Equilibrium Glassy Phase in a Polydisperse Hard-Sphere System

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(Received 29 March 2005; published 8 December 2005)

The phase diagram of a polydisperse hard-sphere system is examined by numerical minimization of a discretized form of the Ramakrishnan-Yussouff free-energy functional. Crystalline and glassy local minima of the free energy are located and the phase diagram in the density-polydispersity plane is mapped out by comparing the free energies of different local minima. The crystalline phase disappears and the glass becomes the equilibrium phase beyond a "terminal" value of the polydispersity. A crystal-to-glass transition is also observed as the density is increased at high polydispersity. The phase diagram obtained in our study is qualitatively similar to that of hard spheres in a quenched random potential.

Colloidal suspensions of polystyrene spheres coated with thin polymeric layers effectively behave as hard-sphere systems [1], exhibiting fluid and crystalline phases in equilibrium. For such systems, glass (amorphous solid) is believed to be a metastable phase [2], resulting from structural arrest. However, in recent theoretical studies [3] of hard spheres in the presence of a quenched random potential, an equilibrium glassy phase was observed at high disorder strengths. While this phenomenon has not yet been confirmed experimentally, it brings forth the question of whether even the presence of annealed disorder in a system of hard spheres can result in an equilibrium glassy phase (i.e., an amorphous phase with free energy lower than that of the liquid and crystalline phases). The annealed disorder can be realized if the hard spheres have different sizes, which is the case for most colloidal suspensions. The size dispersity can be modeled by assuming that the diameters (σ) are sampled from a continuous distribution $p(\sigma)$, characterized by a parameter δ, known as the polydispersity, and defined as the ratio of the standard deviation and the mean of the diameter distribution. In this Letter we present calculations that show that for a system of polydisperse hard spheres, one does obtain an equilibrium glassy phase. In fact, our results suggest that for hard spheres, quenched and annealed disorder lead to qualitatively similar phase behavior.

The equilibrium phase behavior of polydisperse hard spheres has generated a lot of interest in recent times. Experiments have shown that for such a system, crystallization does not occur beyond a *terminal* polydispersity of $\delta_t \approx 0.12$ [4]. Particle simulations [5] and density-functional studies [6] indicate a similar behavior, except that there is no consensus on the value of δ_t.

It has been observed numerically that the typical height of nucleation barriers for the formation of polydisperse crystals grows anomalously as the polydispersity increases, thus suppressing crystallization at high polydispersities [7]. This feature has been utilized in experiments [8] by using polydisperse hard spheres as a suitable system for studying the glass transition. Molecular dynamics simula-

tions [9] of a supercooled system of polydisperse hard spheres also suggest the presence of dynamical heterogeneity, believed to be a signature of glassiness.

Recently, free-energy calculations [10] found the occurrence of reentrant melting (transition from crystal to liquid as the density is increased) near $\delta = \delta_t$. This conclusion is opposed by calculations that suggest that the equilibrium phase at high polydispersity corresponds to a *fractionated* state [11]. Until now, numerical evidence for fractionation has been found only in simulations [12] in the grand canonical ensemble, which is different from the situation in typical experiments. In a recent experiment on polydisperse hard-sphere colloids in a confined geometry [13], reentrant melting was observed at the colloidal monolayer adjacent to the surface, although no crystallization occurred in the bulk.

Although there have been suggestions [6,10] that at high densities or at high polydispersities the equilibrium phase is a glass, there have been no calculations to substantiate this possibility. We have addressed this question within the framework of density-functional theory (DFT), using the Ramakrishnan-Yussouff (RY) free-energy functional [14], given by,

$$\beta F = \int d\mathbf{r}\{\rho(\mathbf{r})\ln(\rho(\mathbf{r})/\rho_0) - \delta\rho(\mathbf{r})\}$$
$$- \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}' C(|\mathbf{r} - \mathbf{r}'|)\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}'). \quad (1)$$

Here, we have defined $\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0$ as the deviation of the time-averaged local density, $\rho(\mathbf{r})$, from ρ_0, the density of the uniform liquid, and taken the zero of the free energy at its uniform liquid value. In Eq. (1), $\beta = 1/(k_BT)$, T is the temperature and $C(r)$ is the direct pair correlation function of the uniform liquid at density ρ_0.

In order to carry out numerical work, we discretize our system. We introduce for this purpose a simple cubic computational mesh of size L^3 with periodic boundary conditions. On the sites of this mesh, we define density variables $\rho_i \equiv \rho(\mathbf{r}_i)h^3$, where $\rho(\mathbf{r}_i)$ is the density at site i

and h the spacing of the computational mesh. In terms of these quantities, the discretized form for the RY functional, in the polydisperse limit, takes the form

$$\beta F = \sum_i \{\rho_i \ln(\rho_i/\rho_L) - (\rho_i - \rho_L)\}$$
$$- \frac{1}{2} \sum_i \sum_j \bar{c}_{ij}(\rho_i - \rho_L)(\rho_j - \rho_L), \qquad (2)$$

where the sums are over all the sites of the computational mesh, $\rho_L \equiv \rho_0 h^3$, and $\bar{c}_{ij}$ is the discretized form of the direct pair correlation function $\overline{C(r)} = \int d\sigma_i \int d\sigma_j p(\sigma_i)p(\sigma_j)C_{ij}(r)$, $C_{ij}(r)$ being the partial direct correlation function between spheres of size σ_i and σ_j. Our algorithm [15] for the minimization of the discretized RY functional converges to the local free-energy minimum whose basin of attraction contains the initial state. It is known that, for the monodisperse hard-sphere system, numerical minimization of the discretized form of the RY functional yields a crystallization transition at dimensionless density $\rho_l \equiv \rho_0\sigma^3 \simeq 0.945$ if the mesh size h is sufficiently small [15,16].

We have extended this method of calculation to a system of polydisperse hard spheres. In our calculation, the particle size distribution is chosen to be of the Schultz type: $p(\sigma) = \gamma^\alpha \sigma^{\alpha-1} \exp(-\gamma\sigma)/\Gamma(\alpha)$, where $\alpha = 1/\delta^2$ and $\gamma = \alpha/\bar{\sigma}$; δ being the polydispersity and $\bar{\sigma}$ the mean diameter of the system of particles. For the average direct correlation function $\overline{C(r)}$ for a polydisperse hard-sphere system, we use the analytical expression derived using the Percus-Yevick approximation [17].

To study the stability of the crystalline minimum, we use the fcc structure as an input for the free-energy minimization. The fluid-to-crystal transition occurs when the free energy of the minimum obtained this way becomes negative (i.e., lower than that of the uniform fluid). For each value of δ, the dimensionless density ρ_l at which this happens is identified. The resultant phase diagram is shown in Fig. 1. In another method of calculating the free energy [6] of the crystal, the local density $\rho(\mathbf{r})$ is approximated as a sum of Gaussian profiles: $\rho(\mathbf{r}) = (A/\pi^{3/2}\epsilon^3)\sum_R \exp[-(\mathbf{r} - \mathbf{R})^2/\epsilon^2]$. In this expression, $A = (1 + \eta)\rho_0 v_0$, where η is the density change at freezing and v_0 is the unit cell volume of a fcc lattice with spacing a, ϵ is the width of the Gaussians, and $\{\mathbf{R}\}$ are the lattice points. The RY free-energy functional is then minimized with respect to the parameters ϵ, η, and a to find the values of $\{\rho_l, \delta\}$ where the free energy of the crystal becomes negative. In this case, $\rho_l \equiv \rho_0\langle\sigma^3\rangle$ is the polydisperse liquid density, $\langle\sigma^3\rangle$ being the third moment of the distribution $p(\sigma)$. As shown in Fig. 1, the results from the grid-minimization and the Gaussian approximation agree quite well, thereby establishing the correctness of the results obtained by the grid method. Our results corroborate earlier density-functional calculations [6]—there is no
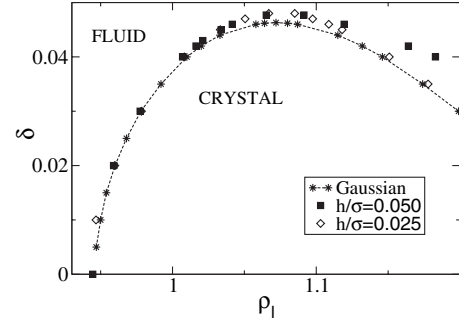

FIG. 1. Fluid-to-crystal transition points in the dimensionless density (ρ_l)-polydispersity (δ) plane. Data for two values of the mesh spacing h used in the grid minimization, and the results obtained from the Gaussian approximation are shown. In all three cases, reentrant melting is observed at high density and high polydispersity.

crystallization beyond a terminal polydispersity $\delta_t \simeq 0.048$. Moreover, our calculations, using both grid minimization and Gaussian approximation, clearly indicate that for values of δ slightly lower than δ_t, there is reentrant melting at high densities, confirming the result of an earlier free-energy calculation [10].

In the density-functional calculations, the value of the terminal polydispersity comes out to be much lower than what is seen in experiments. A possible reason for this difference is that the average direct correlation function $\overline{C(r)}$ used in our calculations underestimates interparticle correlations for relatively large values of δ. The use of a more accurate $\overline{C(r)}$ would probably shift the terminal polydispersity to a higher value without changing other features of the phase diagram.

The question that now needs to be answered is this: What is the equilibrium phase of the polydisperse hard-sphere system at high densities, beyond the point of reentrant melting, and also at polydispersities where crystallization does not occur? Does it remain liquid or does it become a glass? To answer this question, one needs to locate the glassy minima of the free energy and compare their free energy with that of the uniform liquid.

In the density-functional framework, the glassy state corresponds to local minima with inhomogeneous density distributions that exhibit strong nonperiodicity. Such glassy minima have been obtained for the case of monodisperse hard spheres using RY functional [15,18,19], as well as other density functionals [20]. To locate such minima, one first needs to construct appropriate density configurations $\{\rho_i\}$ to be used as inputs for the minimization [21]. In a recent density-functional study of the glass transition in monodisperse hard-sphere systems [19], particle configurations from molecular dynamics (MD) simulations were used to produce the density field for calculating the free energy using the Gaussian approximation for the local density. Similarly, in our discretized method for doing the DFT calculation, the input density

field was constructed from MD simulations of polydisperse hard spheres. The simulations were carried out for 470 particles with their diameters sampled from the Schultz distribution with $\delta = 0.0289$. Using a modified form of the Stillinger-Lubachevsky compression algorithm [23], highly dense configurations of polydisperse hard spheres could be created. The input density field $\{\rho_i\}$ was calculated from these configurations using a computational grid of mesh spacing, $h \approx 0.05\bar{\sigma}$. The RY functional was then minimized in the space of the resulting 4.096×10^6 density variables to obtain the density configuration at the local minimum of the free energy. As in the case of monodisperse hard spheres [22], we obtain, in this case also, free-energy minima with the $\{\rho_i\}$ having a glassy structure. The structure of a local minimum may be characterized by the two-point correlation function $g(r)$ of the local density variables $\{\rho_i\}$ at the minimum. This function is defined as $g(r) = \langle \rho(0)\rho(r)/\rho_0^2 \rangle$. In Fig. 2, we have plotted the $g(r)$ for a glassy free-energy minimum obtained for $\delta = 0.0289$. The glassy nature of the density distribution is indicated by the split second peak of the $g(r)$, with the subpeaks occurring at $1.77\bar{\sigma}$ and $2.02\bar{\sigma}$. These numbers are close to those for a dense random packing of monodisperse hard spheres, where the subpeaks occur at around 1.7σ and 2σ [24].

The density configuration $\{\rho_i\}$ at the local minimum for $\delta = 0.0289$ was thereafter used as input to search for similar glassy minima at other values of the polydispersity. The density at which the free energy of the glassy structure becomes lower than that of the uniform liquid defines the point of the liquid-to-glass transition. Figure 3 shows a plot of the liquid-to-glass transition density for various values of δ. As shown in the plot, one obtains glassy minima for polydispersities higher than δ_t, the terminal value beyond which crystallization does not occur. Also the glass transition point shifts to higher densities as a function of increasing polydispersity and at large enough polydispersity, near $\delta = 0.10$, the glass transition point approaches

the random close packing limit for polydisperse hard spheres [5,25]. When the density configuration for the minimum for $\delta = 0.02$ is used as input for minimizing the RY functional for $\delta = 0.0$, i.e., for a system of monodisperse hard spheres, we obtain a free-energy minimum whose $\{\rho_i\}$ correspond to a polycrystalline structure.

Having determined the densities (ρ_l) beyond which the crystalline and glassy phases, respectively, have lower free energies compared to that of the homogeneous liquid phase, the next task is to determine the final phase diagram, i.e., to determine which phase (crystal, glass, or liquid) is the thermodynamically stable one at different points in the (δ, ρ_l) plane. At any density, if more than one local minima of the free energy are present, the thermodynamically stable phase corresponds to the one with the lowest free energy. Using this criterion, we have obtained the full phase diagram of the polydisperse hard-sphere system, which is shown in Fig. 4. The inset in Fig. 4 shows, for example, how the crystal-to-glass transition line is located—for each polydispersity, the free energies of the glassy and crystalline minima at different values of ρ_l are compared and the value of ρ_l at which the free energy of the glassy minimum becomes lower than that of the crystalline minimum defines the crystal-to-glass transition point.

It is important to note that the reentrant melting shown in Fig. 1 is not present in the final phase diagram. Now, as one moves along a line of fixed polydispersity (for example, $\delta = 0.043$ as shown by the dotted line in Fig. 4), one first encounters the fluid phase, then a crystalline phase and at even higher densities, glass becomes the stable phase (as is clear from Fig. 3). The other significant feature of the phase diagram is that, at a fixed high dimensionless density ($\rho_l > 1.05$), if we increase the polydispersity δ, the crystal undergoes a transition to the glassy state. We find that the crystal-glass transition line is below the fluid-crystal reentrant line in Fig. 1. A possible reason for this behavior is that as the polydispersity increases, the number of smaller particles in the system increases and their presence makes
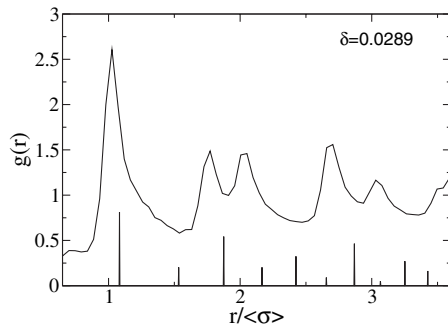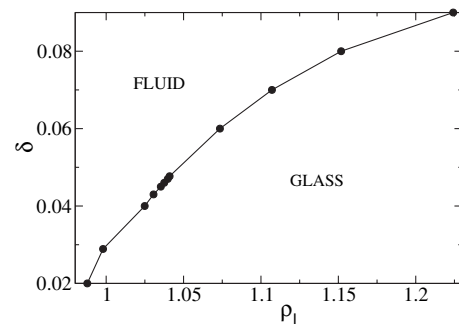

FIG. 2. The two-point density correlation function $g(r)$ for a glassy minimum obtained for a polydispersity value of $\delta = 0.0289$ and dimensionless liquid density $\rho_l = 1.11$. The peaks of the pair distribution function [not drawn in the same scale as $g(r)$ for the glass] for a fcc lattice at this density are plotted.

FIG. 3. Glass transition points, plotted in the dimensionless density (ρ_l)-polydispersity (δ) plane. At these points, the RY free energy of the glassy minimum becomes negative. The line drawn through the data points is a guide to the eye.
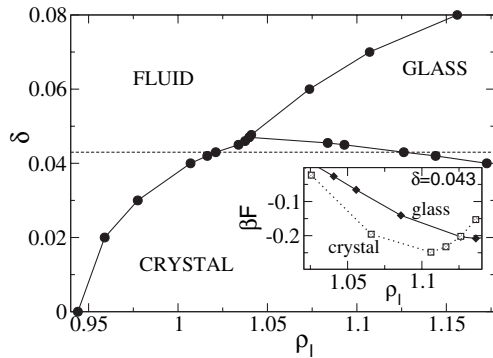
FIG. 4. The overall phase diagram of a system of polydisperse hard spheres in the dimensionless density (ρ_l)-polydispersity (δ) plane showing the presence of the three phases: uniform liquid, crystal, and glass. The lines drawn to denote the phase boundaries are only meant to be guides to the eye. The inset shows the free energies of the glassy and crystalline minima for $\delta = 0.043$ (shown by the dotted line in the main figure). The crystal is the equilibrium phase until $\rho_l \simeq 1.126$, after which the glass becomes the equilibrium phase.

the glassy phase to be entropically favorable as compared to the crystalline phase. Very similar features, including the presence of an equilibrium glassy phase and crystal-to-glass transitions upon increasing density or disorder, have been found [3] in the phase diagram of a system of hard spheres in a quenched random potential. However, in the present case, the disorder in the glassy phase is self-generated, and not imposed externally by a random potential.

Our calculations do not take into account the possibility of having fractionated phases. We need to compare the free energy of the glassy phase with that of fractionated phases at high polydispersities to determine which one is the equilibrium phase. A proper procedure for doing such calculations in the framework of DFT is not yet available. However, one must remember that for many glass-forming liquids, phase separation is possible but may not be observed in experimental time scales. This may be the case for this system as well.

In summary, we have shown, using density-functional theory, that reentrant melting occurs at high densities in a system of polydisperse hard spheres if only the crystal and liquid states are considered. However, the reentrant liquid state is replaced by a glassy state in the full phase diagram because of the presence of glassy minima with lower free energy. At high polydispersity, when crystallization does not occur, our calculations show that the glassy state can be an equilibrium phase for this system.

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