POLYWET
Contact lines on soft solids

Colloque Labex SEAM
12 & 13 November 2018

Robin Masurel

Julien Dervaux
Ioan Ionescu
Laurent Limat
Matthieu Roché

Elasto-capillarity

Deformation of soft solids by capillary forces

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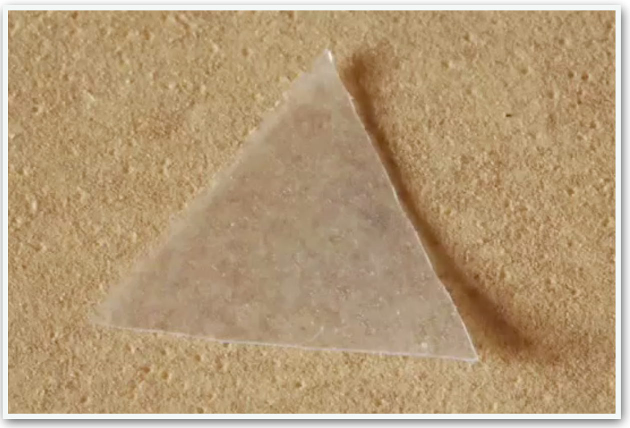
Thin structures (plates, roads)



Py et al (2007)

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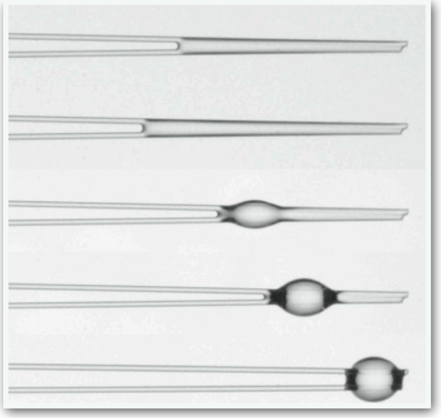

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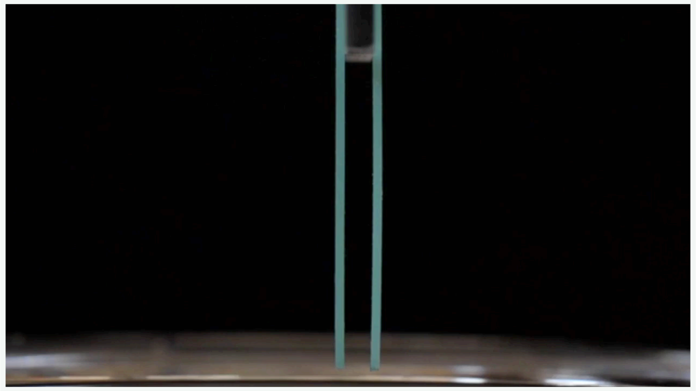

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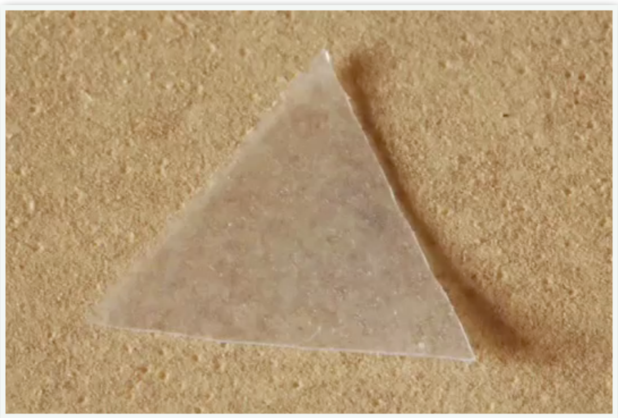

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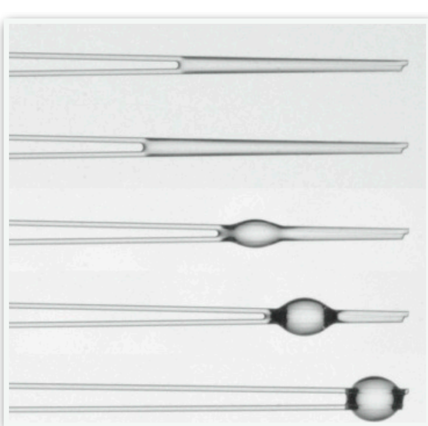

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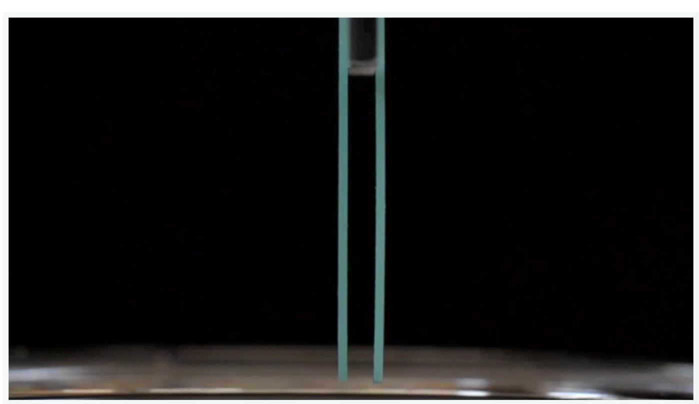

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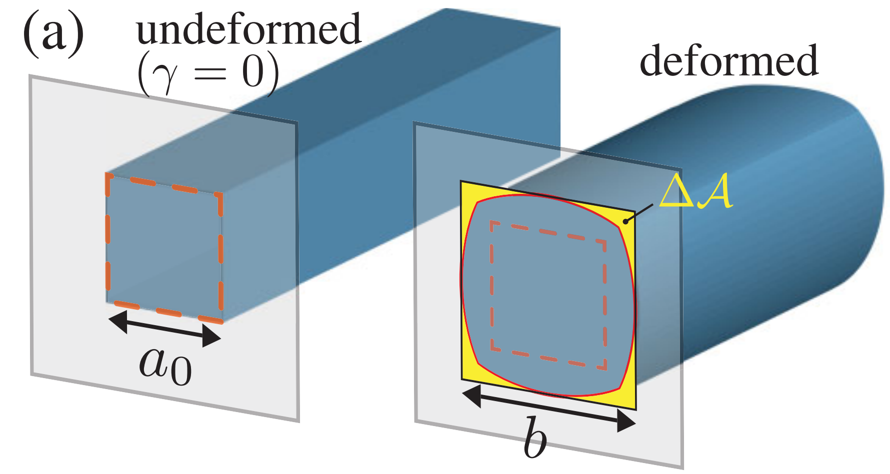
Low shear modulus



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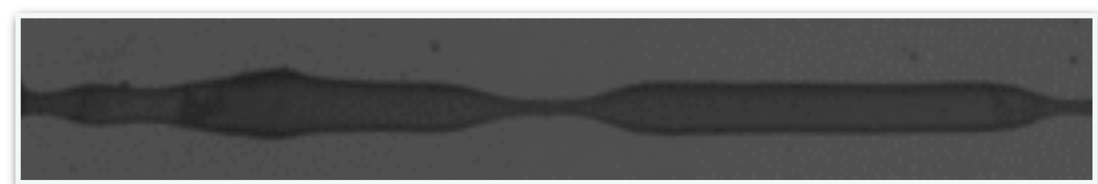

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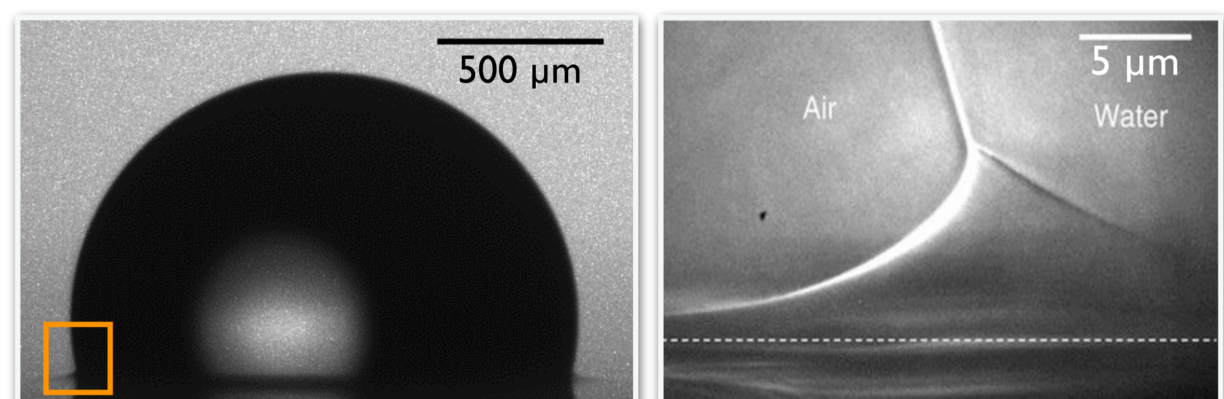

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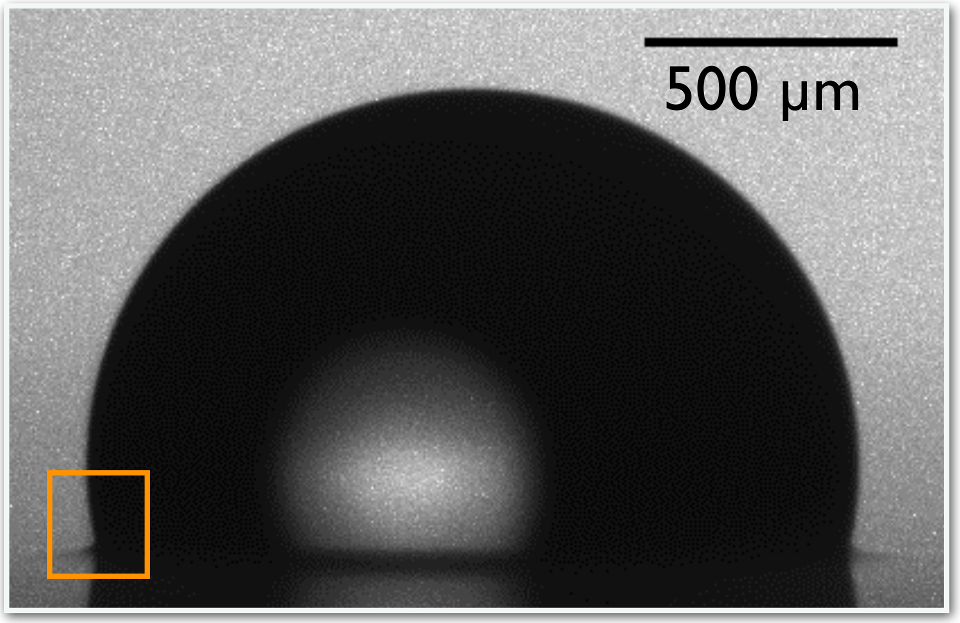
The elastowetting problem

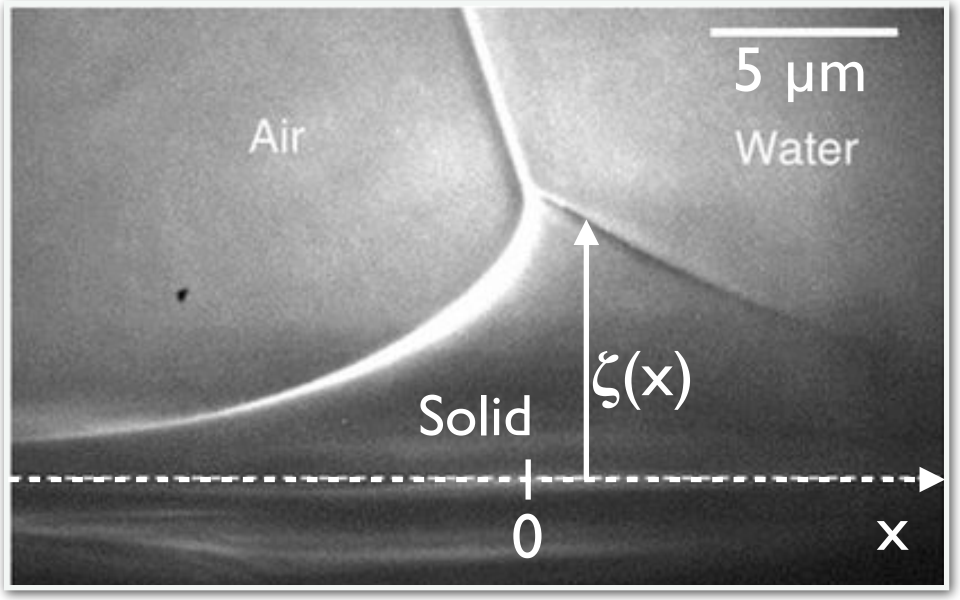
Liquid drops (surface tension γ) on

soft deformable solids

(elastic modulus μ)



Formation of a ridge
beneath the contact line



What is the shape of the ridge $\zeta(x)$?

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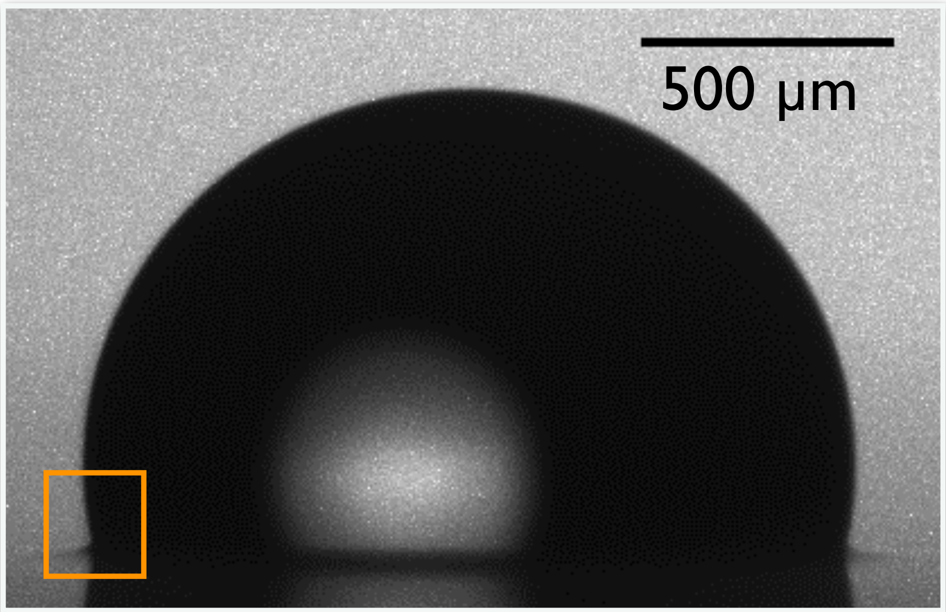

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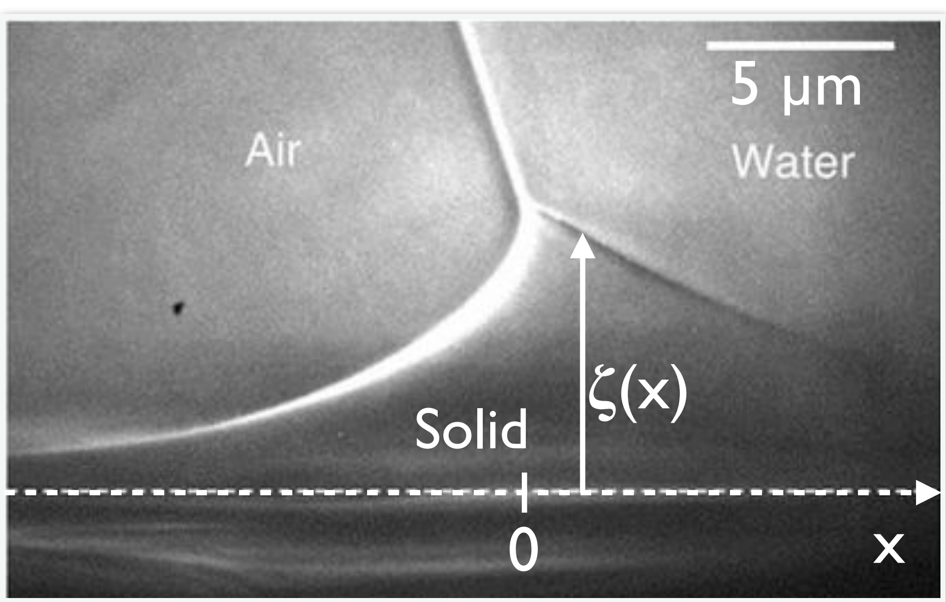

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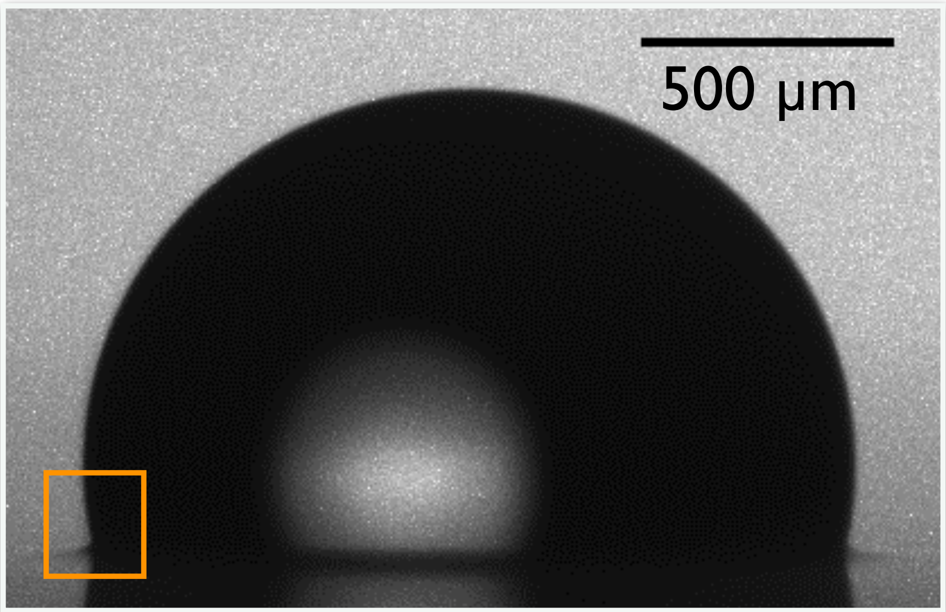

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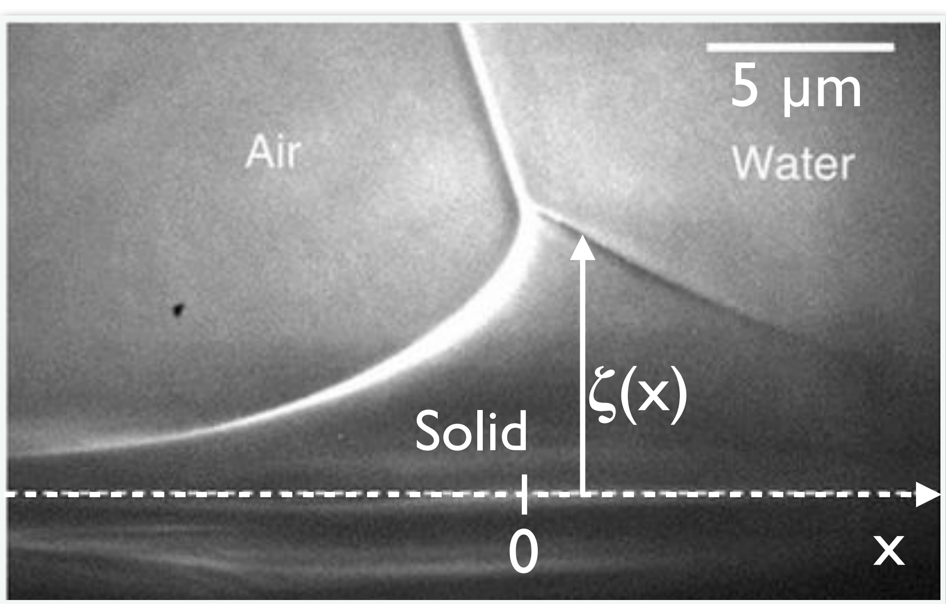

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Dew collection, micro- and nano-devices fabrication, coatings

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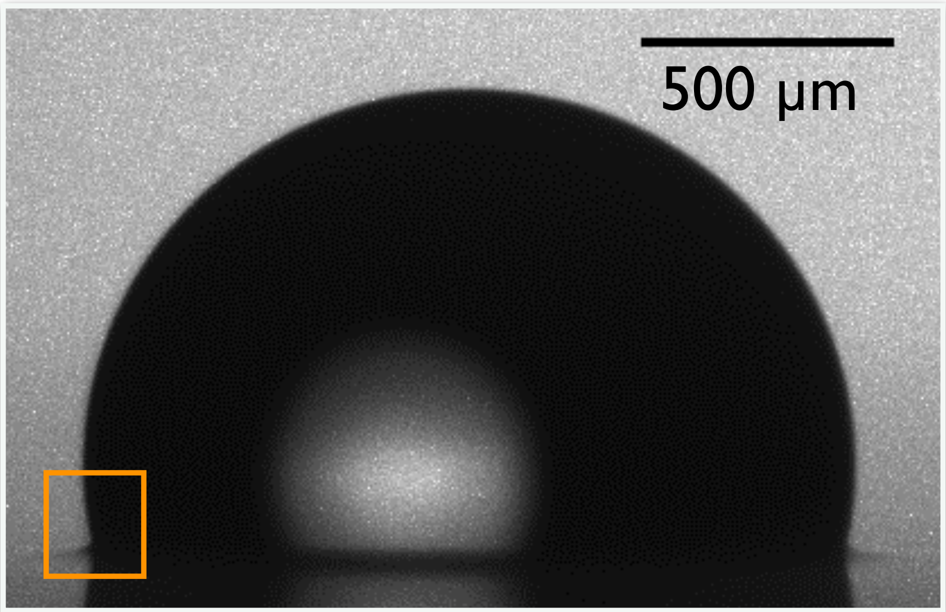

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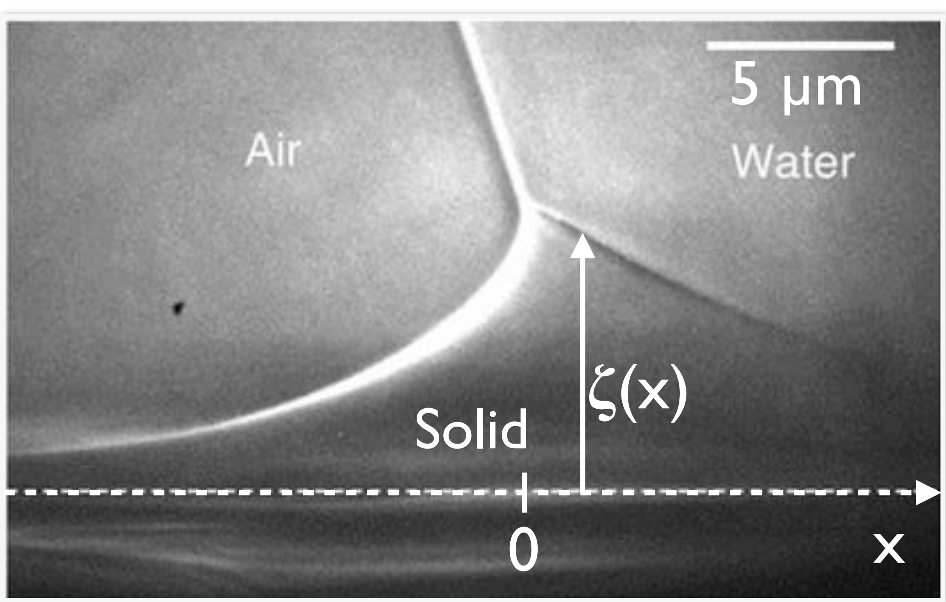

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Direct realization of the Flamant-Boussinesq problem (Green function for many linear problems of contact and fluid-structure interactions)

Rich physics

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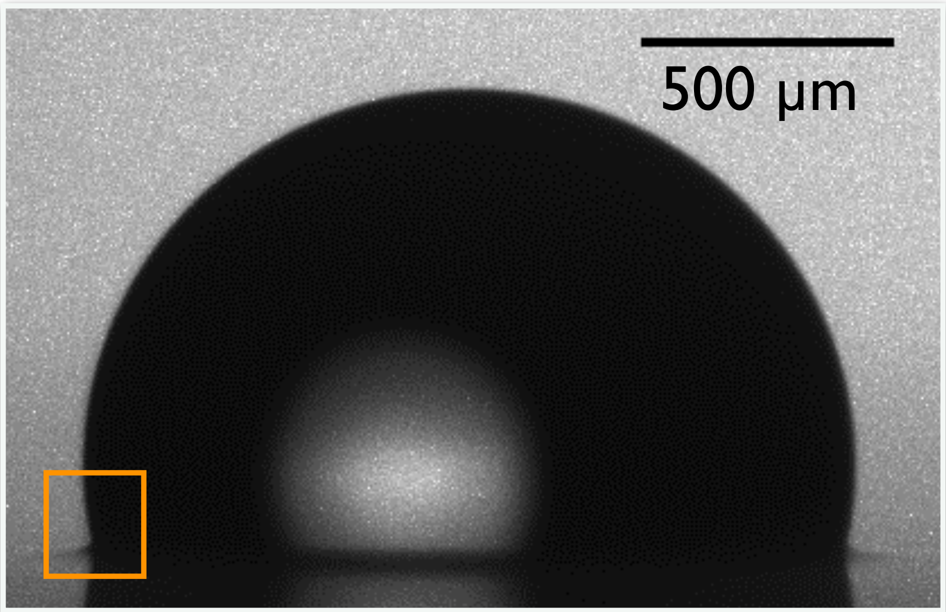

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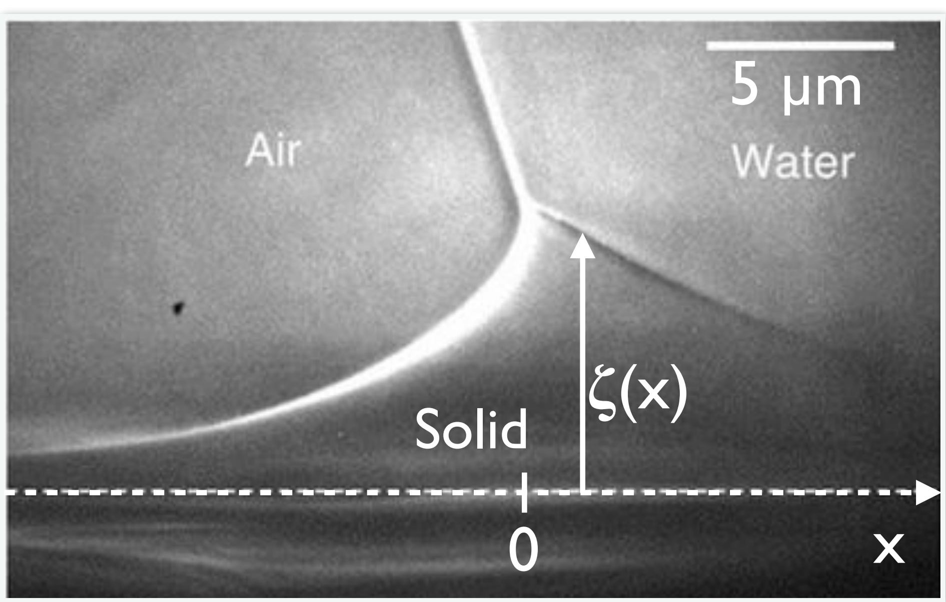

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Not really understood until quite recently

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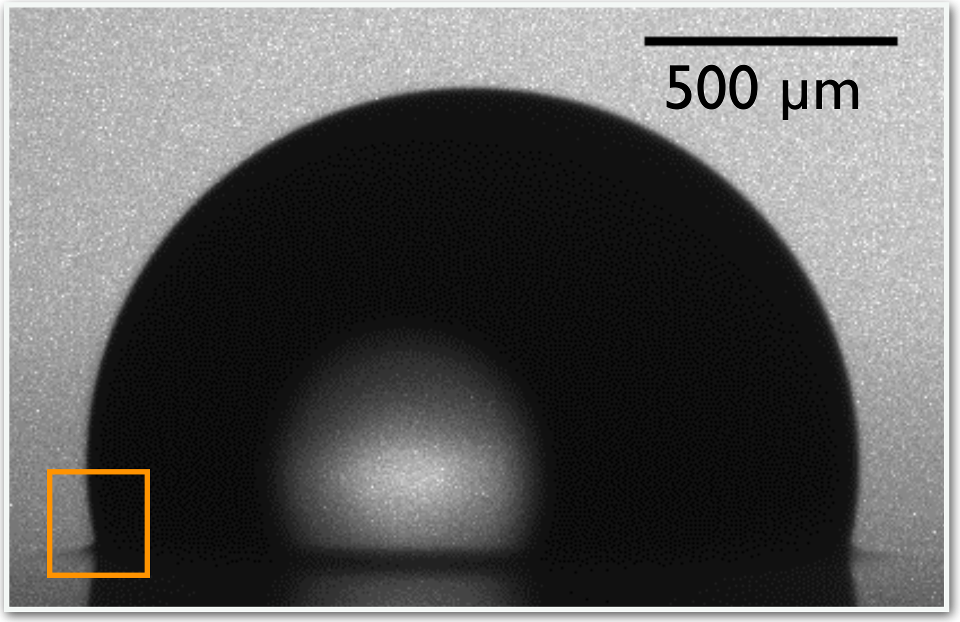
Liquid drops (surface tension γ) on soft deformable solids (elastic modulus μ)



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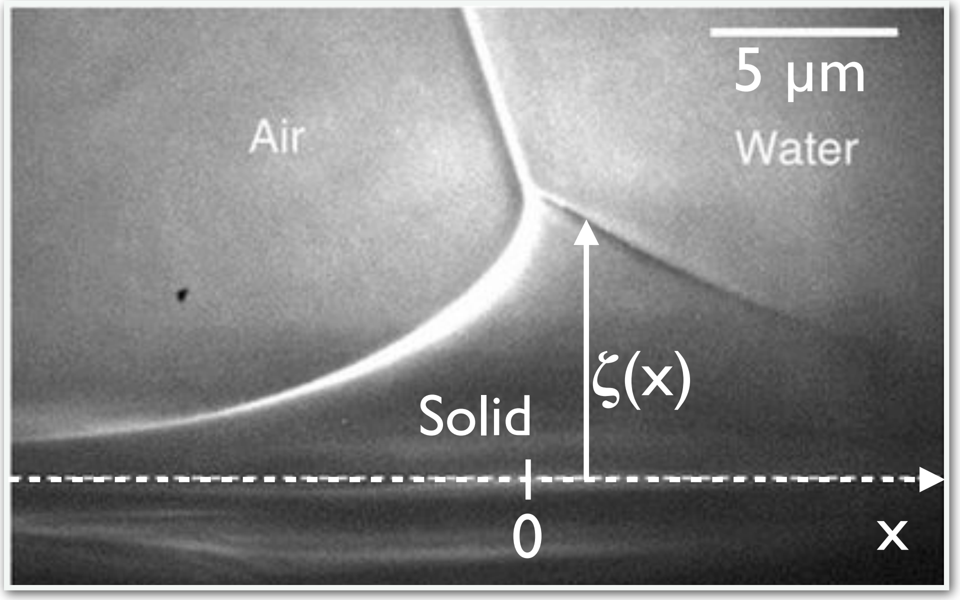

A conceptual difficulty:
(which does not exist for thin structures)

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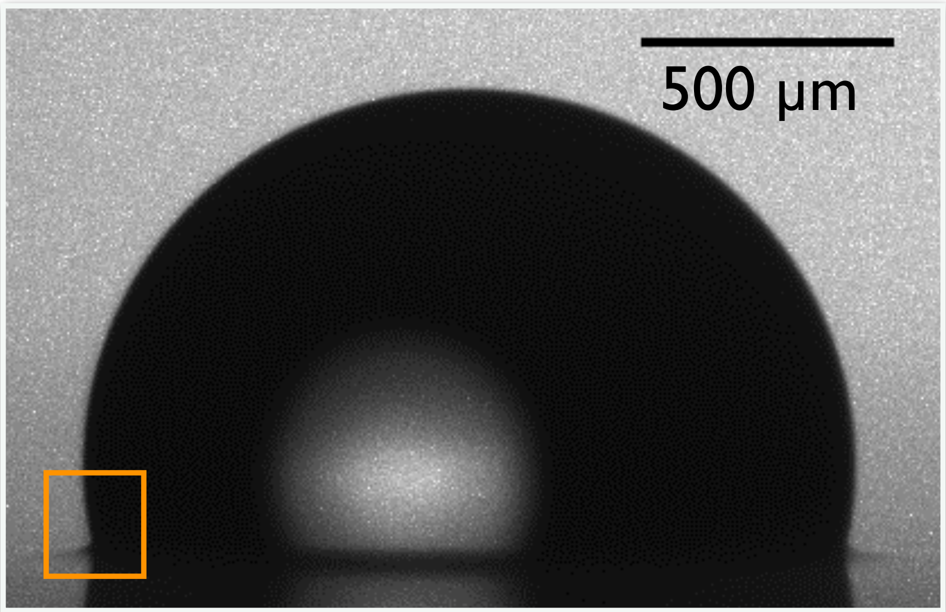

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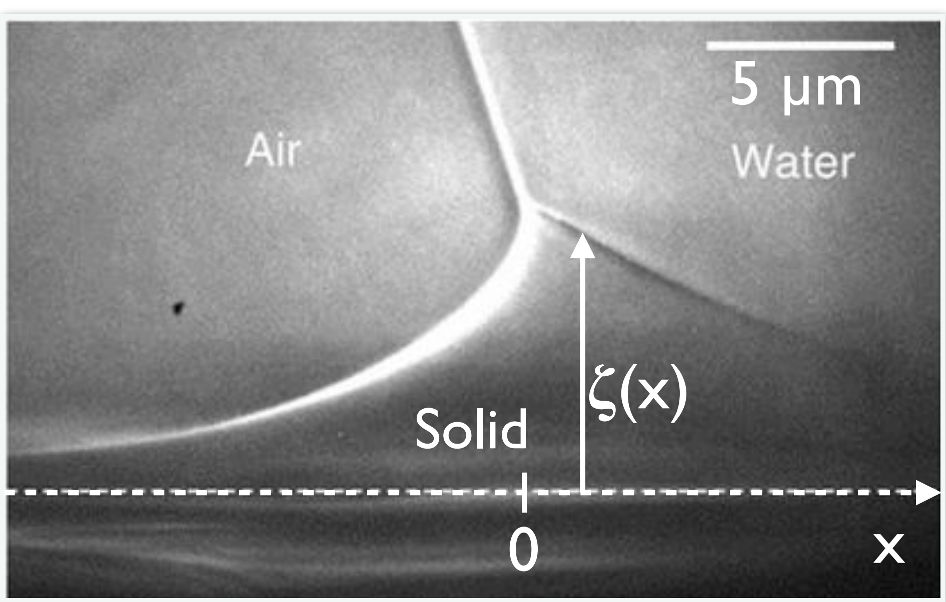

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Dimensional analysis

ridge height: $\zeta(0) \sim \gamma/\mu$

~1 pm on quartz
~ 100 nm on rubber
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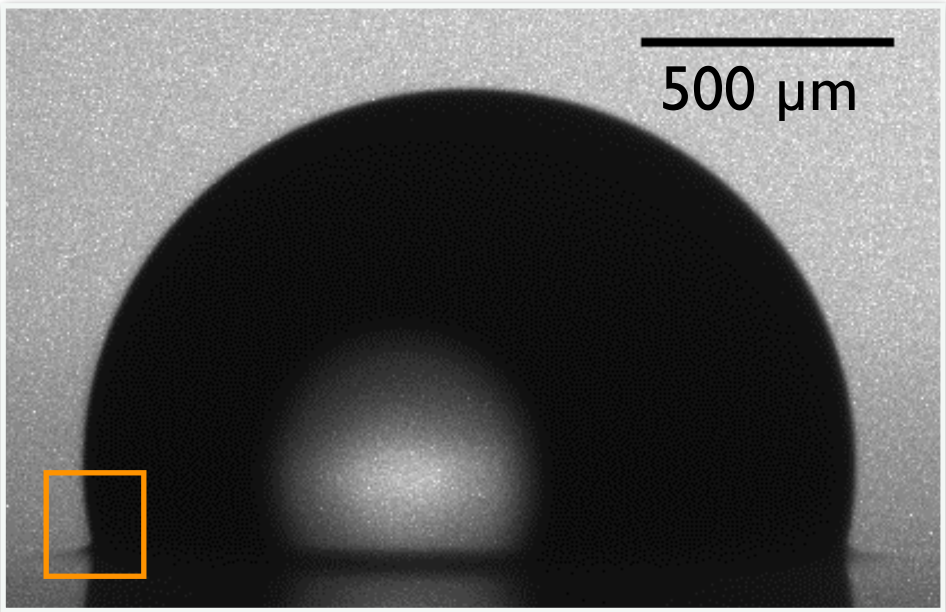

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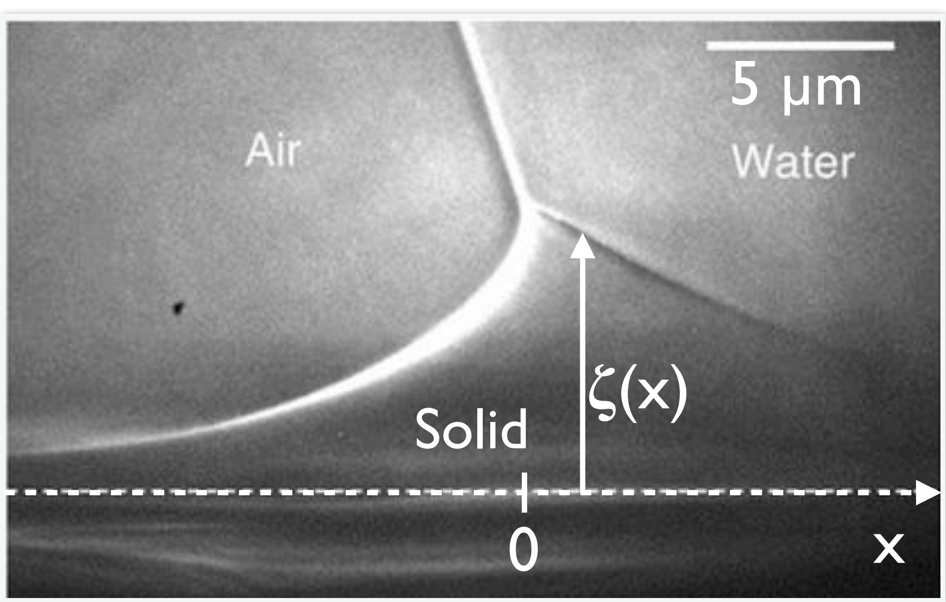

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Line force at the free surface of a half-space

ridge height: $\zeta(0) \rightarrow \infty$

Boussinesq (1892), Flamant (1892)

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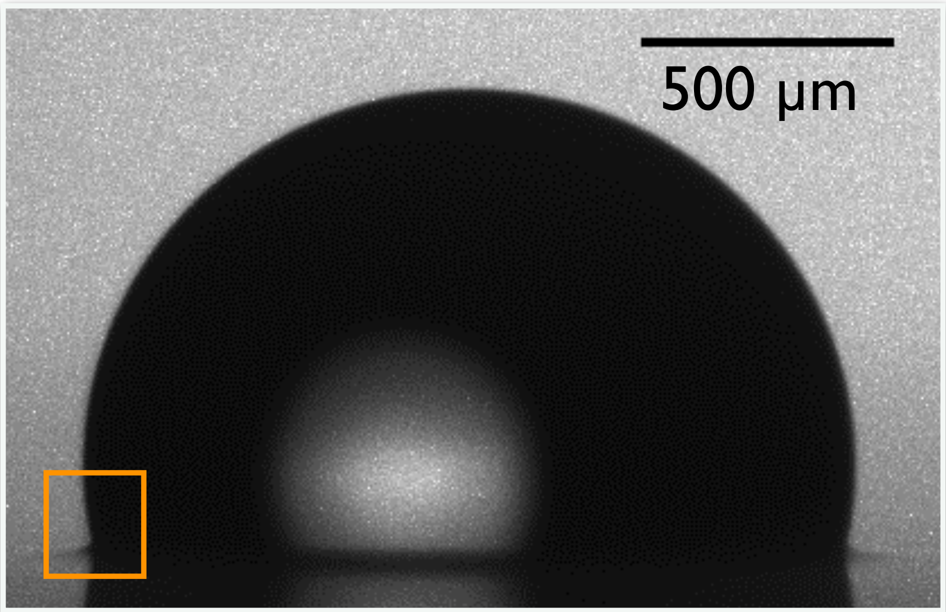

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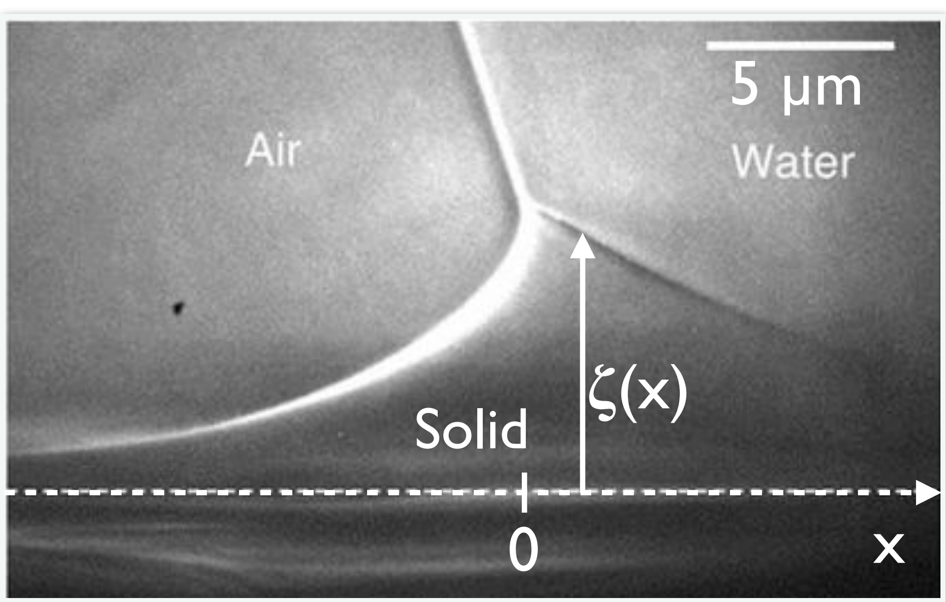

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A regularization mechanism is needed

- non-linearities
- plasticity
- finite width of contact line
- surface tension of the solid
- other ?

Shanahan & de Gennes (1987)

Long et al (1996)

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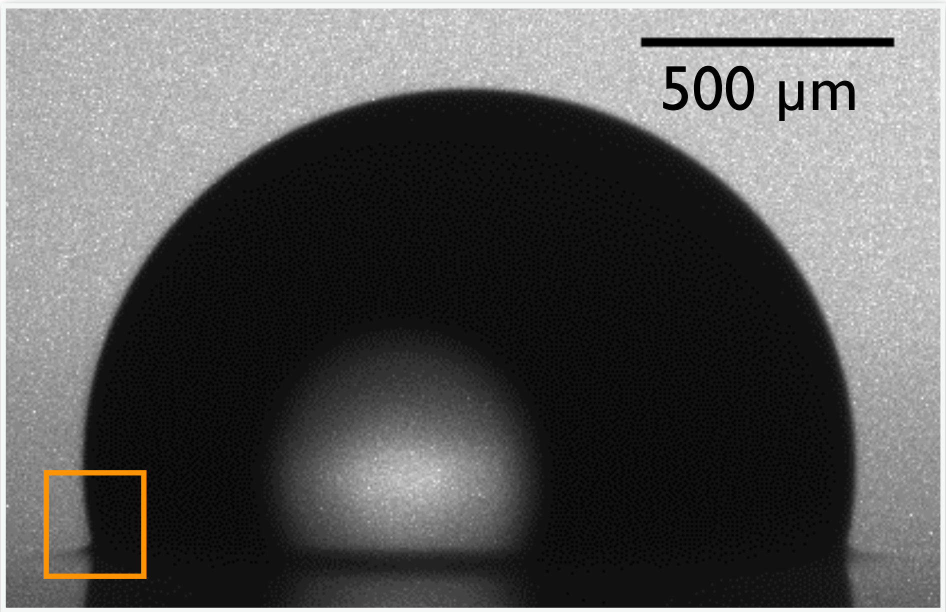

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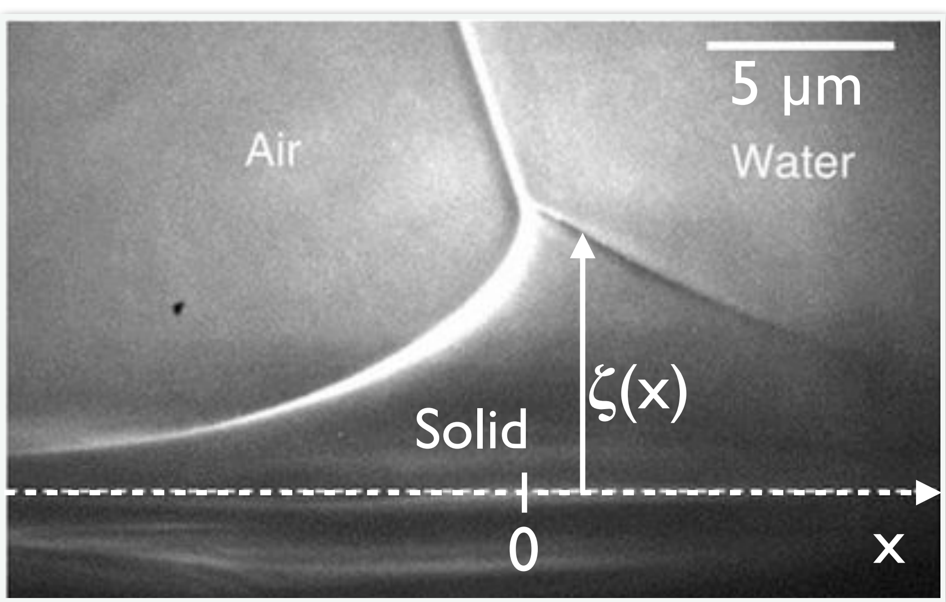

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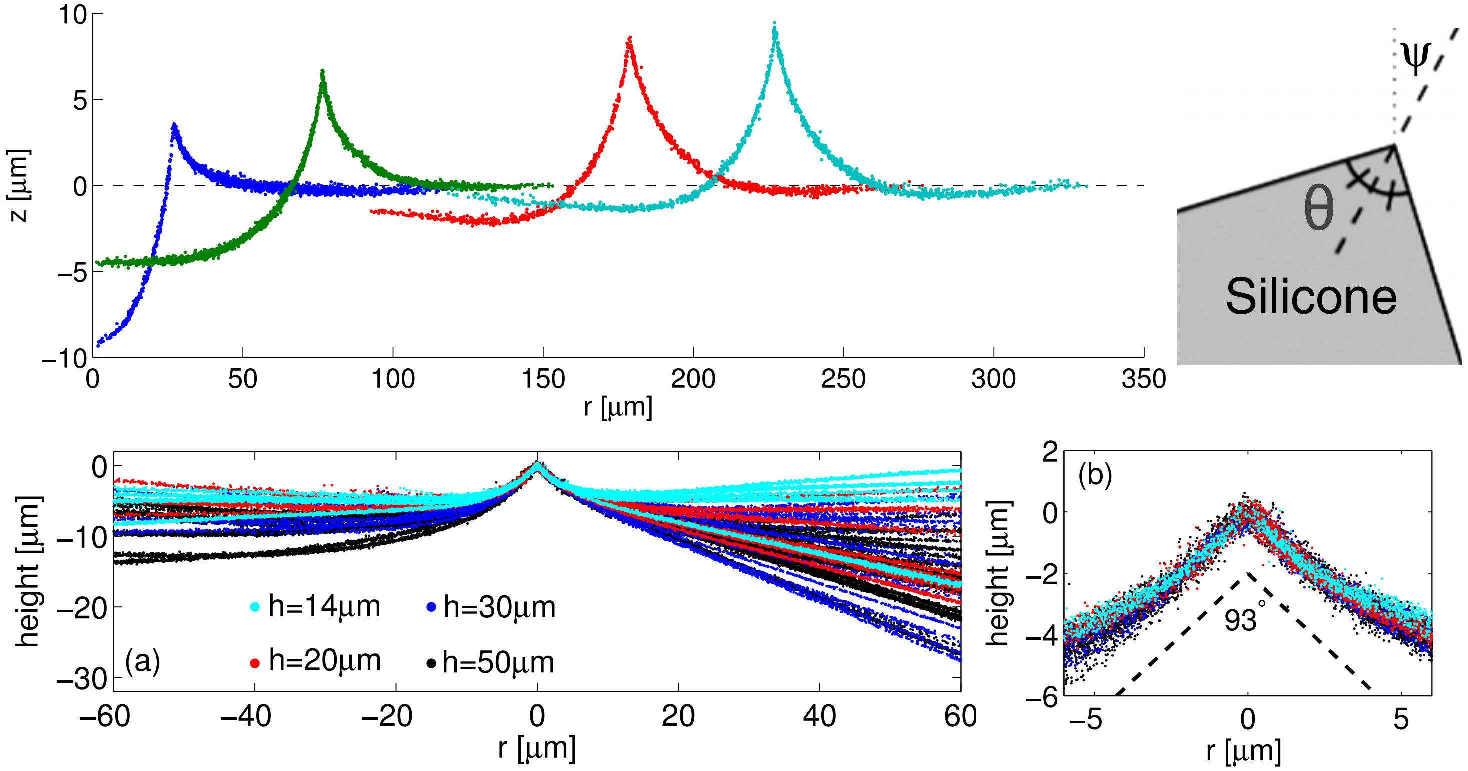
Experimental data at small scales (< 1μm) are needed

Pioneering experimental results

Confocal imaging

Style et al (2013)



The ridge opening angle θ is independent of:

drop radius: R

substrate thickness: H

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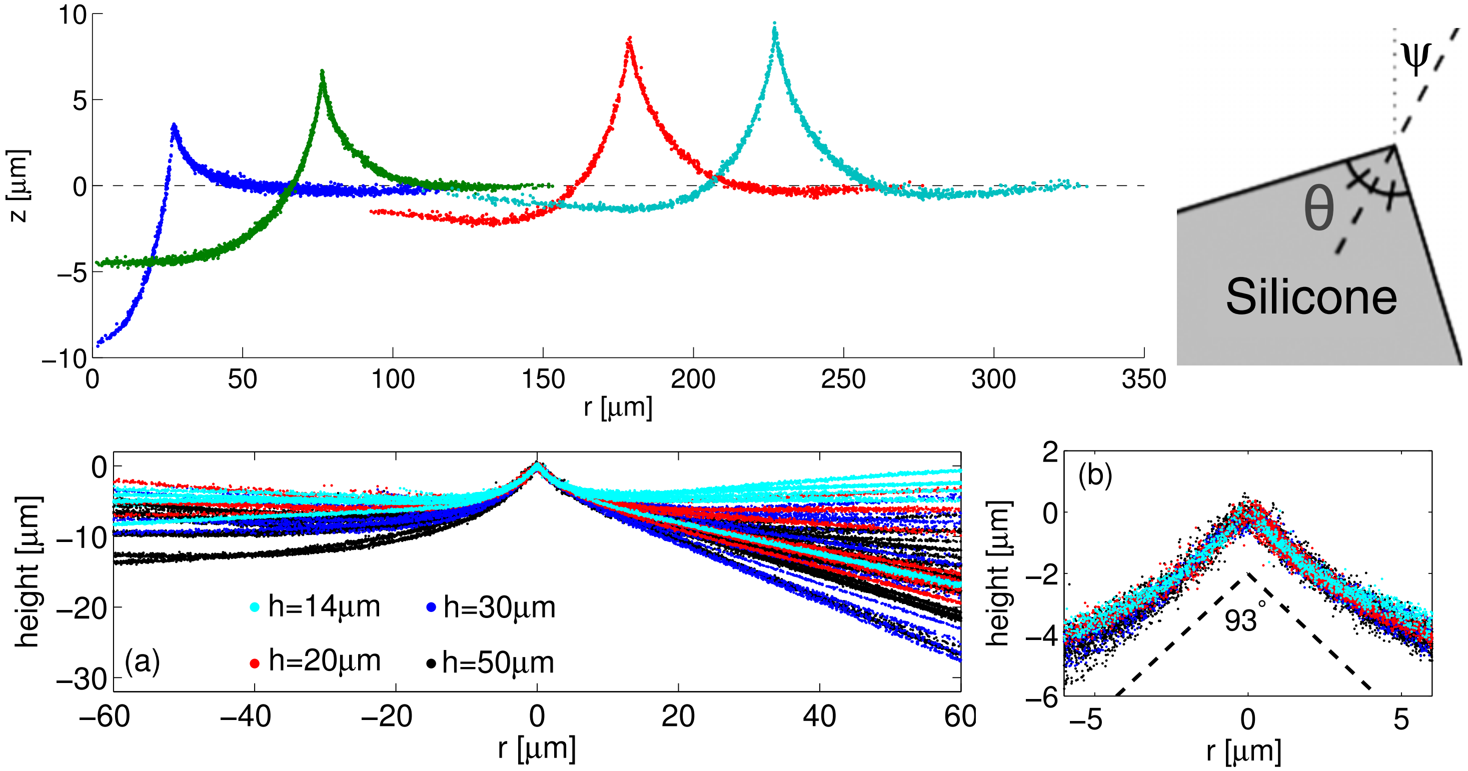
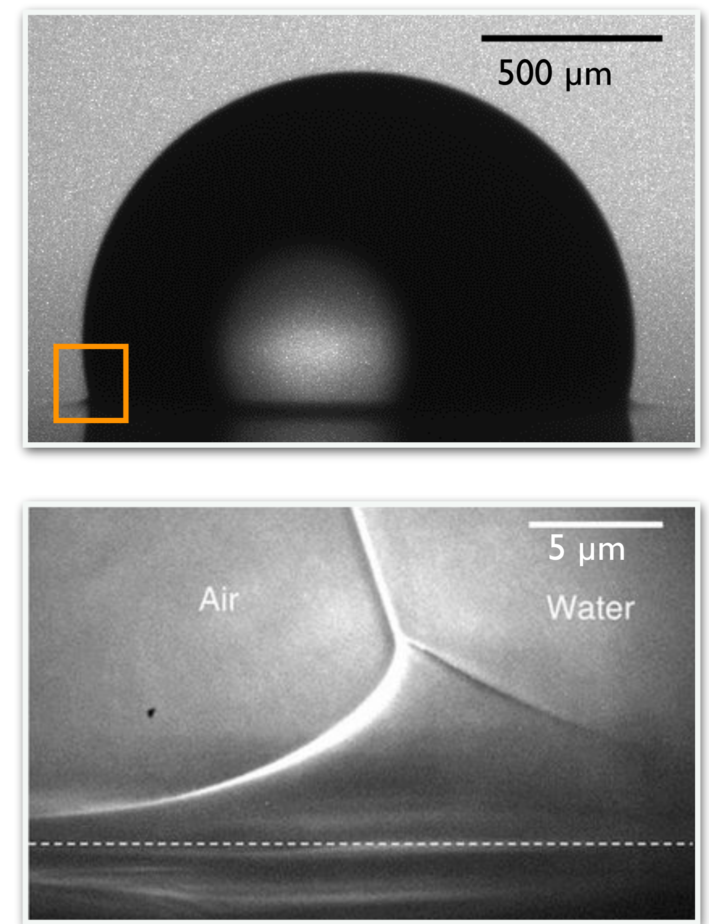
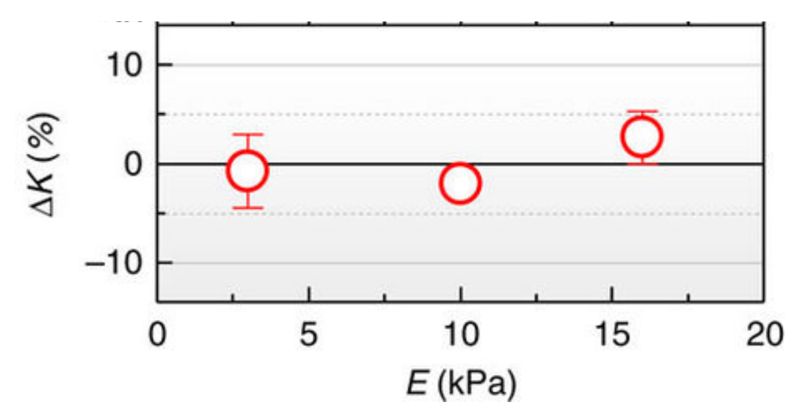


X-ray imaging

Park et al (2014)





The ridge opening angle θ is independent of:

drop radius: R

substrate thickness: H

substrate stiffness: μ

Linear theory of elastowetting

The surface tension of the solid γ_s is the relevant regularization mechanism

Solve a linear elastic problem:

Force balance and incompressibility:

$$\boldsymbol{\nabla} \cdot \boldsymbol{\sigma} = \mathbf{0} \quad \boldsymbol{\nabla} \cdot \boldsymbol{u} = 0$$

Constitutive model:

$$\boldsymbol{\sigma} = \mu(\boldsymbol{\nabla} \boldsymbol{u} + (\boldsymbol{\nabla} \boldsymbol{u})^T) - p\boldsymbol{I}$$

Boundary conditions:

$$\boldsymbol{\sigma n} = \boldsymbol{t} + \gamma_s \boldsymbol{n}(\boldsymbol{\nabla} \cdot \boldsymbol{n})$$

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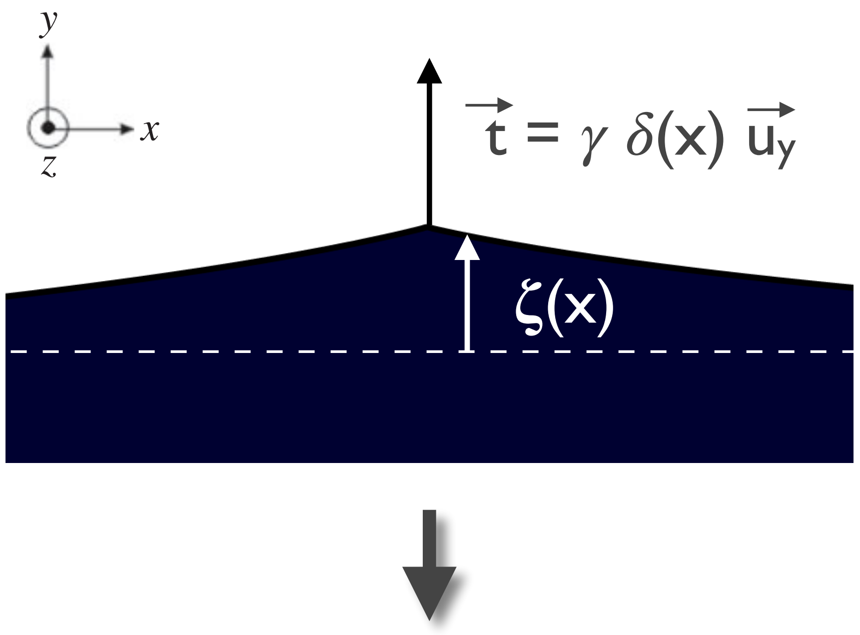
A single 2D vertical contact line:



$$\zeta(x) = \frac{1}{\pi} \int_{1/\Delta}^{\infty} \mathrm{d}k \frac{\gamma \cos kx}{2\mu k + \gamma_s k^2}$$

elasticity ≈ surface tension

at

lengthscale $\ell_s = \gamma_s/(2\mu)$

Linear theory of elastowetting

$$\zeta(x) = \frac{\gamma}{2\pi\mu} \int_{1/\Delta'}^{\infty} \mathrm{d}k \frac{\cos k \frac{x}{\ell_s}}{k + k^2}$$

The solution can be written as:

$\zeta(x) = \gamma/\mu \; f(x/\ell_s)$

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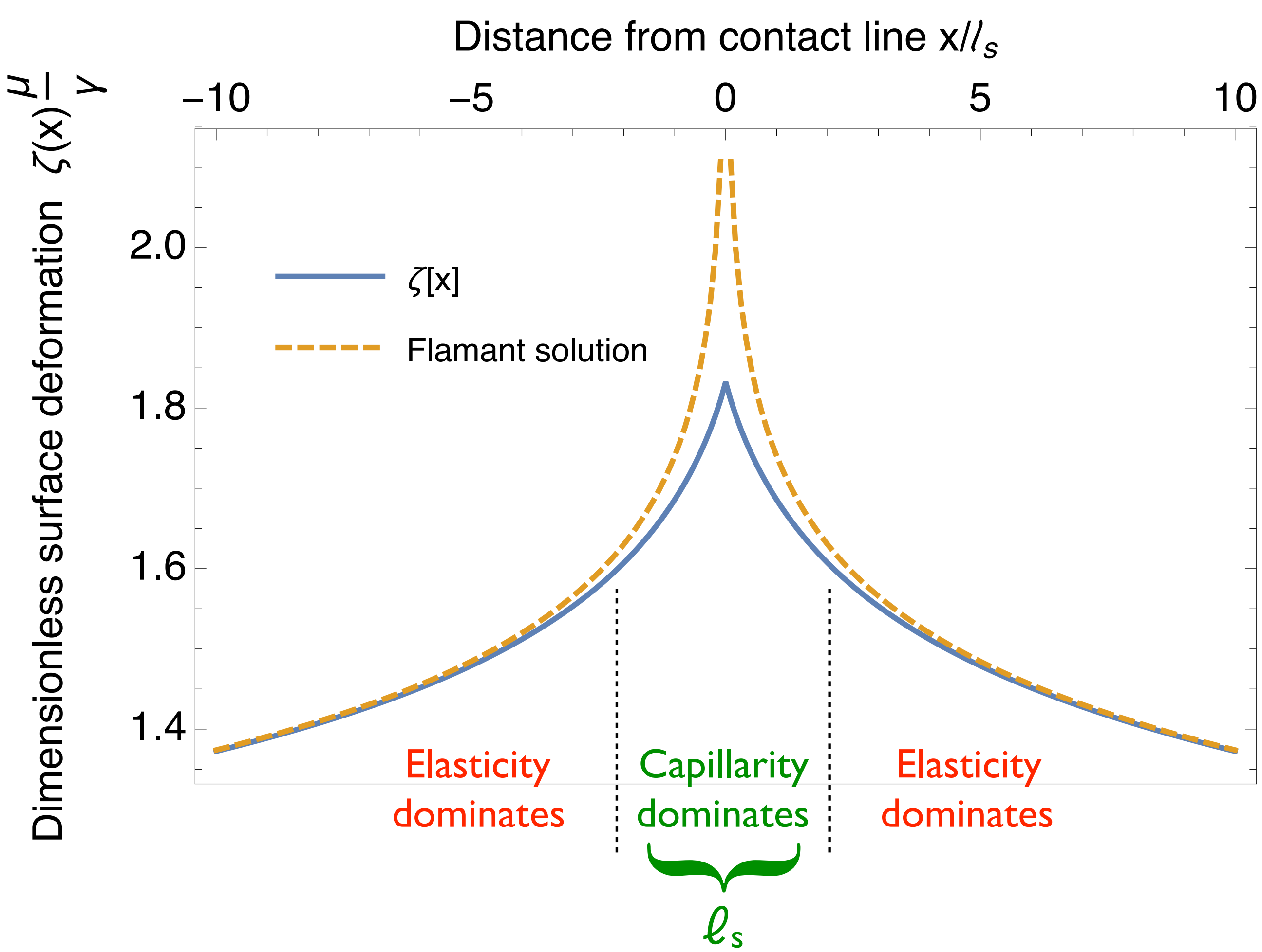
The divergent displacement field is regularized by the surface tension of the soft solid.

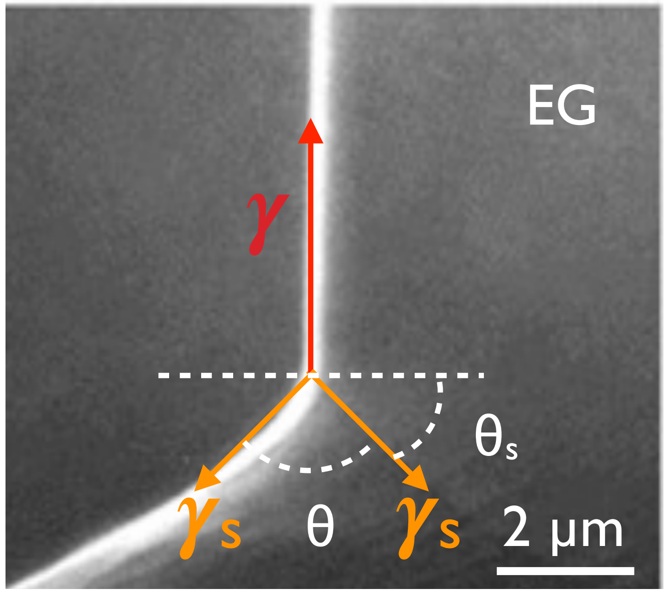
At short distance from the tip ($\ll \ell_s$), capillarity dominates

At large distance from the tip ($\gg \ell_s$), elasticity dominates



Linear theory of elastowetting

At the tip of the ridge:



$\theta_s = \zeta'(0) = \gamma/(2\gamma_s)$

$\theta = \pi - \gamma/\gamma_s$

The opening angle θ of the ridge
is independent of elasticity !

Vertical force balance at the tip:

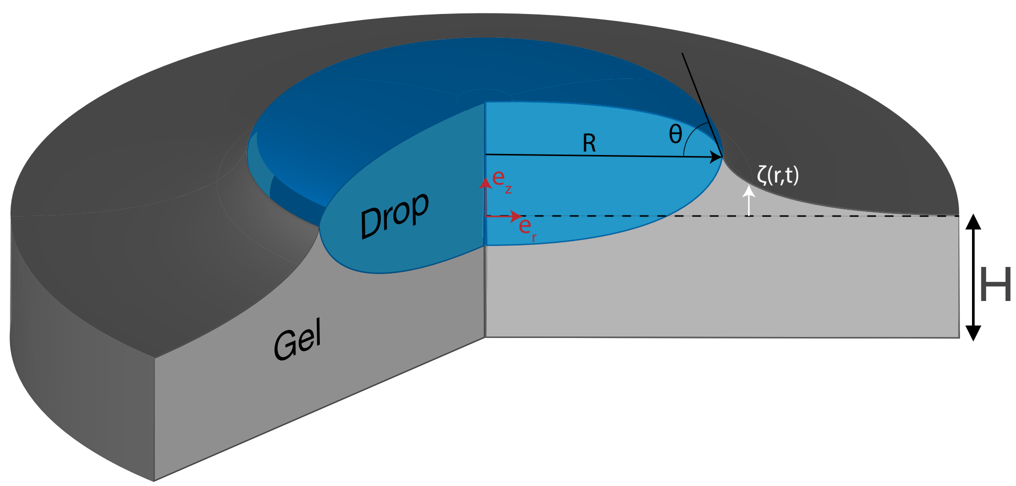
$\gamma = 2\, \gamma_s * \theta_s$

Neumann construction at the tip!

« Liquid-like behavior »

Comparison with static experiments

A drop of radius R resting on a soft substrate with finite thickness H:



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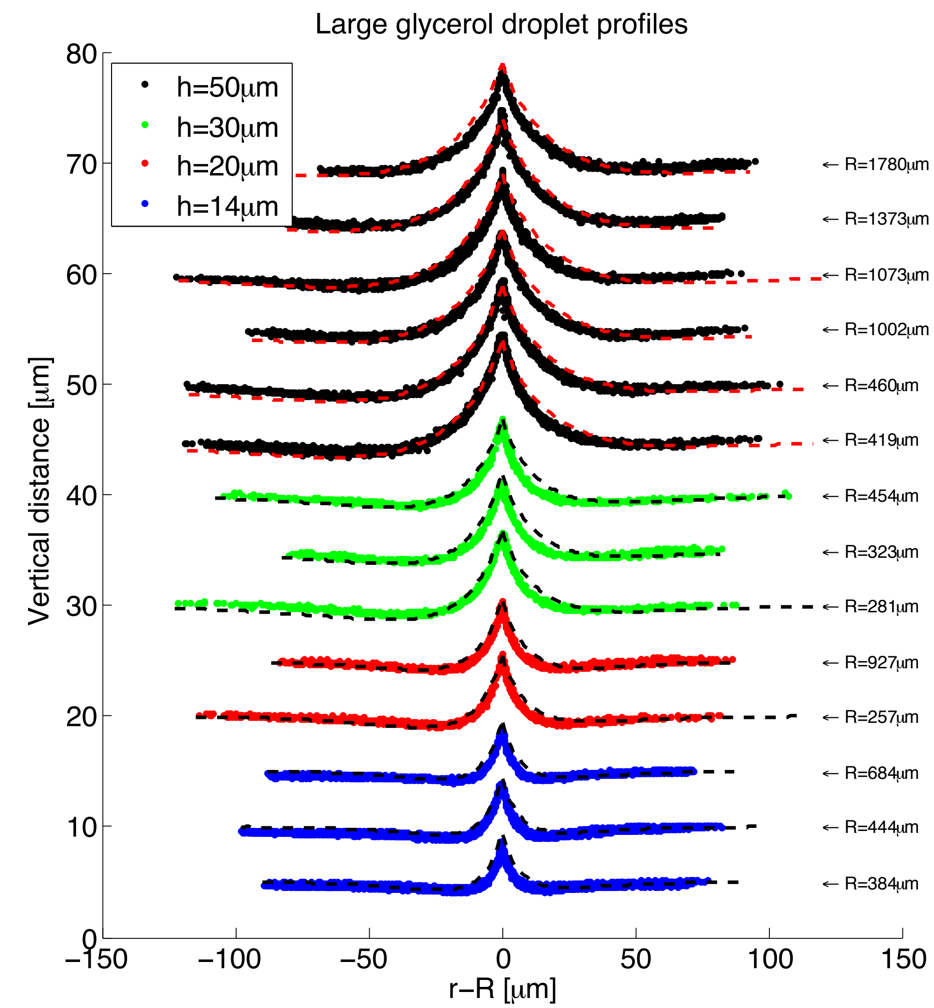
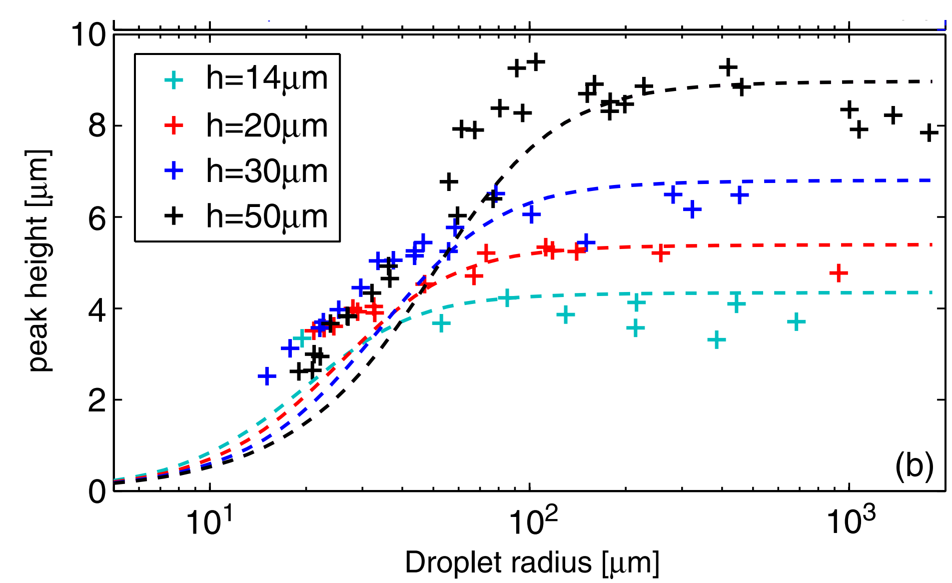
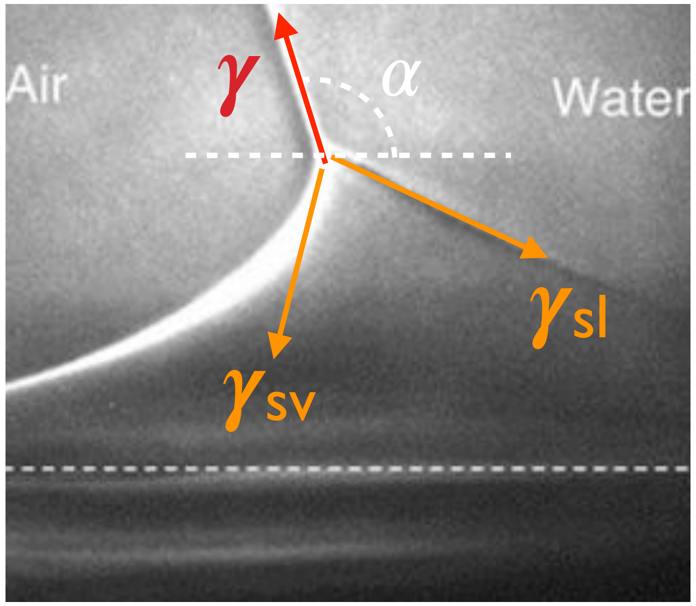




Ridge dimensions decrease with decreasing thickness H and droplet radius R

But the linear theory has strong limitations…

Only macroscopic contact angle
$\alpha = \pi/2$



No predictions for
the general case $\gamma_{SL} \neq \gamma_{SV}$

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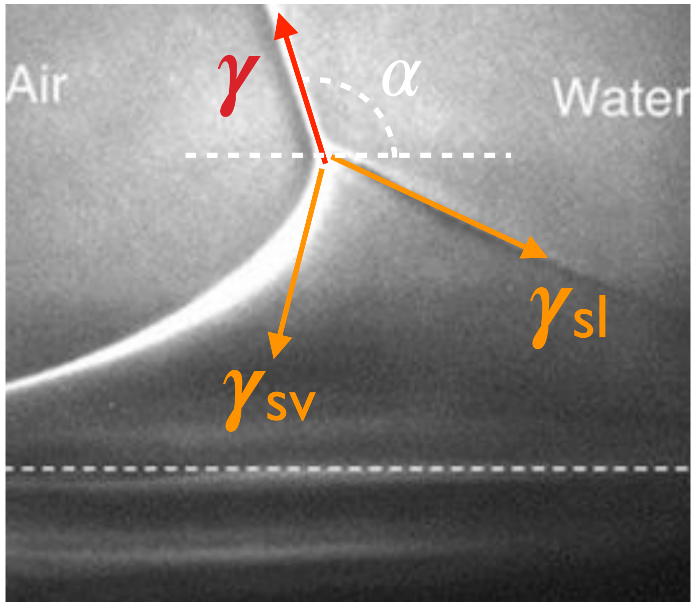

No predictions for
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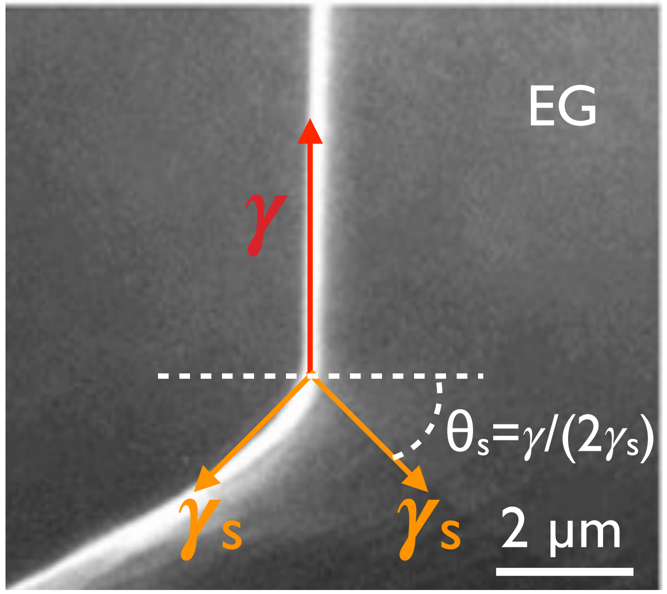
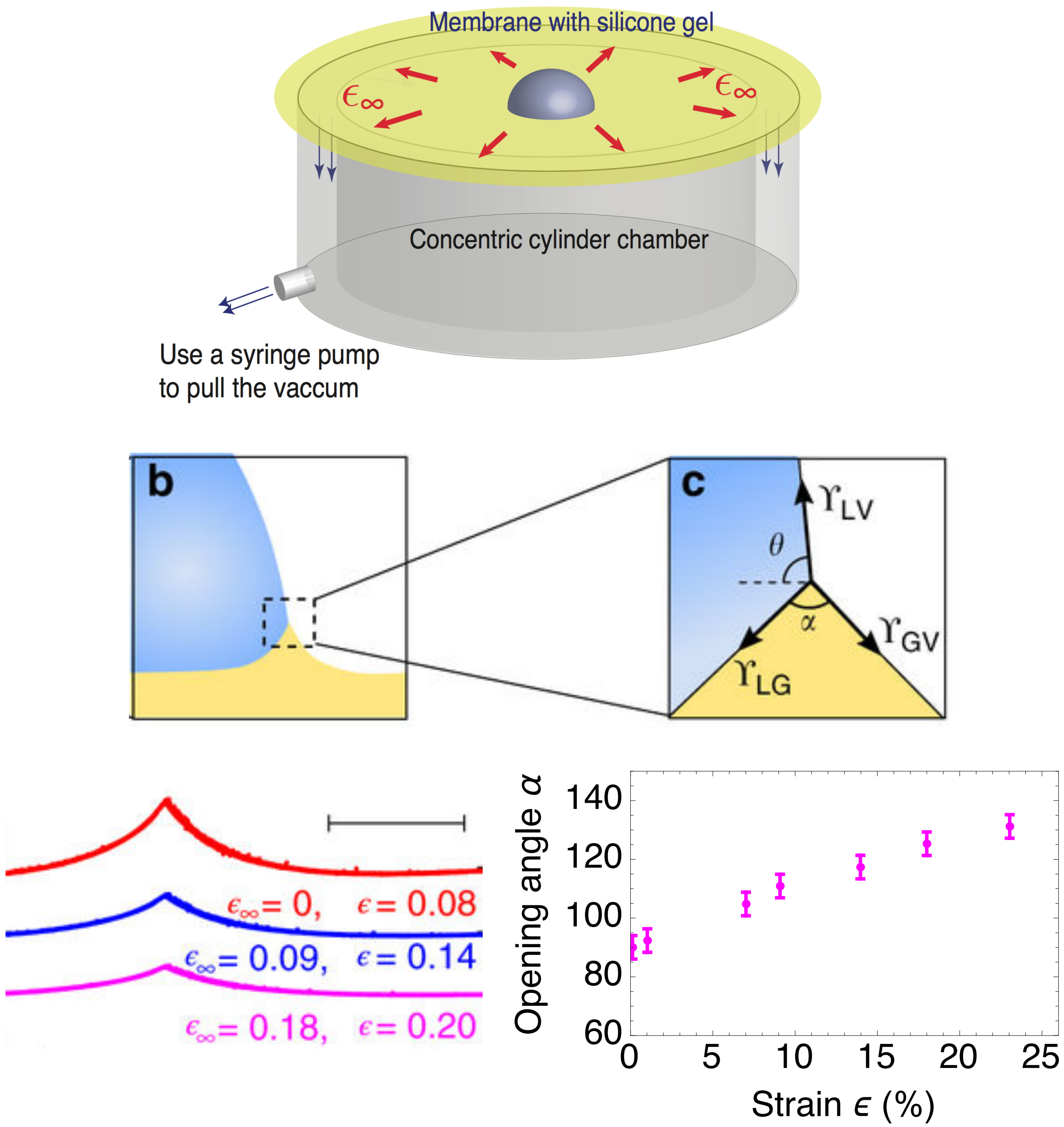
Only small deformations
$\gamma/(2\gamma_s) << 1$



BUT experimentally:
$\zeta'(0) = \theta_s = \gamma/(2\gamma_s) \sim 0.6\text{-}0.8$

Failure of the linear theory at large deformations

Xu et al (Sept 2017)



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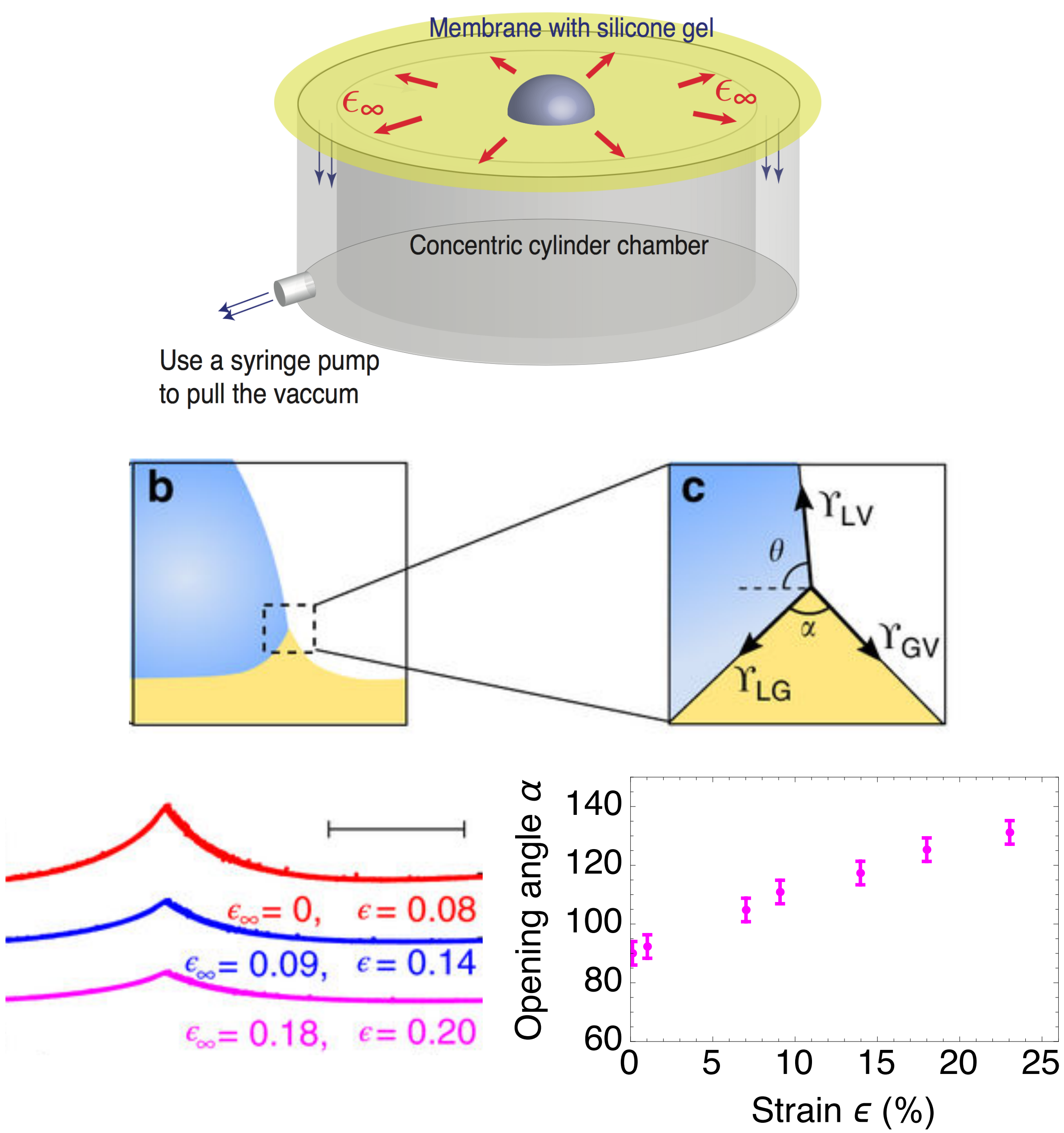

According to the linear theory

γ_s depends on the deformation

Very strong Shuttleworth effect !

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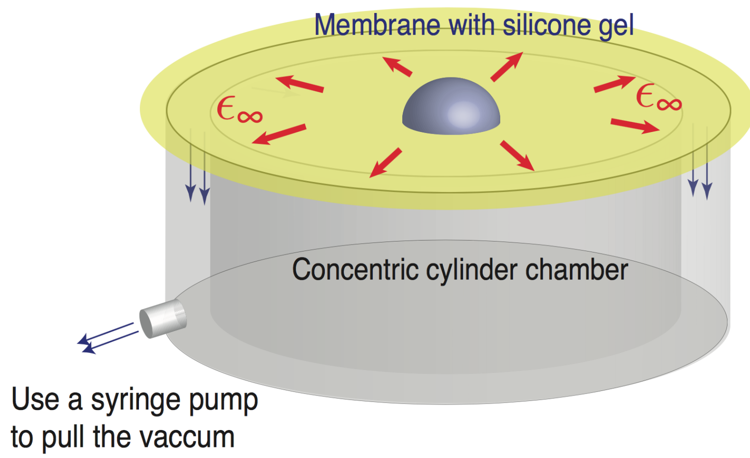
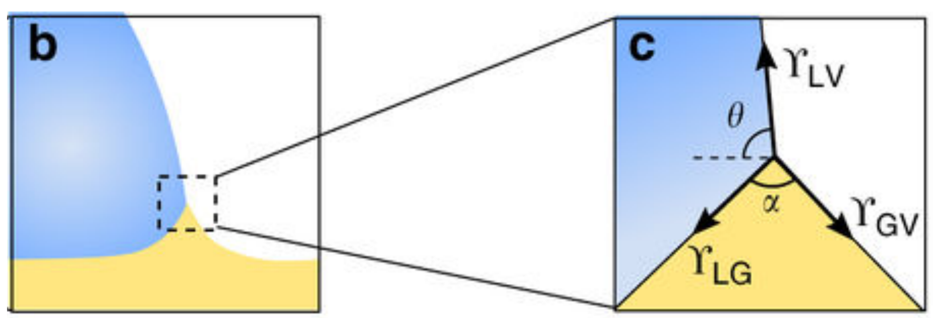
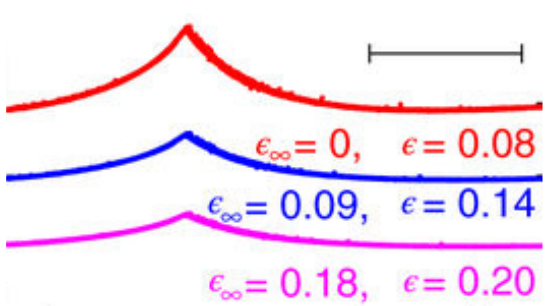
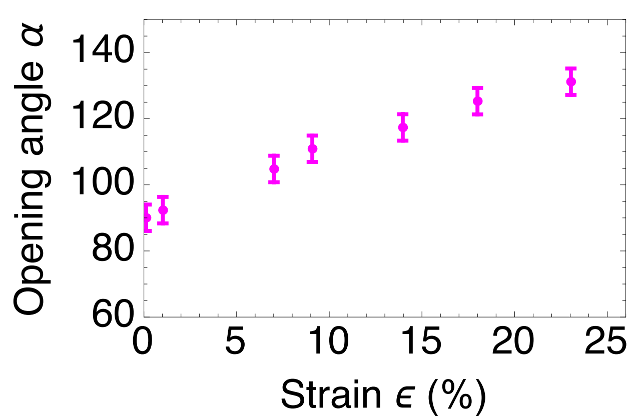
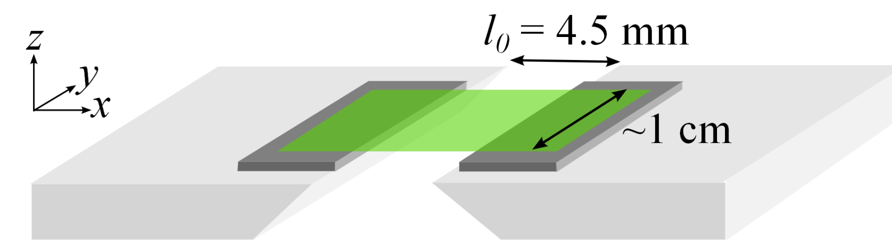


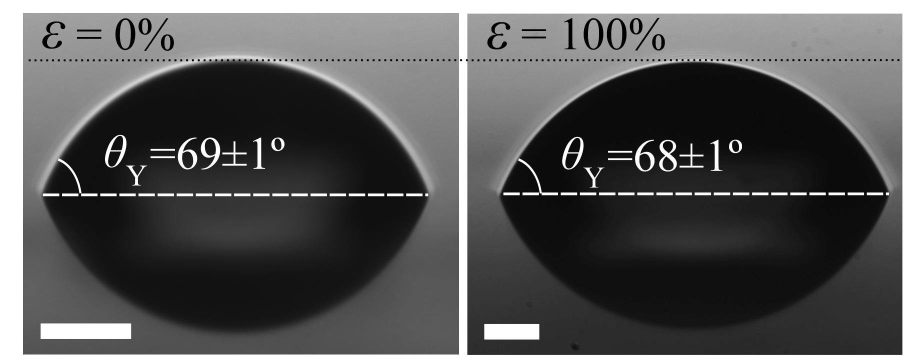


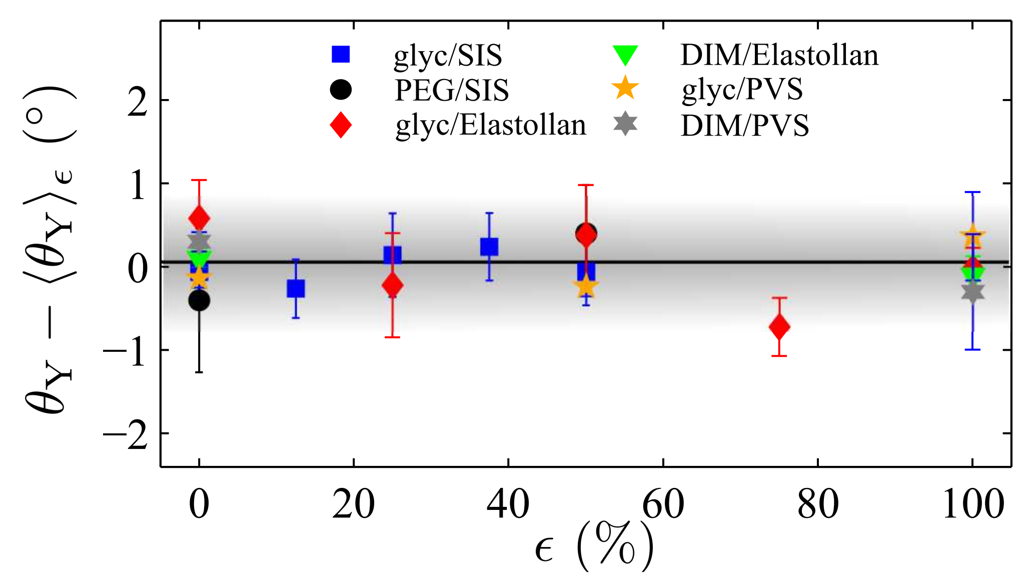




Schulman et al (Dec 2017 on ArXiv)







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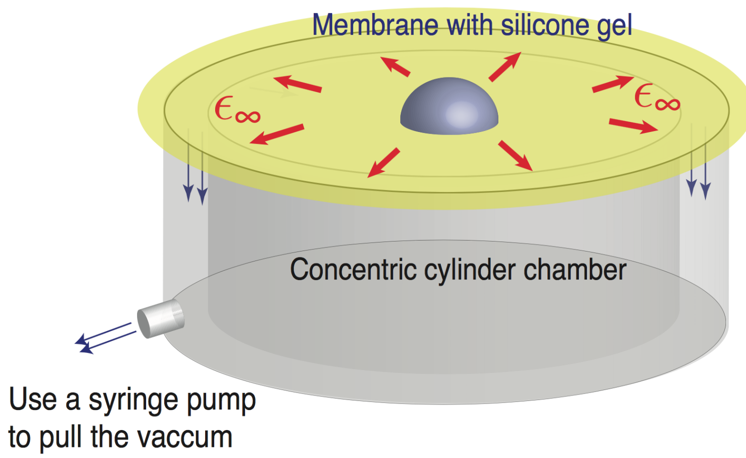
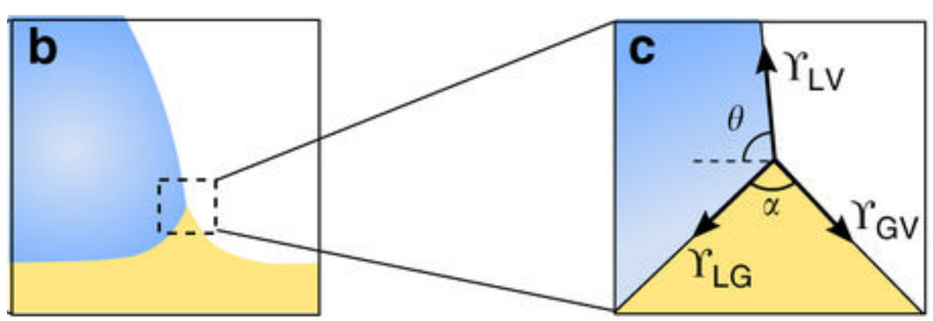
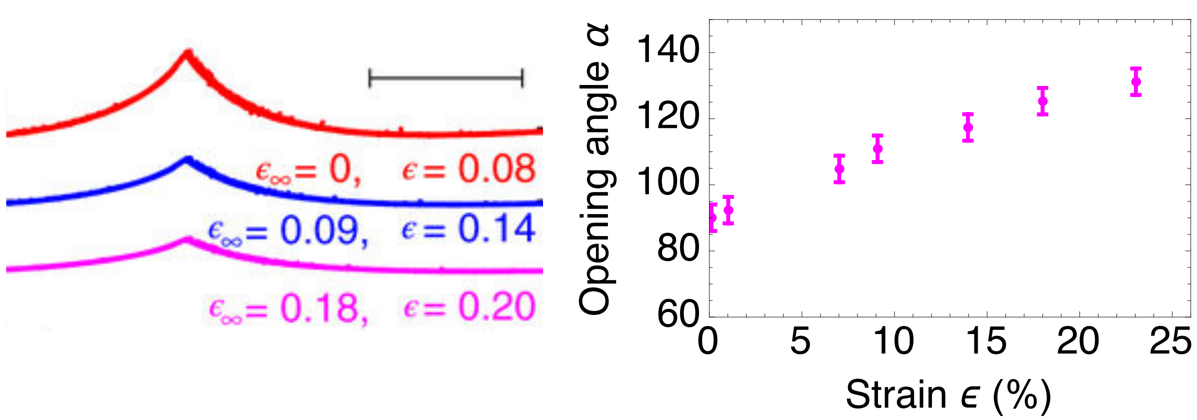
Failure of the linear theory at large deformations

Xu et al (Sept 2017)





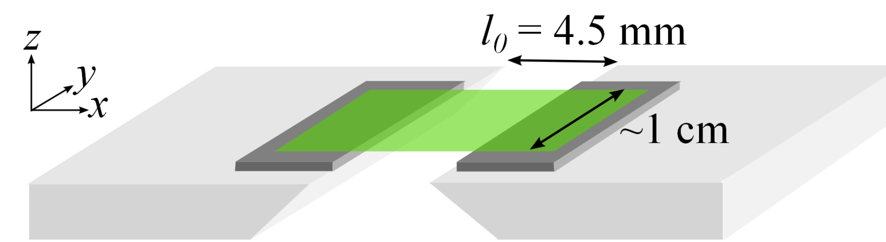


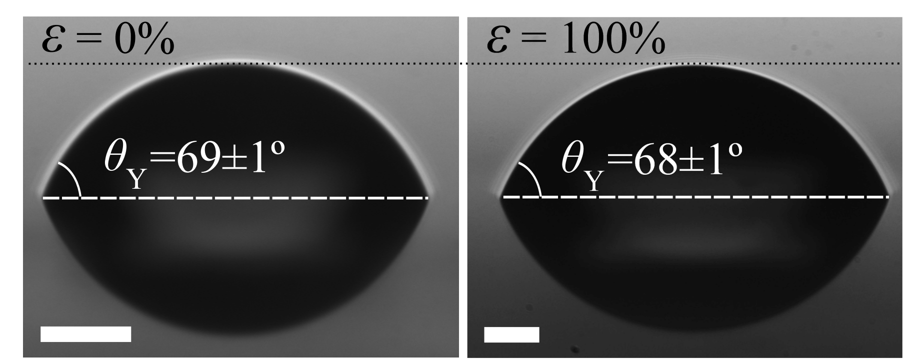
According to the linear theory

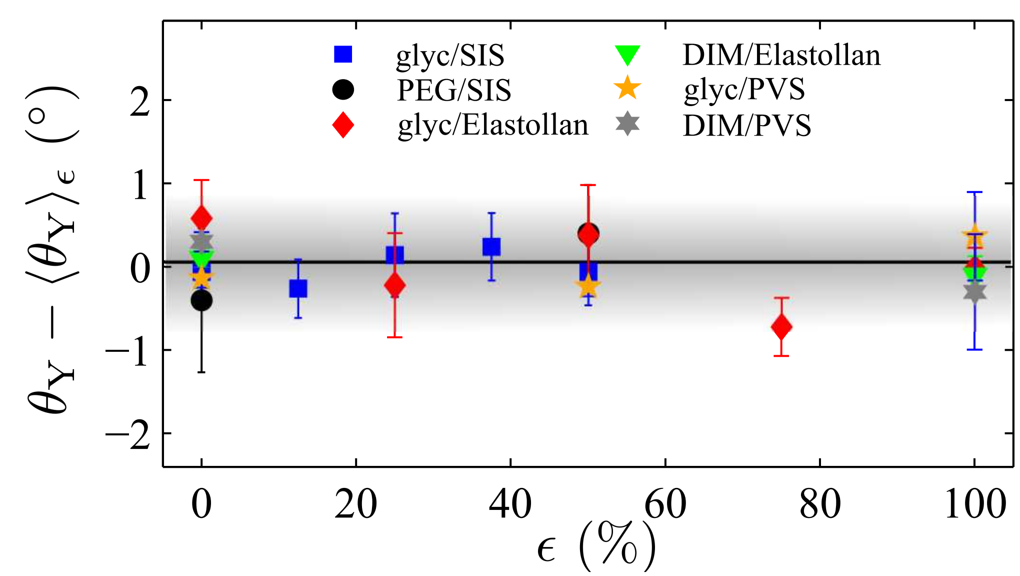
γ_s depends on the deformation

Very strong Shuttleworth effect !

Schulman et al (Dec 2017 on ArXiv)

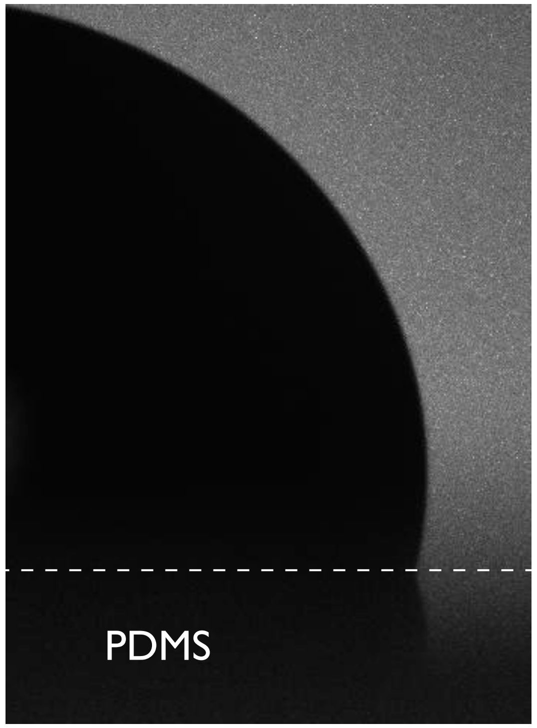


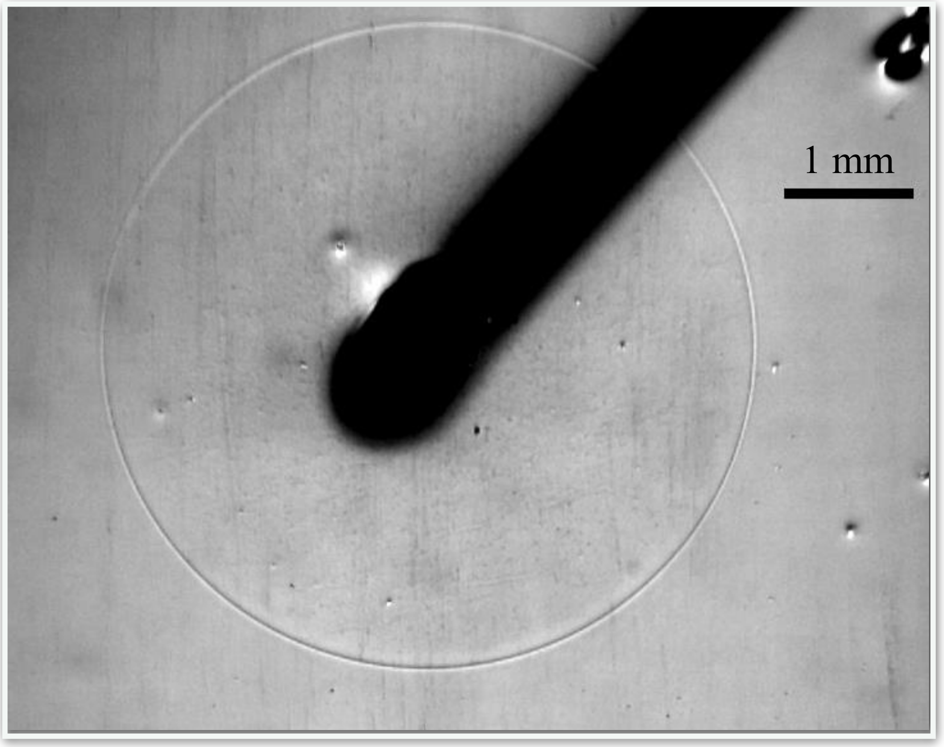




No Shuttleworth effect !

Memory effects in static elastowetting

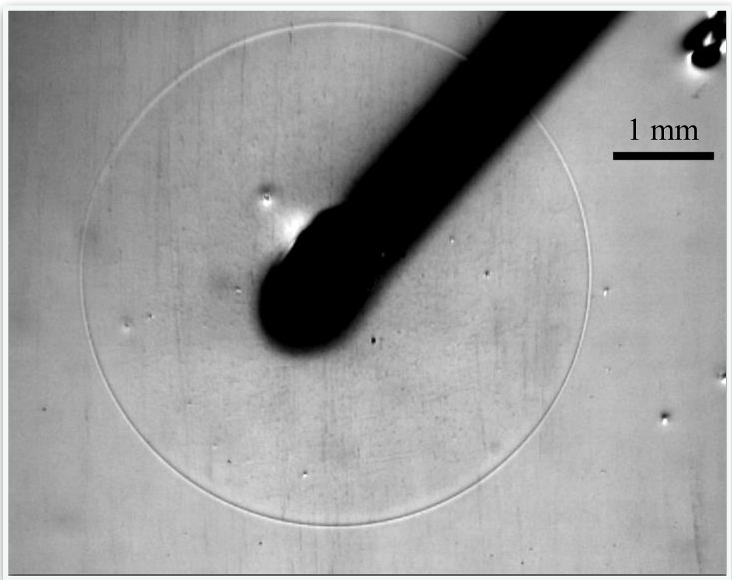




Trace left on PDMS after receding a water droplet

Resting time ~ 30 min
Drop diameter ~ 5 mm
PDMS thickness ~ 100 μm
Shear modulus ~ 1 kPa

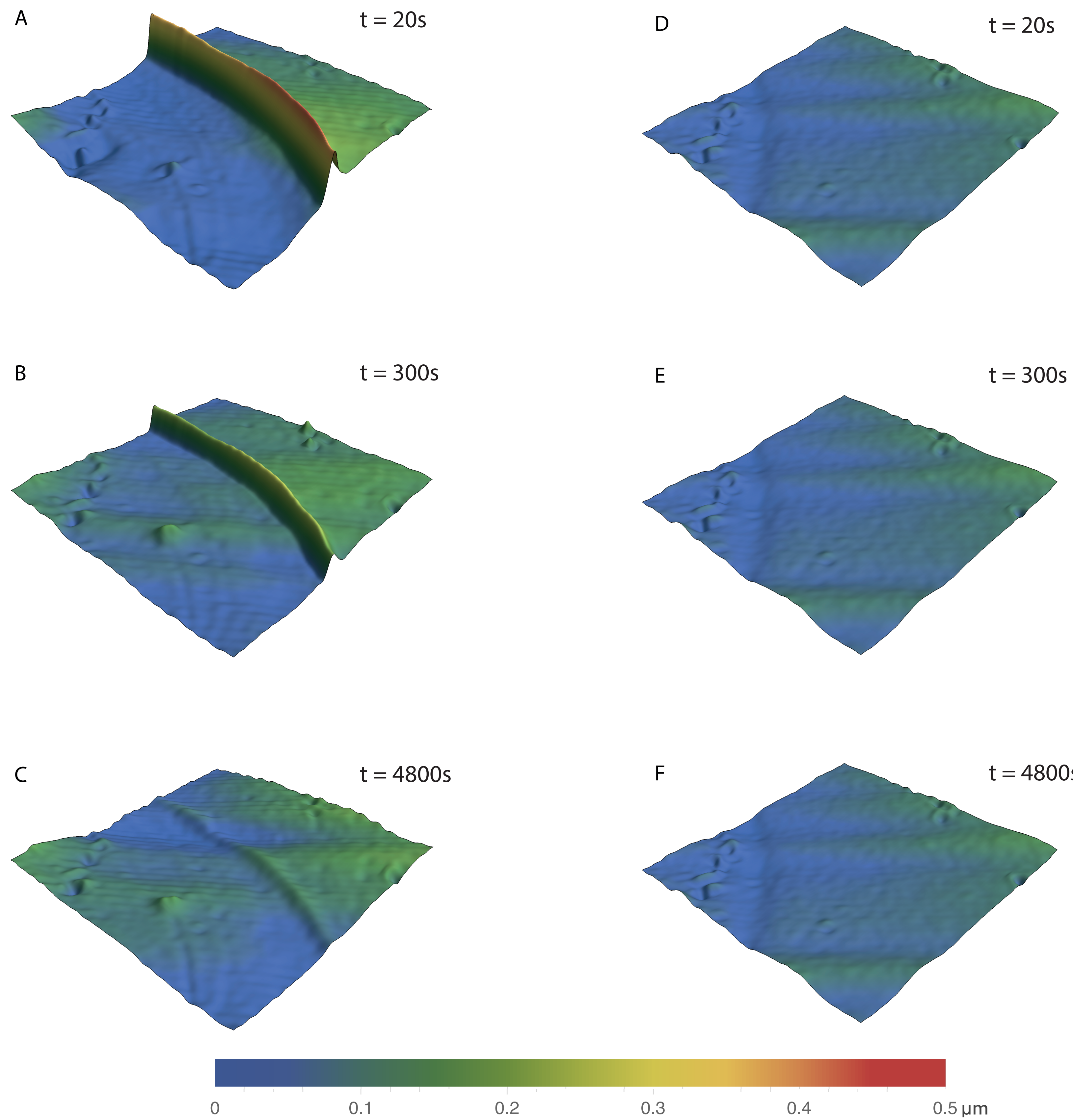
Memory effects in static elastowetting



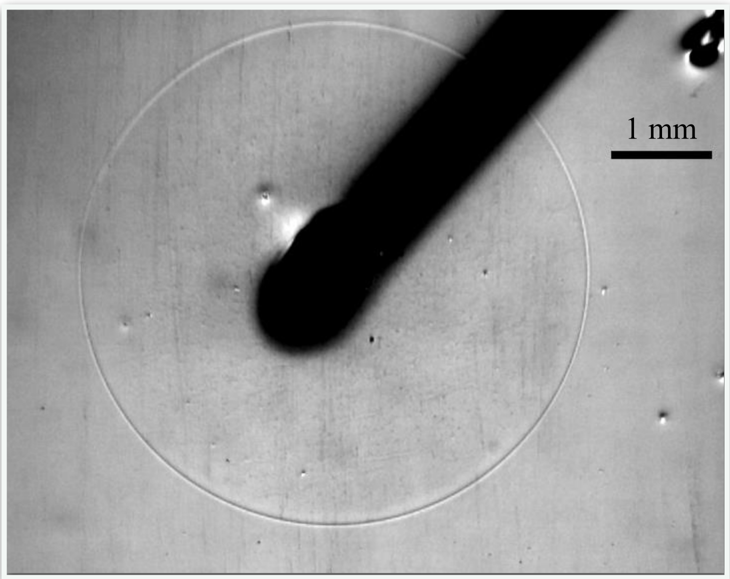
Drop diameter ~ 5 mm
PDMS thickness ~ 100 μm
Shear modulus ~ 1 kPa

Resting time ~ 30 min

Resting time ~ 2 min



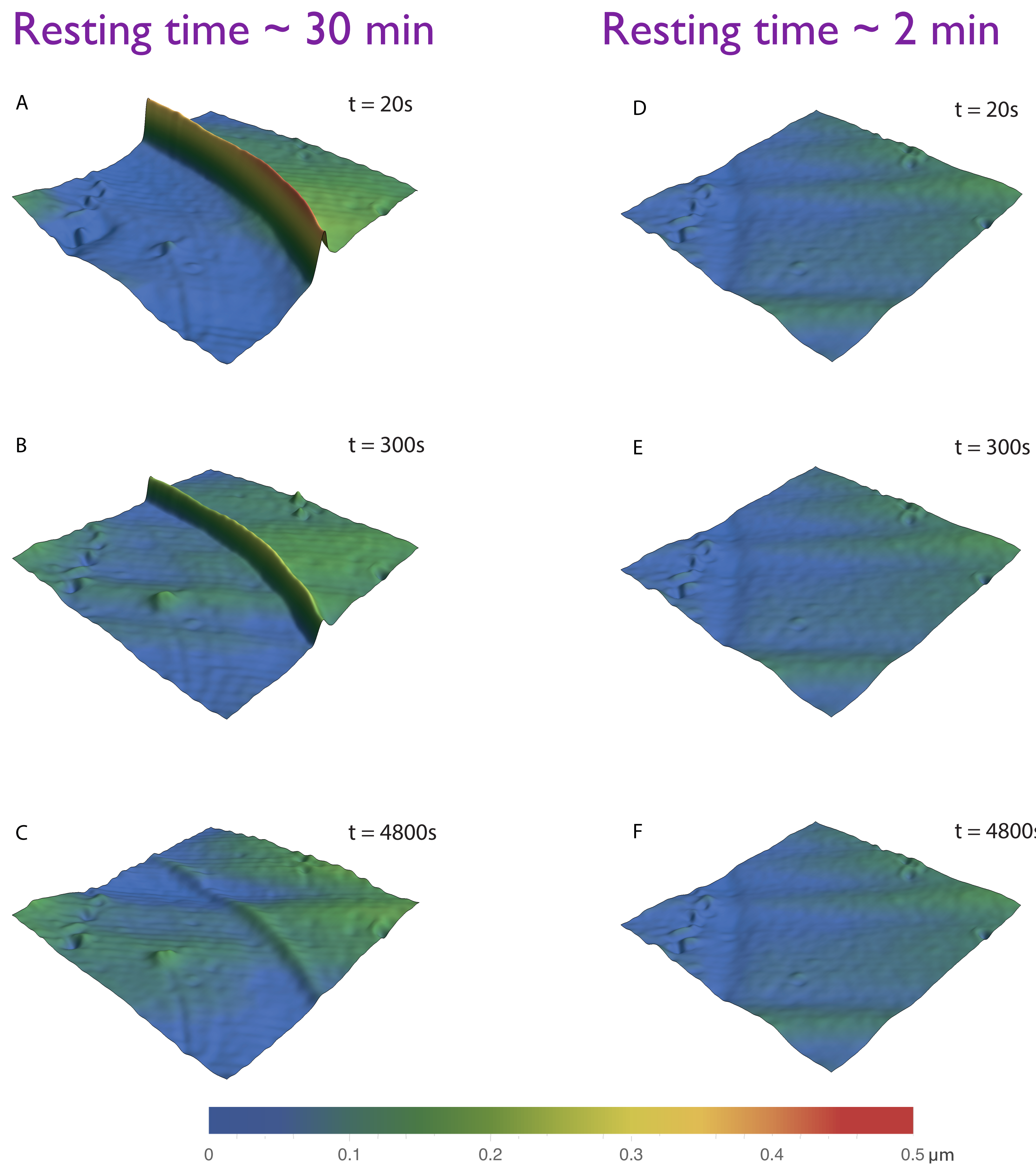
Memory effects in static elastowetting



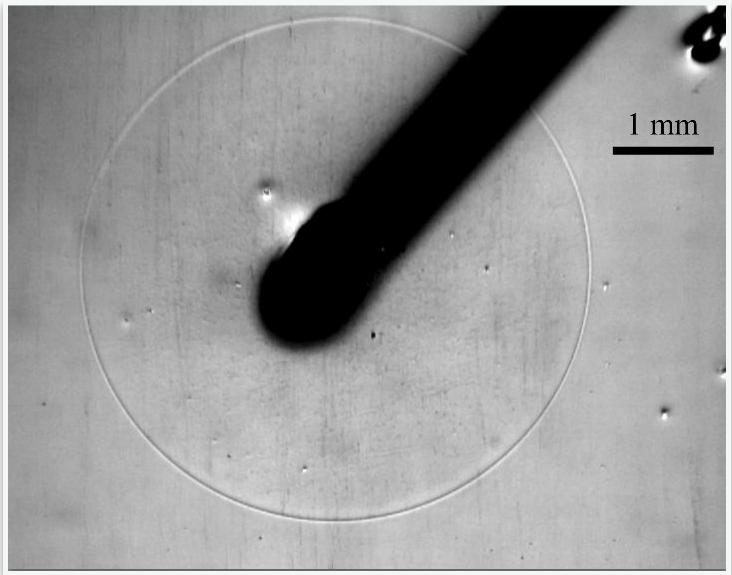
Drop diameter ~ 5 mm
PDMS thickness ~ 100 µm
Shear modulus ~ 1 kPa

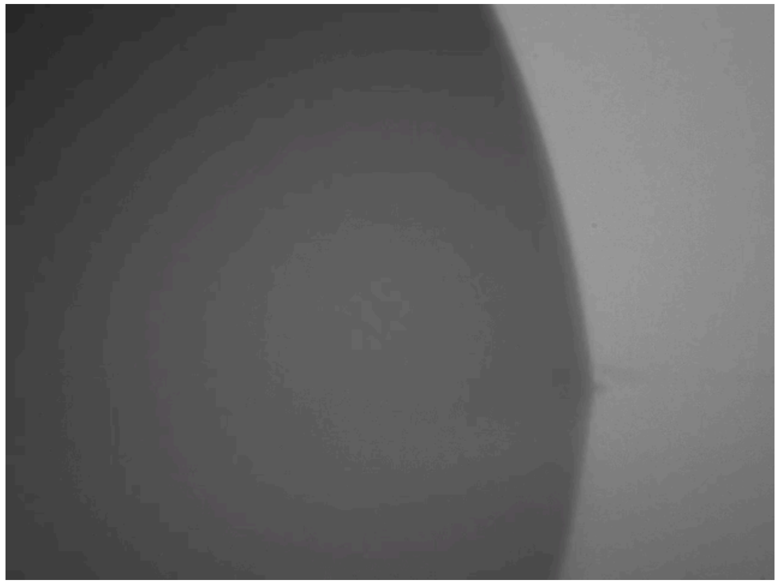
↓

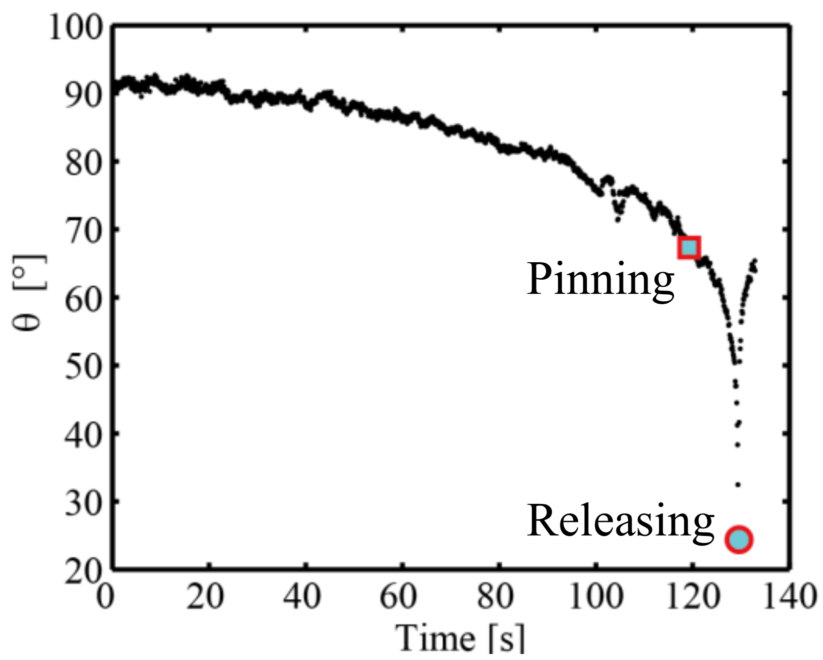
A time-dependent process that depends on the wetting history

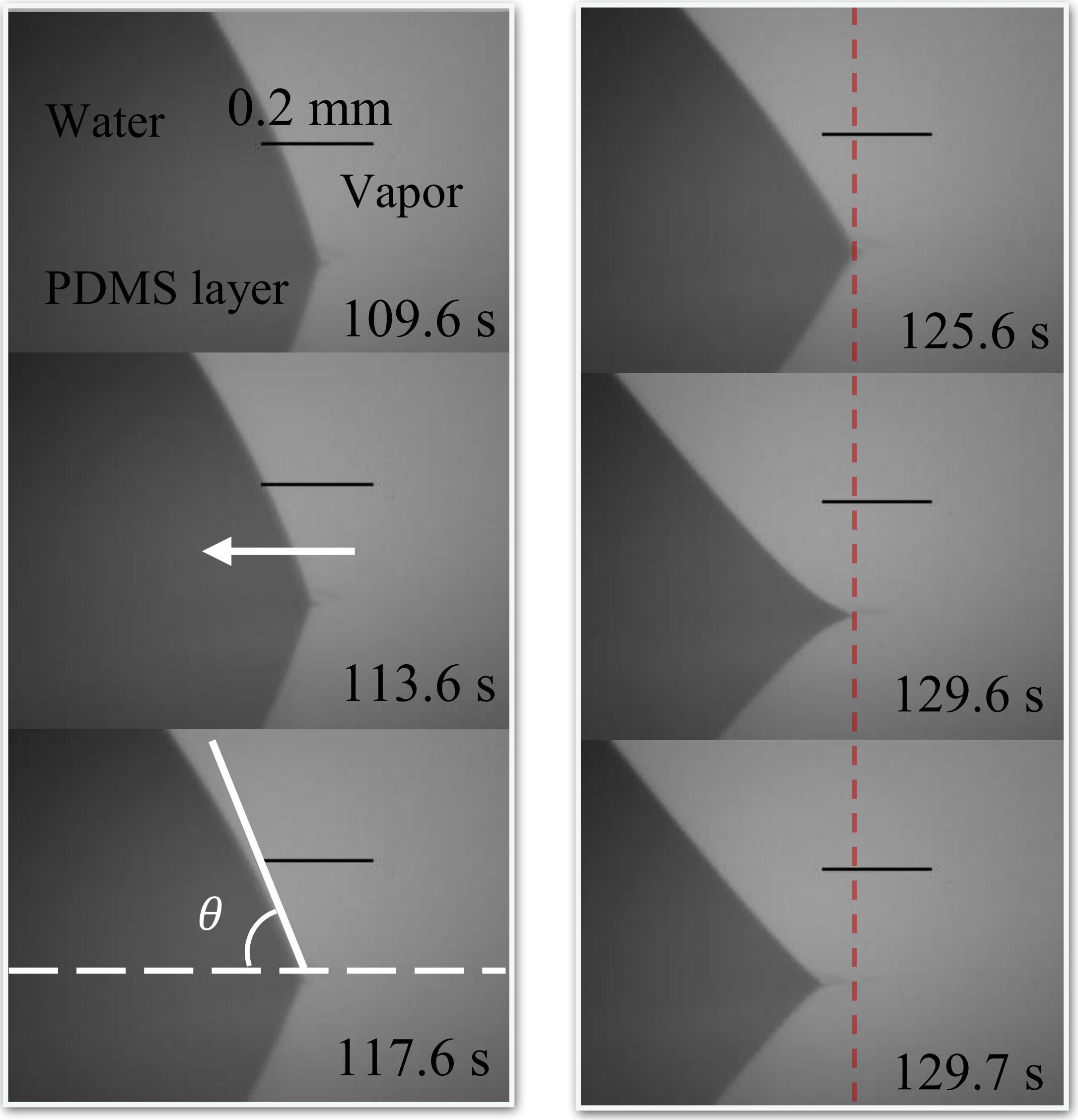


Remnant traces can trap the triple line









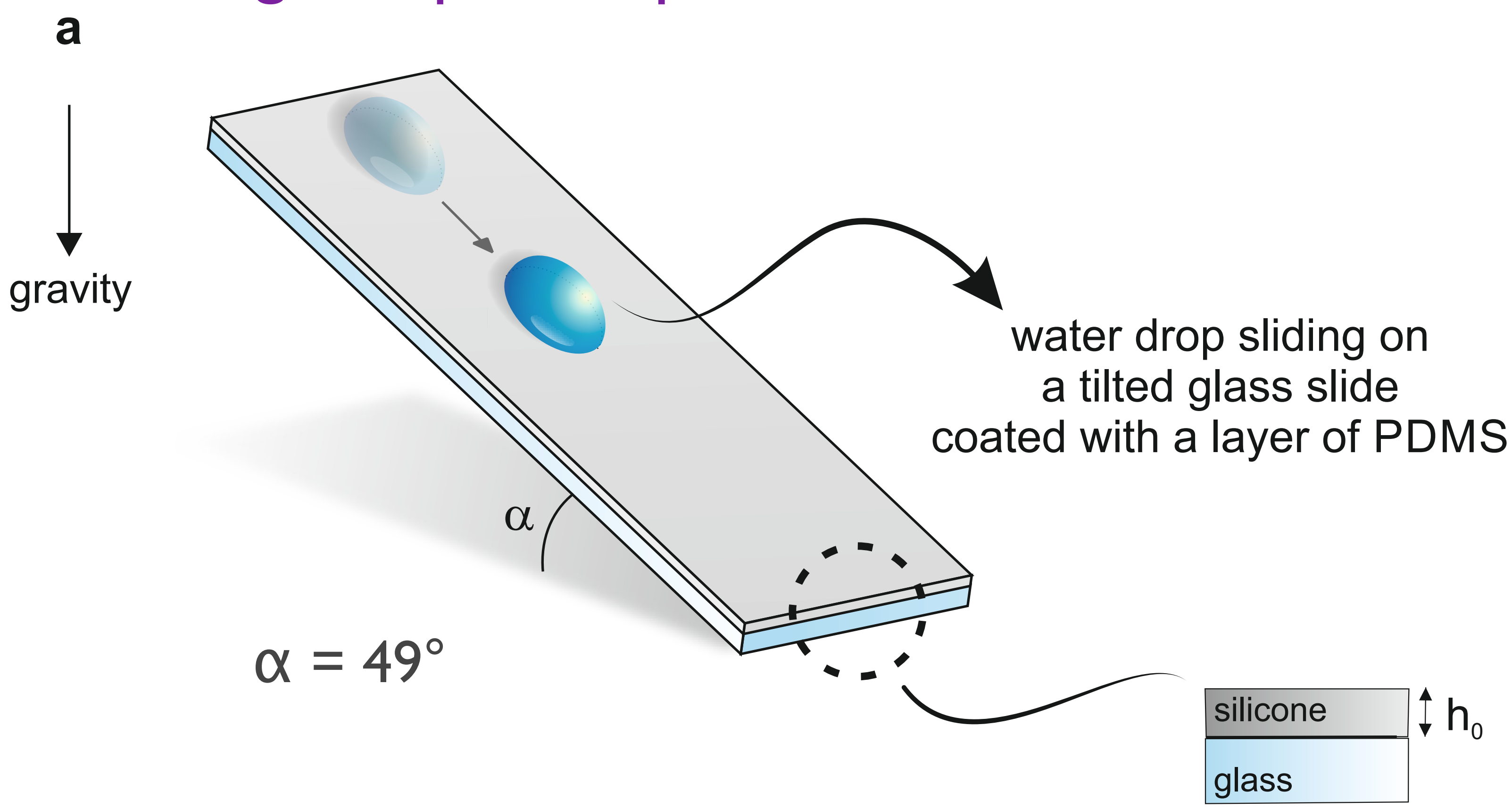
Hysteresis increases from ~5° to ~ 14° on PDMS when the drop is left at rest for 30 minutes on PDMS

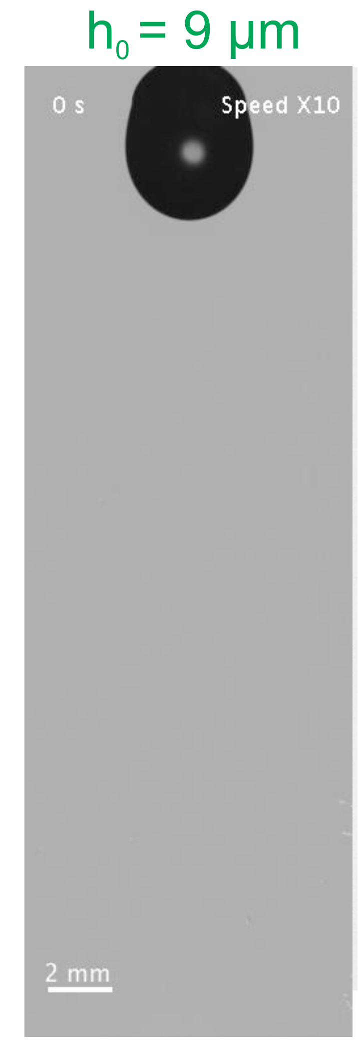
Time-dependent hysteresis was also observed previously on elastomers

Extrand and Kumagai (1996)

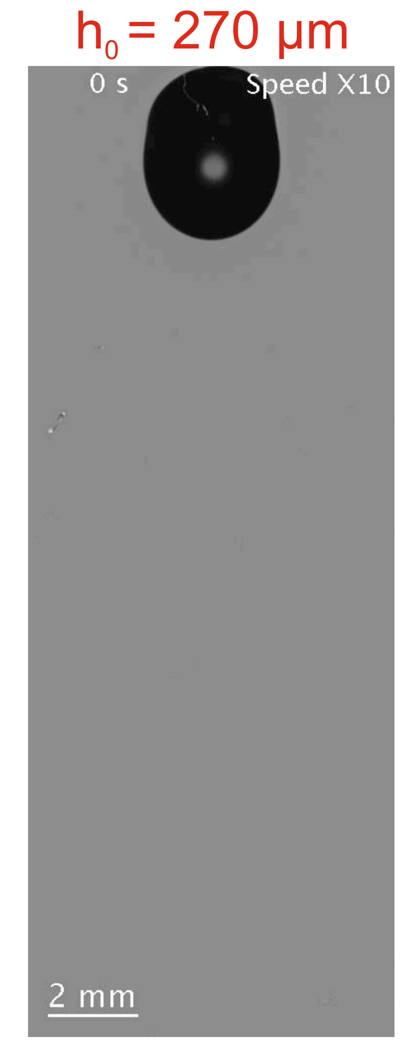
Viscoelastic effects in elastowetting

Sliding of liquid drops on soft deformable solids





$V_{sliding} = 0.6\ mm/s$



$V_{sliding} = 0.04 mm/s$

Sliding velocity on PDMS much smaller
than on bare glass (~ cm/s)

↓

Additional dissipation mechanism: viscoelastic braking

Carré et al (1996), Carré et al (2001), Long et al (1996)

Very sensitive on substrate thickness !

Zhao et al (PNAS, 2018)

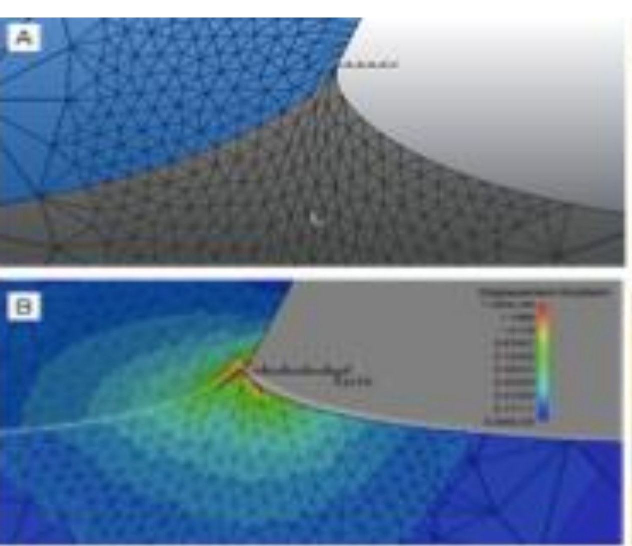
Purpose of the POLYWET Project

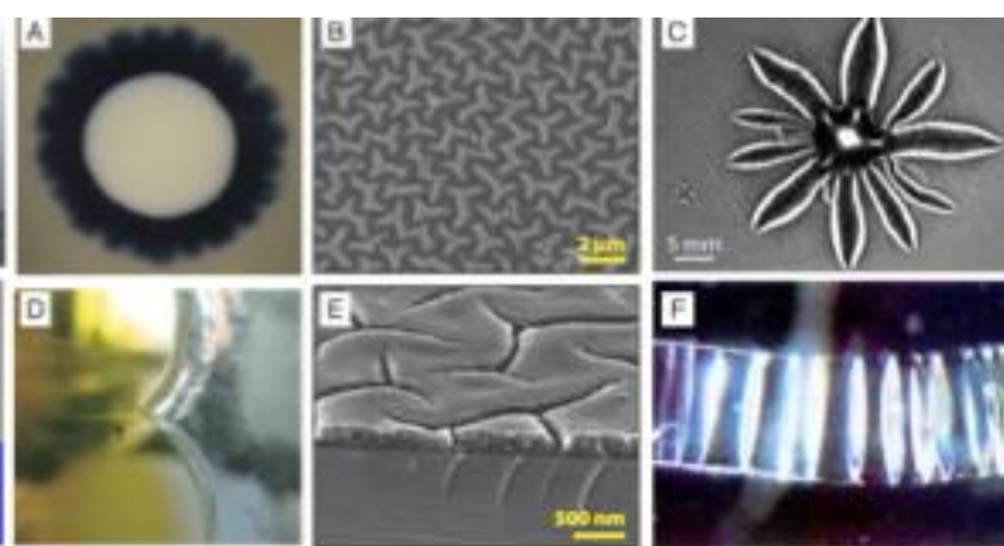
investigate theoretically and numerically
the elastowetting problem

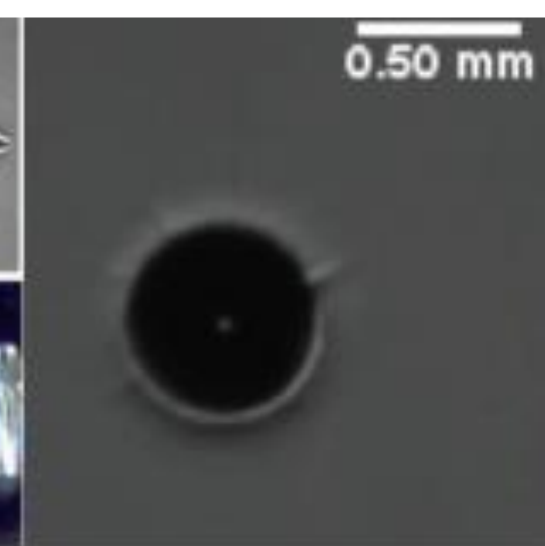
for arbitrary liquid/solid couples
$\gamma_{SL} \neq \gamma_{SV}$

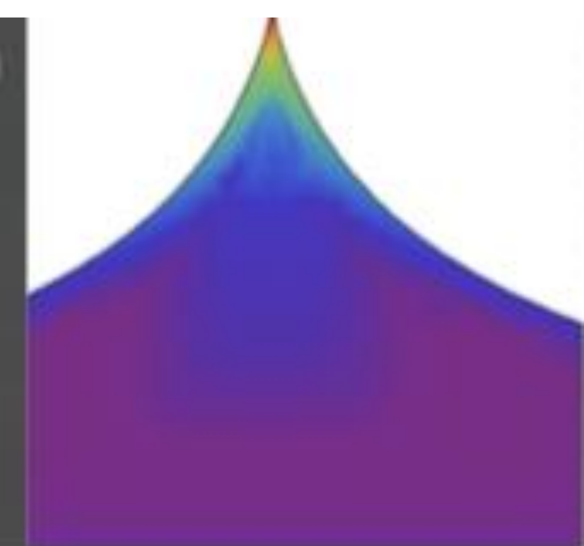
in the nonlinear range
$\gamma/(2\gamma_s) \geq 1$

on complex materials
poro-visco-elastic



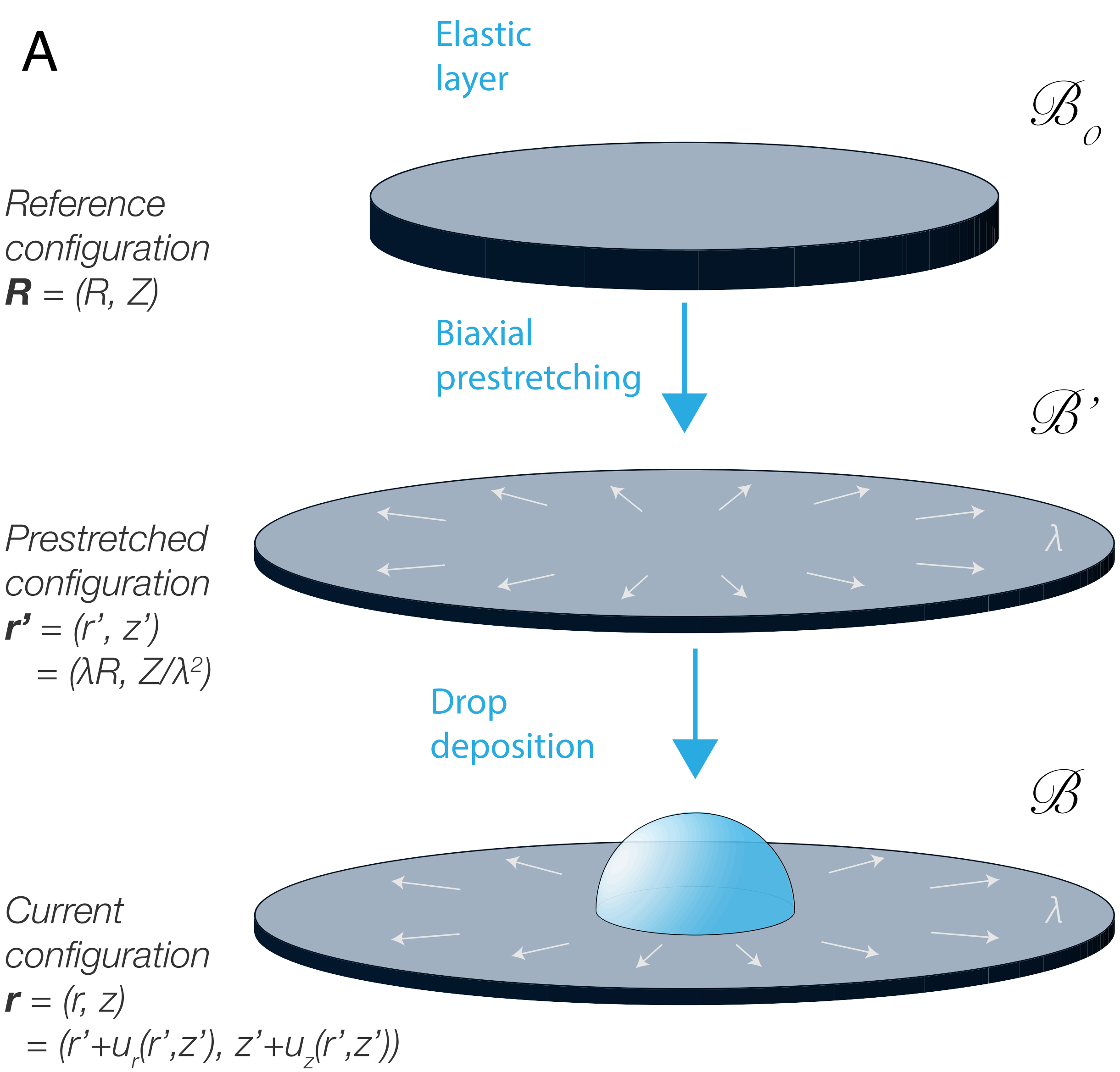






Nonlinear effects in elastowetting

Large deformations of a pre-stretched Neo-Hookean material with constant surface energy:



Elastic energy density:

$$\mathcal{W}_{el}(\boldsymbol{F}) = \frac{\mu}{2}\left\{\mathrm{Tr}(\boldsymbol{F}\boldsymbol{F}^T) - 3\right\}$$

$$\boldsymbol{F} = \frac{\partial \vec{x}}{\partial \vec{X}} \qquad \vec{x} = \vec{X} + \vec{u}(\vec{X})$$

Surface energy density:

$$\mathcal{W}_s = \gamma_s$$

Total energy:

$$\mathcal{W} = \int_{\mathcal{B}_0} \mathcal{W}_{el}(\boldsymbol{F})\mathrm{d}V_0 + \int_{\partial\mathcal{B}} \mathcal{W}_s \mathrm{d}a$$

3D integral over the *reference* volume

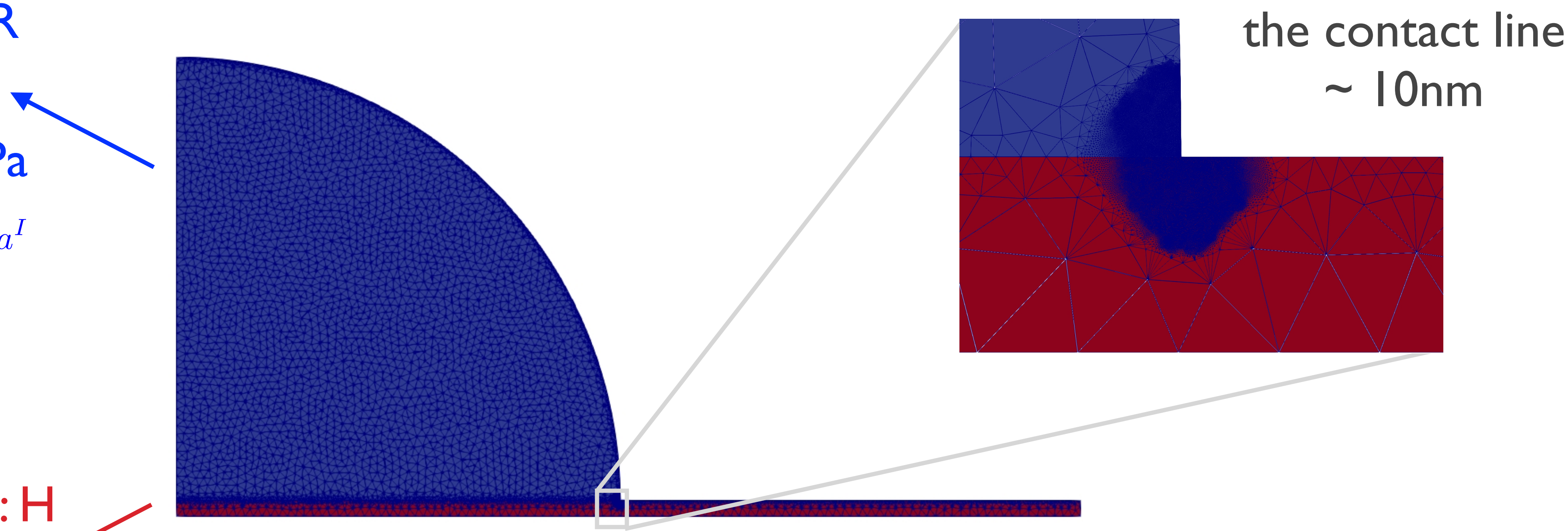
2D integral over the *deformed* area

Nonlinear effects in elastowetting

Approximation of the elastowetting problem as two solids in contact:

Solid I
spherical cap of radius: R
surface energy: γ
elastic modulus: $\mu_I \approx$ mPa

$$\mathcal{W}^I = \int_{\mathcal{B}_0^I} \mathcal{W}_{el}^I(\boldsymbol{F})\mathrm{d}V_0^I + \int_{\partial\mathcal{B}^I} \mathcal{W}_s^I \mathrm{d}a^I$$



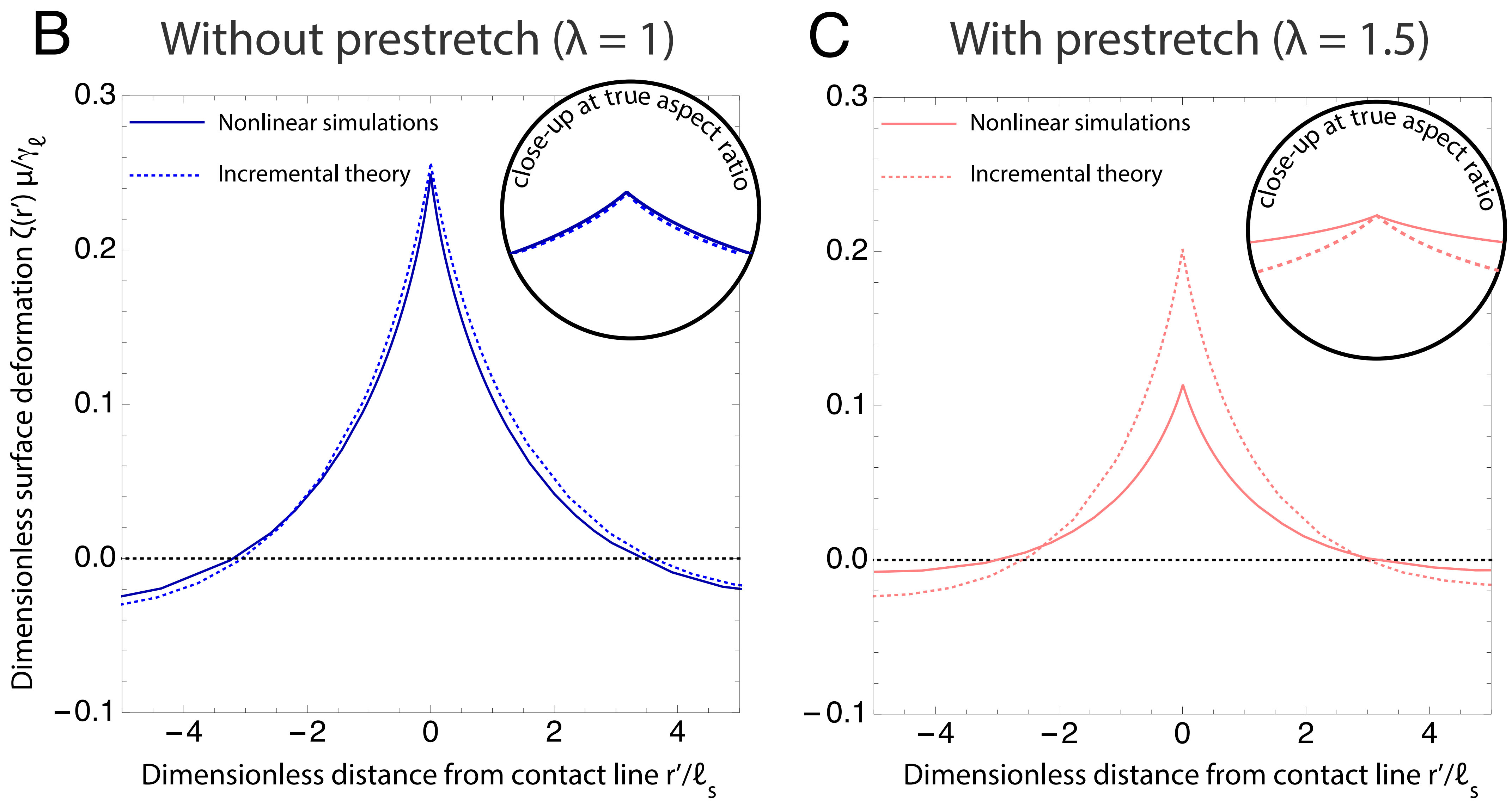
Solid II
circular layer of thickness: H
surface energy: γ_s
elastic modulus: $\mu_{II} \approx$ kPa

$$\mathcal{W}^{II} = \int_{\mathcal{B}_0^{II}} \mathcal{W}_{el}^{II}(\boldsymbol{F})\mathrm{d}V_0^{II} + \int_{\partial\mathcal{B}^{II}} \mathcal{W}_s^{II} \mathrm{d}a^{II}$$

Numerical minimization of the total energy $\mathcal{W}^I + \mathcal{W}^{II}$
is performed by a Finite Element Method under FreeFem++

de Pascalis et al (2018)

Results from the numerical simulations



Drop radius R: 1.3 mm

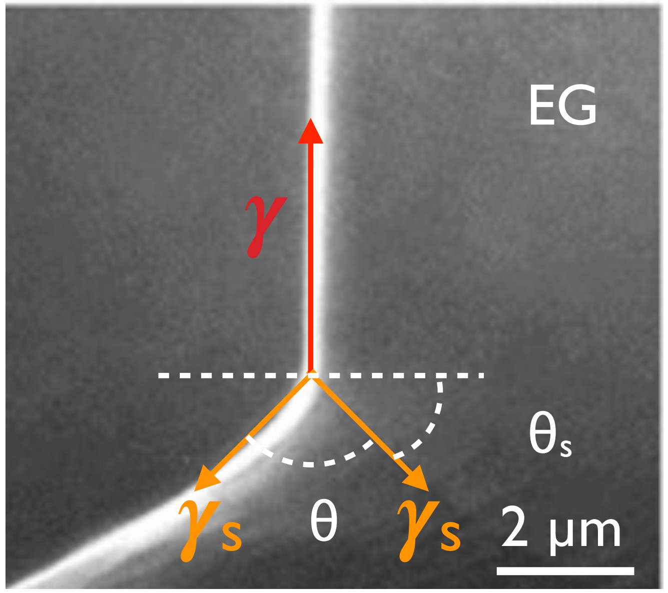
Elastic layer thickness H: 50 μm

Shear modulus μ: 1.6 kPa

Solid surface energy γ_s: 30mN/m

Liquid surface energy γ: 40mN/m

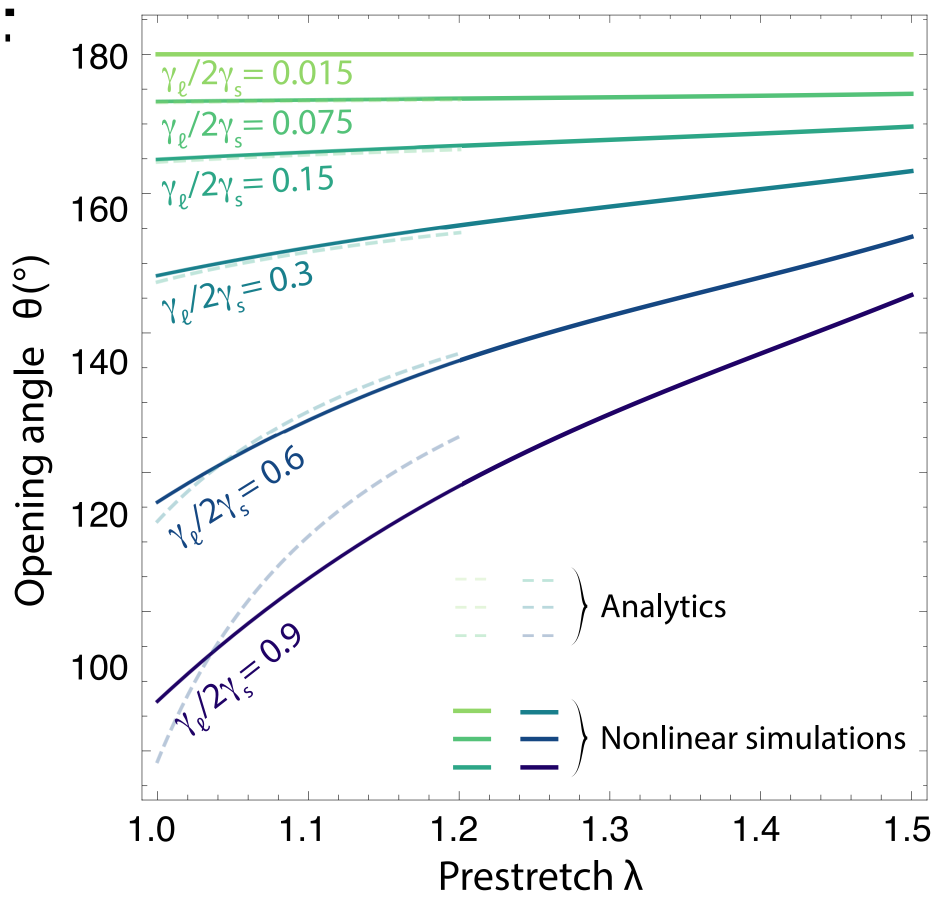
Comparison between linear and nonlinear theories



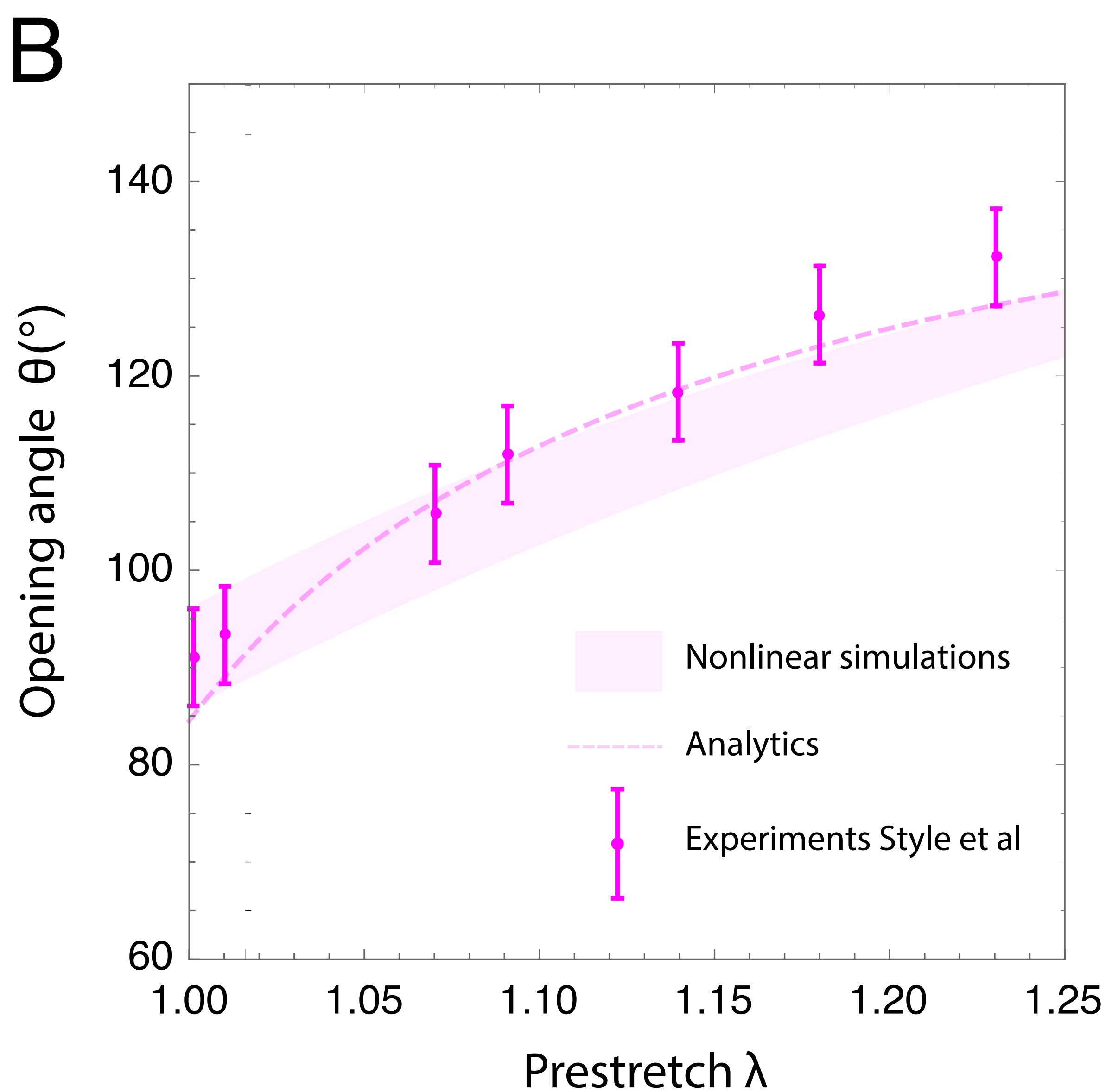
Linear Neumann construction:

$$\gamma = 2\,\gamma_s * \theta_s$$

$$\theta = \pi - \gamma/\gamma_s$$



Comparison between linear and nonlinear theories



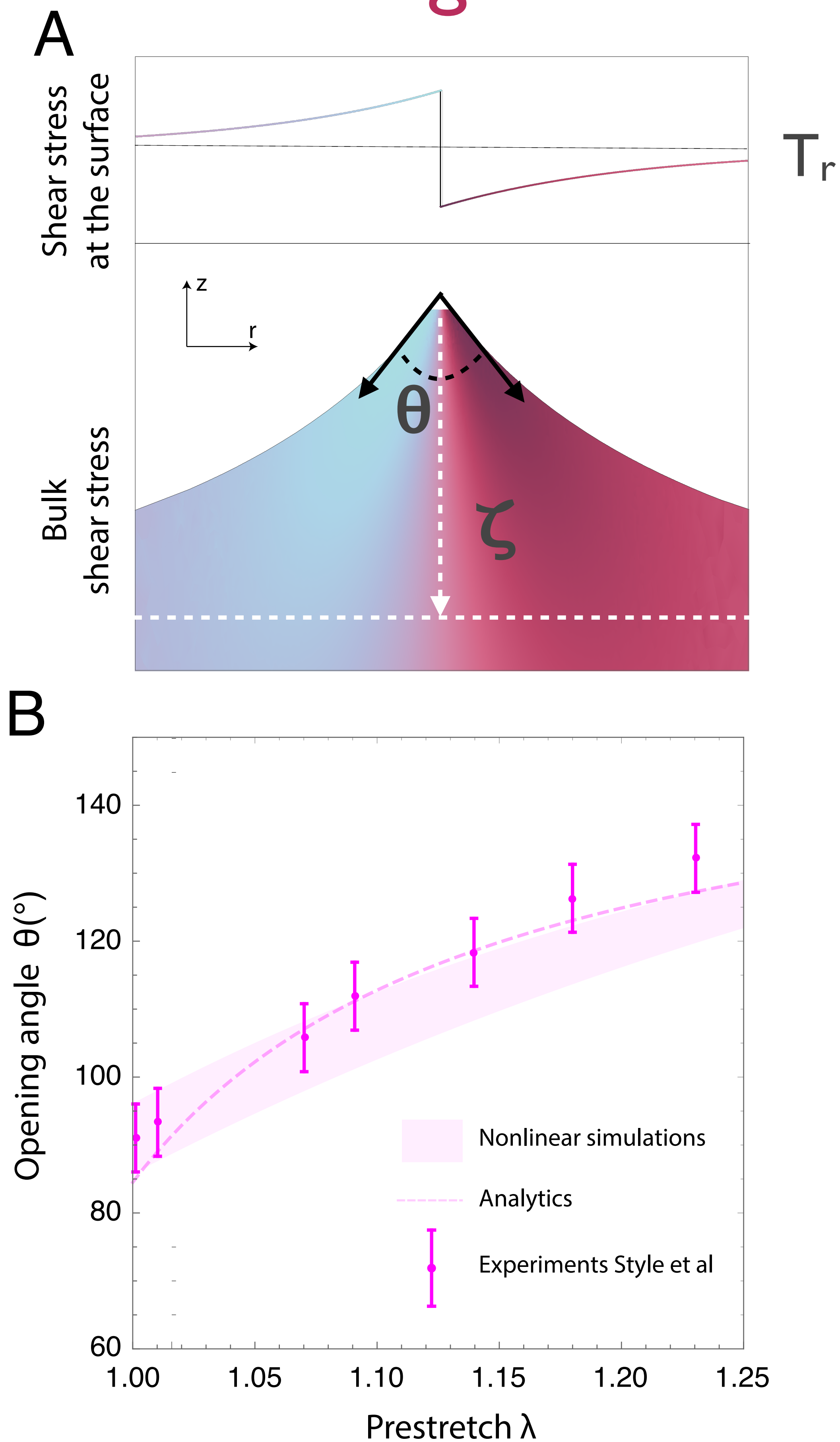
Good agreement between simulations and experiments

No Shuttleworth effect in soft elastomers !

BUT

Nonlinearities are important !

Origin of this nonlinear behavior ?



Elastic force acting at the tip

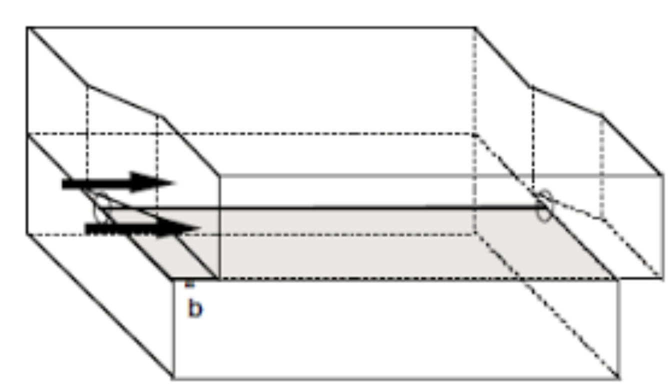
$$\mathbf{f}^E = \lim_{\epsilon \to 0} \int_{\Gamma_\epsilon} \boldsymbol{T} \cdot \boldsymbol{\nu} \mathrm{d}\ell$$

$$f_z^E \propto -\gamma_\ell (\lambda^2 - 1/\lambda^4)(\pi - \theta)$$

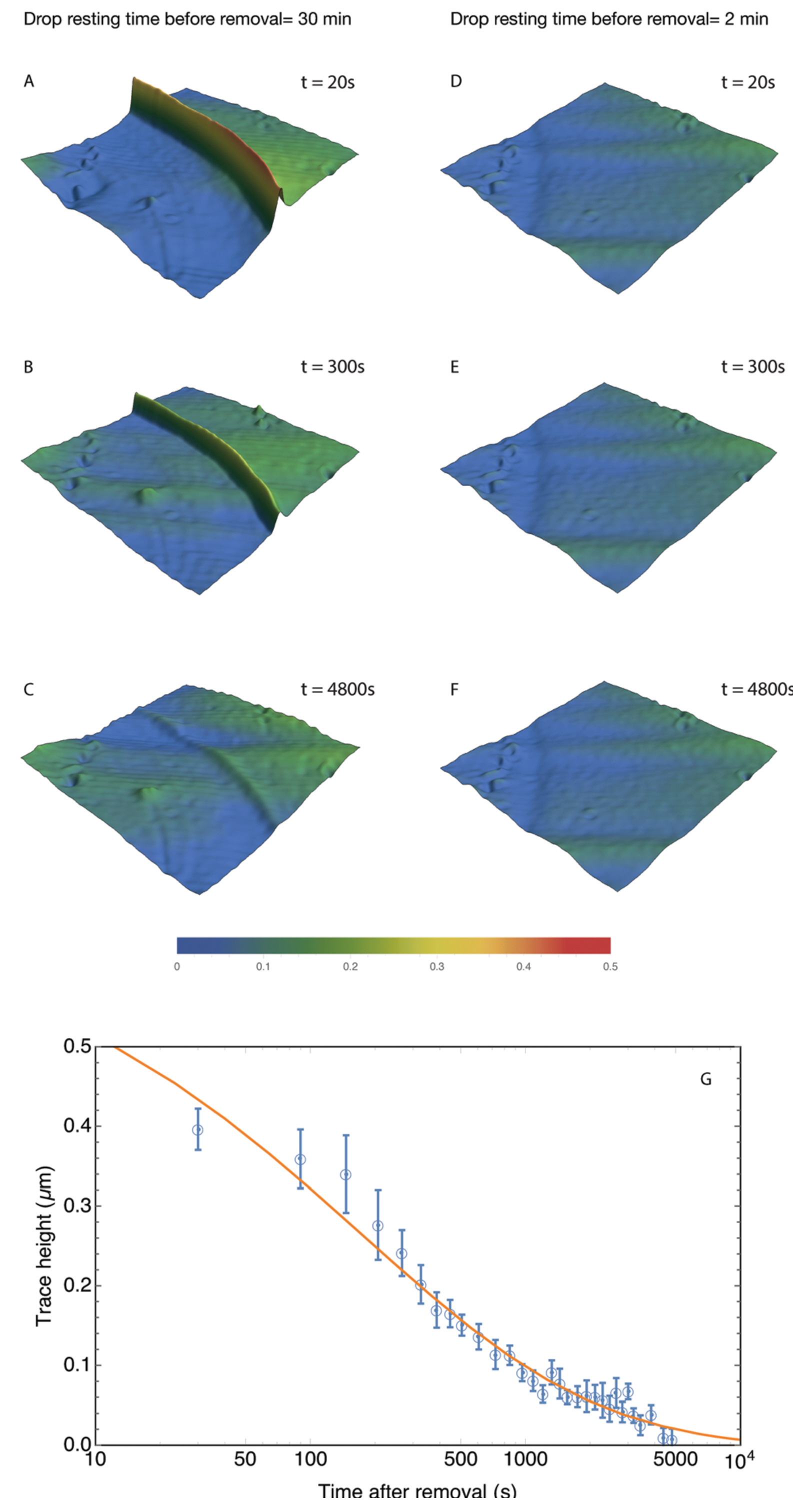
Purely topological force

$$f_z^E \sim 2[T_{rz}\zeta]$$

Analogous to the Peach-Koehler force acting on a dislocation !



Non elastic behaviors in elastowetting



The poro-elasto-wetting theory works well for PDMS

(but more experimental data are needed)

Conclusions

We have developed a powerful numerical tool to investigate the nonlinear elastowetting problem

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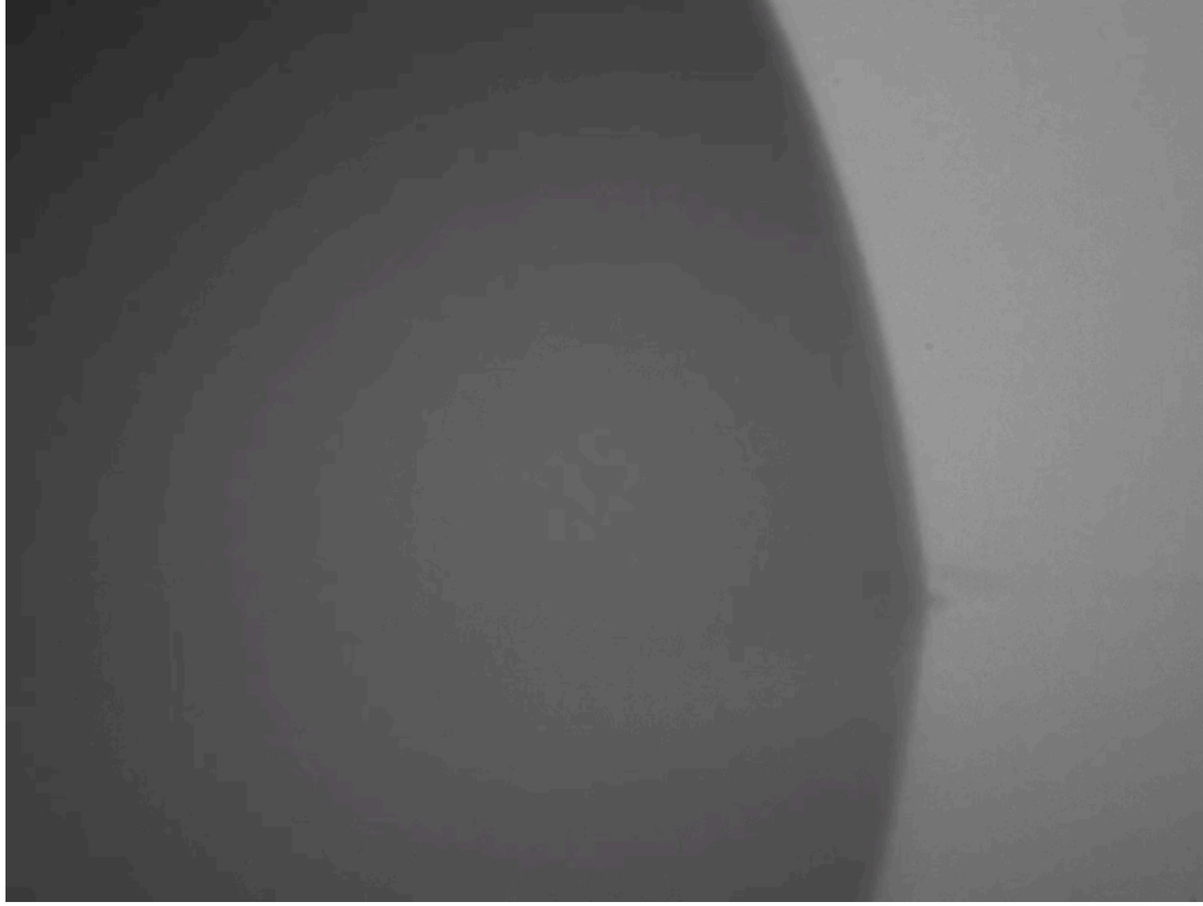
Non trivial behaviors at large deformations ($\gamma/2\gamma_s > 1$)

The elastocapillary ridge behave as a topological defect (a disclination)

Poro-elastic growth and relaxation of the ridge on complex materials



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François Lequeux
Tetsuharu Narita
Menghua Zhao

Dervaux and Limat (PRSA, 2015)
Zhao et al (Soft Matter, 2017)
Zhao et al (PNAS, 2018)
de Pascalis et al (Eur. J. Mech. A , 2018)
Masurel et al (arXiv, under review)