

Computer Simulations of two kinds of Polydisperse Hard-Sphere Systems; Atomic Systems and Colloidal Suspensions

*Tsutomu Shimura*¹, *Hiroyuki Yamazaki*², *Yayoi Terada*¹, *Michio Tokuyama*¹

1. Institute of Fluid Science, Tohoku University, Sendai 980-8577, Japan

2. Fuji Photo Film Co., Ltd, Nishiazabu 2-26-30, Minato-ku, Tokyo 106-8620, Japan

Corresponding author *Tsutomu Shimura* (*shimura@ifs.tohoku.ac.jp*)

Abstract

We perform two kinds of computer simulations on polydisperse hard-sphere systems; a molecular-dynamics simulation on atomic systems and a Brownian-dynamics simulation on colloidal suspensions. Analyses of the mean square displacement, the radial distribution function, and the pressure suggest that there exist three phase regions, a liquid phase region, a metastable phase region, and a crystal phase region, where the freezing and melting points are shifted to the values higher than in monodisperse case. It is also shown that the long-time behavior of colloidal suspensions is exactly the same as that of atomic systems.

Keyword: Brownian Motion, Hard Spheres, Liquid-Solid Phase Transition, Polydispersity

1. Introduction

In recent years, a considerable number of studies have been made on the hard-sphere systems because of their simplicity. In this paper we perform two kinds of computer simulations on polydisperse hard-sphere systems; a molecular-dynamics simulation on atomic systems and a Brownian-dynamics simulation on colloidal suspensions, where the distribution of radii obeys a Gaussian distribution with standard deviation σ divided by a . Here a is a mean particle radius. Then, the atomic particles obey Newton equations with the force F_{ij} , where F_{ij} indicates the force between particle i and particle j . On the other hand, the colloidal particle obeys Langevin-like equation on a time scale of order t_D ,

$$\frac{d}{dt} \mathbf{X}_i(t) = \frac{1}{\gamma_i} \sum_{j \neq i} \mathbf{F}_{ij}(t) + \mathbf{R}_i(t), \quad \langle \mathbf{R}_i(t) \mathbf{R}_j(t') \rangle = 2D_{0i} \delta_{ij} \delta(t - t') \mathbf{I}, \quad (1)$$

where $\mathbf{X}_i(t)$ represents the position vector of particle i , $\gamma_i (= 6\pi\eta a_i)$ the friction coefficient, a_i the particle radius, $D_{0i} (= k_B T / \gamma_i)$ the bare diffusion coefficient, $\mathbf{R}_i(t)$ the Gaussian random velocity with zero mean, and η the viscosity of the fluid. Here $t_D = a^2 / D_0$ indicates structural relaxation time, and $D_0 = k_B T / (6\pi\eta a)$, where k_B Boltzmann constant, and T temperature. For simplicity, we have neglected the hydrodynamic interactions between particles. We assume elastic binary collisions between particles. Our simulations have been performed in the cubic cell which consists of N hard spheres with periodic boundary condition, where $N=10976$ here. As initial configurations, our simulations start from (I) a disordered configuration and (II) an ordered face centered cubic crystal configuration.

2. Results and Discussion

The mean square displacement is given by

$$M_2(t) = \frac{1}{N} \sum_{i=1}^N \langle [\mathbf{X}_i(t) - \mathbf{X}_i(0)]^2 \rangle. \quad (2)$$

Figure 1 shows a log-log plot of $M_2(t)$ versus time t for different volume fractions. In Fig.2, the

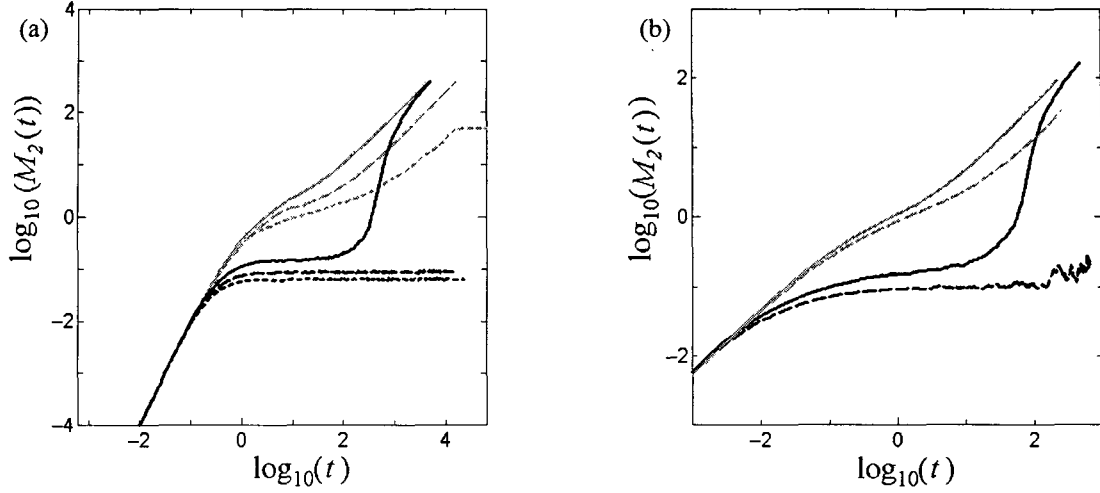


Fig.1. A log-log plot of the mean square displacement $M_2(t)$. (a) the atomic systems and (b) the colloidal suspensions. Solid lines, broken lines, and dotted lines stand for $\phi=0.52, 0.55,$ and $0.57,$ respectively. The black line indicates the results for the ordered initial configuration, and the grey line for the disordered initial configuration.

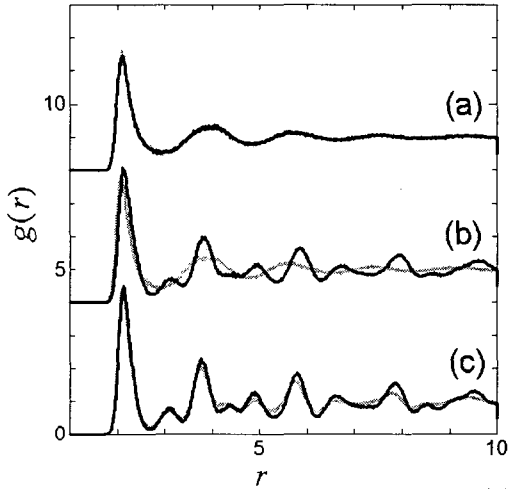


Fig.2. The Radial distribution function $g(r)$ of atomic systems for (a) $\phi=0.52,$ (b) $\phi=0.55,$ and (c) $\phi=0.57.$ The details are the same as in Fig. 1.

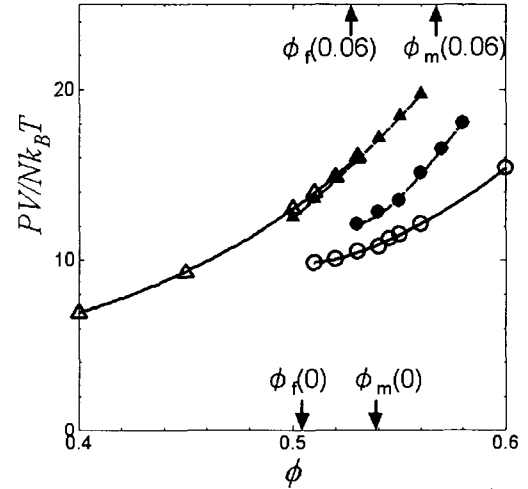


Fig.3. Pressure of atomic systems P versus ϕ . Open symbols and filled symbols indicate the results for a monodisperse case and for a polydisperse case, respectively; triangles in a liquid state, and circles in a crystal state.

radial distribution functions of atomic systems are shown for different volume fractions. In Fig. 3 the pressure P of atomic systems is also shown for a monodisperse case and a polydisperse case. The simulation results suggest that there exist three phase regions, a liquid phase region for $\phi < \phi_f(\sigma)$, a metastable phase region for $\phi_f(\sigma) \leq \phi < \phi_m(\sigma)$, and a crystal phase region for $\phi_m(\sigma) \leq \phi$, where ϕ denotes the volume fraction of the particles, $\phi_f(\sigma)$ the freezing volume fraction, and $\phi_m(\sigma)$ the melting volume fraction. Our simulations show that $\phi_f(\sigma=0) \approx 0.51$, $\phi_m(\sigma=0) \approx 0.54$, and $\phi_f(\sigma=0.06) \approx 0.53$, $\phi_m(\sigma=0.06) \approx 0.57$. In a metastable region, the long time behavior strongly depends on the initial configurations. In case (I) the system remains in a liquid state within our simulation time, while in case (II) it remains in a crystal state. Finally we also show that the long-time behavior of suspensions is the same as that of atomic systems.

This work was partially supported by Grants-in-aid for Science Research with No. 14540348 from Ministry of Education, Culture, Sports, Science and Technology of Japan. The calculations were performed using the ORIGIN 2000 in the Institute of Fluid Science, Tohoku University.