

Dynamic heterogeneous structure relaxation of supercooled liquids

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Molecular dynamics simulations have been carried out on a two-component Morse potential system quenched into supercooled liquid states. The relaxation process and the temperature dependence of the diffusion constants were studied. Using the probability model of relaxation and the dynamic heterogeneities, we give an understanding of the nonexponential structure relaxation in the supercooled liquid state. The relaxation time and its distribution width were obtained. It was found that the distribution width of the relaxation time increases with decreasing temperature, and the relaxation time shows the same temperature dependence as the diffusion constant.

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I. INTRODUCTION

The dynamics of glass-forming systems close to the glass transition is very complicated due to its collective nature and results in different relaxation mechanisms [1,2]. Particle motions in supercooled liquids are severely restricted or jammed, thus giving rise to slow structure relaxations and highly viscoelastic behavior. For a long time, however, it has been expected [3–6] that rearrangements of particle configurations in glass materials should be cooperative, involving many molecules, owing to configuration restriction. In other words, such events occur only in the form of clusters whose sizes increase at low temperature. In the normal liquid states, on the contrary, they are frequent and uncorrelated among one another in space and time. Such an idea was put forth by Adam and Gibbs [3], who invented the concept of rearranging regions. But there are no quantitative predictions.

An outstanding problem in the dynamics of supercooled liquids is to understand why they exhibit nonexponential relaxation of time correlation functions. Two limiting microscopic scenarios have been proposed to explain this behavior [7]. In the so-called “homogeneous” scenario, all the particles relax identically by an intrinsically nonexponential statistical process, while in the “heterogeneous” case the nonexponential relaxation is due to a superposition of individual exponential contributions with different relaxation rates. Recent experiments [8] have given evidence that in the supercooled liquid, the relaxation is not homogeneous. Molecular dynamics (MD) simulation can be a powerful tool to gain insight into the relevant physical process in highly supercooled states. Muranaka and Hiwatari [9], using a simple two-dimension fluid, visualized significant large-scale heterogeneities in particle displacements in a relatively short-time interval. In liquid states, Hurley and Harrowell [10] observed similar kinetic heterogeneities. Donati *et al.* [11] have observed stringlike clusters whose lengths increase at low temperatures in a three-dimensional binary mixture. Kob *et al.* [12], using the non-Gaussian parameter of the self-part of the van Hove correlation function to identify “mobile” particles, found that these particles form clusters whose sizes

grow with decreasing temperature. Doliwa and Heuer [13] studied the three-time correlations for a hard sphere system close to the glass transition and observed anisotropic dynamics. Yamamoto and Onuki [14] studied highly supercooled liquids in two and three dimensions in quiescent and sheared conditions, and they observed that upon structural rearrangements, the bonds between neighboring particle pairs break collectively in the form of clusters whose sizes grow with lowering the temperature. Johnson *et al.* [15] studied a two-component, two-dimensional Lennard-Jones supercooled liquid near the glass transition, and found that the supercooled liquid is spatially heterogeneous and that there are long-lived clusters whose size distribution satisfies a scaling relation up to a cutoff. In addition, Monte Carlo simulation of a dense polymer melt ($d=3$) by Heuer and Okun [16] showed that in this system dynamical heterogeneities occur on short length scales. Monte Carlo simulation of a dense polymer by Ray and Binder [17] showed significant system size dependence of the monomer diffusion constant, which indicates heterogeneities over the system size.

Most previous papers so far have been concerned with either the spatial and dynamical heterogeneities or explaining the nonexponential relaxation. Thus, no direct connection has been made between the heterogeneities and the structure relaxation, and there are no simulation results for the relaxation time distribution, which describes the dynamic heterogeneities. In this paper based on the probability model of relaxation, we give a physical explanation of the heterogeneities and the nonexponential structure relaxation in the supercooled liquid, which may provide new insight into the mechanism of the nonexponential relaxation in supercooled liquids. The distribution of the relaxation times and its temperature dependence is also calculated and discussed.

II. MODEL AND SIMULATION METHODS

We performed MD simulations in three dimensions on binary mixtures of $N_1=192$ atoms of mass m_1 and diameter r_{01} and $N_2=64$ atoms of mass m_2 and diameter r_{02} . They interact via a Morse potential

$$u_{\mu\nu} = \varepsilon(e^{-2\alpha(r-r_{0\mu\nu})} - 2e^{-\alpha(r-r_{0\mu\nu})}), \quad (1)$$

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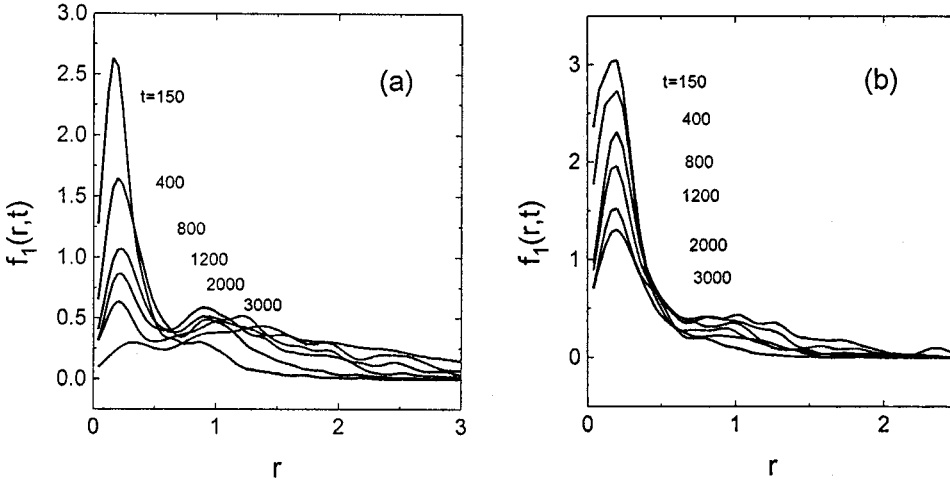


FIG. 1. The van Hove self-correlation function $f_1(r,t)$ for the first kind of particles at two different temperatures. The spatial dependence of the function $f_1(r,t) = 4\pi G_1^s(|\vec{r}|,t)$ is shown for six different times. (a) $T = 0.4$; the times are $t = 150, 400, 800, 1200, 2000, 3000$ (from top to bottom). (b) $T = 0.3$; the times are $t = 150, 400, 800, 1200, 2000, 3000$ (from top to bottom).

where μ and ν are equal to 1 or 2, denoting the two different types of particles, r is the distance between two particles, α is a potential parameter. The diameter is additive: $r_{0\mu\nu} = 1/2(r_{0\mu} + r_{0\nu})$. The units of mass, length, and time are $m_1, r_{01}, \tau_0 = r_{01}\sqrt{m_1/\varepsilon}$, respectively. The temperature unit is ε/k_B . In this study, the potential parameter α is taken as 7.0, and the interaction is truncated at $r_{0\mu\nu}$. The potential using this value of α is close to the Lennard-Jones potential. Nucleation is easily bypassed in a binary mixture and that is the motivation for using a two-component system. The size ratio is $r_{02}/r_{01} = 1.4$. The mass ratio is $m_2/m_1 = 2$. The volume was fixed as $V = 268.85$ so that the number density $\rho^* = N/V = 0.9522$. Periodic boundary conditions were adopted. The temperature of the system was controlled with the Nose-Hoover method [18]. When $T^* > 0.5$, the integration time step was $0.005\tau_0$; and when $T^* \leq 0.5$, it was $0.005\tau_0$ for the first 1×10^5 steps and $0.01\tau_0$ for the later run times.

The two-component system was first heated to $T^* = 3.0$ from a fcc structure. After equilibrating for 5×10^4 steps, 12 configurations were saved at 3×10^3 time-steps interval, to be used as the initial configurations. Then the systems were quenched to low temperatures. The temperatures investigated are $T = 3.0, 2.0, 1.5, 1.0, 0.9, 0.8, 0.7, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, \text{ and } 0.3$. At each temperature, 12 independent runs with different initial configurations were performed to average the quantities. After the quenching, the system was allowed to equilibrate for a time that was longer than the time of the α relaxation, and then the quantities were calculated.

III. RESULTS AND DISCUSSIONS

Since the crystal structure of this binary system is not known, the melting temperature was determined approximately by studying the melting point of a one-component system with an effective diameter, which was obtained via the effective one-component approximation as for the soft-core system [19]

$$r_{0\text{eff}}^3 = \sum_{\mu} \sum_{\nu} x_{\mu} x_{\nu} r_{0\mu\nu}^3, \quad (2)$$

where $x_{\mu} = N_{\mu}/N$. The effective mass is $m_{\text{eff}} = \sum_{\mu} x_{\mu} m_{\mu}$. A fcc crystal of the one-component system of particles of diameter $r_{0\text{eff}}$ and mass m_{eff} (with the same number density

as that of the two-component system) was gradually heated from $T = 0$. Based on the Lindemann criterion [20], the melting temperature of the system was obtained $T_{\text{melt}} = 1.3$.

For the two-component system, the glass transition temperature was obtained through the dynamical diagnostics [21] of the self-parts of the density autocorrelation (or van Hove) functions, namely,

$$G_s^{(\mu)}(\vec{r},t) = \frac{1}{N_{\mu}} \sum_{i=1}^{N_{\mu}} \langle \delta(\vec{r}_i^{\mu}(t) - \vec{r}_i^{\mu}(0) - \vec{r}) \rangle, \quad (3)$$

where $\vec{r}_i^{\mu}(t)$ and $\vec{r}_i^{\mu}(0)$ denote the position of particle i of species μ at time t and 0, respectively.

Both for a liquid in the hydrodynamic limit and a frozen system in the harmonic approximation, the van Hove self-correlation function is a Gaussian

$$G_s^{\mu}(\vec{r},t) = \frac{1}{[\pi\omega_{\mu}^2(t)]^{3/2}} \exp\left[-\frac{r^2}{\omega_{\mu}^2(t)}\right], \quad (4)$$

where the width function $\omega_{\mu}(t)$ is given by $\omega_{\mu}^2(t) = 2D_{\mu}t$ and $\omega_{\mu}^2(t > \tau_D) = A_{\mu}T$, respectively, D_{μ} is the self-diffusion constant for the species μ , A_{μ} is a constant that depends on the vibrational properties of the system, and T is the temperature.

The function $f_{\mu}(r,t) = 4\pi r^2 G_a^{\mu}(|\vec{r}|,t)$ is equal to the probability of finding a particle of species μ at time t at the distance r from its location at time 0. For a liquid, the location of the maximum of $f_{\mu}(r,t)$ as a function of r is changing in time. In a frozen structure, r_{μ}^{max} reaches a constant value after a short time.

Figures 1(a) and 1(b) show the van Hove self-correlation function for the particle 1 at two different temperatures 0.4 and 0.3, respectively. At each temperature $f_1(r,t)$ is shown for a sequence of times. It shows that at $T = 0.4$, the location of the maximum of $f_1(r,t)$ moves, but for $T = 0.3$, it does not change even over the longest time intervals explored in our MD simulations. The disordered structure appears to be frozen over this time scale for $T = 0.3$. Since glass transition is only a dynamic phenomenon which depends on the crossing of the time scale for the experiment (or simulation) and the time scales for molecular rearrangements, and glasses are liquids which are ‘‘frozen’’ on the time scale of experimental observation [1], it is a change in behavior of $f_1(r,t)$ over the

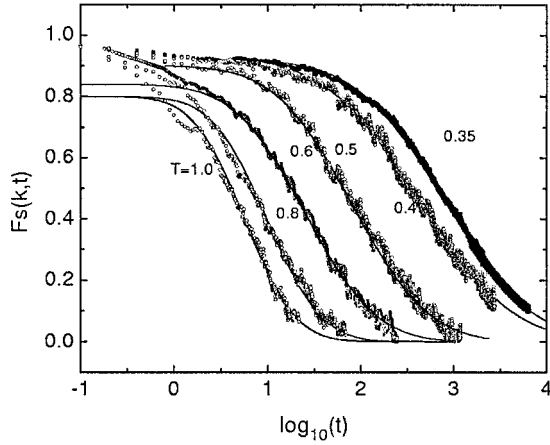


FIG. 2. The density autocorrelation function $F_s^1(k, t)$ for the first kind of particles at six temperatures, $T=1.0, 0.8, 0.6, 0.5, 0.4, 0.35$ (from left to right) for the wave number $k=4.5$. The symbols indicate the values obtained by the MD simulations, the lines are fits to Eq. (6).

time scale of the simulations that determines the glass transition. Thus, the glass transition temperature is about $T_g = 0.3$.

The self-part of the density autocorrelation $F_s^\mu(k, t)$ is relevant to structural relaxation. It is defined as.

$$F_s^\mu(k, t) = \frac{1}{N} \sum_{\mu, j=1}^{N_\mu} \langle \exp\{i\vec{k} \cdot [\vec{r}_j^\mu(t) - \vec{r}_j^\mu(0)]\} \rangle, \quad (5)$$

where \vec{k} is the wave number vector. Since the motion of the particles is essentially ballistic for short times, the correlator usually shows a quadratic dependence on time. For intermediate and long times at low temperatures, a shoulder forms and is accompanied by the nonexponential relaxation. It has been observed [22] that when k is large, the height of the plateau of F_s^μ becomes smaller, and although the relaxation time depends on k , the relaxation times at different k differ only by a constant factor at each temperature. Namely, $\tau_{k1} = a\tau_{k2}$, where τ_{k1} is the relaxation time at $k=k1$, τ_{k2} is the relaxation time at $k=k2$ for the same temperature, and a is a constant uncorrelated to the temperature. When the plateau of F_s^μ becomes smaller, it is inconvenient to extract the relaxation time. So we select $k=4.5$, which is smaller than the main peak of the structure factor located around $k=6.5$.

Figure 2 shows the density autocorrelation function $F_s^1(k, t)$ for a few temperatures determined for $k=4.5$. At low temperatures, for intermediate times, a shoulder begins to form, showing nonexponential relaxation.

It is believed that at short times, a particle is surrounded by an effective cage, which keeps the particle close to its original position. This cage can be thought of as a cooperatively rearranging region (CRR). The particle remains in the cage for the time interval $\tau' = A \exp(E_a/k_B T)$, where E_a is the potential barrier height, T is the temperature, k_B is the Boltzman constant, and A is a constant. Since local equilibrium fluctuations arising in the arrangements of the molecules will always be present, there are many cages with different barrier heights. Then there is a distribution of relaxation times τ , which describes the average lifetime of the

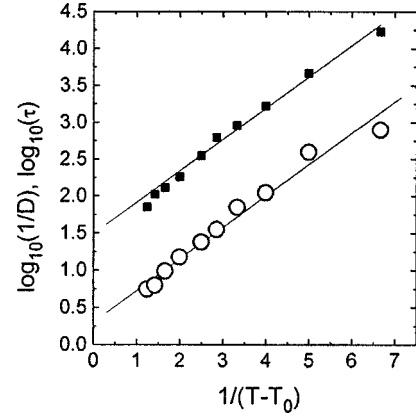


FIG. 3. Temperature dependence of the relaxation time (circle) and self-diffusion constant (square). The solid lines are fits to the Vogel-Fulcher law with $T_0=0.202$.

local structure. Supposing that there are N cages, the lifetime t_i , customarily indicated by $\log_{10}t_i$, of the i th cage is a random variable, and the average lifetime of the cages, i.e., the local relaxation time, is $\log_{10}\tau_i$. Since the CRR can be viewed as independent statistical systems [23], the random variables $\log_{10}t_i$ are independent. Moreover, N is so large that the conditions of the central limit theorem are satisfied. Based on the probability model of relaxation presented by our group [24], the relaxation function $\phi(t)$ can be taken as the density autocorrelation function $F_s(k, t)$, and is proportional to the probability that the lifetime of the system is longer than the observation time. Then the probability, i.e., relaxation function $\phi(t)/\phi_0$, can be written as

$$\frac{\phi(t)}{\phi_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{\log_{10}(t/\tau)}{\sqrt{2}\sigma} \right), \quad (6)$$

where the erfc is the complementary error function, $\log_{10}\tau$ is the relaxation time or the average lifetime of the system, and σ is the half-width of the distribution of the lifetime on a $\log_{10}t$ abscissa.

We now can use this probability model to study the structure relaxation of the supercooled liquid. The lines in Fig. 2 were obtained by fitting the data with Eq. (6), the fitting parameters are σ , ϕ_0 , and τ . In this way, the relaxation time τ and width σ of the the distribution of the relaxation times were obtained. Figure 3 shows temperature dependence of the relaxation time. It can be seen that the temperature-relaxation time relation obeys the Vogel-Fulcher law,

$$\tau = \tau_0 \exp \left(\frac{E}{T - T_0} \right), \quad (7)$$

where $\tau_0 = 1.997$, $E = 0.9802$, $T_0 = 0.202$.

The width of the distribution of lifetimes of the cages is shown in Fig. 4. showing that it increases with decreasing temperature, denoting that the heterogeneity is more prominent at the lower temperatures. It is also seen in experimental measurements on glasses [25,26] that the width of the distribution increasing with decreasing temperature. This can be understood as follows. When the temperature decreases, there are regions whose lifetimes are much longer than others. It is relevant to the observations of Kob *et al.* [12] that

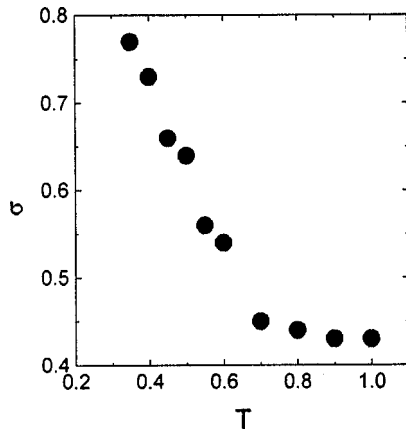


FIG. 4. Temperature dependence of the width of the distribution of the lifetimes of the cages.

there are some “mobile” particles in the supercooled liquid and that of Johnson *et al.* [15] that there are long-lived structures in a two-dimensional Lennard-Jones liquid.

The self-diffusion constants were also calculated by using the Einstein relation

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} [r_i(t) - \vec{r}_i(0)]^2. \quad (8)$$

The temperature dependence of the self-diffusion constant is shown in Fig. 3, and it also obeys the Vogel-Fucher law, $D = D_0 \exp[-E/(T-T_0)]$. With E and T_0 taking the same value as in Eq. (7), we get $D_0 = 0.03238$. It shows that the self-diffusion constant has the same dependence as the relaxation time, suggesting that the nonexponential structure relaxation is related to the particles moving out of the cages.

IV. CONCLUSION

Our two-component MD simulations for a supercooled liquid have shown that the nonexponential structure relaxation is due to the dynamical heterogeneities, and that the distribution width of the lifetime of the local cages, representing the dynamical heterogeneities, increases when the temperature decreases. The relaxation time obtained with this model shows the same temperature dependence as the self-diffusion constant. It denotes that the nonexponential structure relaxation corresponds to the particles moving out of their localized “cages.”

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- [1] M. D. Ediger, C. A. Angell, and S. R. Nagel, *J. Phys. Chem.* **100**, 13 200 (1996).
 - [2] *Structure and Dynamics of Glasses and Glasses Formers*, edited by C. A. Angell, K. L. Ngai, J. Kieff, T. Egami, and G. U. Niehaus, MRS Symposia Proceedings No. 455 (Material Research Society, Pittsburgh, 1997).
 - [3] G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
 - [4] M. H. Cohen and G. Grest, *Phys. Rev. B* **20**, 1077 (1979).
 - [5] F. H. Stillinger, *J. Chem. Phys.* **89**, 6461 (1988).
 - [6] K. L. Ngai, R. W. Rendell, and D. J. Plazek, *J. Chem. Phys.* **94**, 3018 (1991).
 - [7] R. Richert, *J. Non-Cryst. Solids* **172-174**, 209 (1994).
 - [8] K. Schmidi Rohr and H. W. Species, *Phys. Rev. Lett.* **66**, 3020 (1991).
 - [9] T. Muranaka and Y. Hiwatari, *Phys. Rev. E* **51**, R2735 (1995).
 - [10] M. M. Hurley and P. Harrowell, *Phys. Rev. E* **52**, 1694 (1995).
 - [11] C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, *Phys. Rev. Lett.* **80**, 2338 (1998).
 - [12] W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, *Phys. Rev. Lett.* **79**, 2827 (1997).
 - [13] B. Doliwa and A. Heuer, *Phys. Rev. Lett.* **80**, 4915 (1998).
 - [14] R. Yamamoto and A. Onuki, *Phys. Rev. E* **58**, 3515 (1998).
 - [15] G. Johnson, A. I. Mel'cuk, H. Gould, W. Klein and R. D. Mountain, *Phys. Rev. E* **57**, 5707 (1998).
 - [16] A. Heuer and K. Okun, *J. Chem. Phys.* **106**, 6176 (1997).
 - [17] P. Ray and K. Binder, *Europhys. Lett.* **27**, 53 (1994).
 - [18] S. Nose, *Mol. Phys.* **52**, 255 (1984); W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
 - [19] B. Bernu, J. P. Hansen, Y. Hiwatari, and G. Pastore, *Phys. Rev. A* **36**, 4891 (1987).
 - [20] J. N. Roux, J. L. Barrat, and J. P. Hansen, *J. Phys.: Condens. Matter* **1**, 7171 (1989).
 - [21] T. V. Ramakrishnan, *J. Non-Cryst. Solids* **117-118**, 852 (1990).
 - [22] W. Kob and H. C. Andersen, *Phys. Rev. E* **52**, 4134 (1995).
 - [23] D. Thirumalai, R. D. Mountain, and T. R. Kirkpatrick, *Phys. Rev. A* **39**, 3563 (1989).
 - [24] H. Z. Zhuang, X. W. Zou, Z. Z. Jin, and D. C. Tian, *Phys. Rev. B* **55**, 14 047 (1997).
 - [25] P. K. Dixon and S. R. Nagel, *Phys. Rev. Lett.* **61**, 341 (1988).
 - [26] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, *Phys. Rev. Lett.* **65**, 1108 (1990).