Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information

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S1. Square Crystals Formed in the Hanging Drop

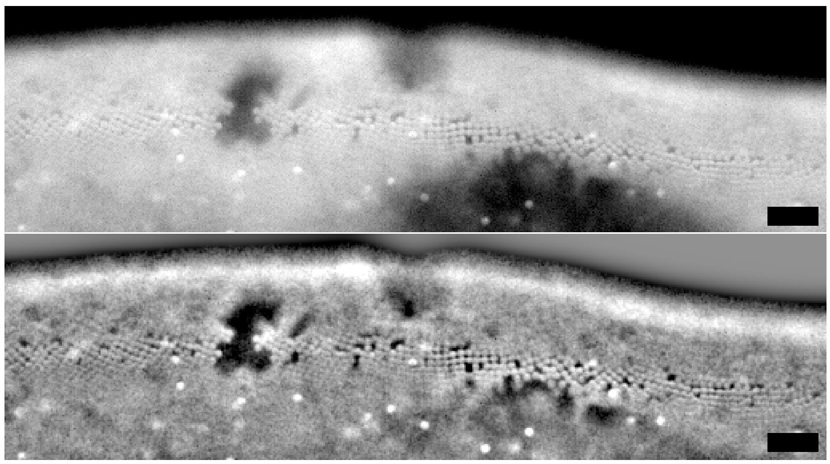

Figure 1: Raw (top) and bandpass filtered (bottom) epifluorescence images of square crystals self-assembled at the contact line of a hanging drop. Filtering accentuates local contrast in the image, making it easier to visualize the square patterning. Scale bars = 5 μm.

S2. Curvature-Induced Quadrupole Pair-Potential Calculations

1 Geometric Model

We model the liquid capillary bridge as an asymmetric, axial section of a catenoid, bounded by two plates separated by a total height h. The catenoid is parametrized by

$$\rho(z) = R\cosh\left(z/R\right) \tag{1}$$

where z is the vertical coordinate whose origin resides at the central waste which has radius R (figure 2).

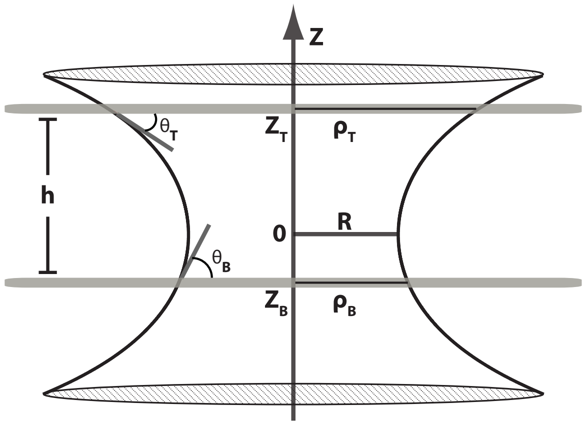

Figure 2: Schematic depicting catenoid model of the capillary bridge.

By definition, the radial boundary of a catenoid has both positive and negative curvature of equal magnitude at point each z. This results in a zero mean curvature surface whose local radii of curvature are given by

$$c(z) = \pm\frac{1}{R\cosh\left(z/R\right)^2} \tag{2}$$

2 Determination of Catenoid Central Width

As shown in figure 2, it is assumed that the plates are positioned on opposite sides of the origin. The physical reasoning behind this assumption stems from constraining the contact angles generated by the liquid at the bounding plates. While $\theta_T \neq \theta_B$, it is known that both $\theta_T, \theta_B < 90^o$. If the plates were positioned on the same side of the origin, one of the contact angles would neccessarily be greater than 90^o.

The height h is a known quantity, given by

$$h = z_T - z_B \tag{3}$$

Rearranging (1) and solving for z_T and z_B yields

$$z_T = R\cosh^{-1}\left(\rho_T/R\right) \tag{4}$$

and

$$z_B = R\cosh^{-1}\left(\rho_B/R\right) \tag{5}$$

However, $z_B < 0$, yet $\mathrm{Re}\left(\cosh^{-1}(x)\right) \geq 0$ for all $x \in (-\infty, \infty)$. Thus, (5) should be

$$z_B = -R\cosh^{-1}\left(\rho_B/R\right) \tag{6}$$

Substituting (4) and (6) into (3) we find

$$h = R\left(\cosh^{-1}\left(\rho_T/R\right) + \cosh^{-1}\left(\rho_B/R\right)\right) \tag{7}$$

The transcendental equation (7) can be solved numerically for R given ρ_T and ρ_B. The radii of the liquid bridge at the top and bottom plates were measured at 2.4 mm and 1.2 mm, respectively, leading to a value of 0.1 mm for R. The values of ρ_T and ρ_B were determined photographically from the images shown in figure 3.

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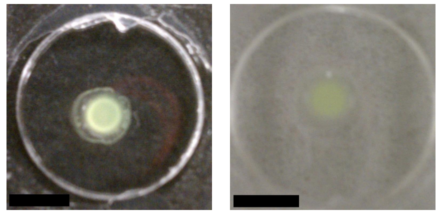

Figure 3: Top-down images of the top (left) and bottom (right) glass coverslips used to form the capillary bridge. Scale bars represent 5 mm.

3 Pair-Potential Calculation

The capillary potential stemming from the quadrupolar deflections produced by particles adhered to a fluid interface with zero mean and constant radii of curvature is given by

$$U(r,\varphi) = -\frac{\pi}{12}\gamma\frac{c^2 a^8 \sin(\theta)^8}{r^4}\cos(4\varphi) \tag{8}$$

Here, γ is the interfacial tension, c is the radius of curvature, a is the particle radius, θ is the particle contact angle at the interface, r is the interparticle separation (center-to-center) and φ is the angle characterizing the orientation of the particle pair relative to the principle axes of curvature. Although c is not constant for a catenoid ((2)), if we strictly consider the interaction between a pair of particles at the same elevation (relative to the catenoid's central waste; $\varphi = 0$) (8) becomes

$$U(r,\Delta z) = -\frac{\pi}{12}\gamma\frac{a^8 \sin(\theta)^8}{r^4 R^2 \cosh\left(^{\Delta z}/_{R}\right)^4} \tag{9}$$

with Δz defined as the vertical distance from the central waste ($z = 0$) of the catenoid. Because θ is not known, we calculate the pair-potential, normalized by the particle thermal energy kT, as a function of Δz and θ. The interparticle separation (r) is set at a constant value of 200 nm (surface-to-surface). Results are shown in figure 4.

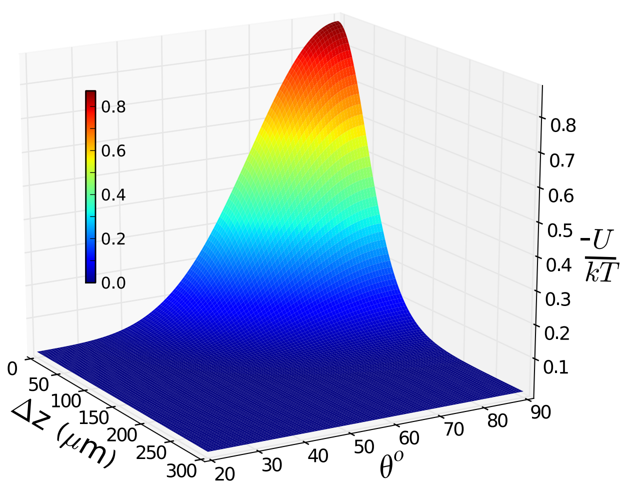

Figure 4: Plot of the normalized capillary pair-potential for particles 1 μm in diameter as a function of vertical position in the catenoid and particle interfacial contact angle. Particle separation is held constant at 200 nm (surface-to-surface).