Supplemental Material for "Crystal Nucleation of Highly-Screened Charged Colloids"

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In this Supplemental Material, we go into more depth on the specific methods used and mentioned in the main paper.

I. ORDER PARAMETER

We use the number of particles of the solid nucleus n as an order parameter for studying crystal nucleation [1–3]. One of the most commonly used techniques for differentiating between liquid and solid on a single-particle level is the one introduced by Ten Wolde *et al.* [1]. This technique uses the bond orientational order parameters q_{lm} to determine the number of solid-like connections ξ of each particle and labels a particle as solid when $\xi \geq \xi_c$, with ξ_c a cutoff value. These bond-orientational order parameters are given by

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j \in \mathcal{N}_b(i)} Y_{lm}\left(\theta_{ij}, \phi_{ij}\right), \tag{S1}$$

where $N_b(i)$ is the number of neighbors of particle i, $\mathcal{N}_b(i)$ is the set of neighbors of i, $Y_{lm}\left(\theta, \phi\right)$ are the spherical harmonics with $m \in [-l, l]$, and θ_{ij} and ϕ_{ij} are the polar and azimuthal angles of $\mathbf{r}_{ij} = \mathbf{r}(j) - \mathbf{r}(i)$, and $\mathbf{r}(i)$ is the position of particle i. The number of solid-like connections of particle i is then determined via

$$\xi(i) = \sum_{j \in \mathcal{N}_b} H\left(d_l(i,j) - d_c\right), \tag{S2}$$

where H is the Heaviside step function, d_c is the dot-product cutoff, and $d_l(i,j)$ is the dot product given by

$$d_l(i,j) = \frac{\sum_{m=-l}^{m=l} q_{lm}(i) q_{lm}^*(j)}{\sqrt{\left(\sum_{m=-l}^{m=l} |q_{lm}(i)|^2\right)\left(\sum_{m=-l}^{m=l} |q_{lm}(j)|^2\right)}}, \tag{S3}$$

with * indicating the complex conjugate. The neighbors of particle i are defined as all particles j with $|\mathbf{r}_{ij}| < r_c$, and a cluster contains all solid particles that have a solid neighbor in the same cluster. For all simulations we use $l = 6$ and the cutoff values $d_c = 0.7$ and $\xi_c = 6$. The nearest neighbor cutoff r_c is chosen to be approximately the position of the first minimum of the radial distribution function for each state point.

II. UMBRELLA SAMPLING

The Gibbs free-energy barrier associated with crystal nucleation can be determined via [2, 3]

$$\beta \Delta G(n) = \text{constant} - \ln P(n), \tag{S4}$$

where $P(n)$ is the probability of observing a cluster of size n. To measure $P(n)$ we use MC simulations in the NPT-ensemble combined with umbrella sampling [4–6]. This technique adds a biasing potential to the interaction potential of the system that drives the simulation to a preferred region of configuration space by artificially making a specific part of phase space more probable. The typical biasing potential used for computing nucleation barriers is given by [1, 7, 8]

$$\beta U_{\text{bias}}\left(n(\mathbf{r}^N)\right) = \frac{\lambda}{2}\left(n(\mathbf{r}^N) - n_c\right)^2, \tag{S5}$$

where λ is a coupling parameter, $n(\mathbf{r}^N)$ is the size of the largest cluster present in the configuration $\mathbf{r}^N$, and n_c is the target cluster size.

Thus, by choosing a suitable value for λ, we can force $n(\mathbf{r}^N)$ to fluctuate around n_c. Then, by performing the simulation for multiple values of n_c, we can compute different "windows" of the barrier. To compute a window, we measure the biased probability distribution $P_{\text{bias}}(n; n_c)$ for clusters of size n and calculate the corresponding Gibbs free energy using

$$\beta \Delta G(n; n_c) = \chi(n_c) - \ln P_{\text{bias}}(n; n_c) - \frac{\lambda}{2} (n - n_c)^2 , \tag{S6}$$

where $\chi(n_c)$ is a constant shift needed to stitch the different windows together nicely [3]. By ensuring that consecutive windows overlap, the shifts can be calculated. For all nucleation barriers, we use $\lambda = 0.02$, take n_c with an interval of 10, and perform 4 independent runs for each window. Note that for the first window, the barrier is determined without the use of a biasing potential and takes all present clusters into account. For the remainder of the barrier the presence of small clusters can be neglected [3].

III. FITTING THE NUCLEATION BARRIER

We compare our nucleation barriers to classical nucleation theory (CNT). In this simple theoretical model, it is assumed that crystal nucleation is controlled by the competition between the free-energy gain of the bulk crystal phase with respect to the fluid phase and the free-energy cost of making a fluid-crystal surface interface. More specifically, the Gibbs free-energy cost for making a spherical nucleus of radius R is given by

$$\Delta G(R) = 4\pi\gamma R^2 - \frac{4}{3}\pi |\Delta\mu| \rho_s R^3, \tag{S7}$$

where γ is the fluid-crystal interfacial free energy, $|\Delta\mu|$ is the difference in chemical potential between the crystal and fluid phases, and ρ_s is the density of the crystal phase. The maximum height ΔG^* and critical radius R^* of the nucleation barrier described by Eq. (S7) are given by

$$\Delta G^* = \frac{16\pi\gamma^3}{3|\Delta\mu|^2\rho_s^2}; \qquad R^* = \frac{2\gamma}{|\Delta\mu|\rho_s}. \tag{S8}$$

The nucleation barrier can be fitted to CNT by realizing that the measured radius depends on the specific choice for d_c and ξ_c. Assuming that the measured radius $R(d_c, \xi_c)$ differs from the unique radius associated with CNT with a constant shift $\alpha(d_c, \xi_c)$ [8], we obtain the equation

$$\beta\Delta G(n; d_c, \xi_c) = \delta + 4\pi\beta\gamma \left[\left(\frac{3n(d_c,\xi_c)}{4\pi\rho_s} \right)^{1/3} - \alpha(d_c,\xi_c) \right]^2 - \frac{4\pi}{3}\beta|\Delta\mu|\rho_s \left[\left(\frac{3n(d_c,\xi_c)}{4\pi\rho_s} \right)^{1/3} - \alpha(d_c,\xi_c) \right]^3 , \tag{S9}$$

where we used that the measured cluster size $n(d_c, \xi_c)$ can be related to the radius $R(d_c, \xi_c)$ by

$$n(d_c, \xi_c) = \frac{4\pi R(d_c,\xi_c)^3 \rho_s}{3}. \tag{S10}$$

The constant shift δ is added to Eq. (S9) for the reason that the nucleation barrier obtained via umbrella sampling is only expected to match CNT near the top of the barrier. For all nucleation barriers, we fit approximately the top third of the barrier. Furthermore, note that the specific choice for d_c and ξ_c does not affect the barrier height, only the width [8], and by using Eq. (S9) to fit the barrier one can also obtain the interfacial free energy γ independent of the choice for d_c and ξ_c.

IV. NUCLEATION RATE

The nucleation rate per unit volume k is related to the nucleation barrier by [2, 9]

$$k = A e^{-\beta\Delta G^*}, \tag{S11}$$

where $e^{-\beta\Delta G^*}$ is the probability of forming a critical nucleus, and A is a kinetic factor, which provides a measure for the rate with which a critical nucleus grows. The latter can be approximated as [2, 3, 9]

$$A \approx \rho f_{n^*} \sqrt{\frac{|\beta\Delta G''(n^*)|}{2\pi}}, \tag{S12}$$

with n^* the size of the critical nucleus, ρ the density of the supersaturated fluid, f_{n^*} the rate at which particles are attached to the critical nucleus, and $\Delta G''(n)$ the second derivative of the nucleation barrier. The attachment rate is related to the mean squared deviation of the cluster size $\langle \Delta n^2(t) \rangle = \langle (n(t) - n^*)^2 \rangle$ at the top of the barrier by [2, 3]

$$f_{n^*} = \frac{1}{2} \frac{\langle \Delta n^2(t) \rangle}{t}. \tag{S13}$$

To compute $\langle \Delta n^2(t) \rangle$, we start numerous kinetic Monte Carlo (KMC) simulations in the NVT-ensemble at the top of the barrier and measure $n(t)$. We then use the long-time behavior of $\langle \Delta n^2(t) \rangle$ to compute f_{n^*} [8]. In the main paper, we report k and f_{n^*} in terms of the long-time diffusion coefficient D_l. To obtain D_l, we simply fit the long-time diffusion of the mean-squared displacement obtained from KMC simulations of the supersaturated fluid at the appropriate packing fraction.

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