Energy invariance in capillary systems
Supplementary Information

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SLIP/Liquid-impregnated surfaces

We used silicon wafers with photolithographically patterned square pillars (90 µm × 90 µm) of SU-8 photoresist (MicroChem) arranged in a square lattice with a centre-to-centre separation between pillars of 100 µm. Patterned surfaces were functionalised and rendered superhydrophobic with a nano-particle based coating (Glaco Mirror Coat, Soft 99 Co.). The surfaces were subsequently immersed in a bath of the silicone oil (Sigma-Aldrich, CAS No. 378348) and withdrawn vertically at a controlled rate of 1 mm s\(^{-1}\) to create a uniform impregnation layer using a Fisnar F4200N robot. Sliding angle and apparent contact angle measurements for water droplets on textured surfaces impregnated with silicone oil were carried out using a Krüss DSA30 Contact Angle meter equipped with a tilt stage, which was levelled prior to each measurement.

Surface tension measurements

Measurements of the interfacial tension of water droplets in contact with a silicone oil reservoir were carried out using the pendant drop method using a Krüss DSA30 Contact Angle Meter equipped with an automated dispensing unit. Water droplets were dispensed at a controlled rate and imaged at 24 fps. A value for the interfacial tension of water was then obtained by analysing the image captured at the moment immediately before the droplet detaches from the syringe needle. An average value for the interfacial tension of water in the presence of air, \(\gamma_{WA} = 71.5 \pm 0.4\) mN m\(^{-1}\), was obtained by averaging 50 measurements. To measure the effective interfacial tension of water in the presence of silicone oil, a small droplet of oil was dispensed onto the area near the tip of the syringe needle where water is dispensed. The oil was then allowed to travel freely downwards, cloaking the water droplet. Droplets were dispensed and analysed until the surface tension measurement stabilised to a constant value \(\gamma = 63.4 \pm 0.5\) mN m\(^{-1}\), averaged over ∼10 consecutive drop counts. Subsequent drops showed a systematic increase in the surface tension that stabilised to the initially measured value of \(\gamma_{WA}\), indicating a depletion of the oil layer.

Wedge experiments

SLIPS wedges were assembled using a levelling stage upon which the bottom substrate was placed. A rotatable sample holder was used to hold the upper substrate. A CCD camera (Thorlabs with LabView controller) was used to image the lateral cross-section of the wedge. For a given experiment, the upper substrate was lowered until one its lower edge made contact with bottom substrate. A droplet of water of known volume (2-5 µL) was then placed on the bottom substrate at a prescribed position from the wedge apex. The top surface holder was then rotated about the apex of the wedge using a dial until the upper substrate made contact with the droplet. Rotation was immediately stopped and the droplet was allowed to move towards its equilibrium position. Time-lapse photography was used to capture images at 1 fps. Images were recorded until a well defined-plateau was observed in the droplet position.

Droplet measurements and data analysis

Raw images were analysed using a bespoke MATLAB programme using a standard image thresholding algorithm. For each individual image the position of the wedge planes and the wedge angle were determined. The intersection with the droplet interface was used to determine the droplet’s average position radius. Time series were used to determine the equilibrium position and radius of the droplets, typically averaged over typically 200 to 300 measurements.

Lattice-Boltzmann simulations

Simulations were carried out using a binary-fluid Lattice-Boltzmann algorithm detailed in Ref. [23]. The geometry of the lattice is a square grid connected to the zeroth, first and second nearest neighbours, and the domain of the simulation is divided into “solid” and “fluid” nodes. At any given fluid node, indicated by a position vector \(\mathbf{r}\), we define two probability distribution functions, \(f_i\) and \(g_i\), where the index \(i\) refers to the advection lattice propagation
integrating over the droplet volume gives
where \( s \) which leads to the result reported in the paper in the limits \( \beta \rightarrow 0 \) and \( \theta \rightarrow \pi/2 \).

**Free-energy landscapes**

The free-energy landscape is constructed by assuming a quasi-spherical barrel shape for the out-of-equilibrium capillary surface [25]. The surface energy of the droplet is given by \( F = \gamma q^2 \sum_i (2 - i) a_i e^i \), where \( q = -\cos \theta X / \sin \beta \) and \( e \) is a small dimensionless parameter quantifying the deviation from a spherical shape. For small wedge angles (\( \beta \sim 10^\circ \)) the constants \( a_i \) read \( a_0 = \pi(\cos 3\theta - 9 \cos \theta)/6 \), \( a_1 = \pi(2\theta - \pi - \sin 2\theta) \), \( a_2 = -2\pi \cos \theta \) and \( a_3 = 0 \). Imposing a constant volume condition on the shape of the droplet gives a relation between \( q \) and \( e \) (see Ref. [25] for details). This leads to the restitution constant, \( k = 6\gamma a_0(1 - 3a_0a_2/a_1)\sin^2 \beta / \cos^2 \theta \), which reduces to the result in the main paper for \( \theta \rightarrow \pi/2 \).

**Jefferey-Hamel flow dissipation**

The bulk dissipation, \( \dot{\mathcal{E}} \), is calculated in the standard way, \( \dot{\mathcal{E}} = \frac{1}{2} \eta \int_V (\nabla \mathbf{u} + (\nabla \mathbf{u}^T) \mathbf{u}) dV \), where \( \mathbf{u} \) is the local velocity field within the droplet. Assuming that the flow is in the radial direction from the apex of the wedge, \( \mathbf{s} \), then (see Ref. [25])

\[
\mathbf{u} = \dot{X} \frac{s_1 + s_2}{2s} \frac{\cos 2\beta - \cos 2\omega}{\cos 2\beta - \beta - \sin 2\beta} \mathbf{s},
\]

where \( s_1 \) and \( s_2 \) are the coordinates of the leading and trailing menisci of the droplet. Using this expression, and integrating over the droplet volume gives

\[
\dot{\mathcal{E}} \approx \frac{32\pi \beta^2 \eta \dot{X}^2 W^2 X^2 [\beta(\cos 4\beta + 3) - \sin 4\beta]}{(4X^2 - W^2)^{3/2}(2\beta \cos 2\beta - \sin 2\beta)^2}.
\]

To calculate the friction coefficient we use (see, e.g., Ref. [19])

\[
\nu = \frac{1}{2} \frac{d^2 \dot{\mathcal{E}}}{dX^2},
\]

which leads to the result reported in the paper in the limits \( \beta \rightarrow 0 \) and \( \theta \rightarrow \pi/2 \).