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Supporting Online Material for

Capillary Wrinkling of Floating Thin Polymer Films

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Supporting Online Material

Materials and Methods

The films were made from solutions of polystyrene ($M_n = 91$ kg/mol, $M_w = 95.5$ kg/mol, Polymer Source Inc., product ID: P3615-S) dissolved in toluene (Anhydrous 99.8%, Sigma-Aldrich Inc.). Subsequently, the solutions with concentrations of 0.5%, 0.75%, 1.08% or 2.16% were filtered through a micropore system (pore size 0.45 μm, Whatman Inc.). Glass slides of $25\times75\times1$ mm^3 were cleaned with acetone and positioned on the holder of a spin coater (Headway Research Inc., model 1-EC101DT-R485). Before applying the PS solution, a layer of acetone was spun off the glass slides at 1000 rpm for 1 minute. Next, the films were prepared on the glass slides by spincoating at speeds varying from 600 to 1800 rpm to get the desired thickness. The reproducibility in thickness of films prepared with this protocol is ±2%.

The plasticizer used was di-octylphthalate (anhydrous, 99%, D201154, from Sigma-Aldrich). The plasticizer was added into PS solution in toluene prior to spin-coating.

The contact angle for water droplets on a PS film was measured by the Sessile Drop Method (Dataphysics Instruments GmbH - Germany) to be 88°±2°. The addition of plasticizer was not found to affect the contact angle within the precision of the measurement.

The water drop was delivered onto the films using a microsyringe (Hamilton, Reno, NV, CAT#80383). A drop of measured volume is ejected from the syringe, and this pendant droplet is gently brought in contact with the film

And the wrinkling pattern was observed in transmission using a long working-distance stereo microscope (Olympus Model SZ 40), typically at a magnification less than 4X. The sample was illuminated from beneath with diffuse white light. Images of the wrinkling pattern were acquire with a commercial consumer digital camera (Olympus Camedia C-770 Zoom) attached to a microscope port.

X-ray reflectivity measurements have been carried out at the W.M. Keck Nanostructure Laboratory (a NSF-MRSEC supported multiuser open access facility), University of Massachusetts Amherst, using a Panalytical X-Pert x-ray diffractometer. The CuK_α radiation from the x-ray source (wavelength $\lambda = 0.154$ nm) is coupled to a parabolic, graded multilayer mirror assembly that produces a low-divergence beam of x-rays. The PS films on the glass substrate are mounted horizontally at the center of a two-circle goniometer and investigated under specular reflection conditions. The modulus of the scattering vector is defined by $q = |\mathbf{q}| = (4\pi/\lambda)\sin\theta$, in which 2θ is the scattering angle. Additional pre-sample and pre-detector slits define the overall resolution in the vertical scattering plane. The intensity is integrated over the horizontal direction. At small incident angles above the critical angle, the incident x-ray beam is reflected both at the front and the back interface of the film, leading to constructive or destructive interference in dependence of q_z (Kiessig fringes). The period δq of the fringes is related to the film thickness by $h = 2\pi/\delta q$. By averaging over several fringes in the range $0.5 < 2\theta < 3.0^o$, the thickness has been determined with a precision of the order of ± 0.5 nm.

Wrinkling using other methods of loading

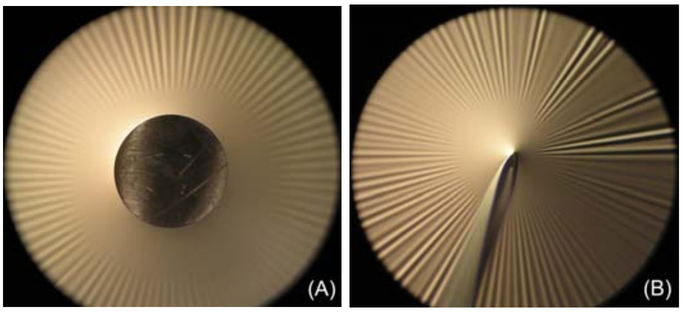

Figure S1. **A.** Loading by a weighted metal disc of radius = 2 mm and mass = 45 mg. **B.** Loading by poking with a needle. The thickness *h* of the film is 233 nm in both situations.

In Figure S1, we indicate two other methods of inducing wrinkles. The mass required to achieve the situation in Fig. S1 A is considerably greater than the mass of the water drops used in Figure 1. Unlike the capillary wrinkling situation, here the wrinkles do not extend to the centre of the load, and there is a central region of pure stretching reminiscent of the core stretching region seen near the apex of a developable cone.

Hysteresis in the wrinkling pattern

We show an example of hysteresis in the number, N, and length, L, of wrinkles in Figure S2 below, where we track these quantities as the droplet shrinks as it evaporates. The droplet radius, *a*, decreases with time (Fig. S2 A) with no apparent of pinning of the contact line as it recedes. N shows no change at all as a decreases, and L changes along a different path than predicted by the scaling law.

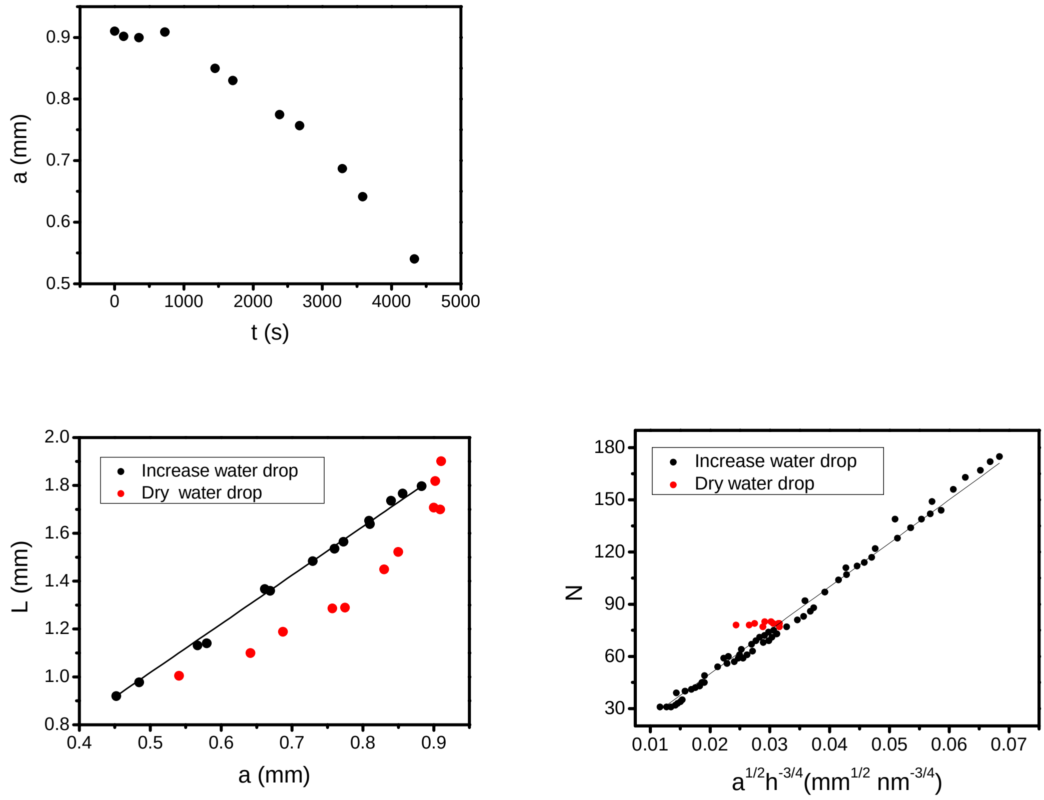

Figure S2. **A.** Radius of drop, a, versus time in seconds. **B.** Length of wrinkle, L, versus a for an advancing (black) and receding (red) contact line. **C.** Number of wrinkles, N, versus a for an advancing (black) and receding (red) contact line. Thickness of the film used here is 94 nm.

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