Dynamical Study of Polydisperse Hard-Sphere System

Tomoaki Nogawa, Nobuyasu Ito
Department of Applied Physics, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Hiroshi Watanabe
Supercomputing Division, Information Technology Center,
University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8658, Japan

We study the interplay between the fluid-crystal transition and the glass transition of elastic sphere system with polydispersity using nonequilibrium molecular dynamics simulations. It is found that the end point of the crystal-fluid transition line, which corresponds to the critical polydispersity above which the crystal state is unstable, is on the glass transition line. This means that crystal and fluid states at the melting point becomes less distinguishable as polydispersity increases and finally they become identical state, i.e., marginal glass state, at critical polydispersity.

I. INTRODUCTION

Recently, jammed (amorphous) solid has attracted more attention in two aspects; 1) the origin of rigidity which fluid lacks, and 2) whether some essential differences exists between the jammed solid and crystal except for the positional order. The former corresponds to the long standing problem of glass transition [1] and jamming transition [2], and the latter is related to the dense packing problem [3]. Since whether the solid has or lacks the positional order is complexly related to properties of materials, it is difficult to find which factor is important. Systematic study is, however, possible in polydisperse particle system, which consists of multiple ingredients with various sizes or shapes. It is empirically known that binary fluid mixture, with more than 10% size-dispersion, often exhibits glass transition while monodisperse simple fluid exhibits crystallization transition. Therefore, polydispersity is one of the most important factors for the glass transition. While the system may involve the glass transition for high enough polydispersity and the simple crystallization for low enough polydispersity, there remains a gap in knowledge between these two regimes. In order to study the effect of polydispersity, accurate control of polydispersity is required, which is difficult in experiments.

Here, we consider the polydisperse hard-sphere (HS) system, which is one of the simplest models to exhibit both of fluid and crystal phases. While it is well known that monodisperse HS system takes a first order melting/crystallization transition, so-called the Alder transition, by increasing/decreasing pressure or density [4, 5], much attention recently has been attracted to the problem; how polydispersity affects this transition. Most remarkable finding is that the discontinuity at the melting point, i.e., density gap between the fluid and the crystal, decreases as the strength of polydispersity increases and finally vanishes at a certain critical point (see Fig. 1). This is similar to the well-known liquid-gas criticality in systems with attractive interactions but there are some differences. The fluid and crystal states are distinguished by their spatial periodicity and fluidity, in addition to their density. Therefore, there is another transition(s) corresponding to the two properties in the supercritical region. When periodic order is not established even after fluidity is lost, there must be an intermediate phase, which is considered the glass phase [10]. The transition from fluid to glass is considered to be dynamical transition corresponding to ergodicity breaking [11, 12].

The phase behavior of a polydisperse HS system still remains under discussion. Bartlett and Warren studied polydisperse systems using a density functional theory (DFT) and claimed that the thermodynamic function does not have a singularity at the point of equal concentration and that the first-order transition line is extended to high-density region to surround the crystal phase [13]. Furthermore, Fasolo et al. pointed out the importance [14].

\[ \Delta P \]

FIG. 1: (color online) Phase diagram showing the polydispersity vs packing fraction (or pressure, inset) plane. There are three equilibrium phases: fluid, crystal, fluid-crystal coexistence. The boundary between the fluid and the disordered solid indicates a dynamical transition.
of fractionation; segregation into multiple crystals. Each crystal has different mean radius and relative dispersion is small inside it. By considering the free energies of mixed states, a lot of coexisting phases appears and the phase diagram becomes very complicated. Although such fractionated states is reasonable in thermal equilibrium state, these phases are not observed in experiments or numerical simulations. One reason is that the system is glassy in the regime where fractionation is predicted. Therefore diffusion of particles over long distance, which is necessary for segregation, is suppressed.

In the present paper, we don’t treat fractionation but consider long surviving homogeneous state including both of equilibrium and nonequilibrium ones. Especially, we discuss the relation between the fluid-crystal transition for small dispersity and the fluid-glass transition for large dispersity. We perform nonequilibrium molecular-dynamics (MD) simulations, which is not only useful to study nonequilibrium dynamics but also gives clue to reveal equilibrium property. We study the fluid-crystal transition in equilibrium for low dispersity by nonequilibrium simulation. On this aspect, a number of numerical studies on polydisperse hardcore systems has been previously reported. But these have been highly restricted to two-dimensional hard-disc systems. Since two-dimensional systems show peculiar properties owing to the low dimensionality, the study of three-dimensional systems is necessary. On the other hand, it is difficult to perform simulations with sufficiently large linear dimensions in three dimensions, thus finite size effect often makes the conclusions ambiguous. Nonequilibrium analysis without time-consuming equilibration makes large-scale simulations possible.

Let us denote the contents of the present paper. In the next section, the detail of the model and method of a numerical simulation is explained. From section III to V, we investigate three transitions among fluid, crystal and glass states to obtain the nonequilibrium phase diagram shown in Fig. 1. The final section is devoted for the concluding remarks.

II. MODEL: HARD ELASTIC SPHERES

We perform MD simulations of elastic spheres with a fixed number of particle $N$, temperature $T$ and pressure $P$ using the Nosé-Hoover method and the Parinello-Rahman method. The reason we did not employ the standard event-driven simulation of HSs is that pressure control, which is essential in the following analysis of first order transition, cannot be implemented efficiently to this method. Since hard-sphere system is widely accepted as one of reference models for solid-fluid transitions, we estimate hard-limit of elastic modulus by extrapolation, which is described later. Hereafter, we use the units with which temperature $k_B T = 1$, mean radius $\bar{r} = 1$, and the mass of the particle to be $m_i = 1$.

Polydispersity is introduced by a uniform distribution of particle radii. The strength of polydispersity is measured by the standard deviation, $\Delta = \sqrt{\langle r_i^2 \rangle - \langle r_i \rangle^2}$, where $r_i$ is the radius of particle $i$ and $\langle \rangle$ denotes the average over all particles. It is known that the quantitative properties of a polydisperse system are well described only by $\Delta$ and that the detailed form of the distribution function of $r_i$ is irrelevant when polydispersity is not too strong.

The interaction between contacting particles, $i$ and $j$, is given by the Hertzian contact potential, $\phi_{hc} = (4\pi/3V) \sum_i \left( \bar{r} - c_0 E_0^{-2/5} \right)^3$ with a calibration constant $c_0$. This constant is determined to be $c_0 = 0.48$ by performing preliminary simulations, with which we confirmed that the extrapolated state equation exhibits good agreement with the result of event-driven simulation of the true HS system. This correction is used throughout the letter. For example, $\phi_{hc}$ is 0.6% smaller than $(4\pi/3V) \sum_i \bar{r}_i^3$ for $E_0 = 10^6$.

We adopt two types of initial particle configuration: FCC and random configurations. The radii of particles are assigned randomly in accordance with the distribution mentioned above and independently of the positions. For random initial state, we perform simulations with overdamped dynamics before integrating Hamilton’s equations of motion until the maximum kinetic energy of the particles decreases below 200 to avoid the rapid acceleration of strongly coalesced particle pairs. After that, the initial velocities are randomly assigned by the Boltzmann distribution.

The observed quantities discussed below are the data for $E_0 = 10^6$ averaged over 4 samples with $N = 55296$, unless otherwise stated. We confirm that our conclusions do not change in a larger system with $N = 131072$. Time integration is performed by the fourth-order predictor-corrector method using a discrete time step of $\Delta t = 0.0004 - 0.02$ and typical number of integration step is $4 \times 10^6$.

III. CRYSTAL MELTING TRANSITION

First, we analyze the polydispersity dependence of the fluid-crystal transition and clarify the existence of the predicted critical point $(P_c, \Delta_c)$. The order parameter
corresponding to this criticality is the density gap $\delta \phi$ between the bistable phases at the melting point. This is calculated by a two-step simulation. As a first step, we determine the melting pressure $P_m(\Delta)$ for a given $\Delta(< \Delta_c)$ from the nonequilibrium analysis discussed later. After that, we observe the packing fractions of the bistable states, $\phi_{\text{fluid}}(\Delta, P_m(\Delta))$ and $\phi_{\text{solid}}(\Delta, P_m(\Delta))$, individually by performing equilibrium simulations with both fluid (random) and crystal (FCC) initial conditions. The packing fraction of the fluid/crystal at the melting point gives the lower/upper bound of the coexisting phase at a fixed $\phi$ condition (see Fig. 1) and its width is $\delta \phi(\Delta) = \phi_{\text{solid}}(\Delta, P_m(\Delta)) - \phi_{\text{fluid}}(\Delta, P_m(\Delta))$.

To determine the melting point, we observe the nonequilibrium relaxation from the mixed initial state [21, 22]; a half of the cubic space is occupied by the crystal and the remaining part is occupied by the random packing (fluid). Thus the two regions are separated by a flat interface, which is perpendicular to the (100)-direction of the FCC structure at time $t = 0$. As $t$ increases, the interface moves so that the fraction of the phase with lower free energy increases. The melting pressure $P_m$ can be determined as the point where the sign of $d\phi/dt$ in the steady state changes, since positive and negative values of $d\phi/dt$ indicate that crystallization and melting occur at the interface, respectively. This method requires a relatively short-time simulation compared to the equilibrium method and enables us to treat larger systems and reduce the finite-size effect. Figure 2 shows the pressure dependence of $d\phi/dt$ and obtained $P_m(\Delta)$ gives the phase boundary between fluid and crystal phases in the inset of Fig. 1.

By this steady interface motion, we can compare equilibrium stability of FCC and fluid states. There remains a possibility, however, that there can be more stable state, such as other types of crystal structure. But we expect that it is not the case for polydispersity, $\Delta < 0.088$.

Performing additional equilibrium simulations at these $P_m(\Delta)$, we eventually obtain $\Delta$-dependence of the $d\phi$ shown in Fig. 3. This order parameter approaches zero as $\delta \phi \propto (\Delta_c - \Delta)^\beta$ with $\Delta_c = 0.088(2)$ and $\beta = 0.7(2)$. The critical pressure $P_c = 3.0(2)$ and the critical packing fraction $\phi_c = 0.576(4)$ are also obtained. We also calculate the FCC order parameter of the crystal state; $m = \cos[K_{\text{FCC}} \cdot (q_i(t) - q_i(0))]$, where $K_{\text{FCC}}$ is the fundamental reciprocal vector of the FCC crystal. The inset of Fig. 3 indicates a power-law; $m \propto \delta \phi(\Delta)^{\beta_m}/\beta \propto (\Delta_c - \Delta)^{\beta_m}$ with $\beta_m = 0.04(1)$. The range of observed value of $m$ is, however, too narrow to conclude the existence of the power-law.

IV. GLASS TRANSITION

We next investigate the transition between the fluid and glass phases by scanning $P$ at fixed $\Delta(> \Delta_c)$. Significant change is observed around a certain threshold $P_g(\Delta)$; the mobility of particles markedly decreases approaching $P_g$, which denotes the glass transition point.

Figure 4 shows the $P$-dependence of the diffusion constant, $D(t_w) = |q_i(2t_w) - q_i(t_w)|^2/t_w$, with waiting time $t_w$ under the random initial condition. Here we make the time interval to measure the displacement equivalent with $t_w$ so that only single time scale is introduced. While the $D(t_w)$ converges to a certain equilibrium value by increasing $t_w$ for $P < P_g \approx 3.0$, the relaxation is so slow for $P > P_g$ that equilibrium state cannot be obtained for used values of $t_w$. Instead, we remarks on the aging property, i.e., the persistent waiting-time dependence; $D(t_w)$ continues to decrease with $t_w$, roughly in a power-law, above $P_g$. This indicates that as the relaxation proceeds, the system becomes trapped in an increasingly stable metastable state and the dynamics becomes slower.

As clearly observed in Fig. 4 the $D(t_w)$ vs $P$ curves.

FIG. 2: (color online) Time derivatives of the mean density is plotted with respect to pressure for $\Delta = 0.0 - 0.085$. The derivative $d\phi/dt$ is approximated by $[\phi(2t_w) - \phi(t_w)]/t_w$ with $t_w/0.001 = 2^{18}$ and $2^{20}$.

FIG. 3: (color online) Polydispersity dependence of the density gap between the fluid and crystal states on the melting line. The results for different Young’s moduli are shown together but very little difference is observed. The solid curve denotes $\delta \phi = 0.45 \times (0.088 - \Delta)^{0.73}$. (inset) Log-log plot of the relation between the density gap and the crystalline order parameter on the melting line.
hardly depend on $\Delta$ for $\Delta \leq 0.12$. Thus $P_g(\Delta)$ is also independent of $\Delta$ and equals to 3.0, similar to the value of $P_c$. In general, the effect of polydispersity is small except in the crystal phase. In addition, almost the same behavior is observed even in the subcritical region ($\Delta < \Delta_c$), as a supersaturation phenomena [12]. Any sign of crystal nucleation is not observed for $\Delta \geq 0.60$. It is known that polydispersity drastically reduces the nucleation rate of the crystal [4]. In the inset of Fig. 4, $\phi_{nc}$ is plotted with respect to $P$. The packing fraction also has little dependence on $\Delta$ (slightly increases with $\Delta$) both in the fluid and glass phases. Therefore, the glass transition density $\phi_g(\Delta) \equiv \phi(P_g(\Delta))$ also has little dependence on $\Delta$ and $\phi_g \approx 0.57 \approx \phi_c$. The extrapolated value, $\phi_g(\Delta \to 0) \approx 0.57$, agrees with the value, $\phi_d \approx 0.58$, predicted by mode-coupling theory [11] or mean field theory, which corresponds to the appearance of the exponentially many metastable states in the fluid [23].

Above the threshold pressure $P_g$, $\phi_{nc}$ gradually approaches the random close packing (RCP) fraction $\phi_{RCP}(\Delta)$ [24], which equals 0.635 for the monodisperse ($\Delta = 0$) system and increases very slowly with $\Delta$ [23].

V. CRYSTAL-AMORPHOUS TRANSITION

Finally, we consider the transition between the crystal and glass states, which is driven by sweeping $\Delta$ at fixed $P(> P_c)$. In Fig. 5 we plot the $\Delta$-dependence of $\phi_{nc}$, estimated by simulations under both crystal and random (glass) initial conditions. Both the crystal and glass states are (meta)stable for a long time in the high-pressure region since there is too little free volume for the local structures to reconfigure. The packing fraction of the crystal is larger than that of the glass for small $\Delta$ but they becomes indistinguishable above a certain threshold $\Delta_{am}(P)$. This threshold appears to be universal, i.e., it hardly depends on $P$. In addition, its value is very similar to $\Delta_c \approx 0.088$. The density difference continuously decreases to zero as $\Delta$ approaches $\Delta_{am}$. Similar behavior is observed for the crystalline order parameter under the FCC initial condition.

VI. CONCLUSIONS

In summary, we investigated the dynamical transitions of a polydisperse elastic sphere system by MD simulations by remarking on nonequilibrium states including metastable states. The obtained transition lines with respect to the packing fraction and polydispersity are summarized in Fig. 1. It was confirmed that the first-order transition between the fluid and crystal phases terminates at the critical point $(\phi_c, \Delta_c)$ and that the other two phase boundaries begin from the critical point to surround the glass phase. The glass state has intermediate properties between those of the fluids and crystal states; it exhibits temporal freezing but does not have periodic order. The fluid-glass and crystal-glass boundaries can be drawn in a surprisingly simple way and are expressed as $P \approx P_c$ (or $\phi \approx \phi_c$) and $\Delta \approx \Delta_c$, respectively. The glass transition line passes through the critical point, which is reasonable because the continuous breakdown of the crystal requires marginal fluidity at the critical point. While softening of the interaction potential will not make essential change in the phase behavior, that of a system with attractive interactions is an interesting open problem.

The transition between the fluid and glass states is not considered to be an equilibrium transition but a dy-
namical one since the static quantities do not exhibit any singular behavior and the transition line is elongated into the crystal phase in equilibrium. This continuous relationship from the supercritical region to the supersaturating monodisperse system suggests the equivalence of the dynamical glass transitions in the monodisperse and polydisperse systems. Let us note that the critical packing fraction is close to the random loose parking (RLP) fraction, \( \phi_{\text{RLP}} \approx 0.56 \), which is considered to be the minimum packing fraction required to maintain the internal stress for highly frictional particles [26]. This coincidence seems natural considering that RLP gives a criterion related to the excluded volume effect. The free volume of particles is very small above \( \phi_{\text{RLP}} \) and diffusion is highly suppressed.

Let us consider the meaning of the boundary between the crystal and glass states. The transitions at this boundary are continuous in terms of density, in contrast to those of fluid-crystal boundary in the subcritical region. It is natural that the first-order transition line and a continuous transition line should meet at the multicritical point. But this is conflict with the prediction of first order transition by Bartlett and Warren [13]. Our nonequilibrium analysis cannot eliminate the possibility that the crystal phase is metastable below \( \Delta_{\text{am}} \), which is estimated by nonequilibrium simulations, and first-order transition occurs at \( \Delta < \Delta_{\text{am}} \). We wonder, however, whether a mean-field-like approach in the DFT scheme can treat the state around the terminal point, where the fluid exhibits singular behavior in dynamics and the periodicity of the crystal is damaged. Our numerical result suggests the possibility that criticality remains.

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