Glass Transition and Re-entrant Melting in a Polydisperse Hard-Sphere Fluid

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Recently, the possibility whether re-entrant melting (transition from crystal to liquid) occurs or not in polydisperse hard spheres as the density is increased was examined by free energy calculations [1]. In this paper, we perform extensive molecular-dynamics simulations on a polydisperse hard-sphere fluid and analyze the simulation results by employing the mean-field theory recently proposed by Tokuyama [2]. We then examine the equilibrium phase diagram of a polydisperse hard-sphere fluid from a new unified point of view. Thus, we find that depending on the values of the volume fraction ϕ, there exist five phase regions at polydispersity $\sigma = 0.06$ [3]. The first is a liquid region [L] for $\phi < \phi_\beta (\simeq 0.5524)$. The second is a supercooled liquid region [S_I] for $\phi_\beta \leq \phi < \phi_m^{(1)} (\simeq 0.5630)$. The third is a crystal region [C] for $\phi_m^{(1)} \leq \phi \leq \phi_m^{(2)} (\simeq 0.5750)$. The fourth is a supercooled liquid region [S_{II}] for $\phi_m^{(2)} < \phi < \phi_g (\simeq 0.6005)$. The last is a glass region [G] for $\phi_g \leq \phi$. This is a first simulation result for a 6% polydisperse hard-sphere fluid to show the existence of transiton from supercoole liquid to crystal, the occurrence of re-entrant melting from crystal to supercooled liquid, and the prediction of the galss transition. In Fig. 1 the phase diagram is shown in the pressure-volume fraction plane. The existence of those phases is confirmed by calculating the mean-square displacement $M_2(t)$ (see Fig. 2). This is also confirmed by calculating the radial distribution function and the non-Gaussian parameter. The long-time self-diffusion coefficient $D_S^L(\phi)$ is calculated by using the relation $D_S^L = \lim_{t \gg 1} M_2(t)/(6t)$. Then, we show that D_S^L obeys the same type of a non-singular function as that found in the experiment for hard-sphere colloids [4]. Hence no divergence of any characteristic times, such as β-relaxation time, is found. Thus, the possibility of the glass transition at $\phi \simeq 0.6005$ is also suggested from a unified point of view.

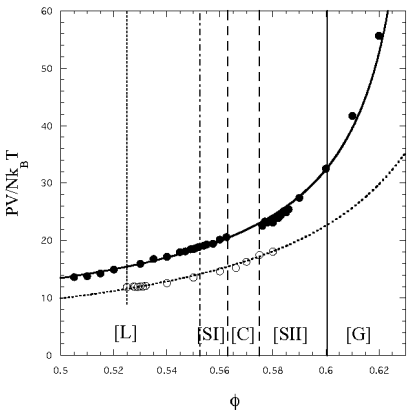

Figure 1: Pressure versus volume fraction. The open circles indicate the simulation results in a crystal state and the filled circles in a liquid state. The solid and the dotted lines indicate the fitting line $(1 - \phi/0.64)^{-0.7}$ for the liquid branch and $(1 - \phi/0.69)^{-1.1}$ for the crystal branch, respectively. The vertical dashed line indicates the freezing point $\phi_f \simeq 0.5250$, the dashed-dot line the crossover point $\phi_\beta \simeq 0.5524$, the long-dashed lines the melting points $\phi_m^{(1)} \simeq 0.5630$ and $\phi_m^{(2)} \simeq 0.5750$, and the solid line the glass transition point $\phi_g \simeq 0.6005$.

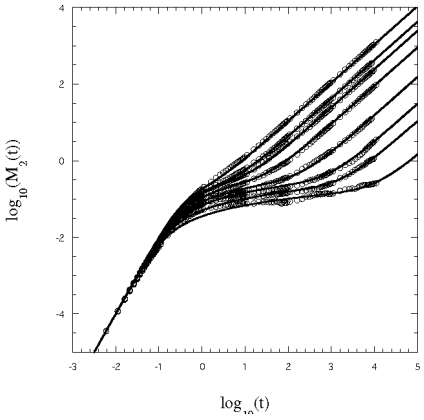

Figure 2: A log-log plot of $M_2(t)$ versus time at $\sigma = 0.06$ in the liquid state for different volume fractions ϕ: [L] 0.5100, 0.5400, 0.5500, [S_I] 0.5625, [S_{II}] 0.5760, 0.5800, 0.5850, and [G] 0.6000 (from left to right). The open circles indicate the simulation results and the solid lines the mean-field results from Refs. [2, 3].

References

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