Supporting Online Material for

Imaging the Sublimation Dynamics of Colloidal Crystallites

J. R. Savage, D. W. Blair, A. J. Levine, R. A. Guyer, A. D. Dinsmore*

*To whom correspondence should be addressed. E-mail: dinsmore@physics.umass.edu

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Supporting Online Material

Colloidal experiments:

Our samples consist of sealed glass cells containing polystyrene spheres in aqueous solution with surfactant micelles. Particles were used as received from Interfacial Dynamics, Portland, OR; (Product # 1-1400, polydispersity 3.5% according to manufacturer). The micelles (~4-20 nm \(S1\)) induce a depletion attraction between the polystyrene spheres, owing to their exclusion from the volume between two nearby spheres \(S2-S4\). The magnitude of the change in free energy upon moving two spheres into contact is approximately \(U_d/k_B T = -2\pi RR_m(T)^2c_m(T)\), where \(k_B T\) is Boltzmann’s constant times the absolute temperature, \(R = 0.70 \mu m\) is the sphere radius, and \(c_m(T)\) and \(R_m(T)\) are the temperature-dependent concentration and radius of the micelles. The concentration of micelles \(c_m(T)\) is proportional to the difference between the concentration of surfactant \(c_s\) and the critical micelle concentration (cmc) divided by the number of surfactant molecules per micelle at that temperature \(S1, 5\). The key to our experiments is that \(U/k_B T\) changes dramatically with modest temperature changes. With the anionic surfactant sodium dodecyl sulfate (SDS; cmc ~ 8.3 mM at 23°C), we used \(c_s = 32\) mM. Crystals form at room temperature and melt when \(T\) exceeds approximately 27°C. With the non-ionic surfactant hexaethylene glycol monododecyl ether \(C_{12}E_6;\ cmc \sim 8.7 \times 10^{-5} \) M at 25°C), we used \(c_s = 4.44 \times 10^{-2}\) M. In this case, micelles shrink when \(T\)
is reduced. Crystals form at $T = 28^\circ C$ and – contrary to the usual case – melt at lower temperatures.

Our procedure consisted of allowing the colloidal spheres to crystallize for 24-48 h. During this time, the particles slowly sedimented to the bottom glass coverslip, then were held there by the depletion attraction to the wall, which is twice as strong as that between two spheres ($S6$). Large numbers of crystallites of various sizes and shapes were formed throughout the bottom surface. All crystallites were of triangular symmetry and apparently close-packed, as expected from the short-range attraction. Owing to the depletion attraction, the number of particles in the suspension was negligible, even during melting.

Samples were mounted on an inverted optical microscope and images were obtained using an oil-coupled objective (63×, N.A. = 1.3) and a monochrome video camera. The apparatus allows rapid, uniform heating of the sample without temperature gradients or convection that would damage the crystallites. The microscope was thermally isolated and heated to allow rapid heating of the sample. Samples were heated from above with resistive heater (Warner TC-324B) transparent sapphire disk, which was attached to the top of the sample chamber. The sapphire plate (which is thermally conductive) eliminated in-plane temperature gradients near the imaged region, which was near the center of the plate. The samples were simultaneously heated from below with an objective heater (Zeiss Tempcontrol 37). Both heaters operated with feedback, and temperature fluctuations were less than 0.1° C. When heating to 65° C, we also wrapped the objective with heating tape connected to a rheostat to decrease the heating time. The microscope was located on a floating table inside an insulating box. Additional heaters...
were mounted inside the insulating box to further alleviate temperature gradients. To begin the heating process, we heated the sample from above while simultaneously heating the objective while it was out of contact with the sample. The objective was brought into contact with the sample after it reached the desired temperature. Remote motorized focus control (ASI MFC-2000) was used to maintain focus while keeping the microscope sealed. Approximately 1 min was required for the temperature to become constant, as evident from thermocouple measurements and from the thermal expansion of the sample stage, which changes the focal plane.

All of the data shown here were acquired well after the sample reached a steady temperature. Images were recorded on S-VHS- format videotape. After acquisition, images were digitized and analyzed using routines written for the Interactive Data Language (IDL) software (S7). The tracking software provides the center-of-mass position of each particle in the field of view with an uncertainty of approximately 30 nm. We then identified crystals and analyzed the dynamics of melting/freezing based on our criteria for being bonded. By our definition, bonds existed between all particles whose inter-particle separation \( r_{ij} \) fell below a cutoff value that was derived from the first minimum of the radial distribution function and that is comparable to the expected value derived from the range of the depletion potential and the uncertainty in the particle positions.

An estimate of the change in the depletion potential \( (U_d) \) with changing \( T \) was obtained by measuring of the lifetime \( \tau \) of several dimers on the surface. We then fit the probability distribution of \( \tau \) to the form \( P(\tau) = \langle \tau \rangle^{-1} \exp(-\tau/\langle \tau \rangle) \), where \( \langle \tau \rangle \) is the mean lifetime. In samples formed with SDS micelles, we obtained \( \tau = 2.5 \) s and 0.77 s at 30
and 65°C. Since the rate of bond breaking is limited by diffusion of the particle in its energy well, $\tau \propto D^{-1} \exp(U_d/k_B T)$, where $D$ is the diffusion constant of an individual sphere moving along the glass surface. From our particle-tracking data, $D = 0.173 \pm 0.002 \, \mu m^2/s$ at 65°C, but is $0.107 \pm 0.001 \, \mu m^2/s$ at 30°C. We thus estimate that the effective potential is approximately $0.7 \kappa_B T$ weaker at the higher $T$. The change of $U_d$ in the C$_{12}$E$_6$ system was less than $0.1 \kappa_B T$ when $T$ is changed from 28°C to 27°C.

**Measured sublimation rate of single-layer crystallites formed in the presence of SDS:**

Figure S1 shows the measured $N$ vs. time for all 7 crystallites that melted at $T = 65 \, ^\circ C$. The data from two of these crystallites are also shown in Fig. 2B.

**Measured sublimation rate of multi-layer crystallites:**

Some of the crystallites in our samples contain multiple layers of colloidal spheres, allowing us to probe the behavior of three-dimensional crystallites. Figure S2 shows the measured $N$ vs. rescaled time for clusters that are three layers in thickness. In these cases the individual particles are not tracked, owing to the distortion of the image by the upper layers. Rather, for each image the perimeter of the cluster was drawn, and the area inside measured using ImageJ ($S8$). The number of particles $N$ was then calculated from the measured area divided by the area per particle.

**Brownian dynamics simulations:**

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Our Brownian dynamics computer simulations were accomplished using the GROMACS simulation package using the “bd” integration option (S9, S10). The equations of motion for the colloidal particles are: 

\[ \frac{d^2 \mathbf{r}_i}{dt^2} = -U(\mathbf{r}_i) - \gamma \frac{d\mathbf{r}_i}{dt} + W_i(t), \]

where \( \mathbf{r}_i \) is the position of the center of mass of each sphere, \( \gamma \) is the single-sphere friction coefficient and \( W_i \) is a Gaussian-distributed random force with zero mean that obeys the 3-D fluctuation-dissipation relation. Hydrodynamic interactions are omitted. GROMACS simulates particle dynamics in three dimensions (3D); a quasi-2D system was created by application of a large harmonic potential along the third dimension using the “position restraint” option. The inter-particle potential used was 

\[ U(r) = \frac{4}{(10r - 9)^{12}} - 400a(r - r_o)^2 \]

for \( r \leq r_o \), \( U(r) = 0 \) for \( r > r_o \) (Fig. S3). The first term in \( U(r) \) for \( r \leq r_o \) is intended to mimic a repulsive hard-core-like interaction, and the second term resembles the two-body depletion potential. The parameters \( a \) and \( r_o \) were chosen to yield potentials of the desired width while maintaining a particle diameter \( \sigma = 1.0 \) and a constant well depth \( U_0 \) \( (U_0/k_B = 258.5 \) Kelvin, in GROMACS units). We define the width of the potential to be \( w \equiv (r_o - \sigma) \). For the simulation data in Figs. 2C and 3C, \( a = 1.0, r_o = 1.1 \), and thus the width \( w \) equals 10% of the particle diameter. A temperature \( T \) was chosen that results in low superheating of the crystallite. For Figs. 2C and 3C \( (w = 10\% \) of the diameter), the temperature is 75.0 (in GROMACS units), so that \( U_0/k_B T = 3.45 \). For all simulations, the friction coefficient \( \gamma \) is 40.0, and a time step of \( 2.5 \times 10^{-5} \) was used. Periodic boundary conditions were enforced to minimize boundary effects, with a periodic box of linear size \( L = 18.0 \sigma \). In all simulations, the system consists of 100 particles; the sphere area fraction is 24%. The data in Figs. 2C and 3C have as their initial configuration an “equilibrium” crystallite configuration; this was generated by beginning with a perfect
diamond-shaped hexagonal crystallite of 100 particles, and running the simulation for $10^9$ time steps. During this process, the size $N$ of the largest cluster in the system seemed to reach an equilibrium value $N_{\text{equil}} < 100$; this equilibrium state was checked by beginning another simulation with a cluster of size $N < N_{\text{equil}}$ and running for $10^9$ time steps; $N$ again settled to a value $\sim N_{\text{equil}}$. A snapshot of a crystallite resulting from this equilibration process is shown in Fig. S4A. For the data with $w = 80\%$ of $\sigma$ (which generated liquid droplet-like behavior), referred to at the end of the paper, $a = 0.0096$, $r_o = 1.8$, and $T = 95.0$ Kelvin (GROMACS units; $U_0/k_B T = 2.72$). Here we began with a perfect diamond-shaped hexagonal crystallite. A snapshot of this simulation is shown in Fig. S4B. For this run, $|\psi_6|^2_{\text{av}} \approx 0.25$ for the liquid droplet.

**Bibliography**


**Fig. S1.** Measured number of particles in clusters, $N$, vs. time, $t-t_0$ in seconds, for seven crystallites formed in the presence of SDS micelles and heated to 65 °C.

**Fig. S2.** Measured number of particles in clusters, $N$, vs. time, $t$, normalized by the characteristic diffusion time $R^2/D$. Data are shown for clusters that are three layers in thickness. (A) In the presence of SDS micelles at $T = 50$ °C. (B) In the presence of C$_{12}$E$_6$ micelles at $T = 27$ °C. For legibility, approximately every 40th data point is plotted.
**Fig. S3.** Plot of the interparticle potential $U(r)$ used in the GROMACS Brownian Dynamics simulation. Shown is the $U(r)$ for which the potential width is 10% of the particle diameter, $\sigma$.

**Fig. S4.** Snapshots of the configurations from the Brownian dynamics simulations. Colored red are those particles in the largest cluster, as identified by the cluster identification algorithm; all other particles in the system are colored blue. (A) An equilibrated crystallite for which the potential $U(r)$ had width $w$ equal to 10% of the particle diameter. (B) A liquid droplet, for which $w$ was 80% of the particle diameter.