

# The shapes of water

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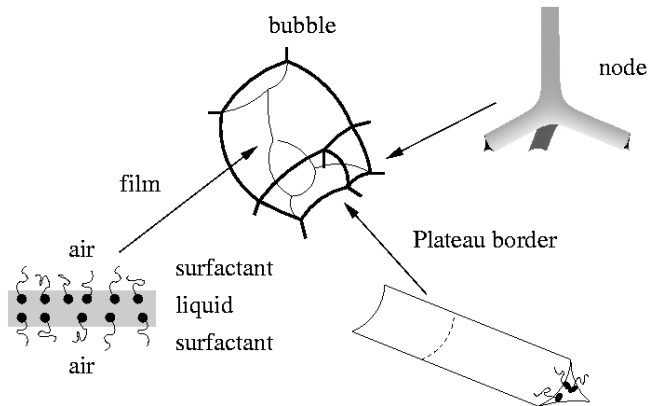
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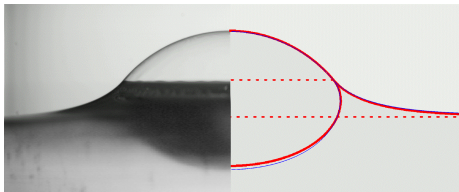
# Consider a foam

- A foam consists of pockets, called cells or bubbles, of gas or liquid enclosed in liquid – liquid foams – or solid – solid foams.
- In liquid foams, liquid is distributed over films, Plateau borders (PBs), and nodes.



# Bubble bubble, toil and trouble

- The building blocks of foams are bubbles.
- Previously we studied the shapes of bubbles on a **liquid** surface:



Teixeira *et al.*. *Langmuir* **31**, 13708–13717 (2015).

- On a **solid** surface, they can have unusual shapes:



- ... but curved geometries are difficult.

# Consider a *confined* foam

- In confined foams there exist wall PBs, or menisci, where the films meet the confining substrates.

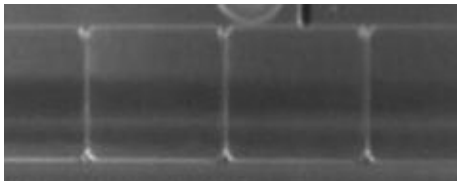


Photo courtesy of M. F. Vaz.

- One usually assumes that the liquid wets the substrates completely, but this need not be so.
- What is the shape of a PB on a surface of a given wettability (i.e., contact angle  $\theta_c$ )? **Can that surface support a foam?**
- This is important for firefighting foams, containers for foamy foodstuffs, etc.

# Theory: model PB and the Young-Laplace equation

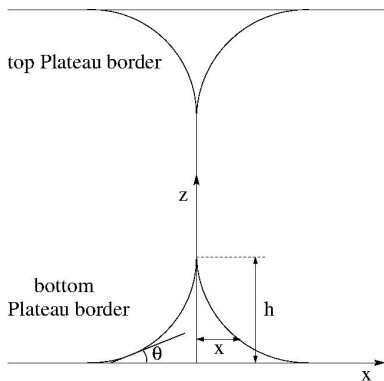
Young-Laplace equation for PBs where flat film meets planar substrate:

$$\left[ 1 + \left( \frac{dx}{dz} \right)^2 \right]^{-3/2} \frac{d^2x}{dz^2} = - \frac{\Delta p}{\gamma}$$

$\Delta p = [p_b(z=0) - \rho g z] - p_a$   
is pressure difference across the interface ( $\propto$  curvature),  $\gamma$  is liquid-gas surface tension.

Boundary conditions:

- 1  $dx/dz(z=0) = -\cot \theta_c$  (solid substrate);
- 2  $dz/dx(x=0) = +\infty$  (PB apex).



# Theory: solving the Young-Laplace equation

- Rewrite equation in terms of film inclination  $\theta(z)$ : boundary conditions are  $\theta(0) = \theta_c$ ,  $\theta(h) = \pi/2$ .
- Assume hydrostatic PBs, normalise lengths by  $h$  and introduce Bond number  $Bo = \rho gh^2/\gamma$ .
- Analytically exact solutions for bottom (+) and top (-) PBs:

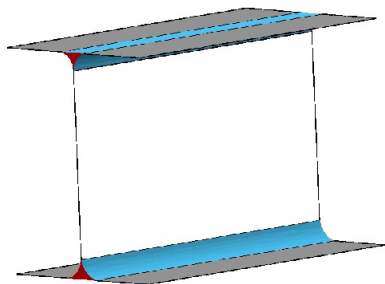
$$x'(z') = \int_{z'}^1 \frac{(1 - z'') (\cos \theta_c \pm \frac{Bo}{2} z'') dz''}{\left[1 - (1 - z'')^2 (\cos \theta_c \pm \frac{Bo}{2} z'')^2\right]^{1/2}}$$

- In zero gravity ( $Bo = 0$ , top=bottom):

$$x'(z') = \frac{1}{\cos \theta_c} \left\{ 1 - \left[1 - (1 - z')^2 \cos^2 \theta_c\right]^{1/2} \right\}$$

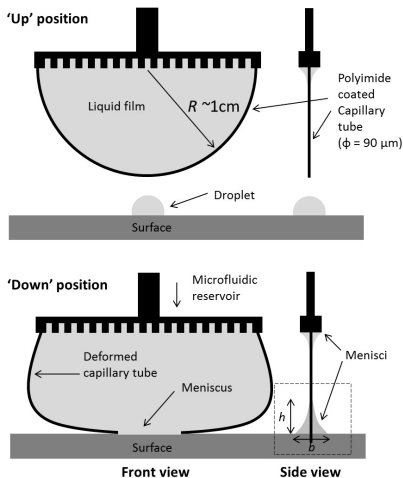
# Simulation: Surface Evolver (SE)

- Discretise each interface and perform direct numerical minimisation of surface energy for a fixed PB area.
- Only half PB is simulated, by symmetry.
- Discretisation induces a small, unphysical, 'contact' angle where the PBs meet the vertical film.



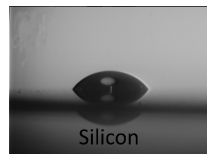
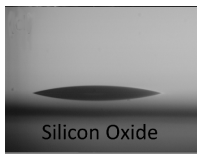
# Experiment: set-up

- Contact angle meter (GBX Scientific Instruments, France).
- Commercially available soap solution (Pustefix, Germany), surface tension  $\gamma = 28.2 \pm 0.3 \text{ mJ m}^{-2}$ ,  $\lambda_c \approx 1.7 \text{ mm}$ .
- In-house microfluidic tool consisting of (i) microfluidic reservoir with a number of capillary slots, made of ABS plastic; (ii) thin, flexible, hydrophilic loop which supports liquid film, made of polyimide-coated capillary tubing (Molex, USA). **Gives bottom PB shape only, not top.**
- We measure: meniscus width at substrate  $2x$ ; meniscus height  $h$ .

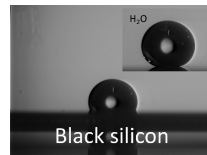
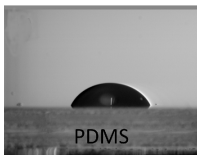




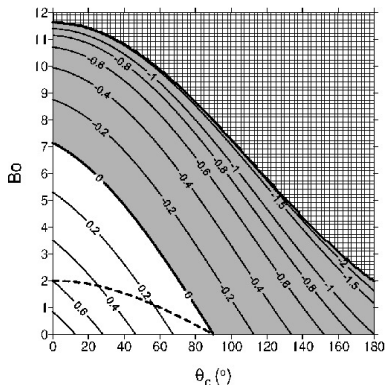
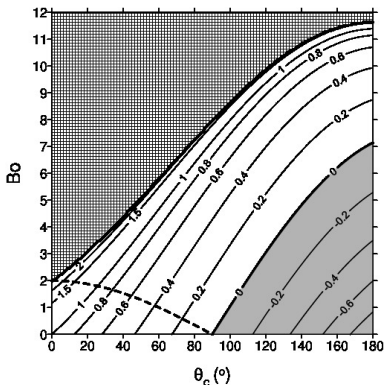
# Experiment: substrates studied



Material	$\theta_c$ ( $^\circ$ )
SiO <sub>2</sub>	18.2 $\pm$ 2.8
Teflonised polished Si	51.7 $\pm$ 0.3
PDMS elastomer	61.0 $\pm$ 2.1
Teflonised rough Si	64.0 $\pm$ 0.4
Teflonised black Si	109.3 $\pm$ 0.3

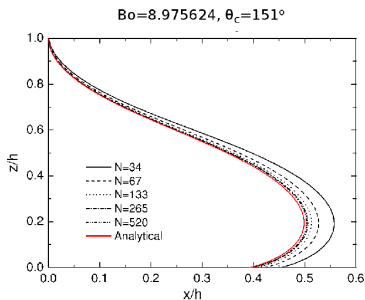
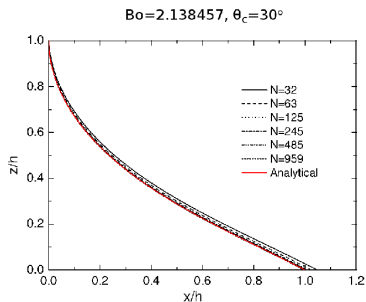


# Results: foam-phobia and foam-philìa, theory



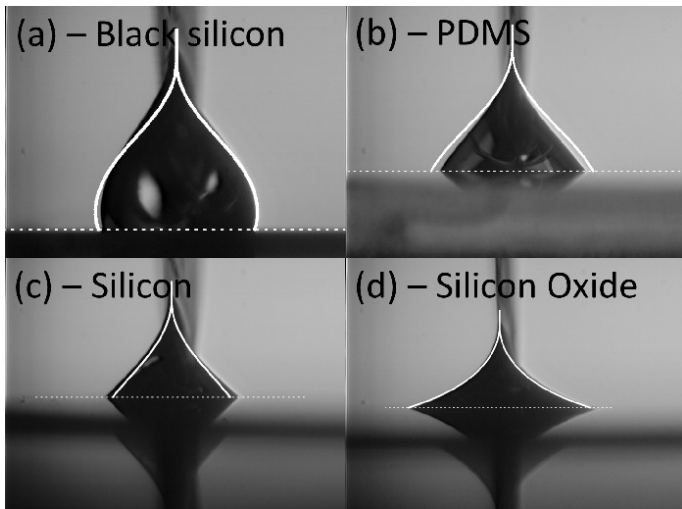
Domains of allowed (white, below dashed line only in right panel) and forbidden (elsewhere) PBs in  $(\theta_c, Bo)$  space, at the bottom (left) and top (right) substrates. The solid lines are loci of constant  $x'(z' = 0)$ . The dashed line is  $Bo = 2 \cos \theta_c$ .

# Results: bottom PB shapes, theory + SE



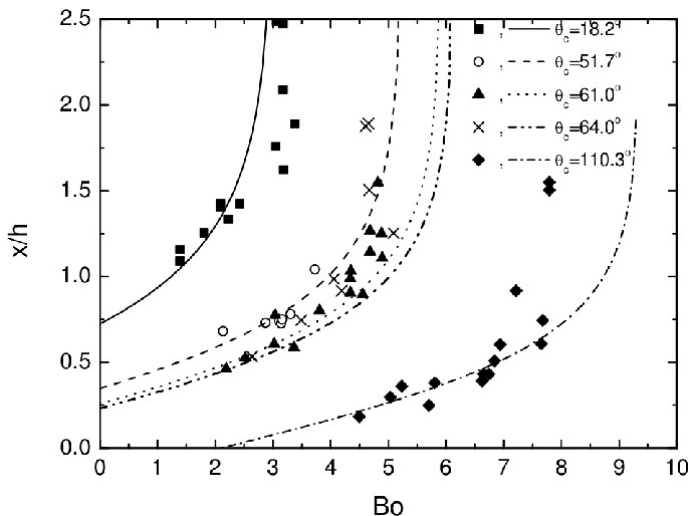
Comparison of bottom PB shapes from analytical theory and Surface Evolver.

# Results: bottom PB shapes, theory + experiment I



PBs at four of the five surfaces used in the experiments.

# Results: bottom PB shapes, theory + experiment II



Scaled PB half-width  $x(z=0)/h$  vs Bond number, from theory (curves) and experiment (symbols).

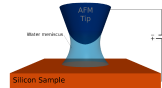
# Liquid bridges

- If the film connecting the two PBs is not infinitesimally thin we have a liquid bridge or capillary bridge. May cause repulsion or attraction.
- Liquid bridges are relevant in many contexts:

- Sand art



- AFM in high-humidity environments



- Soldering



- Lungs, closing small airways and impairing gas exchange

- Wet adhesion of insects and tree frogs



# Theory: the physics of liquid bridge shape

- Bridge shape is determined by the balance of gravity, surface tension, and liquid contact angles. So a key dimensionless quantity is the Bond number ( $H$  is substrate separation):

$$\text{Bo} = \frac{\rho g H^2}{\gamma}$$

- Relevant lengthscale is the capillary length:

$$\lambda_c = \left( \frac{\gamma}{\rho g} \right)^{1/2}$$

- Starting with Lagrange, a lot of work has been done on axisymmetric bridges.
- We solve the Young-Laplace equation with gravity for a planar bridge between two horizontal, flat substrates, to predict the bridge shape.

# Theory: liquid bridge and the Young-Laplace equation

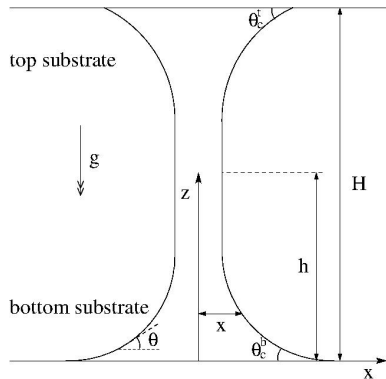
Young-Laplace equation for liquid bridge between two planar substrates:

$$\left[ 1 + \left( \frac{dx}{dz} \right)^2 \right]^{-3/2} \frac{d^2x}{dz^2} = - \frac{\Delta p}{\gamma}$$

$\Delta p = [p_b(z=0) - \rho g z] - p_a$   
is pressure difference across the interface ( $\propto$  curvature),  $\gamma$  is liquid-gas surface tension.

Boundary conditions:

- 1  $dx/dz(z=0) = -\cot \theta_c^b$  (bottom substrate);
- 2  $dz/dx(x=H) = \cot \theta_c^t$  (top substrate).





# Theory: solving the Young-Laplace equation

- Rewrite equation in terms of film inclination  $\theta(z)$ : boundary conditions are  $\theta(0) = \theta_c^b$ ,  $\theta(H) = \theta_c^t$ :

$$\sin \theta \frac{d\theta}{dz} = -\frac{\Delta p}{\gamma}$$

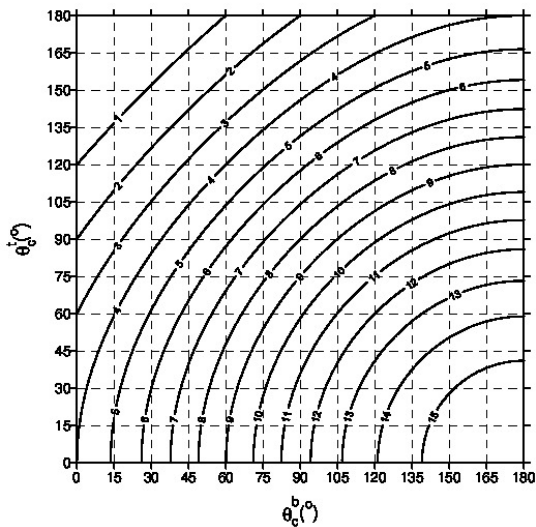
- Analytically exact solution (lengths in units of  $H$ ):

$$x'(z') = x'(0) - \int_0^{z'} \frac{-\cos \theta_c^t z'' + (1 - z'') \left( \cos \theta_c^b + \frac{Bo}{2} z'' \right)}{\left\{ 1 - \left[ -\cos \theta_c^t z'' + (1 - z'') \left( \cos \theta_c^b + \frac{Bo}{2} z'' \right) \right]^2 \right\}^{1/2}} dz''$$

- In zero gravity ( $Bo = 0$ , top=bottom):

$$x'(z') = x'(0) + \frac{\sin \theta_c^b - \left\{ 1 - \left[ \cos \theta_c^b - (\cos \theta_c^b + \cos \theta_c^t) z' \right]^2 \right\}^{1/2}}{\cos \theta_c^b + \cos \theta_c^t}$$

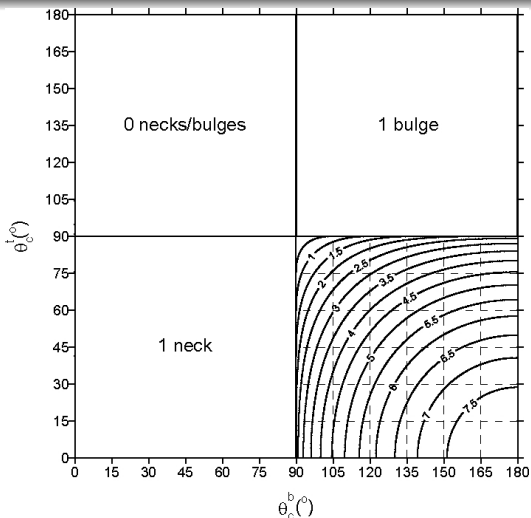
# Results: when does a bridge bridge?



From requiring that  $-1 \leq \cos \theta(z) \leq 1$ :

$$Bo \leq Bo^{\max} = 2 \left( 2 - \cos \theta_c^b + \cos \theta_c^t \right) + 4 \sqrt{(1 - \cos \theta_c^b)(1 + \cos \theta_c^t)}$$

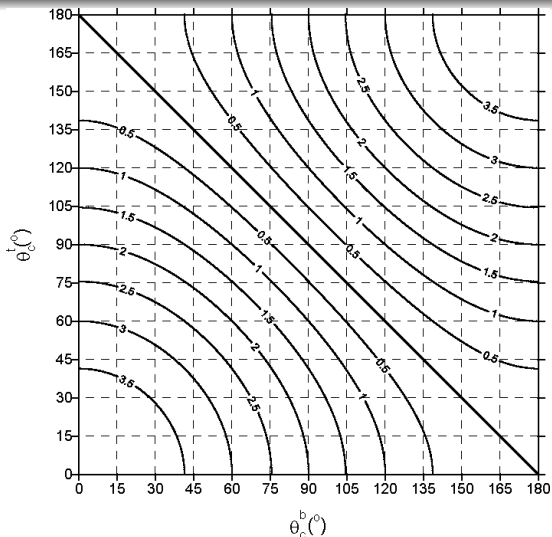
# Results: how many necks and bulges?



From requiring that  $\theta(z) = 90^\circ$  (in units of  $H$ ):

$$h' = \frac{Bo - 2(\cos \theta_c^b + \cos \theta_c^t) \pm \sqrt{Bo^2 - 4(\cos \theta_c^t - \cos \theta_c^b)Bo + 4(\cos \theta_c^t + \cos \theta_c^b)^2}}{2Bo}$$

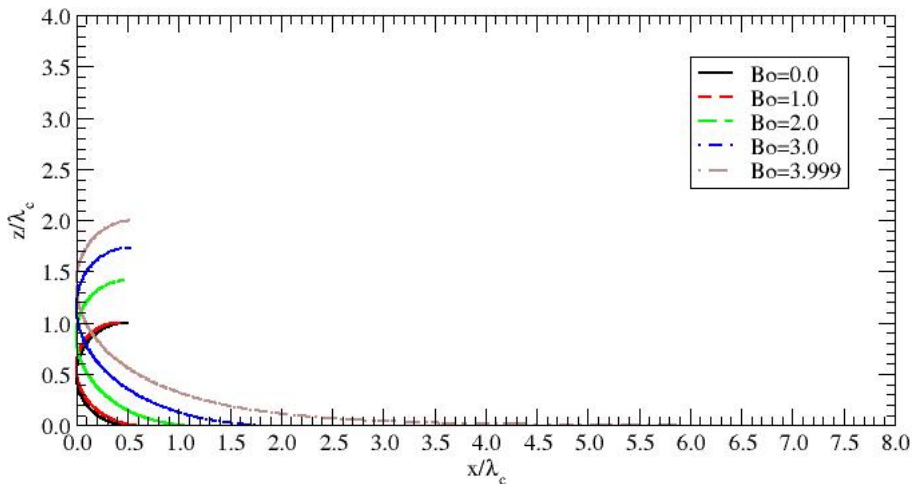
# Results: are there inflection points?



From requiring that  $d\theta(z)/dz = 0$  (in units of  $H$ ):

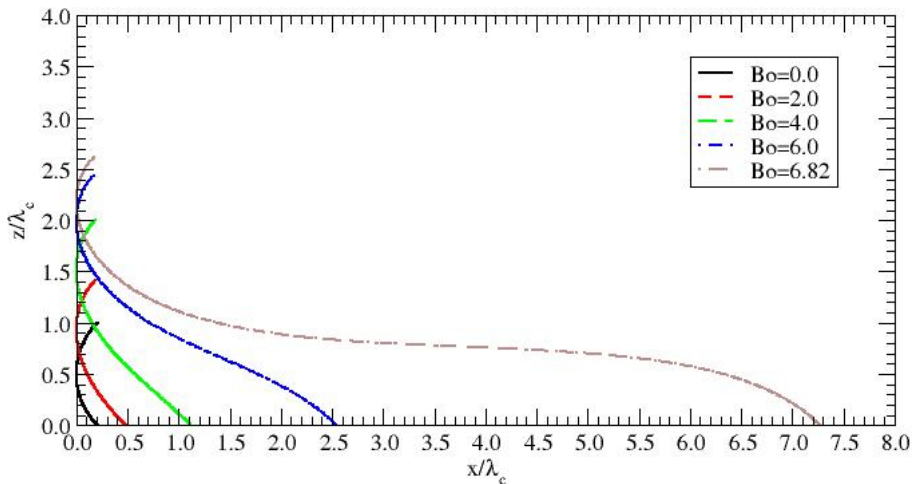
$$\tilde{h}' = \frac{1}{2} - \frac{\cos \theta_c^b + \cos \theta_c^t}{\text{Bo}}$$

# Results: bridge shapes vs $Bo$ , $\theta_c^b = \theta_c^t = 0^\circ$



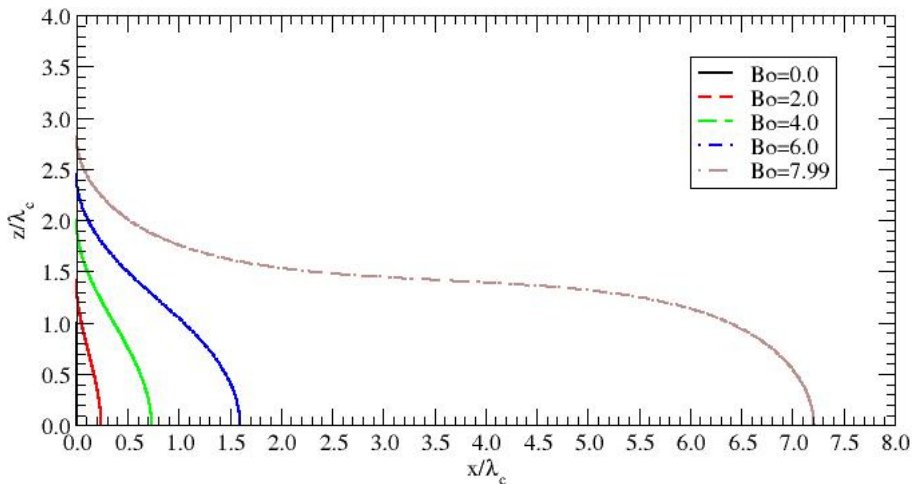
Lengths scaled by capillary length  $\lambda_c$ .

# Results: bridge shapes vs $Bo$ , $\theta_c^b = \theta_c^t = 45^\circ$



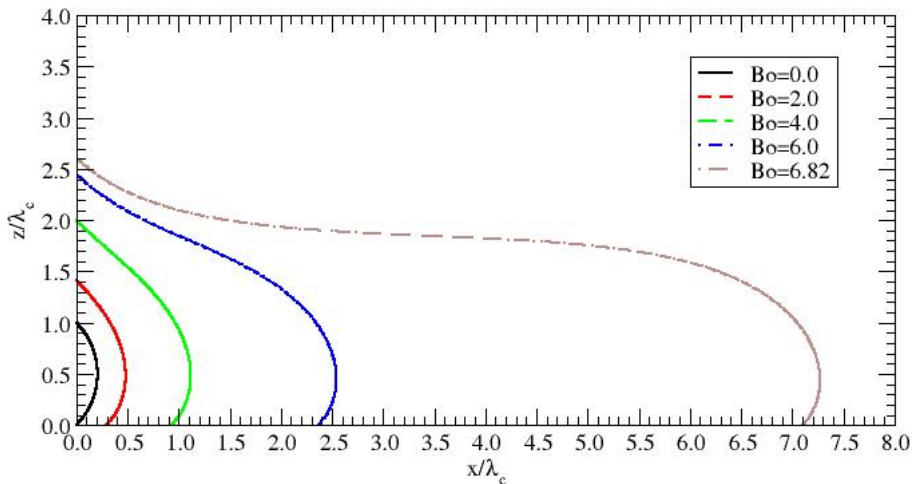
Lengths scaled by capillary length  $\lambda_c$ .

# Results: bridge shapes vs $Bo$ , $\theta_c^b = \theta_c^t = 90^\circ$



Lengths scaled by capillary length  $\lambda_c$ .

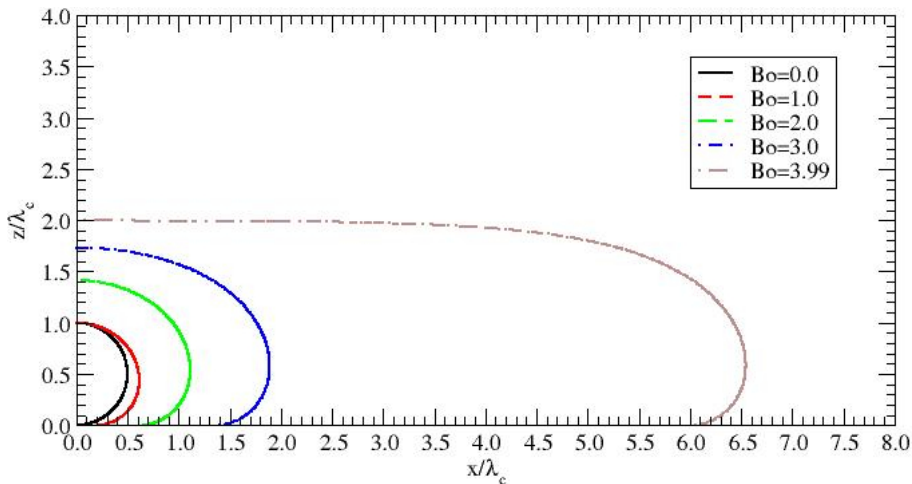
# Results: bridge shapes vs $Bo$ , $\theta_c^b = \theta_c^t = 135^\circ$



Lengths scaled by capillary length  $\lambda_c$ .

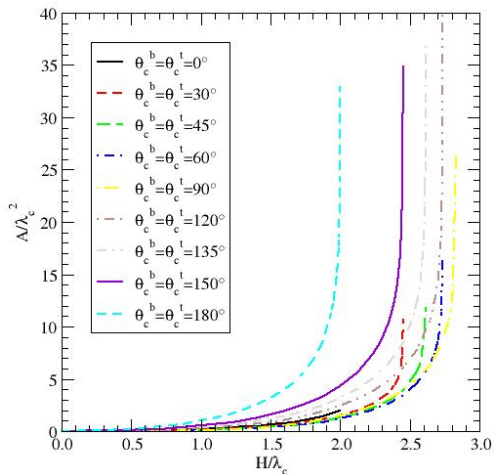


# Results: bridge shapes vs $Bo$ , $\theta_c^b = \theta_c^t = 180^\circ$



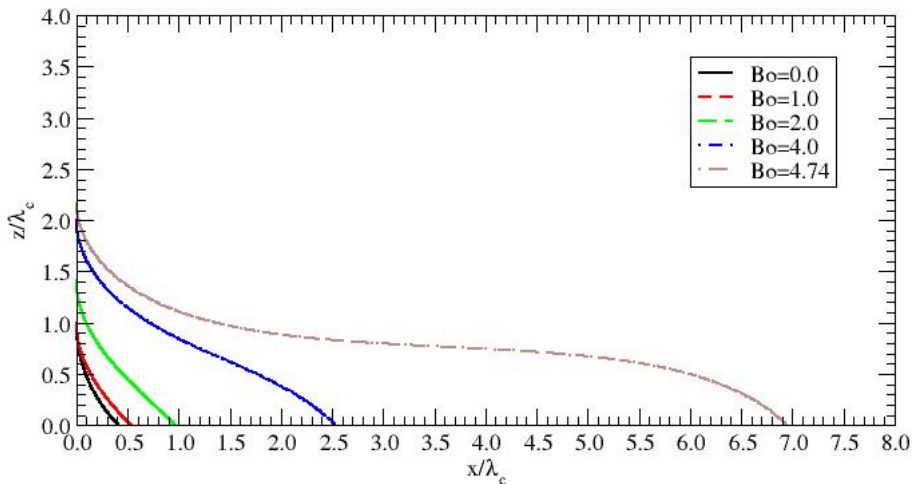
Lengths scaled by capillary length  $\lambda_c$ .

# Results: minimum X-sectional area, $\theta_c^b = \theta_c^t$



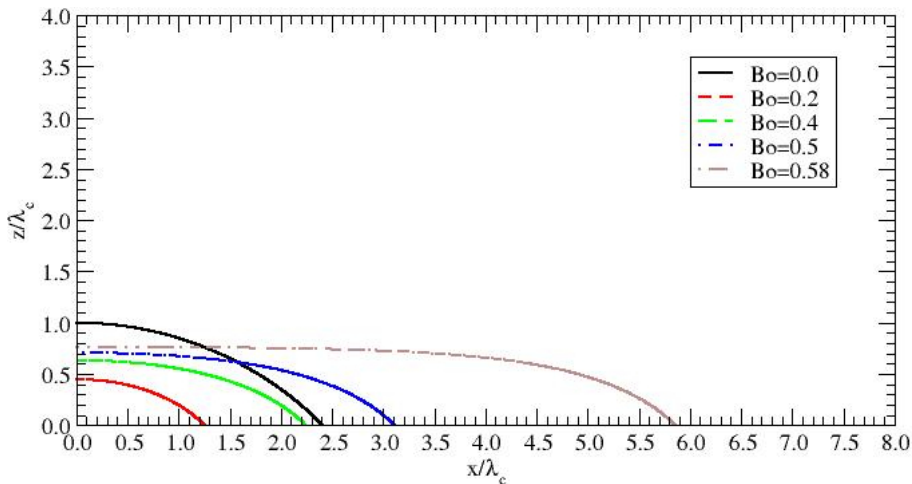
Lengths scaled by capillary length  $\lambda_c$ .

# Results: bridge shapes vs $Bo$ , $\theta_c^b = 45^\circ$ , $\theta_c^t = 90^\circ$



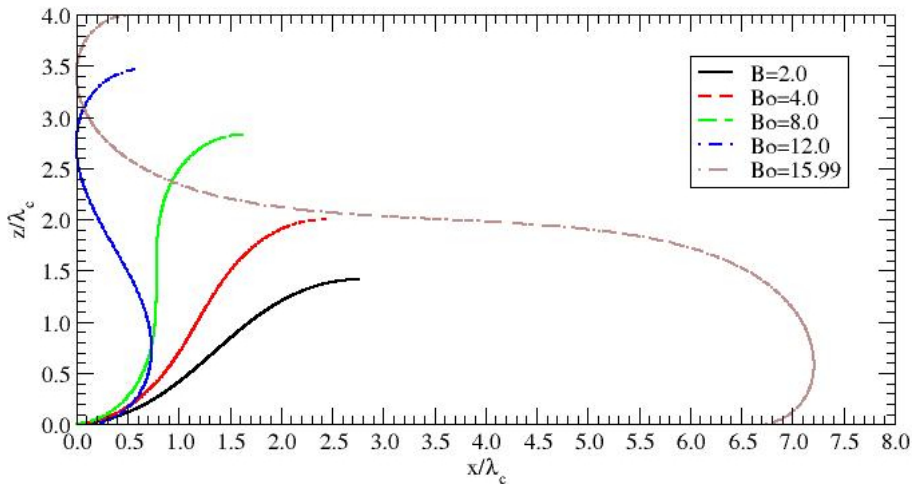
Lengths scaled by capillary length  $\lambda_c$ .

# Results: bridge shapes vs $Bo$ , $\theta_c^b = 45^\circ$ , $\theta_c^t = 180^\circ$



Lengths scaled by capillary length  $\lambda_c$ .

# Results: bridge shapes vs $Bo$ , $\theta_c^b = 180^\circ$ , $\theta_c^t = 0^\circ$

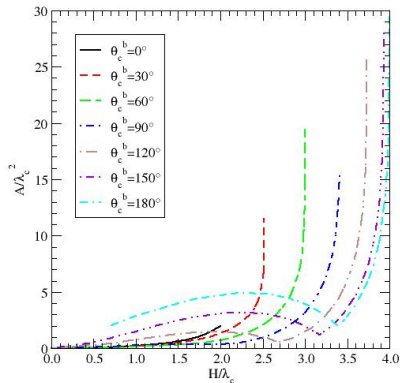
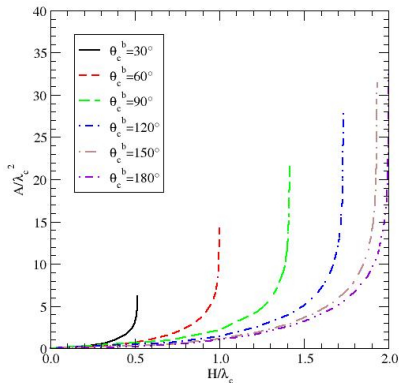


Lengths scaled by capillary length  $\lambda_c$ .

# Results: minimum X-sectional area, $\theta_c^b \neq \theta_c^t$

$$\theta_c^b \leq \theta_c^t = 180^\circ$$

$$\theta_c^b \geq \theta_c^t = 0^\circ$$



Lengths scaled by capillary length  $\lambda_c$ .

# Summary and conclusions

- We have integrated the Young-Laplace equation (quasi-)analytically to find the shape of the 2D PBs along which a planar vertical film meets two horizontal flat substrates of given wettabilities.
- The combination of a particular surface ( $\theta_c$ ) in contact with a particular foam ( $\rho$  and  $\gamma$ ) leads to allowed and forbidden surface PBs: a surface can be **foam-philic** or **foam-phobic**.
  - PBs at the top substrate can only exist in a small region of  $(\theta_c, Bo)$  space; in particular, one must have  $\theta_c < 90^\circ$ .
  - PBs at the bottom substrate have a wider range of existence, requiring larger  $\theta_c$  at higher  $Bo$  or vice versa.
- Predictions are in fairly good agreement with experiment.
- This was then generalised to a 2D liquid bridge: we established the range of substrate separations for which the bridge can exist, as well as the positions of any necks/bulges and inflection points on its surface. These results are analytically exact.
- We also obtained the minimum cross-sectional area of such a liquid bridge, as a function of contact angles and substrate separation.

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- Fundação para a Ciência e Tecnologia (Portugal) through grants EXCL/FIS-NAN/0083/2012 and UID/FIS/00618/2013.
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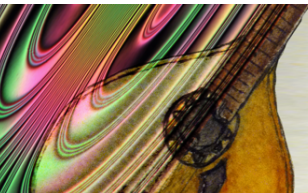


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# ILCC2020

28<sup>th</sup> International Liquid Crystal Conference

26<sup>th</sup> to 31<sup>st</sup> July 2020

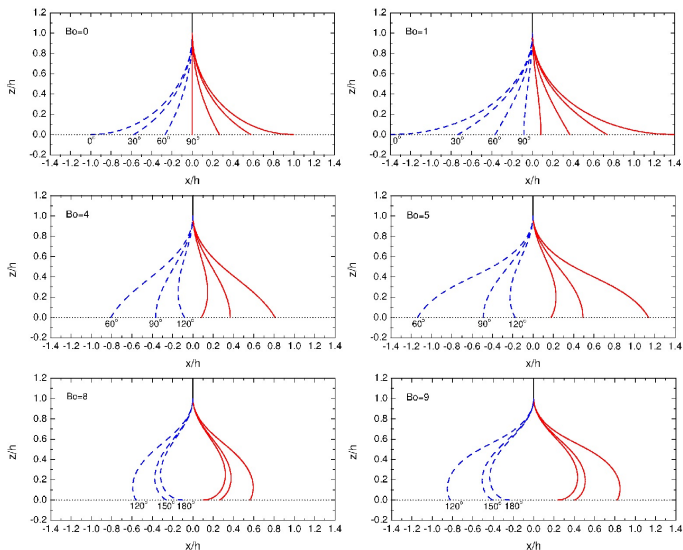
Lisbon, Portugal

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## Topics

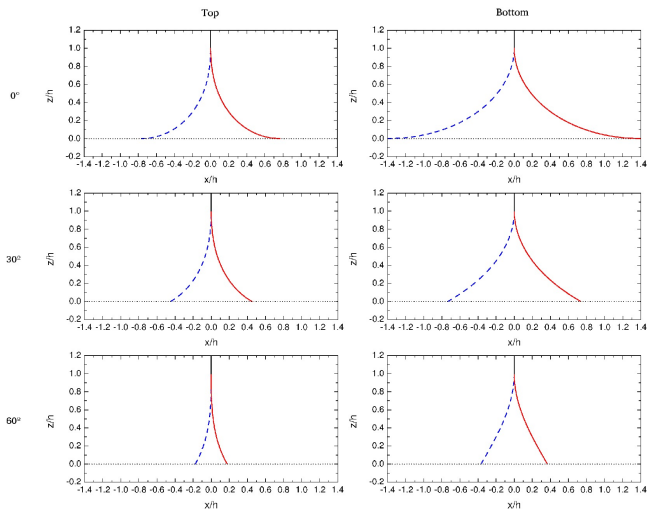
- Liquid Crystals in Biology and Active Matter
- Macromolecular Liquid Crystals
- Confined Liquid Crystals
- Design of New Materials
- Mathematical Modelling, Symmetry and Topology
- Novel Applications

# Results: bottom PB shapes, theory



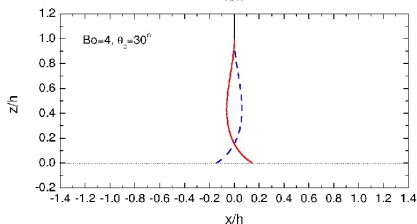
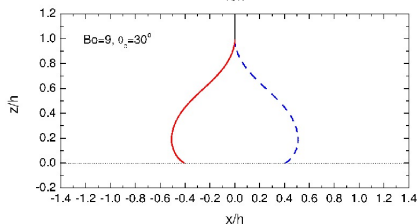
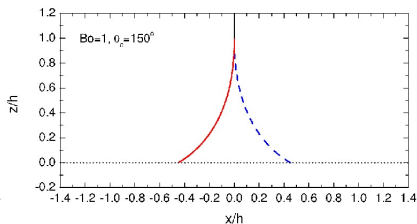
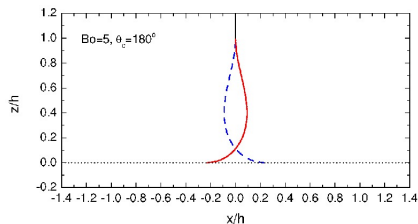
Analytically-calculated PB shapes at bottom substrate, for various combinations of  $Bo$  and  $\theta_c$ .

# Results: top and bottom PB shapes, theory



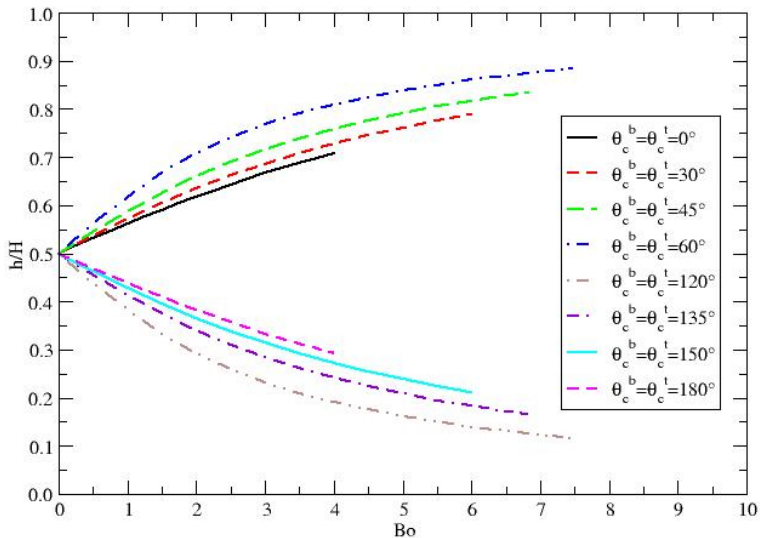
Analytically-calculated PB shapes at top (left column) and bottom (right column) substrates, for  $Bo = 1$  and  $\theta_c = 0^\circ$  (top row),  $30^\circ$  (centre row) and  $60^\circ$  (bottom row).

# Results: unphysical PB shapes, theory



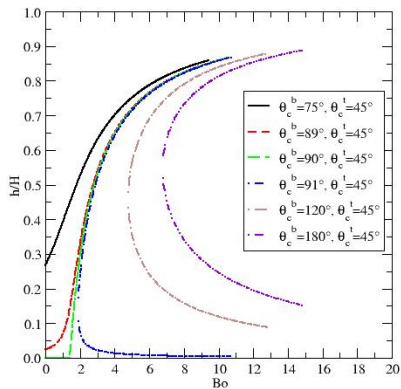
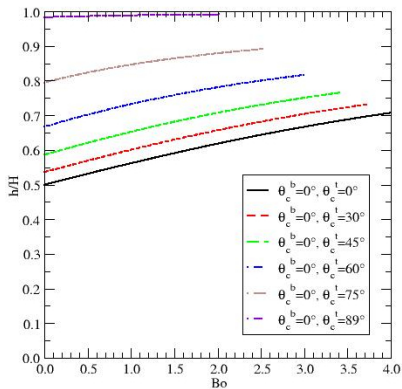
Examples of unphysical bottom PBs (top row) and top PBs (bottom row).

# Results: position of neck/bulge vs $Bo$ , $\theta_c^b = \theta_c^t$



Lengths scaled by substrate separation  $H$ .

# Results: position of neck/bulge vs $Bo$ , $\theta_c^b \neq \theta_c^t$



Lengths scaled by substrate separation  $H$ .