How Different is the Dynamics of a Lennard-Jones Binary Fluid from One-Component Lennard-Jones Fluid?[1]

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Summary

We investigate the dynamics of liquids and supercooled liquids whose pair interaction is described by the Lennard-Jones potential by means of extensive molecular dynamics simulations and analyze the simulation results using the mean field theory for liquids and supercooled liquids suggested by Tokuyama. From comparing the results between the one-component system and the binary-mixture system in which we adopt the Kob-Andersen model, we confirm the universality for the long-time self-diffusion coefficient over the both systems. In addition, we also confirm that it is suitable for representing the dynamics of liquids and supercooled liquids in the both systems to use the long-time self-diffusion coefficient as a control parameter.

1. Introduction

Liquids can become glasses followed by supercooled liquids if crystallization does not occur. Studies of glasses and supercooled liquids have long history [1, 2]. However, the mechanisms of the glass transition and the origin of the slow dynamics near the glass transition point have not been theoretically elucidated yet. Recently, dynamical heterogeneity of the supercooled liquids near the glass transition point has received attention [3]. It is considered that the heterogeneity is related to the origin of the glass transition mechanisms lead us to the slow dynamics.

The most mainstream theory in study of glasses and supercooled liquids is the mode coupling theory for supercooled liquids [4, 5]. This brightened up the study of glasses and supercooled liquids. However, there are some problems for applying the mode coupling theory to the dynamics of glasses and supercooled liquids because that is the theory developed for critical phenomena originally. It is not clear whether the glass transition is critical phenomenon or not. The mean field theory (MFT) for liquids and supercooled liquids has been suggested by Tokuyama [6]. It predicts the dynamics of the supercooled liquids and gives suggestions that universality exists over glass-forming systems [7].

According to the above discussion, we investigate the dynamics of liquids or supercooled liquids for an one-component system and a binary-mixture system by means of extensive molecular dynamics simulations. In the both systems, we set a pair-interaction as the Lennard-Jones potential. Especially, in the binary-mixture system we adopt the Kob-Andersen model [8, 9] as a simulation model. It is known that in that model crystallization does not occur, and stable supercooled liquids and glasses are obtained after a long time calculation.

The goal of our study is to elucidate the mechanisms of the glass transition and the origin of the slow dynamics. In this paper, we aim to understand the universality over the one-component system and the binary-mixture system. In the next section, we introduce the equations of the mean square displacement and the long-time self-diffusion coefficient predicted by the MFT. The simulation model we used is explained in section three, and we show and discuss the simulation results in section four. Finally, we conclude this paper in the last section.

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2. Mean Field Theory for Supercooled liquids

We consider a three-dimensional equilibrium system whose temperature is T, whose volume V, and which contains N particles with mass m and radius a. The mean square displacement is defined as

$$M_2(t) := \frac{1}{N}\sum_{i=1}^{N}\left\langle \{\boldsymbol{X}_i(t) - \boldsymbol{X}_i(0)\}^2 \right\rangle, \qquad (1)$$

where $\boldsymbol{X}_i(t)$ denotes the position vector of i-th particle at time t and the brackets the canonical ensemble average. The mean field theory (MFT) predicts that the mean square displacement for molecular systems obeys the following differential equation [6]:

$$\frac{\mathrm{d}}{\mathrm{d}t}M_2(t) = 6D_s^L + 6\left(\frac{{v_0}^2}{3}t - D_s^L\right)e^{-\frac{M_2(t)}{l^2}}, \qquad (2)$$

where $v_0(=\sqrt{3k_BT/m})$ denotes the average velocity of a particle, D_s^L the long-time self-diffusion coefficient, and l the mean-free path. The long-time self-diffusion coefficient and the mean-free path depend on the control parameter such as an inverse temperature and a volume fraction. The solution of Eq.(2) is obtained by

$$\begin{aligned} M_2(t) &= 6D_s^L t + l^2 \ln\left[e^{-\frac{6D_s^L t}{l^2}}\right. \\ &+ \left.\frac{l^2{v_0}^2}{6{D_s^L}^2}\left\{1 - \left(1 + \frac{6D_s^L t}{l^2}\right)e^{-\frac{6D_s^L t}{l^2}}\right\}\right]. \end{aligned} \qquad (3)$$

Characteristic times, τ_f and τ_L, are defined as $\tau_f := l/v_0$ and $\tau_L := a^2/D_s^L$, respectively. Here, one can obtain the following asymptotic forms for the each characteristic time

$$M_2(t) \simeq \begin{cases} (v_0 t)^2 & \text{for } t \ll \tau_f, \\ 6D_s^L t & \text{for } \tau_L \ll t. \end{cases} \qquad (4)$$

The long-time self-diffusion coefficient D_s^L is determined by the second equation of Eq.(4) and the mean-free path l by a fitting with experimental or simulation data.

The MFT also predicts that the long-time self-diffusion coefficient for molecular systems is described by the following singular type function [6]:

$$D_s^L(p) = \frac{1}{1 + \epsilon\left(\frac{p}{p_c}\right)\left(1 - \frac{p}{p_c}\right)^{-2}}, \qquad (5)$$

where p denotes the control parameter, ϵ a fitting parameter dominated by only interactions among particles, and p_c a singular point which reflects the details of system.

Tokuyama has suggested a "non-singular type" function for the long-time self-diffusion coefficient [10]. Although the singular type MFT (5) deviates from the experimental or simulation results at low temperature range in general, it is still effective when we investigate the universality over glass-forming systems. Therefore, we analyze the simulation data using the singular type equation (5) in this paper.

3. Simulation Model

We consider an one-component molecular system which contains uniform particles (particle O) where the number of O particles is given by N_O, and a binary-mixture molecular system which contains two kinds of particle (particle A and particle B) where the numbers of A particles and B particles are given by N_A and N_B, respectively. In both systems, the particles are confined in a certain space domain with volume V, and we do not consider the interaction with the boundary of the domain. We investigate the dynamics of those systems in which the control parameter is given by the inverse temperature $\beta(= 1/k_BT)$ where k_B denotes the Boltzmann constant.

The motion of particles is described by the Newton equation

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\boldsymbol{X}_i(t) = -\nabla_i \sum_{j(\neq i)}^{N} \phi_{\eta\xi}(X_{ij}), \qquad (6)$$

where ∇_i denotes derivative with respect to $\boldsymbol{X}_i$, $X_{ij} = |\boldsymbol{X}_i - \boldsymbol{X}_j|$, and the pair interaction $\phi_{\eta\xi}(r)$ is described by the Lennard-Jones potential

$$\phi_{\eta\xi}(r) = 4\varepsilon_{\eta\xi}\left[\left(\frac{\sigma_{\eta\xi}}{r}\right)^{12} - \left(\frac{\sigma_{\eta\xi}}{r}\right)^{6}\right], \qquad (7)$$

where $\sigma_{\eta\xi}$ denotes a Lennard-Jones potential parameter which corresponds to the diameter of the particle, $\varepsilon_{\eta\xi}$ another parameter which has energy dimension and corresponds to the depth of the potential, and η and ξ a kind of particle; $\{\eta, \xi\} \in \{O, A, B\}$. In the one-component system, parameters are $\sigma_{OO} =: \sigma$ and $\varepsilon_{OO} =: \varepsilon$, and we set the number density as $0.90\sigma^{-3}$. Furthermore, in the binary-mixture system, we adopt the Kob-Andersen model [8] in which the parameters of the Lennard-Jones potential are given by

$$\frac{\sigma_{AB}}{\sigma_{AA}} = 0.8,\ \frac{\sigma_{BB}}{\sigma_{AA}} = 0.88,\ \frac{\varepsilon_{AB}}{\varepsilon_{AA}} = 1.5,\ \frac{\varepsilon_{BB}}{\varepsilon_{AA}} = 0.5, \tag{8}$$

and the number density is set as $1.2{\sigma_{AA}}^{-3}$.

In order to perform the simulations, we use the Lennard-Jones units. In the one-component system, the length is scaled with σ, the energy with ε, the temperature with ε/k_B, and the time with $\sigma\sqrt{m/48\varepsilon}$. Similarly, in the binary-mixture system the length is scaled with σ_{AA}, the energy with ε_{AA}, the temperature with ε_{AA}/k_B, and the time with $\sigma_{AA}\sqrt{m/48\varepsilon_{AA}}$. The number of particles is given by $N_O = 10976$ in the one-component system and $N_A = 8780$ and $N_B = 2196$ in the binary-mixture system, where $N_A + N_B = 10976$. The particles are in a cubic cell with the length $L_{\mathrm{OC}} = 23.00\sigma$ in the one-component system, and $L_{\mathrm{BM}} = 20.89\sigma_{AA}$ in the binary-mixture system. The periodic boundary conditions are employed and the cutoff distance of the interaction is set as 2.5σ and $2.5\sigma_{AA}$ in the one-component and the binary-mixture system, respectively. We employ the face-centered cubic (FCC) configuration as the initial configuration in the one-component system, while a random configuration in the binary-mixture system. In order to observe equilibrium data, we firstly wait for time which is ten times as long as the relaxation time for each temperature, and then we measure simulation data.

4. Results

4.1 Mean Square Displacement

Figs. 1 and 2 show the results of the mean square displacement for the O particle in the one-component and for the A particle in the binary-mixture system, respectively.

In the one-component system, the results of the mean square displacement are in good agreement with the MFT fitting. In the binary-mixture system, the results agree with the Eq.(3) for higher temperature, while those deviate slightly from the Eq.(3) at an intermediate time for dimensionless temperature lower than 0.500. This must be because the system is still not equilibrium. Since a reorientation time is very long, the systems at low temperature could stay in the non-equilibrium metastable state.

4.2 Long-Time Self-Diffusive Coefficient

Fig. 3 shows the fitting results of the long-time self-diffusion coefficient in the one-component and the binary-mixture systems. In the one-component system, one can not measure them since crystallization occurs for $T < 0.724$ ($\beta > 1.38$).

In the high temperature region, the results of the long-time self-diffusion coefficient are good agreement

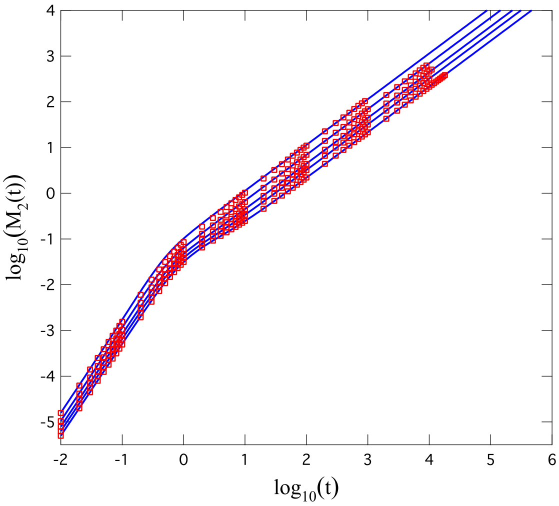

Fig.1 A log-log plot of the results of the mean square displacement versus time in the one-component system for different dimensionless temperatures T =2.50, 1.67, 1.25, 1.00, and 0.794 (from up to bottom). The open squares indicate the simulation results and the solid lines the MFT fitting lines.

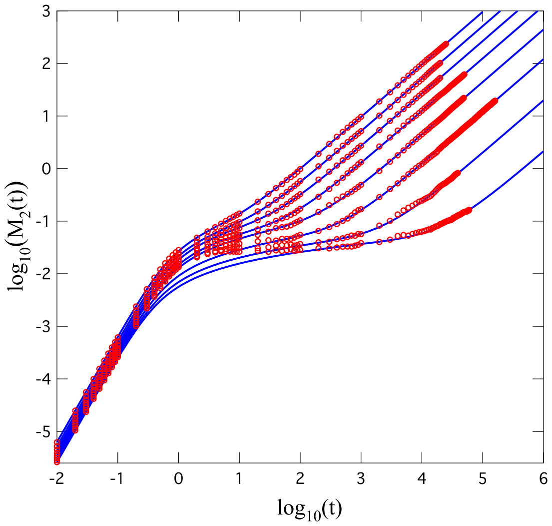

Fig.2 A log-log plot of the results of the mean square displacement versus time in the binary-mixture system for different dimensionless temperatures T =1.00, 0.833, 0.714, 0.625, 0.556, 0.500, 0.455, and 0.417 (from up to bottom). The open circles indicate the simulation results and the solid lines the MFT fitting lines.

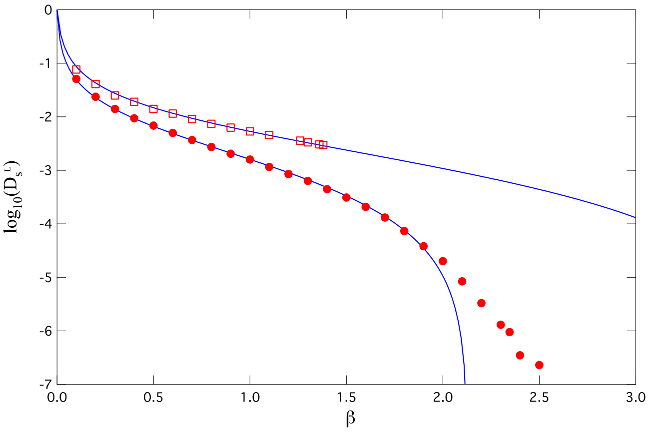

Fig.3 A semi-log plot of the results of the long-time self-diffusive coefficient versus the dimensionless inverse temperature β in the one-component and the binary-mixture systems. The open squares indicate the simulation results in the one-component system, the closed circles in the binary-mixture system, and the solid lines the MFT fitting lines with $\epsilon = 374$ and $\beta_c = 3.74$ in the one-component system and with $\epsilon = 374$ and $\beta_c = 2.13$ in the binary-mixture system.

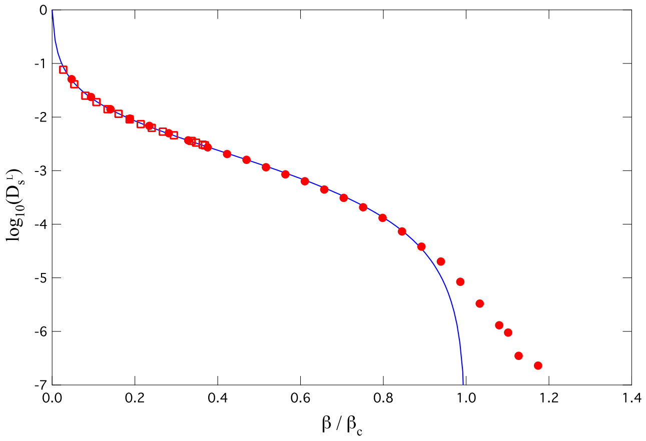

Fig.4 A semi-log plot of the results of the long-time self-diffusive coefficient versus the inverse temperature scaled by the value of singular point in the one-component (open squares) and the binary-mixture (closed circles) systems.

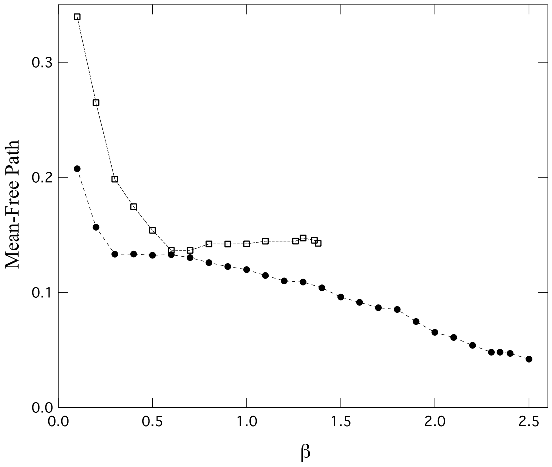

Fig.5 A plot of the results of the mean-free path versus the inverse temperature in the one-component and the binary-mixture systems. The open squares indicate the simulation results in the one-component system and the closed circles in the binary-mixture system.

with the singular type MFT equation (5). However, the simulation results deviate from fitting line by the MFT in the low temperature region. The parameters for fitting are $\epsilon = 374$, $\beta_c = 3.74$ in the one-component system and $\epsilon = 374$, $\beta_c = 2.13$ in the binary-mixture system. As mentioned in [10], it is known that the parameter ϵ in Eq.(5) depends on type of the interactions but does not depend on the details of the system, while the singular point p_c (in our system, $p_c = \beta_c$) depends on the details.

A semi-log plot of the simulation results of the long-time self-diffusion coefficient is shown versus β/β_c in Fig. 4. If one regards the variable as the β/β_c instead of β, a parameter of the singular type MFT equation is given by only ϵ. This is one of universalities that the MFT suggests over the glass-forming systems described by the same type of interactions. In fact, the results of the one-component system agree with that of the binary-mixture system (see Fig.4). Moreover, Gallo's system, which is the simulation model dominated by the Lennard-Jones potential and contains huge particles in simulation cell [11], has the same value of ϵ [10][1].

4.3 Mean-Free Path

Fig. 5 shows the fitting results of the mean-free path in the one-component and the binary-mixture systems. The mean-free path corresponds to a length in which a particle can do ballistic motion without any interactions. In the both systems, the mean-free path decreases rapidly in higher temperature (lower inverse temperature) region, and the plateaus appear at intermediate temperature region. In the one-component system, one can not measure the mean-free path as well as the long-time self-diffusion coefficient for $T < 0.724$ ($\beta > 1.38$). In the binary-mixture system, the mean-free path decreases gently in lower temperature

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[1] Note that the unit to perform the simulation is different between this paper and [10].

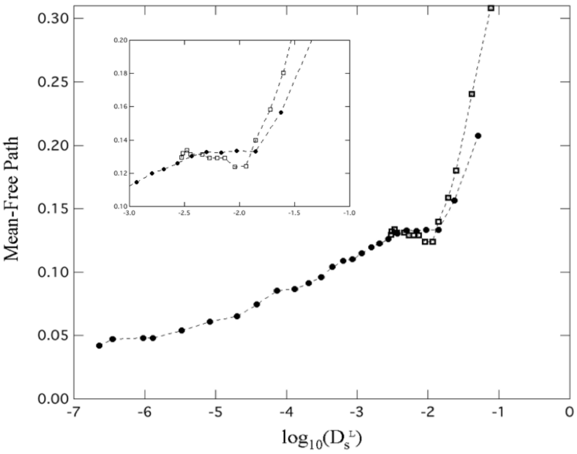

Fig.6 A semi-log plot of the results of the mean-free path versus the long-time self-diffusion coefficient in the one-component and the binary-mixture systems. The open squares indicate the simulation results in the one-component system and the closed circles in the binary-mixture system. The mean-free path results of the one-component system are multiplied by $L_{\mathrm{BM}}/L_{\mathrm{OC}}$ =20.89/23.00.

(higher inverse temperature) region.

In Fig.6 a semi-log plot of the results of the mean-free path is shown versus the long-time self-diffusion coefficient. In order to compare the mean-free path in the one-component system to that in the binary-mixture system, the results of the one-component system are rescaled by $L_{\mathrm{BM}}/L_{\mathrm{OC}}$ =20.89/23.00. In Fig. 6 the behavior of the mean-free path in the one-component system is good agreement with that in the binary-mixture system. This is another universality over the both systems.

5. Conclusions

We have analyzed the dynamics of liquids or supercooled liquids, in which the pair-interaction is described by the Lennard-Jones potential, according to the mean field theory for liquids and supercooled liquids. In comparison between the one-component system and the binary-mixture system, we reveal the universality of the long-time self-diffusion coefficient over the both systems, i.e. those of the systems dominated by the same interactions could be described by the master curve. Furthermore, we confirm that the long-time self-diffusion coefficient is suitable as a control parameter for representing the universality over the both systems. Existence of universality leads us to treat simpler and more fundamental model.

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