Supporting Online Material for

Direct Measurements of Island Growth and Step-Edge Barriers in Colloidal Epitaxy

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Depletion interaction

In a suspension containing particles of two different radii, the attractive depletion interaction arises due to the exclusion of smaller spheres from a region formed by the overlapping excluded volumes of the larger spheres [S1]. This is schematically shown in Fig. S1. The concentration gradient of the small spheres between the overlapping region (shown by the blue region in Fig. S1B) and the bulk leads to an unbalanced osmotic pressure which pushes the larger spheres together leading to an effective attractive interaction between them. The range of the depletion interaction is set by the diameter of the small spheres and the strength of the depletion attraction depends on the concentration of the small spheres.

Fig. S1. (A) The black and the red spheres represent colloids of two radii. The dashed blue line shows the excluded volume around the large spheres due to the small spheres. (B) Shows two large spheres with their excluded volumes overlapping. The red spheres are excluded from the filled blue region.

Fabrication of colloid monolayers

To fabricate our substrates we first lithographically pattern an array of 0.96μm (or 1.26μm) diameter holes in a 500 nm thick polymethylmethacrylate layer that we spin coat on an indium-tin oxide coated coverslip. This conducting coverslip acts as the bottom electrode of an electrophoretic flow cell as shown in Fig. S2. The flow cell is filled with a suspension of silica particles that does not contain any depletant. When approximately 20 layers have sedimented, the negatively charged particles are pushed into the holes. Applying a DC electric field of about 14 kV/m between the top and bottom electrodes permanently binds the silica particles to the indium-tin oxide layer at the bottom of the holes. Simultaneously, the cell is flushed with pure de-ionized water and all layers except the first are washed away. Figure 1A and 1B show con-
focal micrographs of a typical monolayer of colloids pinned to a triangular lattice and square lattice respectively.

**Fig. S2.** Schematic of the flow cell used to make the substrates in our experiments. The pattern of holes is made on the conducting side of an ITO coated coverslip. The monolayers are formed for a typical electrode separation of $\approx 175 \mu m$. This height was increased to achieve complete thin film coverage in experiments performed at a low $F$. We typically form monolayers with greater than 99% coverage.

**Measurement of diffusion constant**

To determine $D$ we track [S2] individual silica particles diffusing on these colloidal monolayers in the presence of our depletant (movie S1). We measure the mean-squared displacement $\Delta r^2$ as a function of time $t$, while carefully ignoring particles with intralayer interactions (particle-particle and/or particle-island). We find that $\Delta r^2 \propto t$ and use the two-dimensional Stokes-Einstein relation to determine $D$. The units of $D$ in epitaxial growth is lattice constant$^2$/s ($LC^2/s$). In our experiments the lattice constant is 1 $\mu m$ and hence $1LC^2/s = 1 \mu m^2/s$.

**Monolayer and island fabrication using holographic optical tweezers**

To make small monolayers and islands for our step-edge barrier measurements, we use the holographic optical tweezers to trap and place individual particles into the lithographically patterned holes in the presence of a depletant (movie S4). The islands are assembled on the colloidal monolayer using a similar procedure. The overlap volume that is freed up when a particle interacts with a hole is larger than the overlap volume freed up when a particle interacts with another particle. Thus the depletion interaction between the first layer of particles and the holes is significantly stronger compared to the depletion interaction between particles on subsequent
Island size and morphology

In our island growth experiments, we observe that the average size of the islands decreases with the deposition flux \( F \) and increases with the monomer surface diffusion coefficient \( D \). A similar dependence of island size with \( D \) and \( F \) is also seen in atomic epitaxy experiments. For two experiments performed at the same \( D \) but at different \( F \), smaller islands are obtained at the higher \( F \) due to the increased probability of a monomer meeting another monomer which leads to an increase in the density of nucleation sites for island growth [S3]. Figure S3A shows the distribution of island sizes, at saturation value \( n_s \), for different \( D/F \) values on a square lattice (black circles correspond to a \( D/F \approx 5.7 \) and the red circles correspond to a \( D/F = 1300 \pm 100 \)). \( D \) also determines island morphology. Compact islands are seen for higher values of \( D \) and fractal and dendritic island growth is seen for smaller \( D \) values. The compactness/fractal nature of islands is decided by the ease with which monomers can cross island corners (Fig. 3A). Fig. S3B shows a log-log plot of the island perimeter versus island area. The fractal exponent, the slope obtained from a power-law fit, is a measure of the roughness and should be 0.5 for compact islands. Our data suggests that the fractal exponent increases with decreasing \( D \) (\( D \approx 5 \times 10^{-4} \mu m^2/s \) for the black circles and \( D \approx 3 \times 10^{-3} \mu m^2/s \) for the red circles) and this is consistent with the trend predicted by kinetic Monte Carlo simulations [S4].

**Fig. S3.** (A) Island size distributions at \( D/F = 5.7 \) (black circles) and \( D/F = 1300 \pm 100 \) (red circles). (B) Island perimeter versus island area for the same \( D/F \) values as in (A). \( D \approx 5 \times 10^{-4} \mu m^2/s \) (black circles) and \( D \approx 3 \times 10^{-3} \mu m^2/s \) (red circles). The red and black lines are least-squares fits to the data.
Determination of path length ratio

For an island with triangular symmetry, the particle on top of the island and its nearest neighbors below form a regular tetrahedron (line segments joining vertices ABCD in Fig. S4A). As the particle moves from one interstitial site to another site on the island or down a step edge, it sweeps an arc. The radius of this arc is shown by the line segment EC in Fig. S4A and S4B. If \( a \) is the particle radius, then the radius of this arc is \( \sqrt{3}a \). The path lengths traveled scale with the angle swept, \( \theta \), since the radius of the arc remains the same for moves on and off the island. The angle made by the face of the tetrahedron (denoted by the plane ADC) with the vertical can be found using the law of cosines. Thus for moves from one interstitial site to another site in the island interior the angle swept is \( \theta_i = 38.9^\circ \) and for particle moves down step edges \( \theta_s = 109.4^\circ \). The ratio of path lengths is \( \frac{\theta_s}{\theta_i} \approx 2.8 \).

Fig. S4. (A) Particle on top of a 3-particle island. ABCD form a regular tetrahedron. (B) Particle midway during the hop. The radius of the arc is shown by the line segment EC.

Simulations of residence time distributions

Our experiments show that to move from one interstitial site to another a particle must break a bond at the initial site and diffuse along the valley between two of the three underlying particles as depicted by the energy landscape in Fig. 3H. This process can be modeled as a 1D random walk on a segment of length \( L \) (Fig. S5A). The distribution of residence times in such a model can be determined by considering an ensemble of independent random walkers that enter from the left edge of the segment at the bond breaking rate. The motion of the walkers on the segment is governed by the diffusion rate. The right edge is absorbing, and the rate of absorption of walkers as a function of time yields the distribution of residence times.

To allow for numerical simulations, we discretize the path into \( N \) sites separated by a distance \( \Delta L = L/N \). The walkers move between adjacent sites according to the scaled diffusion rate \( \gamma = 2D/\Delta L^2 \) and the bond breaking rate \( \Gamma \). Initially, all walkers are located in the first site.
Fig. S5 (A) Schematic of the 1D random walk model for a single pathway with \( N \) segments of length \( \Delta L \). (B) Schematic of the 1D random walk model for 3 pathways \( \{a, b, c\} \). Here pathways \( a \) and \( b \) correspond to descent and are thus longer than pathway \( c \).

At the left edge, and the current \( J = \frac{\partial n}{\partial t} \) of walkers into the first two sites is given by

\[
\begin{align*}
\frac{\partial n_1}{\partial t} &= -\Gamma n_1 + \gamma n_2 \\
\frac{\partial n_2}{\partial t} &= -2\gamma n_2 + \Gamma n_1 + \gamma n_3,
\end{align*}
\]

where we note that the first site loses walkers at the bond breaking rate \( \Gamma \) but gains walkers that randomly walk back to it at the diffusion rate \( \gamma \). Since the right boundary is absorbing, the current of walkers into the last two sites is given by

\[
\begin{align*}
\frac{\partial n_{N-1}}{\partial t} &= -2\gamma n_{N-1} + \gamma n_{N-2} \\
\frac{\partial n_N}{\partial t} &= \gamma n_{N-1}.
\end{align*}
\]

Here the \( N \)th site only gains walkers and does not give any to its neighbor. The current \( J_i \) into any other site is simply

\[
\frac{\partial n_i}{\partial t} = -2\gamma n_i + \gamma (n_{i-1} + n_{i+1}).
\]

While this description is accurate for a walker on a single pathway, in our experiments a particle departing from one interstitial site has three possible exit pathways \( \{a, b, c\} \) that share the same origin (Fig. S5B). To model this scenario, the current of random walkers into each site of the three pathways is given by
Here the first site is shared by the three pathways, and the length of each pathway can be varied by tuning $N^\alpha = L^\alpha / \Delta L$. This formulation allows comparison of residence times in interstitial sites with different numbers of descent pathways $p$ by fixing the ratio of descent path lengths to non-descent path lengths to be $2.8$, as derived above. To calculate the distributions of residence times $\tau$, we numerically evaluate these walker currents at each simulation cycle and monitor the total current

$$J_N = \sum_{\alpha=a,b,c} \frac{\partial n^\alpha_{N^\alpha}}{\partial t},$$

which is the number of walkers that successfully complete the journey along any pathway as a function of time. By tuning the bond breaking rate $\Gamma$ relative to the diffusion rate $\gamma$, the residence time distributions can be calculated for both limits: when $\Gamma \ll \gamma$, the bond breaking time dominates, and when $\Gamma = \gamma$, the residence time can be described by diffusion alone. These distributions are shown for both limits in Fig. S6A and S6B, where the strong bond limit is approximated by $\Gamma = \gamma / 10^5$. To explore the scaling of the mean residence time $\langle \tau \rangle$ with the length of the descent pathway, we plot the mean residence time scaled by the mean residence time for an internal interstitial site where $p = 0$ (Fig. 3I). The scaled residence times are consistent with the intuition that in the diffusion limit, $\langle \tau_{p=3} \rangle / \langle \tau_{p=0} \rangle \approx 2.8^2$, while in the strong bond limit $\langle \tau_{p=3} \rangle / \langle \tau_{p=0} \rangle \approx 2.8$. 

\[
\begin{align*}
\frac{\partial n^1}{\partial t} &= -3 \Gamma n^1 + \gamma (n^a_2 + n^b_2 + n^c_2) \\
\frac{\partial n^a_2}{\partial t} &= -2 \gamma n^a_2 + \Gamma n^1 + \gamma n^a_3, \quad \alpha = \{a, b, c\} \\
\frac{\partial n^a_3}{\partial t} &= -2 \gamma n^a_3 + \gamma (n^a_{i-1} + n^a_{i+1}), \quad \alpha = \{a, b, c\} \\
\frac{\partial n^a_{N^\alpha-1}}{\partial t} &= -2 \gamma n^a_{N^\alpha-1} + \gamma n^a_{N^\alpha-2}, \quad \alpha = \{a, b, c\} \\
\frac{\partial n^a_{N^\alpha}}{\partial t} &= \gamma n^a_{N^\alpha-1}, \quad \alpha = \{a, b, c\}.
\end{align*}
\]
Fig. S6. (A) Distribution of residence times in the limit of strong bonding. (B) Distribution of residence times in the diffusion limit.
References


