

β relaxation in a highly supercooled state via molecular dynamics simulation

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We have studied the β relaxation of the density autocorrelation for a two dimensional model fluid via molecular dynamics (MD) simulation. We have found that correlated motions composed of many particles occur in the time scales of about 20 times the time scales of the thermal oscillations, which corresponds to the β peak frequency of the imaginary self-part of the generalized susceptibility. It is also discussed that the self-part of the density autocorrelation function $F_s(k,t)$ below the glass transition temperature ($\Gamma_{\text{eff}}=1.2-1.3$) presents an oscillatory behavior at the time scales of about 100 times the time scales of the thermal oscillations, which may be caused by the periodic boundary conditions adopted in the MD simulation as usual.

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Neutron spin-echo measurements on $F(k,t)$ [1] revealed two types of distinct relaxations in the ionic system $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ (CKN). Cummins *et al.* [2] have recently measured the dynamical properties of the same material with light scattering, and analyzed both α and β relaxations in detail, leading to a conclusion that their experiments are consistent with the mode-coupling theory [3]. On the other hand, molecular dynamics (MD) simulations [4-6] have found that the jump motion of atoms is an essential nature of the α relaxation in supercooled fluids. Theoretical works have recently been proposed, which take into consideration such jump motions phenomenologically.

In this paper we have carried out an MD simulation using a two dimensional (2D) soft-core model fluid to study the dynamical features in a different (lower) dimensionality, which is also much more advantageous than 3D in visualizing the data.

Since the α relaxation in highly supercooled fluids close to the liquid-glass transition is essentially due to the jump-motion diffusion, to study the α relaxation by MD simulation one inevitably needs a super-long-time calculation [8]. In fact, the jump motions rarely take place near the glass transition temperature: there are only several jump motions for the period of τ [see Eq. (3) for the definition] in a system of 10 000 atoms. In the present work we focus on the β relaxation, which has much less extensively been studied so far in molecular levels. The β relaxation takes place in much shorter time scales than the α relaxation, and is rather insensitive to the temperatures of the system [7]. Thus motives of the present work are as follows: we do not need a super-long-time MD simulation, and the β relaxation can much more easily be studied at low temperatures than is possible for the α relaxation.

The β peak in the imaginary part of the generalized susceptibility $\chi''_s(k,\omega)$ appears in the time scales of the order of several times τ [8]. Since the period of thermal oscillations (Einstein frequency) of atoms turns out to be at least one order of magnitude smaller than the time scale of the β peak, the β peak can be well separated from the peak corresponding to the Einstein frequency. Then, one may ask what type

of atomic motions cause the β relaxation. This is our main concern in this work and for this purpose we have carried out an MD simulation for a two dimensional system composed of 10 000 particles.

The present model is composed of equal numbers of two different species of 5000 atoms each ($N_1=5000$, $N_2=5000$). The smaller (lighter) species has a diameter $\sigma_1=1.0$ and a mass $m_1=1.0$, and the larger (heavier) species has a diameter $\sigma_2=1.4$ and a mass $m_2=2.0$. The periodic boundary conditions were adopted as usual. Numerical time integrations were carried out with the velocity form of the Verlet algorithm [9], and the temperature of the system was controlled with the Nosé algorithm [10].

Atoms interact through the purely repulsive soft-core potentials:

$$v_{\alpha\beta}(r_{ij}) = \varepsilon(\sigma_{\alpha\beta}/r_{ij})^{12}, \quad (1)$$

where

$$\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2, \quad r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|, \quad (2)$$

and α and β are species indices (1 or 2). The cutoff radius of the interaction was chosen to be $4.5\sigma_1$. Hereafter we use the following units: σ_1 (the unit of length), m_1 (the unit of mass), and ε (the unit of energy). The reduced unit of time is chosen to be

$$\tau = \sqrt{m_1\sigma_1^2/\varepsilon}. \quad (3)$$

(For example, τ is 2.45×10^{-12} sec for an argon liquid.) We also use the reduced temperature $T^* = k_B T/\varepsilon$ and the reduced number density $\rho^* = N/S$, where N is the total number of atoms ($=10\,000$) and S is the total area of the system in units of σ_1^2 . In the present work the reduced number density is fixed at $\rho^* = 0.8$.

According to the scaling property of the inverse power potentials, all reduced equilibrium properties of the model fluid depend only on the coupling constant $\Gamma = \rho^*(T^*)^{-1/6}$ apart from the core-size ratio σ_2/σ_1 and the concentration χ_1 or χ_2 , where $\chi_1 = N_1/N$ and $\chi_2 = 1 - \chi_1$. It is convenient to use the following effective coupling constant for the bi-

nary mixtures using the effective one-component approximation [11] as in the case of the three dimensional soft-core system:

$$\Gamma_{\text{eff}} = \Gamma(\sigma_{\text{eff}}/\sigma_1)^2, \quad (4)$$

where

$$\Gamma = \rho^*(T^*)^{-1/6}, \quad \sigma_{\text{eff}}^2 = \sum_{\alpha} \sum_{\beta} \chi_{\alpha} \chi_{\beta} \sigma_{\alpha\beta}^2. \quad (5)$$

In our molecular dynamics simulations, starting from a liquid equilibrated at $\Gamma_{\text{eff}} = 0.8$ ($T^* = 9.685$), which was obtained from initially randomized two species configurations on simple square lattices, we have obtained supercooled states by means of rapid cooling of the liquid. In this paper we investigate a glassy state simulated over the time steps between 1000τ and 1500τ at $\Gamma_{\text{eff}} = 1.4$ ($T^* = 0.3372$). In argon fluid the above condition corresponds to quenching from $T = 1115$ K (liquid) to 38.83 K (glass); the cooling rate becomes of the order of 10^{14} K/sec. The freezing point of the one-component soft-core model is about $\Gamma_{\text{eff}} = 0.987$ [12]. The glass transition point of the present model is around $\Gamma_{\text{eff}} = 1.2-1.3$, which is estimated by the analyses of the pair distribution functions [13].

By analyzing the movements of atoms on the display of our workstation, we have found remarkable correlated motions composed of many atoms in the time scales of several τ to a few dozen τ (Fig. 1). In Fig. 1 movements of atoms from $t = \tau$ to $t = 5\tau$ are shown, after being well equilibrated (annealing). The displacements of atoms for such periods are shorter than σ_1 , but substantially longer than the amplitude of thermal vibrations. Their directions are highly correlated. Previously, two types of correlated displacements of atoms have been reported for a glassy material [14], the linear correlation and the circular correlation. We have found that the circular correlation is very rare for our system. Therefore we assume the linear correlation is a main contribution. Below, we define ‘‘the correlated motion coefficient,’’ which measures the degree of correlated motion between the i th atom and the surrounding near atoms within the cutoff distance r_c . We call it $C_i(r_c, t)$, defined as

$$C_i(r_c, t) = \sum_{r_{ij} \leq r_c}^{N_i} \Delta \mathbf{r}_i(t) \cdot \Delta \mathbf{r}_j(t) / \overline{\Delta r^2(t)} N_i, \quad (6)$$

where $\Delta \mathbf{r}_i(t)$ is the displacement vector of the i th atom for an elapsed time t , $\overline{\Delta r^2(t)}$ is the mean square displacement for an elapsed time t , and N_i is the number of atoms within the distance r_c centered at the i th atom for $t = 0$.

Figure 2 shows the space distribution of $C_i(r_c, t)$. We see that there are large clusters of dark points marked by the highest gradation in the figure, connected to each other throughout the whole simulation cell. This is in contrast with the result obtained for $t = \tau$ (Fig. 3), in which the dark and white points are almost randomly distributed. Note that in the latter case the time scale is of the order of the thermal oscillations, while in the former it is 5τ . The C_i analysis indicates that atoms move in a correlated way for the time scales of several τ . The pattern of the C_i map is significantly

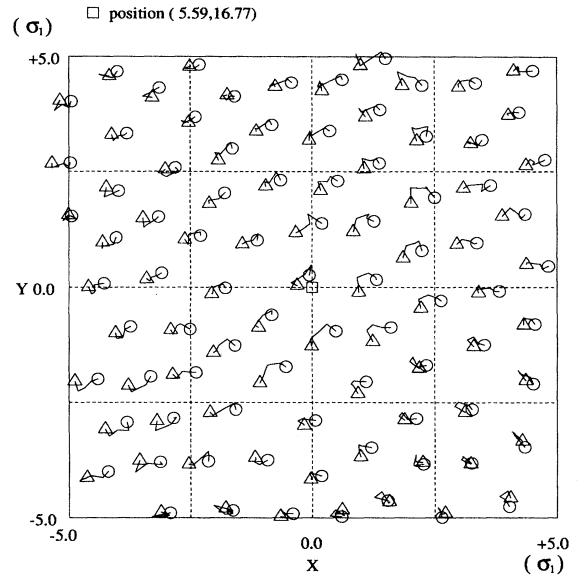


FIG. 1. Movements of atoms near the position (5.59,16.77) (the center of this figure) of the present simulation cell with a side length = $111.80\sigma_1$ for the period from τ to 5τ . The initial positions (at $t = \tau$) of atoms are marked by the circles and the final positions (at $t = 5\tau$) of atoms are marked by the triangles. The axes X, Y are the relative distance from central position (5.59,16.77) in units of σ_1 .

changed with t : The correlation domains change in place and time. It is interesting to note that such a characteristic time scale corresponds to that of the β peak as shown below (see Fig. 5). Figure 4 shows the averaged values of C_i , divided into five successive shells with an equal width $0.25\sigma_1$. It turns out that the values increase as t increases up to several τ and the strength of the correlation decreases as the distance from the origin increases.

The imaginary part of the generalized susceptibility (self-part) is shown in Fig. 5. The peak around $\log_{10}(\omega) \leq 2$ corresponds to the thermal vibrations. The peak between $\log_{10}(\omega) = 0$ and 1 (ω in the unit of τ^{-1}) is the β peak. The characteristic time is of the order of several τ .

Therefore it turns out that the correlated motions which we have obtained above (Figs. 1–4) are the molecular-level origin of the β relaxation. By analyzing the temperature dependence of the C_i , we have found that the correlation areas become significantly larger as the temperature is lowered. We will report on these analyses in detail in a forthcoming paper.

In Fig. 5, the highest and the near scattered data at the left (lower frequency) side of the β peak need special care: These are regarded as spurious results, which may be caused by the periodic boundary conditions imposed by the simulation, because the location of this spurious peak depends strongly on the system size, and it turns out that this is inversely proportional to the length of the simulation cell size.

Such an effect is also observed in $F_s(k, t)$ (see Fig. 6).

$$F_s^{(\alpha)}(k, t) = \left\langle \sum_{j=1}^{N_\alpha} \exp\{i\mathbf{k} \cdot \Delta \mathbf{r}_j^{(\alpha)}(t)\} \right\rangle / N_\alpha, \quad (7)$$

where α denote the species indices, and $\langle \dots \rangle$ denotes an

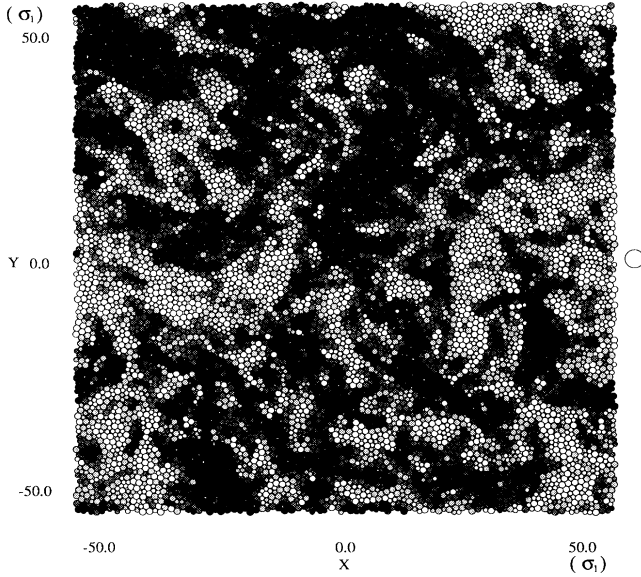


FIG. 2. The correlated motion coefficient $C_i(2.0,5.0)$ is calculated for all atoms ($N=10\,000$). A circle on the right side of this figure denotes the size of the cutoff radius ($r_c=2.0\sigma_1$). All circles indicate the initial positions of atoms with the respective size of each species. The gradation is made according to the (five classed) values of the C_i ; the darker the gradation is, the higher the value of the C_i . The axes X, Y are the absolute distance from central position $(0.0,0.0)$ in units of σ_1 .

initial time average. For large wave numbers the curves decrease monotonously up to $t\sim 15\tau$, then increase up to $t\sim 30\tau$, followed by clear oscillations. The oscillations repeat many times with about the same period (see Fig. 6). This behavior is commonly observed for both species. Mean square displacements and non-Gaussian parameters exhibit similar oscillatory behavior. The curves of $F_s^{(\alpha)}(k,t)$ at $\Gamma_{\text{eff}}=1.3$ also have such oscillatory behaviors, but much less weak. Mean square displacements and non-Gaussian parameters at $\Gamma_{\text{eff}}=1.3$ have the same tendency. Figure 6 was obtained by averaging over 5000 atoms (species 1 only) and 250 initial times. These results show a remarkable contrast to the result of $F_s^{(\alpha)}(k,t)$ obtained for the supercooled liquid at $\Gamma_{\text{eff}}=1.2$, which decreases smoothly without oscillations. The mean square displacement increases linearly as a function of time and the non-Gaussian parameter vanishes quickly (at very short time).

We have attempted to fit the MD data for $F_s^{(\alpha)}(k,t)$ in terms of the stretched exponential function of the form of the Williams-Watts law in the time range between τ and 1000τ :

$$f(t) = A \exp\left\{-\left(t/t_0\right)^\beta\right\}. \quad (8)$$

The best fitted value of β obtained is about 0.7, being significantly smaller than 1.0. This indicates that the system is in a highly supercooled state below the kinetic transition [15]. The present system is probably below the glass transition temperature.

Also we have compared the MD data for $F_s^{(\alpha)}(k,t)$ with the Gaussian approximation [5,16] of it, i.e.,

$$F_s^{(\alpha)}(k,t) \approx \exp\left[-\frac{1}{4}k^2\langle|\mathbf{r}^{(\alpha)}(t) - \mathbf{r}^{(\alpha)}(0)|^2\rangle\right], \quad (9)$$

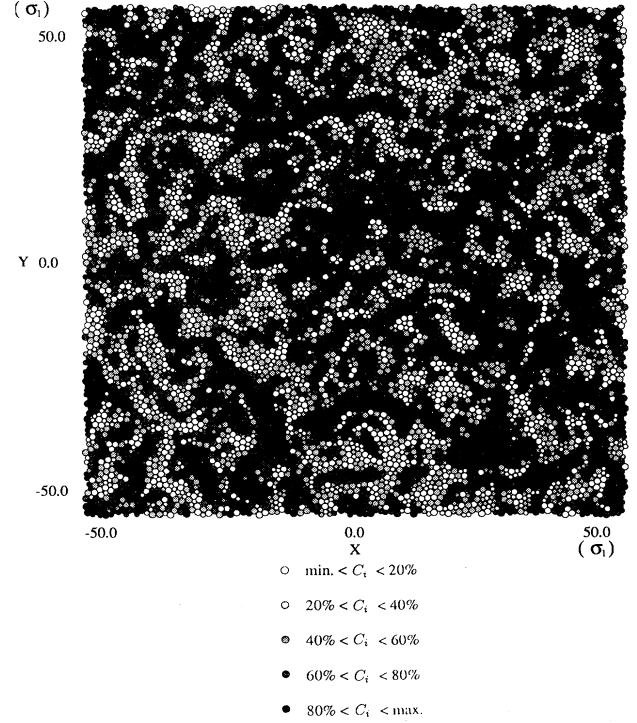


FIG. 3. The correlated motion coefficient $C_i(2.0,1.0)$ is calculated for all atoms ($N=10\,000$). The gradations of the circles are made according to the (five classed) values of the C_i , as shown below the figure; each class gradation has 2000 particles. The axes X, Y are the absolute distance from central position $(0.0,0.0)$ in units of σ_1 .

where $\langle|\mathbf{r}^{(\alpha)}(t) - \mathbf{r}^{(\alpha)}(0)|^2\rangle$ is the mean square displacement. This approximation is obtained by the general cumulant expansion [17] with only the first term taken into account. The result of the comparison for the case $\Gamma_{\text{eff}}=1.4$ and $k=2\pi/\sigma_1$ shows that up to $t=10\tau$ both are in good agreement, but the discrepancy becomes remarkable for $t\geq 10\tau$.

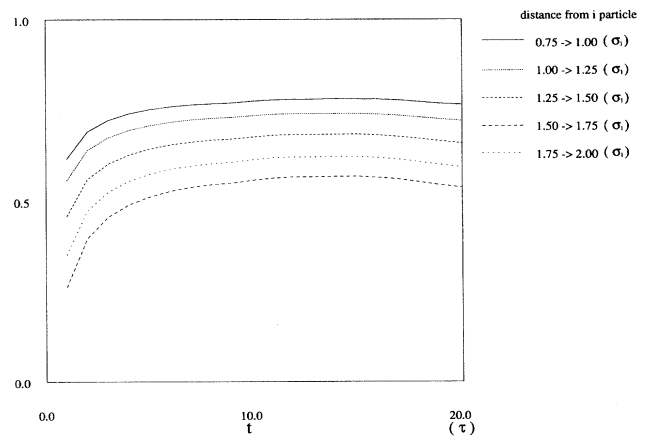


FIG. 4. The averaged value of the correlated motion coefficient $C_i(r_c, t)$ divided into five successive shells with an equal width $0.25\sigma_1$: This average was made over all atoms ($N=10\,000$) and 695 configurations. For example, the solid line is a result of the case that another particle j lies in distances from the i th atom between $0.75\sigma_1$ and $1.00\sigma_1$. The abscissa t is time in units of τ .

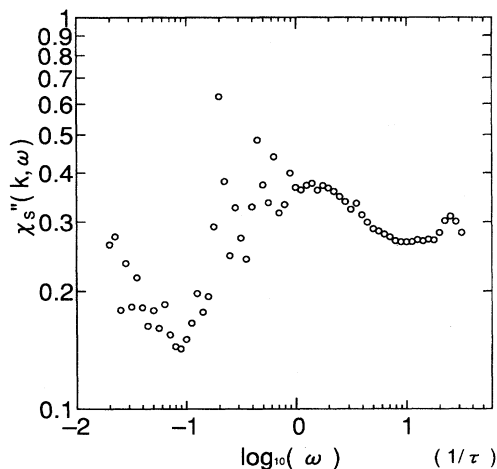


FIG. 5. The imaginary part of the generalized susceptibility (self-part) for species 1 at $\Gamma_{\text{eff}}=1.4$. The reduced wave number is $k=2\pi/1$ (in units of σ_1^{-1}). The abscissa $\log_{10}(\omega)$ is a logarithmic frequency in units of τ^{-1} .

This result indicates that the next term of the cumulant expansion, proportional to the non-Gaussian parameter, plays an important role and the higher-order moments of the cumulant expansion are not negligible.

The full density autocorrelation function $F^{(\alpha)}(k, t)$ was also computed.

$$F^{(\alpha)}(k, t) = \left\langle \left[\sum_{j=1}^{N_\alpha} \exp\{i\mathbf{k} \cdot \mathbf{r}_j^{(\alpha)}(t)\} \right] \times \left[\sum_{j=1}^{N_\alpha} \exp\{-i\mathbf{k} \cdot \mathbf{r}_j^{(\alpha)}(0)\} \right] \right\rangle / N_\alpha. \quad (10)$$

A similar oscillatory behavior to that of $F_s^{(\alpha)}(k, t)$ was also obtained for $F^{(\alpha)}(k, t)$, though the total length of the time

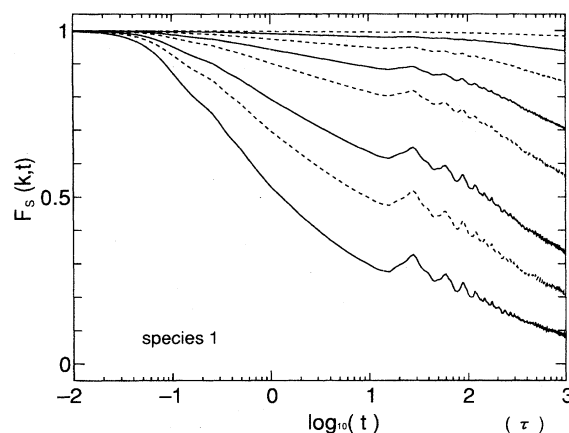


FIG. 6. Self-part of the density autocorrelation function $F_s^{(1)}(k, t)$ for species 1 at $\Gamma_{\text{eff}}=1.4$. Curves, from top to bottom, are for the reduced wave numbers $k=2\pi/10, 2\pi/5, 2\pi/3, 2\pi/2, 2\pi/1.5, 2\pi/1, 2\pi/0.8,$ and $2\pi/0.6$, respectively, in units of σ_1^{-1} . The abscissa $\log_{10}(t)$ is logarithmic time in units of τ .

steps of our MD simulation ($1500\tau=300\,000$ steps) is not enough to obtain $F^{(\alpha)}(k, t)$ as accurately as for $F_s^{(\alpha)}(k, t)$.

Therefore we see such oscillatory behaviors are rather common results obtained from the present MD simulation at a very low temperature. However, as was already mentioned, these oscillatory behaviors are considered to be a spurious effect due to the periodic boundary conditions used in the MD.

We conclude that the averaged value of the correlated motion coefficient increases as t increases in the time scale of several τ and the highly correlated areas increase as well in the same time scale. For this time scale the imaginary part of the generalized susceptibility (self-part) has the β peak. After all, we conclude the correlated motion is the molecular-level origin of the β relaxation.

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