Supporting Information

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SI Text

Film Deformation Due to the Action of Surface Tension, Laplace Pressure, and Gravity

For a linearly elastic material, when bending slopes are small compared with unity, the vertical deflection of the thin film, $w(x)$, is governed by:

$$EI\ \nabla^4 w - \sigma_{II}\nabla^2 w = p(r), \qquad \text{[S1]}$$

where E is the Young's modulus of the film, I is the area moment of inertia, and $p(r)$ is the force distribution (line tension, Laplace pressure, and gravity). Eq. **S1** assumes that the tension inside and outside the contact line is the same. We have solved Eq. **S1** subject to the boundary conditions that w and its first derivative vanish at the outer radius. As shown by Fig. 1*C*, because the drops are small compared with the outer radius of the membrane, the effect of gravity is merely an offset of the entire displacement profile. To investigate the effect of bending, it is sufficient to study the special case where the outer boundary is infinitely distant. As before, the boundary conditions are as follows: (*i*) w and all its derivatives vanish at $r=\infty$; (*ii*) the deflection, slope, and bending moment are continuous at the contact line at $r=c$; and (*iii*) symmetry requires that the slope at $r=0$ is zero. After some detailed calculations, which will be given in a separate paper, the vertical deflection w is found to be:

$$w(r<c) = \frac{2\gamma_{lv} c\sin\theta}{\sigma_{II}}\left[\left(\frac{1}{4}-\varepsilon\right) - \frac{(r/c)^2}{4} + \frac{\sqrt{\varepsilon}C}{2} I_0\left(r/c\sqrt{\varepsilon}\right)\right]$$

$$w(r>c) = \sqrt{\varepsilon}\ \frac{2\gamma_{lv} c\sin\theta}{\sigma_{II}}\left[\frac{I_0(1/\sqrt{\varepsilon})}{2}C - \sqrt{\varepsilon}\right]\frac{K_0(r/c/\sqrt{\varepsilon})}{K_0(1/\sqrt{\varepsilon})}, \qquad \text{[S2 } A \text{ and } B\text{]}$$

where

$$C = \frac{1 + 2\sqrt{\varepsilon}\ \dfrac{K_1(1/\sqrt{\varepsilon})}{K_0(1/\sqrt{\varepsilon})}}{\dfrac{K_1(1/\sqrt{\varepsilon})}{K_0(1/\sqrt{\varepsilon})} I_0(1/\sqrt{\varepsilon}) + I_1(1/\sqrt{\varepsilon})}$$

and

$$\varepsilon = EI/\sigma_{II}c^2, \qquad \text{[S3]}$$

where K_o and K_1 are the modified Bessel functions of the second kind and I_0 and I_1 are modified Bessel functions of the first kind. A posteriori, we find that in most of our experiments, $\sqrt{\varepsilon}$ is small compared with unity. In this limit, the solution is given by:

$$w = \frac{\gamma_{lv} c\sin\theta}{2\sigma_{II}}\left\{\left(1-\left(\frac{r}{c}\right)^2\right) + \left(\sqrt{\varepsilon} - 2\varepsilon\right)\right\} \quad r \le c$$

$$w = \frac{\gamma_{lv} c\sin\theta}{2\sigma_{II}}\frac{K_o(r/c\sqrt{\varepsilon})}{K_o(1/\sqrt{\varepsilon})}\left[\sqrt{\varepsilon} - 2\varepsilon\right] \quad r \ge c. \qquad \text{[S4 } A \text{ and } B\text{]}$$

The main point to be gleaned from Eq. **S4** *A* and *B* is that the effect of bending is confined to a small boundary layer near the contact line ($r=c$). This is due to the rapid decay of the function $K_o(r/c\sqrt{\varepsilon})$ for $r>c$. The shape of the film, particularly its radius of curvature near the axis of symmetry, which is given by the first term on the right-hand side of Eq. **S4*A***, is essentially unaffected by bending. The first term inside the brackets in Eq. **S4*A*** represents membrane-like behavior. The second term, which represents the effect of bending, vanishes for small $\sqrt{\varepsilon}$ (an example is provided in Fig. S1).

We have used data only for conditions where $\sqrt{\varepsilon} \le 0.25$. Thus, we can neglect the influence of bending away from the contact line by analyzing the thin-film deflection near the axis of symmetry, where the film supports mainly biaxial tension:

$$P = 2\sigma_{II}/R, \qquad \text{[S5]}$$

which is just Laplace's equation, where R is the radius of curvature. Additionally, by a force balance between Laplace pressure in the drop and its surface tension, we obtain the following relationship between the tension and easily measurable geometric parameters:

$$\sigma_{II} = \frac{PR}{2} = \frac{R\sigma_{lv}}{c}\sin(\theta-\phi). \qquad \text{[S6]}$$

Eq. **S6** is equivalent to Eq. **2** and replaces it. We obtain the radius of curvature by fitting a sphere to a small region near the center of deformation for various values of c (Fig. S3). The angle θ is measured independently via contact angle experiments on a flat PDMS slab, whereas the angle ϕ is measured by averaging angles from line scans of the vertical deflection at the contact line. Based on known values of the liquid surface tension of the liquids used in this work (1), Eq. **S6** provides the tension in the region where the solid film is in contact with the liquid drop, σ_{II}. The radial equilibrium (Eq. **1**) then gives us the tension in the film just outside the contact line, σ_I.

Shear Force Calculation

To compute the local shear force in the thin film, Q, we use the following expression (2):

$$Q(r) = D\left(\frac{d^3w}{dr^3} + \frac{1}{r}\frac{d^2w}{dr^2} + \frac{1}{r^2}\frac{dw}{dr}\right). \qquad \text{[S7]}$$

We compute the derivatives in Eq. **S7** using a fourth-order central finite difference scheme.

In Fig. S2, we show the local shear force values for three film thicknesses. As expected, the local shear force becomes smaller as the film becomes thinner, and it is then negligible compared with the measured tensions in the film.

Contribution of Stretch to the Tension

Fig. S6 shows that the film stretches due to its deformation. As a result, tension values σ_I and σ_{II} include terms due to stretch in addition to their different surface stresses, σ_{OII} and σ_{OI}. In the main text, we have relied on the intuitive assumption that the stretch contributions vanish as the film thickness reduces to zero. To support this assumption, we have constructed a theoretical model of the in-plane stretching deformation. Analysis of this model confirms that the stretch contribution to tension vanishes as thickness is reduced, supporting the procedure of extrapolating the experimental measurement of tension to zero thickness. Here, we briefly outline our model; details will be presented elsewhere.

We begin with the force equilibrium of the Neumann's triangle:

$$\sigma_I = \sigma_{II} \cos\phi + \sigma_{lv} \cos(\theta - \phi), \quad \textbf{[S8]}$$

$$\sigma_{II} \sin\phi = \sigma_{II} c/R = \sigma_{lv} \sin(\theta - \phi). \quad \textbf{[S9]}$$

Geometric quantities ϕ, θ, c, and R are illustrated in Fig. S5, and σ_{lv} is the surface tension of the liquid droplet. We solve separately the mechanics of deformation in two regions: an inner region, where the liquid is in contact with the membrane, and an outer flat region. In both, equilibrium in the radial direction and strain displacement relations are given by the following:

$$\frac{d\sigma_r}{dr} + \frac{\sigma_r - \sigma_\theta}{r} = 0, \quad \textbf{[S10]}$$

$$\varepsilon_r = \frac{du}{dr};\ \varepsilon_\theta = \frac{u}{r}, \quad \textbf{[S11]}$$

where u is the displacement (Fig. S6). Combining Eqs. **S10** and **S11**, as well as stress–strain relations (including a surface tension), we obtain the governing differential equation for the radial displacement u in region I:

$$\frac{d^2u}{dr^2} + \frac{1}{r}\frac{du}{dr} - \frac{u}{r^2} = 0, \quad \textbf{[S12]}$$

and obtain its solution. For region II, we assume that the deformed shape is a spherical cap under equal biaxial stress and strain. Finally, we impose the condition that the displacement u at $r = c$ be continuous. After some manipulation, we obtain the following equations that relate total measured tensions to surface tension:

$$\sigma_I = \sigma_{oI} - \frac{Et}{1+\nu}\frac{u}{c}$$
$$\sigma_{II} = \sigma_{oII} + \frac{Et}{2(1-\nu)}\left(\frac{h}{c}\right)^2 + \frac{Et}{(1-\nu)}\frac{u}{c}. \quad \textbf{[S13]}$$

As film thickness t reduces, both h and u increase, but they remain bounded (by the solution in the membrane limit). Therefore, in the limit of vanishing thickness:

$$\sigma_I = \sigma_{oI};\ \sigma_{II} = \sigma_{oII}, \quad \textbf{[S14]}$$

which supports the interpretation of tension extrapolated to zero thickness as the surface tension.

1. Jasper JJ (1972) The surface tension of pure liquid compounds. *J Phys Chem Ref Data* 1:841.
2. Timoshenko S, Woinowsky-Krieger S (1959) *Theory of Plates and Shells* (McGraw–Hill, New York).

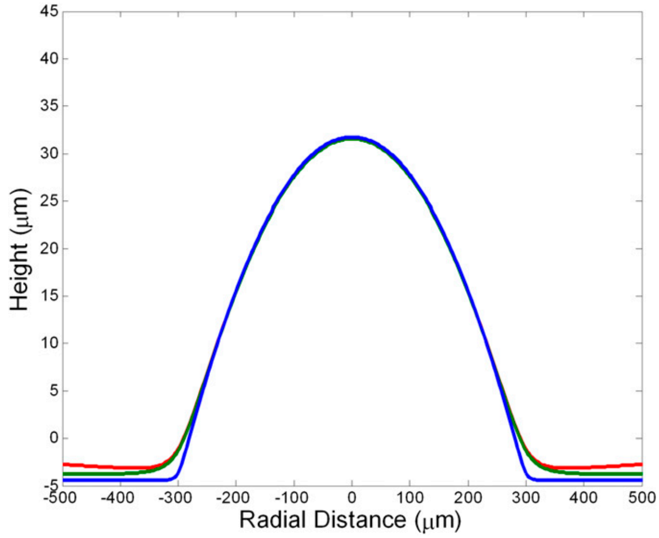

Fig. S1. Calculated deflection of an 11.0-μm thick membrane with radius of 4 mm with a deionized water (DI) drop with a radius of 0.3 mm placed under it. The deflected shapes have been shifted vertically to match at the axis of symmetry to permit easier comparison of the shape in its vicinity. The curve in blue is the deflection based on membrane theory with negligible bending and gravity. The curve in green includes bending but neglects gravity. Finally, the curve in red includes gravity as well. Note that the shape of the membrane near its axis of symmetry is essentially indistinguishable between the three cases. Other parameters for this calculation are as follows: Young's modulus = 2.85 MPa, tension = 0.3 N/m, and liquid surface tension = 72.5 mN/m.

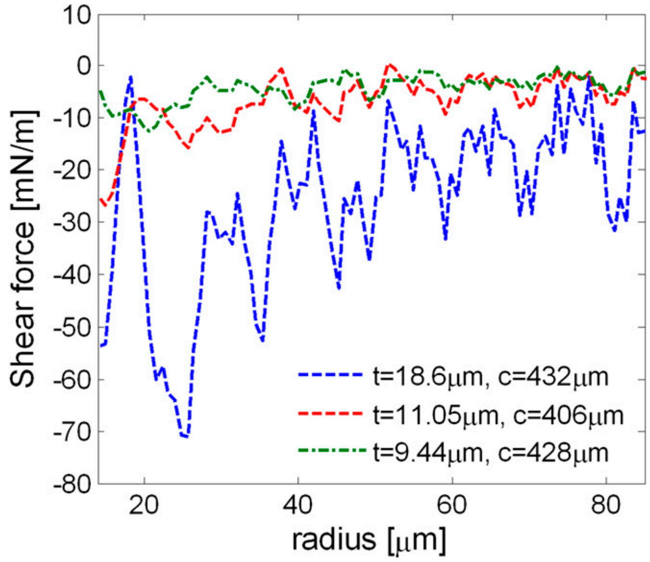

Fig. S2. Local shear force for three film thicknesses. The shear force decreases for smaller film thicknesses, as expected.

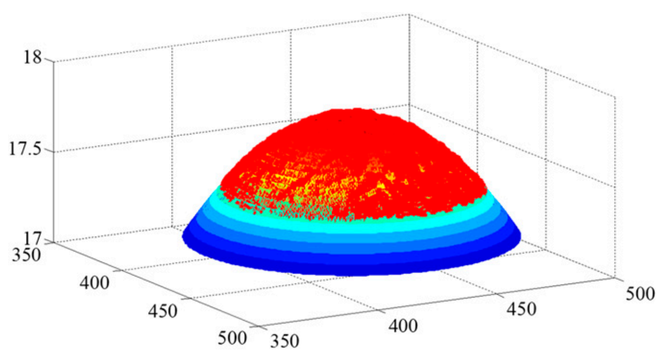

Fig. S3. Data of the deformed shape near its axis of symmetry (red points) are fitted by a spherical surface to estimate the local radius of curvature.

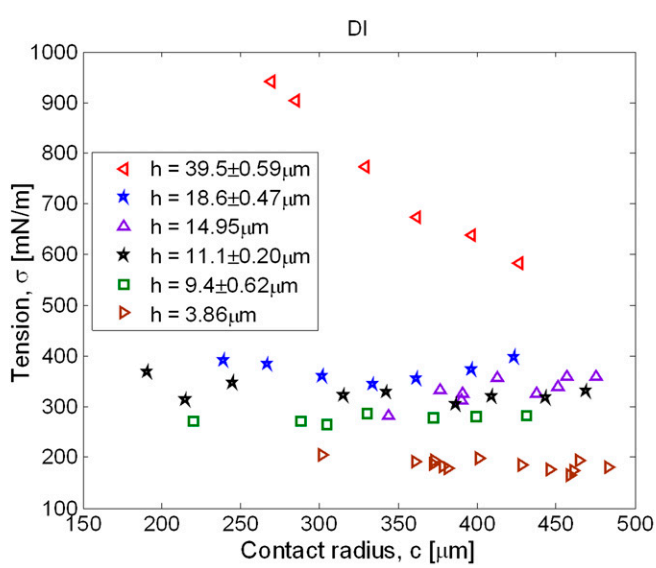

Fig. S4. Measured tension is substantially independent of the contact radius for several film thicknesses. However, for a sufficiently thick film, bending becomes important and the measured tension no longer remains approximately constant as the drop dries.

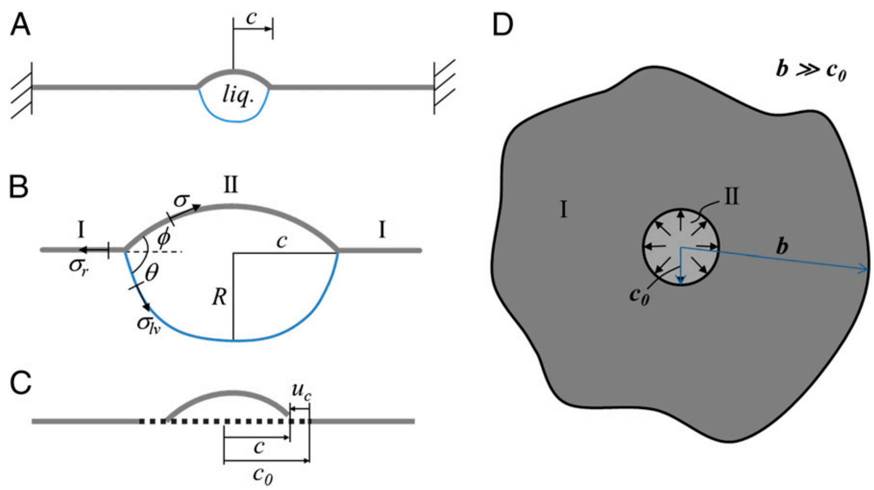

Fig. S5. Schematic of deformation due to a liquid droplet on a thin film. (*A*) Liquid droplet on a thin film, where *c* denotes the radius of the contact line. (*B*) Schematic shows relevant geometric parameters, as well as the tension in the thin film and the liquid surface tension. We split the geometry into two regions, region I (outside the contact line) and region II (inside the contact line). (*C*) Schematic shows the stretch due to droplet-driven deformation. (*D*) View of the thin film near the droplet from above. The radius of region I is much greater than the radius of the contact line. The arrows inside region II indicate the tension there.

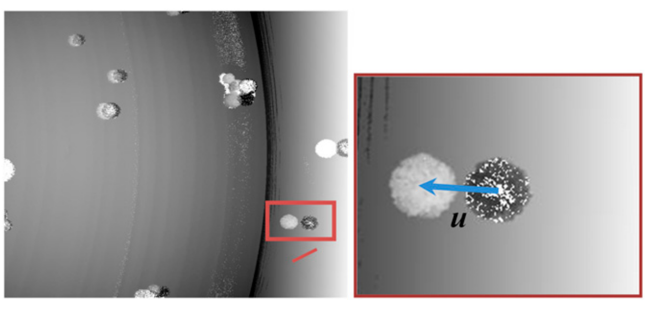

Fig. S6. Difference scan shows the displacement of silica marker particles (~8 μm) due to deformation. The undeformed case (darker particles), where there is no droplet, is subtracted from the case where there is droplet-driven deformation. The DI droplet is in contact with the thin film to the left of the black curve (region II). Deformation of the thin film over the droplet causes the silica particles to move toward the center of the drop (to the left).