Supplementary Information Using Depletion to Control Colloidal Crystal Assemblies of Hard Cuboctahedra

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FORMATION OF SIMPLE CUBIC CRYSTAL WITH q = 0.07

Henzie et al. [1] previously studied the sedimentation-driven assembly of cuboctahedra in systems with and without depletion. In their system, the cuboctahedra had an edge length of 145 nm and they employed a depleting polymer with a radius of gyration equal to 10 nm; this corresponds to $q = \sigma_{dep}/\sigma_{col} = 0.069$. In experiments and simulations employing effective potentials to capture depletion effects, they observed cuboctahedra forming a face-centered tetragonal structure with I4/mmm symmetry. They reported this structure to form in Monte Carlo simulations when effective potentials represented penetrable hard sphere depletants at a packing fraction within the system of 0.03.

We have tested our simulations against their results by using the implicit depletant method [2] as well as by explicitly simulating penetrable hard sphere depletants, a significantly more laborious calculation. Figure S1(a,b) shows cuboctahedra forming a simple cubic crystal with q = 0.07 in simulations with implicit and explicit depletants. In both simulations, the colloid density is set to $\phi_{col} = 0.50$. The simulation with implicit depletants contains $N_{col} = 512$ with $\phi_{dep}^{r} = 0.08$, which corresponds to a system depletant packing fraction of 0.03. The simulation with explicit depletants contains $N_{col} = 216$ and a packing fraction of depletants leads us to believe that gravity or some other force that our model does not include leads to the formation of the previously reported face-centered tetragonal structure.



FIG. S1. The assembly of a simple cubic crystal using (a) the implicit depletion method and (b) explicit depletants. In both cases, the depletants have q = 0.07 and the concentration is set so that the depletant packing fraction in the system is 0.03. Particles in the solid are colored yellow, and identified using a Q4 spherical harmonic order parameter[3]. Additionally, we include a bond order diagram of a single crystal cluster and a diffraction pattern of the solid particles viewed along one of the four-fold axes.



FIG. S2. Coexistence curves for gas-liquid phase separation observed in simulation and predicted from Free Volume Theory. For the simulations, we employ a Gibbs ensemble with a total N = 250 cuboctahedra at an initial packing fraction $\phi_{col} = 0.275$. Simulation data was averaged across four independent runs.

GAS - LIQUID COEXISTENCE

In order to further confirm the phase behavior predicted from Free Volume Theory, we ran simulations to observe gas-liquid coexistence. The standard procedure for doing this is to run simulations in the Gibbs ensemble [4]. In the Gibbs ensemble, we simulate two systems which are allowed to exchange volume and particles with one another, but the total volume and number of particles is held constant. The results from these simulations are summarized in Figure S2. As we observed with fluid-crystal coexistence, theory tends to underestimate the critical depletant concentration needed for phase separation. Our implementation of the Gibbs ensemble is described in Ref. [2].

FREE ENERGY CALCULATIONS

In a semigrand ensemble, such as the one we consider, the full expression for the free energy is: [5]

$$F(N_{\rm col},\mu_{\rm dep},V,T) = F(N_{\rm col},\mu_{\rm dep}\to-\infty,V,T) - \int_{-\infty}^{\mu_{\rm dep}} N_{\rm dep}d\mu_{\rm dep}$$
(S1)

Here, N_{dep} is the number of depletants in the system. According to the Widom insertion theorem [6], the chemical potential of depletants in the system is $\mu_{dep} = \text{const} + k_B T \ln(N_{dep}/\langle V_{free} \rangle)$ and, by definition, the chemical potential in the external reservoir is $\mu_{dep} = \text{const} + k_B T \ln(n_{dep}^r)$. Equating these terms leads to the result $N_{dep} = n_{dep}^r \langle V_{free} \rangle$. Substituting these expressions into the free energy relationship, and making the critical assumption that $\langle V_{free} \rangle$ can be treated as a constant as the depletion concentration varies leads to:

$$F(N_{\rm col}, \mu_{\rm dep}, V, T) \approx A(N_{\rm col}, V, T) - n_{\rm dep}^{\rm r} \langle V_{\rm free} \rangle k_B T$$
(S2)

 $\langle V_{\text{free}} \rangle$ can be replaced by definition with αV . In doing our analysis with a common tangent construction, we work with the free energy density $f(\phi_{\text{col}}, \mu_{\text{dep}}) = F(N_{\text{col}}, \mu_{\text{dep}}, V)v_0/V$ where v_0 is the volume of a single colloid. The purpose of the common tangent construction is to find densities at which two phases will coexist, meaning that they have an equal pressures and chemical potentials. The pressure is defined as:

$$P = -\left[\frac{\partial F}{\partial V}\right] = -\frac{1}{v_0} \left[\frac{\partial (Vf)}{\partial V}\right] = -\frac{1}{v_0} \left[f - \phi_{\rm col}\frac{\partial f}{\partial \phi_{\rm col}}\right]$$
(S3)

The chemical potential is:

$$\mu = \frac{\partial F}{\partial N} = \frac{1}{v_0} \left[\frac{\partial (Vf)}{\partial N} \right] = \frac{\partial f}{\partial \phi_{\text{col}}}$$
(S4)

For more on common tangent construction use with FVT, we refer the interested reader to reference [7].

As mentioned earlier, we rely on numerical calculations of the free energy. For the SC and sBCC crystals, we computed the Helmholtz free energy through Frenkel-Ladd integration [8] of the bulk solid using the method described by Haji-Akbari et al. [9]. This implementation for anisotropic particles considers both the translational and rotational degrees of freedom by tethering particles to springs about their average positions and orientations in the lattice. We performed the calculations on bulk SC and sBCC crystals for a variety of different crystal densities, ϕ_{col} , up to the densest packings (~ 0.833 for SC and ~ 0.917 for sBCC).

We rely on data from the cuboctahedra equation of state when calculating free energies of the other phases. We first ran NPT simulations of systems with 4096 particles. From this, we computed the compressibility factor $Z = PV/Nk_BT$. We then used Widom particle insertion [6] to determine the chemical potential of the system at a reference density of $\phi_{col,0} = 0.20$. We calculate the chemical potential at the reference density as:

$$\mu_0(\phi_{\text{col},0}) = \ln(\phi_{\text{col},0}) - \ln(B_i) - \ln(2\pi^2)$$
(S5)

where B_i is the probability of randomly inserting a particle without generating an overlap, and the last term is necessary to make the normalization of the fluid free energy consistent with the free energy computed in our Frenkel-Ladd calculations. Because we express rotations using normalized quaternions $q^2 = 1$, the factor of $2\pi^2$ measures the surface of the 3-sphere.

This value for the chemical potential at a reference density allows us to determine the absolute free energy by integrating over the compressibility factor:

$$f(\phi_{\rm col}) = \phi_{\rm col} \left[\mu_0(\phi_{\rm col,0}) - Z_0(\phi_{\rm col,0}) + \int_{\phi_{\rm col,0}}^{\phi_{\rm col}} \frac{Z(\phi_{\rm col})}{\phi_{\rm col}} d\phi_{\rm col} \right]$$
(S6)

We similarly integrate over the equation of state to describe the rotator BCC phase and part of the sBCC phase. When integrating the equation of state in these cases, we use an integration constant in order to match the pressure and chemical potential for the unperturbed fluid-rotator BCC coexistence and the rotator BCC-sBCC coexistence from reference [10].

To calculate the depletant contribution to free energy, we used Monte Carlo integration to determine the free volume as a function of depletant size across different colloid densities and phases and in both the SC and sBCC crystals. This allowed us to have an expression for $\alpha = \langle V_{\text{free}} \rangle / V$ across the full range of colloid densities (pictured in Figure S3).

We include calculations of the free energy density f, the pressure, and chemical potential for three depletant conditions in Figure S4.

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FIG. S3. Plots of $\alpha = \langle V_{\text{free}} \rangle / V$ for (a) q = 0.10 and (b) q = 0.25. For $\phi_{\text{col}} < 0.4$, α follows a linear relationship as α goes to 1.0 when $\phi_{\text{col}} = 0$. As q increases, the α will go to a value of zero for both the SC and sBCC structures.



FIG. S4. Plots showing the free energy density, pressure, and chemical potential in the fluid, rotator BCC, sBCC, and SC phases at different depletant conditions. (a) With no depletants, the SC phase is never stable and the sBCC phase is only stable at high ϕ_{col} . (b) At q = 0.1 & $\phi_{dep}^{r} = 0.10$, the fluid-SC coexistence becomes stable. (c) At q = 0.25 & $\phi_{dep}^{r} = 0.50$, the system will phase separate into a fluid and sBCC crystal.

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