Supporting Information for: Using magnetic cylindrical particles at liquid interfaces to create switchable colloidal monolayers

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1 Accuracy of Approximating Cylinders as Super-Ellipsoids

As discussed in the main paper, one numerical problem when analysing the orientational behaviour of cylinders is the fact that Surface Evolver becomes unstable when the three phase contact line crosses the sharp edge of the cylinder. In order to overcome this problem, in our Surface Evolver simulations, we approximate the cylinders as super-ellipsoids (eq.8 in the main paper) with a sharpness parameter $\eta = 20$. In this section, we estimate the accuracy of this approximation. In Figure 1(b), we plot the projection of the particle surface onto the horizontal x-y plane for different values of η for super-ellipsoids with $\alpha = 2.5$. We see that $\eta = 20$ yields a reasonably accurate approximation to the shape of an infinitely sharp cylinder. In Figure 1(a), we plot $\frac{1}{\cos\theta_t}\frac{\partial \overline{F}_{st}}{\partial \theta_t}$ as a function of θ_t for different values η for cylinders with $\alpha = 2.5$, $\theta_w = 90°$, assuming the liquid meniscus around the particle remains flat. The reason for assuming a flat meniscus is because exact results for the orientational behaviour are known for this case. Specifically, in Figure 1(a), the infinitely sharp cylinder curve was calculated using the flat interface model (see section 2 of the main paper) while the results for all other values of η were calculated using Surface Evolver with the interface constrained to remain flat. Note that the position and magnitude of the maxima in $\frac{1}{\cos\theta_t}\frac{\partial \overline{F}_{st}}{\partial \theta_t}$ corresponds to the critical angle and critical field for the irreversible transition from the tilted state to the end-on state (see next section). We see that the Surface Evolver calculations with $\eta = 20$ reproduces

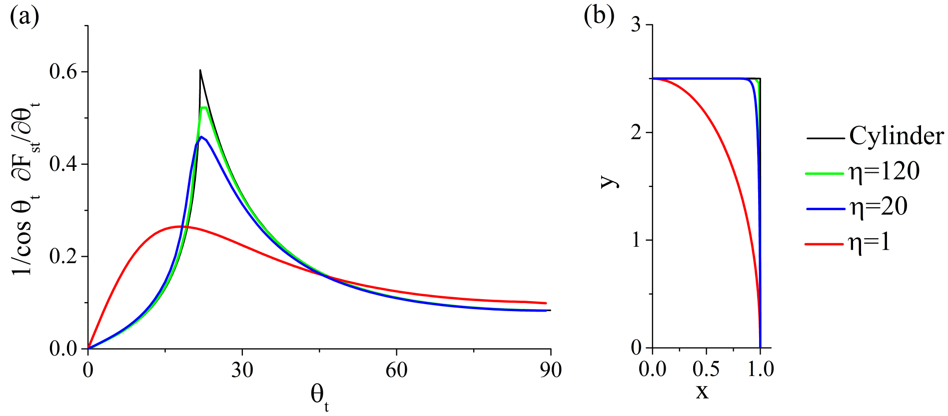

Figure 1: (a)$\frac{1}{\cos\theta_t}\frac{\partial \bar{F}_{st}}{\partial \theta_t}$ as a function of tilt angle θ_t for an infinitely sharp cylinder calculated from flat interface theory and for rounded cylinders with different η calculated from Surface Evolver simulations where the interface is constrained to be flat. (b) Projection of cylinders with different values of η onto the horizontal plane.

the exact curve accurately except for very close to the maximum. Specifically, the $\eta = 20$ curve under predicts the magnitude of the maximum (and hence the critical field) by around 25% but it under predicts the position of the maximum (and hence the critical angle) by only 2%. Considering the fact that in the exact theory, the maximum is a cusp which is extremely challenging to capture numerically, this level of accuracy is reasonably good. Indeed, in order to reduce the error in the critical field to 10%, we would need to increase the sharpness parameter to $\eta = 120$ (see Figure 1(a)), which is not achievable numerically if we incorporate realistic deformations of the liquid meniscus. Finally, for cylinders in the side-on state, it is possible to use Surface Evolver to calculate meniscus deformations around cylinders with infinitely sharp corners. For typical cylinders in the side-on state (say $\alpha = 3$, $\theta_w = 80°$), we find that the difference $z_{max} - z_{min}$ between the maximum and minimum contact line heights using Surface Evolver simulations with $\eta = 20$ deviates only by around 10% from the results for an infinitely sharp cylinder. Taking all these estimates into account, we conclude that the value $\eta = 20$ represents a good compromise between numerical stability and accuracy in our Surface Evolver simulations.

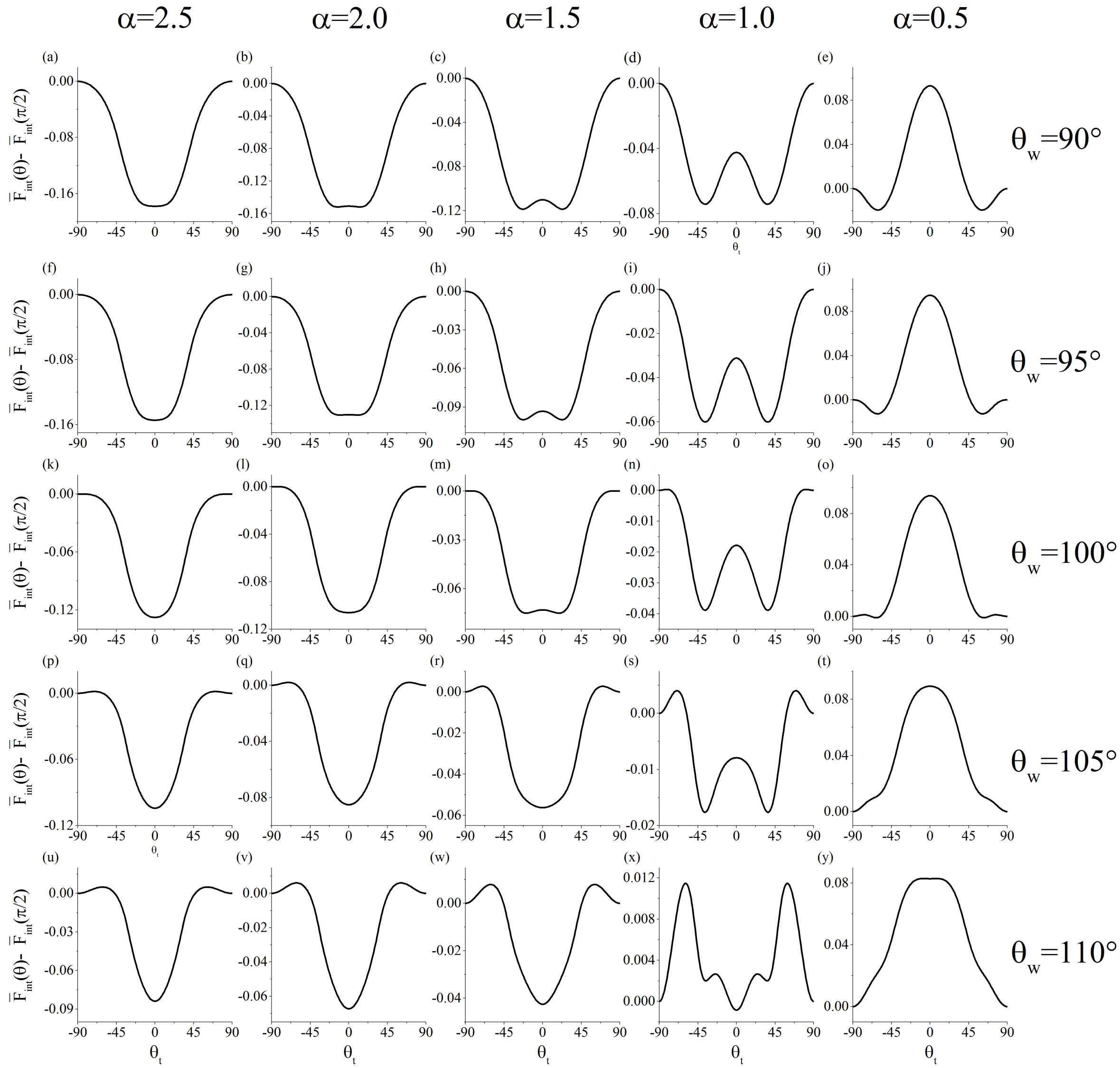

Figure 2: Surface Evolver results for the dimensionless free energy (relative to the end-on state) as a function of tilt angle for cylinders with $\eta = 20$ in the absence of an external field and different aspect ratios α and contact angles θ_w.

2 Orientational Free Energy and Numerical Method for Determining Magnetic Response of Particles

In Figure 2, we plot the Surface Evolver results for the dimensionless free energy as a function of tilt angle for cylinders with $\eta = 20$ in the absence of an external field for $\theta_w = 90^\circ \to 110^\circ$ and aspect ratios $\alpha = 0.5 \to 2.5$ in order to obtain a systematic picture of how changing θ_w and α impacts the orientational free energy landscape.

In our study, the magnetic response of the system, including the stationary tilt angles (i.e., tilt angles corresponding to local minima or maxima in the free energy) for a given

α	θ_0 (°)	θ_{c1} (°)	$\overline{B}_{c1}$
2.0	13.0	7.6	0.007
1.5	23.1	14.1	0.034
1.0	36.4	21.1	0.088
0.5	60.8	30.7	0.213
0.25	82.6	42.0	0.370

Table 1: Surface Evolver results for binodal tilt angles θ_0 and spinodal points $(\theta_{c1}, \overline{B}_{c1})$ for neutrally wetting cylinders with different aspect ratios α.

magnetic field and the magnetic fields and tilt angles at the binodal points or points where irreversible orientational transitions occur (including spinodal points) are determined by solving eq.3 in the main paper. To illustrate this method, in Figure 3, we plot $\frac{1}{\cos\theta_t}\frac{\partial \overline{F}_{st}}{\partial \theta_t}$ for different state points, with (a),(b) corresponding to state points reported in Figure 5 (a), (c) of the main paper respectively and (e),(d),(f) corresponding to state points reported in Figure 12(a), (b), (c) of the main paper respectively. For an arbitrary magnetic field $\overline{B}$, which is represented by a horizontal line in Figure 3, the intersection of the horizontal line with the $\frac{1}{\cos\theta_t}\frac{\partial \overline{F}_{st}}{\partial \theta_t}$ curve corresponds to either a local minimum or maximum of the free energy curve. The binodal tilt angles are obtained from the intersection between the $\overline{B} = 0$ line and the $\frac{1}{\cos\theta_t}\frac{\partial \overline{F}_{st}}{\partial \theta_t}$ curve (filled circles in Figure 3(b),(d)). On the other hand, the maxima and minima in the $\frac{1}{\cos\theta_t}\frac{\partial \overline{F}_{st}}{\partial \theta_t}$ curves correspond to the field strengths and tilt angles where local maxima and minima in the free energy curve merge, i.e., where local minima disappear. We can therefore use the the maxima or minima of the $\frac{1}{\cos\theta_t}\frac{\partial \overline{F}_{st}}{\partial \theta_t}$ curves to determine the spinodal points (open circles in Figure 3(b),(d)) or the position of the irreversible orientational transitions at higher fields. This is illustrated in the plots in Figure 3, where the critical angles and field strengths for the state points reported in Figures 5 and 12 of the main paper are explicitly labelled. A more detailed discussion of this method can be found in ref.[1]

Finally, we report numerical values from Surface Evolver simulations for the binodal and spinodal points for neutrally wetting cylinders with different aspect ratios in Table 1 and critical aspect ratio α_c as a function of contact angle for cylinders in Table 2.

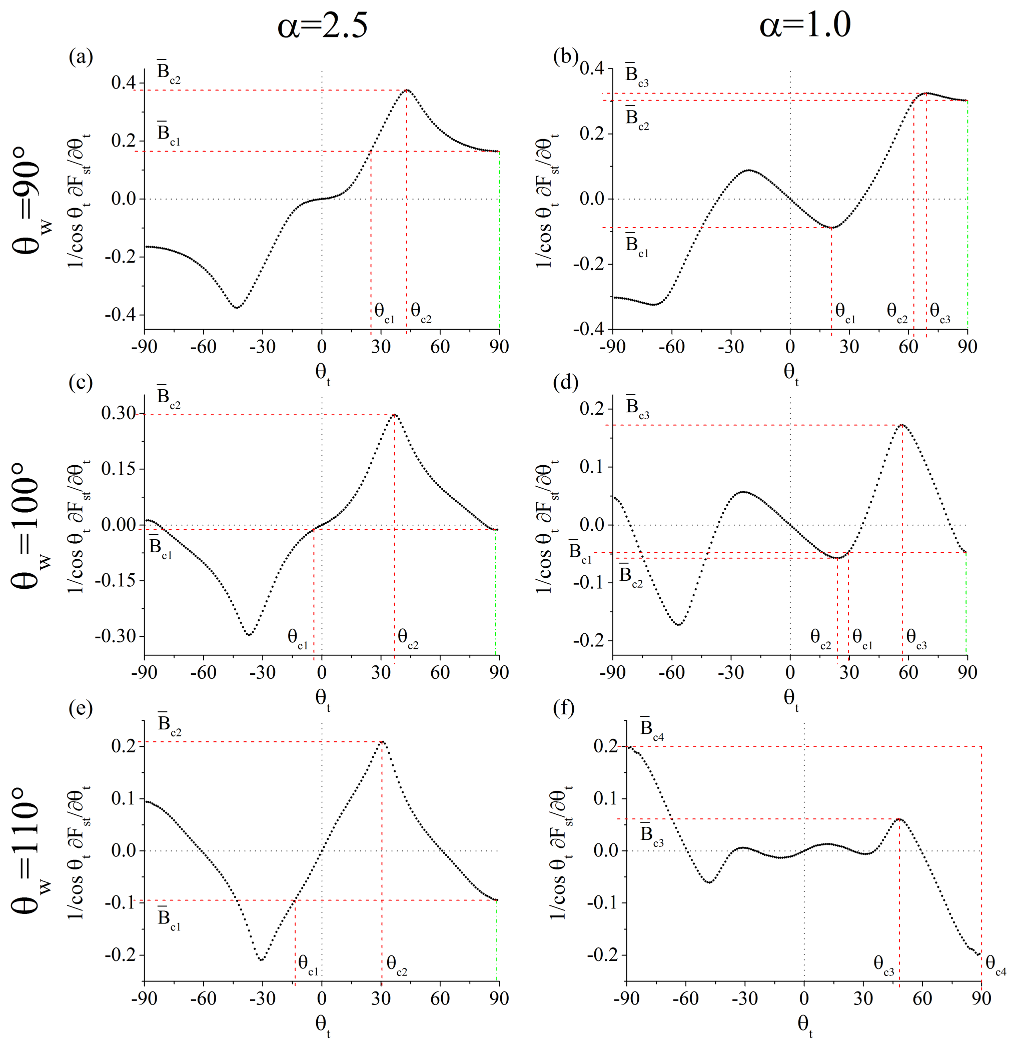

Figure 3: Surface Evolver results for $\frac{1}{\cos\theta_t}\frac{\partial \bar{F}_{st}}{\partial \theta_t}$ vs. θ_t for cylinders with $\eta = 20$ for different combinations of contact angles θ_w and aspect ratios α. The critical field strengths and tilt angles where the cylindrical particles undergo an irreversible transition to a different local minima correspond to the maxima or minima of the curves and are explicitly labelled. See main text for details.

θ_w (°)	α_c
90	2.3
95	2.2
100	1.8
105	1.2

Table 2: Surface Evolver results for the critical aspect ratio α_c as a function of contact angle θ_w for cylinders

References

1. Newton, B. J.; Brakke, K. A.; Buzza, D. M. A. *Physical Chemistry Chemical Physics* **2014,** *16*, 26051.