Line tension at wetting

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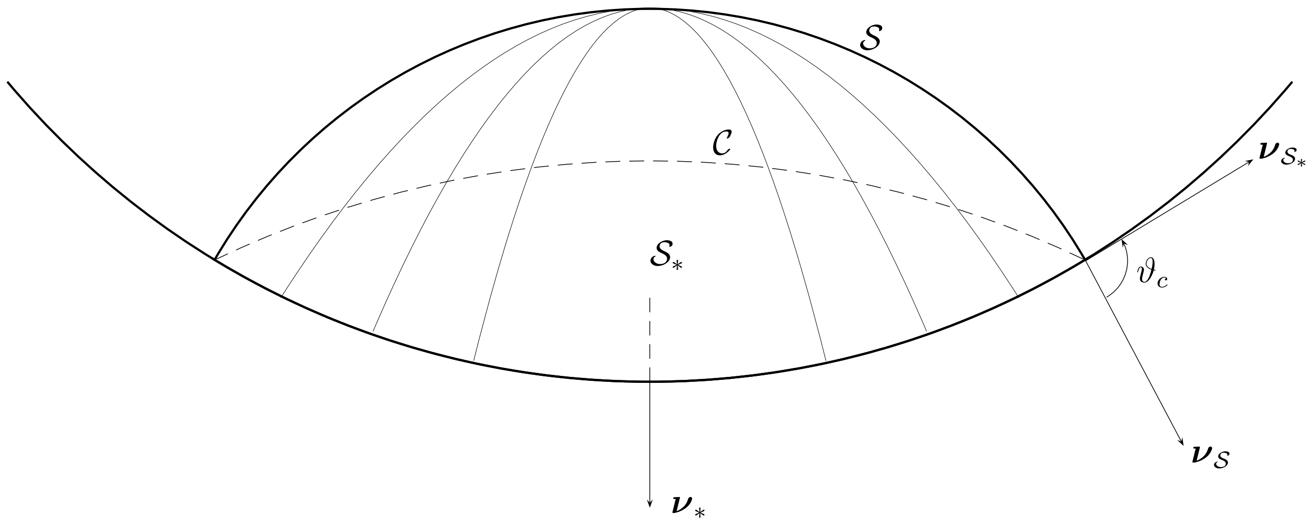
Outline

- What is line tension?
- Effects of line tension
- The sign of line tension
- Stability criterion
- Liquid bridges
- Sessile droplets
- Residual stability
- Conclusions and prospects

• What is line tension?



$\mathcal{S}$, $\mathcal{S}_*$: the free and the adhering surface of the droplet $\mathcal{B}$.

$\mathcal{C}$: contact line.

$\boldsymbol{\nu}$ and $\boldsymbol{\nu}_*$: outer unit normal vectors to $\mathcal{S}$ and $\mathcal{S}_*$.

$\boldsymbol{\nu}_{\mathcal{S}}$ and $\boldsymbol{\nu}_{\mathcal{S}_*}$: conormal unit vectors of $\mathcal{C}$ on $\mathcal{S}$ and $\mathcal{S}_*$.

$\vartheta_c \in [0, \pi]$: the contact angle.

$\vartheta_c = 0$: wetting; $\vartheta_c = \pi$: dewetting.

Continuum approach

The simplest free-energy functional

$$\mathcal{F}[\mathcal{B}] = \gamma \int_{\mathcal{S}} da + (\gamma - w) \int_{\mathcal{S}_*} da + \tau \int_{\mathcal{C}} ds$$

$\gamma := \gamma_{LV} > 0$: surface tension between the droplet and the vapour phase.

$w := \gamma_{LV} + \gamma_{SL} - \gamma_{SV} > 0$: adhesion potential.

τ: line tension.

Constraints

- vol $\mathcal{B} = const.$
- $\mathcal{S}_*$ is in contact with the substrate.

Remark: No bulk contributions in $\mathcal{F}$.

Historical remarks

Line tension was first introduced by Gibbs in his paper

On the equilibrium of heterogeneous substances:

“[Contact lines] might be treated in a manner entirely analogous to that in which we have treated surfaces of discontinuity”.

However, Gibbs also remarked that

“We may here add that the linear tension there mentioned (*i.e.* line tension) may have a *negative* value.”

Both theoretical computations (statistical mechanics) and experimental results predict (measure) both positive and negative line tensions.

• Effects of line tension

At equilibrium: $\mathcal{S}$ is a surface with constant mean curvature.

ϑ_c^0: the bare contact angle such that

$\cos\vartheta_c^0 = \frac{w-\gamma}{\gamma} \quad \in (-1, 1)$.

$\xi := \frac{\tau}{\gamma}$ is the characteristic length of the problem.

κ_{g*}: the geodesic curvature of $\mathcal{C}$, viewed as a curve on $\mathcal{S}_*$.

Along $\mathcal{C}$ the following generalized Young equation holds:

$$\cos\vartheta_c = \cos\vartheta_c^0 + \xi\kappa_{g*}$$

[Vesselovsky & Pertzov (1936), Pethica (1961), Gretz (1966)]

[variable τ: Swain & Lipowsky (1998)]

Comments

- According to recent estimates (Wang *et al.* 2001), $|\xi|$ ranges from 10^{-8} to 10^{-6}m.

- Line tension effects can be appreciated for small droplets, with typical linear dimensions of some microns.

- κ_{g*} in general depends upon the contact angle ϑ_c.

- If $\kappa_{g*} = 0$ (*e.g.* $\mathcal{C}$ is a straight line, as in liquid bridges) line tension does not affect the contact angle at equilibrium.

- τ can be measured indirectly through ϑ_c

• The sign of line tension

$$\tau \int_{\mathcal{C}} ds \,.$$

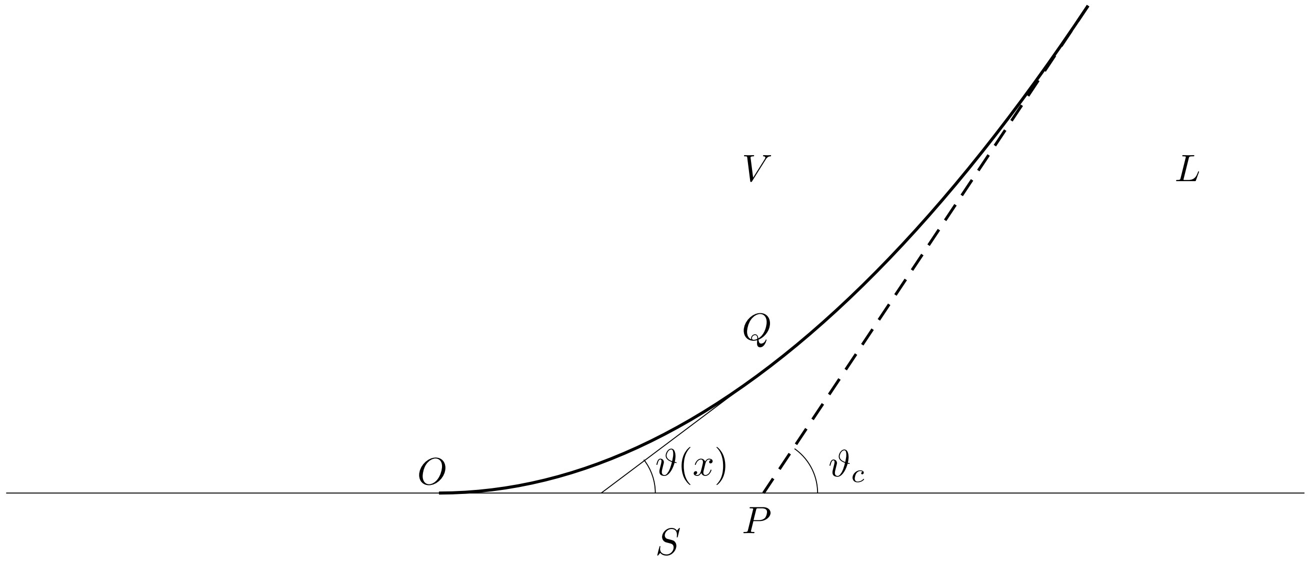
A negative τ makes $\mathcal{C}$ unstable against perturbations with a short wavelength (Steigmann & Li 1995).

The objection

"in the three-phase equilibrium the contact line cannot pucker to increase its length without at the same time changing the areas of the two-phase interfaces –which are of positive tension– in such a way as to increase the free energy of the whole system" (p. 237 of Rowlinson & Widom, 2002).

is weak.

Microscopic approach to line tension



Theoretical computations based on microscopic models do not forbid negative line tensions.

Consistency requirement: The typical length scale of the destabilizing modes should not be to small.

• Stability criterion

A stability criterion is needed to understand the main properties of the destabilizing modes.

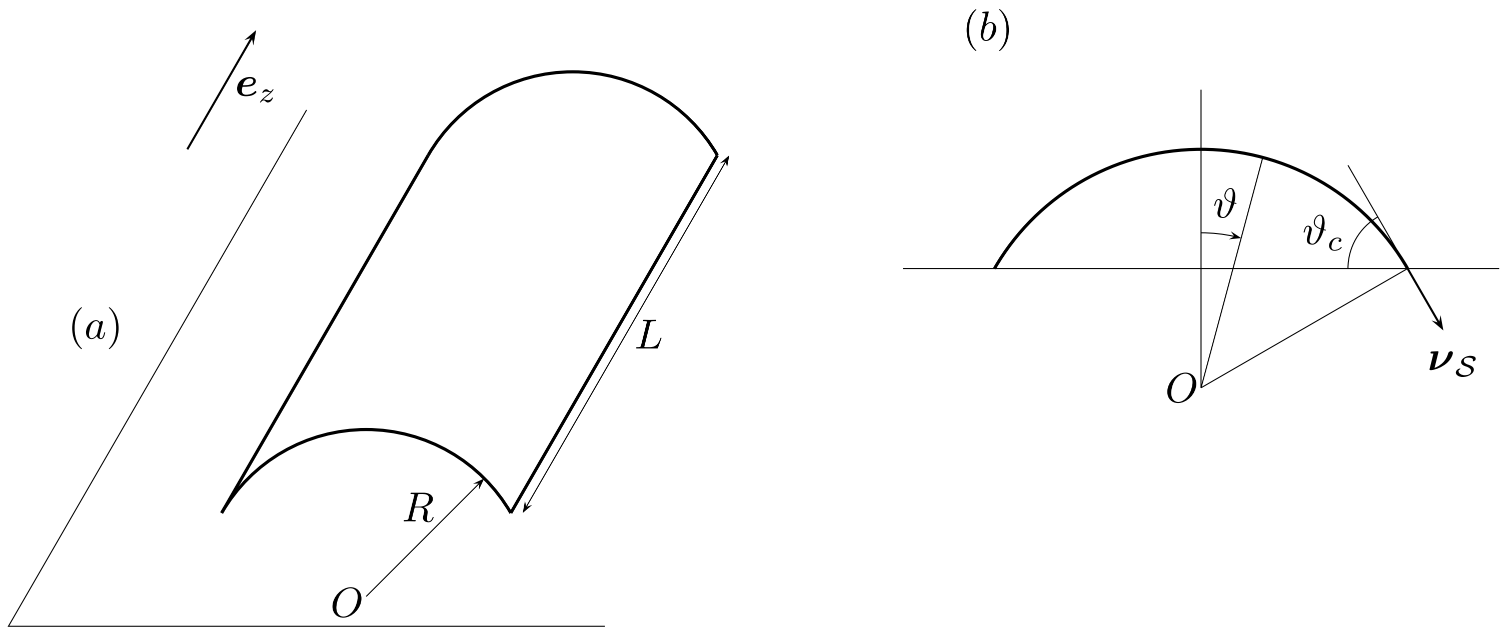
[Rosso & Virga (2003, 2004); Brinkmann, Kierfeld, & Lipowsky (2004)]

Strategy

- Compute the second variation $\delta^2\mathcal{F}$ of the free-energy functional.
- Account for the constraints up to second order.
- Minimize $\delta^2\mathcal{F}$ on a suitable set.

• Liquid bridges

(Rosso & Virga 2004; Brinkmann, Kierfeld, & Lipowsky 2005)



The substrate is flat.

$\mathcal{C}$: two straight-line segments: $\kappa_{g*} = 0$.

At equilibrium $\vartheta_c = \vartheta_c^0$, independently of line tension.

Stability analysis

$u(\vartheta, z)$: perturbation along the normal to the bridge free surface.

λ: multiplier associated with the volume constraint.

The second variation $\delta^2\mathcal{F}$ is minimized on the set

$$\int_{\mathcal{S}} u^2 da = 1 \tag{1}$$

μ is the corresponding multiplier.

Eigenvalue problem

The Euler-Lagrange equation for $\delta^2\mathcal{F}$ is

$$\frac{1}{R^2}\frac{\partial^2 u}{\partial\vartheta^2}+\frac{\partial^2 u}{\partial z^2}+(\mu+\frac{1}{R^2})u+\lambda=0 \tag{2}$$

subject to

$$\frac{1}{R}\sin^2\vartheta_c\left.\frac{\partial u}{\partial\vartheta}\right|_{\vartheta=\vartheta_c}-\xi\left.\frac{\partial^2 u}{\partial z^2}\right|_{\vartheta=\vartheta_c}-\frac{1}{R}\sin\vartheta_c\cos\vartheta_c u(\vartheta_c,z)=0\,. \tag{3}$$

L measures the perturbed length of the bridge:

$$u(\vartheta,0)=u(\vartheta,L)=0\,,\quad \forall\vartheta\in[0,\vartheta_c]\,.$$

Symmetry requirement

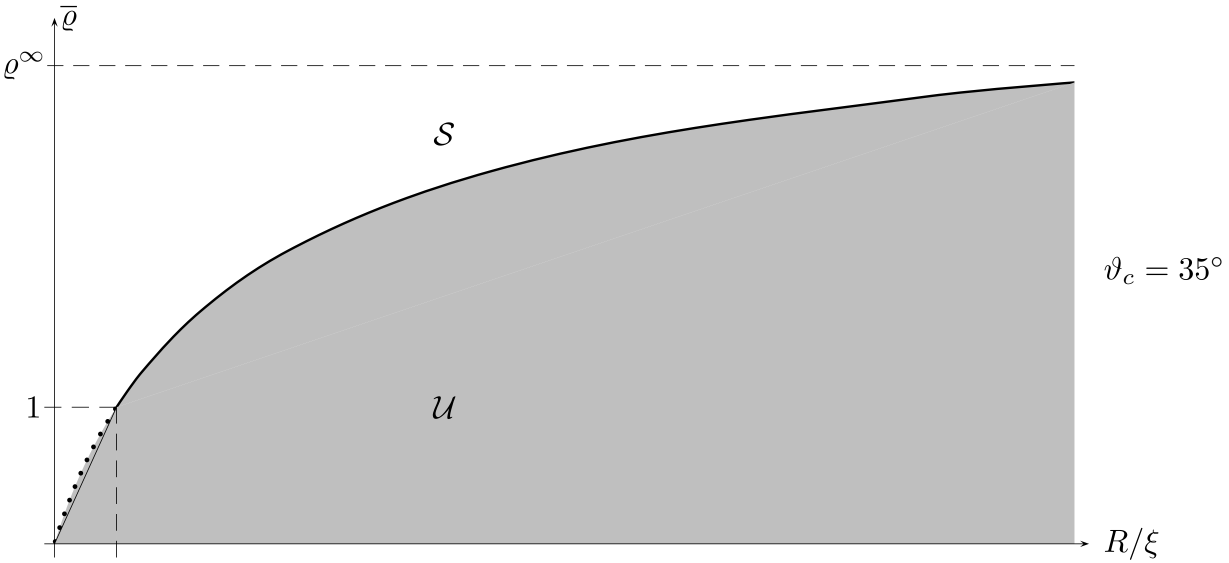
$$\left.\frac{\partial u}{\partial\vartheta}\right|_{\vartheta=0}=0\quad\forall z\in[0,L]\,.$$

The smallest eigenvalue $\mu_{\min}$ for which (2)-(3) can be solved coincides with the minimum of $\delta^2\mathcal{F}$ on the set (1).

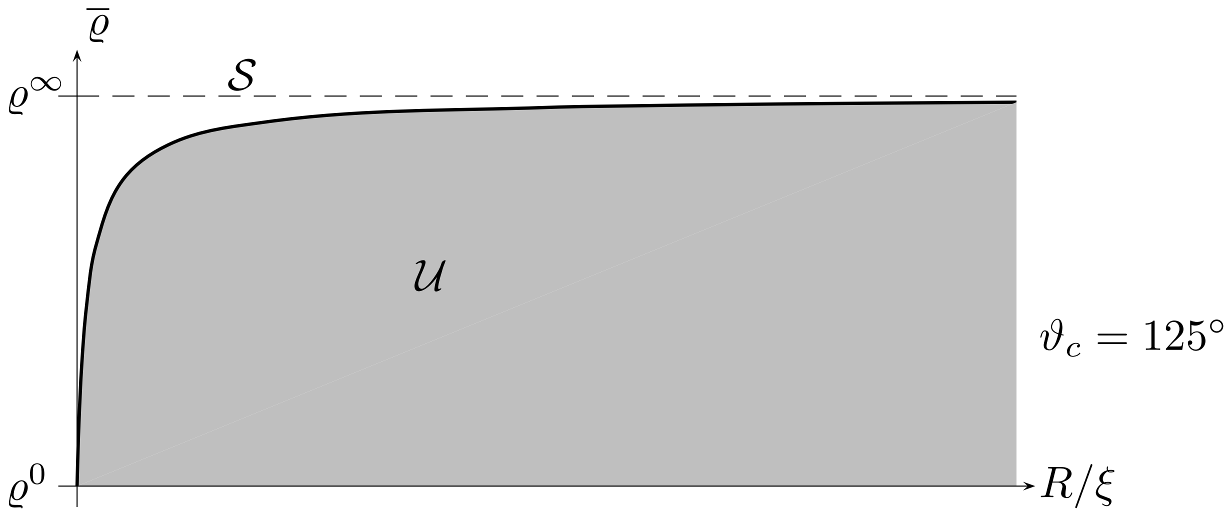
Stability diagrams I: $\xi := \frac{\tau}{\gamma} > 0$, $\vartheta_c \in (0, \frac{\pi}{2})$

$$u(\vartheta, z) = u_0(\vartheta) + \sum_{n=1}^{\infty} \sin\left(\frac{2n\pi}{L} z\right) u_n(\vartheta) .$$

Bridges are stable when $\varrho_n := \left(\frac{2\pi n R}{L}\right)^2 > \overline{\varrho}(\vartheta_c, \frac{R}{\xi})$.



Stability diagrams II: $\xi := \frac{\tau}{\gamma} > 0,\ \vartheta_c \in (\frac{\pi}{2}, \pi)$



Remarks

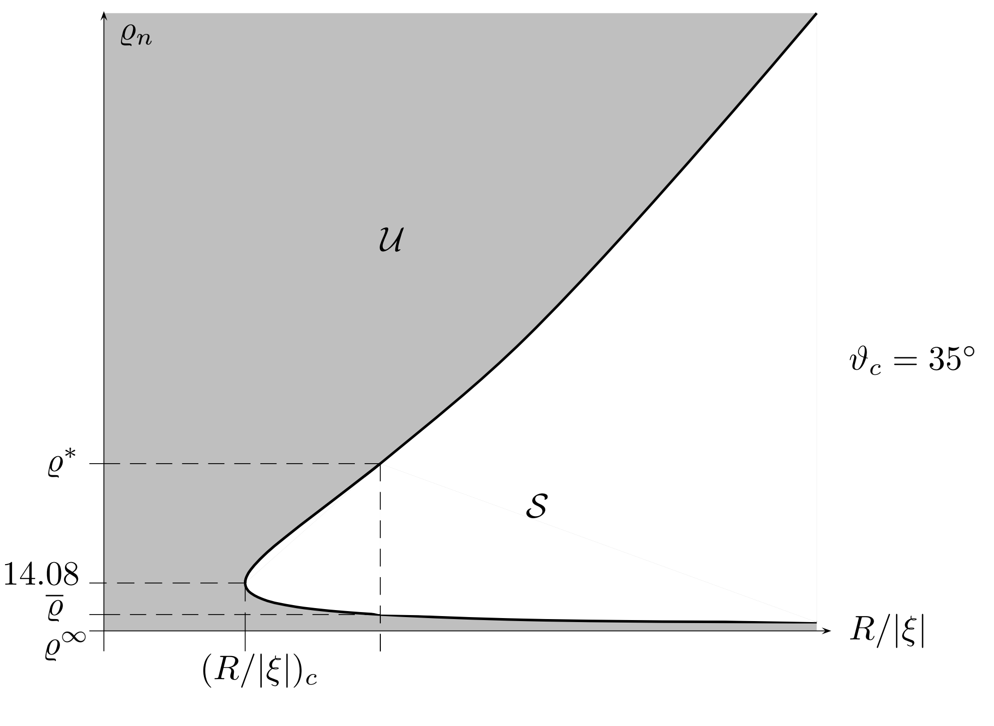
- The most dangerous modes have $n = 1$.
- $\varrho_\infty(\frac{\pi}{2}) = 1$: Rayleigh instability
- A positive line tension broadens the stability region. When $\vartheta_c \in (\frac{\pi}{2}, \pi)$ unstable modes exist also when τ is large.

Stability diagrams III: $\xi := \frac{\tau}{\gamma} < 0$.

If $R/|\xi| < (R/|\xi|)_c(\vartheta_c)$, no stable mode exists: line tension has a completely destabilizing effect.

If $0 < (R/|\xi|)_c(\vartheta_c) < R/|\xi|$, stable modes exist when

$$\overline{\varrho} < \varrho_n < \varrho^*$$

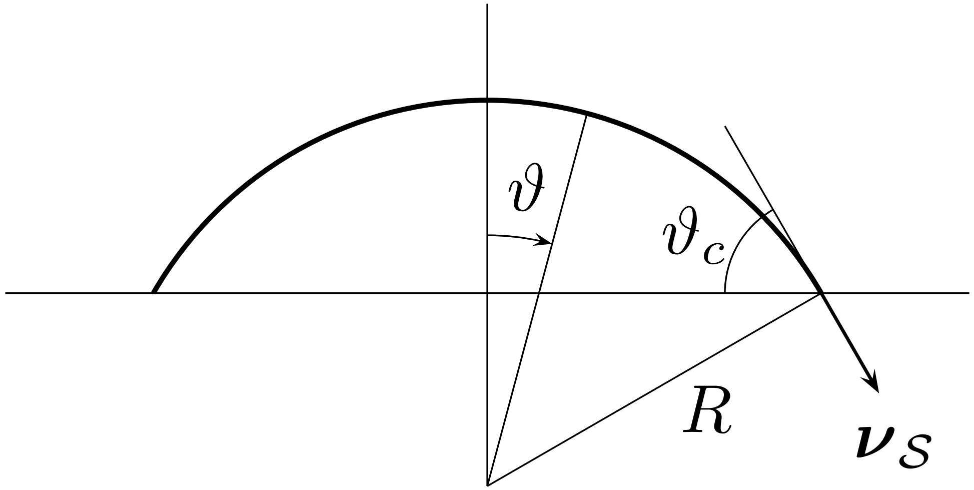


Remarks

- A notion of conditional stability can be established for $\tau < 0$, provided $|\tau|$ is not too large.
- When n increases, instability definitively occurs.

• Sessile droplets

(Widom, 1995; Guzzardi, Rosso & Virga 2005)

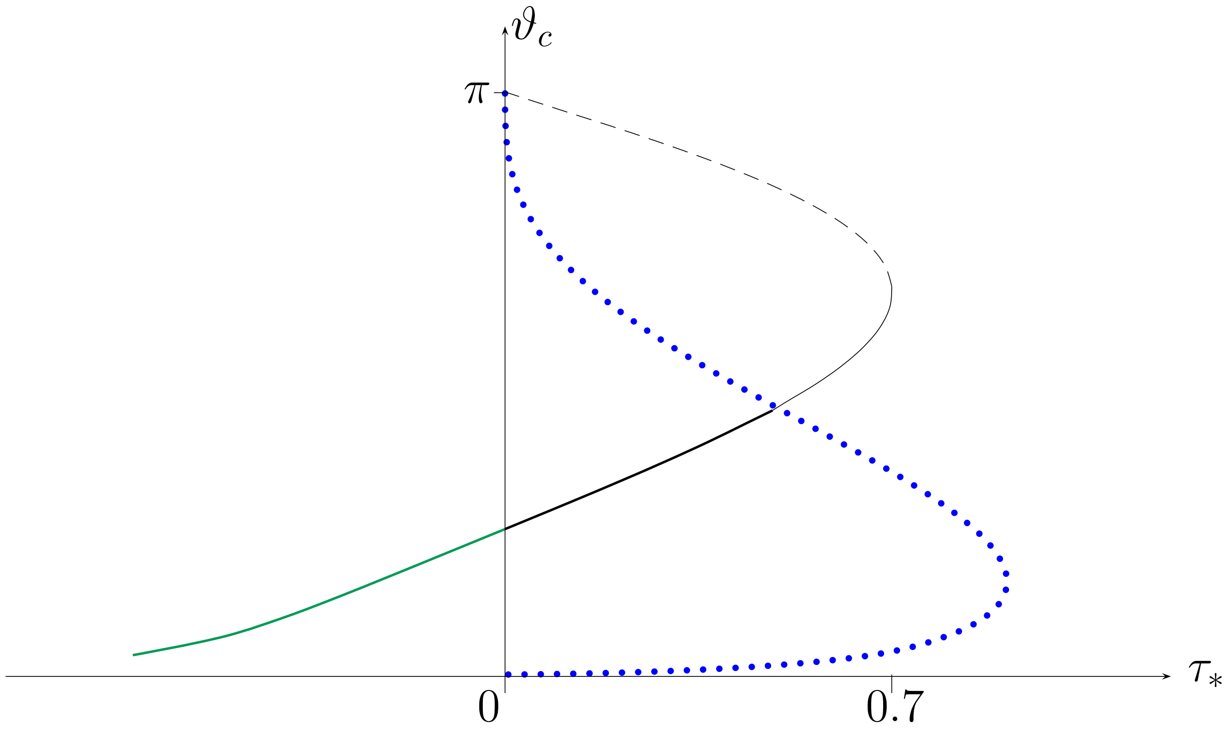


Motivation: Extend Widom's stability analysis of a spherical cap laid on a flat substrate, which applied to the restricted class of perturbations that map spheres into spheres.

Fix $\vartheta_c^0 \in (0, \pi)$ and the volume V of $\mathcal{B}$.

Dimensionless line tension $\tau_* := \frac{\xi}{\sqrt[3]{\frac{3V}{\pi}}}$

Widom's results



Dotted line: locus of first-order drying transitions.

Local stability is predicted for negative line tensions.

Improved stability analysis

Set $\varepsilon := \frac{\xi}{R}$

Equilibrium equation for $\delta^2\mathcal{F}$ on $\mathcal{S}$

$$\Delta_s u + (\mu + 2)u = \lambda$$

boundary condition along $\mathcal{C}$

$$\left[\frac{\partial u}{\partial\vartheta} - \frac{\varepsilon}{(\sin\vartheta_c)^4}\frac{\partial^2 u}{\partial\varphi^2} - \frac{\varepsilon + \sin^3\vartheta_c\cos\vartheta_c}{(\sin\vartheta_c)^4}u\right]\Bigg|_{\vartheta=\vartheta_c} = 0$$

Δ_s: Laplace operator on the sphere.

Set $u = \overline{u} + c$ $\qquad\qquad \Delta_s\overline{u} + (\mu + 2)\overline{u} = 0$

Expansion

$$\overline{u} = \sum_{m=0}^{\infty} a_m u_m(\vartheta)\mathrm{trig}(m\varphi)\,, \tag{4}$$

where

$$\mathrm{trig}(m\,\varphi) := \begin{cases} \sin(m\varphi) \quad \text{or} \quad \cos(m\varphi) & \text{if } m \neq 0 \\ 1 & \text{if } m = 0, \end{cases}$$

$u_m(\vartheta) = P_\nu^m(\cos\vartheta)$: associated Legendre functions with

$$\mu + 2 = \nu(\nu + 1)$$

Unstable modes

$$\nu \in \mathcal{U} := \left\{ \left[-\frac{1}{2} + \mathrm{i}0\,,\ -\frac{1}{2} + \mathrm{i}\infty \right[\cup \left[-\frac{1}{2}\,,\ 1 \right[\right\}\,.$$

Insert each mode into the boundary condition along $\mathcal{C}$, and solve for ε

If $m \neq 0, 1$

$$\varepsilon_\nu^m(\vartheta_c) = -(\sin\vartheta_c)^4 \frac{\left(\cot\vartheta_c \; P_\nu^m(\cos\vartheta_c) - \left.\frac{\partial P_\nu^m(\cos\vartheta)}{\partial\vartheta}\right|_{\vartheta_c}\right)}{(1-m^2)\, P_\nu^m(\cos\vartheta_c)}$$

If $m = 0$

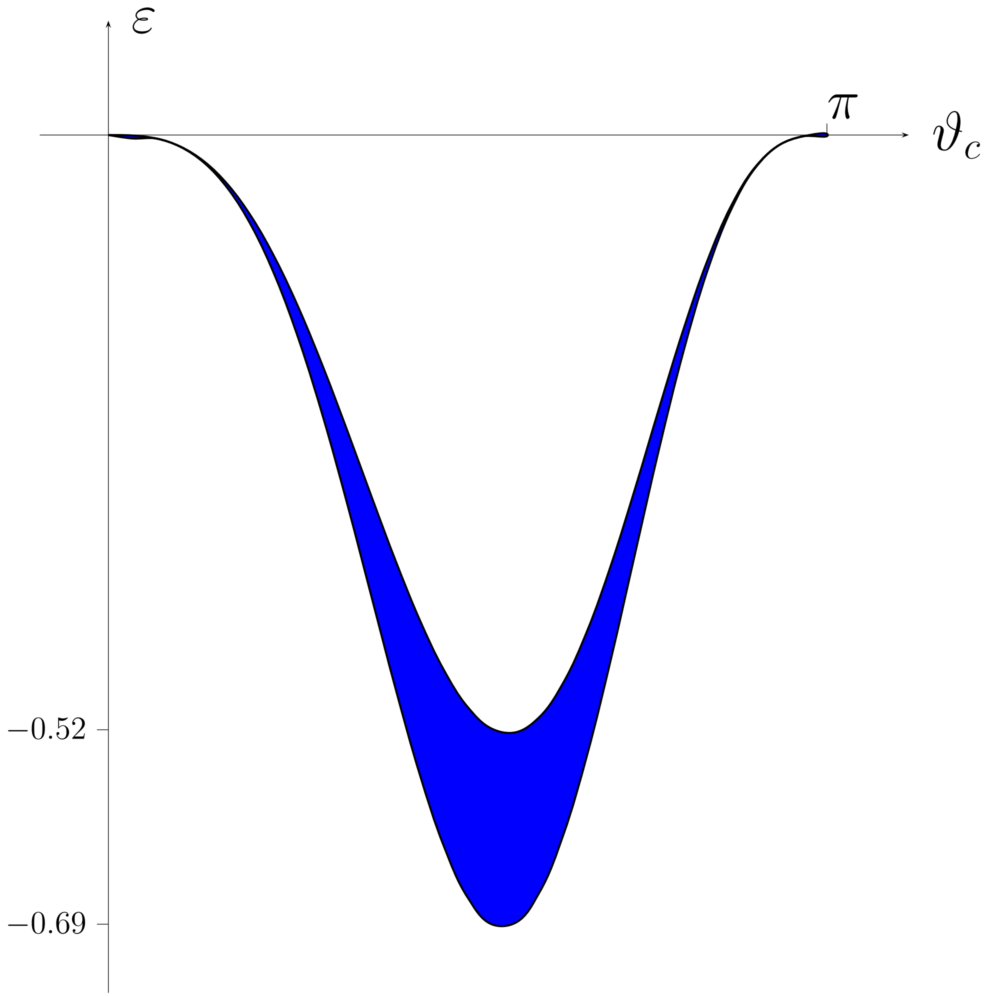
$$\varepsilon_\nu^m(\vartheta_c) = -(\sin\vartheta_c)^4 \frac{\left(\cot\vartheta_c (P_\nu(\cos\vartheta_c) + c(\vartheta_c,\, \nu, 0)) - \left.\frac{\partial P_\nu(\cos\vartheta)}{\partial\vartheta}\right|_{\vartheta_c}\right)}{c(\vartheta_c, \nu, 0) + P_\nu(\cos\vartheta_c)}$$

If the representative point $(\vartheta_c, \varepsilon)$ of an equilibrium configuration belongs to the graph of $\varepsilon_\nu^m(\vartheta_c)$ with $\nu \in \mathcal{U}$, the equilibrium configuration is unstable.

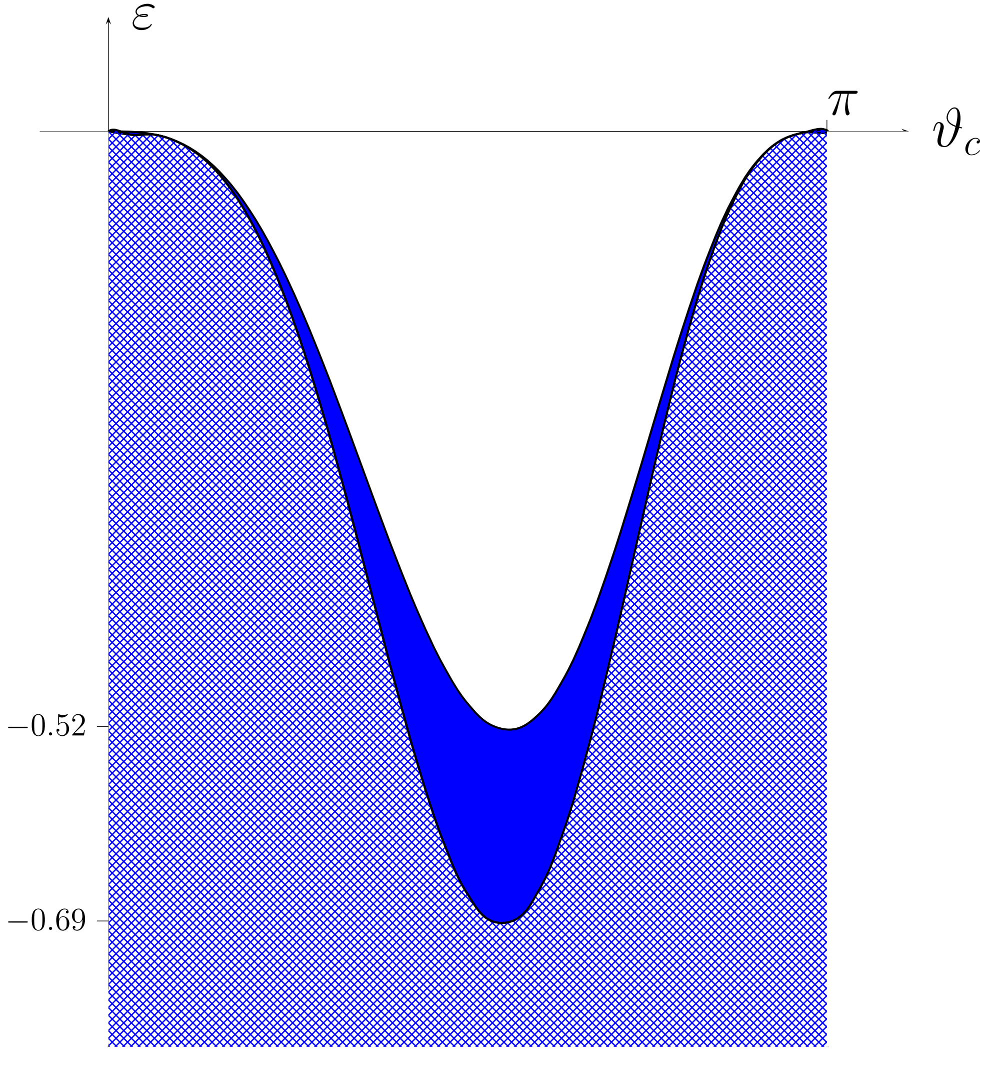
Results

- Unstable modes with $m = 0$: effective only for positive line tensions (as in Widom, 1995).
- $m = 1$: marginal modes, translations.
- Unstable modes with $m > 1$: effective only for negative line tensions.

$m = 2$, spherical ($\nu \in [-\frac{1}{2}, 1[$) unstable modes

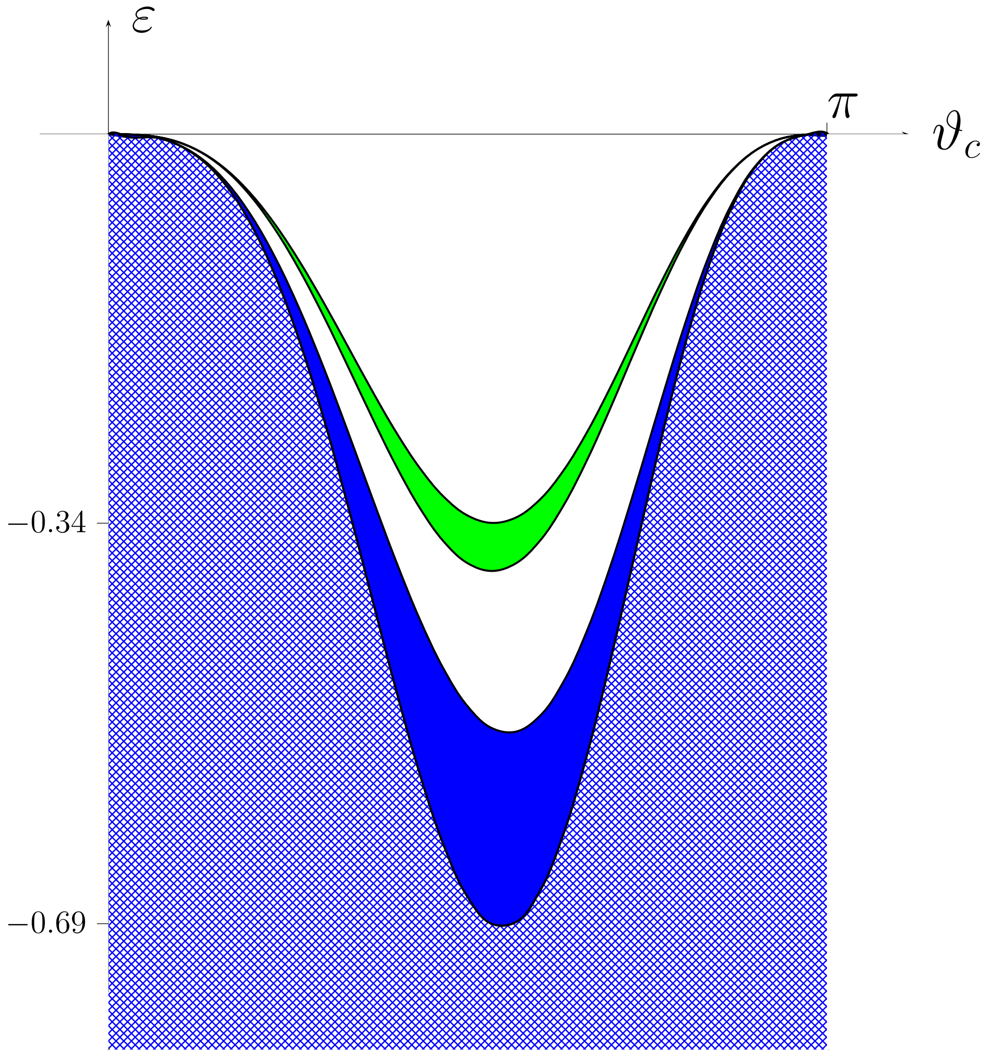


$m = 2$, spherical and conical $(\nu \in \left[-\frac{1}{2} + \mathrm{i}0\,,\ -\frac{1}{2} + \mathrm{i}\infty\right[)$ unstable modes

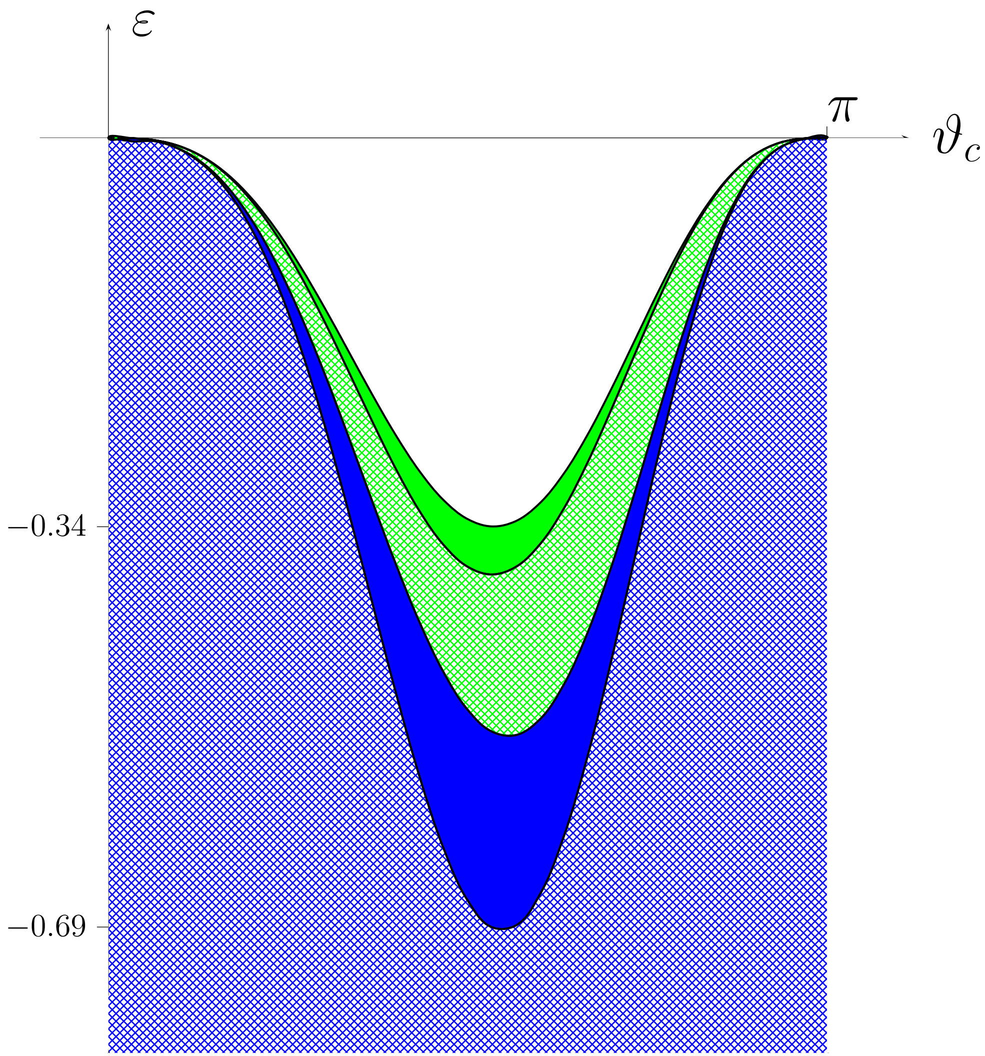


$m = 2$, spherical and conical unstable modes

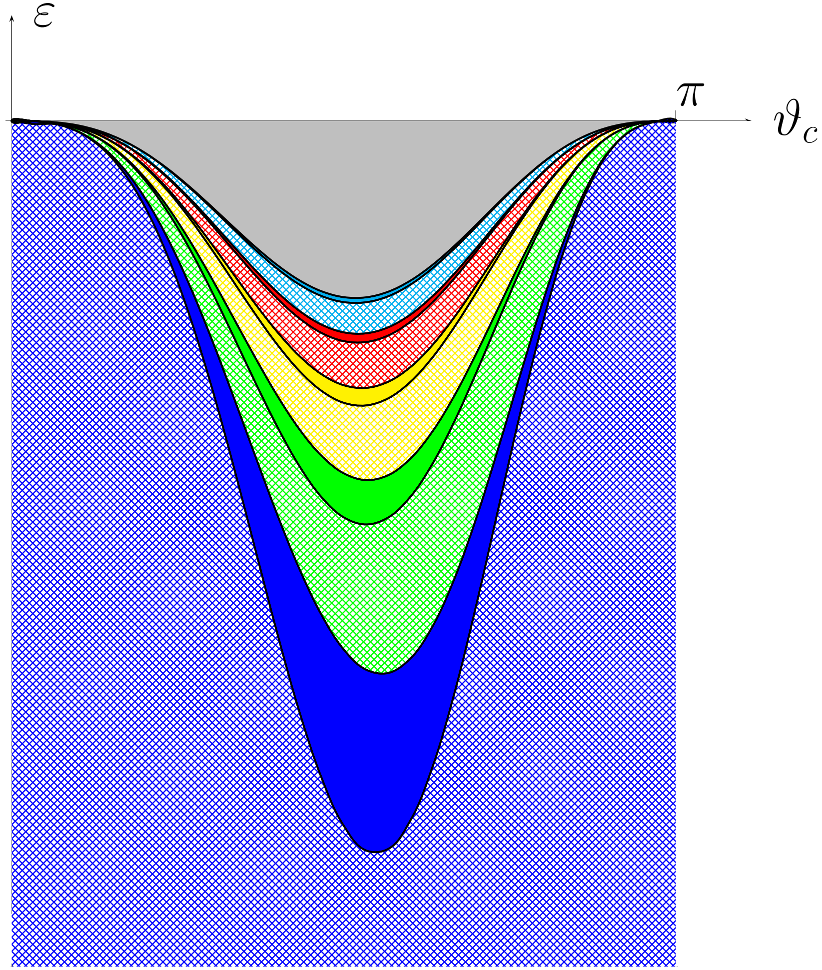
$m = 3$, spherical unstable modes



$m = 2,3$: spherical and conical unstable modes

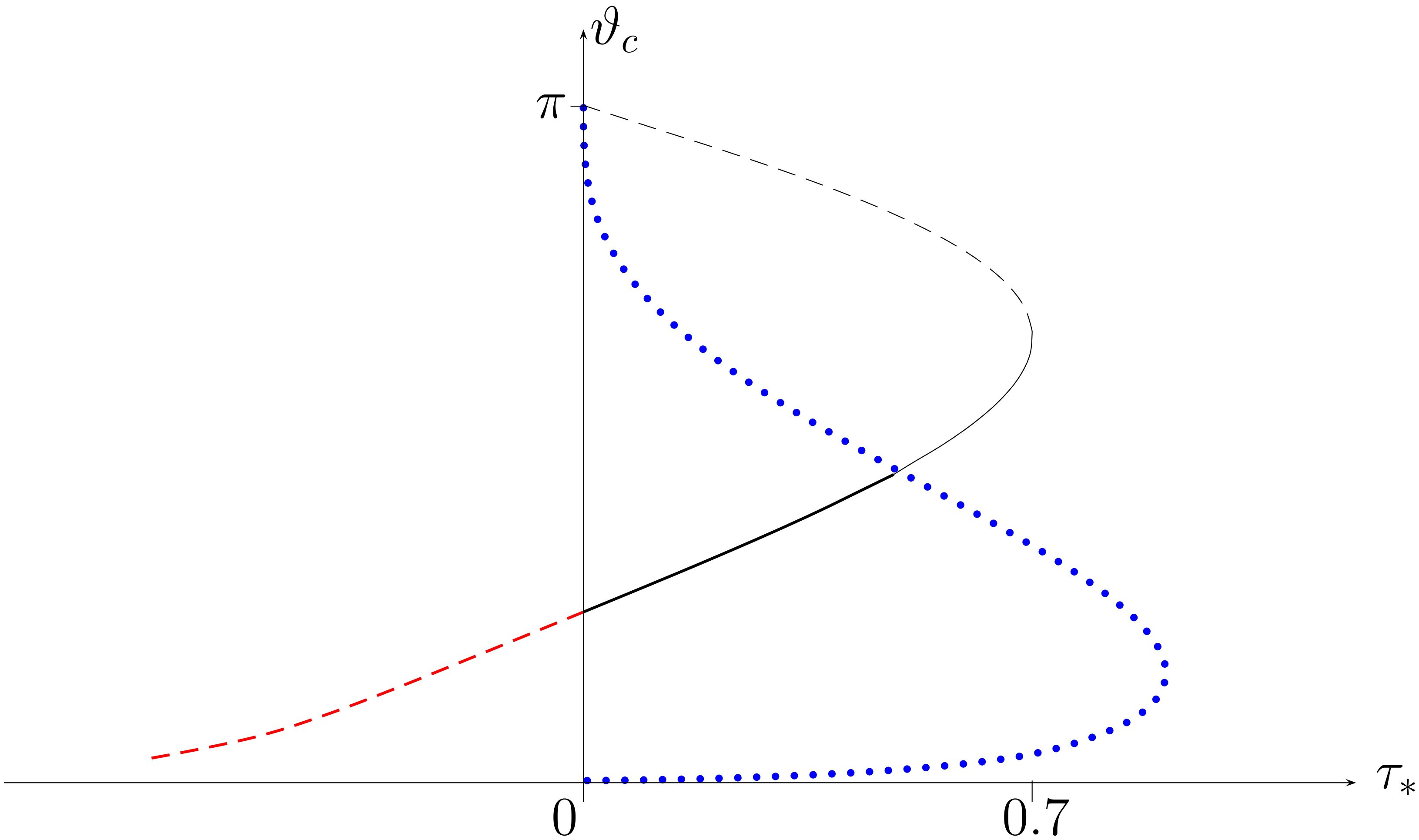


$m > 2$: spherical and conical unstable modes



On increasing m, all equilibria are destabilized.

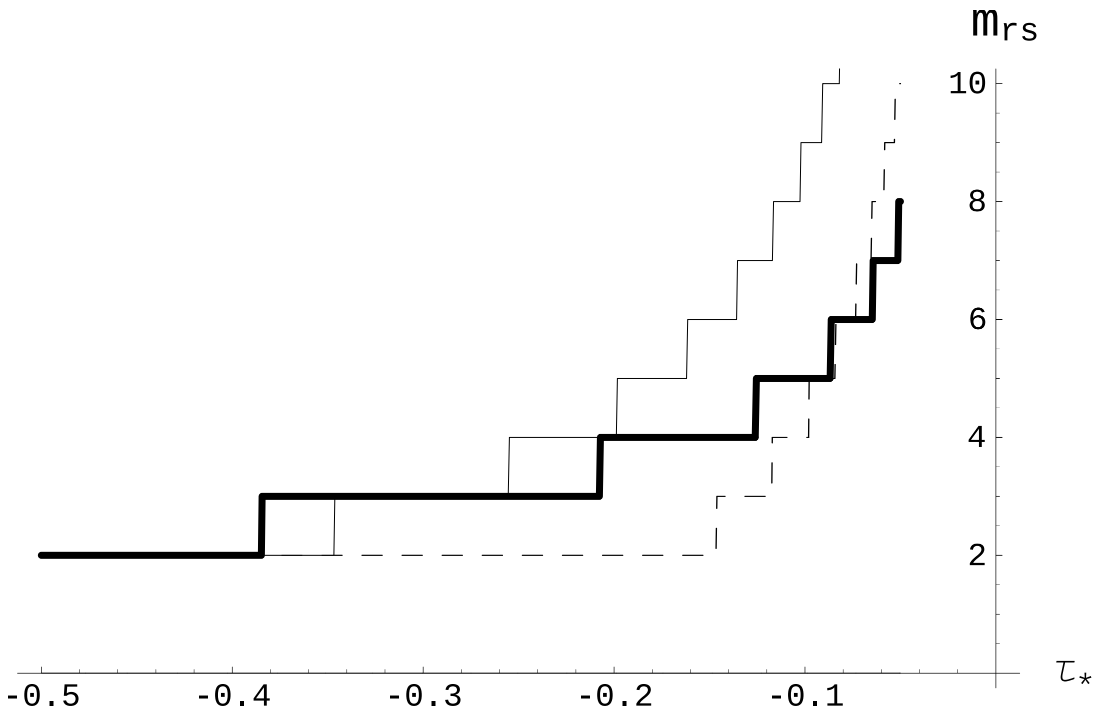
Amendend bifurcation diagram



• Residual stability (negative line tension)

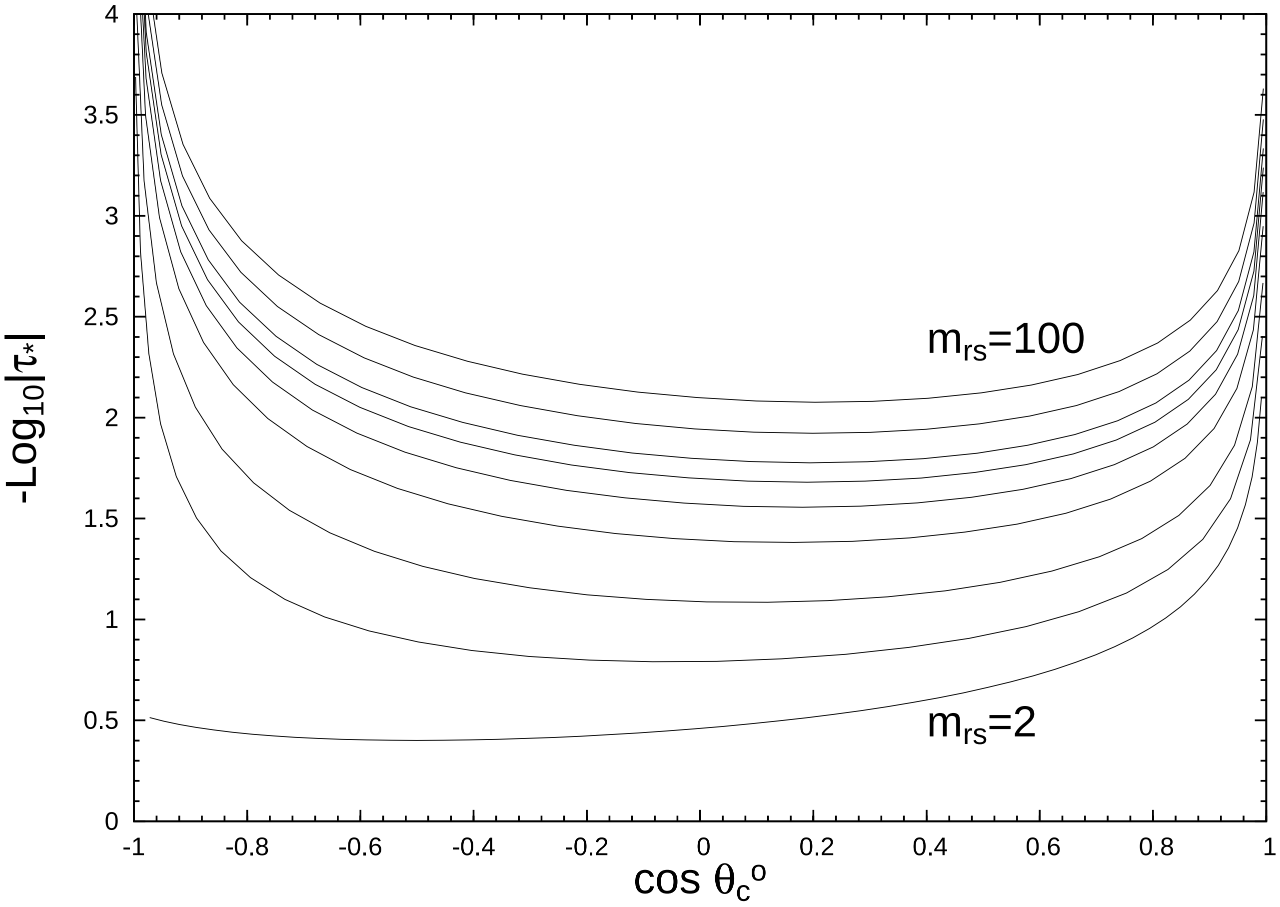
For a given equilibrium configuration, find the smallest value m_{rs} of m for which the corresponding modes are unstable.

For $\tau_* \approx -0.063$ (Widom's estimate)



For the values of ϑ_c^0 plotted here $(\pi/4,\, \pi/2,\, 3\pi/4)$, $m_{\mathrm{rs}} > 6$.

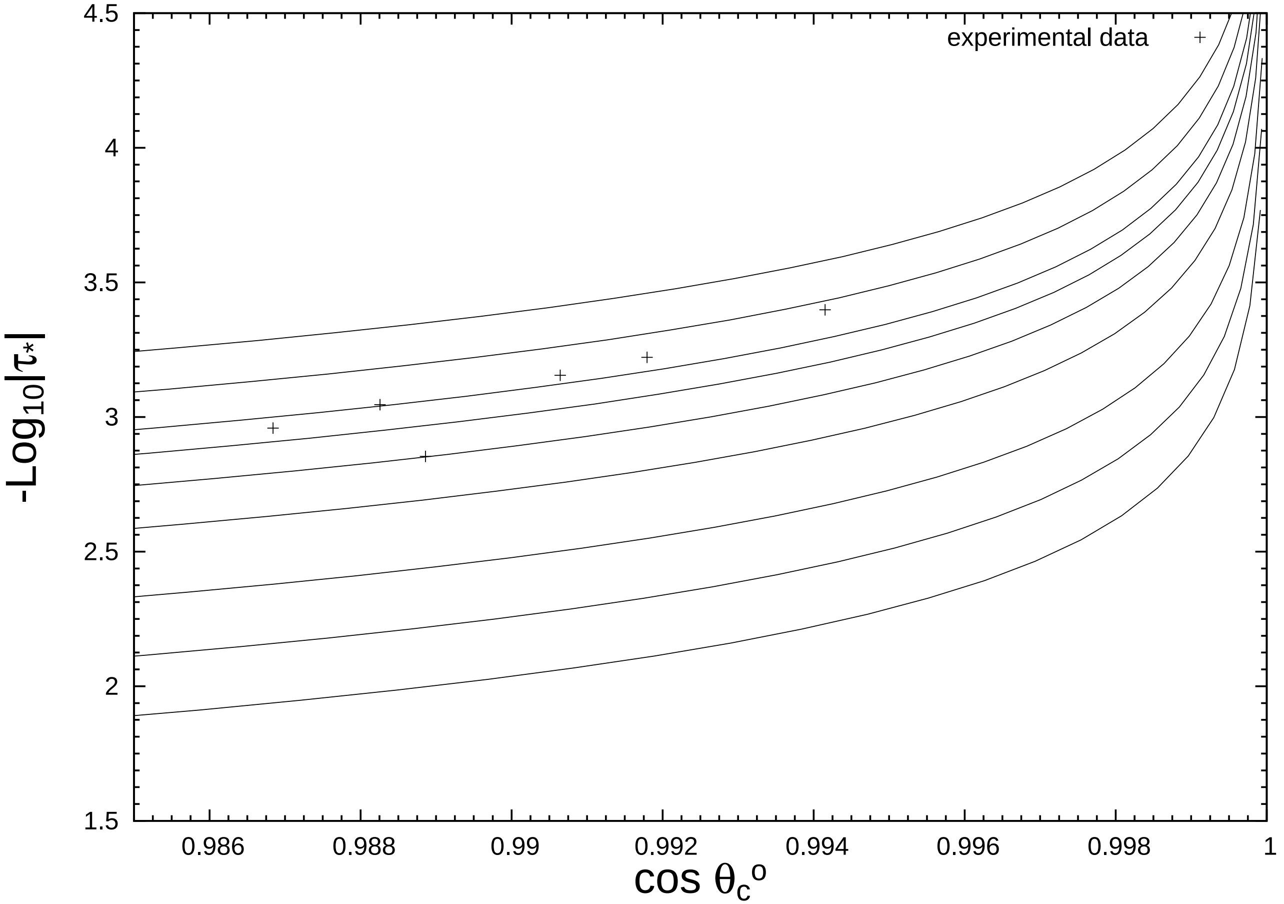
On varying (ϑ_c^0, τ_*), the loci with $m_{\rm rs}$ constant are as below



How to use this information?

Comparison with experimental data

(Wang, Betelu, & Law 2001)



Most experimental points fall across the same curve $m_{\rm rs} = 50$.

• Conclusions...

- A notion of residual stability has been introduced, which applies to droplets with negative line tensions τ, provided that $|\tau|$ is not too large.

- The index $m_{\rm rs}$ of residual stability, which counts the stable modes, estimates the degree of reliability for negative measurements of τ.

- We propose $m_{\rm rs}$ as a means to settle within the continuum model the controversy about the measurability of negative line tensions.

• ...and prospects

- Explore the rôle of curved substrates (Guzzardi & Rosso, 200...)

- Study the stabilizing rôle of the curvature σ of $\mathcal{C}$ by adding, in the spirit of Boruvka & Neumann (1977), a term like $\alpha \int_{\mathcal{C}} \sigma^2 ds$ to the free energy (Rosso & Virga 20...).

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Graphs of $\varrho^{\infty}(\vartheta_c)$ and $\varrho^{0}(\vartheta_c)$