Supporting Information: Morphological Transitions of Liquid Droplets on Circular Surface Domains

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This Supporting Information consists of appendices with derivations of free energies for all droplet regimes, the stability criterion for two-droplet morphologies, details on the bifurcation analysis method and resulting expressions for transition lines and instability lines.

As in the main text, we use dimensionless free energies and dimensionless volumes defined by

$$f \equiv F/2\pi\Sigma_{\alpha\beta}a^2 \tag{1}$$

$$v_\beta \equiv V_\beta/(2\pi/3)a^3. \tag{2}$$

In these dimensionless units a half sphere corresponds to a volume $v_\beta = 1$ and its $\alpha\beta$ interface has a surface energy $f = 1$.

I. FREE ENERGIES IN SINGLE-DROPLET REGIMES

In the main text we derived the free energies of single droplets in regimes I and III,

$$f_{\mathrm{I}}(v_\beta) = \frac{1}{2}(2v_\beta)^{2/3}(2 - 3w_\gamma + w_\gamma^3)^{1/3} \tag{3}$$

$$f_{\mathrm{III}}(v_\beta) = \frac{1}{2}(2v_\beta)^{2/3}(2 - 3w_\delta + w_\delta^3)^{1/3} + \frac{1}{2}(w_\delta - w_\gamma). \tag{4}$$

For regime II, we obtained the implicit result

$$f_{\mathrm{II}}(\cos\theta) = \frac{1}{1+\cos\theta} - \frac{1}{2}w_\gamma \tag{5}$$

$$v_\beta = \frac{1}{2}\frac{2 - 3\cos\theta + \cos^3\theta}{\sin^3\theta}. \tag{6}$$

By solving for $\cos\theta$ in equation (6), we obtain the explicit volume dependence $f_{\mathrm{II}}(v_\beta)$:

$$\cos\theta(v_\beta) = -1 + \frac{1}{h(4v_\beta^2)} + \frac{h(4v_\beta^2)}{1+4v_\beta^2} \tag{7}$$

$$f_{\mathrm{II}}(v_\beta) = \frac{h(4v_\beta^2)(1+4v_\beta^2)}{1+4v_\beta^2 + h^2(4v_\beta^2)} - \frac{1}{2}w_\gamma, \tag{8}$$

with a function $h(x) \equiv (1 + (x(1+x)^3)^{1/2} + x(2+x))^{1/3}$.

These are explicit expressions for the free energy of a single droplet $f = f(v_\beta)$ through all three wetting regimes:

$$f(v_\beta) = \begin{cases} f_{\mathrm{I}}(v_\beta), & v_\beta < v_{\beta,\mathrm{pin}}, & \text{regime I} \\ f_{\mathrm{II}}(v_\beta), & v_{\beta,\mathrm{pin}} < v_\beta < v_{\beta,\mathrm{dep}}, & \text{regime II} \\ f_{\mathrm{III}}(v_\beta), & v_{\beta,dep} < v_\beta, & \text{regime III} \end{cases} \tag{9}$$

with $v_{\beta,\mathrm{pin}}$ and $v_{\beta,\mathrm{dep}}$ as in eq (11) and (12) in the main text.

II. STABILITY CRITERION

For two droplets, which can exchange volume we want to derive the following stability criterion:

> States with two droplets can only be stable if at least one of the droplets is pinned and has a contact angle $\theta < \pi/2$. (10)

A. Laplace pressure

From the expression for the free energy (9) of a single droplet, the Laplace equation is recovered for each wetting regime by taking the derivative with respect to the volume:

$$\frac{a}{3\Sigma_{\alpha\beta}}\Delta P = \frac{\partial f}{\partial v_\beta} = \frac{2}{3}\frac{a}{R}. \tag{11}$$

The first equality is by thermodynamic definition of the pressure, the second by explicit calculation in each regime. This gives the Laplace equation

$$\Delta P = 2\frac{\Sigma_{\alpha\beta}}{R} = P_\beta - P_\alpha. \tag{12}$$

Using (11) we can obtain explicit results for the Laplace pressure (or the mean curvature $2/R$) as a function of the volume. Because of the contact line pinning, the Laplace pressure becomes a *non-monotonic* function of the volume, see Fig. 8.

For a small unpinned droplet in the γ-domain with $v_\beta < v_{\beta,\mathrm{pin}}$, the Laplace pressure is *decreasing* with increasing volume. Then the droplet gets pinned and the curvature and, thus, the Laplace pressure starts to *increase* for $v_{\beta,\mathrm{pin}} \le v_\beta \le 1$ up to the volume $v_\beta = 1$, corresponding to a half sphere, and decreases again for $v_\beta > 1$. The Laplace pressure as a function of the volume assumes the form shown in Fig. 8.

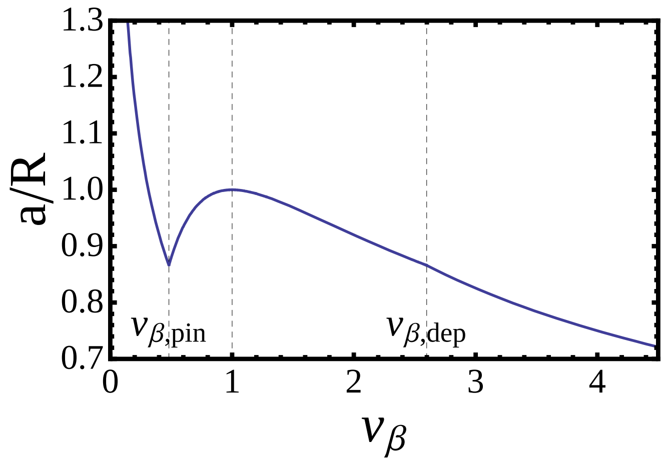

FIG. 8: Reduced mean curvature, a/R, which is proportional to the Laplace pressure, as a function of the dimensionless volume v_β for $w_\gamma = 0.6$ and $w_\delta = -0.6$. The mean curvature a/R is equal to the reduced Laplace pressure $P_{\text{La}} = a/2\Sigma_{\alpha\beta}$. For $v_\beta < v_{\beta,\text{pin}} = 0.4$ the Laplace pressure is *decreasing*, for $v_{\beta,\text{pin}} \leq v_\beta \leq 1$ it is *increasing* and for $v_\beta > 1$ it is again *decreasing* with increasing volume. The local maximum of the mean curvature is attained at $v_\beta = 1$ corresponding to a single droplet with the shape of a half sphere.

B. Laplace pressure and stability

Two droplets (1 and 2) with volumes $v_\beta^{(1)}$ and $v_\beta^{(2)}$ and with a fixed total volume, $v_\beta = v_\beta^{(1)} + v_\beta^{(2)}$, have a total energy

$$f_{2d}(v_\beta, v_\beta^{(1)}) = f(v_\beta^{(1)}) + f(v_\beta - v_\beta^{(1)}) \tag{13}$$

with the free energy $f(v_\beta)$ of a single droplet as given by eq (9).

The equilibrium condition $\partial f_{2d}/\partial v_\beta^{(1)} = 0$ for two droplets on two neighboring domains, which can exchange volume, implies $\partial f/\partial v_\beta^{(1)} = \partial f/\partial(v_\beta - v_\beta^{(1)})$. Since each of the derivatives in the latter expression correspond to the Laplace pressure or the inverse of the radius of curvature of each droplet (see Fig. 8), this implies equal radii of curvature or equal Laplace pressure.

We can show the necessary condition (10) for stability by considering an equilibrium of two droplets which violate the condition and, thus, have both Laplace pressures, which are a *decreasing* function of their volume. If one of the droplets shrinks by a perturbative volume exchange, its Laplace pressure is raised whereas the other droplet grows and, consequently, its Laplace pressure is lowered. The resulting pressure difference with higher Laplace pressure in the shrinking droplet leads to further volume transfer from the shrinking droplet to the growing droplet and, thus, this type of equilibrium is always unstable.

III. FREE ENERGIES IN TWO-DROPLET REGIMES

In this appendix, we derive the expressions for the free energies and volumes in each possible (meta)stable regime involving two droplets. We do this in terms of the total volume v_β and the corresponding wettabilities w_γ and w_δ. We only assume that the domain is more lyophilic than the substrate, i.e., $w_\gamma > w_\delta$, and that the domain is lyophilic, i.e., $w_\gamma > 0$.

A. Regime 2S

In regime 2S, both droplets are pinned and have equal volumes $v_\beta^{(1)} = v_\beta^{(2)} = v_\beta/2$, and, thus, the total free energy is given by

$$\begin{aligned} f_{2S}(v_\beta) &= 2 f_{\text{II}}(v_\beta/2) \\ f_{2S}(\cos\theta^{(1)}) &= \frac{2}{1+\cos\theta^{(1)}} - w_\gamma \end{aligned} \tag{14}$$

with f_{II} from (8).

For droplet volumes and contact angles the corresponding formula (6) from regime II for droplet volume $v_\beta^{(i)} = v_\beta/2$ apply:

$$v_\beta = \frac{(2+\cos\theta^{(1)})(1-\cos\theta^{(1)})^{1/2}}{(1+\cos\theta^{(1)})^{3/2}} \tag{15}$$

B. Regime 2C

In regime 2C, both droplets are pinned and have complementary volumes (say droplet 1 is smaller than droplet 2), i.e., their contac angles satisfy $\cos\theta^{(1)} = -\cos\theta^{(2)} > 0$ and $\sin\theta^{(1)} = \sin\theta^{(2)}$. According to eq (6), the volumes are given by

$$v_\beta^{(1,2)} = \frac{1}{2\sin^3\theta^{(1)}}(2 \pm \cos\theta^{(1)})(1 \mp \cos\theta^{(1)})^2, \tag{16}$$

and the total volume can therefore be written as

$$v_\beta = v_\beta^{(1)} + v_\beta^{(2)} = \frac{2}{\sin^3\theta^{(1)}}. \tag{17}$$

Using all of these formulas and the expression (5) for the free energy of each droplet in regime II, we obtain a closed expression for the free energy in regime 2C as a function of the total volume v_β,

$$\begin{aligned} f_{2C} &= f_{\text{II}}(v_\beta^{(1)}) + f_{\text{II}}(v_\beta - v_\beta^{(1)}) \\ f_{2C}(\cos\theta^{(1)}) &= \frac{2}{\sin^2\theta^{(1)}} - w_\gamma \\ f_{2C}(v_\beta) &= 2(v_\beta/2)^{2/3} - w_\gamma \end{aligned} \tag{18}$$

From (17), it is clear that regime 2C is only accessible for $v_\beta \geq 2$.

C. Regime 5

In regime 5, the larger droplet (say 2) is unpinned and wetting the δ-substrate with $\cos\theta^{(2)} = w_\delta$, whereas the smaller droplet is pinned with $w_\delta \le \cos\theta^{(1)} \le w_\gamma$. i.e., it has a smaller contact angle $\theta^{(1)} < \theta^{(2)}$. Because both droplets have equal radii of curvature, the pinned droplet must have a contact angle $\theta^{(1)} < \pi/2$ and $\cos\theta^{(1)} > -\cos\theta^{(2)}$. Therefore, regime 5 can only be realized for wettabilities with $w_\gamma > -w_\delta$.

The condition that both droplets have the same radii of curvature in equilibrium leads to

$$\begin{aligned}\frac{1}{\sin^2\theta^{(1)}} &= \left(\frac{R^{(1)}}{a}\right)^2 = \left(\frac{R^{(2)}}{a}\right)^2 \\ &= (2v_\beta^{(2)})^{2/3}(1-w_\delta)^{-4/3}(2+w_\delta)^{-2/3} \\ v_\beta^{(2)} &= \frac{(1-w_\delta)^2(2+w_\delta)}{2(1-\cos^2\theta^{(1)})^{3/2}}\end{aligned} \tag{19}$$

i.e., a relation between the volume $v_\beta^{(2)}$ of the unpinned droplet and the free contact angle $\theta^{(1)}$ of the pinned droplet. For the volume $v_\beta^{(1)}$ of the pinned droplet we have

$$v_\beta^{(1)} = \frac{1}{2}\frac{(2+\cos\theta^{(1)})(1-\cos\theta^{(1)})^{1/2}}{(1+\cos\theta^{(1)})^{3/2}} \tag{20}$$

and the resulting total volume as a function of $\cos\theta^{(1)}$ is:

$$\begin{aligned}v_\beta(\cos\theta^{(1)}) &= v_\beta^{(1)} + v_\beta^{(2)} \\ &= \frac{(1-w_\delta)^2(2+w_\delta)}{2(1-\cos^2\theta^{(1)})^{3/2}}\times \\ &\quad \left[1+\frac{(1-\cos\theta^{(1)})^2(2+\cos\theta^{(1)})}{(1-w_\delta)^2(2+w_\delta)}\right].\end{aligned} \tag{21}$$

The free energy in regime 5 is

$$\begin{aligned}f_5(\cos\theta^{(1)}) =& f_{\rm III}(v_\beta^{(2)}) + f_{\rm II}(v_\beta^{(1)}) \\ =& \frac{1}{2}\frac{(1-w_\delta)^2(2+w_\delta)}{1-\cos^2\theta^{(1)}} + \\ & \frac{1}{1+\cos\theta^{(1)}} + \frac{1}{2}(w_\delta - 2w_\gamma),\end{aligned} \tag{22}$$

which gives together with eq (21) a parametric representation of $f = f(v_\beta)$ in terms of the parameter $\cos\theta^{(1)}$.

D. Regime 4

In regime 4, the larger droplet (say 1) is pinned with $w_\delta \le \cos\theta^{(1)} \le w_\gamma$. The smaller droplet is unpinned and on the γ-domain, with $\cos\theta^{(2)} = w_\gamma$. Following stability arguments as in section II A, morphologies in regime 4 can only be stable if the pinned droplet has a contact angle $\theta^{(1)} < \pi/2$, i.e., for $v_\beta^{(1)} < 1$ and $v_\beta < 2$.

The formulae for volumes and free energies are analogous to regime 5. As in regime 5 we can only obtain a parametric representation of $f = f(v_\beta)$ in terms of the parameter $\cos\theta^{(1)}$. For the volume $v_\beta^{(2)}$ of the unpinned droplet and the free contact angle $\cos\theta^{(2)}$ of the pinned droplet one obtains

$$v_\beta^{(2)} = \frac{(1-w_\gamma)^2(2+w_\gamma)}{2(1-\cos^2\theta^{(1)})^{3/2}} \tag{23}$$

For the volume $v_\beta^{(1)}$ of the pinned droplet and the total volume we find

$$\begin{aligned}v_\beta^{(1)} =& \frac{1}{2}\frac{(2+\cos\theta^{(1)})(1-\cos\theta^{(1)})^{1/2}}{(1+\cos\theta^{(1)})^{3/2}} \\ v_\beta(\cos\theta^{(1)}) =& \frac{(1-w_\gamma)^2(2+w_\gamma)}{2(1-\cos^2\theta^{(1)})^{3/2}}\times \\ & \left[1+\frac{(1-\cos\theta^{(1)})^2(2+\cos\theta^{(1)})}{(1-w_\gamma)^2(2+w_\gamma)}\right].\end{aligned} \tag{24}$$

The free energy in regime 4 is

$$\begin{aligned}f_4(\cos\theta^{(1)}) =& f_{\rm I}(v_\beta^{(2)}) + f_{\rm II}(v_\beta^{(1)}) \\ =& \frac{1}{2}\frac{(1-w_\gamma)^2(2+w_\gamma)}{1-\cos^2\theta^{(1)}} + \\ & \frac{1}{1+\cos\theta^{(1)}} - \frac{1}{2}w_\gamma,\end{aligned} \tag{25}$$

which gives together with eq (24) the parametric representation of $f = f(v_\beta)$ in terms of the parameter $\cos\theta^{(1)}$.

In discussing the transition lines between regimes 2S and 4 below we will show that morphologies in regime 4 never represent a global free energy minimum, i.e., they are at most *metastable*.

IV. TRANSITION AND INSTABILITY LINES

In this section we will derive expressions for all transition and instability lines, which are shown in the morphology diagrams in Figs. 3 and 4 and the stability diagrams in Fig. 5 in the main text.

A. Transition lines between single-droplet regimes I, II, and III

At small total total volumes $v_\beta \le v_{\beta,\rm pin}$ there is only one single droplet in regime I, i.e., within the γ-domain. Upon increasing the volume, pinning to the domain boundary occurs, and the droplet enters regime II. The transition from morphology I to morphology II is a *pinning transition* and takes place at

$$v_{\beta,\rm I-II} = v_{\beta,\rm pin} = \frac{1}{2}\frac{(2+w_\gamma)(1-w_\gamma)^{1/2}}{(1+w_\gamma)^{3/2}} \quad \text{continuous pinning transition I-II.} \tag{26}$$

This transition depends only on w_γ and is *continuous.* (as long as we ignore additional line tension effects, see Ref. [2]).

In regime II, the single droplet is pinned and depins from the domain upon further increasing the volume to $v_\beta \geq v_{\beta,\text{dep}}$. Then it starts to wet the δ-domain and enters regime III. The transition between morphologies II and III is a *depinning transition* and takes place at

$$v_{\beta,\text{II}-\text{III}} = v_{\beta,\text{dep}} = \frac{1}{2}\frac{(2+w_\delta)(1-w_\delta)^{1/2}}{(1+w_\delta)^{3/2}} \quad \text{continuous depinning transition II-III.} \tag{27}$$

This transition depends only on w_δ and is also *continuous.*

B. Bifurcation analysis for transition lines between two-droplet regimes 2S, 2C, 4, and 5

Transitions between two different two-droplet morphologies are either *symmetry breaking transitions* (SBTs), where the permutation symmetry of the two spherical caps is lost or *depinning transitions*, where a pinned droplet spreads onto the δ-substrate (2S/2C-5) or retracts onto the γ-domain (2S-4), or combinations of both types.

Morphological transitions between different two-droplet states can be analyzed by studying bifurcations of the branches $f_{2S}(v_\beta)$, $f_{2C}(v_\beta)$, $f_4(v_\beta)$, $f_5(v_\beta)$. The bifurcation analysis of the free energies is difficult because we have only parametric representations of $f_4(v_\beta)$ and $f_5(v_\beta)$ in terms of the parameter $\cos\theta^{(1)}$ (where $\theta^{(1)}$ is the contact angle of the pinned droplet). Therefore, it is more convenient to consider the total volume v_β of both droplets as a function of $\cos\theta^{(1)}$ instead, where $\theta^{(1)}$ is the contact angle of the droplet which remains pinned with $\theta^{(1)} < \pi/2$. Such a droplet must exist according to our above criterion (10). Each (meta)stable stationary droplet morphology with volume v_β has to give a solution $\theta^{(1)}$ of the equation

$$v_\beta = v_\beta(\cos\theta^{(1)}) \quad \text{with } 0, w_\delta \leq \cos\theta^{(1)} \leq w_\gamma \tag{28}$$

where $0 < \cos\theta^{(1)}$ holds because of $\theta^{(1)} < \pi/2$ (this restriction also lifts the permutation symmetry between droplets) and $w_\delta \leq \cos\theta^{(1)}$ and $\cos\theta^{(1)} \leq w_\gamma$ hold because otherwise the pinned droplet will depin and the configuration becomes unstable according to our above stability criterion because no pinned droplet is left. In regimes 5 and 2C we have additional conditions: In regime 5, $\cos\theta^{(1)} > -w_\delta$ assures that the larger unpinned droplet wets the δ-substrate. Analogously, in regime 2C, $\cos\theta^{(1)} < -w_\delta$ assures that the larger droplet does not wet the δ-substrate. The function $v_\beta(\cos\theta^{(1)})$ on the r.h.s. of eq (28) is given by eq (17) in regime 2C, eq (15) in regime 2S, eq (21) in regime 5, and eq (24) in regime 4. The four branches of the function $v_\beta(\cos\theta^{(1)})$ give four possible branches of solutions of (28) corresponding to the two-droplet morphologies 2S, 2C, 4, and 5.

At a morphological transition or an instability of the two-droplet morphologies 2S, 2C, 4, and 5, the corresponding free energy branches $f(v_\beta)$ either terminate (instability), intersect (discontinuous transition), or join smoothly (continuous transition). Right at the transition or in the presence of metastable states and unstable free energy maxima we find several free energy branches for the same volume v_β. Therefore, we will also find several solutions to eq (28) in the parametric representation. Instead of studying the bifurcations of the free energy branches $f(v_\beta)$, we can therefore study the corresponding bifurcations of the solutions of eq (28). Morphological transitions correspond to intersection points of two branches $v_\beta(\cos\theta^{(1)})$. If no solution exists for all four branches, the two-droplet morphologies have become unstable with respect to one of the single-droplet morphologies. If a bifurcation from a single solution of eq (28) to three solutions on two different branches occurs, a discontinuous morphological transition takes place between the corresponding shapes (which involves an additional metastable free energy minimum and an additional unstable maximum). If the total number of solutions of eq (28) is unchanged the corresponding morphological transition is continuous. Using this method we can obtain all instability lines associated with discontinuous transitions and all continuous transition lines. In order to obtain the discontinuous transition lines it is not sufficient to consider $v_\beta(\cos\theta^{(1)})$ but we also have to compare the free energies $f(\cos\theta^{(1)})$ in order to find the intersection points of different branches $f(v_\beta)$.

C. Symmetry breaking transition 2S-2C

The *symmetry breaking transition* (SBT) between morphologies 2S and 2C takes place at

$$v_{\beta,\text{SBT}} = 2 \quad \text{continuous SBT 2S-2C} \tag{29}$$

independent of the wettabilities [1].

The SBT corresponds to a bifurcation of the solutions of (28) at $\cos\theta^{(1)} = 0$, and there is one solution for each of the two branches given by eq (17) in regime 2C and eq (15) in regime 2S within $0 < \cos\theta^{(1)} \leq w_\gamma$, see Fig. 9. Therefore, the SBT is *continuous.*

The SBT line ends in a *critical endpoint* on the first order transition line between regimes 2S/2C and regime 5 for $w_\delta = w_{\delta,c}$, see Fig. 3 in the main text. For $w_\delta > w_{\delta,c}$ the SBT line continues as transition line between metastable states. It terminates at $w_\delta = 0$, where it meets the instability line of the 2S regime. For $w_\delta > 0$, no transition between 2S and 2C is possible because the 2S morphology becomes unstable with respect to depinning and spreading onto the δ-substrate before the contact angle $\theta = \pi/2$ for the SBT can be reached.

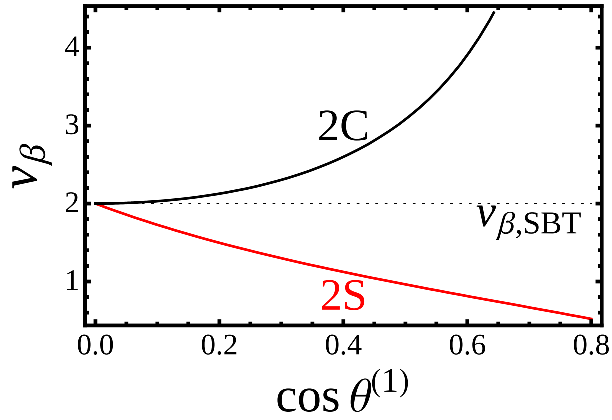

FIG. 9: Bifurcation of solutions to eq. (28) for the SBT between morphologies 2S and 2C for $w_\gamma = 0.8$. The SBT is continuous. The dotted line corresponds to the transition volume $v_{\beta,\mathrm{SBT}} = 2$, see eq. (29).

D. Depinning transitions 2S/2C-5

The *depinning transition* from morphologies 2S or 2C to morphology 5 takes place if the larger droplet wets the δ-substrate. It only depends on the wettability w_δ and the volume v_β. For $w_\delta < w_{\delta,c}$, we find a depinning transition from 2C to 5, for $w_\delta > w_{\delta,c}$ we find a transition from morphology 2S to 5, which is then also a symmetry breaking transition. The point $w_\delta = w_{\delta,c}$ with

$$w_{\delta,c} = \frac{6-\sqrt{51}}{10} \simeq -0.114 \tag{30}$$

separating these two regimes is the *critical endpoint* of the continuous SBT line $v_{\beta,\mathrm{SBT}} = 2$. The depinning transition from 2C or 2S to 5 is *discontinuous* for a range of wettabilities $w_{\delta,c-} < w_\delta < w_{\delta,c+}$, which is given by two *tricritical points* $w_{\delta,c-}$ and $w_{\delta,c+}$ with

$$\begin{aligned} w_{\delta,c-} &\simeq -0.225, \\ w_{\delta,c+} &= -1+\sqrt{2} \simeq 0.414. \end{aligned} \tag{31}$$

For wettabilities $w_\delta > w_{\delta,c+}$ or $w_\delta < w_{\delta,c-}$ the depinning transitions from morphologies 2C or 2S to 5 are *continuous*.

These results are obtained from the bifurcation analysis of the solutions to eq (28). The curves $v_\beta(\cos\theta^{(1)})$ for regimes 2S/2C and 5 intersect for $\cos\theta^{(1)} = \pm w_\delta$ corresponding to the situation $\cos\theta^{(2)} = w_\delta$ that the larger droplet starts to wet the δ-substrate.

The bifurcation behavior is qualitatively different depending on whether the curve $v_\beta(\cos\theta^{(1)})$ for regime 5 according to eq (21) is an increasing function of $\cos\theta^{(1)}$ at the intersection point, see Figs. 10 (a) and (c), which leads to *continuous* depinning transitions or a decreasing function of $\cos\theta^{(1)}$ at the intersection point, see Figs. 10 (b) and (d), which leads to *discontinuous* depinning transitions according to our above discussion of eq (28).

For a *discontinuous* depinning transition with a monotonously decreasing function $v_\beta(\cos\theta^{(1)})$ at the intersection points, see Figs. 10 (b) and (d), the intersection points correspond to instabilities of morphologies 2C and 2S with respect to a depinning into morphology 5,

$$v_{\beta,\mathrm{ins\ 2Ca}} = 2(1-w_\delta^2)^{-3/2} \tag{32}$$

depinning instability 2C ($w_{\delta,c-} < w_\delta < 0$)

$$v_{\beta,\mathrm{ins\ 2Sa}} = \frac{(2+w_\delta)(1-w_\delta^2)^{1/2}}{(1+w_\delta)^{3/2}} = 2v_{\beta,\mathrm{dep}} \tag{33}$$

depinning instability 2S ($0 < w_\delta < w_{\delta,c+}$)

The instability lines $v_{\beta,\mathrm{ins\ 2Sa}}$ and $v_{\beta,\mathrm{ins\ 2Ca}}$ meet at $w_\delta = 0$ and $v_\beta = v_{\beta,\mathrm{SBT}} = 2$, where also the SBT line terminates in the metastable regime. These instability lines are shown as dashed green lines to the right of the solid green transition line in Fig. 3 in the main text.

The corresponding pinning instability lines of regime 5 are given by the *smallest* volume, for which a solution of eq (28) for the volume (21) in regime 5 exists. This volume is obtained as the minimal value that the volume given by eq (21) attains for $|w_\delta| < \cos\theta^{(1)} \le w_\gamma$,

$$v_{\beta,\mathrm{ins\ 5a}} = \min_{|w_\delta|<\cos\theta^{(1)}\le w_\gamma} \left\{ \frac{(1-w_\delta)^2(2+w_\delta)}{2(1-\cos^2\theta^{(1)})^{3/2}} \times \left[1+\frac{(1-\cos\theta^{(1)})^2(2+\cos\theta^{(1)})}{(1-w_\delta)^2(2+w_\delta)}\right]\right\} \tag{34}$$

pinning instability 5 ($w_{\delta,c-} < w_\delta < w_{\delta,c+}$)

The minimum is attained for a value $\cos\theta^{(1)} = \cos\theta_5^{(1)}$, which solves the quadratic equation

$$0 = 1 + (\cos\theta_5^{(1)})^2 - \cos\theta_5^{(1)}\left(4-3w_\delta+w_\delta^3\right) \tag{35}$$

resulting in a closed, but lengthy expression for the instability line $v_{\beta,\mathrm{ins\ 5a}} = v_{\beta,\mathrm{ins\ 5a}}(w_\delta)$ according to (34). The resulting pinning instability lines of regime 5 are shown as dashed green lines to the left of the solid green transition line in Fig. 3 in the main text.

The instability lines $v_{\beta,\mathrm{ins\ 2S/2Ca}}$ and $v_{\beta,\mathrm{ins\ 5a}}$ meet if the minimum is attained for $\cos\theta_5^{(1)} = |w_\delta|$, where the transition between morphologies 2S/2C and morphology 5 becomes *continuous*. This is also the condition that the function $v_\beta(\cos\theta^{(1)})$ has a vanishing derivative at the intersection points and, hence, changes its monotony behavior. This leads to the two *tricritical points* at $w_\delta = w_{\delta,c\pm}$, which are given by the condition

$$0 = 1 + w_{\delta,c\pm}^2 \mp w_{\delta,c\pm}\left(4-3w_{\delta,c\pm}+w_{\delta,c\pm}^3\right) \tag{36}$$

The solutions of these quartic equations give the above results (31).

For $w_\delta > w_{\delta,c+}$ and $w_\delta < w_{\delta,c-}$ the function $v_\beta(\cos\theta^{(1)})$ becomes monotonously increasing at the intersection point, see Figs. 10 (a) and (c), and the depinning transition between morphologies 2S or 2C and 5 is *continuous*. The corresponding transition lines are given by the same equations as the instability lines (32) and (33),

$$v_{\beta,2\mathrm{C}-5} = 2(1-w_\delta^2)^{-3/2} \tag{37}$$
cont. depinning transition 2C-5 ($w_\delta < w_{\delta,c-}$)

$$v_{\beta,2\mathrm{S}-5} = \frac{(2+w_\delta)(1-w_\delta^2)^{1/2}}{(1+w_\delta)^{3/2}} = 2v_{\beta,\mathrm{dep}} \tag{38}$$
cont. depinning transition 2S-5 ($w_\delta > w_{\delta,c+}$)

and are shown as solid black lines in Fig. 3 in the main text.

For $w_{\delta,c-} < w_\delta < w_{\delta,c+}$ the depinning transition between morphologies 2S/2C and 5 is *discontinuous* and we have derived already all instability lines. At the transition lines of the discontinuous transition the free energies f_5 (22) and $f_{2\mathrm{C}}$ (18) or $f_{2\mathrm{S}}$ (14) corresponding to the solutions of (28) are equal. Therefore, in order to find the transition lines of the discontinuous depinning transition between regimes 2S/2C and 5, we have to find simultaneous solutions of the two equations

$$\begin{aligned} v_{\beta,2\mathrm{S}/2\mathrm{C}}(\cos\theta_1^{(1)}) &= v_{\beta,5}(\cos\theta_2^{(1)}) \\ f_{2\mathrm{S}/2\mathrm{C}}(\cos\theta_1^{(1)}) &= f_{2\mathrm{S}/2\mathrm{C}}(\cos\theta_2^{(1)}). \end{aligned} \tag{39}$$

for the two contact angles $\theta_1^{(1)}$ and $\theta_2^{(1)}$, which coexist at the discontinuous transition. This can only be done numerically and gives transition lines $v_{\beta,2\mathrm{S}-5}$ and $v_{\beta,2\mathrm{C}-5}$ between the corresponding instability lines, $v_{\beta,\mathrm{ins}\ 5\mathrm{a}} < v_{\beta,2\mathrm{S}/2\mathrm{C}-5} < v_{\beta,\mathrm{ins}\ 2\mathrm{S}/2\mathrm{Ca}}$, which are shown as solid green lines in Fig. 3 in the main text.

If in addition to eqs (39) the condition $\cos\theta^{(1)} = 0$ or $v_\beta = 2$ is fulfilled the discontinuous transition 2C-5 becomes a discontinuous transition 2S-5, which defines the *critical endpoint* $w_{\delta,c}$ of the SBT line, where $w_{\delta,2\mathrm{S}-5} = w_{\delta,2\mathrm{C}-5} = w_{\delta,c}$. Solving eqs (39) simultaneously with $\cos\theta^{(1)} = 0$ we find the analytical result eq (30) for the critical endpoint.

E. Metastable depinning transition 2S-4

The *depinning transition* from morphology 2S to morphology 4 takes place if the smaller droplet retracts to the γ-domain. This depinning transition is also a symmetry breaking transition. It depends only on the wettability w_γ and the volume v_β. A transition from morphology 2S to 4 is possible for sufficiently lyophilic domains γ, i.e., for $w_\gamma > w_{\gamma,c}$, where $w_{\gamma,c}$ is a *critical point* with

$$w_{\gamma,c} = -1+\sqrt{2}. \tag{40}$$

The depinning and symmetry breaking transition exists for $w_\gamma > w_{\gamma,c}$ and is *continuous* for this range of wettabilities. For $w_\gamma < w_{\gamma,c}$, there is no transition from morphology 2S to morphology 4 but a direct dewetting instability of morphology 2S with respect to the single-droplet morphology II (we consider $w_\gamma > 0$ only). At $w_\gamma = w_{\gamma,c}$, the continuous transition line terminates in the instability line of the 2S state. Because morphologies in regime 4 are at most metastable, the transition from morphology 2S to morphology 4 is a transition between two metastable states, while the stable configuration is the single-droplet morphology II.

These results are obtained from the bifurcation analysis of the solutions to eq (28). The curves $v_\beta(\cos\theta^{(1)})$ for regimes 2S and 4 intersect for $\cos\theta^{(1)} = w_\gamma$. This condition corresponds to the situation that one droplet starts to retract into the γ-domain.

The bifurcation behavior is qualitatively different depending on whether the curve $v_\beta(\cos\theta^{(1)})$ for regime 4, see eq (24), is an increasing function of $\cos\theta^{(1)}$ at the intersection point, see Figs. 11 (a), or a decreasing function of $\cos\theta^{(1)}$ at the intersection point, see Figs. 11 (b). For a monotonously increasing function $v_\beta(\cos\theta^{(1)})$ at the intersection point, the intersection point corresponds to a *continuous* depinning transition between morphologies 2S and 4. The transition line is given by $\cos\theta^{(1)} = w_\gamma$, which gives according to eq (15)

$$v_{\beta,2\mathrm{S}-4} = \frac{(2+w_\gamma)(1-w_\gamma)^{1/2}}{(1+w_\gamma)^{3/2}} \tag{41}$$
cont. transition 2S-4 (metastable, $w_\gamma > w_{\gamma,c}$)

Using $\cos\theta^{(1)} = w_\gamma$, we find a free energy $f_{2S} = 2/(1+w_\gamma) - w_\gamma$ at the transitions. Comparing with $f_{II}(v_{\beta,2\mathrm{S}-4}(w_\gamma))$ as given by eqs (8) and (41) we can check that $f_{2S} > f_{II}$ at the transition lines between regimes 2S and 4. Therefore, morphology 4 is only *metastable* and the continuous depinning transition between morphologies 2S and 4 is a transition between metastable states. Therefore, the transition line (41) appears only in the stability diagrams in Fig. 5 of the main text as solid black line.

Upon further decreasing the volume below $v_{\beta,2\mathrm{S}-4}$ the solutions of eq (28) are found in regime 4 until a minimal value that the volume given by (24) attains for $0 < \cos\theta^{(1)} \le w_\gamma$ is reached. This minimum determines the instability lines of regime 4,

$$v_{\beta,\mathrm{ins}\ 4} = \min_{|w_\delta|<\cos\theta^{(1)}\le w_\gamma} \left\{ \frac{(1-w_\gamma)^2(2+w_\gamma)}{2(1-\cos^2\theta^{(1)})^{3/2}} \times \left[1 + \frac{(1-\cos\theta^{(1)})^2(2+\cos\theta^{(1)})}{(1-w_\gamma)^2(2+w_\gamma)}\right]\right\} \tag{42}$$
dewetting instability 4 ($w_\gamma > w_{\gamma,c}$)

because there is no solution of eq (28) possible for smaller total volumes. This instability of morphology 4 is an instability with respect to dewetting into a single-droplet morphology II or III because there is no solution branch of eq (28) for any of the two-droplet regimes left for $v_\beta < v_{\beta,\mathrm{ins}\ 4}$. The minimum is attained for a value $\cos\theta^{(1)} =$

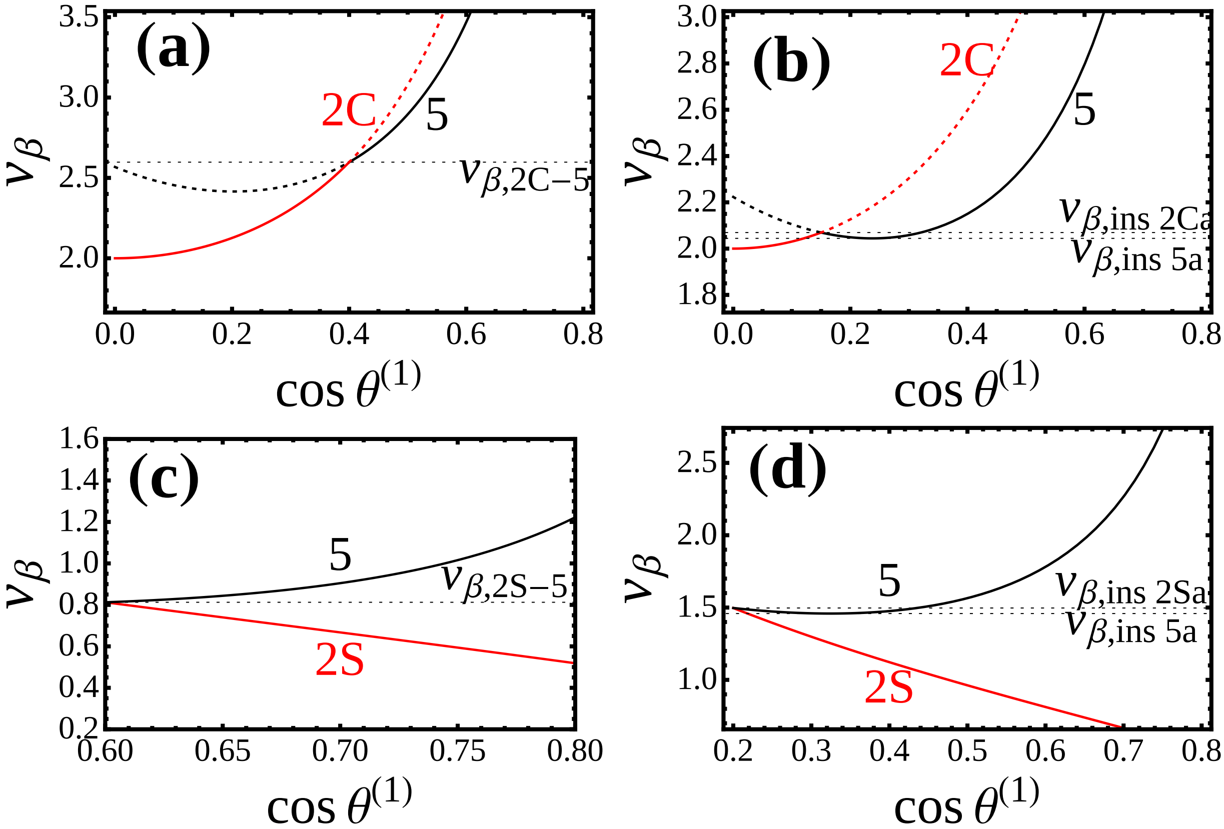

FIG. 10: Bifurcation of solutions to eq. (28) for the transition between morphologies 2C and 5 for $w_\gamma = 0.8$ and $w_\delta = -0.4$ (a) and $w_\delta = -0.15$ (b) and for the transition between morphologies 2S and 5 for $w_\gamma = 0.8$ and $w_\delta = 0.6$ (c) and $w_\delta = 0.2$ (d). The transition 2C-5 is continuous for $w_\delta < w_{\delta,c-} \simeq -0.225$ (a) and discontinuous for $w_{\delta,c-} < w_\delta < w_{\delta,c} \simeq -0.114$ (b). The dotted line on the left side shows the transition volume $v_{\beta,2C-5} \simeq 2.60$, see eq. (37) The dotted lines on the right side show the instability lines $v_{\beta,\text{ins 2Ca}} \simeq 2.07$, see eq. (32) and $v_{\beta,\text{ins 5a}} \simeq 2.04$, see eq. (34). The transition 2S-5 is continuous for $w_\delta > w_{\delta,c+} = -1+\sqrt{2}$ (c) and discontinuous for $w_{\delta,c+} > w_\delta > w_{\delta,c} \simeq -0.114$ (d). The dotted line on the left shows the transition volume $v_{\beta,2S-5} \simeq 0.81$, see eq. (38). The dotted lines on the right side show the instability lines $v_{\beta,\text{ins 2Sa}} \simeq 1.63$, see eq. (33) and $v_{\beta,\text{ins 5a}} \simeq 1.72$, see eq. (34).

$\cos\theta_4^{(1)}$, which solves the quadratic equation

$$0 = 1 + (\cos\theta_4^{(1)})^2 - \cos\theta_4^{(1)}\left(4 - 3w_\gamma + w_\gamma^3\right) \tag{43}$$

resulting in a closed, but lengthy expression for the instability line $v_{\beta,\text{ins }4} = v_{\beta,\text{ins }4}(w_\gamma)$ according to (42). This instability line is shown as dashed dark green line in Fig. 5 in the main text.

The instability line $v_{\beta,\text{ins }4}$ and the transition line $v_{\beta,2S-4}$ meet if the minimum is attained for $\cos\theta_4^{(1)} = w_\gamma$. Then the transition line between regimes 2S and 4 ends in a critical point. This is also the condition that the function $v_\beta(\cos\theta^{(1)})$ has a vanishing derivative at the intersection points and, hence, changes its monotony behavior. The critical point $w_\gamma = w_{\gamma,c}$ is given by the condition

$$0 = 1 + w_{\gamma,c}^2 - w_{\gamma,c}\left(4 - 3w_{\gamma,c} + w_{\gamma,c}^3\right) \tag{44}$$

The solutions of these quartic equations give the above result $w_{\gamma,c} = -1 + \sqrt{2}$, see eq (40).

For $w_\gamma < w_{\gamma,c}$, the function $v_\beta(\cos\theta^{(1)})$ becomes monotonously decreasing at the intersection point and there is no transition from morphology 2S to morphology 4 possible. Instead there are no solutions of eq (28) possible for volumes smaller than the corresponding instability line of regime 2S, which is given by the same equation as the transition line (41),

$$v_{\beta,\text{ins 2Sb}} = \frac{(2+w_\gamma)(1-w_\gamma)^{1/2}}{(1+w_\gamma)^{3/2}} \tag{45}$$

dewetting instability 2S (no trans. 2S-4, $w_\gamma < w_{\gamma,c}$)

Note that as for the instability line of regime 4, this instability of morphology 2S is an instability with respect to dewetting into a single-droplet morphology II or III because there is no solution branch of eq (28) for any of the two-droplet regimes left for $v_\beta < v_{\beta,\text{ins 2Sb}}$. For $w_\gamma < w_{\gamma,c}$, the depinning of one droplet leads to a direct instability of morphology 2S. The instability line (45) is shown as dashed black line in Fig. 5 in the main text.

Finally, we can exclude the possibility of a transition between morphologies 2C and 4 because in such a depinning transition the larger pinned droplet would have a contact angle $\theta^{(1)} > \pi/2$ and morphology 4 would be unstable.

F. Dewetting transition lines between single- and two-droplet regimes

In terms of the total free energy $f_{2d}(v_\beta, v_\beta^{(1)})$ transitions between single- and two-droplet morphologies represent transitions between a boundary minimum at $v_\beta^{(1)} = 0$ (or $v_\beta^{(1)} = v_\beta$) corresponding to a single droplet and some state with two droplets corresponding to a local minimum with $v_\beta^{(1)} > 0$ (or the complementary minimum at $v_\beta - v_\beta^{(1)}$). As such, all of these transitions are *discontinuous*, i.e., associated with a jump $\Delta v_\beta^{(1)}$ in the equilibrium volume of the droplet.

This is not possible if the single droplet is in regime I within the γ-domain because then only two smaller droplets within the γ-domain could occur which are unstable as shown before in the instability discussion based on the Laplace pressure. So there are no transitions from morphology I to any two-droplet morphology. Therefore, all transitions between single- and two-droplet morphologies can only involve the single-droplet morphologies II or III.

1. *Transition lines between regimes 2S,2C, or 5 and regime II*

For $v_\beta < v_{\beta,\mathrm{SBT}} = 2$ and $v_\beta < v_{\beta,\mathrm{dep}}$, there can be a dewetting transition from morphology 2S into morphology II. From the condition

$$f_{\mathrm{II}}(v_\beta) = f_{2\mathrm{S}}(v_\beta) = 2f_{\mathrm{II}}(v_\beta/2) \tag{46}$$

[with $f_{2\mathrm{S}}$ from (14) and f_{II} from (8)] we obtain

$$w_{\gamma,\mathrm{II-2S}}(v_\beta) = \frac{4}{1+\cos\theta(v_\beta/2)} - \frac{2}{1+\cos\theta(v_\beta)} \tag{47}$$

discont. dewetting transition II-2S

where $\cos\theta(v_\beta)$ is given by (7). This result is independent of w_δ. The dewetting transition line (47) is shown as solid black line in the morphology diagrams in Fig. 4 in the main text.

The dewetting transition line $w_{\gamma,\mathrm{II-2S}}(v_\beta)$ has a minimum as a function of v_β. Along the transition line, the free energies of regimes II and 2S are equal, and a Clausius-Clapeyron-like equation holds,

$$\left(w'_\gamma(v_\beta)\frac{\partial}{\partial w_\gamma} + \frac{\partial}{\partial v_\beta}\right) f_{\mathrm{II}}(w_\gamma(v_\beta), v_\beta) = \left(w'_\gamma(v_\beta)\frac{\partial}{\partial w_\gamma} + \frac{\partial}{\partial v_\beta}\right) f_{2\mathrm{S}}(w_\gamma(v_\beta), v_\beta) \tag{48}$$

At the minimum of the transitions line, we have $w'_\gamma(v_\beta) = 0$ and find the additional condition $\partial_{v_\beta} f_{\mathrm{II}}(v_\beta) = \partial_{v_\beta} f_{2\mathrm{S}}(v_\beta) = \partial_{v_\beta} f_{\mathrm{II}}(v_\beta/2)$. This means that the 2S and II states at both sides of the transition line must have *equal* Laplace pressures, i.e., the contact angles θ_{II} in regime II and θ_{2S} in regime 2S fulfill $\cos\theta_{II} = -\cos\theta_{2S}$ or $v_\beta(-\cos\theta_{2S}) = 2v_\beta(\cos\theta_{2S})$ with the function $v_\beta(\cos\theta)$ given by eq. (6). This gives a cubic equation for $\cos\theta^*_{2S}$, the contact angle of morphology 2S in the minimum of the transition line $w_{\gamma,\mathrm{II-2S}}(v_\beta)$,

$$0 = -2 + 9\cos\theta^*_{2S} - 3(\cos\theta^*_{2S})^3 \tag{49}$$

$$\cos\theta^*_{2S} \simeq 0.226 \tag{50}$$

[3] The corresponding *universal* values for volume and wettability in the minimum of the the transition line $w_{\gamma,\mathrm{II-2S}}(v_\beta)$ are

$$v^*_\beta = 2v_\beta(\cos\theta^*_{2S}) \simeq 1.443 \tag{51}$$

$$w^*_\gamma = w_{\gamma,\mathrm{II-2S}}(v^*_\beta) \simeq 0.678 \tag{52}$$

$$\theta^*_\gamma \simeq 47.3^\circ \tag{53}$$

For domain wettabilities $w_\gamma \geq w^*_\gamma$ or contact angles $\theta_\gamma \leq \theta^*_\gamma$, one of the domains always dewets, independent of the total volume.

The results (51 and (52) apply as long as $v^*_\beta \leq v_{\beta,\mathrm{dep}}$ or $-\cos\theta^*_{2S} > w_\delta$. For $w_\delta > -0.226$ the depinning transition from the state II to state III of a single droplet happens at smaller volumes, before the minimum w^*_γ is attained. Then the minimum w^*_γ of the transition curve between the single- and two-droplet regimes is obtained from the dewetting transition line $w_{\gamma,\mathrm{III-2S}}(v_\beta)$, which is derived below. This minimum is no longer independent of w_δ.

The dewetting transition between 2S and II is possible for $v_\beta \leq v_{\beta,\mathrm{SBT}} = 2$, where $w_{\gamma,\mathrm{II-2S}}(v_{\beta,\mathrm{SBT}}) \simeq 0.712$ according to (47). At the SBT transition the two symmetric droplets become unstable, and for $v_\beta > 2$ we have to search for a dewetting transition between the morphology 2C with two complementary droplets and morphology II (or III). Note that $v^*_\beta < 2$, such that the minimum of the transition line between single- and two-droplet regimes is always attained for transitions II-2S (or III-2S, see below).

For $2 < v_\beta < v_{\beta,\mathrm{dep}}$, there can be a dewetting transition from morphology 2C into morphology II. From the condition

$$f_{\mathrm{II}}(v_\beta) = f_{2\mathrm{C}}(v_\beta) \tag{54}$$

[with $f_{2\mathrm{C}}$ from (18) and f_{II} from (5)] we obtain

$$w_{\gamma,\mathrm{II-2C}} = 4(v_\beta/2)^{2/3} - \frac{2}{1+\cos\theta(v_\beta)} \tag{55}$$

discont. dewetting transition II-2C

where $\cos\theta(v_\beta)$ is given by (7). This result is also independent of w_δ.

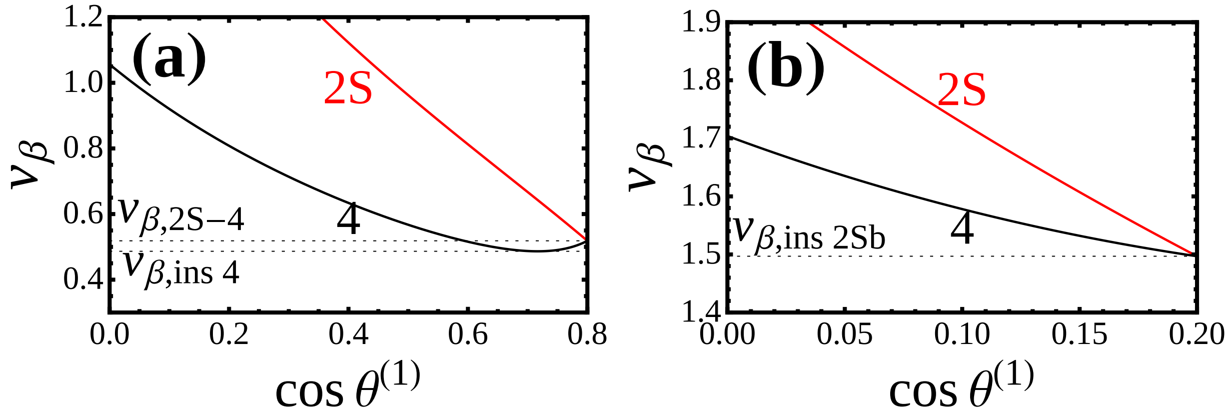

FIG. 11: Bifurcation of solutions to eq. (28) for the transition between morphologies 2S and 4 for $w_\gamma = 0.8$ (a) and for a direct instability of morphology 2S for $w_\gamma = 0.2$ (b). There exists a continuous transition 2S-4 for $w_\gamma > w_{\gamma,c} = -1 + \sqrt{2}$ (a). The dotted lines on the left side correspond to the transition volume $v_{\beta,2S-4} \simeq 0.52$, see eq. (41) and the instability line $v_{\beta,\text{ins }4} \simeq 0.49$, see eq. (42). For $w_\gamma < w_{\gamma,c}$ there is no transition but a direct instability of morphology 2S. The dotted line on the right side corresponds to the instability line $v_{\beta,\text{ins 2Sb}} \simeq 1.46$, see eq. (45).

It is *not* possible to have a transition between a two-droplet morphology 5 and a single-droplet morphology II. In regime 5, the unpinned droplet has a volume $v_\beta^{(2)} > v_{\beta,\text{dep}}$. Thus, we also have $v_\beta > v_\beta^{(2)} > v_{\beta,\text{dep}}$ in regime 5, and a transition to morphology II with $v_\beta < v_{\beta,\text{dep}}$ is not possible.

2. Transition lines between regimes 2S,2C, or 5 and regime III

For $v_{\beta,\text{dep}} < v_\beta < 2$, there can be a dewetting transition from morphology 2S to morphology III. From the condition

$$f_{\text{III}}(v_\beta) = f_{2\text{S}}(v_\beta) = 2 f_{\text{II}}(v_\beta/2) \tag{56}$$

[with $f_{2\text{S}}$ from (14) and f_{III} from (4)] we obtain

$$\begin{aligned} w_{\gamma,\text{III}-2\text{S}} =& \frac{4}{1+\cos\theta(v_\beta/2)} \\ & -(2v_\beta)^{2/3}(1-w_\delta)^{2/3}(2+w_\delta)^{1/3} - w_\delta \\ & \text{discont. dewetting transition III-2S} \end{aligned} \tag{57}$$

which depends also on w_δ. The dewetting transition line (57) is shown as solid black line in the morphology diagrams in Fig. 4 in the main text.

For $v_\beta^* \geq v_{\beta,\text{dep}}$ with v_β^* from eq (51), the dewetting transition line $w_{\gamma,\text{III}-2\text{S}}(v_\beta)$ attains a minimum. Again, a Clausius-Clapeyron relation holds at this minimum value, from which it follows that the coexisting 2S and III morphologies at both sides of the transition curve must have *equal* Laplace pressures, i.e., the same radii of curvature in regime III and in regime 2S. It follows that at the minimum

$$\begin{aligned} v_{\beta,\text{III}} &= \frac{1}{2}\left(\frac{R}{a}\right)^3 (2+w_\delta)(1-w_\delta)^2 \\ &= \frac{1}{2}\frac{(2+w_\delta)(1-w_\delta)^2}{(\sin\theta_{2S})^3} \\ = 2v_{\beta,\text{II}} &= \frac{(2+\cos\theta_{2S})(1-\cos\theta_{2S})^2}{(\sin\theta_{2S})^3} \end{aligned} \tag{58}$$

This gives a cubic equation for $\cos\theta_{2S}^*$, the contact angle that each of the droplets in regime 2S attains at the minimum of the transition line $w_{\gamma,\text{III}-2\text{S}}(v_\beta)$,

$$(2+\cos\theta_{2S}^*)(1-\cos\theta_{2S}^*)^2 = \frac{1}{2}(2+w_\delta)(1-w_\delta)^2. \tag{59}$$

The corresponding volume and wettability in the minimum, $v_\beta^* = 2v_\beta(\cos\theta_{2S}^*)$ and $w_\gamma^* = w_{\gamma,\text{III}-2\text{S}}(v_\beta^*)$ become increasing functions of w_δ for the transition line to regime III.

For $2 < v_{\beta,\text{dep}} < v_\beta < v_{\beta,2\text{C}-5}$, there can be a dewetting transition from morphology 2C into morphology III. From the condition

$$f_{\text{III}}(v_\beta) = f_{2\text{C}}(v_\beta) = 2(v_\beta/2)^{2/3} - w_\gamma \tag{60}$$

[with $f_{2\text{C}}$ from (18) and f_{III} from (4)] we obtain the transition line

$$\begin{aligned} w_{\gamma,\text{III}-2\text{C}} &= (4v_\beta)^{2/3}\left[1 - \frac{(1-w_\delta)^{2/3}(2+w_\delta)^{1/3}}{2^{2/3}}\right] - w_\delta \\ v_{\beta,\text{III}-2\text{C}} &= \left(\frac{w_\gamma + w_\delta}{2^{4/3} - 2^{2/3}(1-w_\delta)^{2/3}(2+w_\delta)^{1/3}}\right)^{3/2} \\ & \text{discont. dewetting transition III-2C} \end{aligned} \tag{61}$$

where $\cos\theta(v_\beta)$ is given by (7) and which depends on *both* w_γ and w_δ. The dewetting transition line (61) appears as solid red line in the morphology diagrams in Fig. 4 (b) and (c) in the main text.

For $v_\beta > v_{\beta,2C-5}, v_{\beta,2S-5}$, there is a dewetting transition from morphology 5 into morphology III, which can be calculated from the condition

$$f_{III}(v_\beta) = f_5(v_\beta) \tag{62}$$

[with f_5 from (22) and f_{III} from (4)]. Because there is no closed analytic expression for $f_5(v_\beta)$ as a function of v_β this condition has to be solved numerically. to obtain $w_{\gamma,III-5}$. The result depends on w_δ and is shown in Fig. 4 as solid green lines.

G. Instability lines

We determined all lines of discontinuous dewetting transitions between two- and single-droplet regimes, i.e., between regimes II-2S, II-2C, III-2S, III-2C, and III-5. The transition lines $w_{\gamma,II-2S}$ (eq (47)), $w_{\gamma,II-2C}$ (eq (55)), $v_{\beta,III-2X}$ (eq (57)), $v_{\beta,III-2C}$ (eq (61)), and $w_{\gamma,III-5}$ join smoothly to give a single line of *discontinuous dewetting transitions* between two- and single-droplet regimes. At these discontinuous transitions two branches of local minima of the free energy $f(v_\beta) = \min_{v_\beta^{(1)}}[f_{2d}(v_\beta, v_\beta^{(1)})]$ intersect and we find hysteresis, i.e., the energetically unfavorable state remains metastable up to an *instability line* (or spinodal). At the instability line the corresponding metastable minimum becomes an unstable saddle point such that $\partial f_{2d}/\partial v_\beta^{(1)} = 0$ and $\partial^2 f_{2d}/(\partial v_\beta^{(1)})^2 = 0$.

We first consider the instability of the single-droplet morphologies II and III with respect to wetting, i.e., a two-droplet morphology. As shown above there is no transition between the single-droplet morphology I and and any two-droplet morphology. Therefore, regime I has no instability line and we only have to discuss the instability lines of regimes II and III. The single-droplet states are boundary minima of $f_{2d}(v_\beta, v_\beta^{(1)})$ at $v_\beta^{(1)} = 0$ or $v_\beta^{(1)} = v_\beta$. It can be easily shown that $\partial f_{2d}/\partial v_\beta^{(1)}|_{v_\beta^{(1)}} > 0$ for all $w_\gamma < 1$ (because of the $((1-w_\gamma)v_\beta^{(1)})^{2/3}$-dependence of the free energy f_I). Therefore, the single-droplet states II and III remain metastable for all domain wettabilities such that the instability line for the single-droplet regimes II and III is the line

$$w_{\gamma,\mathrm{insII,III}} = 1 \quad \text{wetting instability II,III} \tag{63}$$

The continuous depinning transition between morphologies II and III at $v_{\beta,II-III}$ (see eq (27)) continues to exist in the metastable regime, i.e., above the discontinuous transition line between the single- and two-droplet regimes.

Next, we consider the instability lines of the two-droplet regimes with respect to dewetting into a single-droplet regime. There are additional instability lines for the instabilities with respect a depinning into other two-droplet regimes, which we have already discussed above. We have already discussed the instability lines of regime 2S in our discussion of depinning transitions between different two-droplet regimes: For $w_\gamma > w_{\gamma,c} = -1 + \sqrt{2}$, morphology 2S first undergoes a depinning transition into morphology 4 at $v_{\beta,2S-4}$, see (41) while it is only a metastable state, before morphology 4 becomes unstable at $v_{\beta,\mathrm{ins}\ 4}$, see eq. (42), with respect to dewetting. For $w_\gamma < w_{\gamma,c}$, on the other hand, there is a direct dewetting instability of morphology 2S without a transition into morphology 4 at $v_{\beta,\mathrm{ins}\ 2Sb}$, see eq. (45). This is a dewetting instability with respect to morphology II for $v_\beta < v_{\beta,\mathrm{dep}}$ and an instability with respect to morphology III for $v_\beta > v_{\beta,\mathrm{dep}}$.

We also discussed already one depinning instability line for regime 2C, the instability line (32), where the larger droplet depins and starts to wet the δ-substrate for $\cos\theta^{(2)} = w_\delta$. Another dewetting instability is encountered if the smaller droplet starts to depin and retract onto the γ-domain for $\cos\theta^{(1)} = w_\gamma$. This leads to a second instability line

$$v_{\beta,\mathrm{ins2Cb}} = 2(1-w_\gamma^2)^{-3/2} \tag{64}$$
$$\text{dewetting instability 2C}$$

This is a dewetting instability with respect to a single-droplet morphology because an intermediate transition into morphology 4 is not possible as discussed above. The instability line (64 is shown as dashed red line in Fig. 5 in the main text. The lines $v_{\beta,\mathrm{ins}\ 2Cb}$ and $v_{\beta,\mathrm{ins}\ 2Sb}$ meet and terminate at $w_\gamma = 0$ and $v_\beta = v_{\beta,SBT} = 2$.

Similarly, morphology 5 will become unstable with respect to dewetting if the smaller droplet starts to depin and retract onto the γ-domain for $\cos\theta^{(1)} = w_\gamma$.

$$v_{\beta,\mathrm{ins5b}} = \frac{1}{2}\frac{(1-w_\gamma)^2(2+w_\gamma) + (1-w_\delta)^2(2+w_\delta)}{(1-w_\gamma^2)^{3/2}}$$
$$\text{dewetting instability 5} \tag{65}$$

This instability line is shown as dashed light green line in Fig. 5 in the main text.

[1] P. Lenz and R. Lipowsky, Phys. Rev. Lett. **80**, 1920 (1998).

[2] P. Blecua, R. Lipowsky and J. Kierfeld, Langmuir **22**, 11041 (2006).

[3] Note that the numerical value for $\cos\theta^*_{2S}$ is very close to the value of $w_{\delta,c-}$ but that these two values are *different*,

as can be shown from their defining cubic and quartic eqs. (49) and (36).