

Two-step relaxation and the breakdown of the Stokes-Einstein relation in glass-forming liquidsBaicheng Mei¹, Yuyuan Lu^{1,*}, Lijia An^{1,†} and Zhen-Gang Wang^{2,‡}¹State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China²Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA

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It is well known that glass-forming liquids exhibit a number of anomalous dynamical phenomena, most notably a two-step relaxation in the self-intermediate scattering function and the breakdown of the Stokes-Einstein (SE) relation, as they are cooled toward the glass transition temperature. While these phenomena are generally ascribed to dynamic heterogeneity, specifically to the presence of slow- and fast-moving particles, a quantitative elucidation of the two-step relaxation and the violation of the SE relation in terms of these concepts has not been successful. In this work, we propose a classification of particles according to the rank order of their displacements (from an arbitrarily defined origin of time), and we divide the particles into long-distance (LD), medium-distance, and short-distance (SD) traveling particle groups. Using molecular-dynamics simulation data of the Kob-Andersen model, we show quantitatively that the LD group is responsible for the fast relaxation in the two-step relaxation process in the intermediate scattering function, while the SD group gives rise to the slow (α) relaxation. Furthermore, our analysis reveals that τ_α is controlled by the SD group, while the ensemble-averaged diffusion coefficient D is controlled by both the LD and SD groups. The combination of these two features provides a natural explanation for the breakdown in the SE relation at low temperature. In addition, we find that the α -relaxation time, τ_α , of the overall system is related to the relaxation time of the LD particles, τ_{LD} , as $\tau_\alpha = \tau_0 \exp(\Omega \tau_{LD}/k_B T)$.

DOI: [10.1103/PhysRevE.100.052607](https://doi.org/10.1103/PhysRevE.100.052607)**I. INTRODUCTION**

Glass-forming liquids exhibit a number of anomalous dynamical phenomena as the temperature is cooled toward the glass-transition temperature [1–4]. For example, the self-intermediate scattering function $F_s(\mathbf{q}, t)$, the self-part of the relaxation of the density-density correlation function, shows a distinct two-step relaxation—a fast relaxation followed by a plateau due to the cage effect before the final nonexponential decay in the form of the Kohlrausch-Williams-Watts (KWW) function [5,6]. Such a two-step relaxation has been loosely attributed to the presence of dynamic heterogeneity [2,6,7] in glass-forming liquids at low temperatures, i.e., the presence of numerous heterogeneous regions of mesoscopic sizes, with some regions comprising fast-moving particles having fluidlike characteristics with low viscosity, and other regions made up of slow-moving particles exhibiting highly viscous characteristics. However, application of these concepts to $F_s(\mathbf{q}, t)$ has not established a clear correlation between these two kinds of particles on the one hand, and the two kinds of relaxations in this function on the other. For example, an $F_s(\mathbf{q}, t)$ defined solely in terms of the fast or slow particles, which is expected to show a simple one-step relaxation, still exhibits a two-step relaxation [5,8].

Another anomalous behavior in the glass-forming liquids is the breakdown of the Stokes-Einstein (SE) relation, which relates the self-diffusion coefficient D to the viscosity or equivalently to the relaxation time τ_α [9–12]. While for normal liquids the product $D\tau_\alpha$ is temperature-independent, numerous studies [13–19] in recent decades have shown that this relation is violated in glass-forming liquids at low temperatures. Conceptually, Hodgdon and Stillinger [20,21] associated this violation with dynamic heterogeneity; however, there is considerable debate as to the mechanistic explanation. It has been argued that slow particles determine the relaxation time τ_α , whereas the average diffusion coefficient D is dominated by the fast particles [4]. A similar view [11,15] is that the slow and fast particles obey the SE relation separately, but the combined effect leads to a breakdown in the SE relation from the standpoint of the average relaxation time and diffusion coefficient [6]. However, some simulation studies find that the SE relation only holds for the slow particles and does not hold for the fast particles [22,23], while other studies suggest that the SE relation is violated for both the fast and slow particles [24,25].

In this work, we investigate the origin of the two-step relaxation and the breakdown of the SE relation by conducting molecular-dynamics simulations of the classical Kob-Andersen model [26–28] consisting of a binary Lennard-Jones (LJ) glass-forming liquid. Different from the slow- and fast-moving particles invoked in the literature, we propose an alternative classification according to the rank order of the particles measured by their observed displacements at any given time, where the small proportion of particles with

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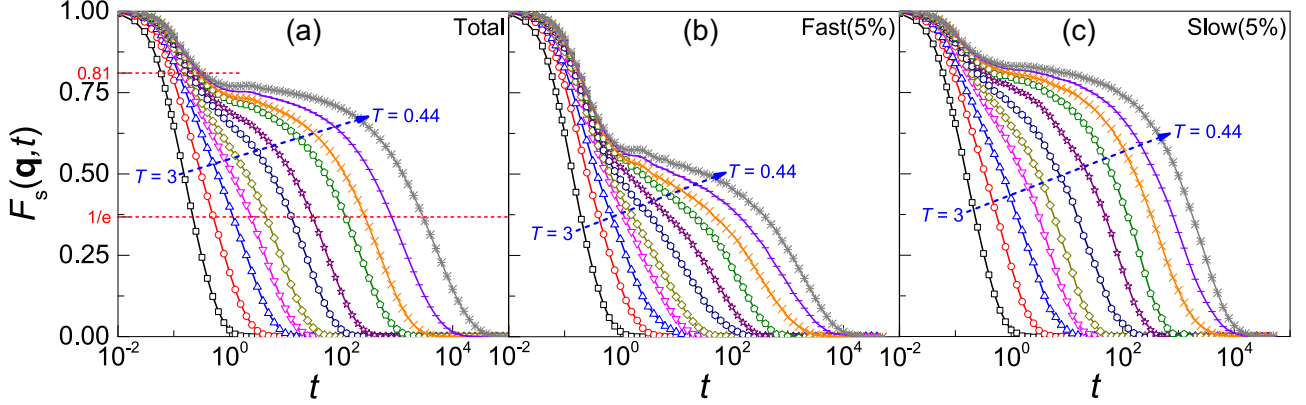


FIG. 1. The self-intermediate scattering function for all particles (a), and particles in LD (b) and SD (c) groups, at a series of temperatures. From left to right, the temperatures are 3.0, 1.5, 1.0, 0.8, 0.7, 0.6, 0.55, 0.5, 0.48, 0.46, and 0.44, respectively. The red horizontal lines define the corresponding structural relaxation times.

the largest displacements is denoted as a long-distance (LD) traveler group, and those with the smallest displacements are denoted as a short-distance (SD) traveler group, while the remainder are denoted as a medium-distance (MD) traveler group. We find that the fast and slow relaxations in the self-intermediate scattering function can be unambiguously associated with the dynamics of the LD and SD groups, respectively. The relaxation times of the LD and SD groups, together with their diffusion coefficients, allow a straightforward elucidation of the mechanism of the breakdown in the SE relation at low temperatures. Further analysis reveals that there exists a strong correlation between different relaxation times: both the relaxation time for the SD group and the system relaxation (α -relaxation) times depend exponentially on the relaxation time of the LD group, implying that the α -relaxation originates from multiple short-time rearrangement events. Finally, we present evidence for nonergodicity that persists to several orders of the system relaxation time.

II. MODEL AND METHODS

We performed molecular-dynamics simulation of the classical Kob-Anderson model [26–28] for a binary Lennard-Jones mixture of particles A and B, which can mimic an amorphous metal or metalloid alloy Ni₈₀P₂₀ [29]. The interaction potential is given by

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right], \quad (1)$$

where $\alpha, \beta \in [A, B]$, $\epsilon_{\alpha\beta}$ represents the depth of the potential well, r is the distance between particles, and $\sigma_{\alpha\beta}$ is the value of r for which $V_{\alpha\beta}$ is zero. All quantities are presented in reduced units, with the lengths given in units of σ_{AA} , temperature in units of ϵ_{AA} over the Boltzmann constant k_B , and time in units of $\sqrt{m\sigma_{AA}^2/\epsilon_{AA}}$. The mass of each particle is assumed to be the same, $m = 1.0$. Other LJ parameters are $\sigma_{AB} = 0.8\sigma_{AA}$, $\sigma_{BB} = 0.88\sigma_{AA}$, $\epsilon_{AB} = 1.5\epsilon_{AA}$, and $\epsilon_{BB} = 0.5\epsilon_{AA}$. These parameters are identical to those used by previous researchers [27,28]. We employ a cutoff distance of $r_c = 2.5$, beyond which $V_{\alpha\beta}$ is assumed to be zero. The number of particles N is 1080 with 80% (864) A and 20% (216) B. A cubic box with size $L_x = L_y = L_z = 9.655$ is used, corresponding to a

number density ρ of 1.2. For this system, the mode-coupling transition temperature is $T_c = 0.435$ [28,30,31]. The simulations were conducted in the NVT ensemble, and periodic boundary conditions were applied in all three directions. The equations of motion were integrated using the velocity form of the Verlet algorithm with a time step of 0.0025. The system was equilibrated for at least $10\tau_\alpha$ prior to the collection of statistical data. Simulations were performed for a series of temperatures starting at the highest $T = 3.0$ down to $T = 0.42$.

III. RESULTS

A. Decomposition of the self-intermediate scattering function

In Fig. 1(a), we present the time evolution of the self-intermediate scattering function for the entire system, $F_s(\mathbf{q}, t) = \langle \frac{1}{N} \sum_{j=1}^N \exp\{i\mathbf{q} \cdot [\mathbf{r}_j(t + t_0) - \mathbf{r}_j(t_0)]\} \rangle$, with $|\mathbf{q}|$ set to correspond to the first peak of the static structure factor, and $\langle \dots \rangle$ represents the thermal average, which is obtained by averaging over both different t_0 and different samples. At high temperatures, $F_s(\mathbf{q}, t)$ exhibits a single-step fast relaxation. With decreasing T , a shoulder appears at intermediate times, which reflects the caged motion of particles in glassy systems and divides the structural relaxation into two contributions representative of a two-step relaxation, where the primary peak corresponds to the short-time rapid relaxation and the shoulder corresponds to the long-time α -relaxation [6]. Note that the α -relaxation time τ_α is defined as the time required for $F_s(\mathbf{q}, t)$ to decay to $1/e$.

In the literature, the fast- and slow-moving particles are defined by the square of their displacement, $\mathbf{r}_i^2(\tau^*) = [\mathbf{r}_i(t_0 + \tau^*) - \mathbf{r}_i(t_0)]^2$, over some characteristic time τ^* [15,32], where t_0 is an arbitrarily chosen origin of time. A particular particle i will be defined as a fast- or slow-moving particle, respectively, if $\mathbf{r}_i^2(\tau^*)$ belongs to the top or bottom few percent, say 5%, of all particles. τ^* is usually selected as the time t^* when the corresponding non-Gaussian parameter is at its maximum [5,8,33], which is slightly shorter than τ_α . Instead of the self-intermediate scattering function for all the particles, we define $F_s(\mathbf{q}, t)$ for particles belonging only to the fast- and slow-moving particle groups, respectively.

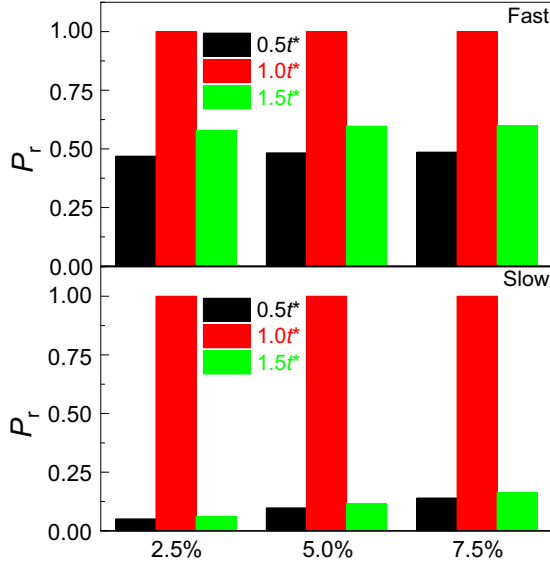


FIG. 2. Upper panel: fast-moving particles; lower panel: slow-moving particles. The histograms show the fraction of fast- and slow-moving particles defined at $t = t^*$ that remain in the same respective groups at earlier ($0.5t^*$, black) and later ($1.5t^*$, green) times. 2.5%, 5%, and 7.5% are the different thresholds used to define the fast- and slow-moving groups.

This is done by restricting the summation in the definition of $F_s(\mathbf{q}, t)$ to include only particles in the fast- or slow-moving particle groups. We observe in Figs. 1(b) and 1(c) that both groups exhibit similar two-step relaxation behaviors to that for the entire particle set at low temperatures. Note that in this classification scheme, the motion state of a particle (i.e., whether a particle is slow- or fast-moving) was permanently assigned to a specific particle index i according to its displacement at $t = t^*$, i.e., the identities of the particles in the fast- and slow-moving groups do not change with time. Thus, when examining the self-intermediate scattering function or the diffusion, any given particle carries the same state label, even though a fast particle in the top 5% measured by its displacement at $t = t^*$ may not belong to the top 5% of particles with the largest displacements at earlier or later times. Indeed, at $t = 0.5t^*$, only 48.3% of the fast particles defined using $t = t^*$ were actually fast, while at $t = 1.5t^*$, the fraction is 59.7%. Even fewer overlaps are observed for the slow particles; see the lower panel in Fig. 2. In other words, the fast- and slow-moving particles defined by their displacements at $t = \tau^*$ do not inform their actual displacements at earlier or later times.

We propose a classification of particles according to their displacements at any given time t (measured from $t_0 = 0$), and we divide the particles into LD, MD, and SD groups based on the rank order of their displacements. At any given moment, the small fraction of particles (e.g., 5%) with the largest displacements is considered to form the LD group, and those (e.g., 5%) with the smallest displacements are assigned to the SD group, while the remainder (90%) are considered to belong to the MD group. We have also used threshold values of 2.5% and 7.5% in ranking the particles; the results only show small quantitative differences. For clarity, we focus

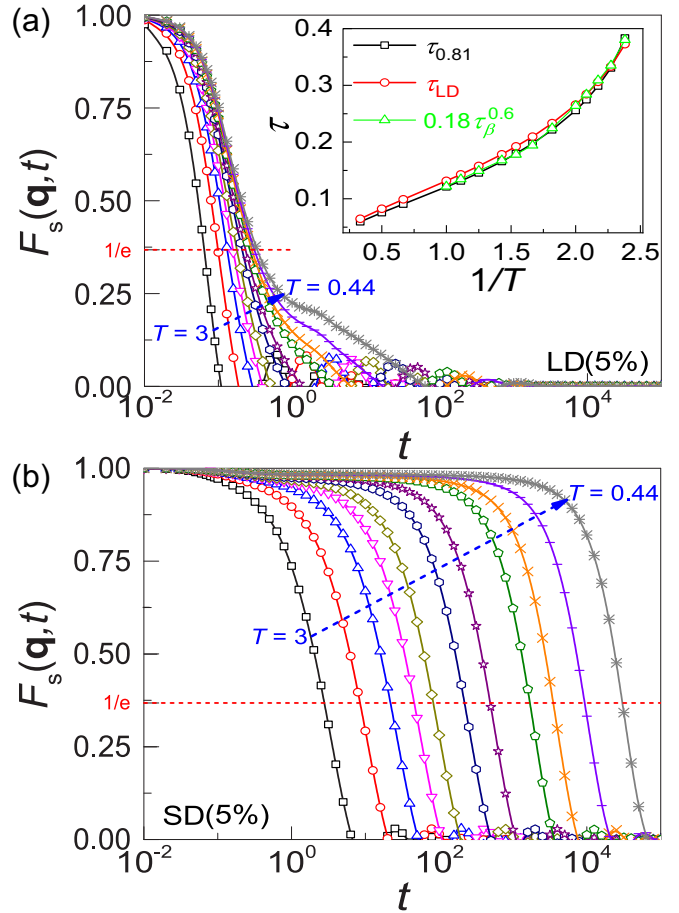


FIG. 3. The self-intermediate scattering function for (a) the LD traveling group (the top 5% of total particles) and (b) the SD traveling group (the bottom 5% of total particles) at a series of temperatures. The red horizontal lines define the corresponding structural relaxation times. The inset in (a) displays the temperature dependence of the relaxation times corresponding to the LD group, the time required for the $F_s(\mathbf{q}, t)$ of all particles to decay to 0.81 ($\tau_{0.81}$), and $0.18\tau_\beta^{0.6}$, where τ_β is the β -relaxation time, defined using the inflection in the log-log plot of the mean squared displacement (MSD) of a particle system vs time [34].

on results obtained using the 5% threshold. Note that in this definition, the particle index is unimportant, i.e., a randomly chosen particle i can change between the LD, MD, and SD groups with the evolution of time, but at each given time, the assignment of LD, SD, and MD will always be based on the rank order of the particles according to their displacements, regardless of the particle index. We now demonstrate that this classification leads to a natural explanation of the two-step relaxation process and the breakdown of the SE relation.

In Figs. 3(a) and 3(b), we present these restricted self-intermediate scattering functions for the LD and SD groups over the same range of T . Rather than the two-step relaxation behavior obtained for all particles, we observe that the $F_s(\mathbf{q}, t)$ values for both LD and SD groups exhibit single-step relaxation behaviors, each with their own relaxation times, τ_{LD} and τ_{SD} . If we normalize the time in Figs. 3(a) and 3(b) using their corresponding relaxation times, we obtain the results shown in Figs. 4(a) and 4(b). We find that the normalized curves

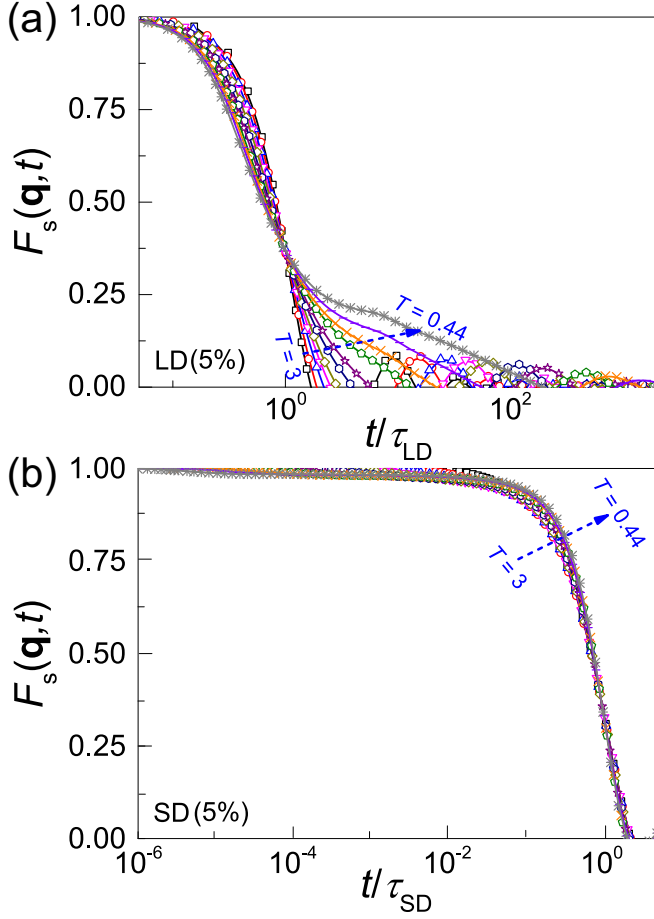


FIG. 4. The values of the self-intermediate scattering function for the LD group (a) and the SD group (b) with t normalized by the corresponding relaxation time at a series of temperatures.

for the respective LD and SD groups approximately coincide, indicating that the LD and SD groups each exhibit similar relaxation behavior at different temperatures. The differences at long times observed in Fig. 4(a) are due to particle exchanges; see the discussions in Sec. III E.

The relaxation time of the SD group τ_{SD} is found to be comparable to the overall relaxation time τ_α , but is far greater than that of the LD group τ_{LD} . We can introduce another characteristic time $\tau_{0.81}$ for all particles, which is defined as the time required for $F_s(\mathbf{q}, t)$ to decay to 0.81; see Fig. 1(a). As is clear from the inset of Fig. 3(a), $\tau_{0.81}$ is approximately equal to τ_{LD} at all temperatures considered. This analysis demonstrates a clear correspondence between the rapid relaxation with the dynamics of the LD group, and the slow relaxation with the SD group.

B. Temperature dependence of time scales

Figure 5 shows the temperature dependence of the different relaxation times. It is clear that τ_{LD} exhibits Arrhenius behavior, with a small slope in the $1/T$ plot, suggesting a low activation barrier. τ_{SD} , on the other hand, shows clearly super-Arrhenius behavior; the curves can be well fitted by the classical Vogel-Fulcher-Tammann equation $\tau = \tau_0 \exp[BT_0/(T - T_0)]$ [35–37], where B and T_0 are fitting parameters, and τ_0

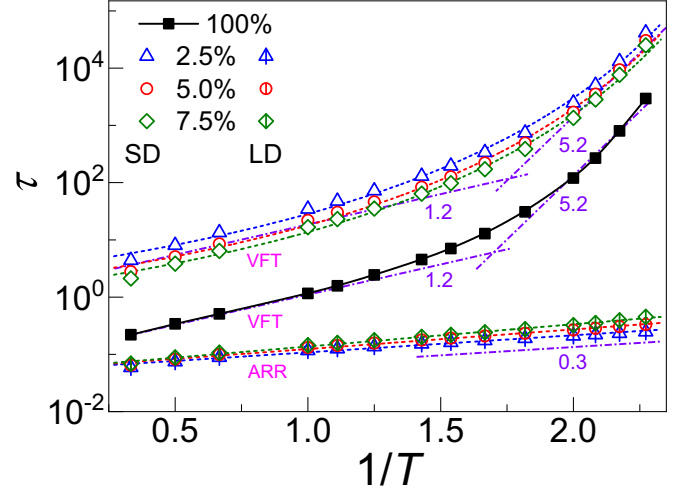


FIG. 5. Temperature dependence of the relaxation times for all particles, the LD group (based on the 2.5%, 5%, or 7.5% thresholds), and the SD group (based on the 2.5%, 5%, or 7.5% thresholds).

represents the relaxation time in the high-temperature limit. Moreover, the temperature dependence of τ_{SD} is similar to that of the system relaxation time τ_α . In particular, the slopes of both relaxation times with respect to $1/T$ in the semilog plot in the Arrhenius regime are identical (≈ 1.2), as are the limiting slopes in the super-Arrhenius regime (≈ 5.2). Note that the limiting slopes in the super-Arrhenius regime are indicated for convenience of discussion and do not imply the existence of a linear dependence in the logarithm of the relaxation time on $1/T$.

The Arrhenius temperature dependence in τ_{LD} implies a simple activated process. To demonstrate this, we plot the probability distribution of r [i.e., $P(r)$] for all particles at $t = \tau_{LD}$ in Fig. 6(a). We observe that the population of LD particles are those that have undergone displacements exceeding half the particle radius $r \approx 0.24$. If we consider this as a threshold value for a particle to escape its local cage, we can identify τ_{LD} as the timescale for this activated event. This reasoning is corroborated by applying the nonlinear Langevin equation (NLE) theory of Schweizer and co-workers [38–40], which provides the following r -dependent dynamic free energy $F_{dyn}(r)$ for a tagged particle:

$$\beta F_{dyn}(r) = -3 \ln(r) - \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{\rho C^2(q) S(q)}{1 + S^{-1}(q)} e^{-\frac{(qr)^2}{6} [1 + S^{-1}(q)]}. \quad (2)$$

Here, $\beta = 1/k_B T$, ρ is the number density of the particles, $C(q)$ is the direct correlation function [41,42], and $S(q) = [1 - \rho C(q)]^{-1}$ is the structure factor, where $q = |\mathbf{q}|$ is the wave number. We employed Eq. (2) to obtain the r -dependence of $\beta F_{dyn}(r)$ for our LJ system at different temperatures using the $S(q)$ obtained from our simulation. The results are shown in Fig. 6(b). For low temperatures ($T < 1.0$), $\beta F_{dyn}(r)$ acquires a minimum (transient localized state) at $r < r_B$ and an energy barrier at r_B . This energy barrier indicates the emergence of hopping transport (i.e., activated rearrangement). Importantly, we find $r_B \approx 0.24$,

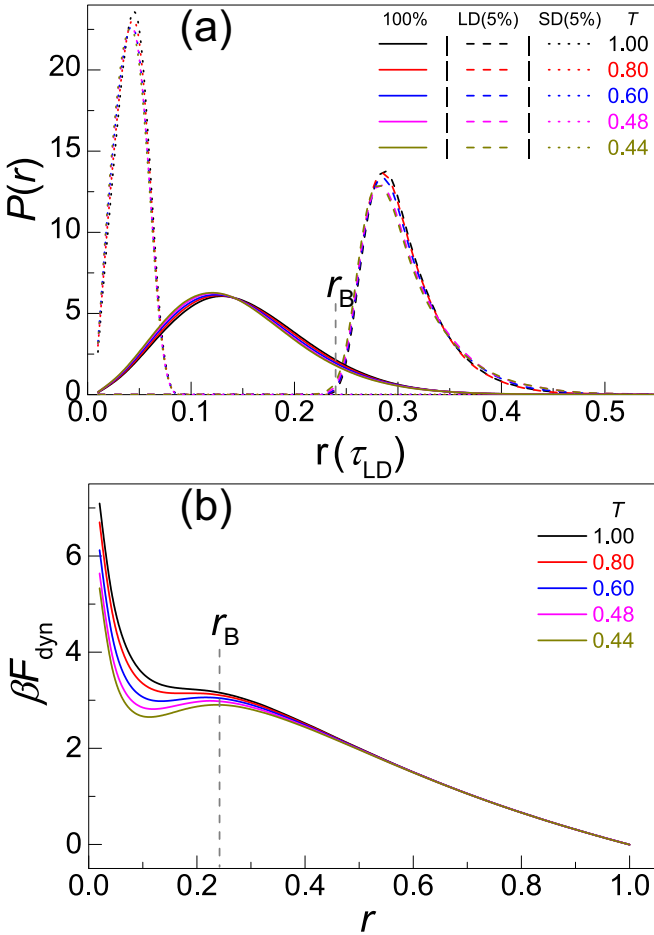


FIG. 6. (a) Probability distribution of particle displacement r for all particles, and particles in LD and SD groups, at a series of temperatures. (b) Nonlinear Langevin equation dynamic free-energy barriers as a function of r at a series of temperatures.

which coincides with the threshold value shown in Fig. 6(a). For comparison, we also show in the same figure the displacement distribution for the SD particles; clearly their displacements are far below $r_B \approx 0.24$. These results are inconsistent with the conventional picture of all the particles performing localized motion within their cages as being responsible for the faster relaxation mode [6].

C. Relationship between different timescales

Fluctuations in the density correlation functions of glass-forming liquids typically approach a plateau value after undergoing an initial rapid relaxation. This relaxation is known as the β -relaxation process [43]. While recent studies [34] have defined τ_β using the inflection in the log-log plot of the mean-squared displacement (MSD) of a particle system versus time, hereafter referred to as $\tau_\beta(\text{MSD})$, our analysis based on the LD and SD classification suggests a similarity between the relaxation of the LD particles and the β relaxation. This implies that the β -relaxation process may originate from the activated relaxation of some of the particles.

The conventional understanding of β - and α -relaxation is that these are two different relaxation modes for the system

that occur on different timescales. However, a recent study has shown that $\tau_\beta(\text{MSD})$ scales with the dynamic heterogeneity length as $\tau_\beta(\text{MSD}) \sim \xi^{0.8}$ [34]. We thus expect a similar relationship between τ_{LD} and ξ , i.e., $\tau_{LD} \sim \xi^z$. This relationship is shown in Fig. 7(a) with different criteria for defining the LD group. The exponent varies between 0.40 and 0.56. Taking the 5% criterion, we get $z \approx 0.5$. On the other hand, according to the recent work of Das *et al.* [44], τ_α satisfies the following relation with ξ :

$$\tau_\alpha = \tau_0 \exp\left(\frac{\Omega \xi^\gamma}{k_B T}\right), \quad (3)$$

where Ω is a T -independent parameter and γ is a universal exponent. This same study found that the average value of γ for a three-dimensional system is approximately 0.5, the same value as our exponent z in scaling between τ_{LD} and ξ . Therefore, we can substitute ξ^γ in Eq. (3) with τ_{LD} , which yields the following relation:

$$\tau_\alpha = \tau_0 \exp\left(\frac{\beta \tau_{LD}}{k_B T}\right). \quad (4)$$

This relation is plotted in Fig. 7(b), which indicates that Eq. (4) holds approximately over the full range of temperatures for all the different LD criteria. Moreover, a similar plot of Eq. (4) in Fig. 7(c), but with τ_α replaced by τ_{LD} , demonstrates good agreement with this relation as well for all the temperatures in the supercooled regime. Combining $\tau_\beta \sim \xi^{0.8}$ and $\tau_{LD} \sim \xi^{0.5}$, we also obtain a relation between the β -relaxation and the LD relaxation processes, i.e., $\tau_{LD} \sim \tau_\beta^{0.6} (\approx \tau_\beta^{5/8})$, with a prefactor about 0.18, as shown in the inset of Fig. 3(a). These results suggest that the β -relaxation process is directly controlled by the short-time activated rearrangements of particles in the LD group, whereas the long-time relaxation process results from multiple, successive activated rearrangements of these particles. Furthermore, an analysis of the spatial correlations of particles within the LD group on a timescale of τ_α indicates that these particles tend to form stringlike structures, which is consistent with earlier observations of correlated stringlike motion of particles near the glass transition [5,33]. This indirectly supports the physical picture of the excitation chain [45–47] and string models [48–50] that stringlike structures are responsible for dynamic relaxation processes.

D. Breakdown of the SE relation

We now turn to the diffusion of the particles and the SE relation. In contrast to the behavior for the relaxation times, the values of $1/D$ for all particles as well as for the separate LD and SD groups all exhibit significant super-Arrhenius behavior with respect to $1/T$ at low temperatures; see Fig. 8(a). Moreover, the slopes of all curves for both groups agree well with the slopes obtained for all particles in the Arrhenius regime. However, in the super-Arrhenius regime the rate of change exhibits some minor differences between the SD and LD groups and all the particles, with the SD group having the largest slope, the LD group having the least, and all the particles intermediate between the SD and LD groups.

From Figs. 5 and 8(a), it is clear that the temperature dependence of $1/D$ for the SD groups follows essentially that

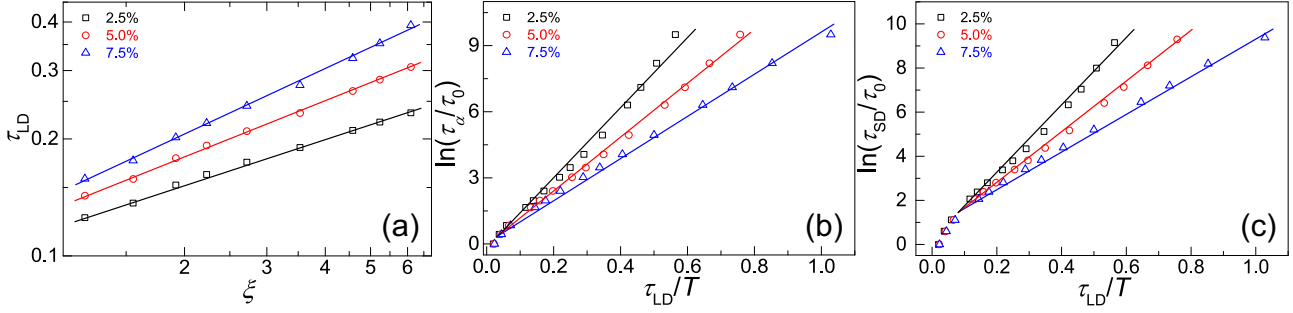


FIG. 7. (a) Relationship between τ_{LD} and the dynamic heterogeneity length ξ for the system with threshold values for the LD group. (b) Correlation between the relaxation time for the system τ_α and τ_{LD} . (c) Correlation between τ_{SD} and τ_{LD} .

of τ_{SD} , implying the SE relation for this group. It is also clear that the SE relation does not hold for the LD group since τ_{LD} increases with $1/T$ much slower than that of the other groups, even in the Arrhenius regime. When all particles are considered, the SE relation is obeyed in the Arrhenius regime, because both τ_α and $1/D$ follow the same temperature dependence. But in the super-Arrhenius regime, the slope in $1/D$ is less than that in τ_α , so there is an upward turn in the product $D\tau_\alpha$, i.e., the SE relation is violated in this regime.

These behaviors are shown in Fig. 8(b), which presents the product $D\tau$ using D and τ for each group.

E. Memory effects and nonergodicity in LD and SD particles

To gain insight into the relationship between the LD and SD particle groups introduced in this work and the fast- and slow-moving particles used in previous work, we return to the overlap fractions for these two groups of particles at different selected times shown in Fig. 2. While the figure demonstrates that the fast- and slow-moving particles are not permanent—which is the main reason that they fail to explain the two-step relaxation in the self-intermediate scattering function—it also reveals that a significant fraction of the fast-moving particles (defined as the longest travelers at time t^*) is also in the LD group at $0.5t^*$ and $1.5t^*$, suggesting some memory effects. The fraction is less for the slow-moving particles, but still significantly higher than the corresponding threshold fraction that defines the group (for example, for the 5% threshold, the overlap is about 10%).

To show this effect more quantitatively, in Fig. 9 we show the time evolution of the retention probability of particles in the LD or the SD group, $P_{\text{ret}}(t) = \langle N_{LD-1}(t) \rangle / N_{LD-0}$ or $\langle N_{SD-1}(t) \rangle / N_{SD-0}$. Here, N_{LD-0} (N_{SD-0}) represents the number

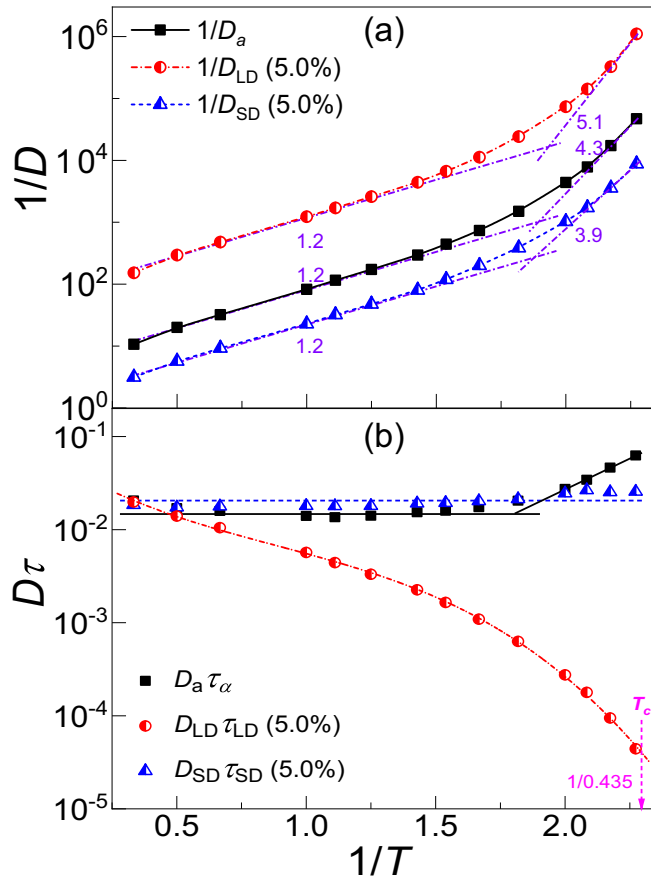


FIG. 8. Temperature dependence of (a) the reciprocal diffusion coefficient and (b) the product of the individual relaxation times τ and the corresponding diffusion coefficient D for all particles, the LD group, and the SD group.

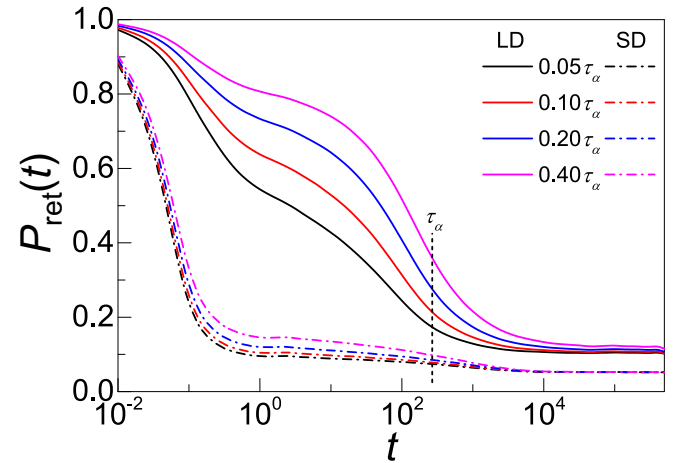


FIG. 9. Time evolution of the retention fraction $P_{\text{ret}}(t)$, i.e., the fraction of LD particles (solid line) and the SD particles (dash-dotted line) defined at time t_0 that remain in their respective groups at $t_0 + t$, for $T = 0.48$. Four reference times t_0 are chosen: $0.05\tau_\alpha$, $0.1\tau_\alpha$, $0.2\tau_\alpha$, and $0.4\tau_\alpha$.

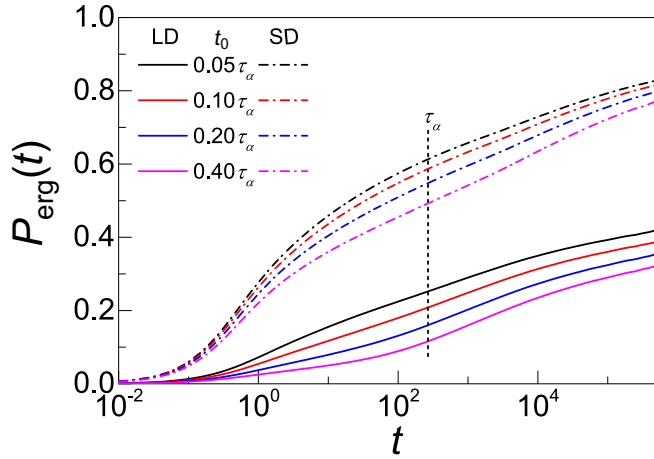


FIG. 10. Time evolution of $P_{\text{erg}}(t)$ at $T = 0.48$ for the LD (solid lines) and the SD (dash-dotted lines) particles. Four reference times t_0 are chosen: $0.05\tau_\alpha$, $0.1\tau_\alpha$, $0.2\tau_\alpha$, and $0.4\tau_\alpha$.

of instantaneous LD (SD) particles at the reference time t_0 for defining the particle groups, and $\langle N_{\text{LD-1}}(t) \rangle$ [$\langle N_{\text{SD-1}}(t) \rangle$] is the average number of particles that remain in their respective group at $t + t_0$. On timescales of τ_α , $P_{\text{ret}}(t)$ has decayed considerably, suggesting that the identity of the particles within the LD (SD) group varies greatly. Note that the retention fraction is larger for the larger reference time, since the difference in the displacement between particles in the LD (SD) group and particles in other groups is larger, and hence it is less frequent that an LD (SD) particle will fall out of that group. On the other hand, $P_{\text{ret}}(t)$ remains appreciably greater than the threshold value employed for defining these groups (5%) on the timescale of τ_α , suggesting that there is substantial overlap between the fast- and slow-moving particles in the literature (defined using a fixed time τ^*) and our LD and SD particles on this time scale. These two results simultaneously explain why the conventional concept of fast- and slow-moving particles fails to offer a clear explanation of the two-step relaxation and the violation of SE relation, but nevertheless has proven useful in describing many classical phenomena in glass-forming liquids.

To further elucidate the memory effects in the LD and SD particles, we define the following function: $P_{\text{erg}}(t) = [(N_{\text{LD}}^*(t)) - N_{\text{LD-0}}]/(N - N_{\text{LD-0}})$ or $[(N_{\text{SD}}^*(t)) - N_{\text{SD-0}}]/(N - N_{\text{SD-0}})$. Here, N is the total number of particles in the system, $N_{\text{LD-0}}$ ($N_{\text{SD-0}}$) is the same instantaneous number of LD (SD) particles defined for $P_{\text{ret}}(t)$, and $N_{\text{LD}}^*(t)$ [$N_{\text{SD}}^*(t)$] is the average number of particles that have been in the LD (SD) group at least once during the period from t_0 to $t_0 + t$. Clearly, $N_{\text{LD}}^*(t=0) = N_{\text{LD-0}}$ [$N_{\text{SD}}^*(t=0) = N_{\text{SD-0}}$], while for $t \rightarrow \infty$, $N_{\text{LD}}^* = N_{\text{SD}}^* = N$, because all the particles will have been in the LD (SD) group at least once if the system is ergodic. Since τ_α is considered the longest relaxation time of the system, it is expected that the function $P_{\text{erg}}(t)$ should approach 1 on timescales of τ_α . Figure 10 shows the time evolutions of $P_{\text{erg}}(t)$ for different choices of t_0 . Surprisingly, the values of $P_{\text{erg}}(t)$ are far less than 1 even for times greater than $10^3\tau_\alpha$. Therefore, judged by the behavior of this function, the relaxation time appears to be greater than $10^3\tau_\alpha$. In other words,

on timescales of $10^3\tau_\alpha$, the system behaves nonergodic. In addition, we note from Fig. 10 that $P_{\text{erg}}(t)$, especially for the SD particles, becomes substantial at τ_α , indicating that a significant fraction of the LD and SD particles have undergone exchanges. The fact that additional time even up to $10^3\tau_\alpha$ does not result in significantly more relaxation suggests that many of the exchanges are futile, i.e., they take place within the same particle group, thus confirming the long-term memory effects in these particle groups.

IV. CONCLUSIONS

In summary, we have proposed a classification of the particles into LD, MD, and SD groups according to their observed displacements to characterize the dynamic heterogeneity in glass-forming liquids. With these newly defined particle groups, the two-step relaxation process in the intermediate scattering function $F_s(\mathbf{q}, t)$ can be naturally assigned to the relaxation of the LD and SD groups, respectively, where the LD group contributes to the first-step (rapid) relaxation at short-time scales and the SD group determines the second-step (α)-relaxation at long times. By analyzing the temperature dependence of the various relaxation times, we have discovered a strong exponential relationship between the relaxation time for the LD particles τ_{LD} on the one hand, and the relaxation time for the SD particles τ_{SD} and the α -relaxation time τ_α on the other. We believe that this exponential dependence implies that the long-time α relaxation results from multiple short-time rearrangement events. Moreover, while the value of τ_α is controlled primarily by the SD particles, the diffusion coefficient is determined by both the LD and SD groups. Therefore, the breakdown of the SE relation at low temperatures can be understood as a direct consequence of the different contributions of the LD and SD groups to the relaxation time and the diffusion coefficient.

We have further analyzed the memory effects in the LD and SD particles by defining a retention probability and a measure of the ergodicity in the particle identity. Our results show that there is a substantial fraction of particles transitioning out of their respective groups on timescales of τ_α , yet a significant fraction remains, thus clarifying why the traditional concept of fast- and slow-moving particles fails to explain the two-step relaxation process and the breakdown of the SE relation, but is nevertheless useful for describing many dynamic phenomena in glass-forming liquids. Surprisingly, we find that the system behaves nonergodic up to three orders of magnitude of τ_α , judged by the ergodicity (or lack thereof) in the particle identity. We hope these results offer some fresh perspectives on the dynamic behavior in glass-forming liquids, and contribute to the development of new theories for describing glass dynamics.

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