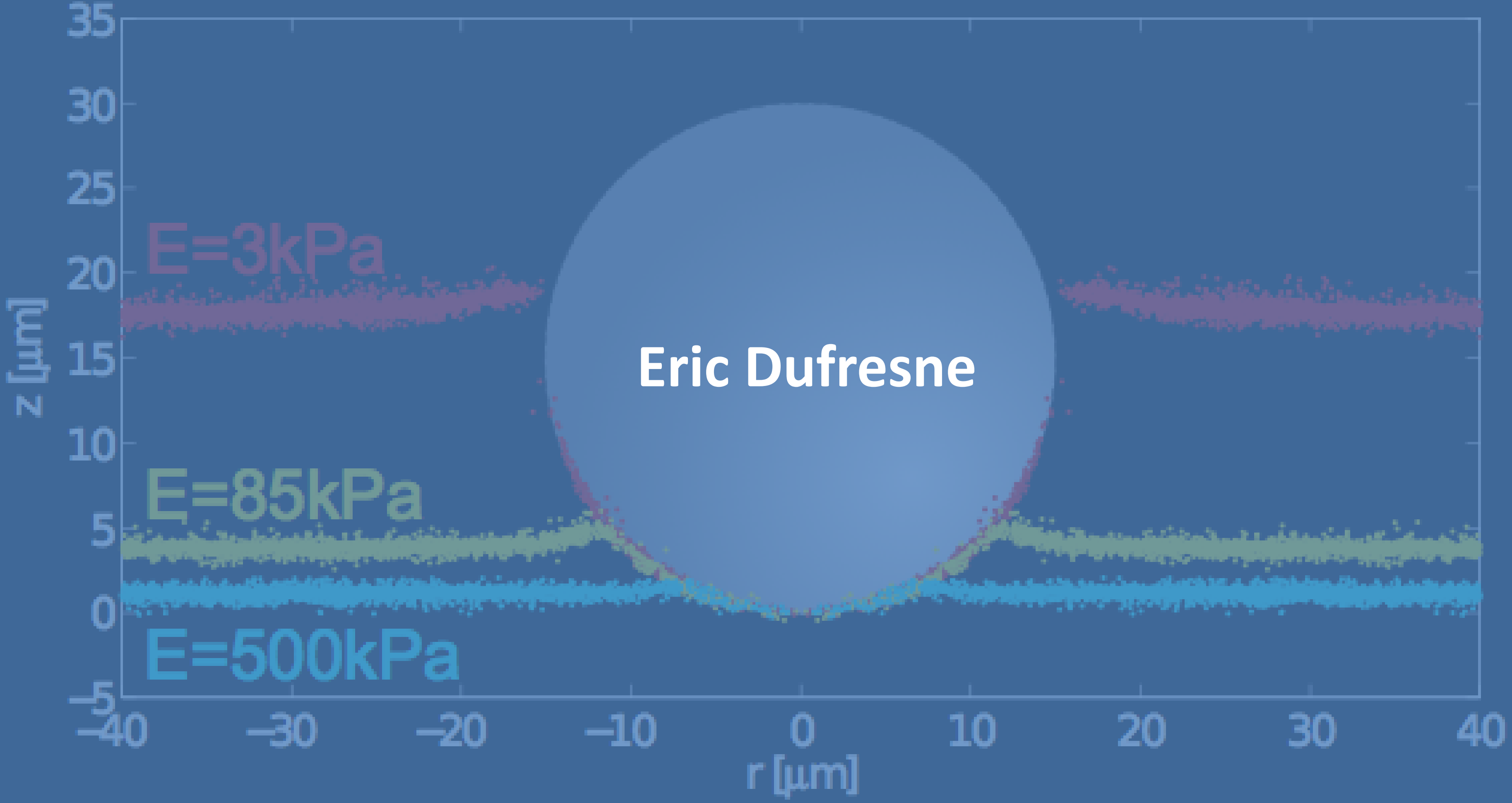
Wetting & Adhesion on Soft Surfaces

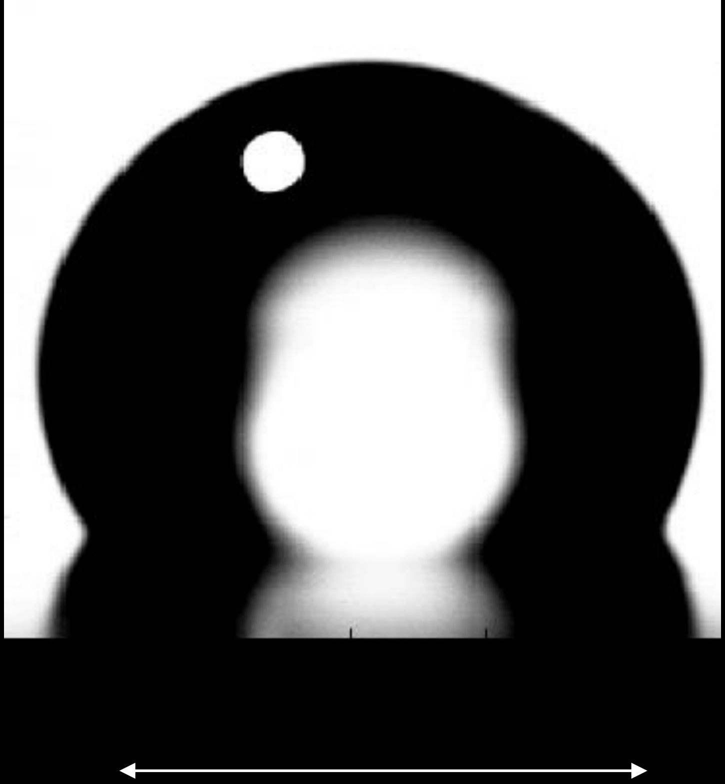
"Young's Law is dead…long live Young's Law"



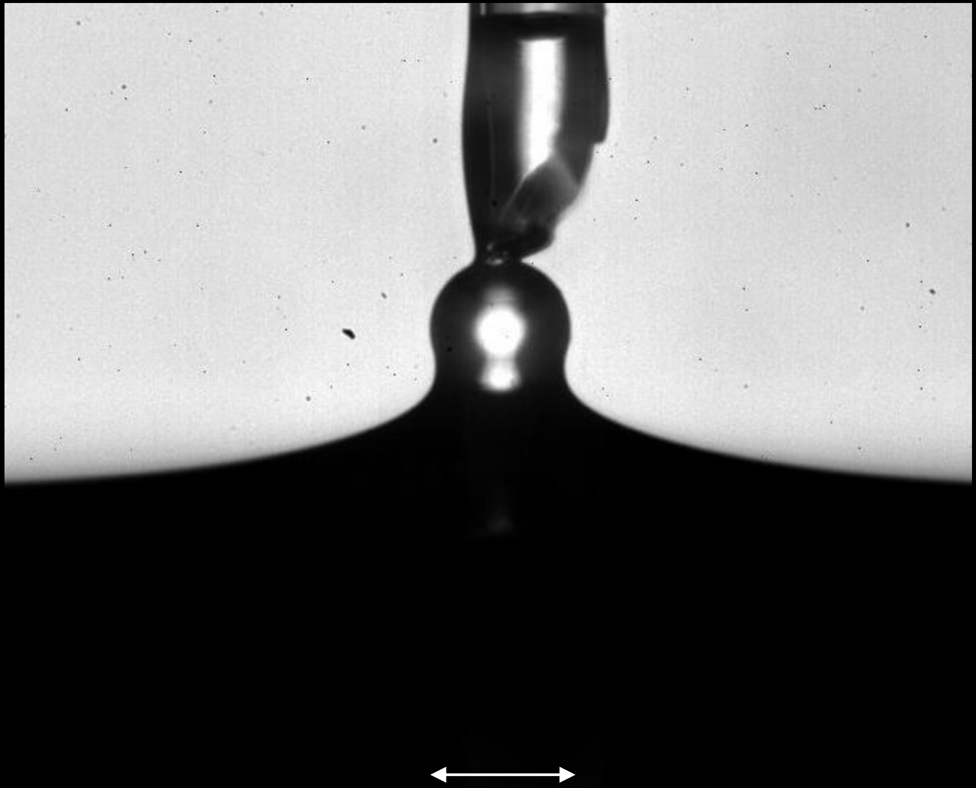
Eric Dufresne

KITP 2014

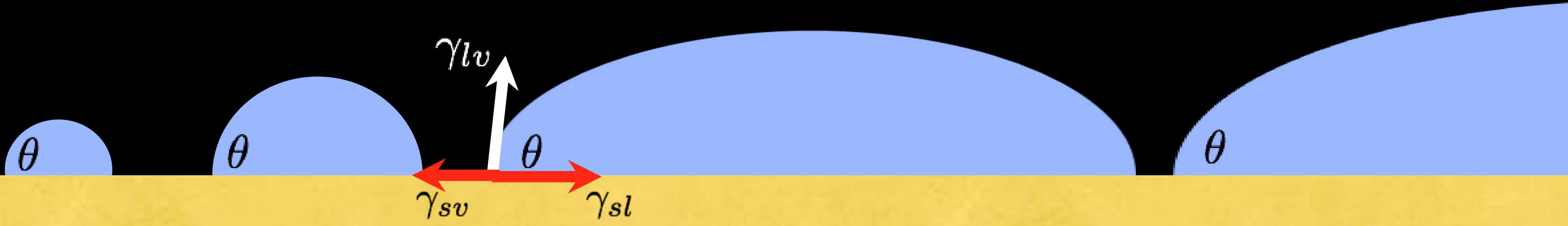
Wetting



Adhesion



Young's Law relates contact line geometry and material properties in equilibrium

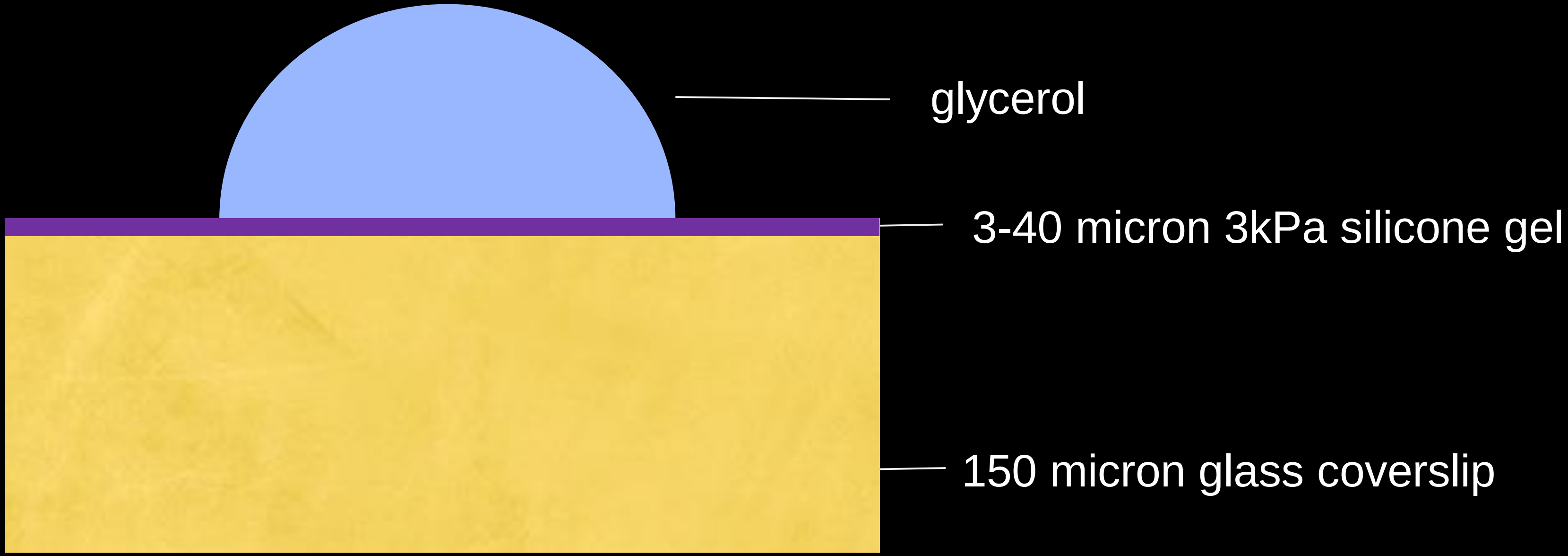


Thomas Young
1773-1829

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

What happens when the solid surface is soft?

Dr. Robert Style

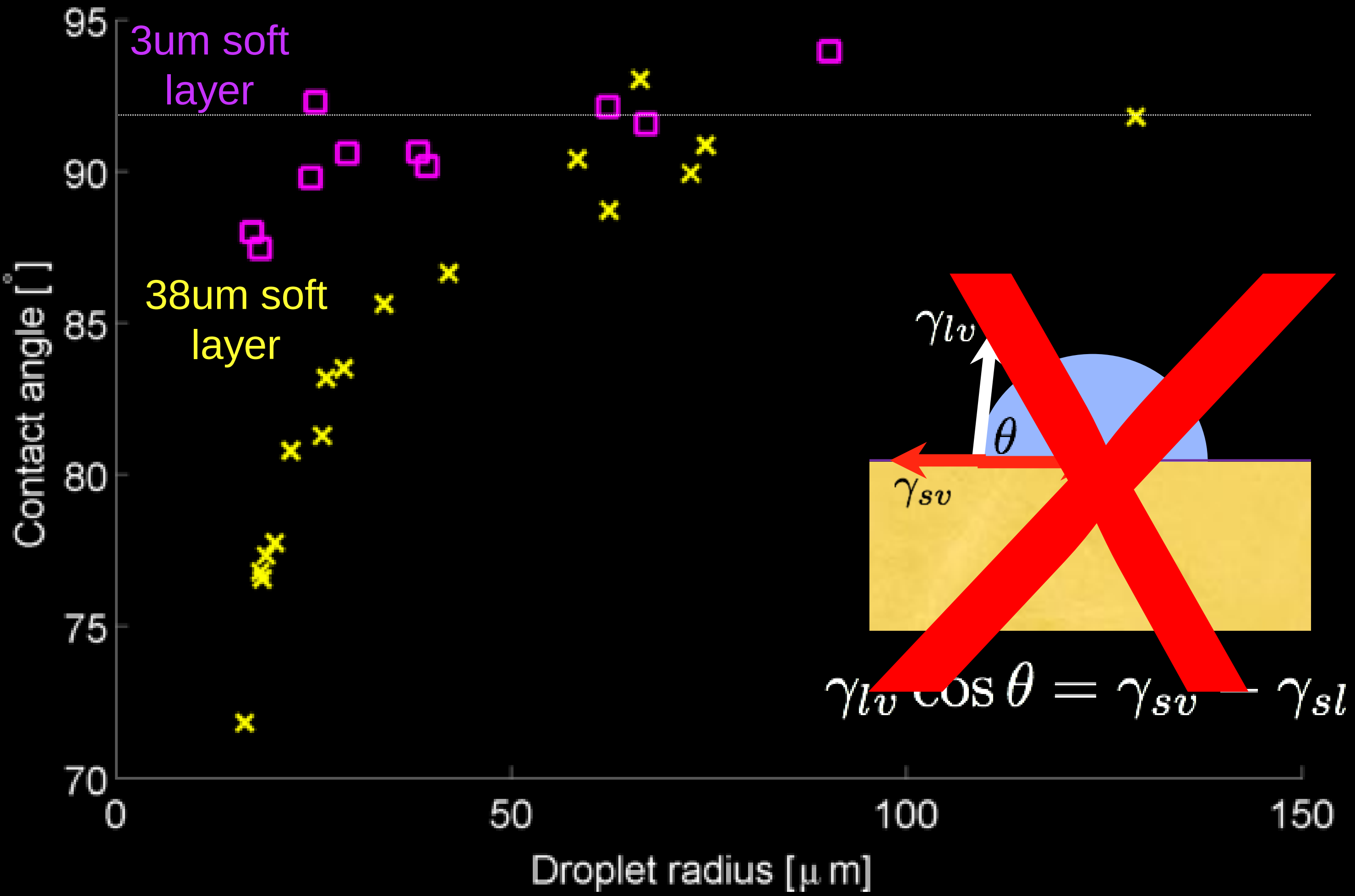


glycerol

3-40 micron 3kPa silicone gel

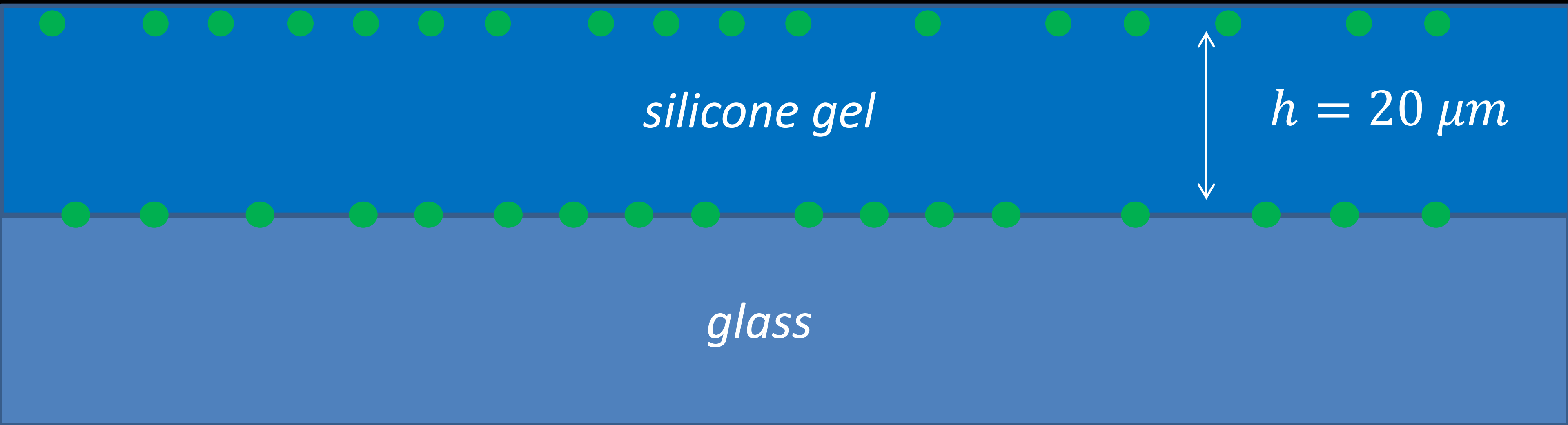
150 micron glass coverslip

On a soft substrate, apparent contact angle depends on droplet size and thickness of soft layer



Glycerol drops on silicone (E=3kPa)
Zygo surface profilometer

Confocal Imaging Near the Contact Line

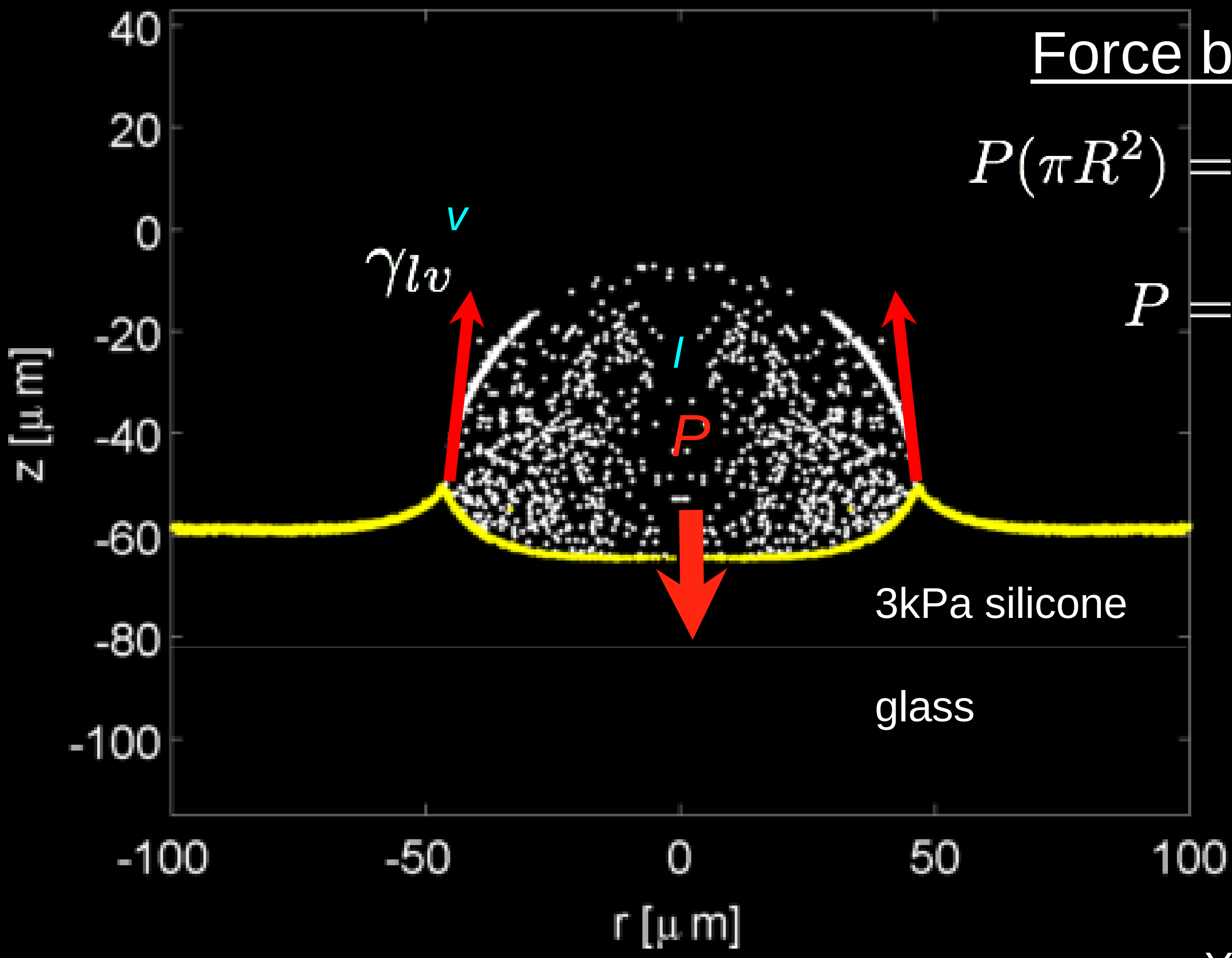


silicone gel

$h = 20\ \mu m$

glass

Droplets Deform Soft Substrates



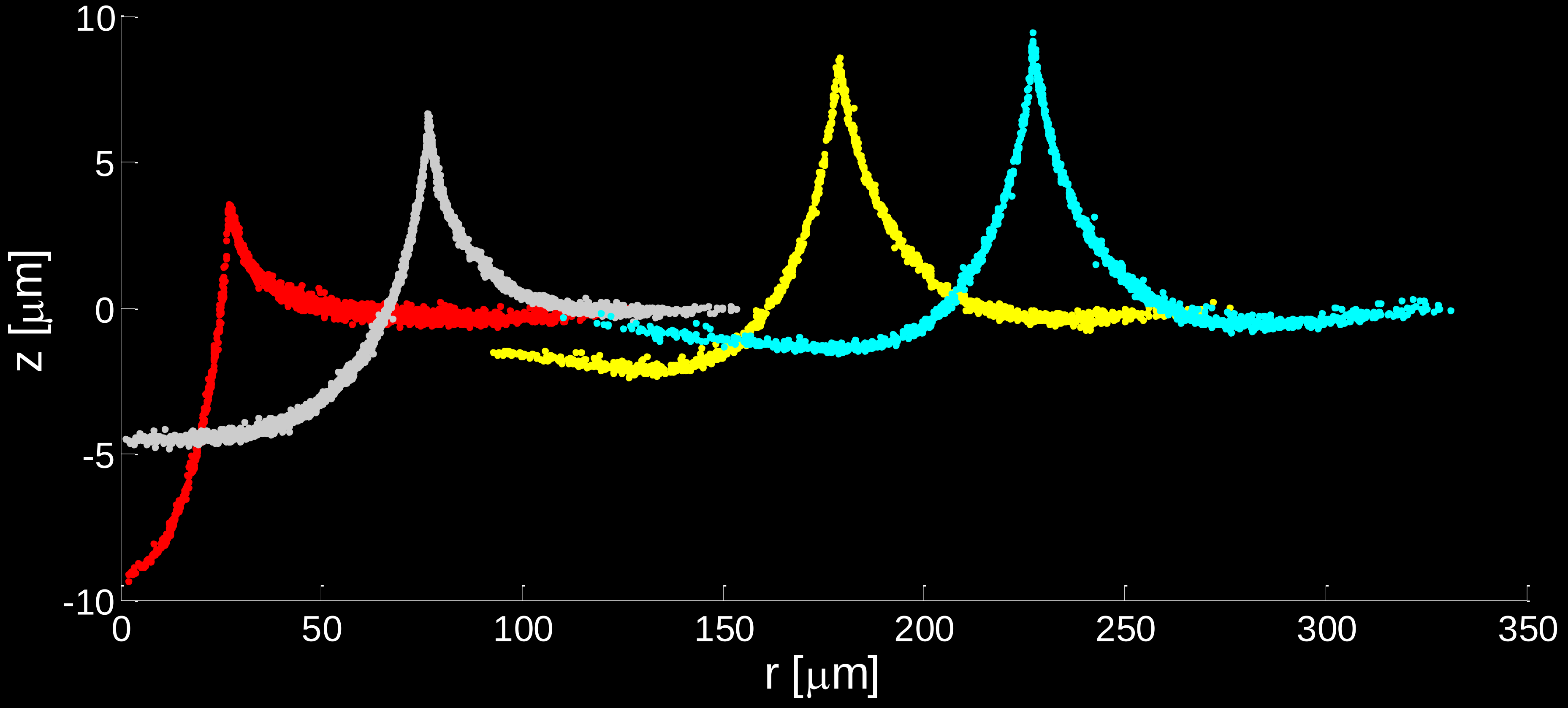
Force balance:

$$P(\pi R^2) = \gamma_{lv}(2\pi R)$$

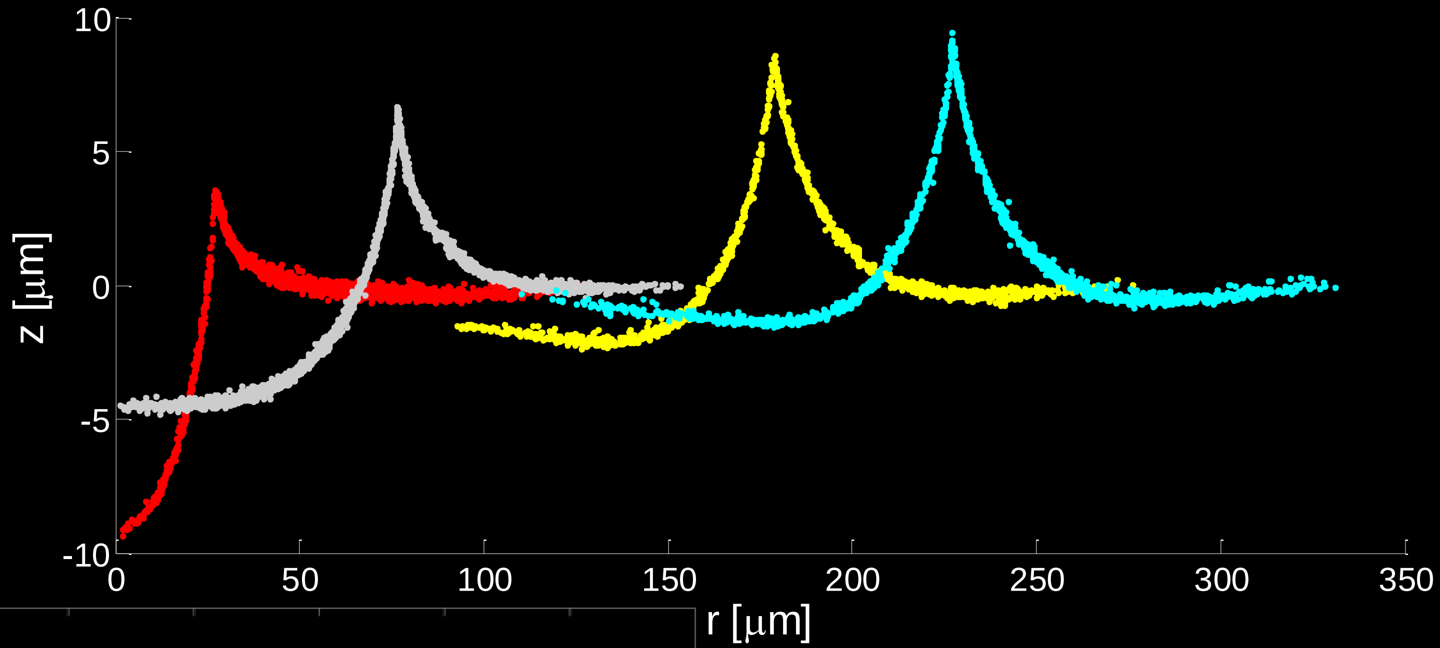
$$P = \frac{2\gamma_{lv}}{R}$$

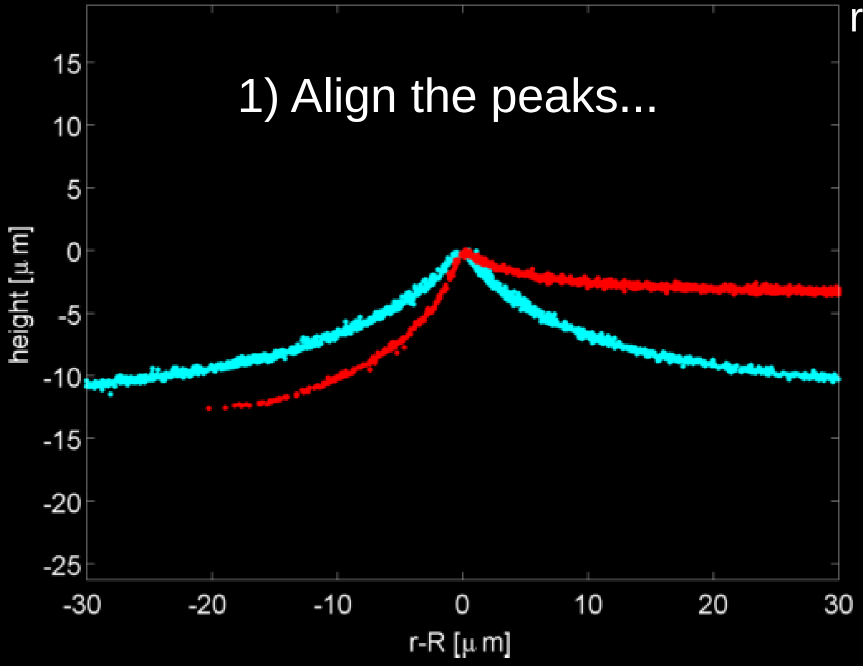
Yonglu Che

Profiles change dramatically with droplet size

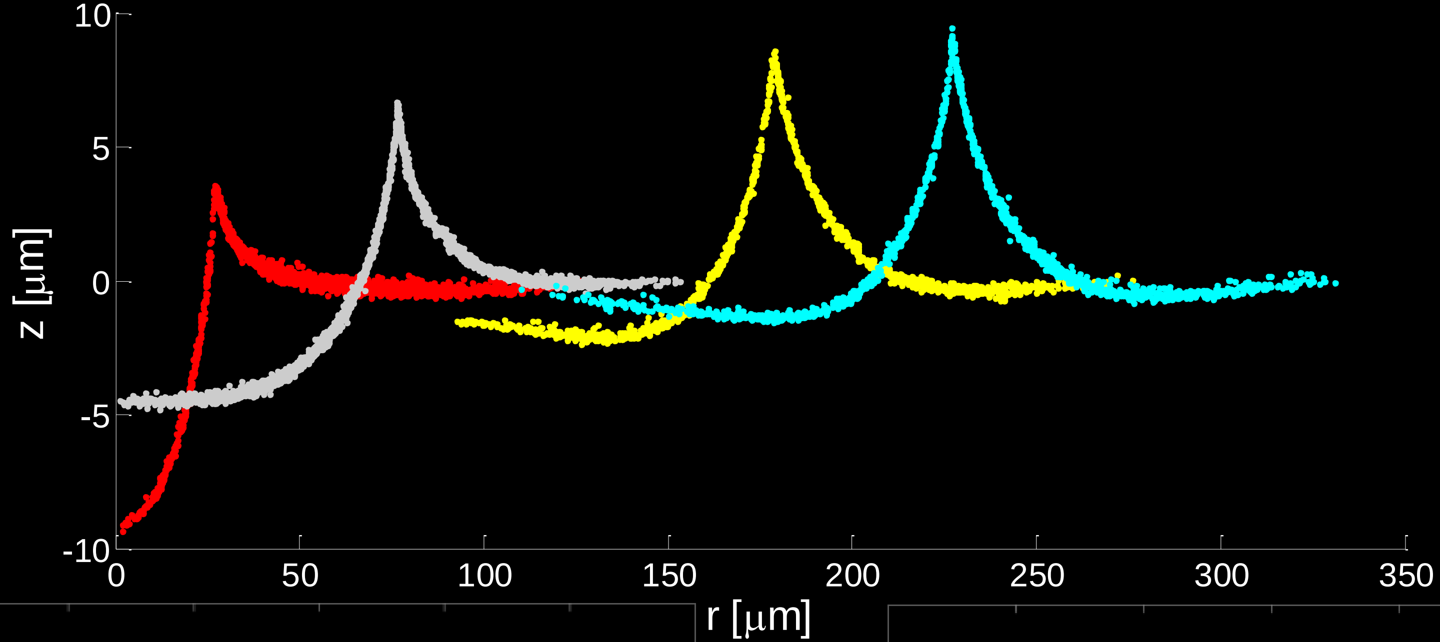


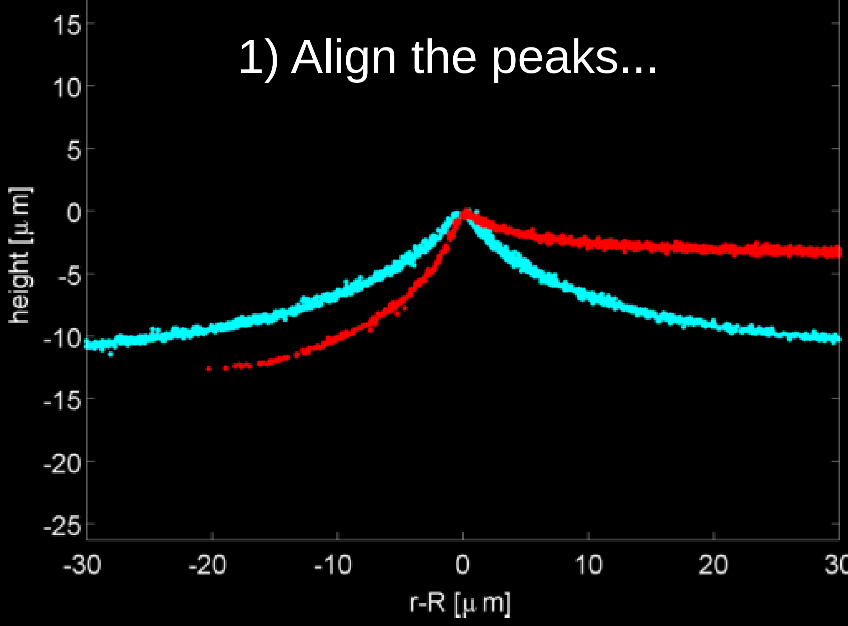
Overall profiles change – but how about the cusp?

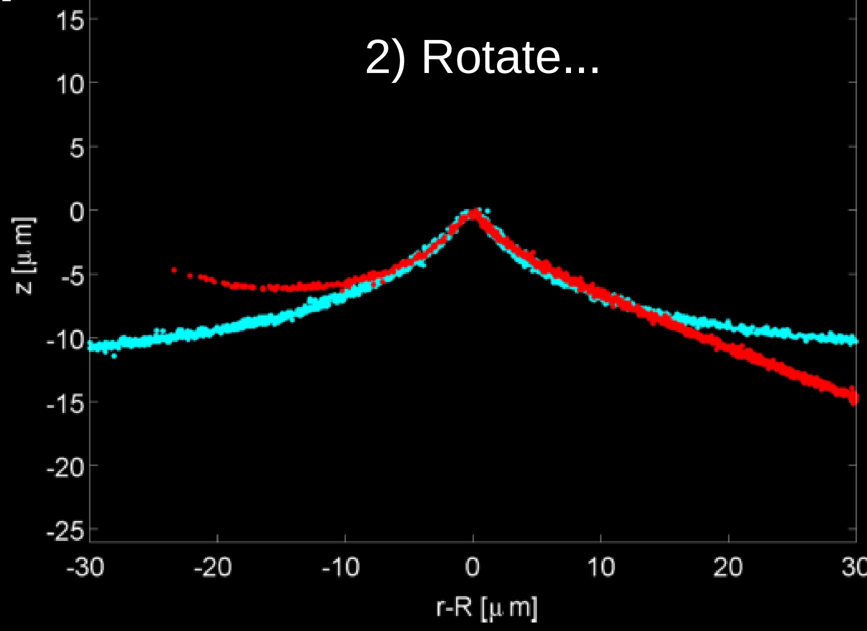



1) Align the peaks...

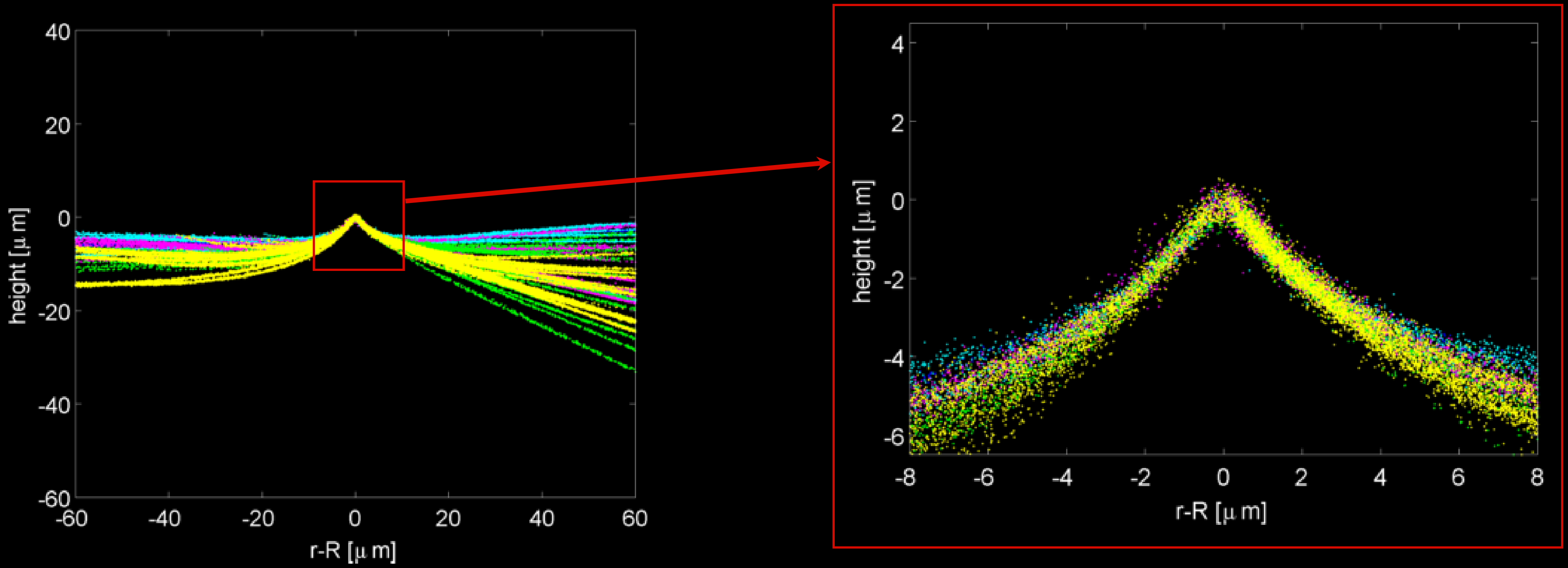
Overall profiles change – but how about the cusp?





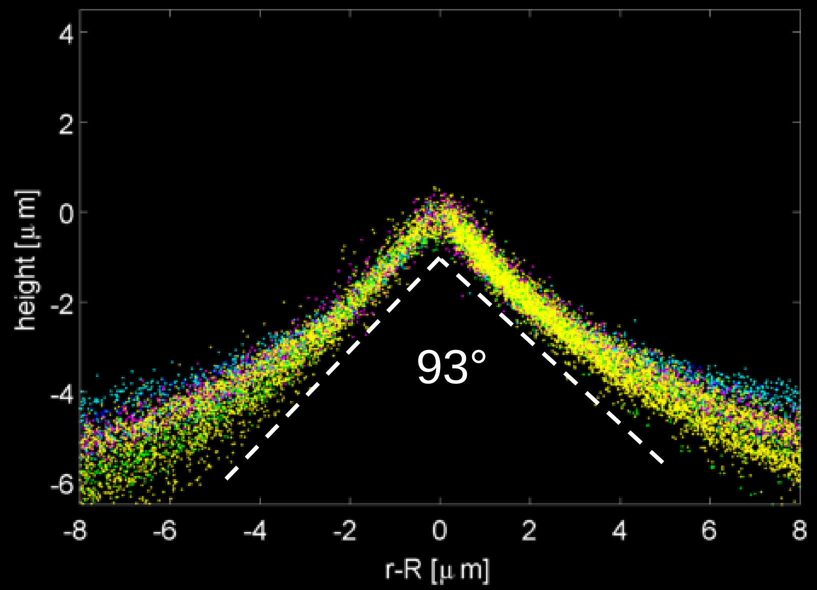


Cusp shape is universal near contact line

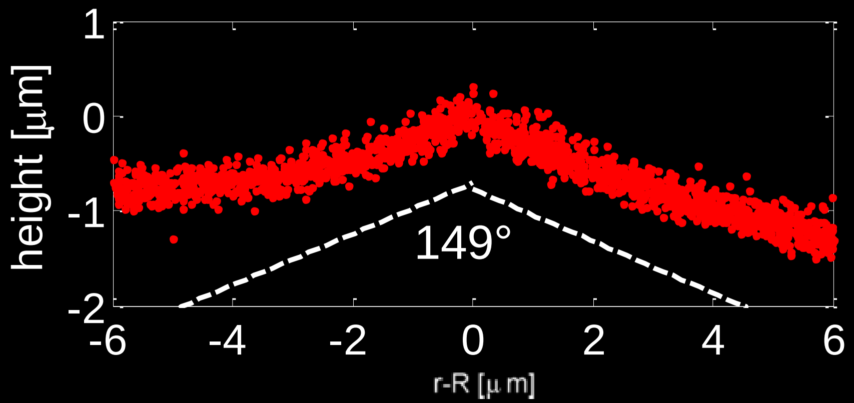


61 glycerol drops
radii: 18um - 1000um
Four different substrates: 13.5 - 50um thick

Contact line geometry depends on the wetting fluid

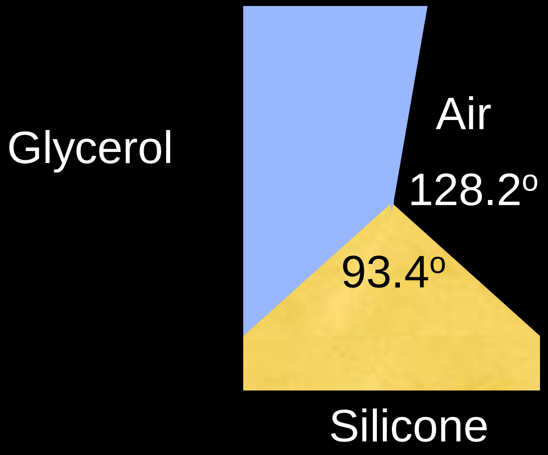


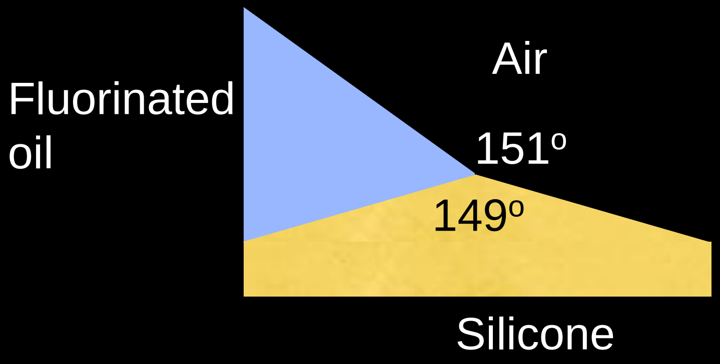
glycerol
61 drops
radii: 18um - 1000um
substrates: 13.5 - 50um thick



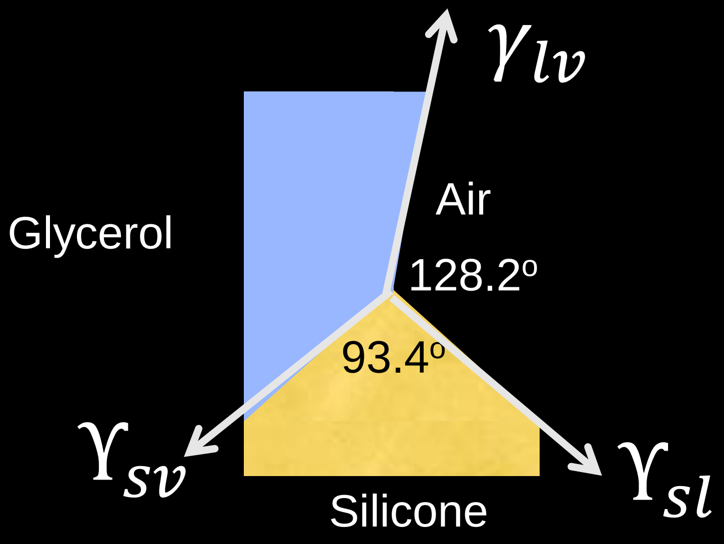
fluorinert fc-70
14 drops
radii: 140um - 270um
substrate: 23 um thick

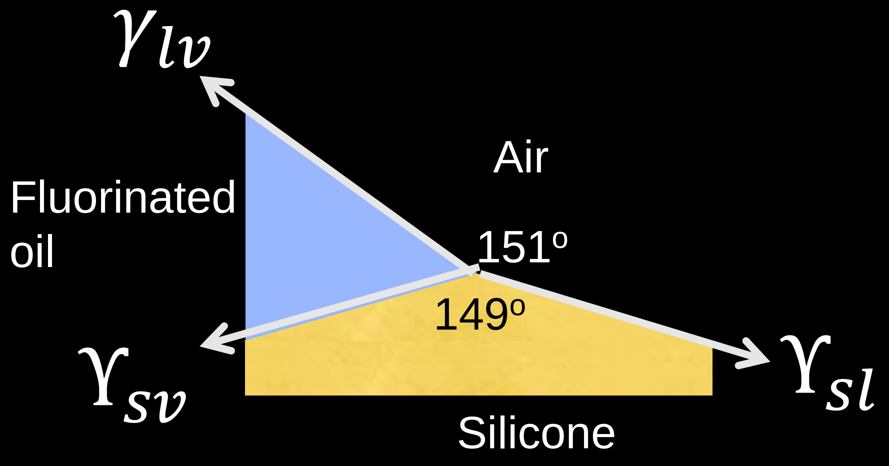
While apparent contact angle depends on boundary conditions… microscopic configuration of interfaces is universal





Hypothesis: geometry at contact line is determined by a vector balance of surface tensions – a la Neumann



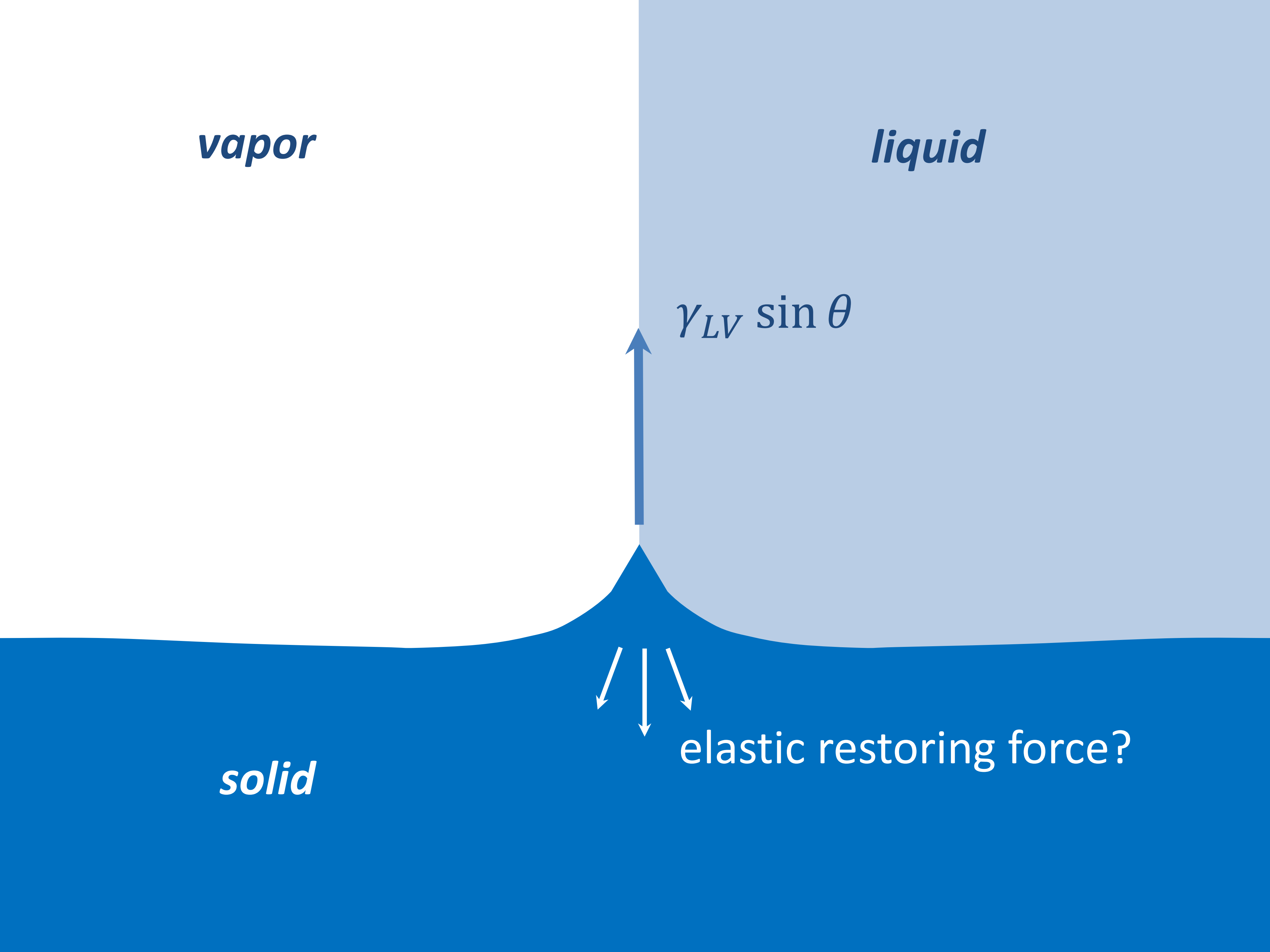


γ_{lv}: l-v surface tension

γ_{sv}: s-v surface tension

γ_{sl}: s-l surface tension

What about solid elasticity?



vapor

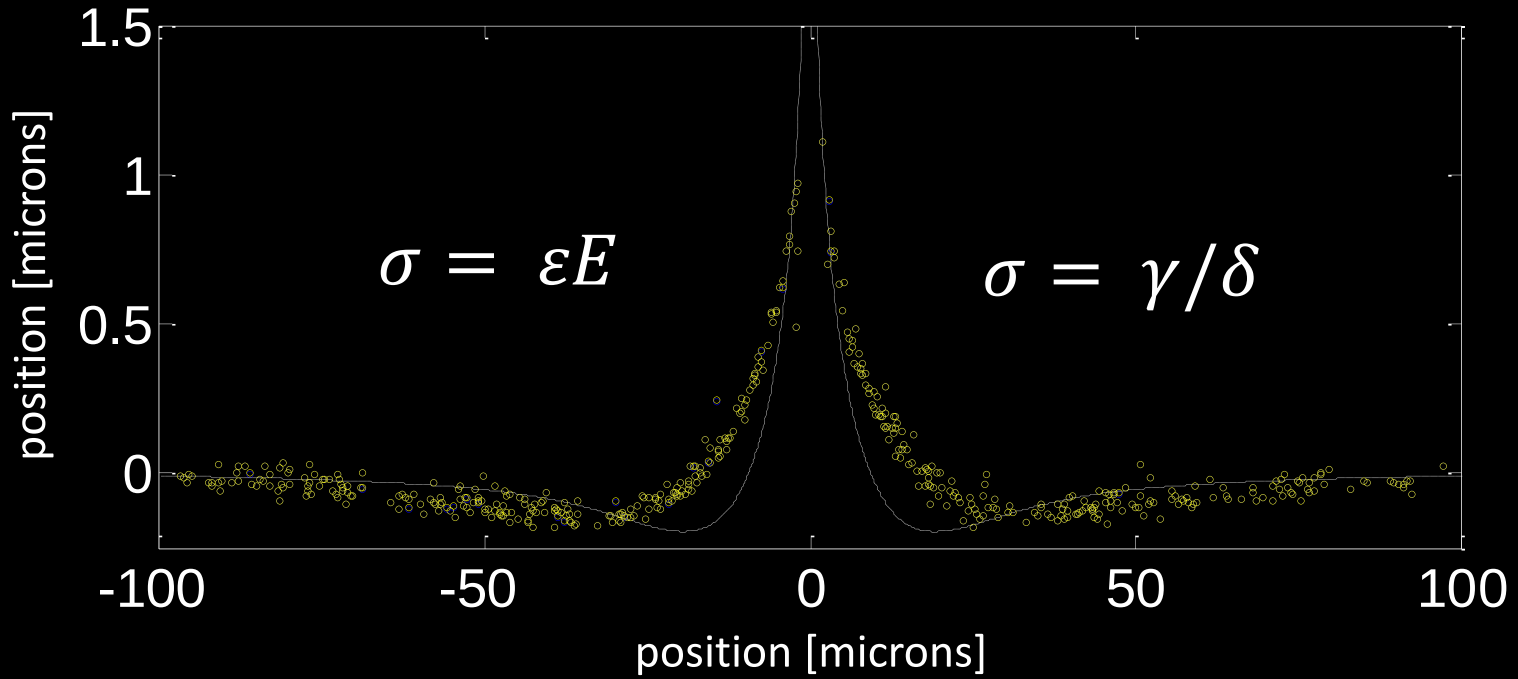
liquid

$\gamma_{LV} \sin\theta$

elastic restoring force?

solid

Elastic Theories Cannot Balance Contact Line Forces

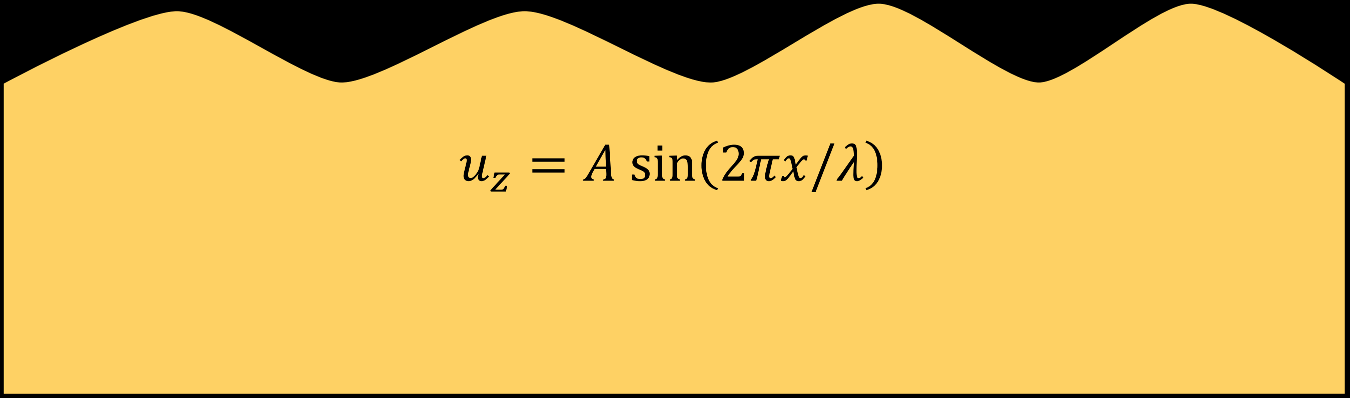


$\sigma = \varepsilon E$

$\sigma = \gamma/\delta$

Reasonable estimates for contact line width lead to unreasonable strains and displacements

Flattening of a linear elastic solid

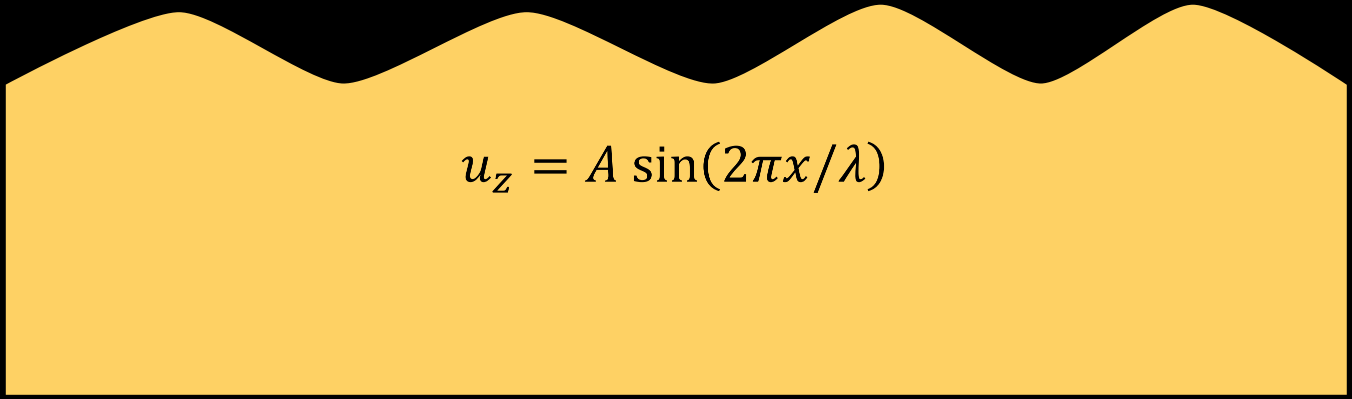


$$u_z = A \sin(2\pi x/\lambda)$$

Elastic restoring force: $\sigma_E = \varepsilon E \sim AE/\lambda$

Flattening of a linear elastic solid by surface tension

Long Ajdari 1996, Jerison Dufresne 2011, Jagota 2012

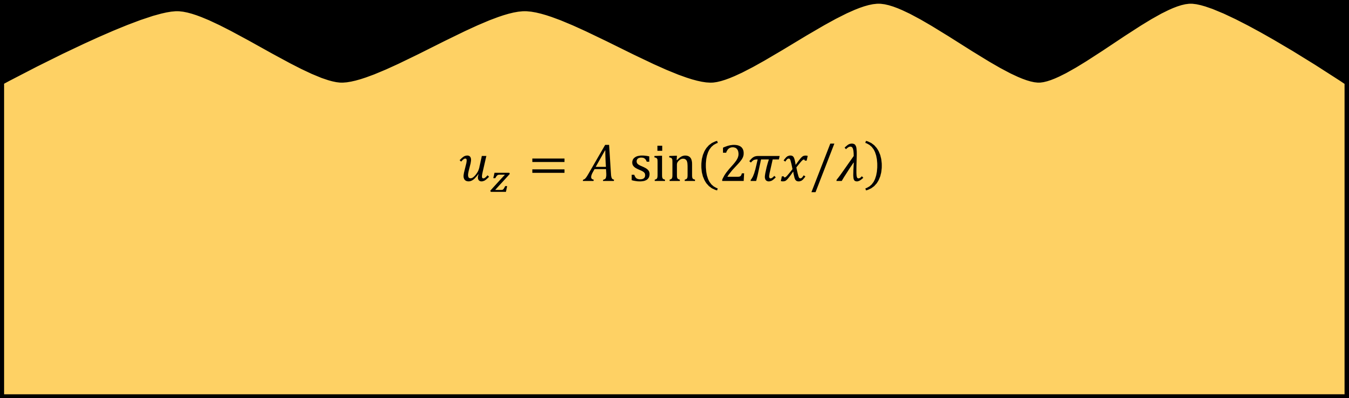

$u_z = A\sin(2\pi x/\lambda)$

Elastic restoring force: $\sigma_E = \varepsilon E \sim AE/\lambda$

Capillary force: $\sigma_\gamma \sim \Upsilon A/\lambda^2$

Υ: solid surface tension

Balance of Elasticity and Capillarity Defines a Length scale



$$\frac{\sigma_E}{\sigma_\Upsilon} \sim \frac{\lambda}{l}$$

$$l = \Upsilon/E$$

Elastocapillary Length

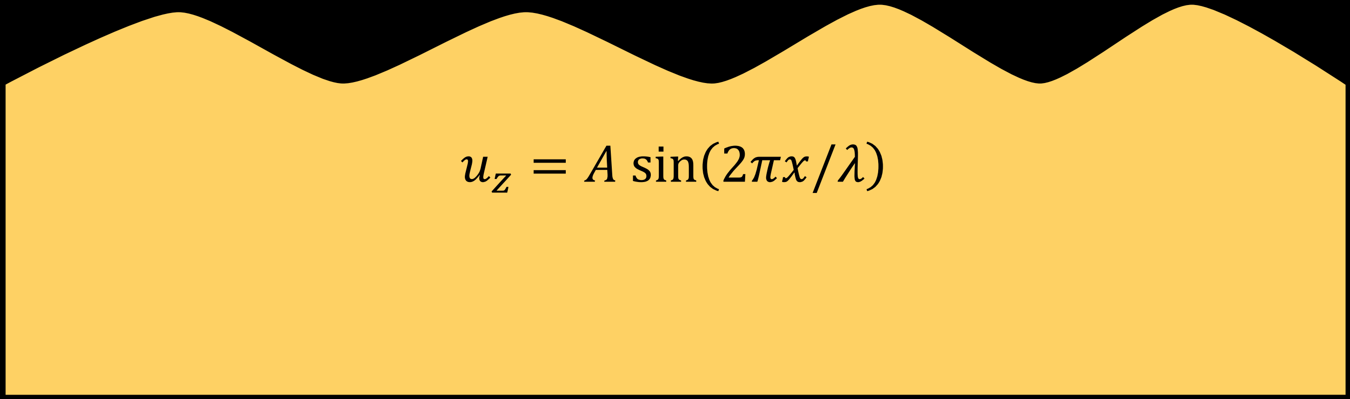
$$\lambda/_{l} \gg 1$$

Elasticity Dominates

$$\lambda/_{l} \ll 1$$

Surface Tension Dominates

Capillarity Dominates at Short Length Scales on Soft Materials



$u_z = A \sin(2\pi x/\lambda)$

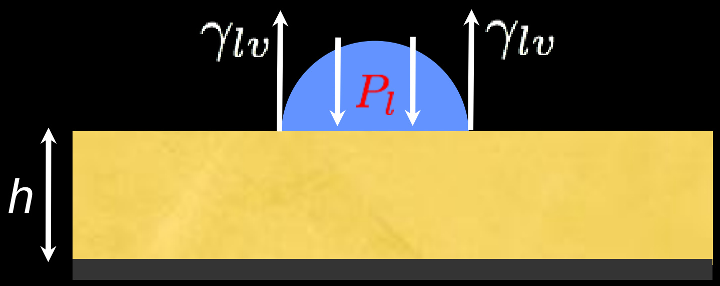
$\Upsilon = 0.03\ \mathrm{N/m}$

$l = 0.1\ \text{Å for } E = 3\ \mathrm{GPa}$

$l = 10\ \text{nm for } E = 3\ \mathrm{MPa}$

$l = 10\ \mu\text{m for } E = 3\ \mathrm{KPa}$

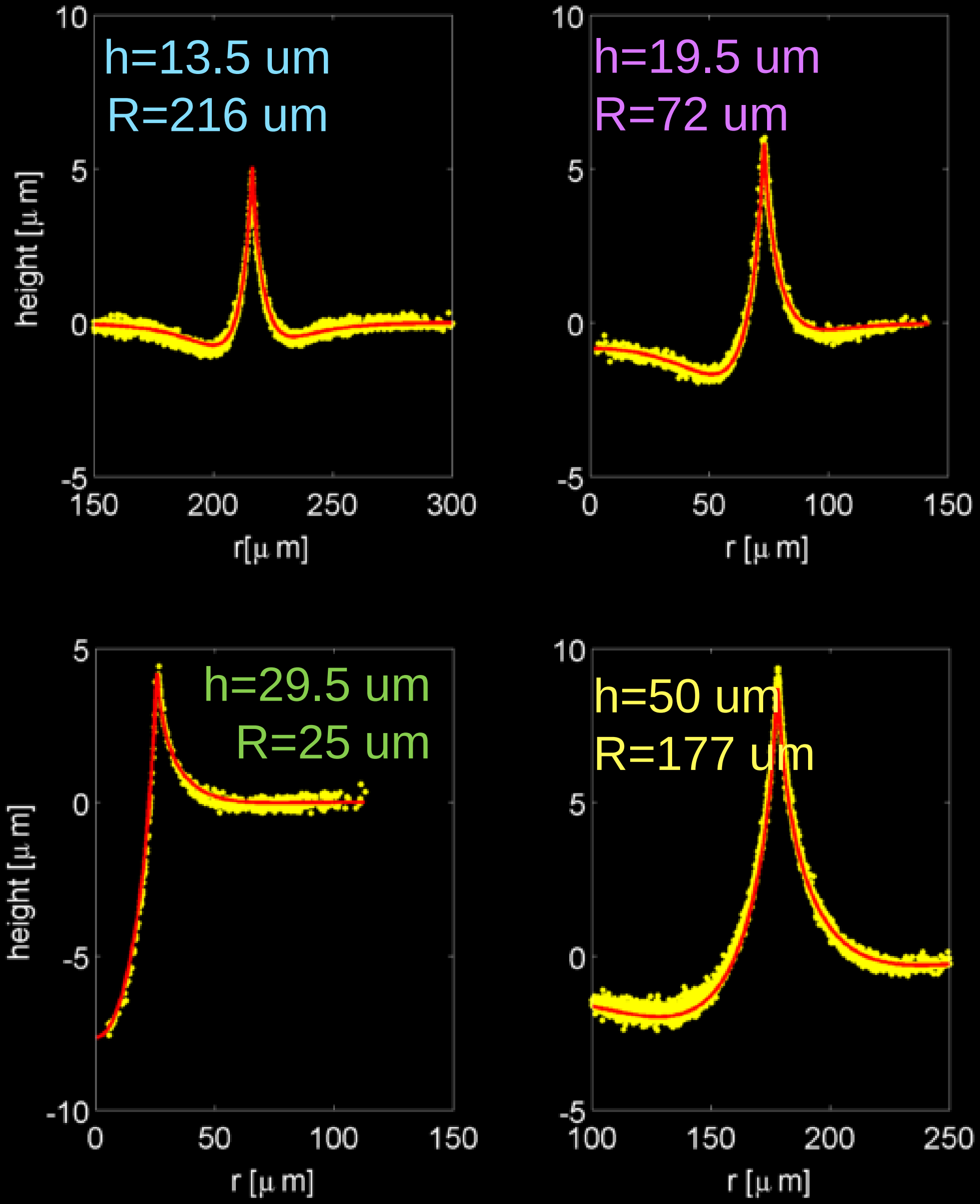
Linear Elasticity Plus Solid Surface Tension Captures Profiles



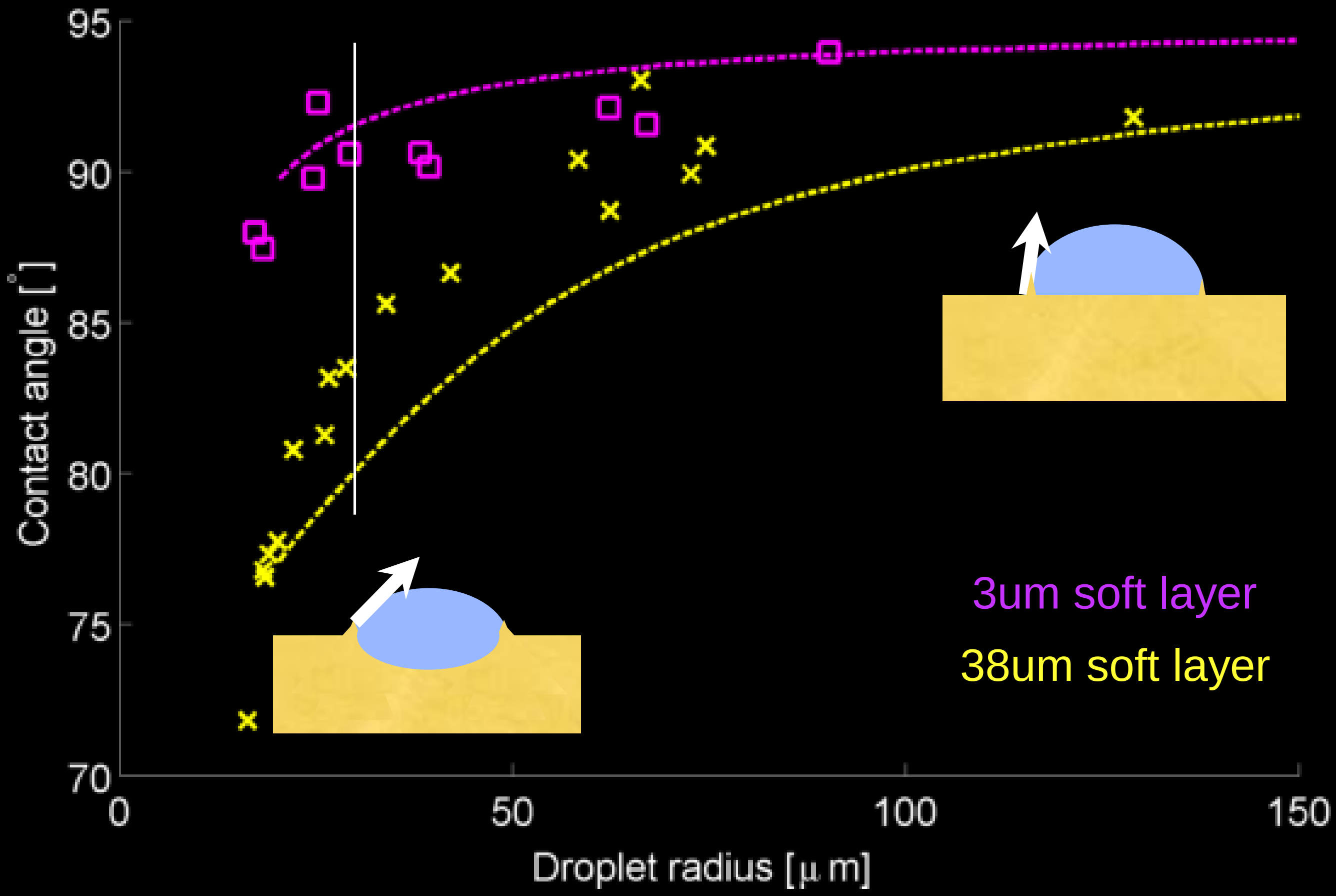
Linear elastic solid with surface tension

Sharp features near contact line are controlled by surface tension.

Far-field determined by elasticity

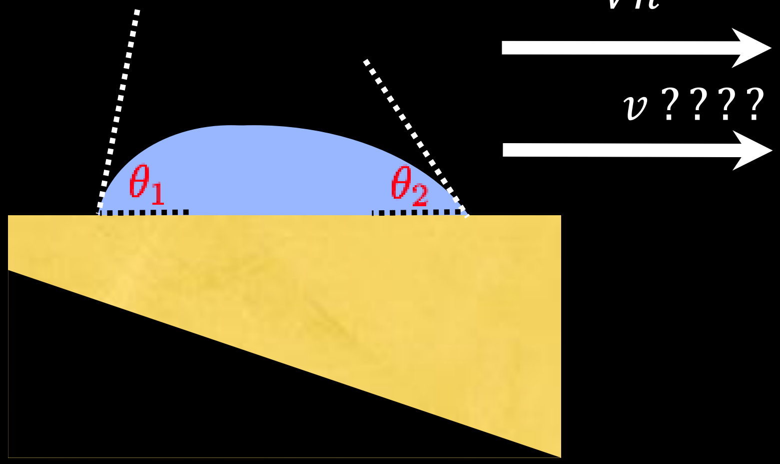


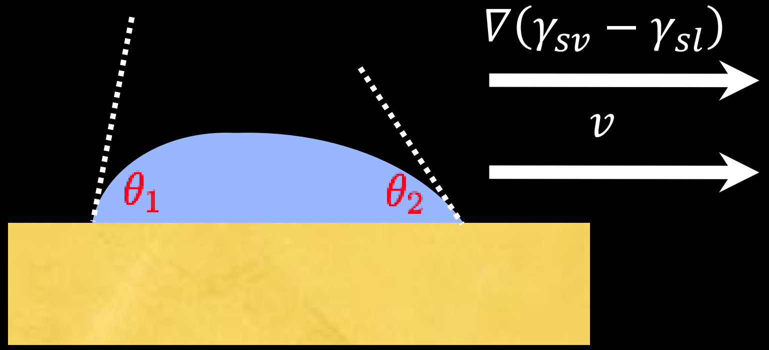
Linear Elasticity Plus Solid Surface Tension Predicts Change in Apparent Contact Angle



Glycerol drops on silicone (E=3kPa)

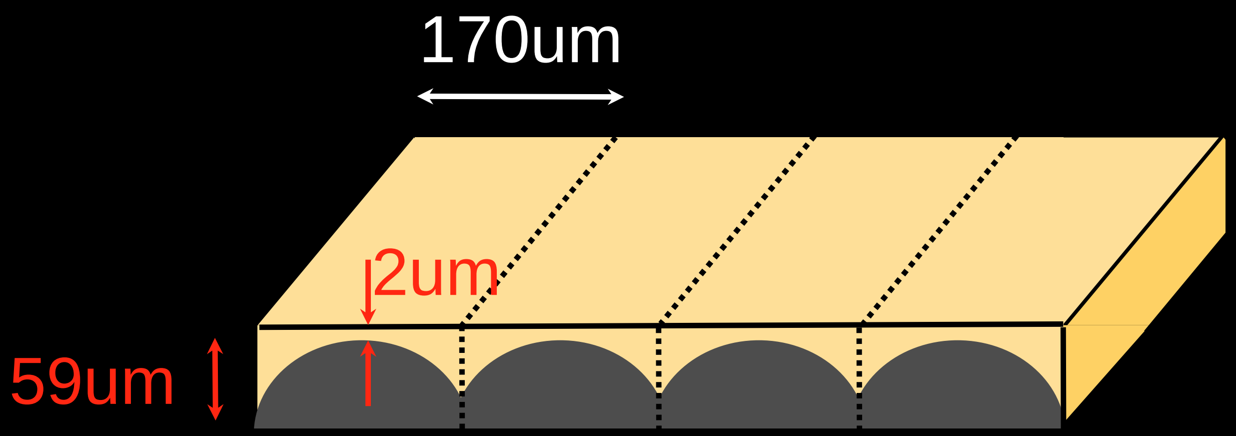
Differences in contact angle drive droplet motion?



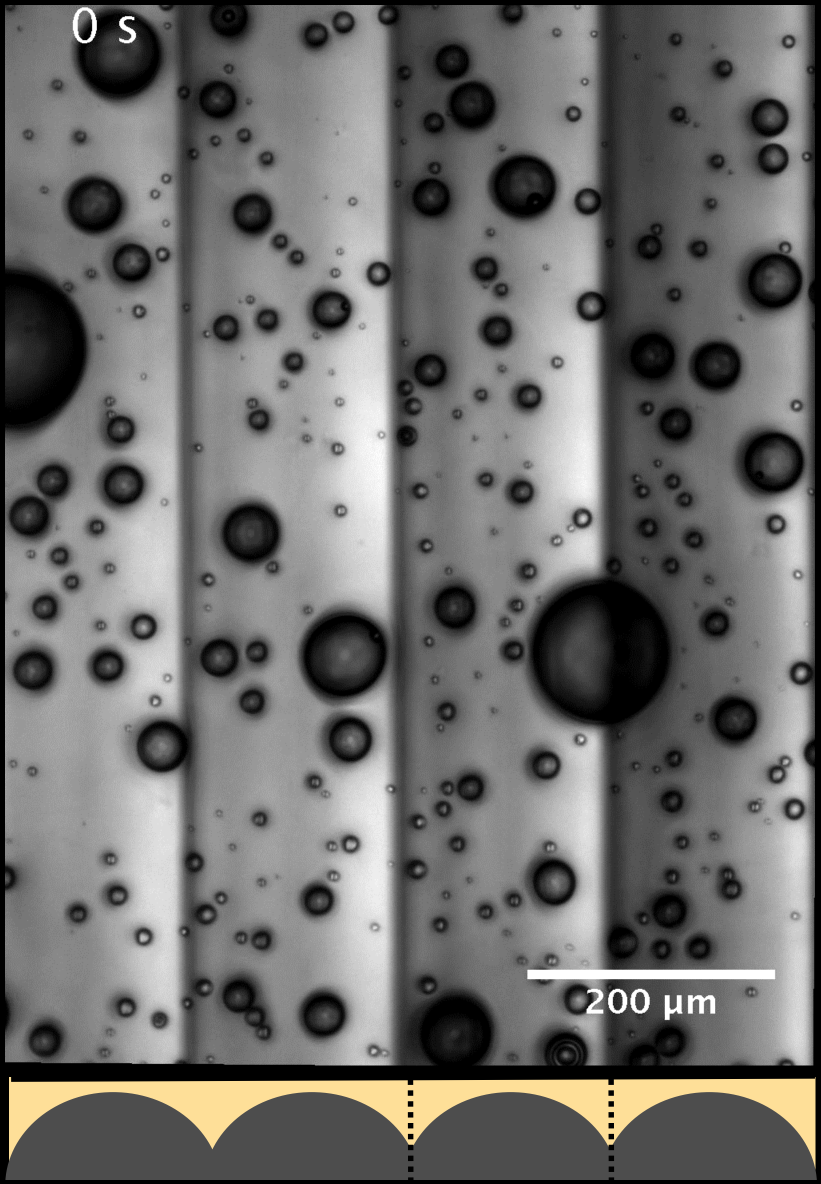


see *e.g.* chaudhury,
whitesides, troian

Making a thickness gradient

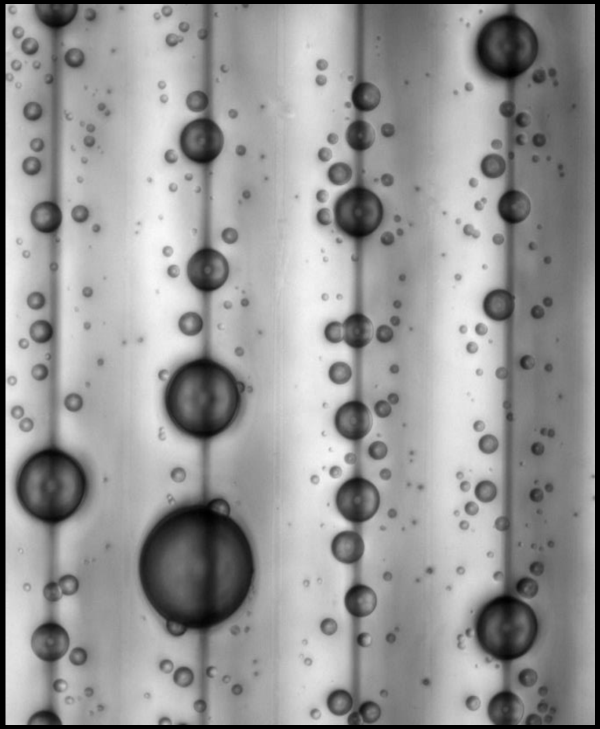


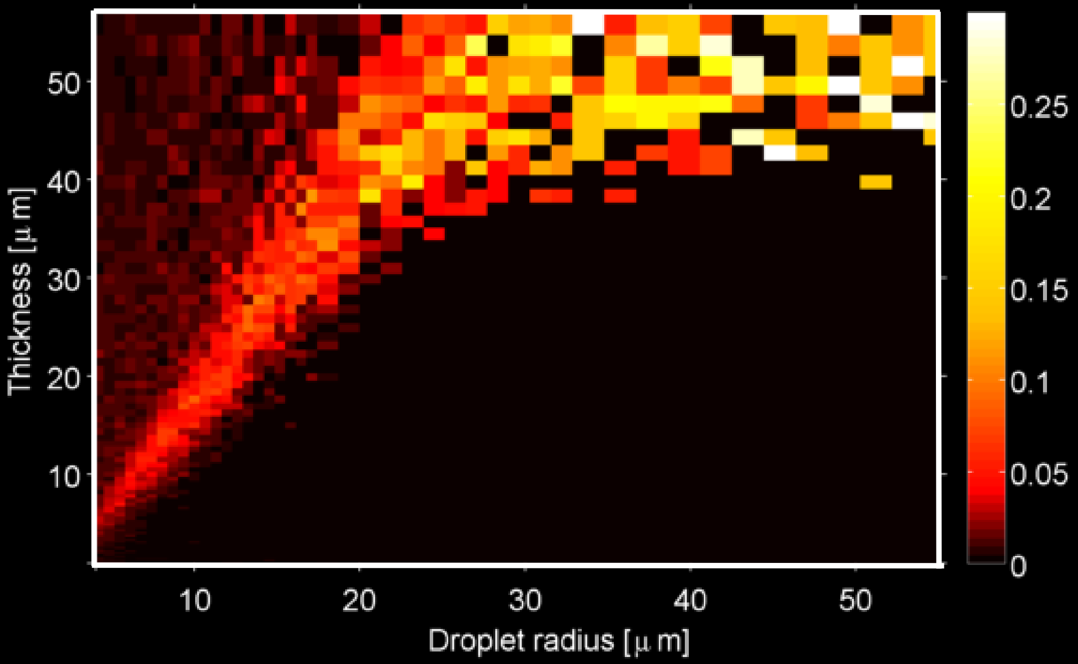
3kPa silicone gel coated on hard substrate
with close-packed cylindrical ridges



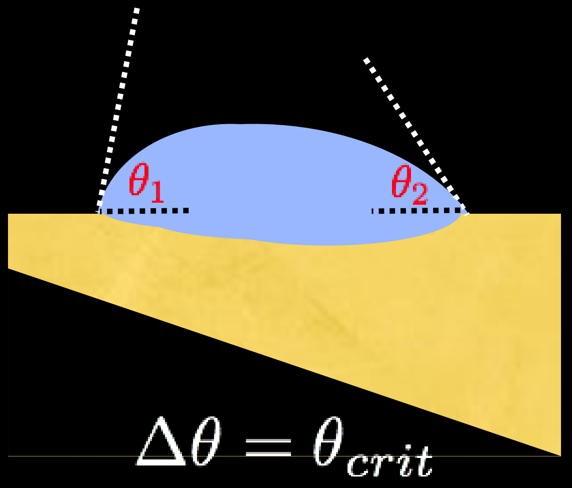
Atomized spray of glycerol on substrate with thickness/stiffness gradient

Resting depth depends on drop size

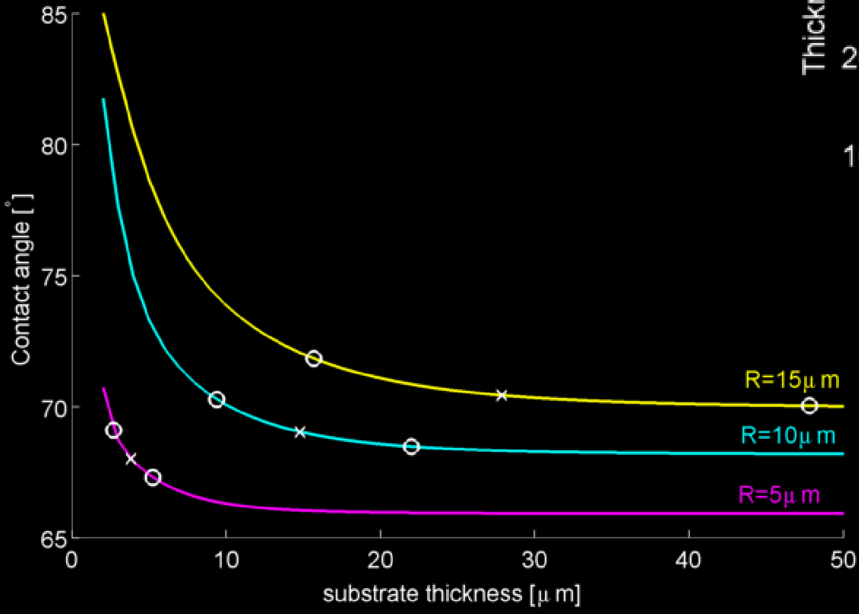



Probability density of `final’ drop position

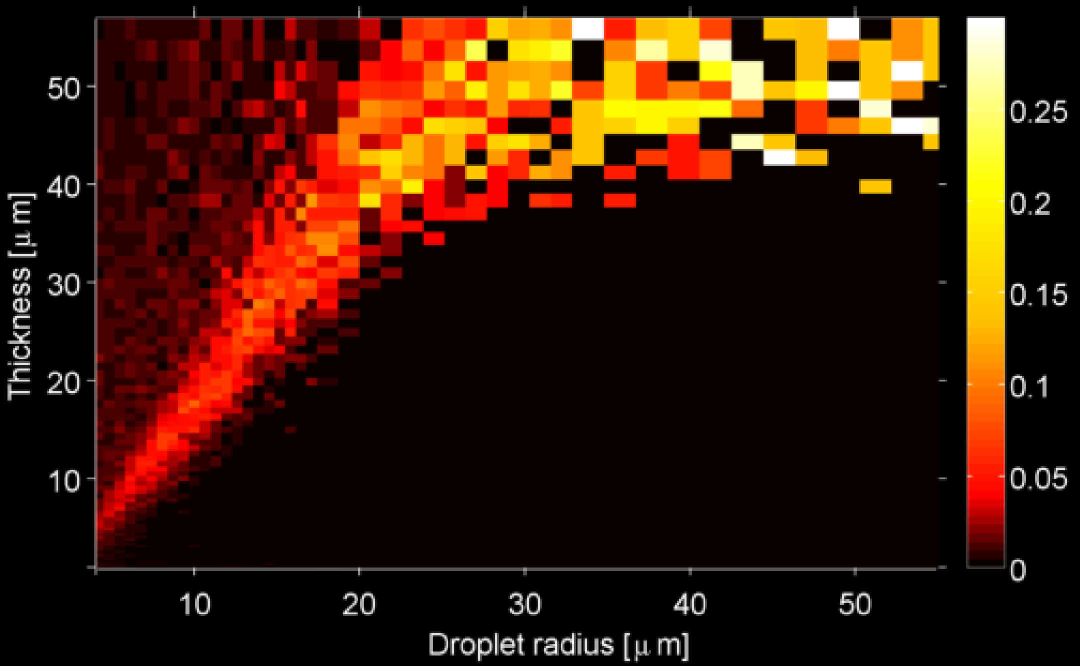
Simple theory for droplet motion on thickness gradient



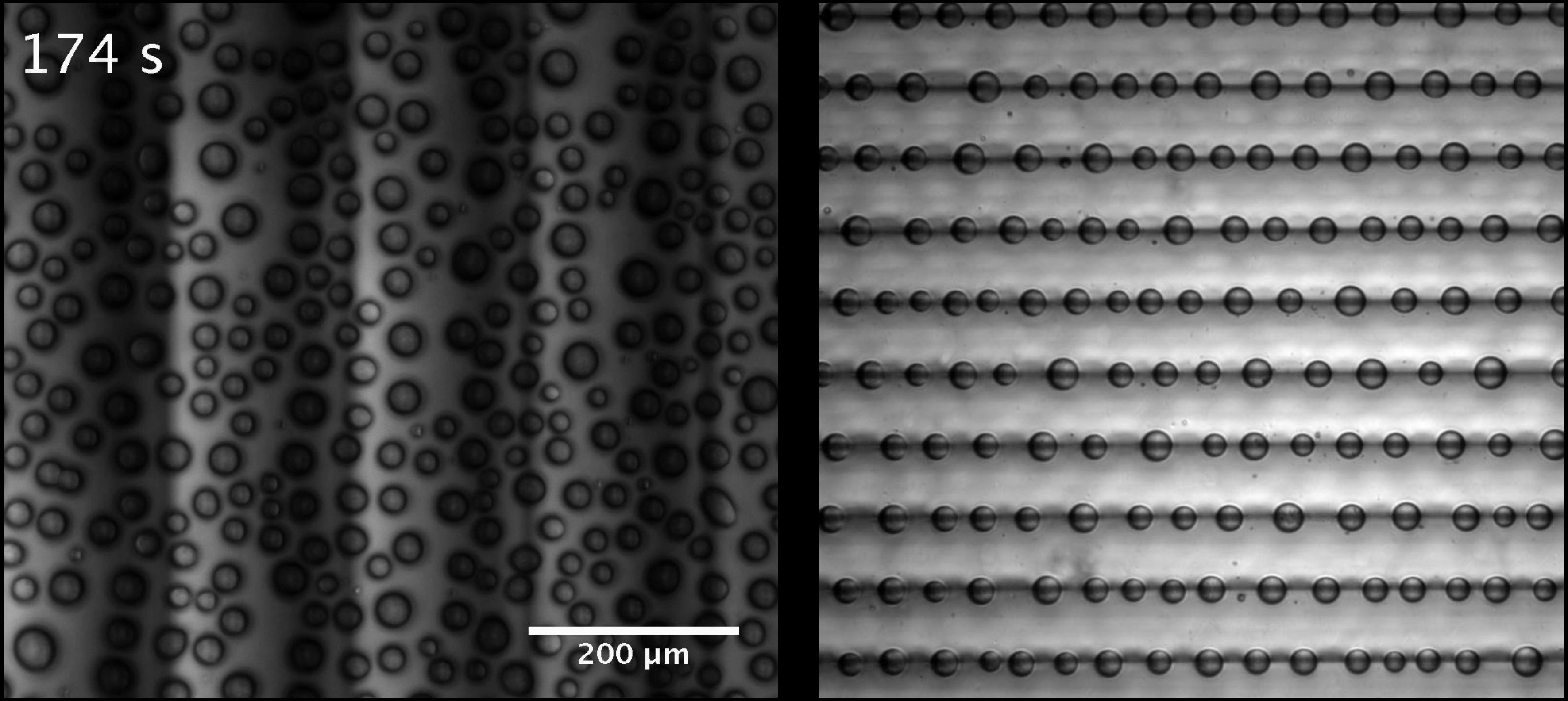
$$\Delta\theta = \theta_{crit}$$



Probability density of `final' drop position

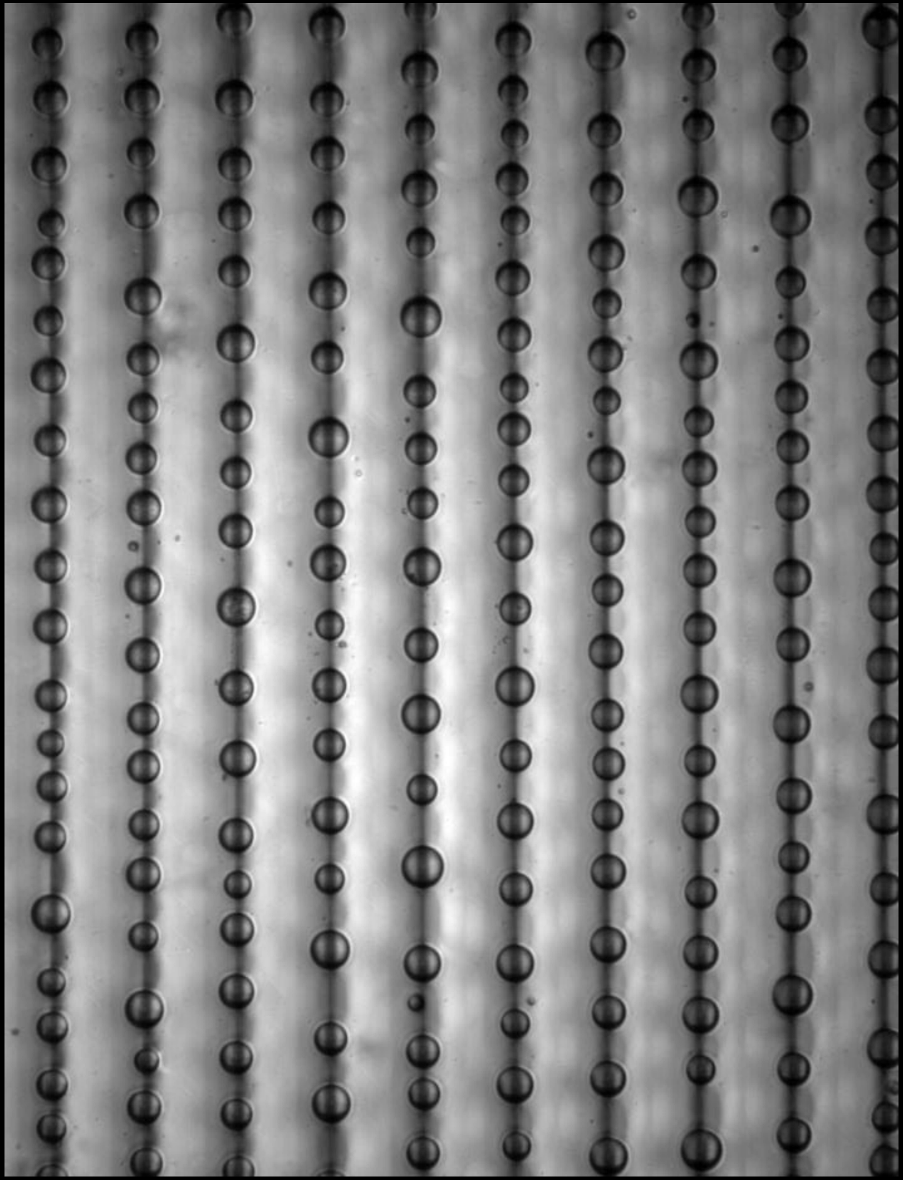


Condensation, coarsening and evaporation enhance patterning



0-600 s cooling by Peltier
>600 s Peltier off

Wetting Summary



Young's law fails on soft substrates as *R* approaches $\gamma/_E$.

The shape of the cusp close to contact line is universal and determined by the surface tensions.

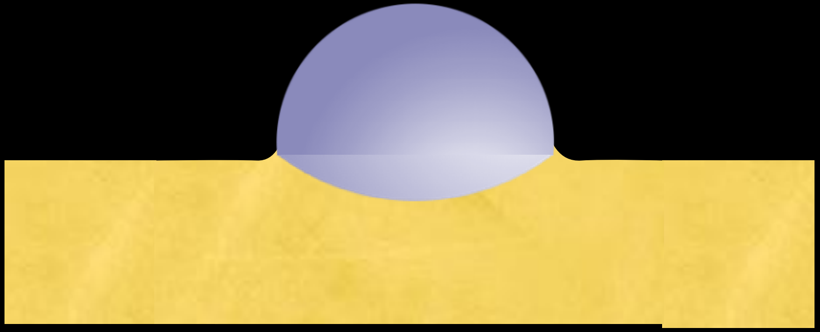
While the apparent contact angle is not universal it seems to drive droplet motion

Theory and preliminary expts:
Jerison *et al Physical Review Letters* 2011
Style *et al Soft Matter* 2012

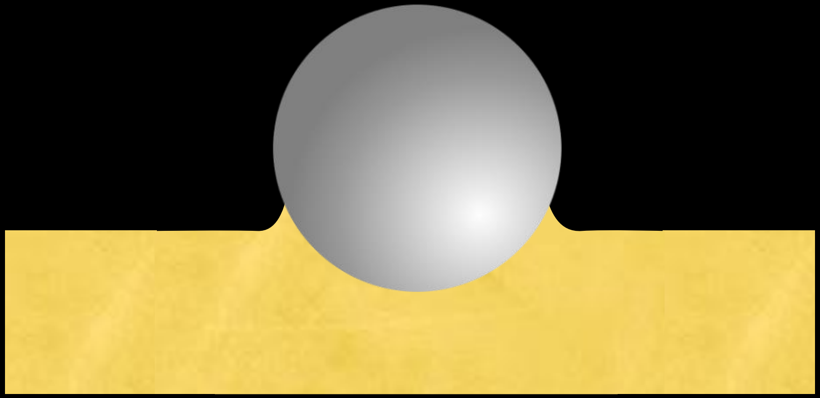
Breakdown of Young's Law
Style *et al Physical Review Letters* 2013

Drop movement
Style et al PNAS 2013

Wetting and adhesion don’t look so different on a soft surface

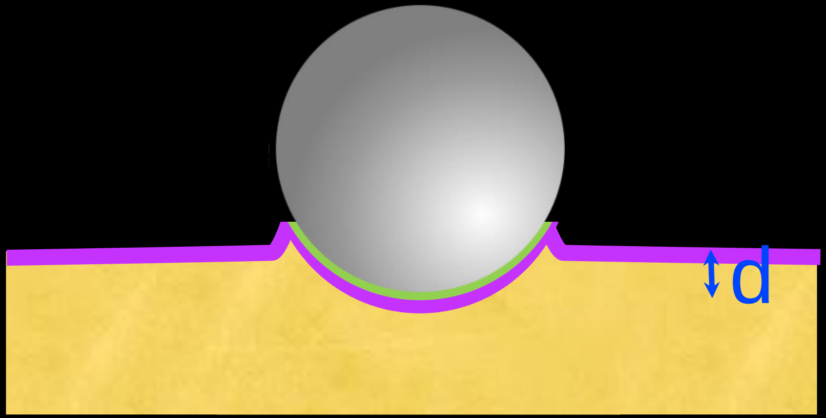


Wetting



Adhesion

Johnson, Kendall & Roberts (1971) – ‘JKR’

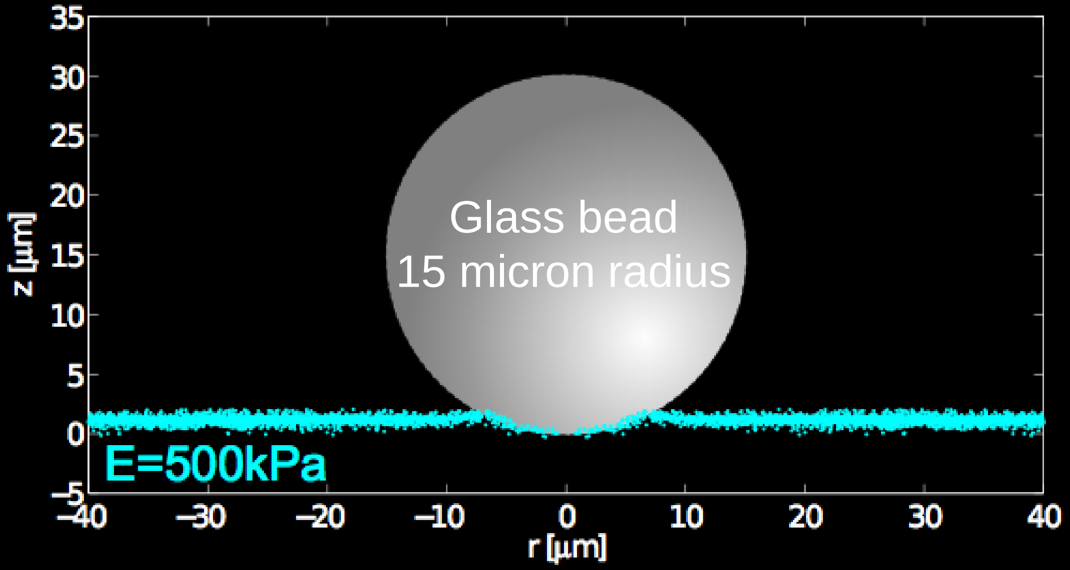


Adhesion Energy, $W = \gamma_{sp} - \gamma_{sv} - \gamma_{pv}$

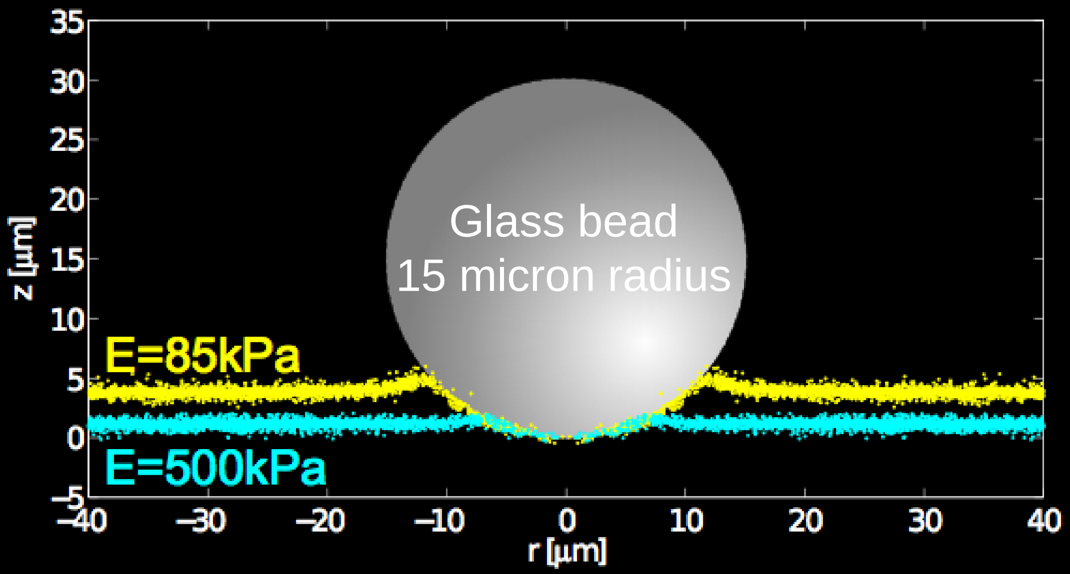
Substrate Elasticity, E

Substrate surface tension, Υ_{sv} ,Υ_{sp}?

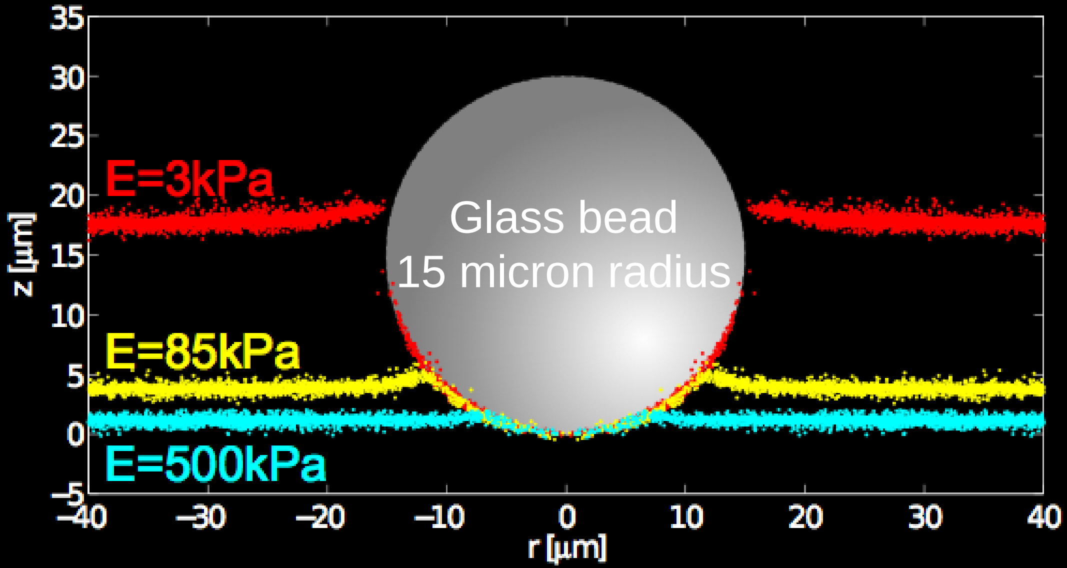
Surface profiles for different stiffness substrates



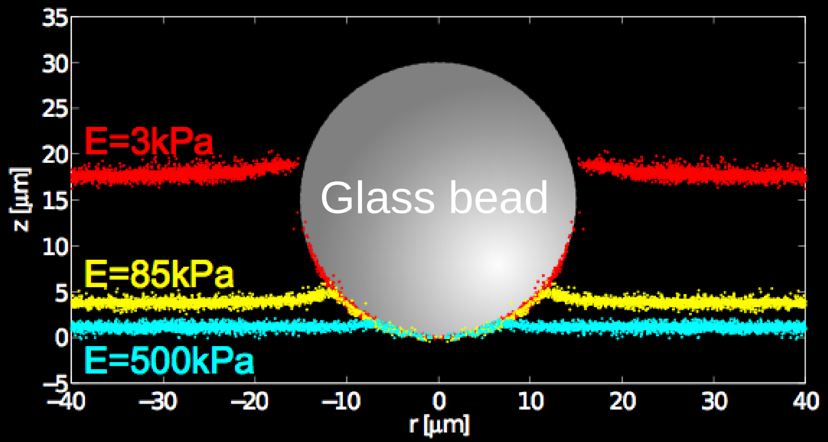
Surface profiles for different stiffness substrates

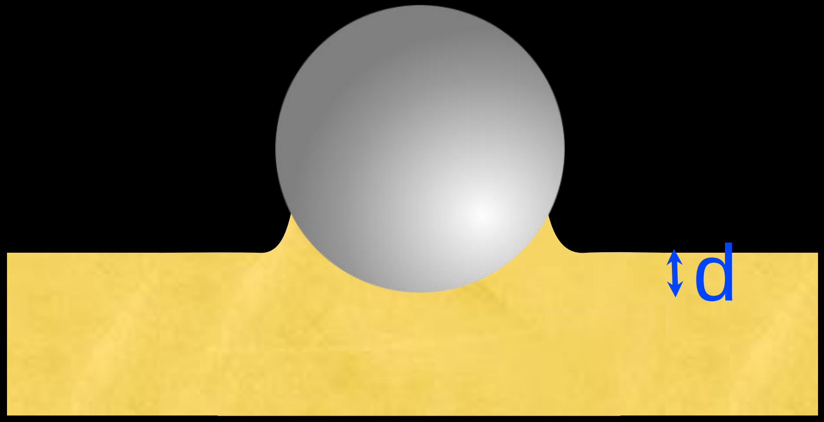


Surface profiles for different stiffness substrates

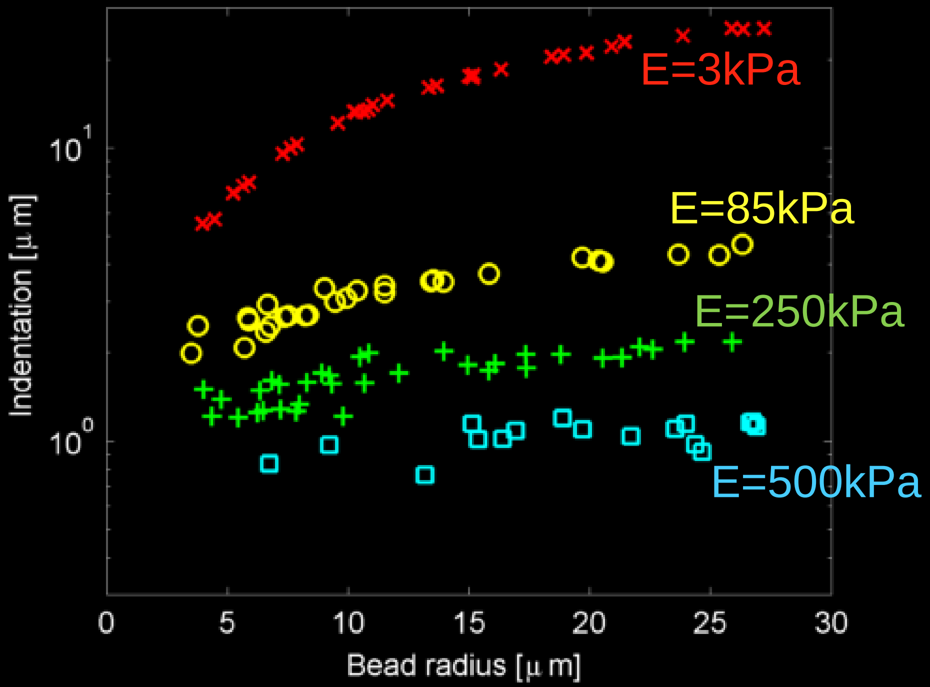


Indentation Depth Changes with Size and Stiffness





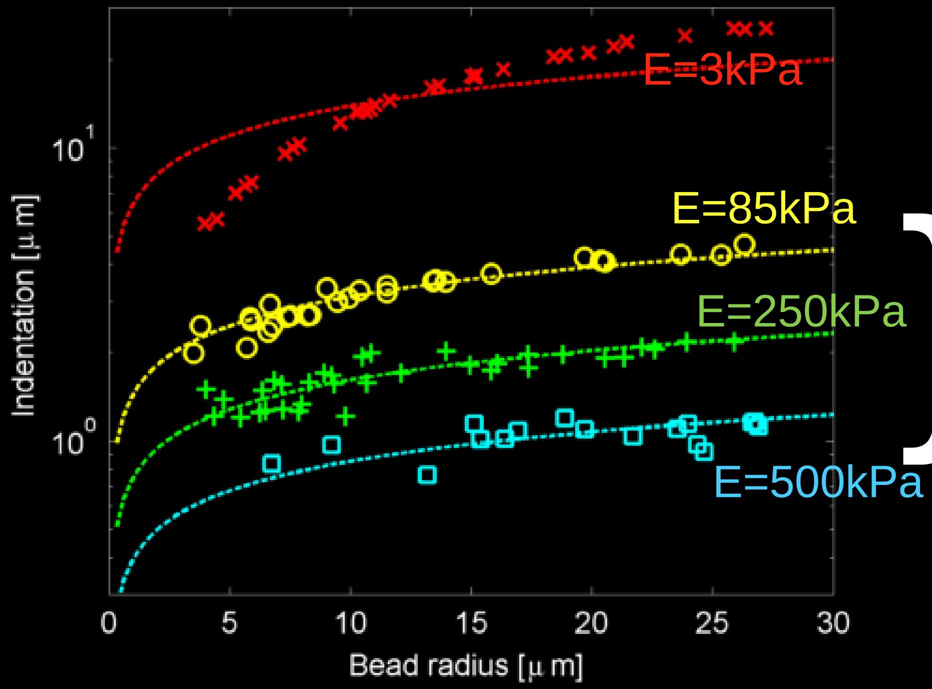
d, indentation



Comparing results with JKR

$$d = \left(\frac{\sqrt{3} W (1 - \nu^2)}{2E} \right)^{2/3} R^{1/3}$$

d,indentation

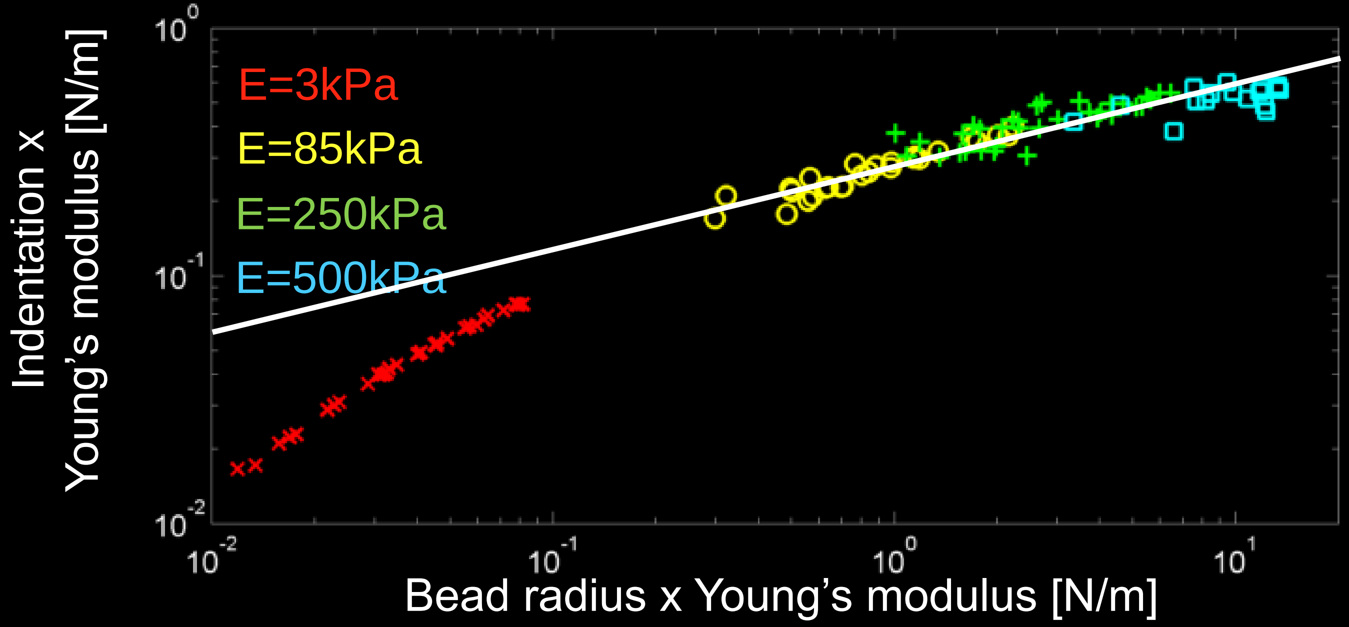


W~25mN/m

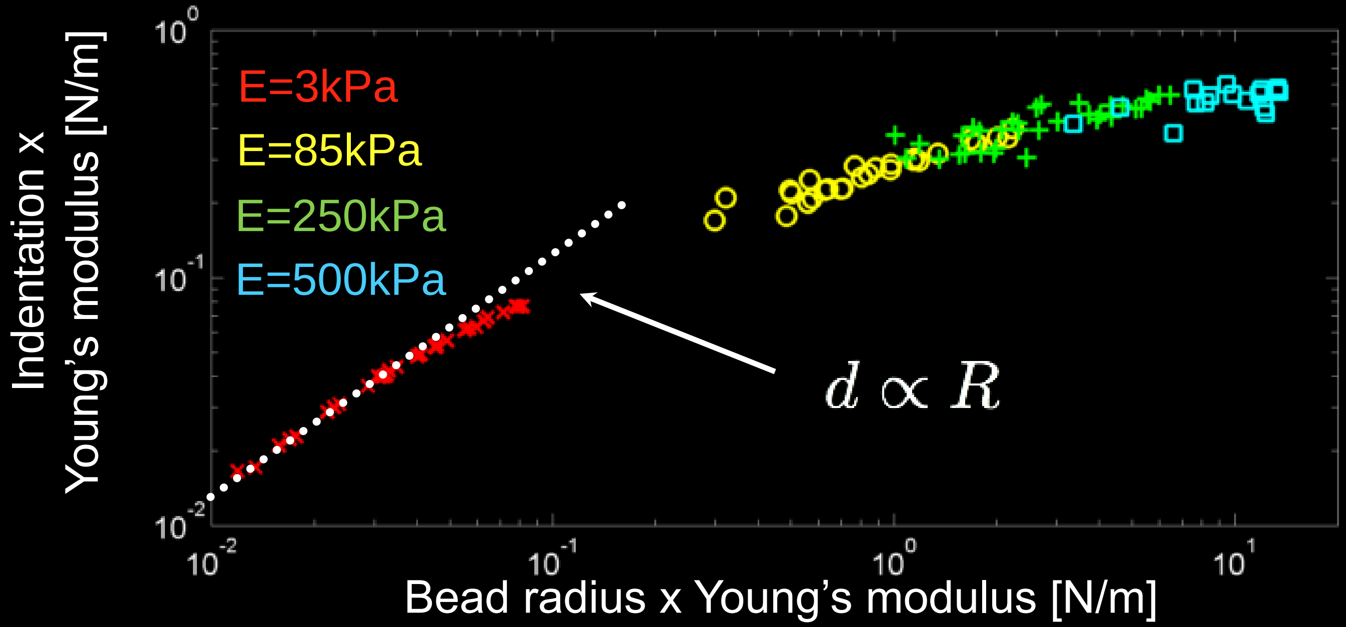
W~70mN/m

Collapsing the data

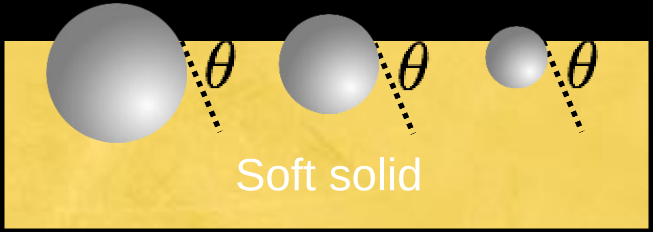
$$dE = \left(\frac{\sqrt{3} W (1-\nu^2)}{2} \right)^{2/3} (RE)^{1/3}$$

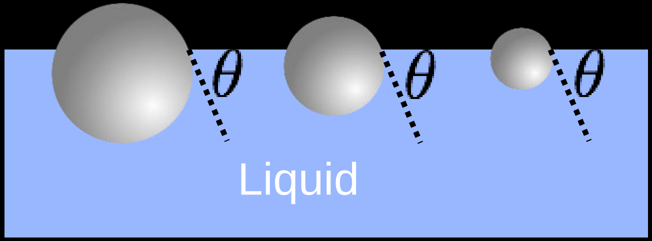


Indentation proportional to bead radius for small beads



Indentation, $d \sim R$ implies constant contact angle





$$\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl}$$

JKR plus surface tension fits data

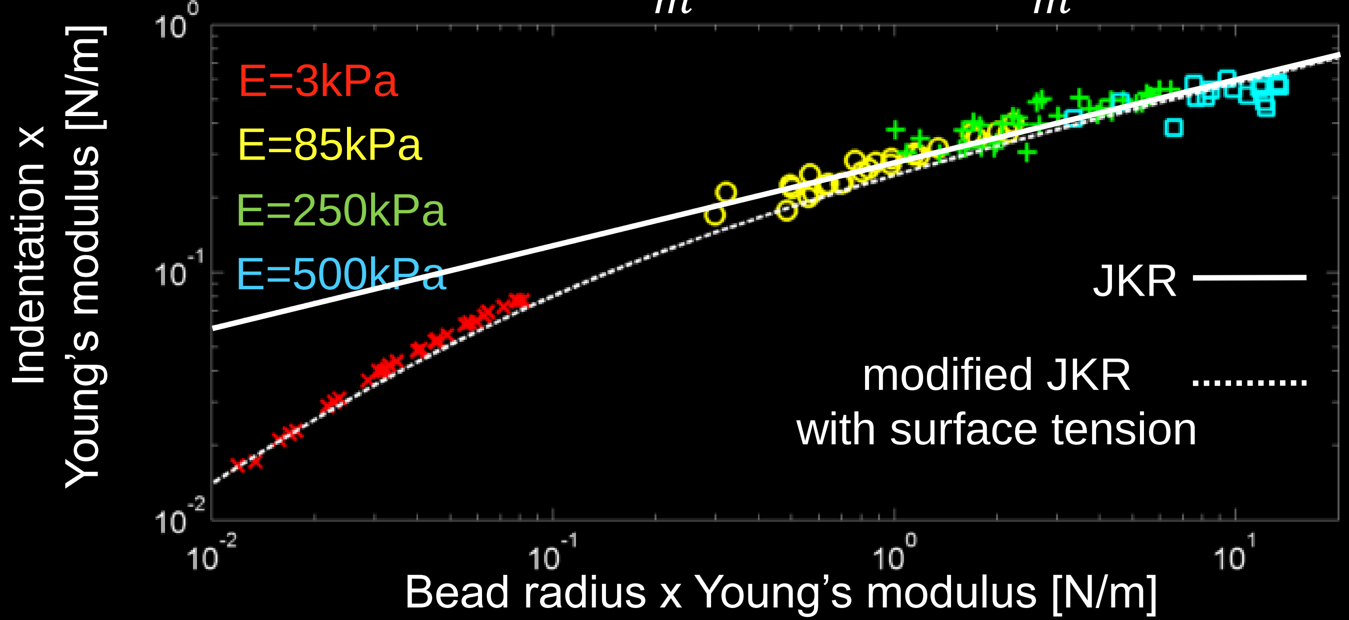
Minimize total energy (a la Carillo/Raphael/Dobrynin 2010):

Elastic energy + Adhesion Energy + Surface Tension

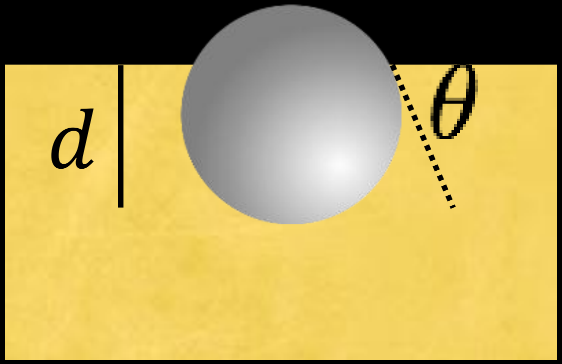
(from JKR)

$$\Upsilon_{sv} \Delta A$$

$$W = 71 \frac{mN}{m}, \qquad \Upsilon_{sv} = 45 \frac{mN}{m}$$



Small contact limit of JKR plus surface tension…



$$d = WR/\Upsilon_{sv}$$

equivalently…

$$\Upsilon_{sv}\cos\theta = W - \Upsilon_{sv}$$

Smells like Young's Law

for $\Upsilon_{sv} = \gamma_{sv}$,

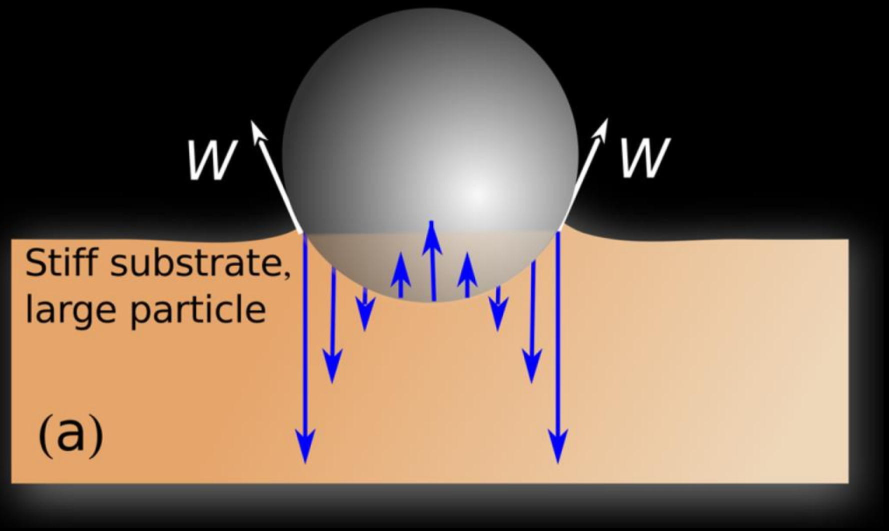
$$\gamma_{sv}\cos\theta = \gamma_{sp} - \gamma_{pv}$$

Young's Law with soft substrate in the place of the liquid

Two Regimes of Contact

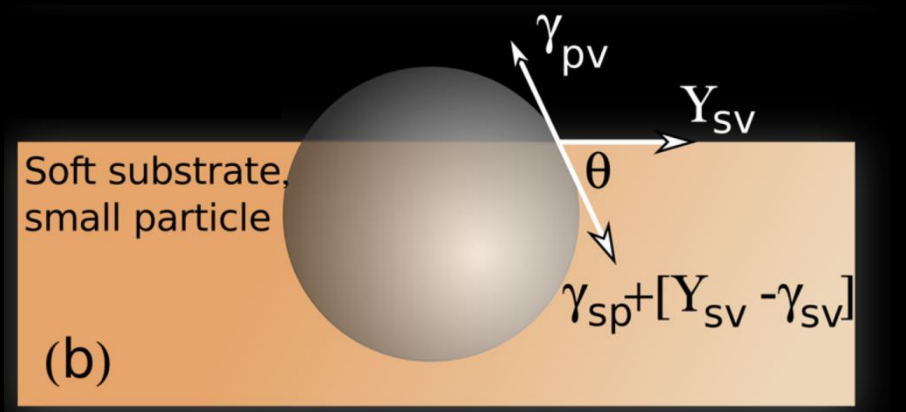
Style, Hyland, Dufresne *Nature Communications 2013*

$a \gg \Upsilon_{sv}/E$



JKR

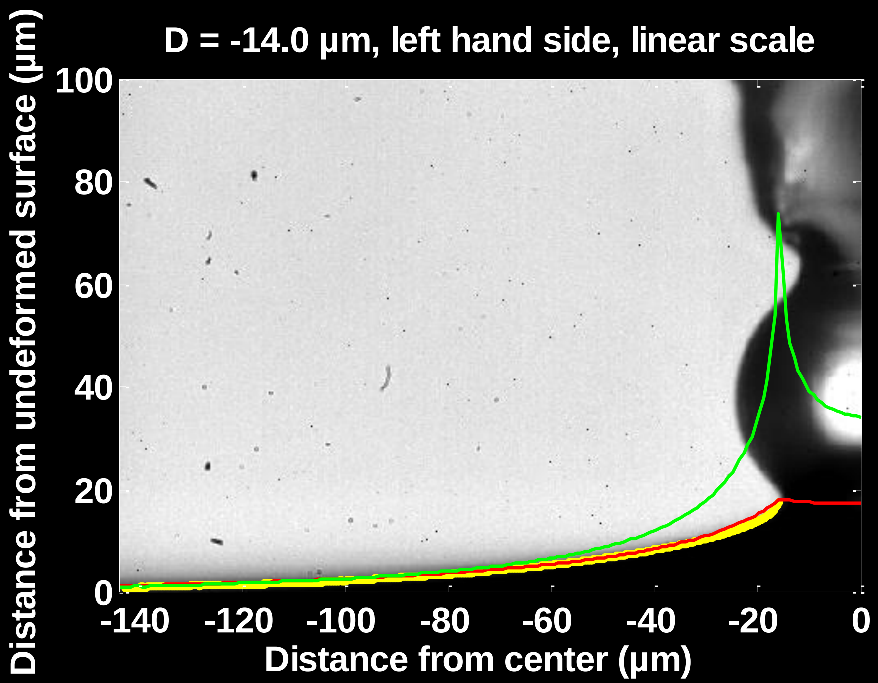
$a \ll \Upsilon_{sv}/E$

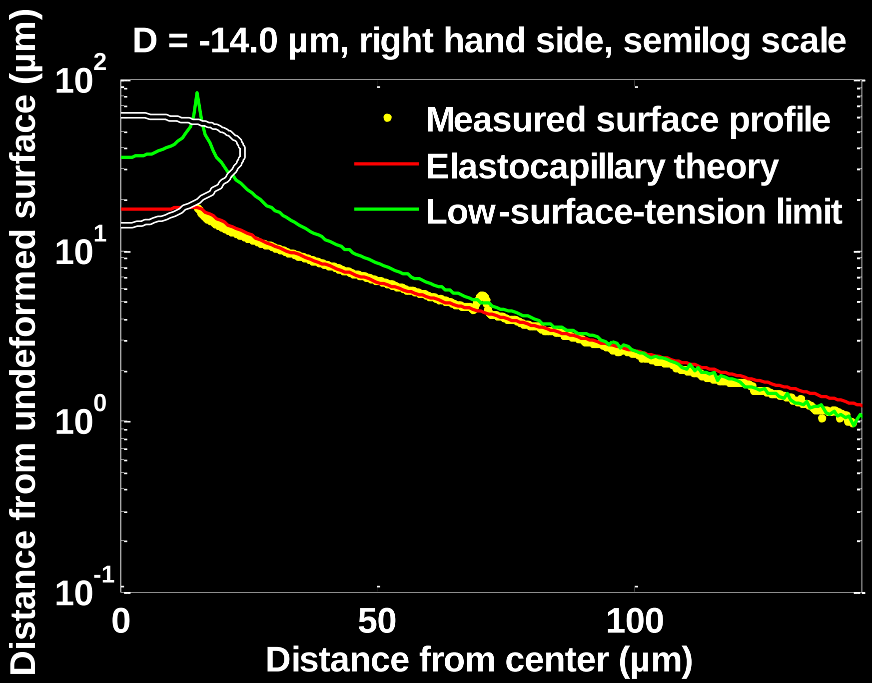


Young's Law

Next Step: How does surface tension modify forced-adhesion?

Kate Jensen


D = -14.0 μm, left hand side, linear scale


D = -14.0 μm, right hand side, semilog scale

Key Findings

- Young’s law doesn’t describe wetting of small drops on soft substrates

- Young’s law does describe adhesion of small particles to soft substrates

- Soft solids have a characteristic length scale $\frac{\Upsilon_{sv}}{E}$, below which elastic response to surface deformation is swamped by surface tension