Entropic Confinement of Colloidal Spheres in Corners on Silicon Substrates

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We have investigated depletion effects among dispersed, submicron, polystyrene spheres of two different sizes near a faceted silicon substrate. The larger spheres were confined to the corners where two silicon facets intersected (as where a wall meets a floor). The entropic confinement potential increased by $1.2 k_B T$ when the small-sphere volume fraction was increased by 14% to 0.37. Large-sphere crystallites nucleated along the corner and grew out along the flat surfaces *before* crystals nucleated on the flat surface or in the bulk. The results demonstrate a novel way to sort particles or to organize them along geometric features in a substrate for microfabrication.

The motions of submicron particles on substrates in contact with suspensions can affect a wide variety of material properties including reactivity of biological systems[1] and flow in porous media or in particle filters. Recent reports have shown that the texture and shape of a substrate strongly perturb the motion of nearby colloidal particles, even when there exist only hard-core interactions among the particles and surfaces. For example, in binary hard-sphere mixtures (containing spheres of two sizes), the larger particles are repelled from the edge of a terrace and are pushed along a wall of continuously changing radius of curvature.[2,3] These effects have been explained using the theory of entropic "depletion" or excluded-volume forces.[4,5]

In this Letter, we report the first use of the depletion mechanism to confine particles at specific positions in the sample. The ability to trap dispersed particles at specific points on a substrate may lead to a useful technique for microfabrication using soft materials. We show that, in a binary hard-sphere mixture, the larger spheres are confined along a corner (for example, where a wall meets a floor, as shown in Figure 1). This confinement is accompanied by an *increase* of the mixture's total entropy. We also explore the effects of substrate shape on the growth of crystallites of the larger spheres. Crystallites nucleate in the corners before nucleating in the bulk or on the flat surface. Furthermore, these crystallites are aligned in a specific direction with respect to the substrate, suggesting a new way to make aligned colloidal crystallites. Finally, we show how the measured entropic potentials differ from the ideal-gas predictions when there exist structural correlations among the smaller particles.[6−8]
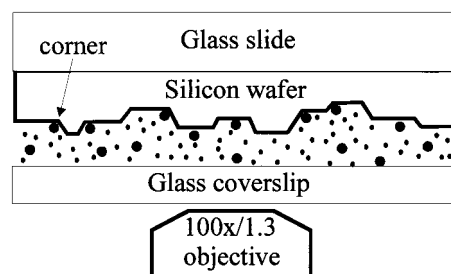

Figure 1. Schematic diagram of the experiment, showing the sample cell and microscope objective. The suspension contains polystyrene spheres (sphere diameters are 0.474 and 0.083 μm; volume fractions are 0.015 and 0.32−0.37).

Our samples contained polystyrene spheres of two different sizes (diameters a_L and $a_S = 0.474$ and 0.083 μm (Seradyn, Inc.; Indianapolis, IN)), suspended in water. The salt concentration was 0.01 M, so that the Debye screening length (approximately 5 nm) was small compared to the particle sizes.[9] Thus, the particles closely resembled hard spheres. The large-sphere volume fraction ϕ_L was 0.015 in all samples (ϕ is the number of spheres multiplied by the volume of each sphere divided by the sample volume). Three different samples were studied. They contained different small-sphere volume fractions, $\phi_S = 0.319$, 0.333, and 0.365, that were measured by viscometry.[10] The sample cell consisted of a glass cover slip glued to a glass slide with a piece of silicon wafer between the two (see Figure 1). We injected approximately 0.30 mL of suspension into the sample cell. The silicon substrate was a small (10 mm by 10 mm) piece of a wafer with the (100) axis normal to the top (polished) surface. The bottom surfaces of such wafers are covered with naturally occurring truncated pyramids that are formed

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(10) The viscometry measurements revealed that the particles are slightly swollen in solution, so that the volume fraction measured by weighing before and after drying underestimated the sphere concentration in solution by approximately 22%.[20]

by the intersections of smooth Si crystal planes. These pyramids conveniently provide a large number of corners with an open angle of approximately 150° (Figure 1). The larger particles were clearly visible using an inverted optical microscope (Zeiss Axiovert 135, 100× objective, numerical aperture = 1.3, with differential interference contrast (DIC)). We recorded images of the samples over a period of days to look for crystallites of larger spheres.

In the absence of small spheres, 0.474-μm spheres were placed in the corner using a laser tweezer[11,12] and then released. These spheres were not confined to the corner; they diffused at least 0.5 μm away within 2 s. In the *binary* suspensions, the tweezers were not needed: the larger spheres spontaneously lined up along the corners. Although these particles were confined for up to several seconds or minutes, they were free to diffuse along the line of the base of each pyramid. To quantify the strength of the potential holding the large spheres in the corner, we measured the average time they were confined there. In the experiment, a large sphere confined to the corner was chosen at random and a timer was started. As soon as the sphere in question diffused away from the surface ("escaped"), the timer was stopped and the elapsed time was recorded. The sphere was considered to have escaped when it had ventured a distance roughly equal to its radius from the corner or when its diffusivity suddenly increased. The latter criterion (suggested and used by Kaplan et al.[13] to distinguish particles at the surface from those in the bulk) relies on the dramatic decrease in hydrodynamic friction when the sphere moves vertically away from the corner. Lifetimes were measured for 100−200 events in each of the three samples. The probability of escape in the short time interval dt is constant, defined here to be dt/τ. Therefore, the probability P that the large sphere escapes after time t is predicted to be $P(t) = (1/\tau) \exp(-t/\tau)$.[14] The experimental data agree with this exponential form (Figure 2a). A robust method to extract the mean lifetime τ from the data is to plot the total number of escape events $N(t_0;t)$, that occurred between t_0 and t:

$$N(t_0;t) = N_{\text{total}} \int_0^t P(t')\, dt' = N_{\text{total}}(\exp(-t_0/\tau) - \exp(-t/\tau)) \quad (1)$$

We chose $t_0 = 2$ s because of the lack of reliable measurements at shorter times. From our data, we counted $N(t_0;t)$; the square root of $N(t_0;t)$ provided an estimate of the statistical uncertainty. We then fit $N(t_0;t)$ to the function in eq 1 and determined that $\tau = 7 \pm 2, 13 \pm 3$, and 32 ± 8 s when the small-sphere volume fraction ϕ_S = 0.319, 0.333, and 0.365, respectively. A 14% increase in ϕ_S caused a factor of 5 increase in τ.

The mean corner occupation time τ is related to F_{trap}, the depth of the free energy well holding the particle in the corner: $\tau = \tau_D \exp(F_{\text{trap}}/(k_B T))$, where τ_D is the average time between attempts to hop across the barrier (the subscript D stands for diffusive).[15,16] In Figure 2b, we plot $\ln(\tau)$ versus ϕ_S. An estimate of τ_D is given by L^2/D, where L is the width of the trap and D is the particle's diffusion
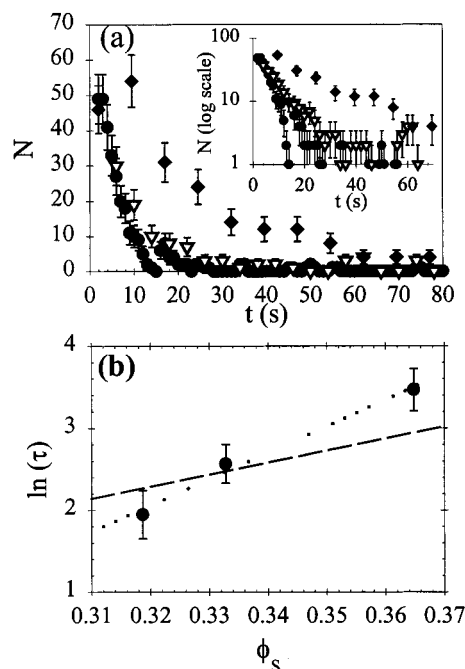

Figure 2. (a) Histogram showing the number of observed escape events N versus elapsed time t. Circles, open triangles, and diamonds correspond to ϕ_S = 0.319, 0.333, and 0.365, respectively. The inset shows the same data with N on a logarithmic scale. (b) The symbols show the measured $\ln(\tau)$ versus ϕ_S, where τ is the mean lifetime of a large sphere in a corner. The dashed line gives the ideal-gas prediction of the free energy of confinement (including the predicted variation in τ_D), which clearly does not agree with the measurement (dotted line).
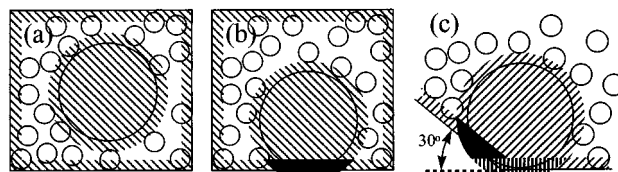

Figure 3. Cartoon illustrating the depletion force. In part a, the volume accessible to the centers of the small spheres is the volume of the box minus the hatched (excluded) regions. In part b, the accessible volume is increased by the volume of the overlap region shown in black. Hence, the entropy of the small spheres is increased. (c) In our experiment, the easiest way for the larger sphere to escape from the corner is along one surface. During the escape, the excluded-volume overlap with one wall is lost (region shown in black), and the entropy decreases.

coefficient. Using the method of ref 17 we estimate that, as ϕ_S increases from 0.32 to 0.37, D decreases by approximately 40%. Using this estimate of the ϕ_S-dependence of τ_D, we infer from the data that F_{trap} increased by $1.2 k_B T$.

To put our results in context, we briefly review the theory of depletion forces in mixtures of hard spheres of two different sizes. Moving a large sphere toward a surface does not change the interaction energy (which is zero for hard spheres and hard walls) but does increase the volume accessible to the other (smaller) spheres due to the overlap of the exclusion zones (Figure 3).[4,18] The gain in entropy (or reduction of free energy) corresponds to a force that pushes the larger particle against the wall. The range of the force is determined by the size of the small spheres,

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and the strength of the force depends on ϕ_S, the ratio of sphere sizes, and the shape of the wall. When the small spheres are treated as an ideal gas, the change in Helmholtz free energy of the mixture ΔF is equal to the osmotic pressure of the small spheres $P_S(\phi_S)$ multiplied by the change in the volume accessible to them: $\Delta F = -P_S(\phi_S)\Delta V_{overlap}$. When the wall is flat, the minimum free energy (which occurs at contact) is approximately given by $F_{contact} = -3\alpha\phi_S k_B T$ ($\alpha \equiv a_L/a_S = 5.71$). In this experiment, a large sphere in the corner is in contact with two walls. When it escapes from the corner, it loses contact with one wall, and the free energy increases by

$$F_{trap} = 3G(\theta)\alpha\phi_S k_B T \qquad (2)$$

where $G(\theta)$ is a calculable geometrical factor that depends on the open angle θ of the corner (Figure 3c). For our experiment, $\theta \sim 30°$ and $G(\theta) = 0.45$. In separate experiments, we found evidence of a weak electrostatic attraction between the silicon surface and the larger particles in a binary mixture.[19] Such nondepletion forces (such as the DLVO potential[9]), however, will not affect the slope of the plot shown in Figure 2b because they are independent of ϕ_S. Therefore, as long as we are looking at the *functional dependence* of $F(\phi_S)$ and not at its absolute magnitude, forces not induced by the small particles drop out of the analysis.

According to the ideal-gas depletion-force prediction in eq 2, the confinement potential F_{trap} should increase by just $0.36 k_B T$ when ϕ_S increases from 0.319 to 0.365. The plot of $\ln(\tau)$ ($=F_{trap}/k_B T + \ln(\tau_D)$) versus ϕ_S in Figure 2b compares the data to the ideal-gas prediction of $\ln(\tau)$, which includes the correction for the ϕ_S-dependence of τ_D, as discussed above, plus an arbitrary constant. The slope of our data is 32 ±10, clearly much steeper than the ideal-gas prediction, which is shown in Figure 2b. We repeat that since the corner confinement depends only on ϕ_S and is absent when $\phi_S = 0$, nondepletion forces (such as electrostatic or van der Waals) are not relevant. A possible explanation for this large deviation is that the small spheres are not an ideal gas. Computer simulations[7,8] and liquid structure theory[6-8] have recently been used to calculate depletion forces in a binary hard-sphere mixtures. Mao *et al.*[6] and Dickman *et al.*[8] have predicted and Crocker *et al.*[20] have found experimentally that the ideal-gas law accurately estimates the minimum ("contact") value of the free energy $F_{contact}$; that is, $F_{contact}$ is proportional to ϕ_S. The ideal-gas model, however, fails to predict a potential-energy *barrier* that reaches a maximum value of F_{barr} when the distance between the surfaces of two large spheres (or between a large sphere and a wall) is approximately $a_S/2$. The quantity F_{barr} grows rapidly with ϕ_S when $\phi_S > 0.1$ and reaches $4 k_B T$ for the sphere + flat wall geometry ($\alpha = 10$ and $\phi_S = 0.30$).[8] The energy well that confines the large sphere in the corner, therefore, is $F_{trap} = F_{contact} + F_{barr}$. Our results are consistent with $F_{barr} \approx 1 k_B T$. Quantitative analysis, however, is complicated by the geometry and by the possibility of electrostatic interactions between the small spheres and the silicon wall. Such interactions would alter the distribution of small spheres in the corner and prevent precise comparison to theoretical hard-sphere predictions.

Finally, the optical micrographs in Figure 4 demonstrate "prefreezing" of large spheres in the corner. Here, we
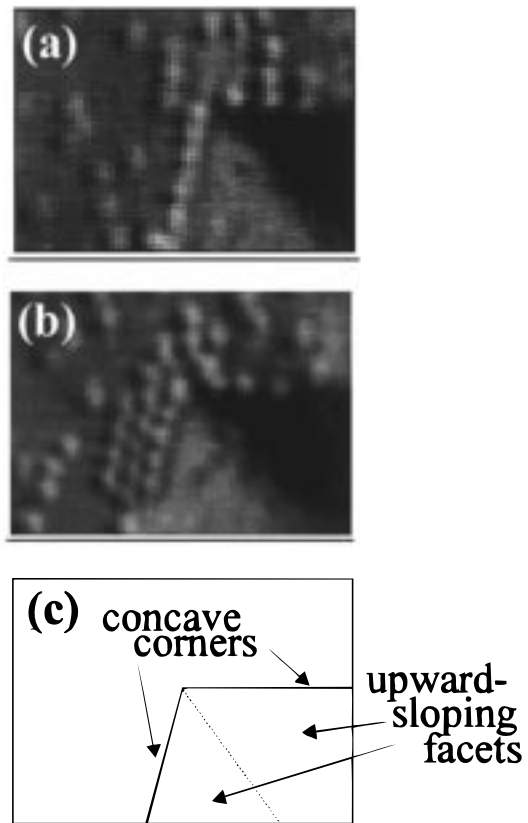
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Figure 4. Optical micrograph of a crystal growing from the corner. The large- and small-sphere volume fractions are $\phi_L = 0.30$ and $\phi_S = 0.35$. The gray circles are large spheres (0.474-μm diameter) moving along the flat surface of the silicon wafer. The small spheres are not visible. A raised pyramid lies at the lower right corner of the surface, as shown in part c. In part a, there is a clearly visible line of particles along the (convex) corner. In part b (10 min later), a two-dimensional crystallite has formed from the first row of particles and is aligned with the corner.

observed nucleation of crystallites in corners but not at the flat surface or in the bulk. Since the equilibrium particle density is higher in the corner, it is reasonable that nucleation would occur there first, just as nucleation along a wall occurs before it does in the bulk.[18,21] We emphasize, moreover, that the corner *aligns* the crystals along a specific direction in the plane, a potentially useful feature when making ordered arrays of particles on a chip.

We have reported on the entropic confinement mechanism. In addition to its potential for use in making patterns of microspheres on surfaces, the method may also be used to sort particles, such as cells, according to size or shape without sensitivity to surface charge or surface chemistry. Finally, an understanding of the behavior of microscopic particles near corners is likely to be relevant to a complete understanding of polydisperse suspensions near rough surfaces or inside porous media.

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