Relationship between the Diffusive Coefficient and the Specific Heat for Lennard-Jones Binary Mixture

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Abstract. We perform the extensive molecular dynamics simulations on the Kob-Andersen type Lennard-Jones binary mixtures. We study not only dynamical behavior near the glass transition but also the static one, including the specific heat. We then analyze the simulation results from a unified point of view suggested by Tokuyama. The view suggests the definition of the glass transition by using the long-time self-diffusion coefficient. Thus, we show that the temperature at the peak of the specific heat coincides with the glass transition temperature calculated from the long-time self-diffusion coefficient. We also discuss the relationship between the specific heat and the long-time self-diffusion coefficient from a new standpoint.

Keywords: Glass transition, Kob-Andersen model, Long-time self-diffusion coefficient, Specific heat
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INTRODUCTION

Glass and supercooled liquid have been studied since antiquity, and we have much knowledge of them [1, 2, 3]. Near the glass transition temperature, glass-forming liquids show slow dynamical behavior: Their viscosity of glass forming liquids increases continuously but rapidly. Moreover, their relaxation functions (e.g. intermediate scattering functions) exhibit some complicated relaxations. However, the mechanisms of the slow dynamics have not been elucidated theoretically yet.

The specific heat also changes drastically at the vicinity of the glass transition point [4, 5, 6]. While the specific heat diverges to infinity in the second-order transition phenomena, it does not in the glass transition. Thus, it is considered that the glass transition is dynamical crossover. In order to understand the mechanisms of the glass transition and slow dynamics, we need to link statics and dynamics like the Adam-Gibbs approach [7].

The viscosity decreasing corresponds to the increasing of the diffusion coefficient. Tokuyama suggests analytic forms of the long-time self-diffusion coefficient (LSD) for fragile glass forming systems (singular [8] and non-singular type [9]). The equations contain a parameter p_c which means a singular point of the diffusion coefficient. However, it is unclear whether a singular point of the diffusion coefficient exists or not. We do not know yet what proper meaning the p_c has.

We also suggest the definition of the glass transition by using the LSD [9]. The purpose of this proceedings is to investigate the validity for the definition via the specific heat at constant volume. We perform the molecular dynamics simulations and measure the specific heat at constant volume (statics) and the LSD (dynamics) for the Kob-Andersen Lennard-Jones binary mixture model [10]. For the Kob-Andersen model, the glass transition temperature is obtained as $T_g = 0.4376$ from the LSD analysis [9]. Note that this temperature corresponds to the glass transition LSD ($\hat{D}_g = 9.16 \times 10^{-6}$), which is based on the experiment performed by van Magen et. al. [11].

MEASUREMENTS

The long-time self-diffusion coefficient (LSD) D_s^L is represented by

$$D_s^L = \lim_{t \to \infty} \frac{M_2(t)}{2d}, \tag{1}$$

where $M_2(t)$ denotes the mean-square displacement and d the spatial dimensionality. The LSD depends on an appropriate control parameter p (e.g. volume fraction, inverse temperature, and so on). Tokuyama has theoretically derived an equation of the LSD for hard-sphere suspensions as [12]

$$D_s^L(\phi) = D_s^S(\phi) \frac{1 - 9\phi/32}{1 + (D_s^S(\phi)/D_0)(\phi/\phi_c)(1 - \phi/\phi_c)^{-2}}, \tag{2}$$

where ϕ denotes the volume fraction, ϕ_c ($\simeq 0.5718$) the critical volume fraction, D_s^S the short-time self-diffusion coefficient, and D_0 the diffusion coefficient of a single particle. The term $9\phi/32$ appears due to the coupling between the hydrodynamic interactions among particles and the direct interactions [12]. Tokuyama considers that the LSD has the universal form which is similar to Eq.

(2), and then extends Eq. (2) to molecular systems as [8]

$$\hat{D}(p) = \frac{D_s^L(p)}{av_0} = \frac{1}{1+\varepsilon(p/p_c)(1-p/p_c)^{-2}}, \quad (3)$$

where a denotes the radius of the molecules, and v_0 the unit velocity. We note that ε and p_c should be treated as fitting parameters in Eq. (3), whereas D_s^S, D_0, and ϕ_c are not fitting parameters in Eq. (2). It is unclear whether the singular point p_c of the LSD exists or not. Results from simulation studies show that the singular point does not exist [13, 14].

Tokuyama also suggests a non-singular type equation of the LSD [9]. To fit the non-singular equation to simulation or experimental data, we use a new fitting parameter α in addition to ε and p_c. Because the singular point p_c is needed even for non-singular fitting, we consider that it has physical meanings even if the singular point does not exist. Using the non-singular fitting line, we can calculate the glass transition point which corresponds to $\hat{D}_g = 9.16 \times 10^{-6}$.

The specific heat c_V per particle at constant volume is defined by

$$c_V := N^{-1}(\partial E/\partial T)_V, \quad (4)$$

where N denotes the number of particle, E the internal energy, T the temperature, and V the volume. When the internal energy is represented by $E = K + \Phi$ where K denotes the kinetic energy and Φ the potential energy, the specific heat can be represented by

$$c_V = c_V^K + c_V^\Phi = dk_B/2 + c_V^\Phi, \quad (5)$$

where c_V^K the specific heat due to the kinetic energy, c_V^Φ that due to the potential energy, and k_B the Boltzmann constant. Because of the equipartition law of energy, one can show that $c_V^K = dk_B/2$. Moreover, $c_V^\Phi = dk_B/2$ in the harmonic oscillator approximation, and thus one can obtain $c_V = dk_B$ in solid states, which is known as the Dulong-Petit law[1]. The behavior of the specific heat is determined by the potential energy part since the specific heat due to the kinetic energy is constant.

MODEL

We consider binary-mixture molecular systems which consist of two kinds of particles (particle A and particle B) where the numbers of A particles and B particles are given by N_A and N_B, respectively. The difference between A and B particle is particle size, but we set them as the

[1] In the lower temperature region, the Dulong-Petit law does not hold and the specific heat is a function of the square of the temperature (Debye model).

same mass m. The particles are confined in a certain three-dimensional space with the volume V constant, and we neglect the interaction with the boundary of the domain. We investigate those systems in which the control parameter is given by the inverse temperature; $p = \beta(= 1/k_B T)$.

The motion of particles is described by the classical Newtonian equation

$$m\frac{d^2}{dt^2}\vec{X}_i(t) = -\nabla_i \sum_{j \neq i} u_{\eta\xi}(X_{ij}), \quad (6)$$

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

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

where $\sigma_{\eta\xi}$ denotes one of the Lennard-Jones potential parameters which corresponds to the size of the particles, $\varepsilon_{\eta\xi}$ another parameter which has energy dimension and corresponds to the depth of the potentials, and η and ξ a kind of particle; $\{\eta,\xi\} \in \{A,B\}$. We adopt the Kob-Andersen model [10] in which the parameters of Eq. (7) are given by

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

and the number density is set as $1.2\sigma_{AA}^{-3}$. This model simulates a metallic alloy $Ni_{80}P_{20}$ [16].

To perform molecular dynamics simulations, we employ the Lennard-Jones units. Length is scaled with σ_{AA}, energy with ε_{AA}, temperature with ε_{AA}/k_B, and time with $\tau = \sigma_{AA}\sqrt{m/48\varepsilon_{AA}}$. The unit velocity v_0 is represented by $v_0 = \sigma_{AA}/4\tau = \sqrt{3\varepsilon_{AA}/m}$. Moreover, the numbers of particles are given by $N_A = 8780$ and $N_B = 2196$. The particles are in a cubic cell with the length $L = 20.89\sigma_{AA}$. The equation of motion is integrated by the velocity Verlet method with a time step 0.01τ. The periodic boundary conditions are employed. The cutoff distance of the interactions for each combination of particles is set as $2.5\sigma_{AA}$. An initial configuration is a random configuration. In order to observe equilibrium data, we firstly wait for time which is ten times longer than the relaxation time for each temperature (preparing calculations), and then we measure physical variables (main calculations). Temperature is adjusted by the velocity scaling method in the preparing calculations.

RESULT AND DISCUSSION

Fig. 1 shows the results of the mean-square displacement of the only A particle. In the range of the inverse temperature less than $\beta = 2.2$ (the temperature more than
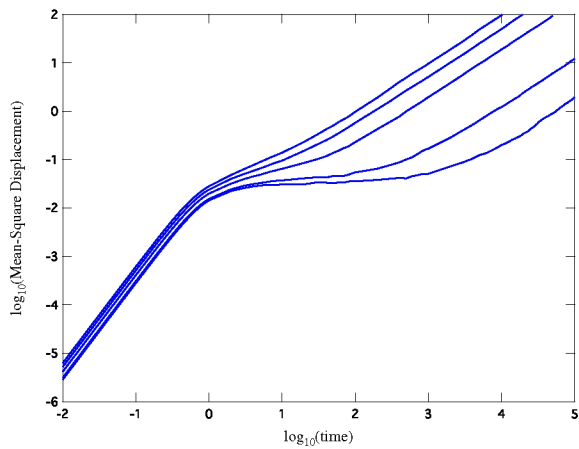
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FIGURE 1. (Color online) Log-log plot of the mean-square displacement of the A particle for $T = 1.0, 0.83, 0.67, 0.50$, and 0.45 (from top to bottom).
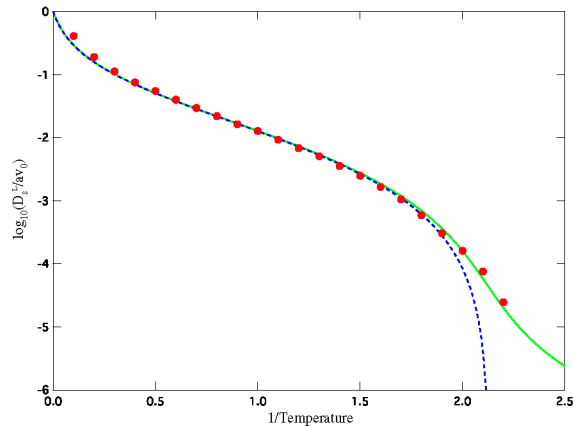

FIGURE 2. (Color online) Plot of the common logarithm of the LSD versus the inverse temperature. The red circles indicate the simulation results, the dashed blue line the singular type fitting (Eq. (3)), and the solid green line the non-singular type fitting [9]. The parameters are $\varepsilon = 46.75$, $\beta_c = 2.13$, and $\alpha = 2.05$.
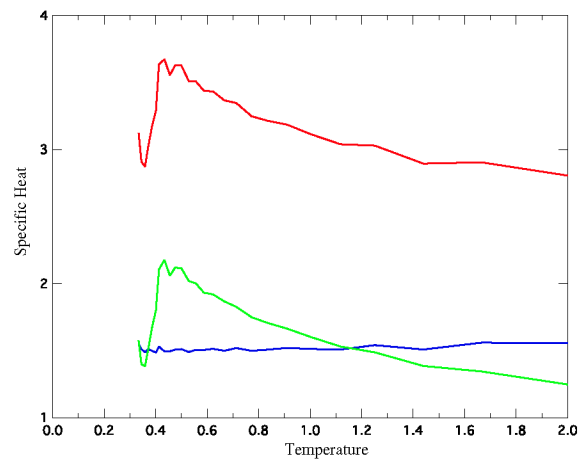

FIGURE 3. (Color online) Plot of the specific heat per particle at constant volume versus the temperature. The red line indicates the specific heat given from Eq. (4), the blue one that due to the kinetic energy, and the green one that due to the potential energy.

good agreement with the simulation results. However, the singular line diverges from the simulation results, while the non-singular line is in good agreement with them. Considering that the simulation results are equilibrium, it seems that the LSD does not have singular effect but non-singular behavior. Thus, the singular point β_c looks superficial. Nevertheless, the non-singular fitting, which contains the superficial singular point β_c as a fitting parameter, is in good agreement with the results. Moreover, the relationship the LSD and the control parameter scaled with the singular point p_c shows universality [8, 15]. Therefore, we consider that β_c (in general, p_c) is still important.

As above mentioned, we suggest the definition of the fragile glass transition by using the LSD [9]. According to the classification, the system in which the LSD $\hat{D}$ is less than $\hat{D}_g = 9.16 \times 10^{-6}$ is glassy state. The glass transition LSD $\hat{D}_g$ corresponds to $T_g = 0.4376$ ($\beta_g = 2.2851$) in the Kob-Andersen model. This transition temperature is calculated by the non-singular LSD fitting line. It is considered that the results of the mean-square displacement in $\beta > \beta_g$ are out of equilibrium.

Fig. 3 shows the results of the specific heat per particle at constant volume. Those results are scaled with the Boltzmann constant. We measure them from Eq. (4). The energy is average over $10^4 \tau$. While the mean-square displacement is not steady-state in $T < 0.434$, the internal, kinetic, and potential energy are equilibrium.

The dimensionless specific heat due to the kinetic energy is constant value 1.5, and it is reasonable. On the other hand, they due to the internal and potential energy increase as the temperature decreases, but rapidly
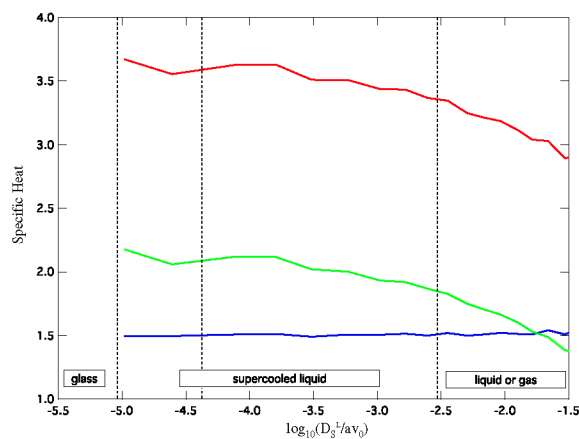
$T = 0.455$), those results are steady-state within error, and then we regard them as equilibrium state. The slope of the log-log plot is unity in large time scale that means the dynamics is dominated by the diffusive motion. On the other hand, in $\beta \geq 2.3$ ($T \leq 0.435$) we have not obtained steady-state results yet. It is unclear whether our calculation time is lacking or the systems show aging.

We can measure the long-time self-diffusion coefficient (LSD) from the long-time limit of the mean-square displacement (Eq. (1)). The results of the LSD are shown in Fig. 2. We note that the LSD is scaled with av_0 in Fig. 2. In higher temperature (lower inverse temperature) region, the both singular and non-singular fitting are in

FIGURE 4. (Color online) Plot of the specific heat per particle at constant volume versus the common logarithm of the LSD. The details are the same as in Fig. 3. The vertical dotted lines denote the supercooled point (right, $\hat{D}_\beta = 2.95 \times 10^{-3}$), the (superficial) singular point (center, $\hat{D}_c = 4.22 \times 10^{-5}$), and the glass transition point (left, $\hat{D}_g = 9.16 \times 10^{-6}$) [9].

decrease below $T = 0.43$. It indicates that dynamics links to statics because the peak of the specific heat (statics) corresponds to the glass transition point $T_g = 0.4376$ obtained from the LSD (dynamics).

The growth of the specific heat due to the potential energy represents the importance of the spatial structuring at the vicinity of the glass transition point. It is consistent in view of the dynamical heterogeneity [17].

We suggest that the LSD has the universal form described by Eq. (3). It means that we treat the LSD as an universal parameter. Fig. 4 shows the relationship between the specific heat and the LSD. The specific heat does not change drastically at the supercooled LSD $\hat{D}_\beta$ and the singular LSD $\hat{D}_c$. As shown in Ref. [18], we should investigate and compare to another systems.

SUMMARY

We have investigated the specific heat at constant volume and the long-time self-diffusion coefficient (LSD) of the Kob-Andersen type Lennard-Jones binary mixture fluids by using molecular dynamics simulations.

Our statement is that the LSD has an universal form for fragile glass-forming systems [8] and we treat the LSD as an universal parameter [18]. When we regard it as an universal parameter, the glass transition LSD is $\hat{D}_g = 9.16 \times 10^{-6}$ [9]. The definition is based on dynamical analysis and the glass transition LSD $\hat{D}_g$ is equivalent over fragile glass-forming liquids. It strongly indicates that the glass transition is based on dynamical behavior. Moreover, using the non-singular type LSD

suggested by Tokuyama [9], one can transform from the glass transition LSD to the glass transition temperature. Thus, we reveal that the definition of the glass transition by using the LSD is reasonable according to the results of the specific heat in the Kob-Andersen model.

Unfortunately, our above statements might not have strong powers of persuasion since we have analyzed the only Kob-Andersen model. We should investigate the relationship between the specific heat and the LSD of other systems and analyze whether the LSD is universal parameter or not. In that regard, what is needed is accuracy of calculation.

ACKNOWLEDGMENTS

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