



Polydispersity Effect on Solid-Fluid Transition in Hard sphere Systems

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The solid-fluid transition of the hard elastic particle system with size polydispersity is studied by molecular dynamics simulations. Using nonequilibrium relaxation from the mixed initial condition we determine the melting point where the first order transition between the solid, fcc crystal, and fluid states occurs. It is found that the density gap between the bistable states decreases with increasing the strength of the polydispersity and continuously approaches to zero at the critical point.

1. Introduction

Hardcore particle system is the simplest model which exhibits both of solid and fluid phases. Which state is stable in thermodynamics is governed only by the configuration entropy and the phase transition is driven by controlling density (volume) or pressure in fixed particle number systems [1,2]. The hardcore system also shows glassy behavior by introducing polydispersity: inhomogeneity of shape or size among particles [3–5]. For sufficiently weak polydispersity the system still shows well distinguishable crystal and fluid phases and exhibits a first order melting transition as well as the monodisperse system. It is, however, predicted that there exists a critical strength of polydispersity above which the system continuously changes the state between fluid and solid without melting transition [4,6]. This crossover is expected to correspond to the glass transition. Therefore the critical point, the end of the melting line in pressure-polydispersity space, must be important to clarify the origin of glassy or amorphous nature of the materials.

There are several studies on the hard disc systems in two dimensions, which supports the existence of the critical point. But two dimensional system is rather exotic and expected to show the two-stage Kosterlitz-Thouless transition instead of a first order transition [7,8]. In this article, we study a hardcore sphere system in three dimensions focusing on the polydispersity dependence of the melting transition to clarify the existence of the critical point mentioned above. On this purpose we provide an efficient technique for the analysis of the first order transition using nonequilibrium relaxation.

2. Model and methods

The molecular dynamics simulation of hardcore particle is usually performed by using the event-driven algorithm. Although this algorithm provides very high precision in the solution the equation of motion, it is not suitable for simulations on the constant-pressure condition or with large scale by multi-thread computation. Thus we treat the hard elastic particle system, which is identical to hard core one in the large elastic modulus limit. The basic Hamiltonian of the system is written as follows,

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \sum_{\langle i,j \rangle} U_{\text{el}}(r_i + r_j - |\mathbf{q}_i - \mathbf{q}_j|), \quad (1)$$

where m_i , r_i , \mathbf{q}_i and \mathbf{p}_i are the mass, radius, position and momentum of the i -th particle, respectively. The elastic interaction is introduced by the Hertzian contact potential, $U_{\text{el}}(x) = E_0 x^{5/2} \Theta(x)$, where E_0 means the elastic modulus and $\Theta(\cdot)$ is the Heaviside's step function. We use the Nose-Hoover thermostat [9] and the Parrinello-Rahman method [10] in order to obtain constant temperature T and pressure P . The time integration of the Hamilton equation is performed by using the fourth order predictor-corrector method.

The polydispersity is introduced by a uniform distribution of the radii of particles in $\bar{r} - \sqrt{3}\Delta < r < \bar{r} + \sqrt{3}\Delta$, which leads average \bar{r} and dispersion Δ^2 . The standard deviation Δ is a parameter to measure the degree of the polydispersity. It is known for the hard disc system that the $\phi - P$ curve only depends on the dispersion not on the detail of the distribution function [4]. We don't consider the distribution of mass and set $m_i = m$ for all i .

We use a cubic space with the linear dimension L_0 and impose the periodic boundary condition. In order to find the melting point, which lies in the metastable region, we observe nonequilibrium relaxation from the mixed initial state [11], where the solid and fluid regions coexist in the same sample. In the metastable region in P , the phase with lower free energy invades the region of the other phase to leave a single phase state. This can be regarded as melting or crystal growth on the domain boundary. The two phases are bistable at the melting point and the interface does not move. In practice we prepare a solid phase with $N/2$ particles in $0 < x < L_0/2$ and a fluid phase with $N/2$ particles in $L_0/2 < x < L_0$ coexist in the same sample. (There are two interfaces in the periodic boundary condition.) The solid phase is given by the fcc crystal and the fluid phase is by random configuration. The interface between them is a plain parallel to the (100)-direction of the fcc. For the polydisperse case we give the random value of particle radius independently of the position of the particle in the both region. Since the random initial configuration in the fluid phase results pair particles which deeply stick to each other at a certain probability, we perform overdamped relaxation to avoid the breakdown of the simulation. The volume fraction of the particles ϕ is set appropriately and those of both regions settle to the equilibrium values, $\phi_{\text{solid}}(P)$ and $\phi_{\text{fluid}}(P)$ for given P as the simulation proceed. Ideally mean density will behaves as

$$\phi(P, t) = \frac{1}{2}[\phi_{\text{solid}}(P) + \phi_{\text{fluid}}(P)] + \frac{2v_{\text{DW}}(P)t}{L}[\phi_{\text{solid}}(P) - \phi_{\text{fluid}}(P)], \quad (2)$$

where $v_{\text{DW}}(P)$ is the velocity of the domain boundary which is negative for $P < P_m$ and positive for $P > P_m$.

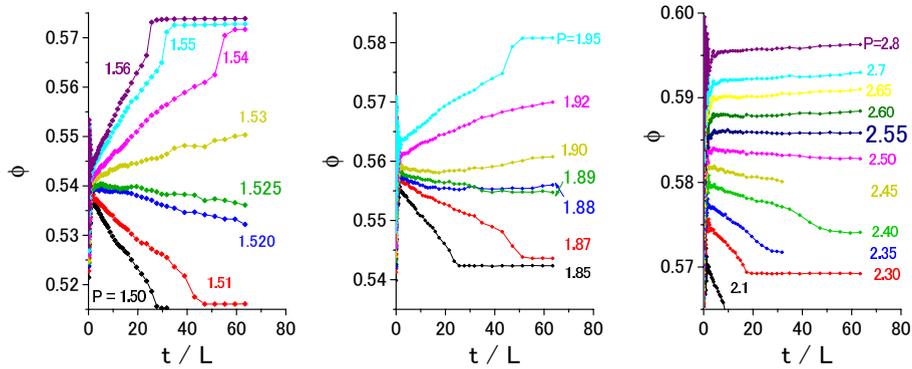


Figure 1. Time evolution of the volume fraction of ϕ for $\Delta = 0.0$ (left), 0.060 (center) and 0.080 (right).

The density gap at the melting point $\phi_g(\Delta) = \phi_{\text{solid}}(P_m) - \phi_{\text{fluid}}(P_m)$ plays a role of the order parameter for the continuous transition corresponding to the symmetry breaking between the solid and fluid states and approaches to zero at Δ_c . After P_m is determined, we estimate $\phi_{\text{solid}}(P_m)$ and $\phi_{\text{fluid}}(P_m)$ by the equilibrium simulations with the *single* phase initial conditions. to obtain $\phi_g(\Delta)$.

3. Results

In this article we use an unit to yield $m = 1, \bar{\tau} = 1$ and $T = 1$ and only show the results for $E_0 = 1.0 \times 10^4$ and $N = 4L^3 = 131072$.

At first, we observe the nonequilibrium relaxation of the monodisperse system. Figure 1(left) shows the time evolution of ϕ . We can find eq. (2) roughly holds and v_{DW} changes its sign between $P = 1.525$ and $P = 1.530$. Thus P_m is estimated as $1.527(3)$. It is confirmed that the melting point and the density gap reproduces those of the true hardcore system by taking the large E_0 limit.

The center and left graphs in Fig. 2 are the results of the polydisperse cases with $\Delta = 0.060$ and 0.080 . The melting point can be found in the same way with the monodisperse case. Larger Δ leads larger P_m and v_{DW} becomes smaller because the particles are packed closely and cannot move easily. This makes it more difficult to determine P_m .

The density gap is plotted as a function of Δ^2 in Fig. 2. The gap shows a tendency to vanish at $\Delta = \Delta_c \approx 0.087$ ($\Delta_c^2 \approx 0.0076$). These suggests that the difference between solid and fluid state disappears above Δ_c and actually we do not observe any obvious singular behavior of transition for $\Delta > \Delta_c$ (not shown here). The phase diagrams in $\Delta^2 - P$ and $\Delta^2 - \phi$ plains is obtained from the simulations for various Δ as shown in Fig. 3. The critical values of the pressure and the packing fraction is roughly estimated as $P_c = 3.0$ and $\phi_c = 0.60$, respectively.

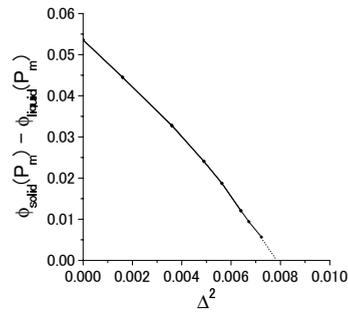


Figure 2. Polydispersity dependence of the density gap, the difference of the volume fractions between the solid and fluid phases at the melting point.

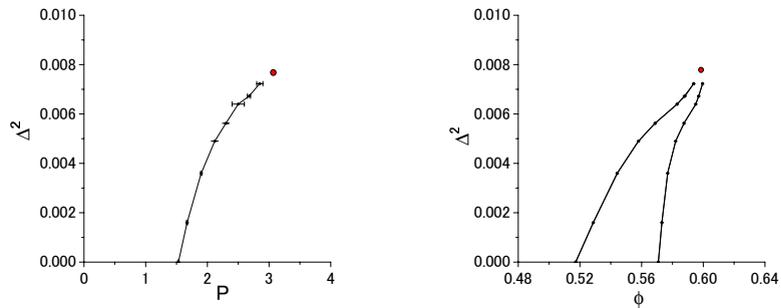


Figure 3. Phase diagrams for the constant-pressure and constant-density conditions. The red point indicates the expected critical point.

4. Summary and Discussion

In conclusion we investigate the melting transition of the polydisperse hard elastic particles by using nonequilibrium relaxation method from the mixed phase initial state. It is confirmed that the discontinuity of the transition decreases as the strength of the polydispersity grows and vanishes at the critical point. In this article E_0 is restricted to a single value E_0 . Although there will be some corrections on the values, Δ_c , P_c and ϕ_c , in the hard core limit, the critical behavior is expected not to change qualitatively as far as the interaction of the particles are repulsive and short-ranged.

There remains open problems about the nature of the transitions between the crystal and amorphous solid phases for $P > P_c$ (or $\phi > \phi_c$) and between the fluid and amorphous solid phases for $\Delta > \Delta_c$.

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