Equilibrium glassy phase in a polydisperse hard sphere system

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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.

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Colloidal suspensions of polystyrene spheres coated with thin polymeric layers effectively behave as hard sphere systems, exhibiting fluid and crystalline phases in equilibrium. For such systems, glass (amorphous solid) is believed to be a metastable phase, resulting from structural arrest. However, in recent theoretical studies 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. 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 ($\sigma$) are sampled from a continuous distribution $p(\sigma)$, characterized by a parameter $\delta$, known as the polydispersity, and defined as the ratio of the standard deviation and the mean of the diameter distribution. In this paper 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 have 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 $\delta_t \approx 0.12^2$. Particle simulations and density functional studies indicate a similar behavior, except that there is no consensus on the value of $\delta_t$.

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. This feature has been utilized in experiments by using polydisperse hard spheres as a suitable system for studying the glass transition. Molecular dynamics simulations 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 found the occurrence of re-entrant 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. Till now, numerical evidence for fractionation has been found only in simulations 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, re-entrant melting was observed at the colloidal monolayer adjacent to the surface, although no crystallization occurred in the bulk. It was claimed that such phenomena could be observed in the bulk as well, only if one waited for sufficiently long time to allow crystallization to occur. The presence of the wall resulted in lowering of the nucleation barrier, thereby allowing crystallization and re-entrant melting to occur.

Although there have been suggestions 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. In DFT, the free energy is expressed as a functional of the time-averaged local density $\rho(r)$.

The RY free energy functional is given by:

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

(1)

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

In the polydisperse limit, the RY functional becomes\[7\]

$$\beta F = \int \text{d}r \{ \rho(r) \ln(\rho(r)/\rho_0) - \delta \rho(r) \}$$

$$- \frac{1}{2} \int \text{d}r \int \text{d}r' C(r-r') \delta \rho(r) \delta \rho(r')$$

(2)

where $C(r) = \int \text{d} \sigma_i \int \text{d} \sigma_j p(\sigma_i) p(\sigma_j) C_{ij}(r)$, $C_{ij}(r-r')$ being the partial direct correlation function between spheres of size $\sigma_i$ and $\sigma_j$.

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 $\rho_i \equiv \rho(r_i) h^3$, where $\rho(r_i)$ 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 takes the form

$$\beta F = \sum_i \{ \rho_i \ln(\rho_i/\rho_L) - (\rho_i - \rho_L) \}$$

$$- \frac{1}{2} \sum_i \sum_j C_{ij}(\rho_i - \rho_L)(\rho_j - \rho_L).$$

(3)

where the sums are over all the sites of the computational mesh, $\rho_L \equiv \rho_0 h^3$, and $C_{ij}$ is the discretized form of the direct pair correlation function $C(r)$ of the uniform liquid. Our algorithm\[18\] 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 $\rho_1 \equiv \rho_0 \sigma^3 \approx 0.945$ if the mesh size $h$ is sufficiently small\[17,18\]. Dasgupta and Valls\[19\] also obtained glassy minima for monodisperse hard sphere systems using this minimization scheme.

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 $\gamma = \alpha/\bar{\sigma}$, $\delta$ being the polydispersity and $\bar{\sigma}$ the mean diameter of the system of particles. For the average direct correlation function $C(r)$ for a polydisperse hard sphere system, we use the analytical expression derived using the Percus-Yevick approximation\[20\].

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 $\delta$, the dimensionless density $\rho_1$ at which this happens is identified. The resultant phase diagram is shown in Figure 1. In another method of calculating the free energy\[2\] of the crystal, the local density $\rho(r)$ is approximated as a sum of Gaussian profiles:

$$\rho(r) = A/\pi^{3/2} \sum_i \exp[-(r - R_i)^2/c_i^2].$$

In this expression, $A = (1 + \eta) \rho_0 v_0$, where $\eta$ is the density change at freezing and $v_0$ is the unit cell volume of a fcc lattice with spacing $a$, $c$ is the width of the Gaussians and $\{R_i\}$ are the lattice points. The RY free energy functional is then minimized with respect to the parameters $\epsilon$, $\eta$, and $a$ to find the values of $\{\rho_i, \delta\}$ where the free energy of the crystal becomes negative. In this case, $\rho_1 \equiv \rho_0 < \sigma^3$ is the polydisperse liquid density, $< \sigma^3 >$ 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\[7\] - there is no crystallization beyond a terminal polydispersity $\delta_t \approx 0.048$. Moreover, our calculations, using both grid-minimization and Gaussian approximation, clearly indicate that for values of $\delta$ slightly lower than $\delta_t$, there is re-entrant melting at high densities, confirming the result of an earlier free-energy calculation\[12\].

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 $C(r)$ used in our calculations underestimates inter-particle correlations for relatively large values of $\delta$. The use of a more accurate $C(r)$ 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: What is the equilibrium phase of the polydisperse hard sphere system at high densities, beyond the point of re-entrant 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 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 non-periodicity [15, 19]. To locate such minima, one first needs to construct appropriate density configurations \( \{ \rho_i \} \) to be used as inputs for the minimization. In a recent density-functional study of the glass transition in monodisperse hard sphere systems [21], particle configurations from molecular dynamics (MD) simulation 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 simulation 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 [22], 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 \( h \approx 0.05 \sigma \). The RY functional was then minimized in the space of the resulting \( 4.096 \times 10^6 \) density variables to obtain the density configuration at the local minimum of the free energy. As in the case of monodisperse hard spheres [23], 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 sub-peaks occurring at 1.77\( \sigma \) and 2.02\( \sigma \). These numbers are close to those for a dense random packing of monodisperse hard spheres, where the sub-peaks occur at around 1.7\( \sigma \) and 2\( \sigma \) [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. Fig. 3 shows a plot of the liquid-to-glass transition density for various values of \( \delta \). As shown in the plot, one obtains glassy minima for polydispersions higher than \( \delta_t \), 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 [6, 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.

![FIG. 2: The two point density correlation function \( g(r) \) for a glassy minimum obtained for a polydisperosity value of \( \delta = 0.0289 \) and dimensionless liquid density \( \rho_l = 1.11 \). Also plotted in the figure are 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.](image)

![FIG. 3: Glass transition points, plotted in the dimensionless density \( (\rho_l) \)-polydispersity \( (\delta) \) 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.](image)

Having determined the densities \( (\rho_l) \) 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 \( (\delta, \rho_l) \) 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 \( \rho_l \) are compared and the value of \( \rho_l \) at which the free energy of the glassy minimum becomes lower than
that of the crystalline minimum defines the crystal-to-glass transition point.

![Diagram of phase diagram](image)

**FIG. 4:** The overall phase diagram of a system of polydisperse hard spheres in the dimensionless density ($\rho_l$)-polydispersity ($\delta$) 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 the glassy and crystalline minima for $\delta = 0.043$ (shown by the dotted line in the main figure). The crystal is the equilibrium phase till $\rho_l \approx 1.126$, after which the glass becomes the equilibrium phase.

It is important to note that the re-entrant 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. 1), 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. 2). 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 $\delta$, the crystal undergoes a transition to the glassy state. We find that the crystal–glass transition line is below the fluid–crystal re-entrant 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 the glassy state 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 in the phase diagram of a system of hard spheres in a quenched 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 re-entrant melting occurs at high densities in a system of polydisperse hard spheres if only the crystal and liquid states are considered. However, the re-entrant 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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