

Abstract. After brief review of our recent simulation studies on kinetic heterogeneity in supercooled liquids, we report finite-size effects observed in computer simulations by decreasing system size from $N = 10^4$ to 10^3 and 108. Although no significant deviation is detected in the static pair correlation functions, it is demonstrated that the structural α relaxation in smaller systems become considerably slower than that in larger systems for temperatures below T_x at which the size of the cooperative particle motions becomes comparable to the unit cell length of the small system. Also the effects of confinements in planar walls are reported.

1. INTRODUCTION

Heterogeneity in the dynamics of supercooled liquids, *i.e.*, coexistence of mobile (cluster- or string-like) and immobile regions, have been detected by a number of molecular dynamics (MD) simulations with various visualization methods [1]-[7]. Those observations strongly suggest that rearrangements of particle configurations in glassy materials are cooperative, involving many molecules. To understand nature of the heterogeneity quantitatively, we have examined bond breakage processes among adjacent particle pairs and found that the spatial distribution of broken bonds in an appropriate time interval ($\sim \tau_\alpha \simeq 0.1\tau_b$, where τ_α is the structural α relaxation time and τ_b is the average bond life time) is very analogous to the critical fluctuation in Ising spin systems. The structure factor of the broken bonds is excellently fitted to the Ornstein-Zernike form [1], and the correlation length ξ thus obtained grows rapidly with decreasing temperature as shown in Table 1. We demonstrated furthermore that ξ is related to τ_α through the dynamical scaling law, $\tau_\alpha \sim \xi^z$ with $z \simeq 4$ in 2D and $z \simeq 2$ in 3D. As shown later, the heterogeneity structure in our bond breakage is essentially the same as that in local diffusivity [2], which leads to a systematic violation of the Stokes-Einstein law in supercooled states. Since the dynamical correlation length ξ in supercooled liquids grows rapidly with lowering the temperature, it seems quite reasonable to expect some kinds of finite-size effects in the dynamics of supercooled liquids when ξ becomes comparable to the system size L , even if no such effect is detectable in the static correlation functions. In this paper, we report apparent finite size effects observed in the dynamics of a simple soft sphere liquid in supercooled conditions [8]. The size effects due to confinements in planar walls are studied, as well as those under the periodic boundary condition (PBC).

2. SIMULATIONS AND RESULTS

We here summarize only important parameters only details of simulations are given in our earlier papers [1, 2]. Our model mixture is composed of two kinds of particles (1 and 2) which interact via the soft-core potential

$$U_{SS}(r) = \epsilon(\sigma_{ab}/r)^{12}, \tag{1}$$

Table 1. Correlation length ξ of the bond breakage processes obtained from $N = 10^4$ system in 3D.

T	0.772	0.473	0.352	0.306	0.267
ξ	2.1	5.8	11.	22.	130.

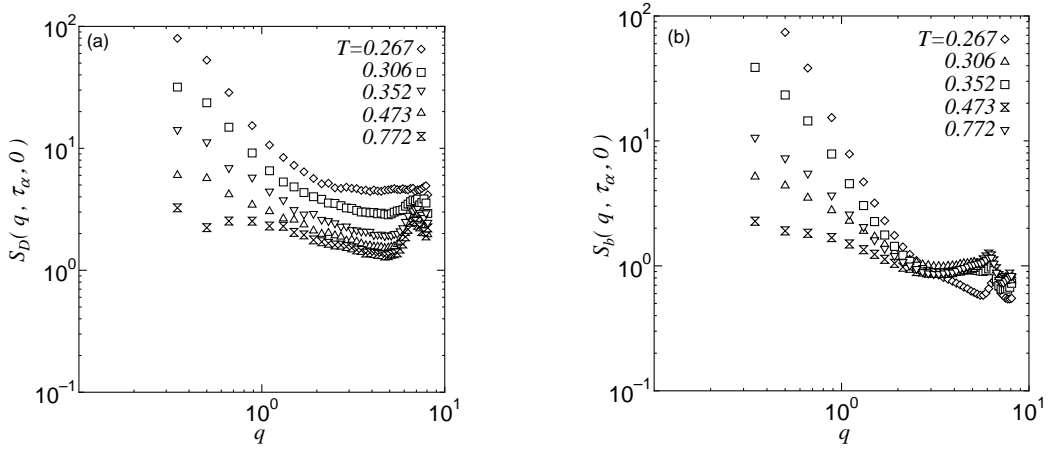


Figure 1. Correlation functions $S_{\mathcal{D}}(q, \tau_{\alpha}, 0)$ in (a) and $S_b(q, \tau_{\alpha}, 0)$ in (b). Large q values of $S_{\mathcal{D}}(q, t, 0)$ are related to the non-Gaussian parameter $A_2(t)$ via $\lim_{q \rightarrow \infty} S_{\mathcal{D}}(q, t, 0) = \langle [\Delta \mathbf{r}^1(t; t_0)]^4 \rangle / \langle [\Delta \mathbf{r}^1(t; t_0)]^2 \rangle^2 = 5(A_2(t) + 1)/3$.

where $\sigma_{ab} = (\sigma_a + \sigma_b)/2$ and $a, b \in 1, 2$. The size ratio $\sigma_1/\sigma_2 = 1/1.2$ and the mass ratio $m_1/m_2 = 1/2$ are taken, while $\epsilon_1 = \epsilon_2 = \epsilon$. The units of length, time, and temperature are $\sigma_1, \tau_0 = (m_1 \sigma_1^2 / \epsilon)^{1/2}$, and ϵ/k_B . Structural relaxations in liquids can be monitored by calculating the coherent or incoherent intermediate scattering functions, $F(q, t)$ or $F_s(q, t)$. Decay profiles of those two functions are known to be very similar at the first peak wave number q_m in $F(q, 0)$. Since $F_s(q, t)$ can be more accurately determined via MD simulations, we calculate the incoherent scattering function for component 1,

$$F_s(q, t) = \left\langle N_1^{-1} \sum_{j=1}^{N_1} \exp[i\mathbf{q} \cdot \Delta \mathbf{r}_j^1(t; t_0)] \right\rangle_{t_0}, \quad (2)$$

where $\Delta \mathbf{r}_j^1(t; t_0) = \mathbf{r}_j^1(t + t_0) - \mathbf{r}_j^1(t_0)$ is the displacement vector in terms of j th particle in component 1, and $\langle \cdots \rangle_{t_0}$ presents an average over initial times t_0 and independent MD runs. We then defined the α relaxation time τ_{α} , by $F_s(q, \tau_{\alpha}) = e^{-1}$ at a dimensionless wave number $q = 2\pi$.

2.1 Heterogeneity in local diffusivity

We have performed MD simulations in three-dimensional space for a system composed of $N = N_1 + N_2 = 10^4$ particles with a fixed density $\rho = N/L^3 = 0.8$ and a composition $x_1 = N_1/N = 0.5$. Simulations were carried out in a cubic box with dimension $L = 23.2$ at temperatures $T = 0.772, 0.473, 0.352, 0.306$ and 0.267 . The PBC was used in all cases. At each temperature, the system was carefully equilibrated in the canonical condition so that no appreciable aging effect takes place. Data were then taken in the microcanonical condition. To characterize the heterogeneity structure [2], we consider the Fourier component of the local *diffusivity* density for component 1 defined by

$$\mathcal{D}_{\mathbf{q}}(t_0, t) \equiv \sum_{j=1}^{N_1} a_j(t)^2 \exp[-i\mathbf{q} \cdot \mathbf{R}_j(t)], \quad (3)$$

where $a_j(t)^2 \equiv [\Delta \mathbf{r}_j^1(t; t_0)]^2 / \langle [\Delta \mathbf{r}^1(t; t_0)]^2 \rangle$ and $\mathbf{R}_j(t) \equiv \frac{1}{2}[\mathbf{r}_j^1(t_0) + \mathbf{r}_j^1(t_0 + t)]$. Note that $\mathcal{D}_{\mathbf{q}}(t_0, t)$ depends on the initial time t_0 and the final time $t_0 + t$. The correlation function $S_{\mathcal{D}}(q, t, \tau) = \langle \mathcal{D}_{\mathbf{q}}(t_0 + \tau, t) \mathcal{D}_{-\mathbf{q}}(t_0, t) \rangle_{t_0}$ is then obtained after averaging over many initial states. We plot $S_{\mathcal{D}}(q, \tau_{\alpha}, 0)$ in Fig.1(a) and also the structure factor of the bond breakage $S_b(q, \tau_{\alpha}, 0)$ in Fig.1(b). It is confirmed that both $S_{\mathcal{D}}(q, \tau_{\alpha}, 0)$ and $S_b(q, \tau_{\alpha}, 0)$ tend to those long wavelength limits for $q \lesssim \xi^{-1}$, where ξ is the correlation length of the bond breakage processes [1]. Time evolutions of the the heterogeneity structure $S_{\mathcal{D}}(q, t, \tau > 0)$ have also been studied [3] but not contained in this paper.

2.2 System size effects with periodic boundary

Besides the $N = 10^4$ system discussed above, we have performed MD simulations also for smaller systems composed of $N = 108$, and 10^3 particles with fixed $\rho = 0.8$ and $x_1 = 0.5$ using the PBC.

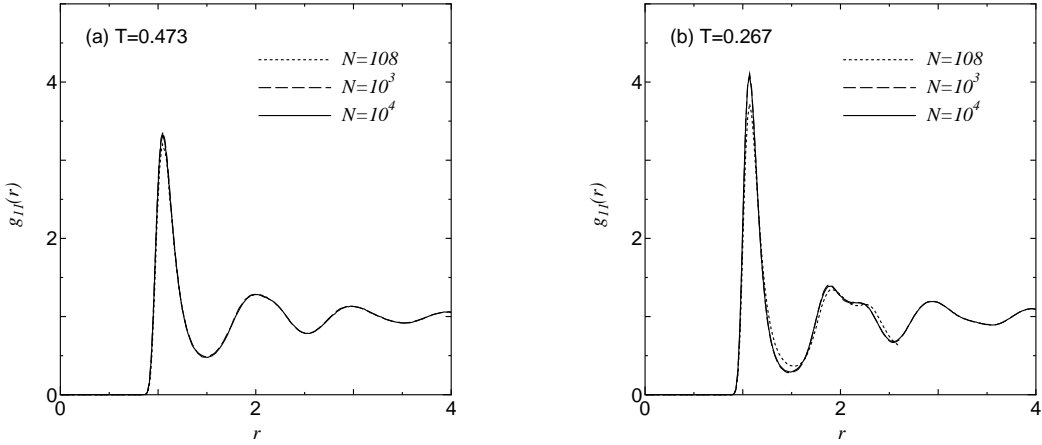


Figure 2. Partial radial distribution function $g_{11}(r)$ at $T = 0.473$ (a) and at $T = 0.267$ (b).

The corresponding system linear dimensions are $L^{N=108} = 5.13$, $L^{N=10^3} = 10.8$, and $L^{N=10^4} = 23.2$. We first calculate the partial radial distribution functions,

$$g_{ab}(r) = [\langle \hat{n}_a(\mathbf{r})\hat{n}_b(\mathbf{0}) \rangle - N_a\delta_{ab}\delta(r)]/x_ax_b\rho N, \quad (4)$$

to investigate whether finite-size effects are detectable in static pair-correlations. Here $\hat{n}_a(\mathbf{r}) = \sum_{j=1}^{N_a} \delta(\mathbf{r} - \mathbf{r}_j^a)$ is the number density of component a . We plot $g_{11}(r)$ for $N = 108$, 10^3 , and 10^4 systems at $T = 0.473$ in Fig.2(a) and $T = 0.267$ in Fig.2(b). One can find that at both temperatures $g_{11}(r)$ for all systems agrees fairly well; no significant size dependence can be detected except for small deviations of $N = 108$ data at $T = 0.267$. Here the height of the first peak is slightly lower for $N = 108$ than others. We examined also 12 and 22 components and confirmed the same tendencies as in $g_{11}(r)$. Our results indicate that finite-size effects are very small or almost negligible in static pair correlations for $N \gtrsim 10^2$, as that is generally expected.

Let us next consider finite-size effects in dynamical properties. Figure 3(a) shows decay profiles of $F_s(q = 2\pi, t)$ obtained for $N = 108$, 10^3 , and 10^4 systems at $T = 0.473$ and 0.267 . At $T = 0.473$, we see that the two curves for $N = 10^3$ and 10^4 entirely coincide, and one for $N = 108$ is also close to them. The relaxation times thus obtained are $\tau_\alpha^{N=108} \simeq 3.5$, $\tau_\alpha^{N=10^3} = \tau_\alpha^{N=10^4} \simeq 2.3$. At $T = 0.267$ where we observe two-step relaxations (the faster and the slower parts are called the fast- β and the α relaxations, respectively) in $F_s(q, t)$, the decay profiles of the three systems differ significantly in the α regime ($t \gtrsim 10^2$), whereas they agree well in the fast- β regime ($t \lesssim 1$). We have determined $\tau_\alpha^{N=108} \simeq 27\,000$, $\tau_\alpha^{N=10^3} \simeq 6500$, and $\tau_\alpha^{N=10^4} \simeq 2000$ at $T = 0.267$. Figure 3(b) shows the temperature dependence of $\tau_\alpha^{N=108}$, $\tau_\alpha^{N=10^3}$, and $\tau_\alpha^{N=10^4}$. At the highest temperature $T = 0.772$, $\tau_\alpha^{N=108}$, $\tau_\alpha^{N=10^3}$, and $\tau_\alpha^{N=10^4}$ are exactly equal. However, $\tau_\alpha^{N=108}$ begins to deviate from the others around $T = 0.473$ at which $\xi = 5.8$ is comparable to $L^{N=108} = 5.13$. The deviation of $\tau_\alpha^{N=108}$ increases with further decreasing temperature, and $\tau_\alpha^{N=108}$ becomes almost one order larger than $\tau_\alpha^{N=10^4}$ for $T \lesssim 0.352$. Similarly, $\tau_\alpha^{N=10^3}$ begins to deviate from $\tau_\alpha^{N=10^4}$ around $T = 0.306$, at which $L^{N=10^3} < \xi < L^{N=10^4}$. We suppose that the present finite-size effects, slower relaxations in smaller systems at low T , are attributable to suppression of cooperative particle motions due to insufficient system size. The structural relaxation time of smaller systems thus tends to show a stronger (super-Arrhenius) temperature dependence as a result of the finite-size effects. Remembering the fact that the static pair-correlations are almost identical in those three systems at all temperatures, higher order correlations in particle configurations may be relevant to this effect. Finite-size effects in the dynamics have already been examined by several authors [9]-[11]. Horbach *et al.* found similar finite-size effects in a model silica glass which is known as a typical *strong* glass former, while the present soft sphere is classified in *fragile* glass former.

To understand what happens in microscopic scale, we visualize individual particle motions in $N = 10^4$ system at $T = 0.267$. First, we pick up mobile particles by the condition $|\Delta\mathbf{r}_j^a(t; t_0)| > l_c^a$, where $t = 0.125\tau_\alpha = 250$, and l_c^a is a cut-off length defined separately for component $a \in 1, 2$ such that the sum of $\Delta\mathbf{r}_j^a(t)^2$ over the mobile particles covers 66% of the total sum $\sum_j^{N_a} \Delta\mathbf{r}_j^a(t)^2$. We now define clusters of the mobile particles by connecting i and j if $|\mathbf{r}_i(t) - \mathbf{r}_j(0)| < 0.3(\sigma_i + \sigma_j)$

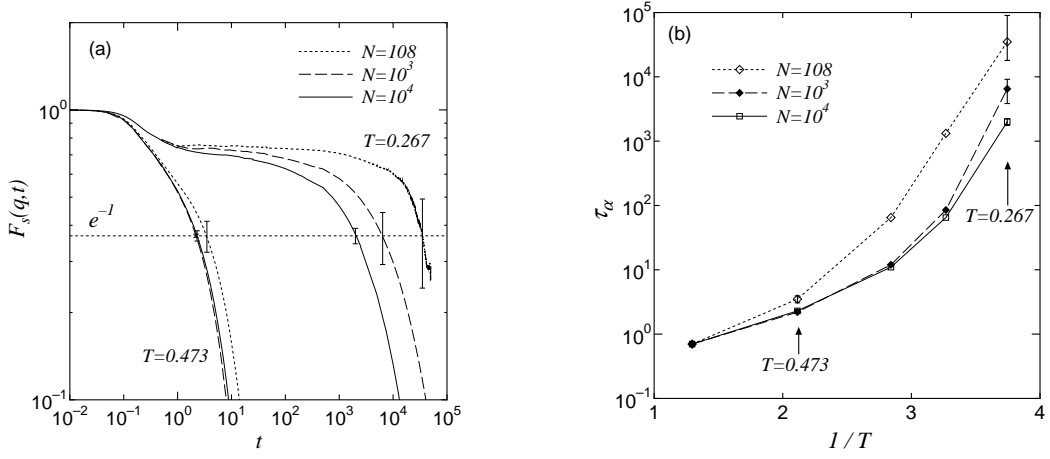


Figure 3. (a) Incoherent intermediate scattering function $F_s(q, t)$ of component 1 with $q = 2\pi$ at $T = 0.473$ and 0.267 . The error bars present the standard deviations $\delta_y = \sqrt{\langle A^2 \rangle_{t_0} - \langle A \rangle_{t_0}^2}$ with $A \equiv \frac{1}{N_1} \sum_{j=1}^{N_1} \exp[i\mathbf{q} \cdot \Delta \mathbf{r}_j^1(\tau_\alpha; t_0)]$. (b) Temperature dependence of τ_α for $N = 108$ (open diamonds), 10^3 (closed diamonds), and 10^4 (open squares). The error bars present

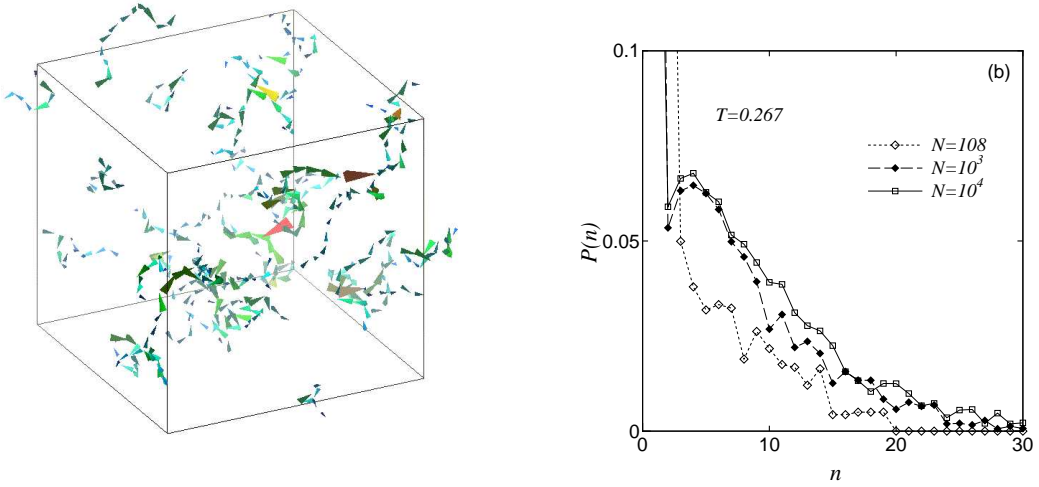


Figure 4. (a) Spatial distribution of particle displacements belonging to clusters with size $n \geq 5$ at $T = 0.267$ for $N = 10^4$. The arrows indicates individual particle displacements. (b) $P(n)$ vs n at $T = 0.267$ for $N = 108$ (open diamonds), 10^3 (closed diamonds), and 10^4 (open squares).

or $|\mathbf{r}_i(0) - \mathbf{r}_j(t)| < 0.3(\sigma_i + \sigma_j)$ similar to Donati *et al.* [7]. In Fig.4(a), we show spatial distribution of the clusters having the size $n \geq 5$; those are all chain-like [7] and exhibit long-range correlations. Although only 5% of the total particles are shown in Fig.4(a), the sum of $\Delta \mathbf{r}_j(t)^2$ covers approximately 40% of the total $\sum_{i=1}^N \Delta \mathbf{r}_j(t)^2$ indicating clearly that the chain-like cooperative motion becomes dominant in glassy dynamics. To investigate possible finite-size effects in the cooperative motions quantitatively, we here introduce the distribution function,

$$P(n) = \frac{\sum_{i=1}^N \Delta \mathbf{r}_j(t)^2 \delta(n - n_i)}{\sum_{i=1}^N \Delta \mathbf{r}_j(t)^2}, \quad (5)$$

where the sum runs over mobile particles only. n_i is the size of the cluster in which the mobile particle i belongs, and thus $\delta(n - n_i)$ is 1 if i is a member of the cluster having the size n and 0 if not. The physical meaning of $P(n)$ is as follows; cooperative motions involving n particles contribute $P(n)$ to the total squared displacements of the mobile particles. In Fig.4(b), we plot $P(n)$ for $N = 108$, 10^3 , and 10^4 at $T = 0.267$ and found that the cooperative motions in $N = 108$ system are strongly suppressed. It is found also that larger scale cooperative motions ($n > 10$) are considerably suppressed in $N = 10^3$ comparing to $N = 10^4$. The characteristic cluster size $\bar{n} = \sum_{i=1}^{\infty} nP(n)$ is 3.38, 6.11, and 7.73 for $N = 108$, 10^3 , and 10^4 , respectively.

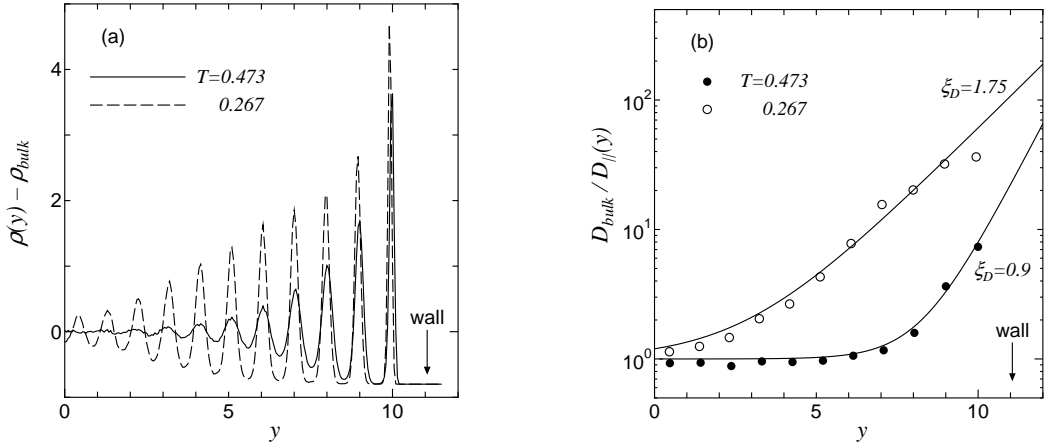


Figure 5. (a) Density profiles as a function of y . (b) Profiles of effective diffusion constants as a function of y . y is the distance from the film center in the direction normal to the wall.

2.3 Effects of confinement in planar walls

We have studied properties of supercooled simple liquids in a thin film geometry where liquids are confined between smooth planar walls. The wall-particle interaction is modeled simply by

$$U_W(r_{w\pm}) = \epsilon[(\sigma_w/r_{w+})^{12} + (\sigma_w/r_{w-})^{12}], \quad (6)$$

where $\sigma_w = (\sigma_a + 1)/2$ and $r_{w\pm} = \pm 0.5h - y_i$. The gap h between two walls follows the over-damped equation of motion

$$dh/dt = \zeta^{-1}(P_w - P_{set}) \quad (7)$$

with $\zeta = 1$, where $P_w = L^{-2} \sum_{i=1}^N (dU_W/dr_{w-} - dU_W/dr_{w+})$. This will fix the normal stress P_w of the film equal to the bulk pressure P_{set} which is an input parameter and already known as a function of T . Figure 5(a) shows density profiles in the direction normal to the film (y) at $T = 0.267$ and 0.473 . Envelopes of the density oscillation are roughly fitted to a simple form

$$\rho(y)/\rho_{bulk} = 1 + A \exp[-(0.5h - y)/\xi_\rho], \quad (8)$$

where A is a fitting parameter and correlation lengths $\xi_\rho = 1.8$ and 3.5 are obtained at $T = 0.473$ and 0.267 , respectively. Figure 5(b) presents profiles of the effective in-plane diffusion constant $D_{||}$ as a function of y . Again $D_{||}$ can be fitted well to the simple form

$$D_{bulk}/D_{||}(y) = 1 + B \exp[-(0.5h - y)/\xi_D], \quad (9)$$

where B is a fitting parameter, and the choice $\xi_D = \xi_\rho/2$ gives better results shown in Fig.5(b). So far from our simulation results in confined geometry, it is still difficult to conclude whether the observed decrease in particle mobility near the wall is solely attributable to (rather trivial) interface effects or suppression of collective motions, because both ξ_ρ and ξ_D grow with lowering T in a similar manner as that for ξ observed in bulk simulations [1].

3. DISCUSSIONS

In the framework of conventional liquid theories [12], changes in static particle configurations upon cooling lead to a drastic slowing-down toward the glass transition. The mode coupling theory (MCT) [13, 14] is the most successful self-consistent approach within this framework. In the original MCT, however, a sharp ergodic/non-ergodic transition is predicted at a temperature T_c which is considerably above T_g . Since such sharp transitions has never been observed in real glassy materials, it is believed that the MCT has some difficulties for describing the true dynamics of supercooled liquids apparently below T_c . The main problem is the fact that the original MCT do not take into account the hopping motions of particles, which must be cooperative and thus long ranged as is seen in recent MD simulations [1]-[7]. It is an interesting fact that the behavior of structural relaxations in small systems, in which cooperative hopping motions are highly suppressed, becomes somehow closer to the original MCT prediction.

In the case of confined supercooled liquids, wall-liquid interface strongly *suppressed* particle mobility in our present simulations for a simple liquid. This seems to contradict to some recent experiments on glass-forming thin films [15]-[18], where particle motions are more *enhanced* in thinner films. Enhancement of particle mobility has also been observed in recent MD simulations for $\text{Ni}_{0.5}\text{Zr}_{0.5}$ metallic glass films, where a free (glass-vacuum) surface was considered [19]. Although the situation is still controversial, we suppose that the dynamics in confined geometries must be strongly affected by characters of the interface. Therefore it seems still difficult to conclude naively that the experimentally observed enhancement in particle mobility is attributable to the finite size effects on the cooperative motions. Very careful treatments to excludes interface effects must be necessary.

4. SUMMARY

We have successfully characterized heterogeneity in the dynamics of supercooled liquids and examined possible system-size effects by use of MD simulations. Significant finite-size effects have been found in the structural relaxation function at low temperatures, whereas no such effect is detectable in static pair-correlation functions. The cooperative particle motions, which leads to the α relaxation in glassy states, are strongly suppressed in smaller systems for temperatures lower than T_x at which ξ becomes comparable to the system size. The present finite-size effects are regarded as a natural consequence of the dynamical heterogeneity appearing in supercooled liquids.

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Heterogeneity and finite size effects in the dynamics of supercooled liquids

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