Supplementary Material (ESI) for Soft Matter

Supporting Information

1 Large drop volume regime

As an additional aspect to Fig. 4 in the main text, we have focused on the large drop volume regime in Fig. S1. The clamshell to barrel branch of the bistability regime curves towards lower angles. This brings out an interesting feature, which we refer to as reentrant behavior. At low contact angles and large drop volumes, a drop in the clamshell state can enter the barrel morphology region by reducing the drop volume. By reducing the volume further with given contact angle, the drop will enter the bistable regime again and eventually decay into a clamshell morphology.

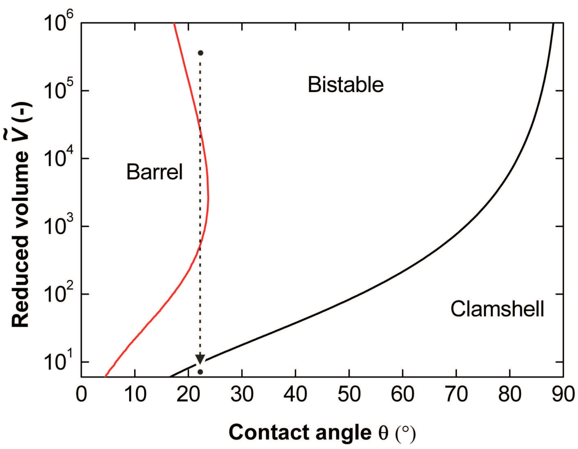

Fig. S1: Morphology diagram of drops on fibers as a function of contact angle θ and reduced volume $\tilde{V}$, extended to large volumes (up to 10^6). The solid lines indicate the numerically determined stability limit of the clamshell (upper red) and the (coinciding) analytically and numerically determined stability limits of the barrel (lower black). The dotted arrow indicates a path showing reentrant behavior with decreasing drop volume.

2 Stability analysis of barrel drops

In the absence of gravity, the liquid-vapor interface of an equilibrated barrel drop wetting a cylindrical fiber is described by segments of Delaunay surfaces which satisfy the condition of Young-Dupré at the contact line [1, 2, 3]. But not all of the shapes constructed in this way represent mechanically stable barrel drops [3]. In order to assess the mechanical stability of the liquid-vapor interface with respect to small variations of its shape, one has to discuss the second variation of the interfacial energy under appropriate constraints. If the second variation is positive for all admissible variations of the interfacial shape the corresponding drop shape is mechanically stable. For further details of the variational calculus, the parameterization of deformations, and the spectral analysis we refer to Refs. [4, 5].

2.1 Jacobi's accessory equation

Let $\mathcal{A}$ be the liquid-vapor interface of the drop. To assess the mechanical stability of a liquid drop in the absence of gravity one has to solve the eigenvalue problem [4, 5]

$$-\nabla^2\nu + (2K - 4H^2)\,\nu = \lambda\nu + \mu \quad \text{on} \quad \mathcal{A} \tag{1}$$

in the normal component of the displacement field ν subject to a linear subsidiary condition

$$\int_{\mathcal{A}} \mathrm{d}A\;\nu = 0 \tag{2}$$

and boundary conditions

$$\mathbf{n}\cdot\nabla\nu + \left(\frac{\hat{c}_\perp}{\sin\theta} - c_\perp\cot\theta\right)\nu = 0 \quad \text{on} \quad \mathcal{L}\;. \tag{3}$$

In local coordinates, the Laplace-Beltrami operator on $\mathcal{A}$ assumes the general form

$$\nabla^2 = \frac{1}{\sqrt{g}}\,\partial_i\sqrt{g}\,g^{ij}\,\partial_j \quad \text{with} \quad i,j = 1,2\;.$$

The Gaussian curvature $K = c_1\,c_2$ and the mean curvature $H = (c_1 + c_2)/2$ are the product and sum, respectively, of the two principal normal curvatures c_1 and c_2 in a point of $\mathcal{A}$, while $c_\perp$ and $\hat{c}_\perp$ are the normal curvatures of $\mathcal{A}$ and of the substrate surface $\hat{\mathcal{A}}$, respectively, on the contact line $\mathcal{L}$ perpendicular to the contact line. The vector $\mathbf{n}$ is the outward pointing conormal of $\mathcal{A}$ in a point of $\mathcal{L}$.

The Lagrange parameter λ and μ have to be chosen such that eqns. (1), (2), and (3) are simultaneously satisfied. Statements about the stability of a drop are thus equivalent to an analysis of the eigenvalue spectrum of a linear operator in the subspace of volume conserving normal displacements. A drop is mechanically stable if the smallest relevant eigenvalue λ_{min} is positive.

Owing to the continuous translational and rotational symmetry of the wetted cylindrical surface each drop in mechanical equilibrium belongs to a whole family of equilibrium configurations generated by a translation along, or a rotation around the symmetry axis of the cylinder. Because each state in such a continuous family of shapes has the same interfacial energy we find Goldstone modes with $\lambda = 0$ in the volume conserving subspace of variations provided that translational and/or rotational symmetry of the drop is broken. Hence, the discussion of eigenvalues and corresponding eigenmodes is restricted to the linear subspace of modes orthogonal to these Goldstone modes.

2.2 Axially symmetric drops

In the following we assume that the liquid-vapor interface of the drop is a surface of revolution. Hence, the components of the metric tensor g_{ij}, the local surface element $\sqrt{g}$, the curvatures $c_\perp$, $c_\parallel$, and the Gaussian curvature K do not depend on the azimuthal angle φ and are solely functions of the parameter u along the contour. After a separation of variables, the displacement field can be written as the product

$$\nu(u,\varphi) = \rho(u)\,\mathrm{e}^{\pm i m\varphi} \ ,$$

and Jacobi's accessory equation (1) reduces to an ordinary differential equation

$$-\frac{1}{g_{11}}\frac{\mathrm{d}^2\rho}{\mathrm{d}^2 u} - \frac{1}{\sqrt{g}}\left[\frac{\mathrm{d}}{\mathrm{d}u}\left(\frac{\sqrt{g}}{g_{22}}\right)\right]\frac{\mathrm{d}\rho}{\mathrm{d}u} + \left(\frac{m^2}{g_{22}} + 2\,K - 4H^2\right)\,\rho = \lambda\,\rho + \mu \ , \tag{4}$$

with a linearized subsidiary constraint of constant volume

$$\int_{u_0}^{\pi-u_0} \mathrm{d}u\,\sqrt{g}\,\rho = 0 \ , \tag{5}$$

and boundary conditions

$$\frac{1}{\sqrt{g_{11}}}\frac{\mathrm{d}\rho}{\mathrm{d}u} \pm c_\perp \cot\theta\,\rho = 0 \quad \text{for} \quad \begin{cases} u = u_0 \\ u = \pi - u_0 \end{cases} \tag{6}$$

at the contact lines.

2.3 Differential geometry of undoloid drops

Following Refs. [1, 2], we will parameterize the contour of a barrel drop in cylindrical coordinates by undoloids

$$z = r_\mathrm{o}\,\mathrm{E}(k,u) + r_\mathrm{i}\,\mathrm{F}(k,u) - \frac{(r_\mathrm{o}^2 - r_\mathrm{i}^2)\cos u\,\sin u}{\sqrt{r_\mathrm{o}^2\,\cos^2 u + r_\mathrm{i}^2\,\sin^2 u}} \quad \text{and} \quad r = \frac{r_\mathrm{o} r_\mathrm{i}}{\sqrt{r_\mathrm{o}^2\,\cos^2 u + r_\mathrm{i}^2\,\sin^2 u}} \ ,$$

with a phase angle $u \in [u_0, \pi - u_0]$ and a modulus $k = \sqrt{(r_\mathrm{o}^2 - r_\mathrm{i}^2)/r_\mathrm{o}^2}$. Here, $\mathrm{F}(k,u)$ and $\mathrm{E}(k,u)$ denote the elliptic integrals of first and second kind (for a definition of the functions see, e.g., Ref.[6]) while r_o and r_i are the largest and smallest distance of the contour from the symmetry axis. The parameter $\tilde{n}$ in the main text becomes identical to r_o after a rescaling of all lengths by the radius of the fiber, r.

The components of the metric tensor of an undoloid drop can be computed as

$$g_{11} = \left[\frac{r_\mathrm{o} r_\mathrm{i}(r_\mathrm{o} + r_\mathrm{i})}{r_\mathrm{o}^2\cos^2 u + r_\mathrm{i}^2\sin^2 u}\right]^2 \qquad \text{and} \qquad g_{22} = \frac{r_\mathrm{o}^2 r_\mathrm{i}^2}{r_\mathrm{o}^2\cos^2 u + r_\mathrm{i}^2\sin^2 u} \ ,$$

where the indices $i = 1, 2$ refer to the coordinate u and to the azimuthal angle φ, respectively. Because of the parameterization of an axially symmetric surface in cylindrical coordinates the off-diagonal elements g_{12} and g_{21} of the metric tensor are simply zero. The area of the local surface element of $\mathcal{A}$ is given by

$$\sqrt{g} = \frac{r_\mathrm{o}^2 r_\mathrm{i}^2(r_\mathrm{o} + r_\mathrm{i})}{\sqrt{(r_\mathrm{o}^2\cos^2 u + r_\mathrm{i}^2\sin^2 u)^3}} \ .$$

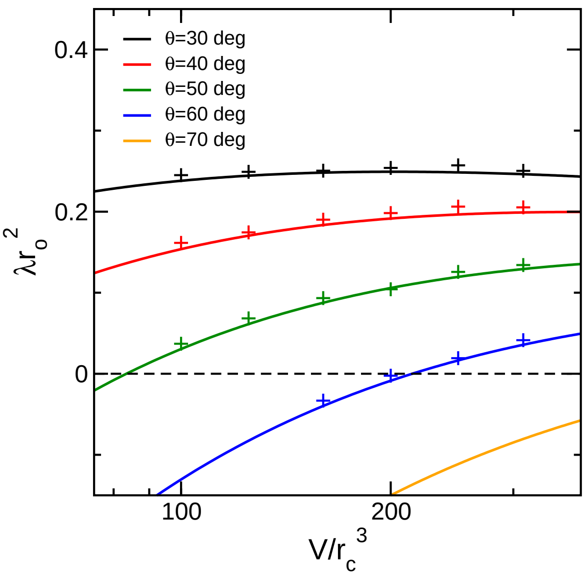

Fig. S2: Dimensionless rescaled eigenvalue $\lambda r_{\rm o}^2$ of the second variation (Jacobi's accessory equation) for barrel drops as function of the rescaled volume $\tilde{V}$. Shown are eigenvalues of the relevant mode with $l = 0$ and $m = 1$ for different values of the contact angle θ. The solid lines indicate the numerical solutions of the boundary value problem eqns. (4), (5), and (6), and the plusses the numerical solutions obtained with Surface Evolver.

The mean and Gaussian curvature on $\mathcal{A}$ assume the form

$$H = \frac{1}{r_{\rm o} + r_{\rm i}} \qquad \text{and} \qquad K = -\frac{(r_{\rm o} - r_{\rm i})\,\left(r_{\rm o}^2 \cos^4 u - r_{\rm i}^2 \sin^4 u\right)}{r_{\rm o}^2 r_{\rm i}^2 (r_{\rm o} + r_{\rm i})} \,,$$

respectively, while the normal curvatures parallel and perpendicular to the cylinder axis are given by

$$c_{\|} = \frac{r_{\rm o} \cos^2 u + r_{\rm i} \sin^2 u}{r_{\rm o} r_{\rm i}} \qquad \text{and} \qquad c_{\perp} = -\frac{(r_{\rm o} - r_{\rm i})\,\left(r_{\rm o} \cos^2 u - r_{\rm i} \sin^2 u\right)}{r_{\rm o} r_{\rm i} (r_{\rm o} + r_{\rm i})} \,,$$

respectively. The cosine of the angle α between the surface normal of the liquid-vapor interface and the radial unit vector reads

$$\cos\alpha = \frac{r_{\rm o} \cos^2 u + r_{\rm i} \sin^2 u}{\sqrt{r_{\rm o}^2 \cos^2 u + r_{\rm i}^2 \sin^2 u}} \,. \tag{7}$$

2.4 Inflection point criterion

Due to the reflection symmetry $u \to \pi - u$ of the undoloid drops and, in consequence, of eqns. (4), (5) and (6), we may consider eigenfunctions ρ which are either symmetric or antisymmetric with respect to the reflection symmetry at $u = \pi/2$. Besides this discrete symmetry, each eigenfunction ν can be labeled by its azimuthal node number m and the number l of zeroes of the function $\rho(u)$.

The rigid translation of the liquid-vapor interface perpendicular to the axis of the cylinder generates a displacement mode

$$\nu(u, \varphi) = \mathrm{e}^{\pm im\varphi} \cos \alpha(u) \tag{8}$$

with azimuthal node number $m = 1$ and longitudinal node number $l = 0$. It can be checked by explicit calculation using eqn. (7) that expression (8) is a solution of Jacobi's accessory equation (4) and the volume constraint given by eqn. (5) for any r_o and r_i. The boundary condition eqn. (6) is satisfied for undoloid curves with an inflection point located on the surface of the cylinder. For undoloids the curvature $c_\perp(u)$ of the contour has the same sign as the derivative of $\rho'(u)$ for $0 < u < \pi/2$ and opposite sign for $\pi/2 < u < \pi$ while $\rho(u)$ is non-zero everywhere. Hence, for contact angles $0 < \theta < \pi/2$, the boundary condition eqn. (6) can only be satisfied if $c_\perp(u_0) = 0$, i.e., the point u_0 must correspond to an inflection point of the drop contour. This finding is corroborated by numerical solutions of the boundary value problem eqns. (4), (5) and (6). The numerically computed dimensionless rescaled eigenvalue λr_o^2 of the mode with $l = 0$ and $m = 1$ as function of the rescaled volume $\tilde{V}$ is displayed in Fig. S2 for different values of the contact angle θ. The numerical analysis shows that shapes without an inflection point are always unstable, while shapes with an inflection point are always mechanically stable.

References

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