

Brownian-Dynamics Simulation of Colloidal Suspensions with Kob-Andersen Type Lennard-Jones Potentials¹

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Summary

Extensive Brownian-dynamics simulations of binary colloidal suspension with Kob-Andersen Lennard-Jones potential are performed in order to study the static and the dynamic properties of supercooled liquid and also to elucidate the mechanism of glass transition. The numerical results of several physical quantities, such as an effective pressure, a radial distribution function, a mean square displacement, a non-Gaussian parameter, and a self-intermediate scattering function, are then investigated. Thus, it is shown that as the temperature is decreased, a crossover from a liquid state to a supercooled state occurs smoothly without any first-order phase transitions. The slow relaxation processes at lower temperatures are also discussed from a unified point of view.

1. Introduction

The glass is a familiar and useful material to the human being from ancient times. The traditional method to obtain the glass is to cool the viscous liquids rapidly from a higher temperature to a lower temperature. With a sufficiently rapid cooling rate, the system can avoid the crystallization at its freezing point and become a supercooled liquid. If one cools the system further, the system finally goes into a glass state. The transition from the supercooled liquid to the glass is called the glass transition. From the physical point of view, however, it is not fully understood yet [1]. Recently, the slow dynamics near the glass transition has attracted remarkable attention [2]. About two decades ago, the appearance of the mode-coupling theory (MCT) triggered that this field was warmed up [3, 4]. However, near the glass transition, MCT fails to describe the whole dynamics of the system since it assumes the singular behavior for physical quantities near the glass transition. Recently, Tokuyama has proposed the mean-field theory (MFT) [5, 6], which was obtained from the nonlinear

stochastic diffusion equation for colloidal suspensions [7, 8], and shown that MFT well describes the universal behavior near the glass transitions. Computer simulations have also provided us with much helpful information for deeper understanding about those phenomena. For a typical example, Kob and Andersen have simulated the model of Ni₈₀P₂₀, which is known as one of metallic glass former, and compared their results with mode-coupling theory [9, 10, 11]. Today, their model, the so-called Kob-Andersen model, is well known as a good glass-forming system on computer simulations. Recently, Flenner *et. al.* have performed the Brownian-dynamics simulations on Kob-Andersen model with 1000 particles [12, 13] and recovered the supercooled state at temperatures lower than those in the original Kob-Andersen model system.

In the present paper, we perform extensive Brownian-dynamics simulations of binary colloidal suspensions with Kob-Andersen type Lennard-Jones potentials with 10976 particles and explore the static and the dynamic properties of the model system from a unified point of view.

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2. Starting Equations

We consider the three-dimensional system which consists of N particles with mass m and radius a in the equilibrium solvent with temperature T and viscosity η . The whole system is given by a cubic box of size $L(=V^{1/3})$, where V is the total volume of the system. There are two types of particles, N_A particles of type A and N_B particles of type B . We assume that the radius a is of order $10^{-6} \sim 10^{-9}$ m. Hence they undergo a Brownian motion. Let $\mathbf{r}_i^\alpha(t)$ be a position vector of i th particle of type α at time t . Then, the particles obey the Langevin equations

$$m \frac{d^2}{dt^2} \mathbf{r}_i^\alpha(t) = -\gamma \frac{d}{dt} \mathbf{r}_i^\alpha(t) + \sum_{\beta} \sum_{j \neq i}^{A,B} \mathbf{F}_{ij}^{\alpha\beta}(t) + \mathbf{R}_i^\alpha(t), \quad (1)$$

where $\gamma(=6\pi\eta a)$ denotes the friction constant and $\mathbf{F}_{ij}^{\alpha\beta}(t)$ the force between i th particle of type α and j th particle of type β . Here $\mathbf{R}_i^\alpha(t)$ denotes the Gaussian, Markov random force and satisfies

$$\langle \mathbf{R}_i^\alpha(t) \rangle = 0, \quad (2)$$

$$\langle \mathbf{R}_i^\alpha(t) \mathbf{R}_j^\beta(t') \rangle = 2\gamma k_B T \delta(t-t') \delta_{ij} \delta_{\alpha\beta} \mathbf{1}, \quad (3)$$

where the brackets $\langle \dots \rangle$ denote the equilibrium ensemble average. Eq. (1) holds on the time scale of order t_B , where $t_B(=m/\gamma)$ is a Brownian relaxation time. In the following, we neglect the hydrodynamic interactions between particles. This is because they are mainly described by the Oseen tensor and show long-range interactions which are difficult to deal with numerically.

We are interested only in the diffusion process on the time scale of order t_D , where $t_D(=a^2/D_0)$ is a structural relaxation time. Here $D_0(=k_B T/\gamma)$ is a single-particle diffusion constant. Since $t_D \gg t_B$, on the time scale of order t_D , we have $d^2 \mathbf{r}_i^\alpha(t)/dt^2 \simeq 0$. Then, Eq. (1) reduces to

$$\frac{d}{dt} \mathbf{r}_i^\alpha(t) = \frac{1}{\gamma} \sum_{\beta} \sum_{j \neq i}^{A,B} \mathbf{F}_{ij}^{\alpha\beta}(t) + \mathbf{f}_i^\alpha(t), \quad (4)$$

where $\mathbf{f}_i^\alpha(t)$ denotes the random velocity given by $\mathbf{f}_i^\alpha(t) = \mathbf{R}_i^\alpha(t)/\gamma$ and satisfies

$$\langle \mathbf{f}_i^\alpha(t) \mathbf{f}_j^\beta(t') \rangle = 2D_0 \delta(t-t') \delta_{ij} \delta_{\alpha\beta} \mathbf{1}. \quad (5)$$

This is a starting equation to solve numerically. We discuss this next.

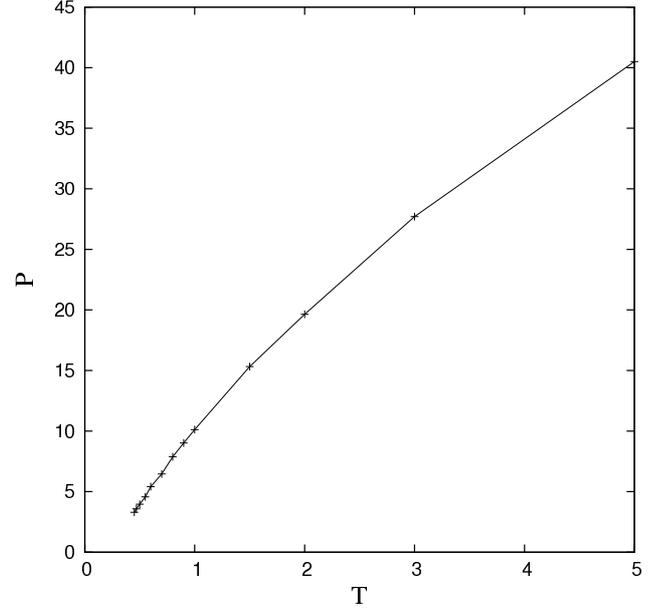


Fig.1 The effective pressure versus temperature.

3. Simulations

We choose $N_A = 8781$ and $N_B = 2195$ here, where $N = 10976$ and $N_A/N \simeq 0.8$. The force between the particles $\mathbf{F}_{ij}^{\alpha\beta}$ is given by the Kob-Andersen type Lennard-Jones potential

$$\mathbf{F}_{ij}^{\alpha\beta} = -\nabla U_{\alpha\beta}(r_{ij}^{\alpha\beta}), \quad (6)$$

$$U_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right], \quad (7)$$

where $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are chosen as in Ref. [9]; $\epsilon^{AA} = 1.0$, $\sigma^{AA} = 1.0$, $\epsilon^{AB} = 1.5$, $\sigma^{AB} = 0.8$, $\epsilon^{BB} = 0.5$, and $\sigma^{BB} = 0.88$. In this model, both the crystallization and the phase separation are known not to occur. The length of force cutoff r_c is set on $2.5\sigma^{AA}$. The system size L is fixed on $20.89\sigma^{AA}$. Length, time, energy, and temperature are scaled by σ_{AA} , t_D , ϵ_{AA} , and ϵ_{AA}/k_B , respectively. Periodic boundary conditions are used. We integrate Eq. (4) at different temperatures by using Euler method with time step $dt = 1 \times 10^{-4}$. The initial configurations are created by the random packing method [14]. Before we take the data, we wait for long times to equilibrate the system.

4. Simulation Results

We first discuss the effective pressure P of the system. One calculates it by using the virial theorem

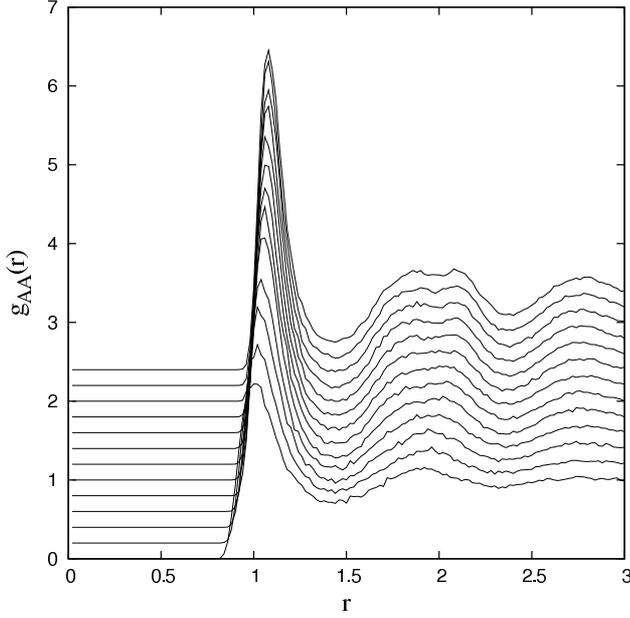


Fig.2 Radial distribution function of A - A correlation for different temperatures $T = 0.45, 0.47, 0.50, 0.55, 0.60, 0.70, 0.80, 0.90, 1.0, 1.5, 2.0, 3.0$ and 5.0 (from top to bottom).

given by

$$P = \frac{Nk_B T}{V} - \frac{1}{6V} \left\langle \sum_{\alpha, \beta}^{A, B} \sum_i^{N_\alpha} \sum_{j \neq i}^{N_\beta} \mathbf{F}_{ij}^{\alpha\beta} \cdot \mathbf{r}_{ij}^{\alpha\beta} \right\rangle, \quad (8)$$

where $\mathbf{r}_{ij}^{\alpha\beta} = \mathbf{r}_i^\alpha - \mathbf{r}_j^\beta$. In Fig. 1, the pressure P is shown versus temperature. As the temperature decreases, the pressure decreases smoothly. There exists no jump in P over a whole temperature region. This means that crystallization does not occur in the present system. Hence we discuss how the structure of the system changes as the temperature decreases. This is done by calculating the radial distribution function for A - A correlation $g_{AA}(r)$ given by

$$g_{AA}(r) = \frac{1}{2N_A \rho_A} \left\langle \sum_i^{N_A} \sum_{j \neq i}^{N_A} \delta(\mathbf{r} - \mathbf{r}_{ij}^{AA}) \right\rangle, \quad (9)$$

where $\rho_A (= N_A/V)$ is the number density of the particles of type A . In Fig. 2, $g_{AA}(r)$ is plotted for various temperatures. At higher temperatures, $g_{AA}(r)$ shows a structure observed in a liquid state. As T decreases, the split generally appears on the second peak of $g_{AA}(r)$. This is well-known as one of characteristic properties of supercooled liquids.

Next, we discuss the dynamics of the system. It is convenient to introduce the mean square displacement

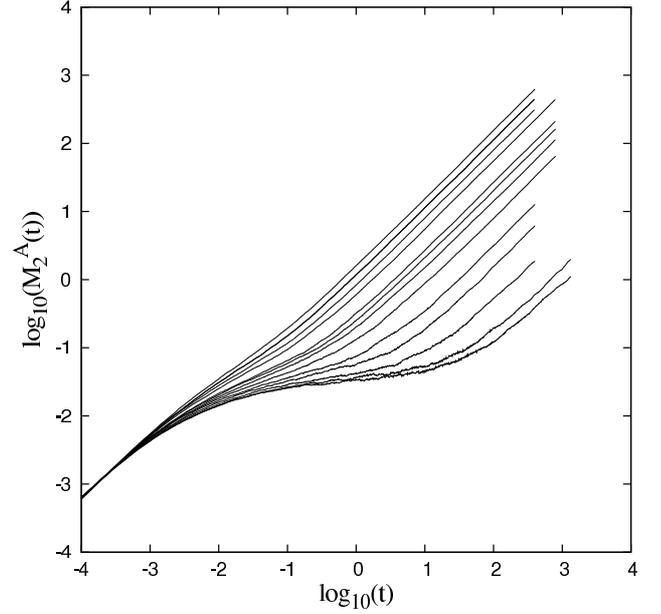


Fig.3 The log-log plot of the mean-square displacement of the particles of type A for different temperatures $T=5.0, 3.0, 2.0, 1.5, 1.0, 0.9, 0.8, 0.7, 0.6, 0.55, 0.5, 0.47$ and 0.45 (from left to right).

M_2^A of the particles of type A by

$$M_2^A(t) = \frac{1}{N_A} \sum_i^{N_A} \langle |\mathbf{r}_i^A(t) - \mathbf{r}_i^A(0)|^2 \rangle. \quad (10)$$

In Fig. 3, the simulation result is shown for different temperatures. In a short-time region, M_2^A obeys a free diffusion process given by

$$M_2^A(t) = 6D_0 t. \quad (11)$$

In a long-time region, it obeys a long-time diffusion process given by

$$M_2^A(t) = 6D_s^{L(A)}(T)t, \quad (12)$$

where $D_s^{L(A)}(T)$ denotes the long-time self-diffusion coefficient and depends on T . Thus, there is a crossover from a free diffusion process to a long-time diffusion process. This crossover is independent of the temperature, although $D_s^{L(A)}$ decreases drastically as the temperature decreases. In an intermediate-time region, however, the dynamics of $M_2^A(t)$ strongly depends on the temperature. After short times, the many-body interactions become important and prevent $M_2^A(t)$ to increase, leading to plateaus at lower temperatures. This is the so-called cage effect.

In order to investigate how the dynamics at lower temperatures is different from that at higher temper-

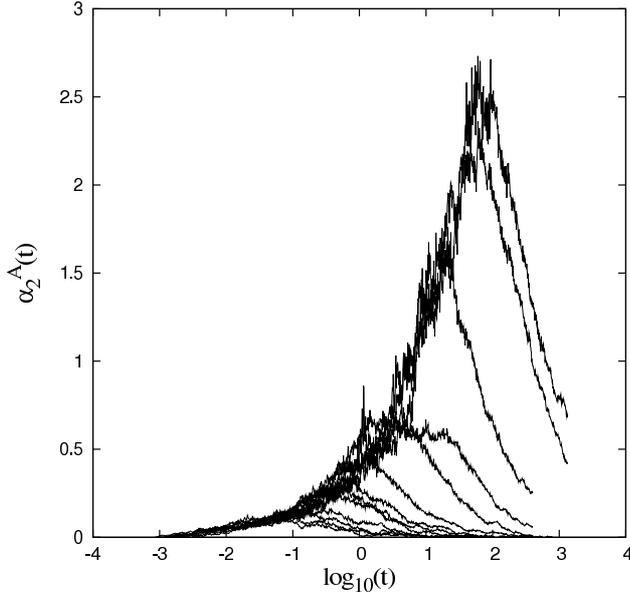


Fig.4 The non-Gaussian parameter of the particles of type A versus time for different temperatures. The details are the same as in Fig. 3.

atures, it is also convenient to introduce the non-Gaussian parameter α_2^A of the particles of type A by

$$\alpha_2^A(t) = \frac{3}{5} \frac{M_4^A(t)}{(M_2^A(t))^2} - 1, \quad (13)$$

where $M_4^A(t)$ is the 4th moment given by

$$M_4^A(t) = \frac{1}{N_A} \sum_i^{N_A} \langle |\mathbf{r}_i^A(t) - \mathbf{r}_i^A(0)|^4 \rangle. \quad (14)$$

In Fig.4, $\alpha_2^A(t)$ is plotted versus time for different temperatures. As the temperature decreases, the peak position τ_α of α_2^A increases and its peak height grows drastically. This shows that the spatial heterogeneities play an important role at lower temperatures. The time τ_α is the so-called α -relaxation time.

Finally, we discuss the self-intermediate scattering function $F_S(k, t)$ of type A , which is given by

$$F_S^A(k, t) = \frac{1}{N_A} \sum_{i=1}^{N_A} \langle e^{i\mathbf{k} \cdot [\mathbf{r}_i^A(t) - \mathbf{r}_i^A(0)]} \rangle, \quad (15)$$

where k denotes the wave number and $F_S^A(k, t=0) = 1$. The value of k is chosen as the first-peak position of the static structure factor $S_{AA}(k)$, which is given by

$$S_{AA}(k) = 1 + 4\pi\rho_A \int_0^\infty [g_{AA}(r) - 1] \frac{\sin(kr)}{kr} r^2 dr. \quad (16)$$

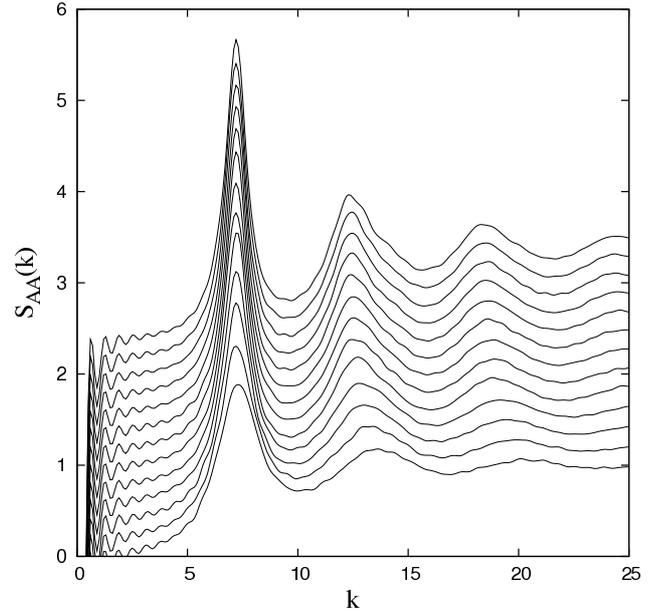


Fig.5 The static structure factor of A - A correlation versus wave number for different temperatures. The details are the same as in Fig. 2

In Fig. 5, $S_{AA}(k)$ is plotted versus wave number for different temperatures. The first-peak position is found around $k = 7.25$. In Fig. 6, $F_S^A(k, t)$ is shown versus time for different temperatures at $k = 7.25$. For higher temperatures, $F_S^A(k, t)$ shows a single exponential like decay. For lower temperatures, one can see the shoulders in the intermediate-time region. This corresponds to the cage effect discussed in the mean-square displacement $M_2^A(t)$. The long-time decays around τ_α are also different from an exponential decay because the non-Gaussian parameter $\alpha_2^A(t)$ is large. This is easily seen if one can transform Eq. (15) into a new form

$$F_S^A(k, t) \simeq \exp \left[-k^2 \frac{M_2^A(t)}{6} + \frac{1}{2} k^4 \left(\frac{M_2^A(t)}{6} \right)^2 \alpha_2^A(t) \right]. \quad (17)$$

Thus, both effects, cage effect and structural effect, are included in the self-intermediate scattering function $F_S^A(k, t)$.

5. Summary

In the present paper, we have performed the Brownian-dynamics simulation on the binary colloidal suspensions with the Kob-Anderson type Lennard-Jones potentials. We have then investigated several physical quantities at different temperatures, such as

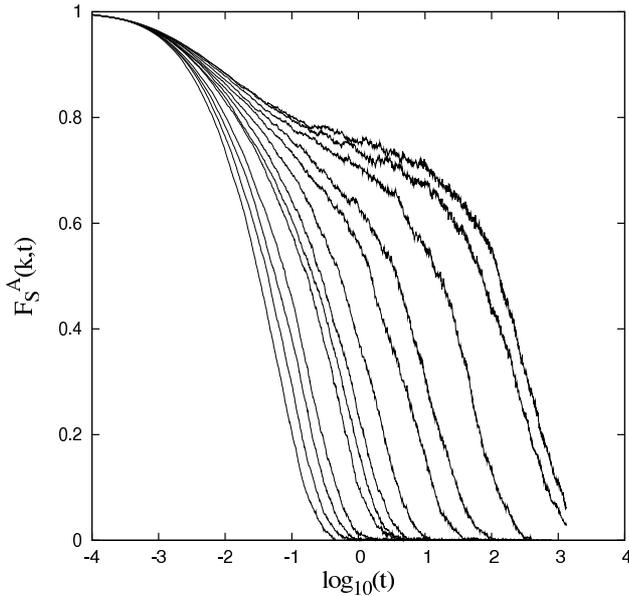


Fig.6 The self-intermediate scattering function of the particles of type *A* versus time for different temperatures at $k = 7.25$. The details are the same as in Fig. 3.

the pressure P , the radial distribution function $g_{AA}(r)$, the mean-square displacement $M_2^A(t)$, and the self-intermediate scattering function $F_S^{AA}(k, t)$. Thus, we have shown that as the temperature decreases, the system smoothly becomes a supercooled state from a liquid state without crystallization. In fact, the pressure P decreases smoothly without any jumps as T decreases. The split of the second peak of $g_{AA}(r)$ are observed at temperatures lower than $T = 0.6$. This is one of signs for a supercooled state. This situation is the same as that in the Lennard-Jones binary mixtures [15].

We have not discussed the long-time self-diffusion coefficient and several characteristic times. In order to study whether the system is in a supercooled state or not and also how the present system is different from Lennard-Jones binary mixtures, we must explore them from a unified point of view. This will be discussed elsewhere together with self-consistent analyses of simulation results by the mean-field theory.

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