EFFECT OF SIZE DISPERSITY ON THE MELTING TRANSITION

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ABSTRACT

We present a molecular dynamics simulation study of the liquid-solid transition in a two dimensional system consisting of particles of two different sizes interacting via a truncated Lennard-Jones potential. We work with equal number of particles of each kind and the dispersity $\Delta$ in the sizes of the particles is varied by changing the ratio of the particle sizes only. For the monodisperse case ($\Delta = 0$) and for small values of $\Delta$, we find a first order liquid-solid transition on increasing the volume fraction $\rho$ of the particles. As we increase $\Delta$, the first-order transition coexistence region weakens gradually and completely disappears at high dispersities around $\Delta = 0.10$. At these values of dispersity the high density phase lacks long range translational order but possesses orientational order with a large but finite correlation length. The consequences of this effect of dispersity on the glass transition and on the melting transition in general are discussed.

INTRODUCTION

The liquid-solid transition in a system of densely-packed interacting particles has attracted considerable attention in recent years\cite{1}. Such a system undergoes a transition from a disordered liquid phase to an ordered solid phase on increasing the volume fraction of the particles. It was further observed that polydispersity in the sizes of the particles has a profound effect on the transition. With increasing dispersion, the solid structure becomes unstable and above a certain degree of dispersity the solid cannot form at all\cite{2}. The consequence of this should be very important from the experimental point of view since colloidal suspensions in general do have particles of various sizes and show the liquid-solid transition \cite{3} and in the simulations of glass transition, particles of different sizes are always considered \cite{4}. Still, the effect of size dispersity on the liquid-solid transition has not received sufficient attention. In this paper, we study the effect of size-dispersity on the liquid-solid transition for interacting particles in two dimensions.

The instability of the solid phase with increasing size dispersity is not striking, as one would intuitively expect that a high dispersity naturally destroys the crystal order needed to form a solid. But molecular dynamics (MD) simulation studies in three dimensions \cite{2}, and similar recent studies in two dimensions \cite{5}, consistently show the gradual weakening of the first order transition with increasing dispersity $\Delta$ and find the existence of a critical value $\Delta_c$ where the line of first-order transitions ends. At $\Delta_c$, one does not see the first order transition. This prediction also arises from a study employing the density functional theory\cite{6} and simpler models of crystals\cite{7}. The phase diagram is remarkably similar to the first order transitions ending in a critical point that one observes in the temperature driven liquid-gas transition. We study the transition at and around $\Delta_c$ by carefully examining the nature of the phases obtained at different densities and dispersities.
Figure 1: Pressure versus density plots for different dispersities. The small dispersity curves show the first order phase transition from the low density liquid phase to the high density 2d-solid phase with the intermediate flat coexistence region. The inset is a blow up of the coexistence regions at different dispersities.

MODEL AND SIMULATION

We report a molecular dynamics simulation study of a 50–50 mixture of Lennard-Jones (LJ) particles of two different sizes. The particles are contained in a two dimensional box of linear size $L$ with periodic boundary condition used on all walls. We have performed our simulations for $N = 400$, 2500 and 10000 particles. To each particle we assign a radius proportional to its LJ diameter and define the density $\rho$ as the ratio of the total area occupied by the particles to the total area of the box.

The degree $\Delta$ of size dispersity is quantified by the relative width of the bimodal particle size distribution function. Here we present results for dispersities $\Delta = 0$, 0.06, 0.07 and 0.10. All physical quantities are measured in reduced units in which the average LJ diameter $\sigma$, LJ energy scale $\epsilon$ and the mass of each particle are one. Our results are all collected from the isothermal hyper-surface of the phase space with $kT = 1.0$, where $k$ is the Boltzmann constant. Pressure $P$ is computed using the virial relation.

RESULTS

Fig. 1 shows the $P - \rho$ diagrams for different dispersities $\Delta$. For small $\Delta$, we observe the flat coexistence region which is a characteristic feature of first order phase transition. This region shrinks as $\Delta$ increases and near $\Delta = 0.1$ disappears completely.

Fig. 2 shows the mean square displacement (MSD) of the particles at different phases for $\Delta = 0$ and 0.1. The plots for $\Delta = 0$ essentially have three features: (i) a late time diffusive regime for low densities (ii) a frozen regime where the diffusion is very small for high densities (iii) a sudden change in the MSD behavior between the two regimes on varying the density. This jump is one of the characteristic features of a first-order phase transition. We observe these features for other $\Delta$ values but with increasing $\Delta$, the magnitude of the jump in the MSD plot decreases and the system goes from liquid to solid regime rather
continuously. On the other hand the MSD plot for $\Delta = 0.10$ shows that at high dispersity, the system does not become solid even at $\rho = 1.0$.

In order to study the translational symmetry at different phases, we measure the total pair distribution function $g(r)$ (Fig. 3). The form of $g(r)$ for the low density phase has a liquid-like structure. On the other hand for $\Delta = 0$, the solid phase at high densities shows a clear 2d solid-like structure with pronounced peaks, and deep dips which persist up to long distances, with the amplitude of the peaks decreasing slowly. This quasi-long-range translational symmetry is expected for solids in two dimensions [9]. For large values of dispersity around $\Delta = 0.10$ and high density the system does not show the solid structure mentioned above and lacks translational order.

Next, we study the orientational order of the phases by measuring the hexagonal order parameter $\psi_6$ [10] which characterizes the local bond orientational order around particles. The absolute value of $\psi_6$ increases from a small positive value to one as the structure changes from disorder to an ordered triangular lattice. We have plotted the distribution of $|\psi_6|$ for all particles (see Fig. 4). The liquid phase has a flat distribution, thus not showing any local orientational order [10]. The solid phase shows a high degree of local orientational order, since it forms a nearly perfect triangular lattice. On the other hand for $\Delta = 0.10$ the $\rho = 1.0$ system shows a hump near unity but also a big tail extending down to zero. The hump confirms the existence of local hexagonal order which has also been observed in experiments on bidisperse hard spheres[11]. The presence of the long tail indicates that there are many orientational defects in the system, as a result of size dispersity. These defects are disclinations and appear as distorted hexagonal or pentagonal and heptagonal neighboring particle arrangements around the particles.

CONCLUSION

We find that a geometrical factor like the dispersity $\Delta$ in the particle sizes has a similar effect on the liquid-solid transition as the temperature (thermal energy) has on the liquid-
gas transition. $\Delta$ weakens the first order transition from the liquid state to the solid state driven by the volume fraction $\rho$ of the particles. This observation supports the earlier similar observations in different systems like in elastic disk systems\[3\] and in colloidal systems \[2\] with polydispersity in the sizes of the particles. We further observe that at high values of $\Delta$, the system always remains at the fluid phase. This is the region where one can observe glass transition. Our study provides a quantitative measure of the size dispersity $\Delta$, which would be needed to observe the glass transition. It further indicates that there may not be any true phase transition (in the thermodynamic sense) in the process of glass transition. We will provide detailed evidence for this conclusion elsewhere\[12\] (see also \[13\]). However, much detailed study, specially on the effect of temperature is needed to say anything conclusively.

ACKNOWLEDGMENTS

We wish to thank L. Amaral, B. Kutnjak-Urbanc and W. Kob for useful discussions and remarks. The Center for Polymer studies is supported by NSF.

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Figure 4: $|\psi_6|$ distribution for two different dispersities; For monodisperse systems, $\rho = 0.7$ plot belonging to the liquid phase shows no orientational order, $\rho = 0.875$ plot has a developing hump along with a very fat tail indicating the coexistence of the solid and liquid phases, $\rho = 0.9$ to $\rho = 1.0$ on the other hand have pronounced peak near one and diminishing tails , indicating a triangular lattice arrangement of the particles. On the other hand, for $\Delta = 0.1$, even at $\rho = 1.0$, we find a long tail in the distribution indicating the presence of many defects in the form of dislocations and disclinations and absence of true long range orientational order.

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