (\sigma_{AA} + \sigma_{bb})/2$, and $\epsilon_{AA} = \epsilon_{bb} = \epsilon_{AB}$. The masses are given by $m_B/m_A = 1/2$. The length of the sample is $L = 7.26\sigma_{AA}$ and the potential was cut and shifted at $2.5\sigma_{AB}$. All quantities are reported in reduced units: $T$ in units of $\epsilon_{AA}$, lengths in units of $\sigma_{AA}$, and in time units of $\tau_{\epsilon} = (m_B\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$. Adopting argon parameters for the A particles gives $\tau_{\epsilon} = 3 \times 10^{-11}$ s.
29 We also calculated $\chi_{4}(t)$ following Ref. 8; we find that although $\tau_\alpha^2(t)$ scales more like $D^{-1}$ than like $\tau_\alpha$, $\tau_M^2$ scales more like $D^{-1}$ than does $\tau_\alpha$. 