Heterogeneous Diffusion in Highly Supercooled Liquids

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The diffusivity of tagged particles is demonstrated to be heterogeneous on time scales comparable to or less than the stress relaxation time \( \equiv \tau_a \) in a highly supercooled model liquid. The particle motions in the relatively active regions dominantly contribute to the mean square displacement, giving rise to a diffusion constant larger than the Stokes-Einstein value. The van Hove self-correlation function \( G_v(r,t) \) is shown to have a large \( r \) tail which can be scaled in terms of \( r/t^{1/2} \) for \( t \approx 3\tau_a \). Its presence indicates heterogeneous diffusion in the active regions. However, the diffusion process becomes homogeneous on time scales longer than the life time of the heterogeneity structure \( (\sim 3\tau_a) \).

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In a wide range of liquid states, the Stokes-Einstein relation \( D \eta a/k_BT = \text{const} \) has been successfully applied between the translational diffusion constant \( D \) of a tagged particle and the viscosity \( \eta \) even when the tagged particle diameter \( a \) is of the same order as that of solvent molecules. However, this relation is systematically violated in fragile supercooled liquids [1–6]. The diffusion process in supercooled liquids thus remains not well understood. In particular, Sillescu et al. observed the power law behavior \( D \propto \eta^{-v} \) with \( v \approx 0.75 \) at low temperatures [2]. Furthermore, Ediger et al. found that smaller probe particles exhibit a more pronounced increase of \( D \eta/T \propto D/D_{SE} \) with decreasing \( T \) [3], where \( D_{SE} = k_BT/2\pi \eta a \) is the Stokes-Einstein diffusion constant. In such experiments the viscosity changes over 12 decades with decreasing \( T \), while the ratio \( D/D_{SE} \) increases from order 1 up to order \( 10^2 \) to \( 10^3 \). The same tendency has been detected by molecular dynamics simulations in a three-dimensional (3D) binary mixture with \( N = 500 \) particles [4] and in a two-dimensional (2D) binary mixture with \( N = 1024 \) [5]. In our recent 3D simulation with \( N = 10^4 \) [6], \( \eta \) and \( D \) both varied over four decades and the power law behavior \( D \propto \eta^{-0.75} \) has been observed. Many authors have attributed the origin of the breakdown to heterogeneous coexistence of relative active and inactive regions, among which the local diffusion constant is expected to vary significantly [2,3,7–9]. The aim of this paper is to demonstrate via molecular dynamics (MD) simulation that the diffusivity of the particles is indeed heterogeneous on time scales shorter than the structural or \( \alpha \) relaxation time \( \tau_a \) but becomes homogeneous on time scales much longer than \( \tau_a \).

A number of recent MD simulations have detected dynamic heterogeneities in supercooled model binary mixtures [10–14]. That is, rearrangements of particle configurations in glassy states are cooperative, involving many molecules, owing to configuration restrictions [15]. In particular, we have examined bond breakage processes among adjacent particle pairs and found that the broken bonds in an appropriate time interval \( (\sim \tau_a) \) are very analogous to the critical fluctuations in Ising spin systems with their structure factor being excellently fitted to the Ornstein-Zernike form [6,12]. The correlation length \( \xi \) thus obtained is related to the \( \alpha \) relaxation time \( \tau_a \) via the dynamic scaling law, \( \tau_a \propto \xi^z \), with \( z = 4 \) in 2D and \( z = 2 \) in 3D. The heterogeneity structure in the bond breakage is essentially the same as that in jump motions of particles from cages or that in the local diffusivity, as will be discussed below. However, there is no theory on these large-scale heterogeneities.

Our 3D binary mixture is composed of two atomic species, 1 and 2, with \( N_1 = N_2 = 5000 \) particles with the system linear dimension \( L = V^{1/3} \) being fixed at 23.2\( \sigma_1 \) [16]. They interact via the soft-core potentials \( v_{ab}(r) = \epsilon(\sigma_{ab}/r)^{12} \) with \( \sigma_{ab} = (\sigma_a + \sigma_b)/2 \), where \( r \) is the distance between two particles and \( a,b \in \{1,2\} \). The interaction is truncated at \( r = 3\sigma_1 \). The mass ratio is \( m_2/m_1 = 2 \). The size ratio is \( \sigma_2/\sigma_1 = 1.2 \), which is known to prevent crystallization [10,16]. No tendency of phase separation is detected at least in our computation times. We fix the particle density at a very high value of \( (N_1 + N_2)/V = 0.8/\sigma_1^3 \), so the particle configurations are severely restricted or jammed. We will measure space and time in units of \( \sigma_1 \) and \( \tau_0 = (m_1\sigma_1^2/\epsilon)^{1/2} \). The temperature \( T \) will be measured in units of \( \epsilon/k_B \), and the viscosity \( \eta \) in units of \( \epsilon\tau_0/\sigma_1^3 \). The time step \( \Delta t = 0.005 \) is used, and very long annealing times \( (2.5 \times 10^5 \text{ for } T = 0.267) \) are chosen in our case. For \( T \geq 0.267 \), no appreciable aging (slow equilibration) effect is detected in various quantities such as the pressure or the density time correlation function, whereas at the lowest temperature, \( T = 0.234 \), a small aging effect remains in the density time correlation function.

Let us consider the incoherent density correlation function, \( F_s(q,t) = \langle \sum_{j=1}^{N_1} \exp[iq \cdot \Delta r_j(t)] \rangle /N_1 \) for the particle species 1, where \( \Delta r_j(t) = r_j(t) - r_j(0) \) is the displacement vector of the \( j \)th particle. This function may be introduced also in shear flow [6]. The \( \alpha \) relaxation time \( \tau_a \) is then defined by \( F_s(q,\tau_a) = e^{-1} \) at \( q = 2\pi \) for various \( T \) (and the shear rate \( \dot{\gamma} \)).
We also calculate the coherent time correlation function, $S_{11}(q, t) = (n_1(q, t)n_1(-q, 0))$, where $n_1(q, t) = \sum_{j=1}^{N_1} \exp\{i q \cdot r_j(t)\}$ is the Fourier component of the density fluctuations of the particle species 1. The decay profiles of $S_{11}(q, t)$ at its first peak wave number $q = q_m \sim 2\pi$ and $F_s(q, t)$ at $q = 2\pi$ nearly coincide in the whole time region studied ($t < 2 \times 10^5$) within 5%. Hence, $S_{11}(q_m, \tau_\alpha)/S_{11}(q_m, 0) \equiv e^{-1}$ holds for any $T$ in our simulation. Such agreement is not obtained for other wave numbers, however. These results are consistent with those for a Lennard-Jones binary mixture [17]. Furthermore, some neutron-spin-echo experiments [18] showed that the decay time of $S_{11}(q_m, t)$ is nearly equal to the stress relaxation time and as a result the viscosity $\eta$ is of order $\tau_\alpha$. In agreement with this experimental result, we obtain a simple linear relation in our simulations:

$$\tau_\alpha \equiv (A_\eta/q_m^2) \eta/T.$$  \hspace{1cm} (1)

The coefficient $A_\eta$ is close to $2\pi$ in our system. Figure 1 shows that Eq. (1) is valid over a wide range of $\tau_\alpha$. Here, we may define a $q$-dependent relaxation time $\tau_q$ by $F(q, \tau_q) = e^{-1}$. Thus, particularly at the peak wave number $q = q_m$, the effective diffusion constant defined by $D_q = 1/q^2 \tau_q$ is given by the Stokes-Einstein form even in highly supercooled liquids.

However, notice that the usual diffusion constant is the long wavelength limit, $D = \lim_{q \to \infty} D_q$. It is usually calculated from the mean square displacement, $(\langle \Delta r(t)^2 \rangle = \langle \sum_{j=1}^{N_1} (\Delta r_j(t))^2 \rangle)/N_1$. The crossover of this quantity from the plateau behavior arising from motions in transient cages to the diffusion behavior $6D\tau_a$ has been found to take place around $t \sim 0.1\tau_a$ [6]. In Fig. 2, we plot $D\tau_a$ versus $\tau_\alpha$, which clearly indicates breakdown of the Stokes-Einstein relation in agreement with the experimental trend.

To examine the diffusion process in more detail, we consider the van Hove self-correlation function, $G_s(r, t) = (\sum_{j=1}^{N_1} \delta(\Delta r_j(t) - r))/N_1$. Then

$$F_s(q, t) = \int_0^\infty dr \frac{\sin(qr)}{qr} 4\pi r^2 G_s(r, t)$$  \hspace{1cm} (2)

is the 3D Fourier transformation of $G_s(r, t)$. At the peak wave number $q = 2\pi$, the integrand in Eq. (2) vanishes at $r = 1$, and the integral in the region $r < 1$ is confirmed to dominantly determine the decay of $F_s(2\pi, t)$. On the other hand, the mean square displacement,

$$\langle (\Delta r(t))^2 \rangle = \int_0^\infty dr d^3r \langle G_s(r, t) \rangle,$$  \hspace{1cm} (3)

is determined by the particle motions out of the cages for $t \geq \tau_\alpha$ in glassy states. In Fig. 3, we display $4\pi r^4 G_s(r, \tau_\alpha)$ versus $r$ at zero shear, where $\tau_\alpha = 3.2$ and 2000 for $T = 0.473$ and 0.267, respectively. These curves may be compared with the Gaussian (Brownian motion) result, $(2/\pi^{1/2})^{-3/2} r^4 \exp(-r^2/2\ell^2)$, where $3\ell^2 = 6D_{SE}\tau_\alpha = 3/2\pi^2$ is the Stokes-Einstein mean square displacement. Because the areas below the curves give $6D\tau_a$, we recognize that the particle motions over large distances $r > 1$ are much enhanced at low $T$, leading to the violation of the Stokes-Einstein relation.

We then visualize the heterogeneity of the diffusivity. To this end, we pick up mobile particles of the species 1 with $|\Delta r_j(t)| > \ell_c$ in a time interval $[t_0, t_0 + t]$ and number them as $j = 1, \ldots, N_m$. Here, $\ell_c$ is defined such that the sum of $\Delta r_j(t)^2$ of the mobile particles is 66% of the total sum ($\equiv 6DtN_1$ for $t \geq 0.1\tau_\alpha$). In Fig. 4, these particles are drawn as spheres with radii

$$a_j(t) \equiv |\Delta r_j(t)|/\sqrt{\langle (\Delta r_j(t))^2 \rangle}$$  \hspace{1cm} (4)

located at $R_j(t) \equiv \frac{1}{2}[r_j(t_0) + r_j(t_0 + t)]$ in three time...
FIG. 3. $4\pi r^4 G_1(r, t)$ versus $r$ at $t = \tau_a$. The solid line is for $T = 0.267$ and the broken line is for $T = 0.473$. The dotted line represents the Brownian motion result. The peaks at $r = 1.2$ and $2$ in the solid line arise from hopping processes in our system at $T = 0.267$. Note that the areas below the curves give $6D\tau_a$.

The reduced at
\begin{align*}
\text{deviations} & = 0.48 \text{ and } 5.71 \text{ in } 4(\text{a}), 1.3 \text{ and } 7.25 \text{ in } 4(\text{b}), \text{ and } 2.9 \text{ and } 13.16 \text{ in } 4(\text{c}), \text{ respectively.}
\end{align*}

Here they approach the Gaussian results, $\ell_c = 0.403$ (taken over many initial states $t_0$) is related to $A_2(t)$ by
\begin{align*}
A_2 &= 3(\Delta r(t)^4)/(\Delta r(t)^2)^2 - 1 = 3N_1(\sum_{j=1}^{N_1} a_j(t)^4)/(\sum_{j=1}^{N_1} a_j(t)^2)^2 - 1 \text{ takes a maximum value of } 3.1 \text{ at } t \approx 0.125\tau_a \text{ at this temperature.}
\end{align*}

This is because the statistical average of $\langle V \rangle$ (taken over many initial times $t_0$) is related to $A_2(t)$ by
\begin{align*}
\langle V \rangle &= \langle 5(c_4)\langle N_m \rangle/(3c_2^2N_1) \rangle [1 + A_2(t) - 1], \text{ where}
\end{align*}

the deviations $c_4$ and $N_m/(\langle N_m \rangle - 1)$ are confirmed to be very small for large $N_1$ and are thus neglected. We may also conclude that the significant rise of $A_2(t)$ in glassy states originates from the heterogeneity in accord with some experimental interpretations [19].

Furthermore, we consider the Fourier component of the diffusivity density defined by
\begin{align*}
D_q(t_0, t) &= \sum_{j=1}^{N_1} a_j(t)^2 \exp[-i\mathbf{q} \cdot \mathbf{R}_j(t)], \quad (5)
\end{align*}

which depends on the initial time $t_0$ and the final time $t_0 + t$. The correlation function $S_D(q, t)$ tends to its long wavelength limit for $q \leq \xi^{-1}$, where $\xi$ coincides with the correlation length of the heterogeneity structure of the bond breakage [6,12]. As the difference $T = 0.267$ and $\tau_h - 3\tau_a$ is the lifetime of the heterogeneity structure. The two-time correlation function among the broken bond density [6,12] also relaxes with $\tau_h$ in the same manner.

We naturally expect that the distribution of the particle displacement $\Delta R_j(t)$ in the active regions should be characterized by the local diffusion constant $D(x, t)$ dependent on the spatial position $x = (x, y, z)$ and the

FIG. 4. Mobile particles of the species $1$ at $T = 0.267$. The time interval $t$ is $0.125\tau_a$ in (a), $\tau_a$ in (b), and $10\tau_a$ in (c). The radii of the spheres are $|\Delta R_j(t)|/\sqrt{\langle (\Delta R_j(t))^2 \rangle}$ and the centers are at $1/2[r_j(t^0) + r_j(t^0 + t)]$. The system linear dimension is $L = 23.2$. The darkness of the spheres represents the depth in the 3D space. The heterogeneity is significant at $0.125\tau_a$ and $\tau_a$ but is much decreased at $10\tau_a$. 4917
time interval $t$. The van Hove correlation function $G_s(r, t)$ may then be expressed as the spatial average of a local function $G_s(x, r, t)$, which is given by $[4\pi D(x, t)]^{-3/2} \exp(-r^2/4D(x, t)t)$. To check this conjecture, we plot the scaled function $\sqrt{6Dt} 4\pi r^2 G_s(r, t)$ versus $r^* = r/\sqrt{6Dt}$ in Fig. 5. The areas below the curves are fixed at 1. At relatively short times $t \lesssim 3\tau_a$, the curves in the region $r \gtrsim 1$ or $r^* \gtrsim (6Dt)^{-1/2}$, which give dominant contributions to $(\Delta r(t))^2$, tend to a master curve quite different from the rapidly decaying Gaussian tail. Note that in each curve the position of the peak at larger $r^*$ corresponds to $r \equiv 1$. This asymptotic law is consistent with the picture of the space-dependent diffusion constant in the active regions. It is also important that the heterogeneity structure remains unchanged in the time region $t \lesssim \tau_h \sim 3\tau_a$. At longer times $t \gtrsim 10\tau_a$, the curves approach the Gaussian form as can be seen in the inset of Fig. 5. Of course, $4\pi r^2 G_s(r, t)$ for $r < 1$ does not scale in the above manner, because it is the probability density of a tagged particle staying within a cage. This short-range behavior determines the decay of $F_s(2\tau, t)$ as noted below Eq. (2).

In conclusion, our MD simulations demonstrate that the diffusivity in supercooled liquids is spatially heterogeneous on time scales shorter than $3\tau_a$, which leads to the breakdown of the Stokes-Einstein relation. The heterogeneity detected is essentially the same as that of the bond breakage in our previous work [6]. We should then investigate how the heterogeneity arises and influences observable quantities in more realistic glass-forming fluids with complex structures.

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[6] R. Yamamoto and A. Onuki, Phys. Rev. E 58, 3515 (1998). Here we define $F_s(q, t)$ in shear flow of the form, $\dot{\gamma}y\kappa$, by setting $\Delta r_j(t) = r_j(t) - \dot{\gamma} \int_0^t dt' y_j(t') \kappa_i - r_j(0)$, where $y_i$ is the unit vector in the direction. Then $F_s(q, t)$ turns out to be almost independent of the angle of $q$. The viscosity and $\tau_a$ under shear satisfy Eq. (1) even in the non-Newtonian regime $\dot{\gamma}\tau_a > 1$.