

Supplementary Material

Numerical and Experimental Investigation of Static Wetting Morphologies of Aqueous Drops on Lubricated Slippery Surfaces Using a Quasi-Static Approach

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S1: Realization of the floating systems using SE simulations for validation:

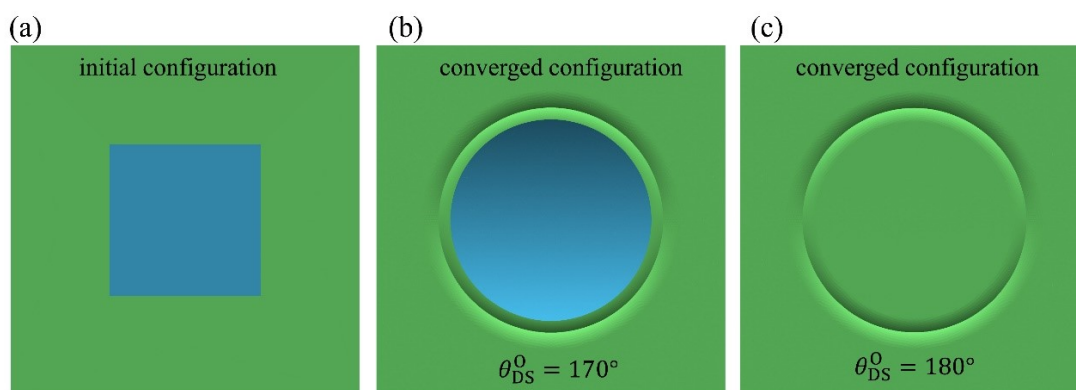


Fig. S1 Snapshots of SE simulation images for (a) initial configuration and the final converged configurations for (b) sinking and (c) floating systems as viewed from the bottom of the solid substrate.

As seen in Fig. S1, an initial configuration (a) converges to the final configuration (b) or (c) depending on the substrate wettability $\theta_{DS}^0 = 170^\circ$ or $\theta_{DS}^0 = 180^\circ$, respectively. A thin film of oil between the drop and the solid surface is energetically preferred when the substrate wettability is set to $\theta_{DS}^0 = 180^\circ$. This is consistent with the floating point condition (referred in the Introduction section of the main manuscript). The results show the validity of SE simulations and the capacity of Surface Evolver to capture such fine details.

S2: Volume estimation of the target ridge volume from SE simulation-1:

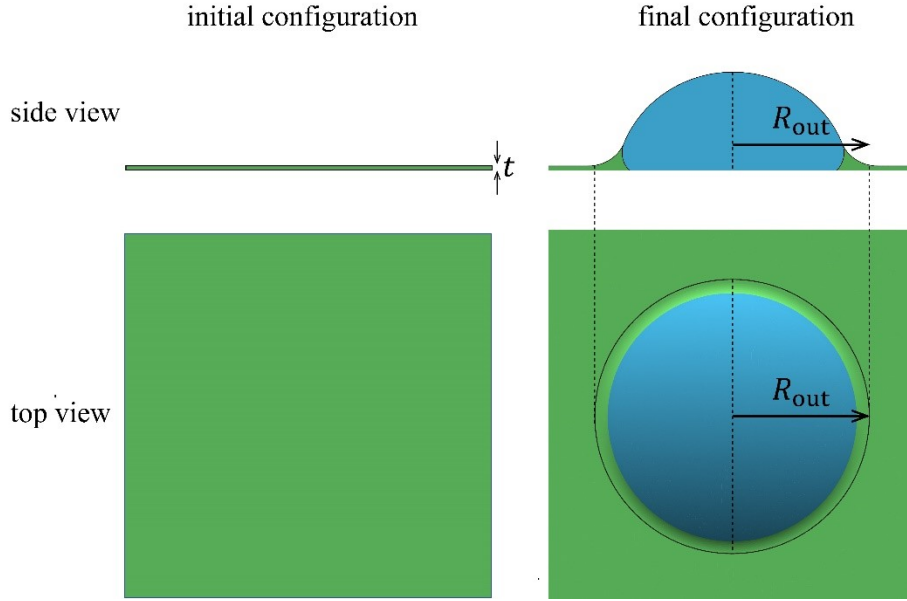


Fig. S2: Schematics of top and side views of a lubricant-coated slippery surface showing initial and final configurations before and after drop deposition.

Figure S2 shows the top view of a drop deposited on a thin lubricating fluid coated surface with lubricant thickness, t , lubricant surface area, $A_{lubricant}$, and volume, $V_{lubricant}$. If the sinking time of the drop, τ_S , is similar to early intermediate times, the volume of the wetting ridge, V_{ridge} , can be derived by conserving the lubricant volume as follows,

$$V_{lubricant} = V_{ridge} + V_{non-ridge} \quad (1)$$

Using $V_{lubricant} = A_{lubricant} t$, $V_{non-ridge} = A_{non-ridge} t$ and $A_{non-ridge} = A_{lubricant} - \pi R_{out}^2$, we get

$$V_{ridge} = \pi R_{out}^2 t \quad (2)$$

where, $A_{non-ridge}$ and $V_{non-ridge}$ is the surface area and volume, respectively, of the lubricant from a region far away from the drop that has not flown to the wetting ridge.

S3: Variation of the drop volume with time:

Environmental exposure to an aqueous drop (80 wt% formamide) on a dry hydrophobic surface under the lab condition (19.8 °C and 55% RH) results in only a 10 % change (increase, due to the hygroscopic nature of formamide) in the volume (found using the spherical cap method) even after 6 h (see Fig S3). Since the sinking time for aqueous drops on a thin lubricating fluid coated surface is about 5-10 min, the environmental exposure does not affect the drop shape during this period.

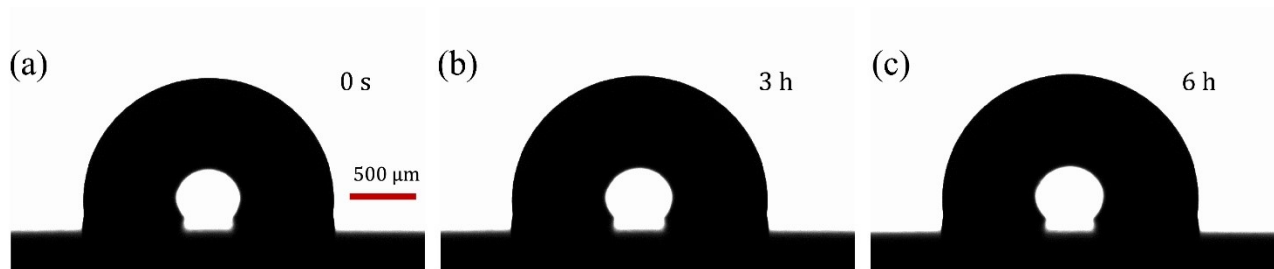


Figure S3: Optical images of 80 wt% formamide drop on a hydrophobic surface after (a) 0 s, (b) 3 h, and (c) 6 h. The drop volume increased from 2.02 μl (0 s) to 2.16 μl (3 h) and 2.25 μl (6 h) under the lab condition.

S4: To find surface and interfacial tension using the pendant drop method:

Various drop-air and drop-oil interfacial tensions were found using the standard pendant drop method with the help of the contact angle goniometer. The optical images of 80 wt % aqueous formamide solution and ethylene glycol pendant drops in air and silicone oil are shown in Fig. S4. Experimentally obtained values are shown in Table S1.

Drop	Interfacial tension (mN/m)	
	Drop-air	Drop-oil
80 wt % aqueous formamide	60.7 (± 0.2)	26.0 (± 0.5)
Ethylene glycol	48.3 (± 0.1)	16.9 (± 0.2)

Table S1: Interfacial tensions of various drop liquids measured using the pendant drop method.

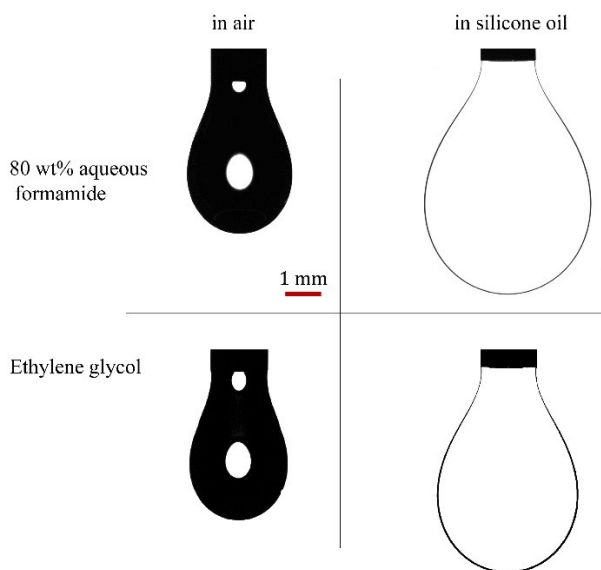


Figure S4: Optical images of 80 wt% aqueous formamide and ethylene glycol (EG) drops in air and in 350 cSt silicone oil just before detaching from the needle to find the surface/interfacial tensions using the pendant drop method.

S5: To find the thickness of spin-coated lubricant films:

The thickness of lubricant films prepared at different spin coating rotation speeds (with fixed spin time and acceleration time as 100 s and 10 s, respectively) was measured using the reflected spectrum from Filmetrics F20-EXR, as shown in Fig. S5 (a). The measured reflected spectra are fitted with a calculated model to extract the thickness of the film. Figure S5 (b) shows the thickness of the lubricating films obtained using different rotation speeds in the spin coater. The solid blue line represents the fitted curve, Eq. 3, indicating that the thickness decreases with a power law, exponentially with the increased rotation speed ω .

$$t = t_0 + Ae^{-B\omega} \quad (3)$$

where $t_0 = 1.45 \mu\text{m}$, $A = 23.94 \mu\text{m}$, and $B = 6.38 \times 10^{-4} \text{rpm}^{-1}$.

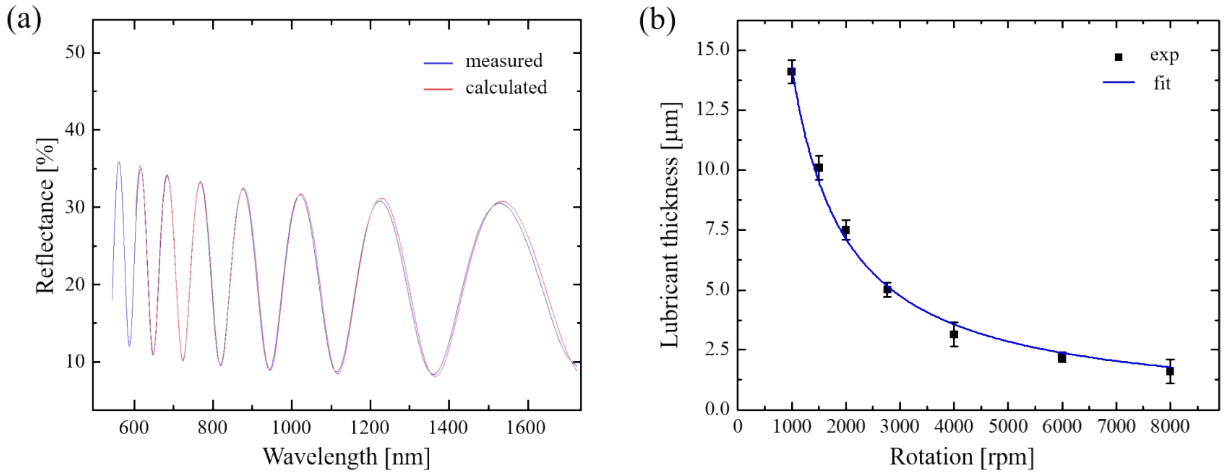


Figure S5: (a) Measured (in blue) and calculated (in red) reflectance with wavelength using the Filmetrics-F20-EXR device for a thin silicone oil film prepared at 6000 rpm. (b) Plot showing the variation of silicone oil thickness with the rotation speed in rpm. The solid blue line represents the inverse power-law fit to the experimental data.

S6: Quasi-static behavior of the system:

To confirm that the quasi-static behavior of the system, we observed the interfacial profiles at the the equivalent Neumann's point. For this, we considered an 80 wt% aqueous formamide drop on a $5.0 (\pm 0.5) \mu m$ thin lubricant film coated on a substrate with wettability, $\theta_{DS,e}^0 = 143.1 (\pm 2.4)^\circ$. after depositing the drop, wetting ridge formed spontaneously and the drop also started sinking. Spreading of the drop, due to the sinking, stopped after about a minute, hence we conclude that the sinking time of the drop is 1 minute. Subsequently, we measured the dynamic behavior (growth) of the wetting ridge by measuring the wetting ridge height as a function of time. As shown in Fig. S6, the wetting ridge grows very slowly as a function of time (increased from about $70 \mu m$ to $90 \mu m$ in 40 minutes). Thus, we conclude that such starved lubricated systems are quasi-static in the intermediate time scales and the proposed methodology can be applied to find various interfacial profiles for such systems.

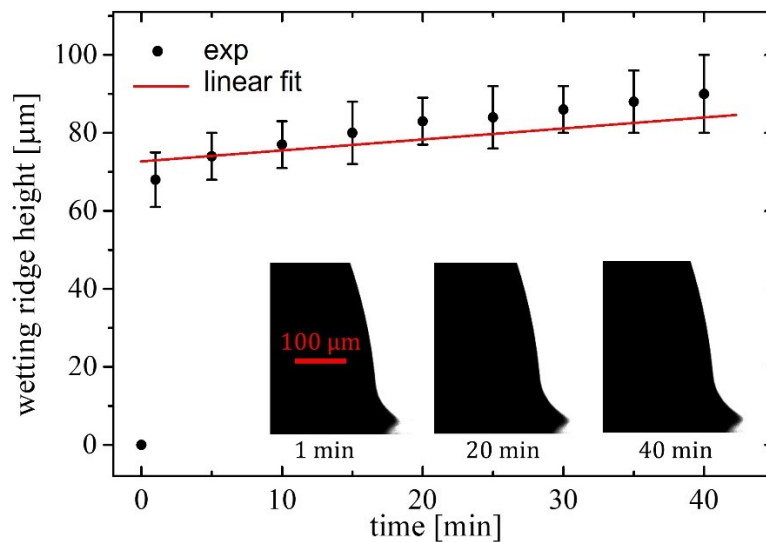


Figure S6: Graph showing the variation in the height of wetting ridge associated with an aqueous 80 wt% formamide drop with time. Red solid line represents a linear fit to the experimental data. Inset shows optical images of the drop and the wetting ridge at different times.

S7: To derive the expression for apparent contact angle:

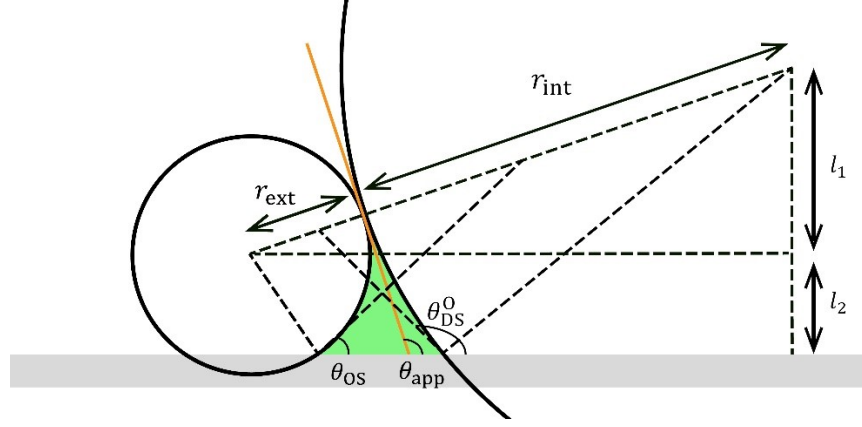


Figure S7: Schematic of a drop on a slippery surface with a negligible wetting ridge.

As shown in Fig. S7, the expression of the apparent contact angle for the negligible wetting ridge can be derived using following assumptions:

- (i) The oil-air and oil-drop interfaces can be fitted with a circle of radius r_{ext} and r_{int} respectively and are very small compared to the radius of curvature, R of the effective drop-

air interface i.e. $r_{ext} \sim r_{int} \ll R$. Then, the ratio $\frac{r_{ext}}{r_{int}} \sim \frac{\gamma_{OA}}{\gamma_{OD}}$ [1].

- (ii) For cloaked drops, the Neumann's angle in oil, $\theta_o = 0^\circ$. Thus, the two circles with radius r_{int} and r_{ext} do not intersect.

Then from the geometry, l_2 and l_1 are,

$$l_2 = r_{ext} \cos \theta_{OS} \text{ and } l_1 = -r_{ext} \cos \theta_{OS} - r_{int} \cos \theta_{DS}^0$$

From the right angled triangle with one side, l_1 , we get,

$$\cos \theta_{app}^S = \frac{(\gamma_{OD} \cos \theta_{DS}^0 + \gamma_{OA} \cos \theta_{OS})}{\gamma_{OD} + \gamma_{OA}} = \frac{(\gamma_{OD} \cos \theta_{DS}^0 + \gamma_{OA} \cos \theta_{OS})}{\gamma_{DA,eff}}$$

S8: Generalizing the simulation for drops of different liquids:

To check the validity of the simulations for other systems, we used ethylene glycol (EG) and water as the other test drops. The interfacial tension of the water-air and water-silicone oil was taken as 72 mN/m and 39 mN/m , respectively, from the literature [2]. The interfacial tension of the EG-air and EG-silicone oil was found from the pendant drop method (see Table S1). Contact angles of EG and water drops on substrate ($\theta_{DS,e}^0$) in air and oil was found using the contact angle goniometer, as shown in Fig. S8. SE simulations were then carried out for these drops to generate the drop profiles resulting in a good agreement between the simulations (solid red profiles) and the experiments (optical images) as shown in Fig S8.

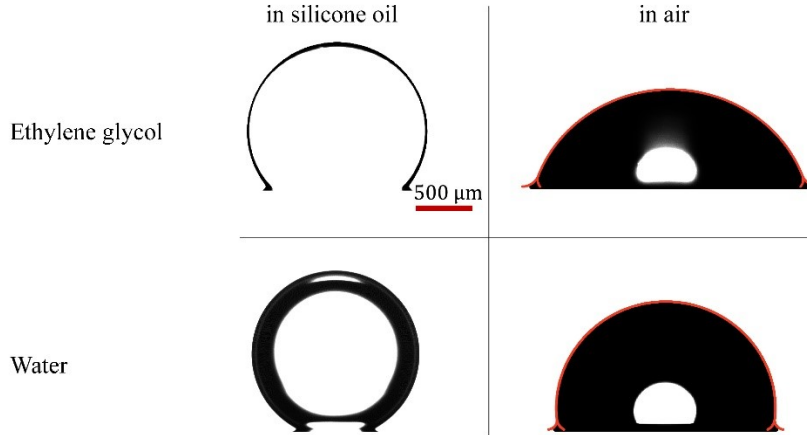


Figure S8: (i) Ethylene glycol and (ii) water drops on silicon surfaces with contact angles $\theta_{DS,e}^0 = 130.7 (\pm 2.3)^\circ$ and $\theta_{DS,e}^0 = 153.3 (\pm 3.0)^\circ$ in (a) ambient silicone oil and (b) ambient air with overlapped experimental and surface evolver simulation results.

References:

1. Kreder, M.J., et al., *Film Dynamics and Lubricant Depletion by Droplets Moving on Lubricated Surfaces*. Phys. Rev. X, 2018. **8**(3): p. 031053.
2. Bergeron, V. and D. Langevin, *Monolayer Spreading of Polydimethylsiloxane Oil on Surfactant Solutions*. Physical Review Letters, 1996. **76**(17): p. 3152-3155.

