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 $\times$ 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 The surfaces were subsequently immersed in a bath of the silicone oil (Sigma-Aldrich, CAS No. 378348) and withdrawn vertically at a controlled rate of 1 mm s^{-1} to create a uniform impregnation layer using a Fisnar F4200N robot.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, $\gamma_{\mathrm{WA}} = 71.5 \pm 0.4$ 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 $\sim$10 consecutive drop counts. Subsequent drops showed a systematic increase in the surface tension that stabilised to the initially measured value of γ_{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 r, we define two probability distribution functions, f_i and g_i, where the index i refers to the advection lattice propagation

directions, $\mathbf{c}_i$. The time evolution is given by the single-relaxation-time lattice-Boltzmann equations, $f_i(\mathbf{r}+\mathbf{c}_i, t+1) = f_i(\mathbf{r},t)+(f_i-f_i^{\rm eq})/\tau_f$ and $g_i(\mathbf{r}+\mathbf{c}_i, t+1) = g_i(\mathbf{r},t)+(g_i-g_i^{\rm eq})/\tau_g$. These include a collision step where the distribution functions relax towards equilibrium values, indicated by the superscript "eq" over the respective relaxation timescales τ_f and τ_g (set to unity in the simulations), followed by a propagation step where the f_i and g_i are advected to their neighbouring sites. The macroscopic variables are recovered through moments of the distribution functions, i.e., the density $\rho = \sum_i f_i$, momentum density $\rho\mathbf{v} = \sum_i \mathbf{c}_i f_i$, and a 'phase field' $\phi = \sum_i g_i$ which labels two binary fluid phases. The instantaneous hydrodynamic fields determine the pressure and chemical potential of the fluid mixture via a Cahn-Hilliard free-energy model. The hydrodynamic behaviour of the fluid, in turn, is governed by the macroscopic variables via collisions of the distribution functions, subject to the mass and momentum conservation conditions, i.e., $\sum_i f_i^{\rm eq} = \rho$, $\sum_i g_i^{\rm eq} = \phi$, $\sum_i \mathbf{c}_i f_i^{\rm eq} = \rho\mathbf{v}$ and $\sum_i \mathbf{c}_i g_i^{\rm eq} = \phi\mathbf{v}$. A suitable choice of the equilibrium distribution functions recovers the macroscopic equations of motion of the fluid in the limit of small Mach numbers.

We set a rectangular domain of 1112×362 lattice nodes. A truncated wedge geometry was set by fixing two solid planes at an angle $\beta = 5°$, implemented by interpolation of the standard bounce-back rules and the phase field. Constant-pressure boundary conditions were imposed at the narrow and wide edges of the wedge, respectively set to be 160 and 354 lattice sites in length. A droplet was initialised by splitting the simulation domain into two phases of equal density and viscosity. Such an initial condition quickly evolved into circular-shaped leading and trailing droplet edges, approximately 20 lattice sites in thickness, which intersect the solid at the prescribed contact angle of the Cahn-Hilliard model, which was set to 120°. The droplet was allowed to evolve for 12,000,000 time steps, until equilibrium was achieved. The transient flow, depicted in Fig. 3(d), corresponds to a snapshot of the simulation after 20,000 time steps.

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 $F = \gamma q^2 \sum_i^3 (3-i) a_i \epsilon^i$, where $q = -\cos\theta X/\sin\beta$ and ϵ is a small dimensionless parameter quantifying the deviation from a spherical shape. For small wedge angles ($\beta \sim 10°$) 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 ϵ (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 $\theta \to \pi/2$.

Jefferey-Hamel flow dissipation

The bulk dissipation, $\dot{\mathcal{E}}$, is calculated in the standard way, $\dot{\mathcal{E}} = \frac{1}{2}\eta \int_V \left(\boldsymbol{\nabla}\mathbf{u} + \boldsymbol{\nabla}\mathbf{u}^T\right)^2 \mathrm{d}V$, 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, $\hat{\boldsymbol{s}}$, then (see Ref. [25])

$$\mathbf{u} = \dot{X}\frac{s_1+s_2}{2s}\frac{\cos 2\beta - \cos 2\omega}{\cos 2\beta - \beta^{-1}\sin 2\beta}\hat{\mathbf{s}},$$

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

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

where $W = s_2 - s_1$ is the width of the droplet.

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

$$\nu = \frac{1}{2}\frac{\mathrm{d}^2\dot{\mathcal{E}}}{\mathrm{d}\dot{X}^2},$$

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