Surface Tension, Droplets, and Contact Lines

Lecture III

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Boulder Condensed Matter Summer School 2015

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->Oxford

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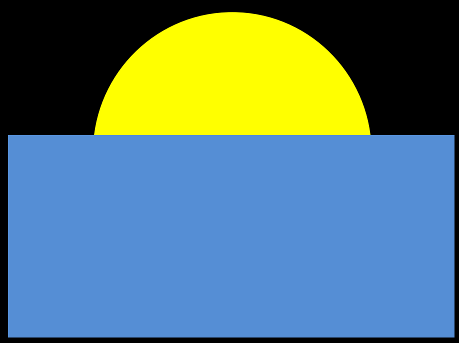
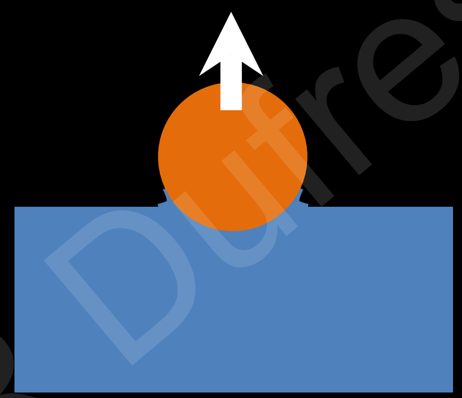
Three Foundational Theories of Interfacial Mechanics

Young-Dupre (18XX)



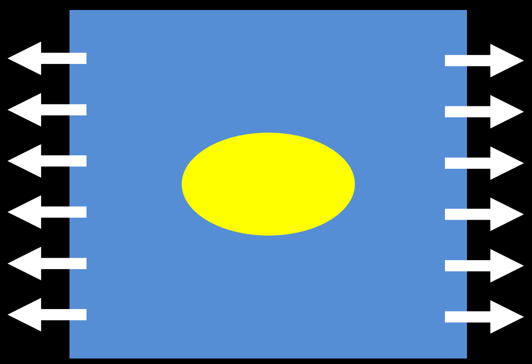
wetting

JKR (1971)



adhesion

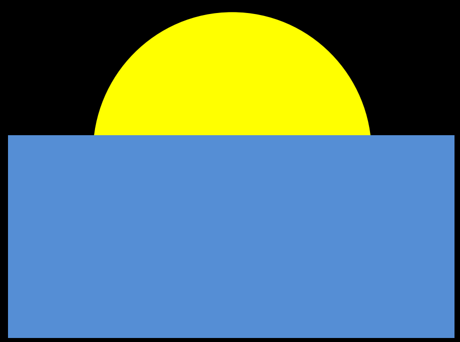
Eshelby (1957)



composites,
fracture,
dislocations

Three Foundational Theories of Interfacial Mechanics

Young-Dupre (18XX)



wetting

JKR (1971)

adhesion

Eshelby (1957)

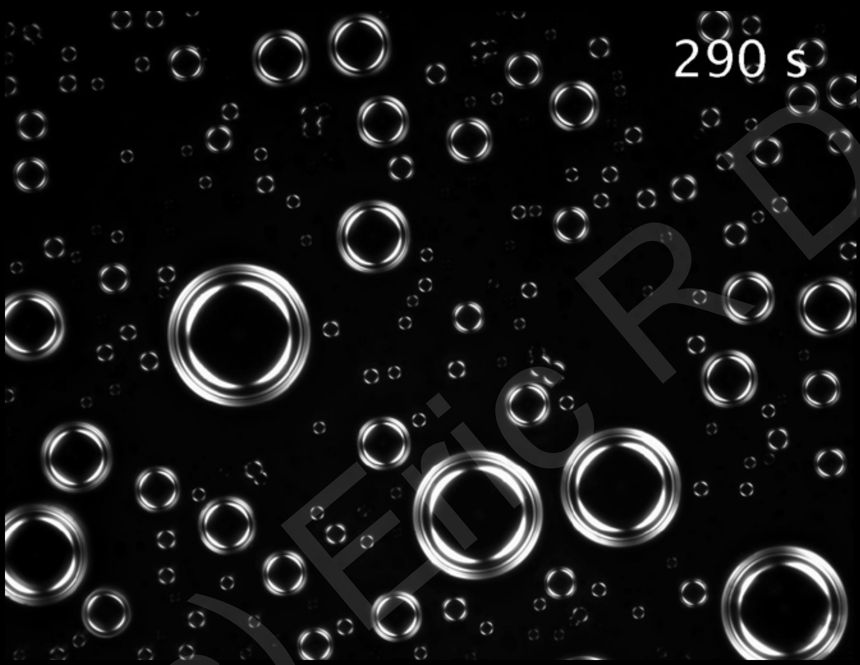
composites,
fracture,
dislocations

3 kPa silicone gel (50 μm)

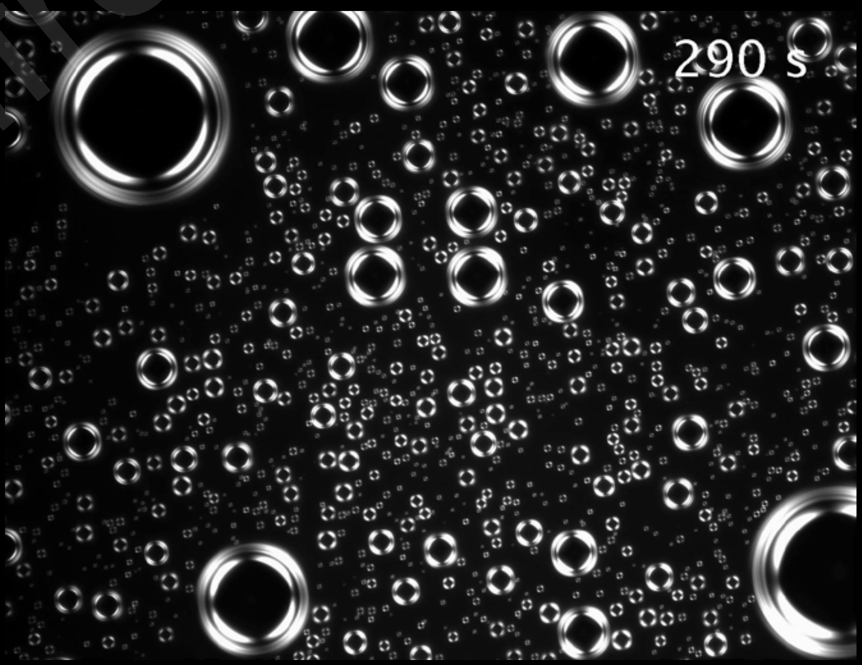
1.8 MPa silicone elastomer (50 μm)

atomized glycerol

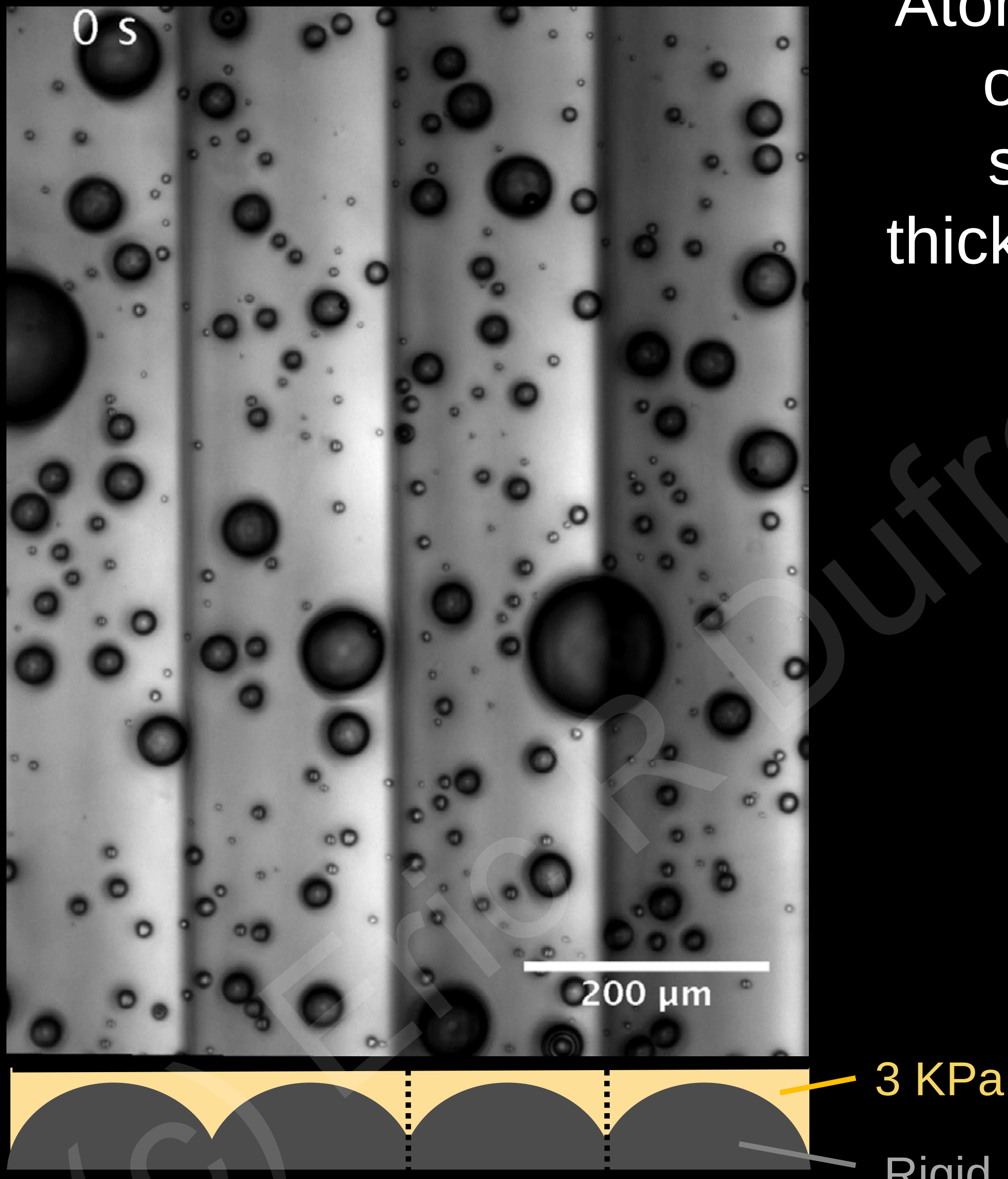
0.3mm



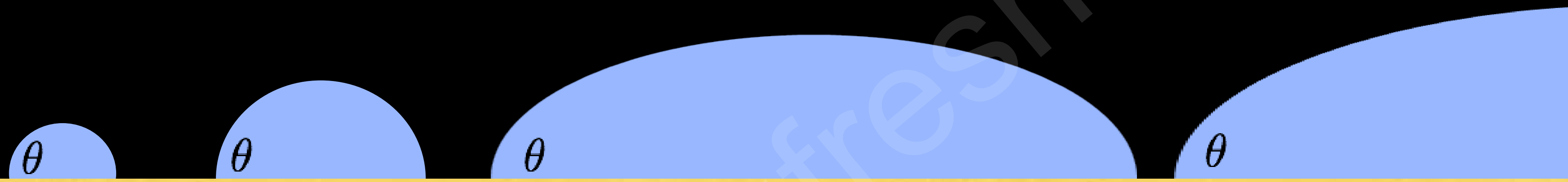
0.3mm



Atomized spray of glycerol on a flat surface of a soft substrate with a thickness/stiffness gradient



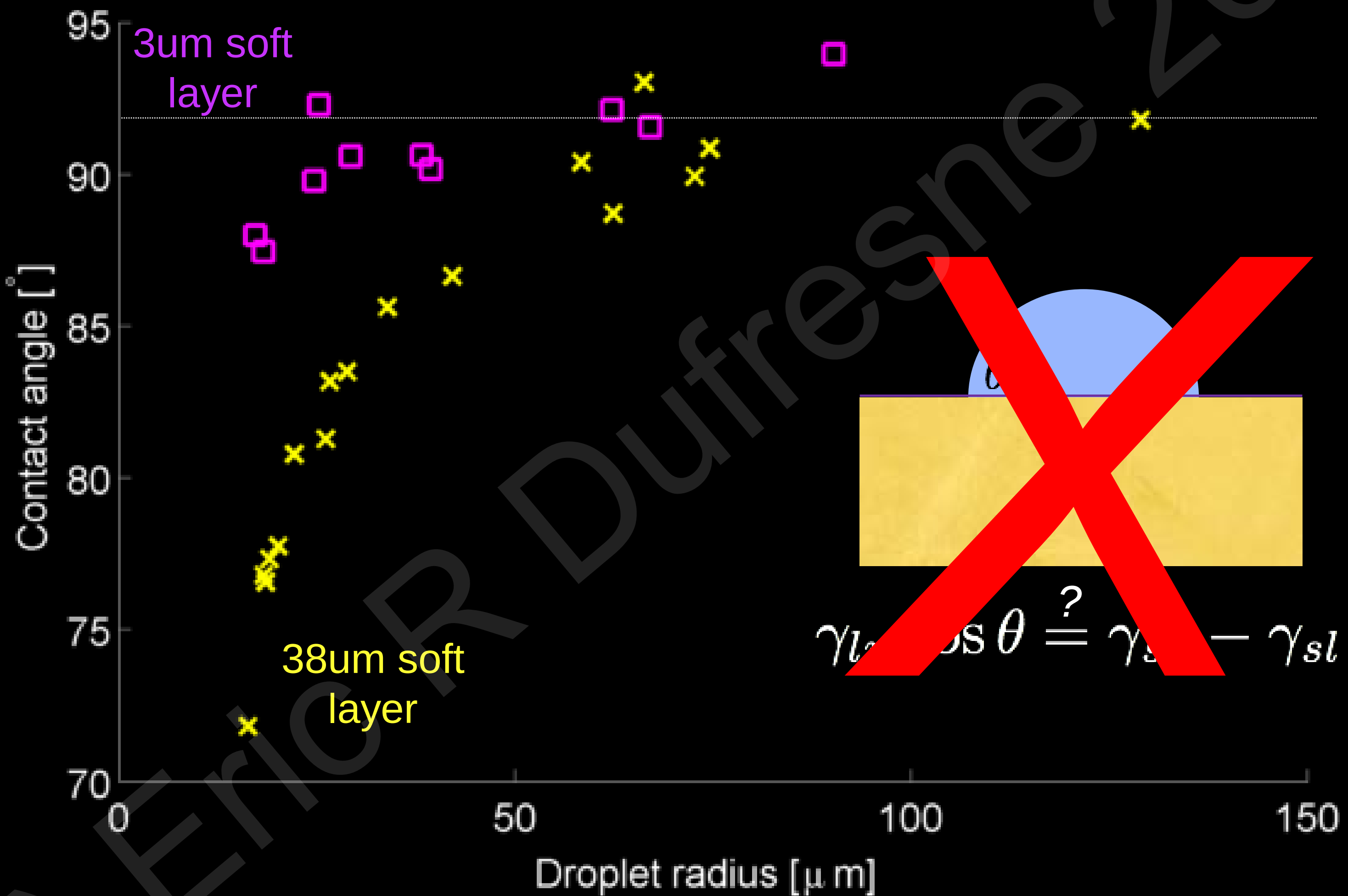
Young-Dupre equation relates contact line geometry and material properties in equilibrium




Thomas Young
1773-1829

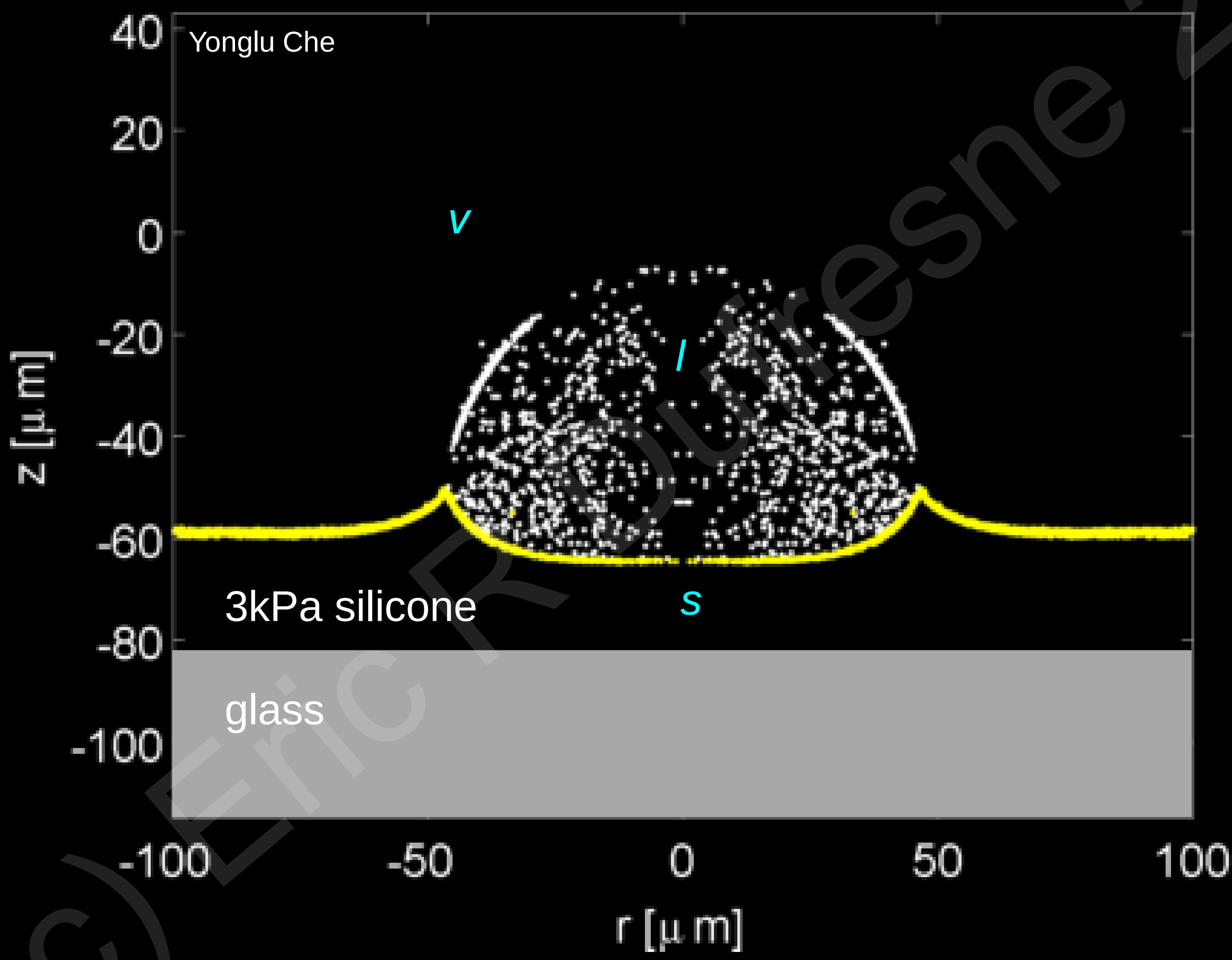
$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

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

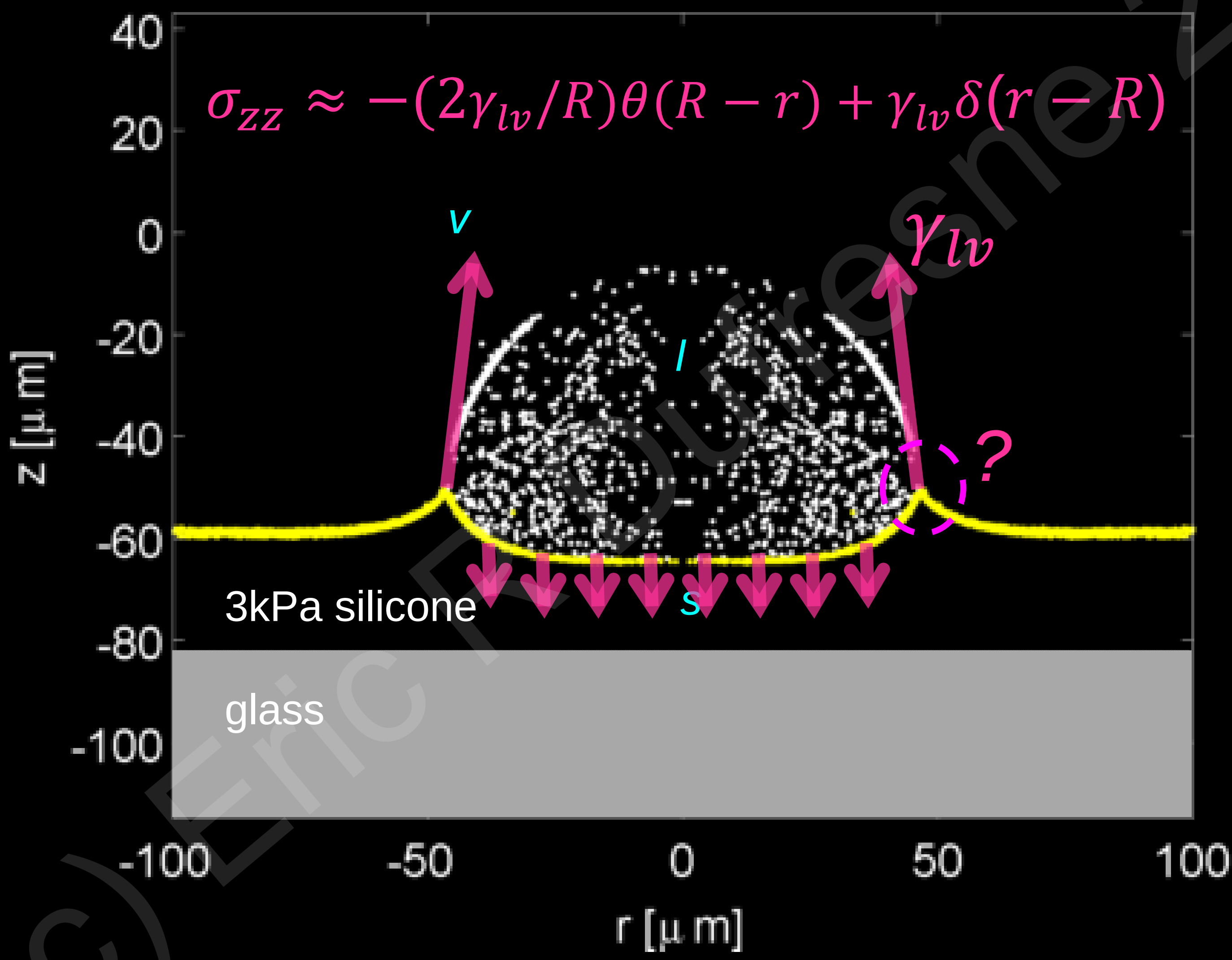


Glycerol drops on silicone (E=3kPa)
Zygo surface profilometer

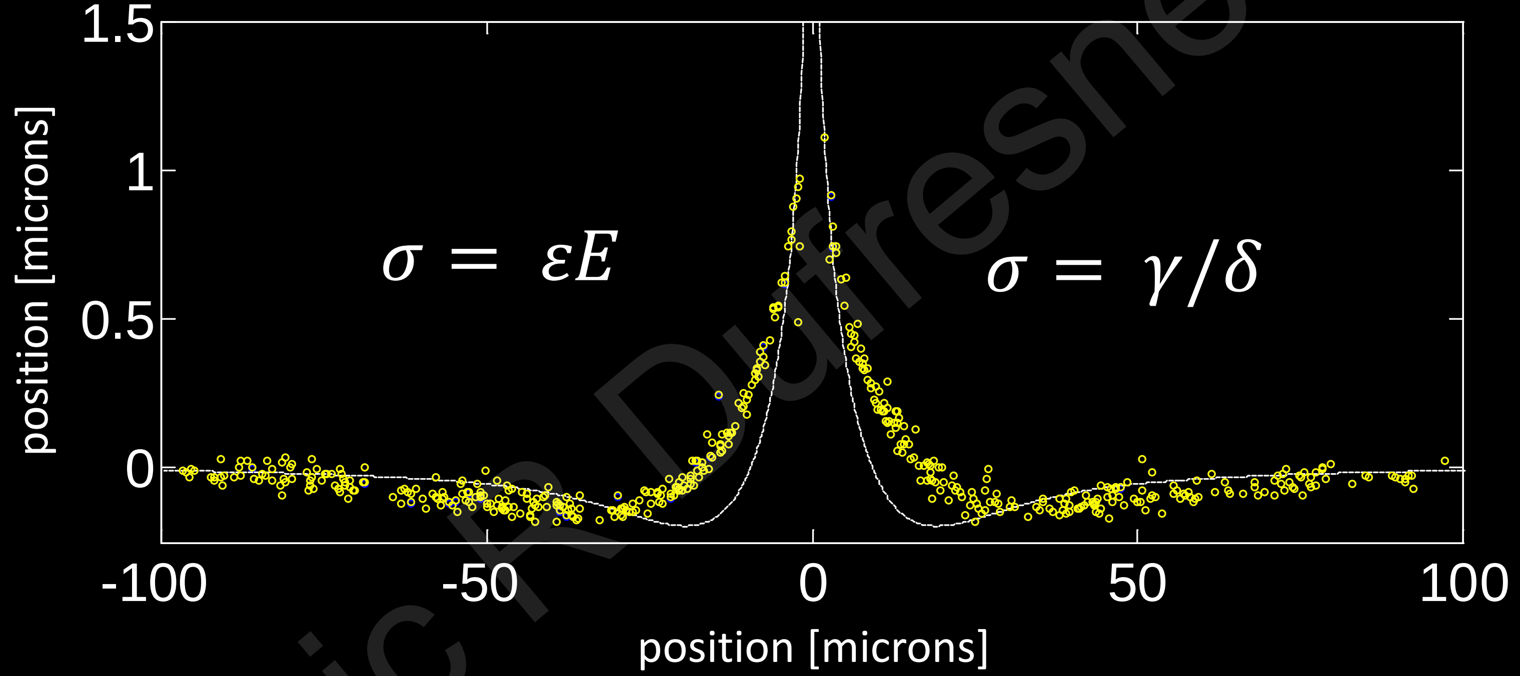
Droplets Deform Soft Substrates



Droplets Deform Soft Substrates

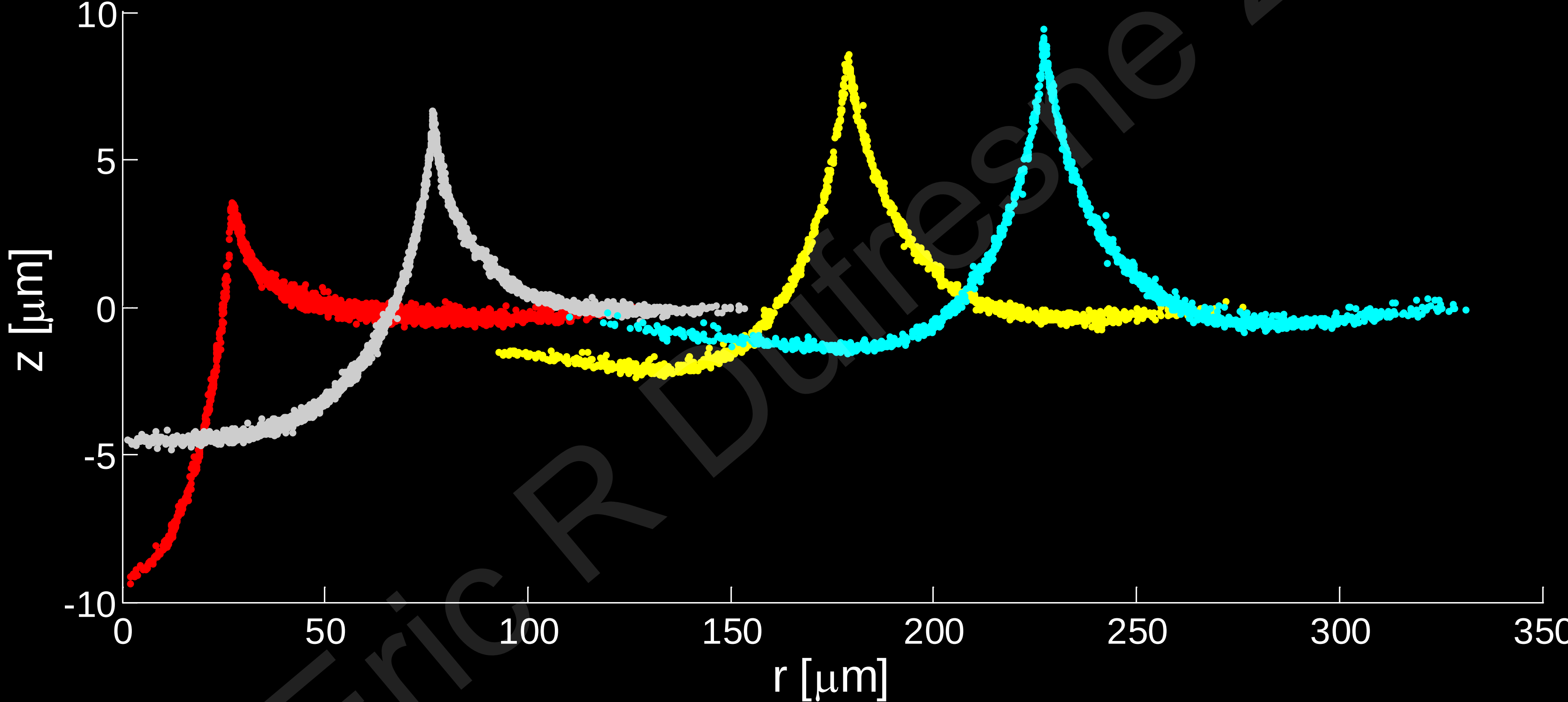


Elastic Theories Cannot Balance Contact Line Forces

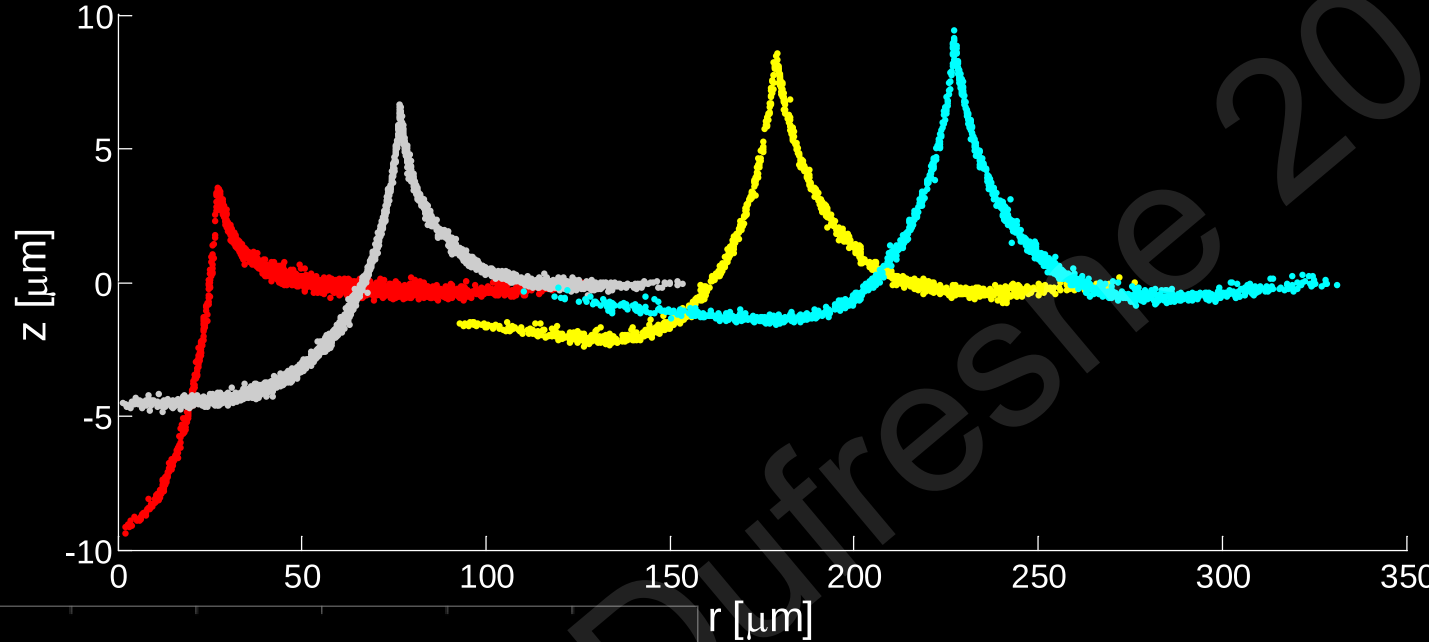


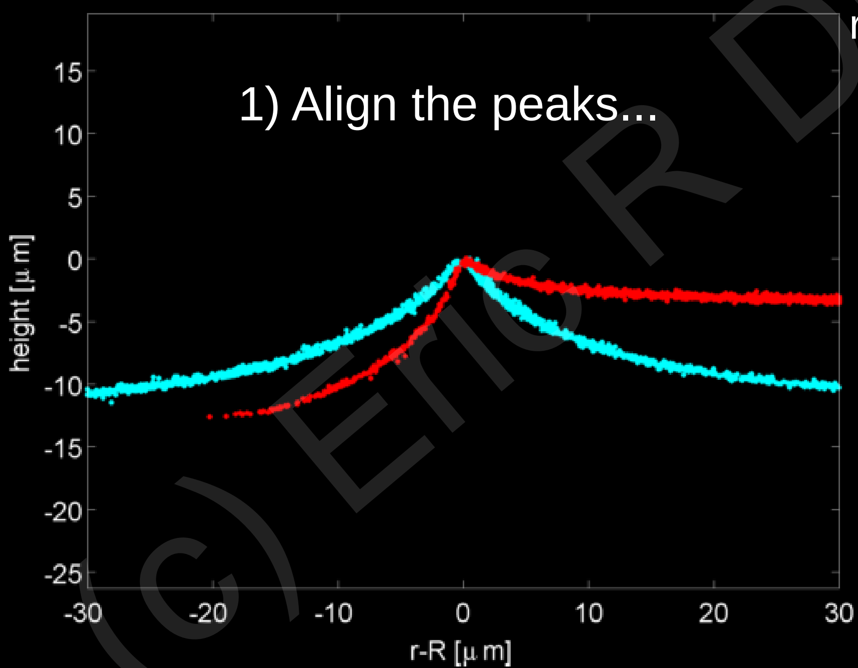
Reasonable estimates for contact line width lead to unreasonable strains and displacements

Profiles change dramatically with droplet size



Overall profiles change – but how about the ridge?





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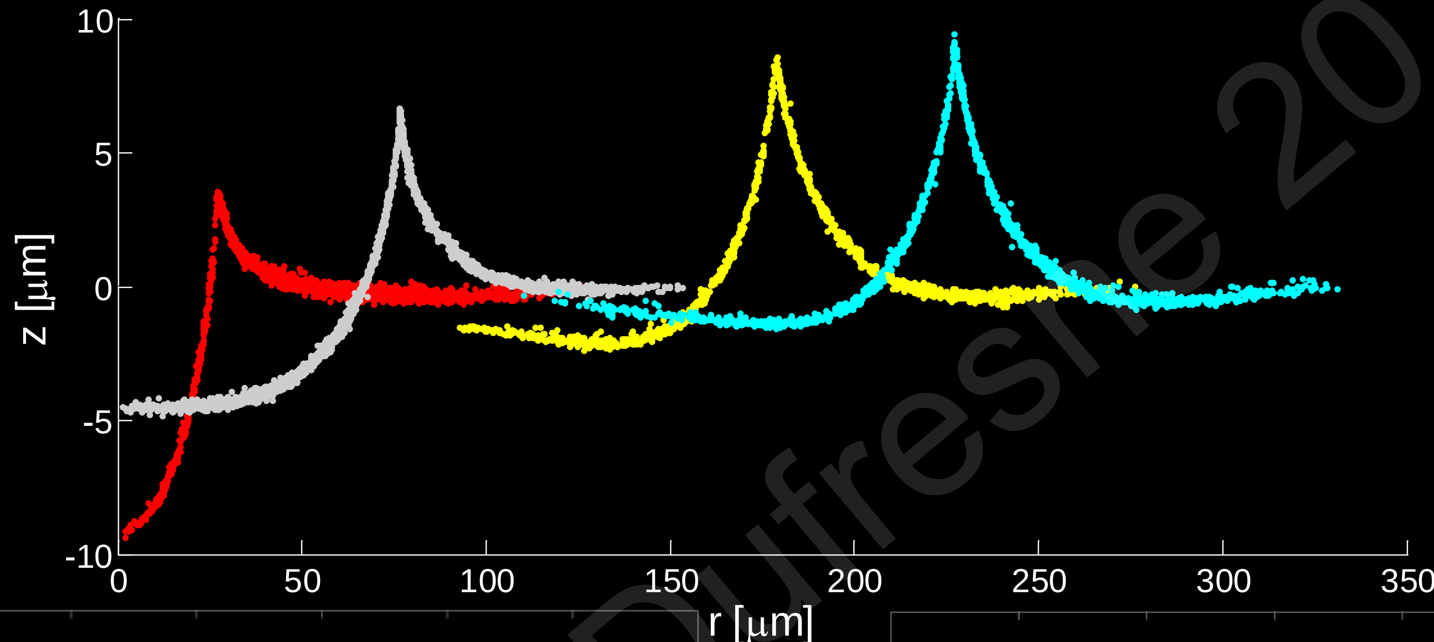
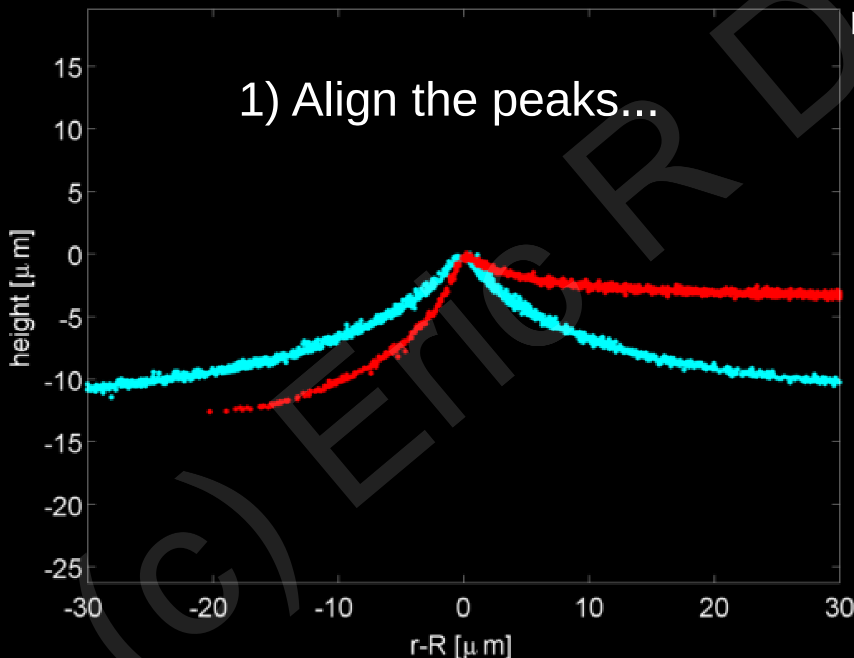
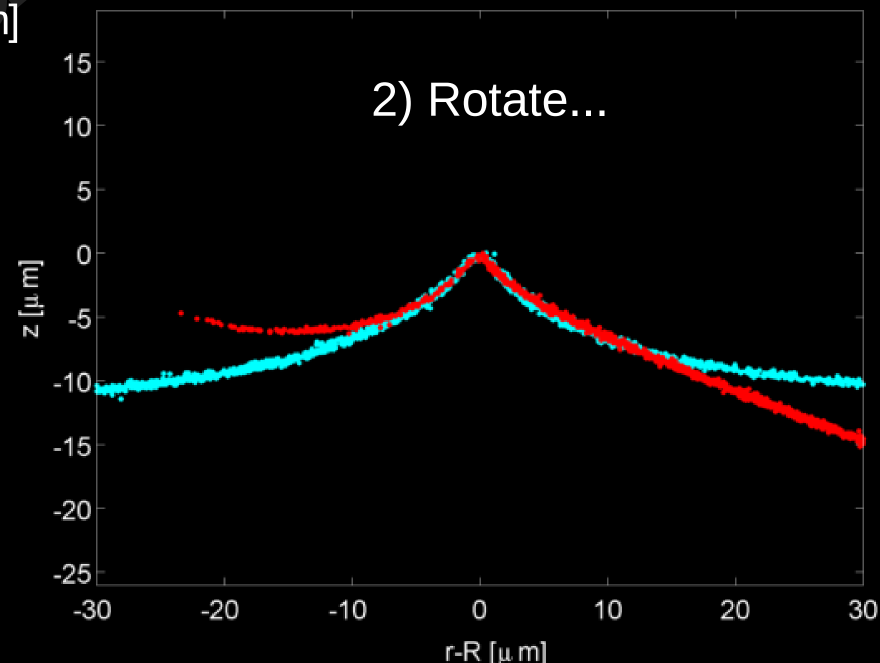
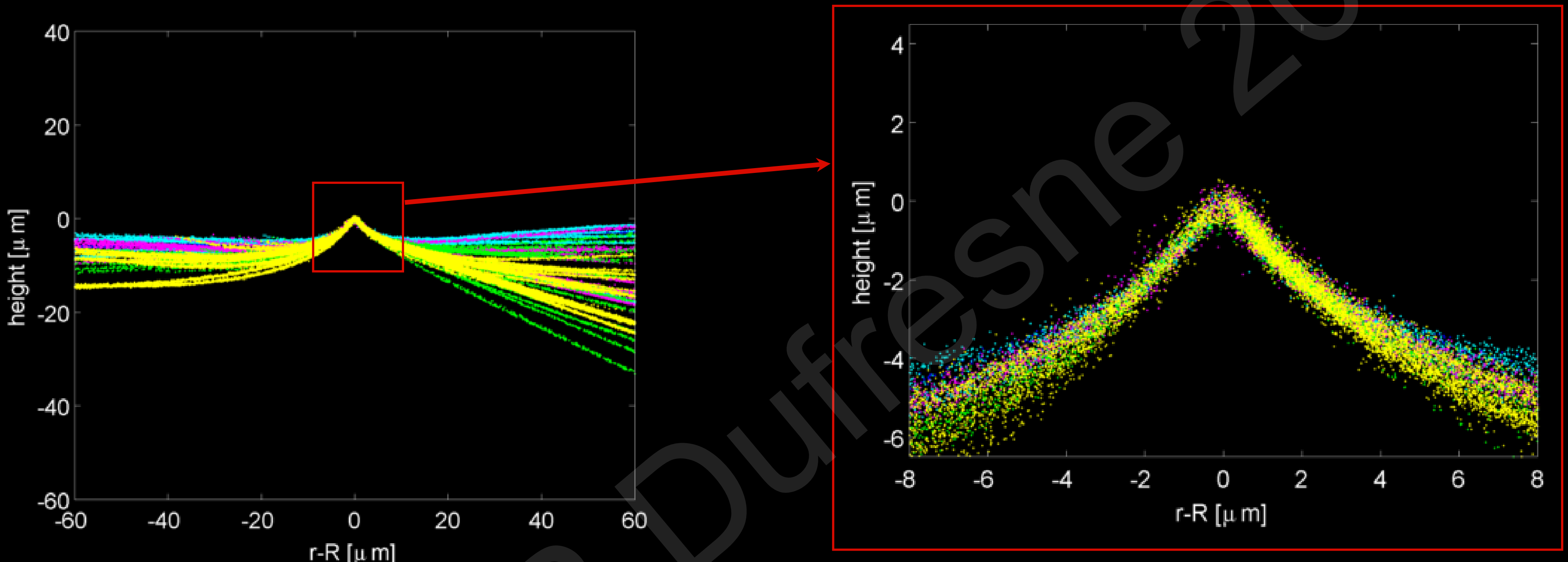




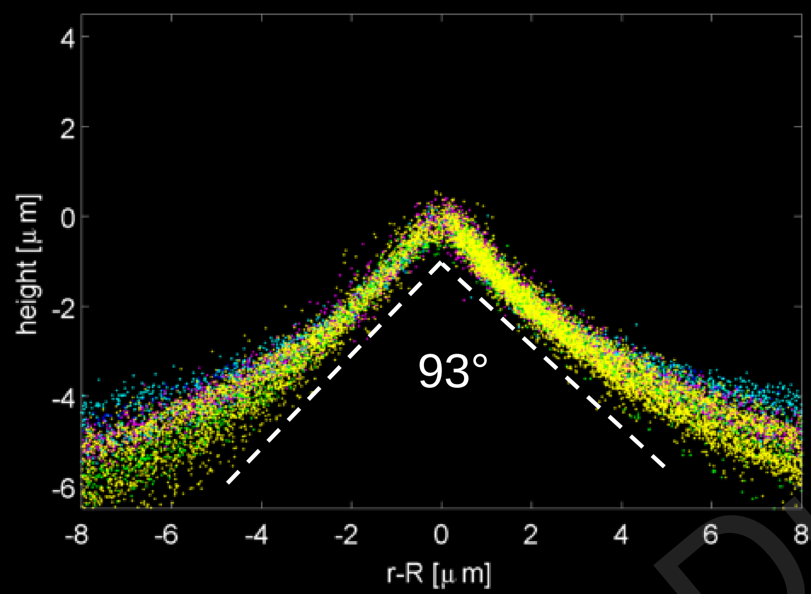


Ridge shape is universal near contact line



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

Contact line geometry depends on the wetting fluid



glycerol
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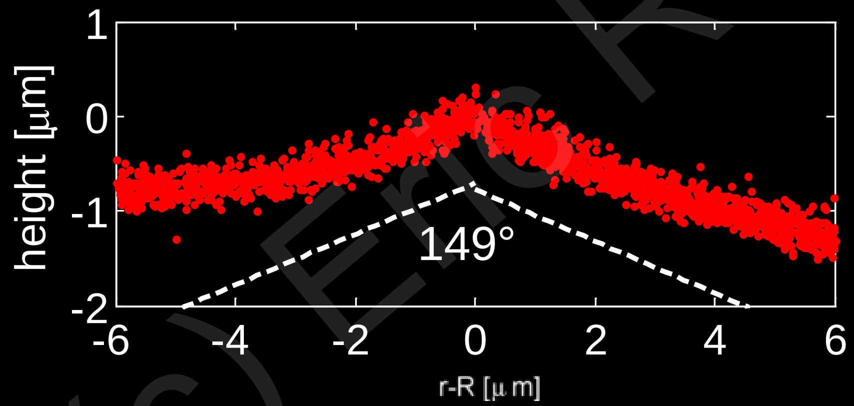
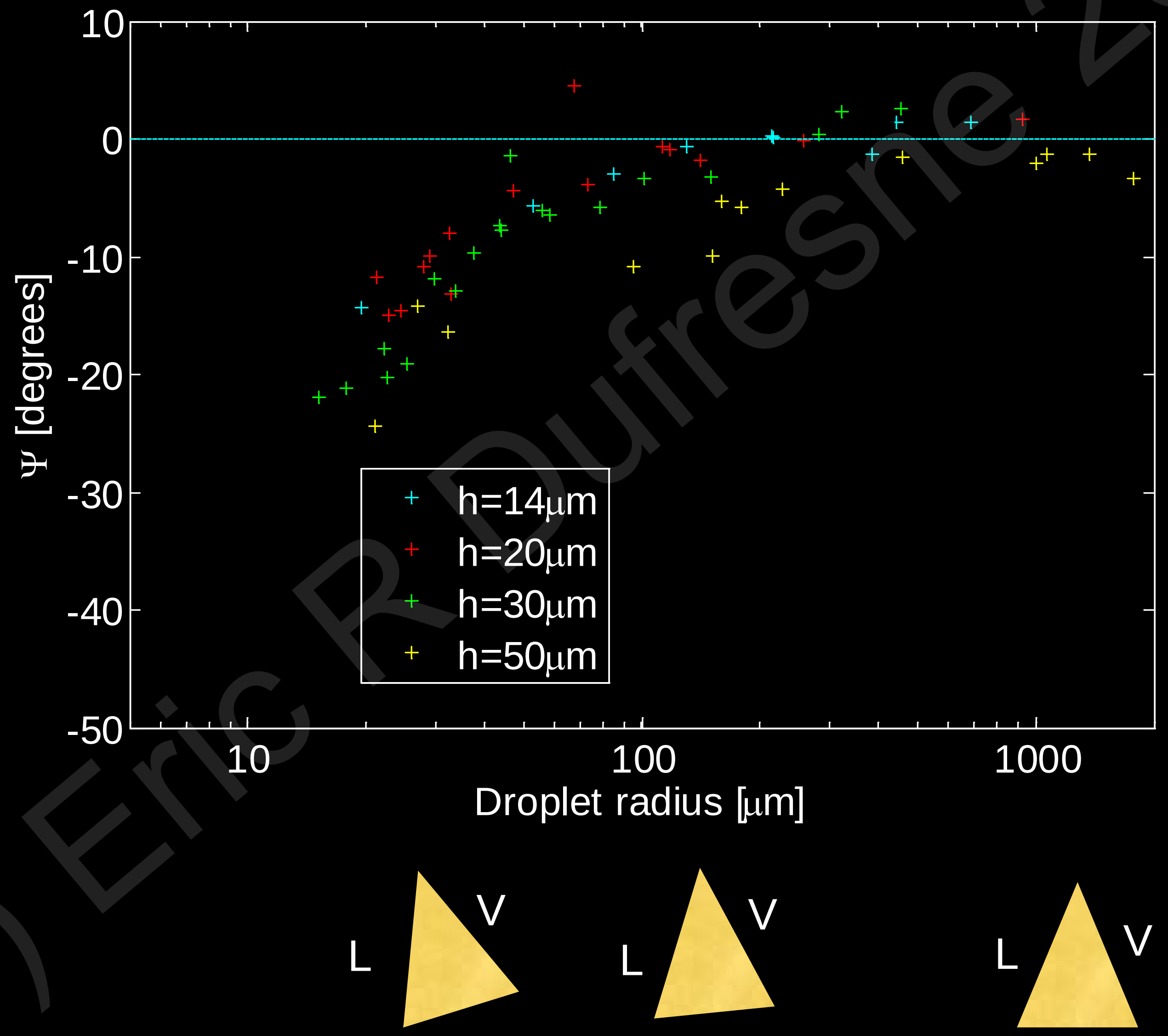
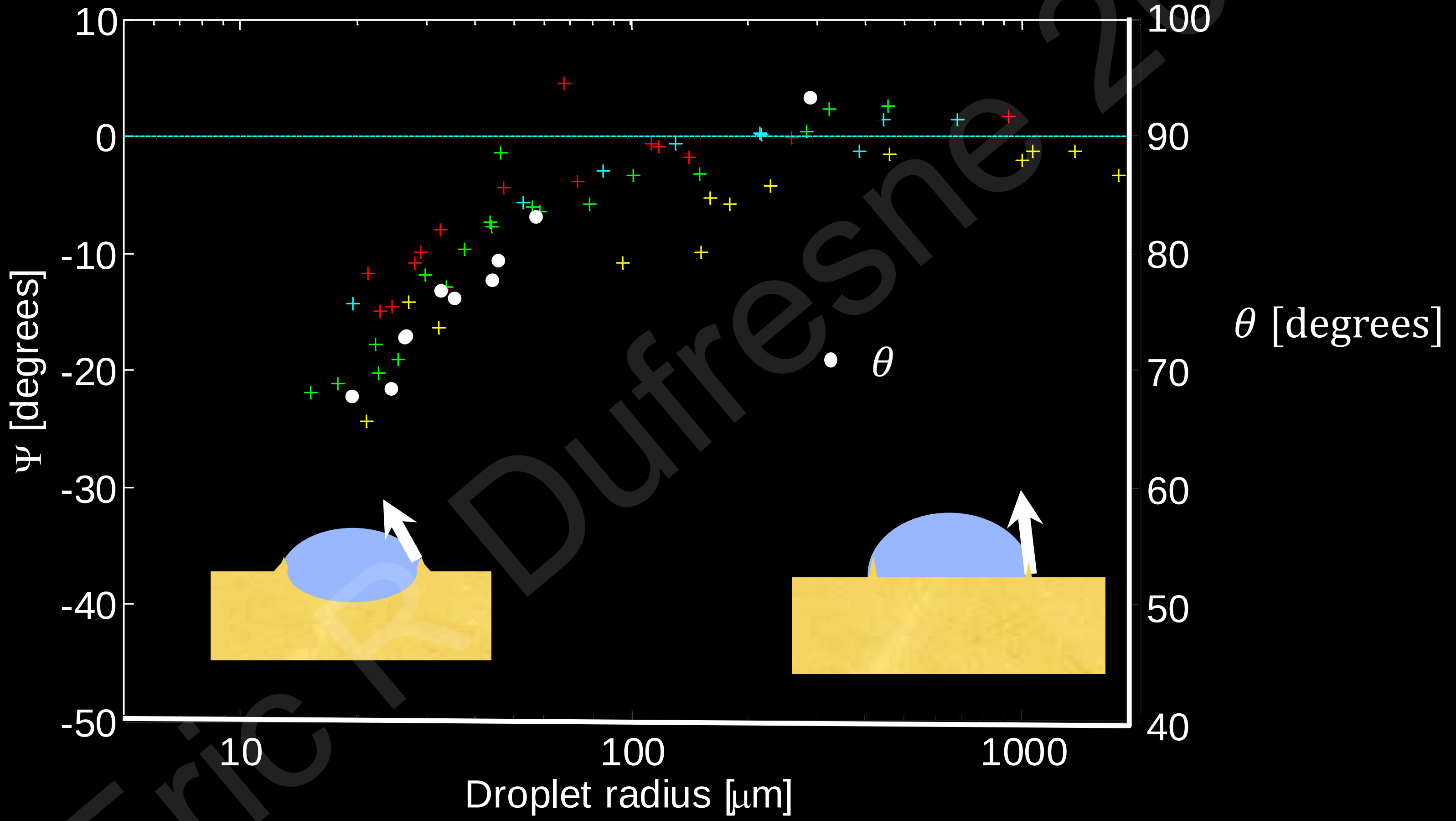


fluorinert fc-70
14 drops
radii: 140um - 270um
substrate: 23 um thick

Cusp rotates as droplets get smaller

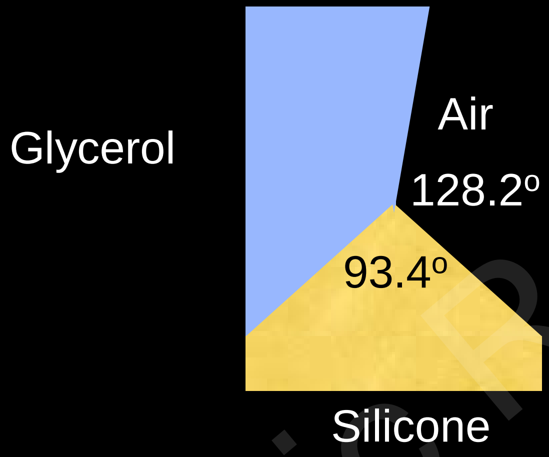


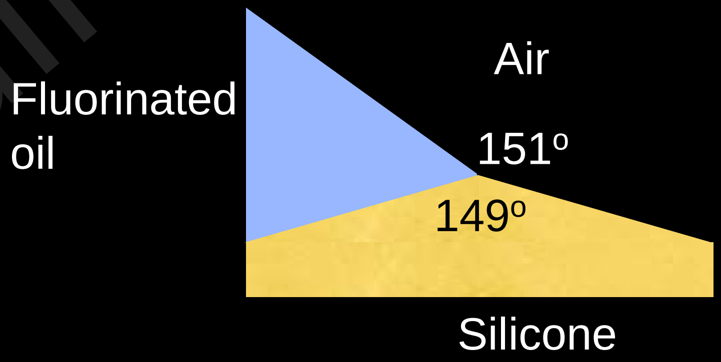
Macroscopic contact angle follows rotation of cusp



Angles between all three interfaces are fixed!

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





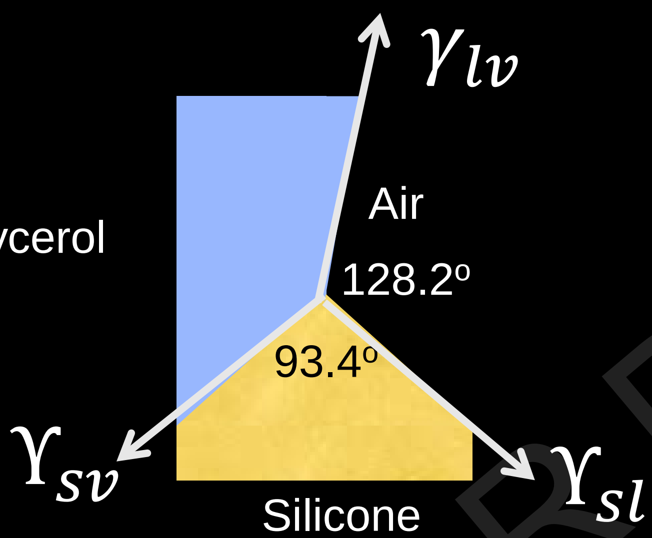
Key Experimental Observations

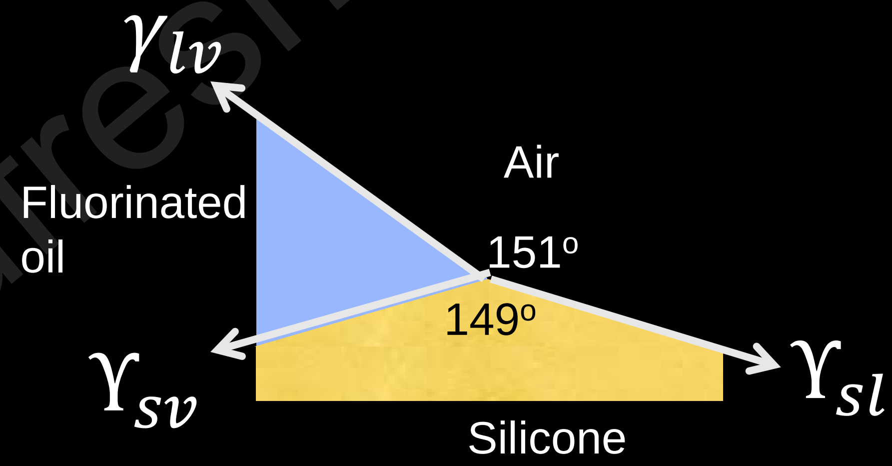
- Young’s law doesn’t work on a 3KPa silicone substrate when glycerol droplets are smaller than about 100 microns. The apparent contact angle drops as the droplet gets smaller.

- For droplets much bigger than 100 microns, you get a size independent contact angle. This contact angle matches that of much stiffer silicone, of order 1MPa, about 90 degrees.

- Within two microns of the contact line, all the interfaces are straight and meet each other at fixed orientations. These orientations depend on the liquid.

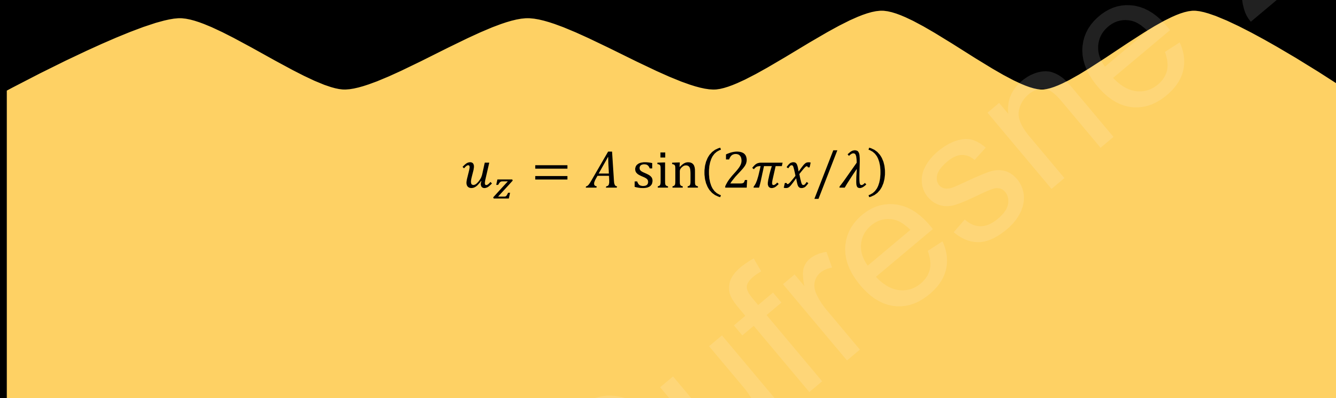
Hypothesis: geometry at contact line is determined by a vector balance of interfacial stresses





γ_{lv}: l-v surface tension Υ_{sv}: s-v surface tension Υ_{sl}: s-l surface tension

Deformation of a linear elastic solid surface

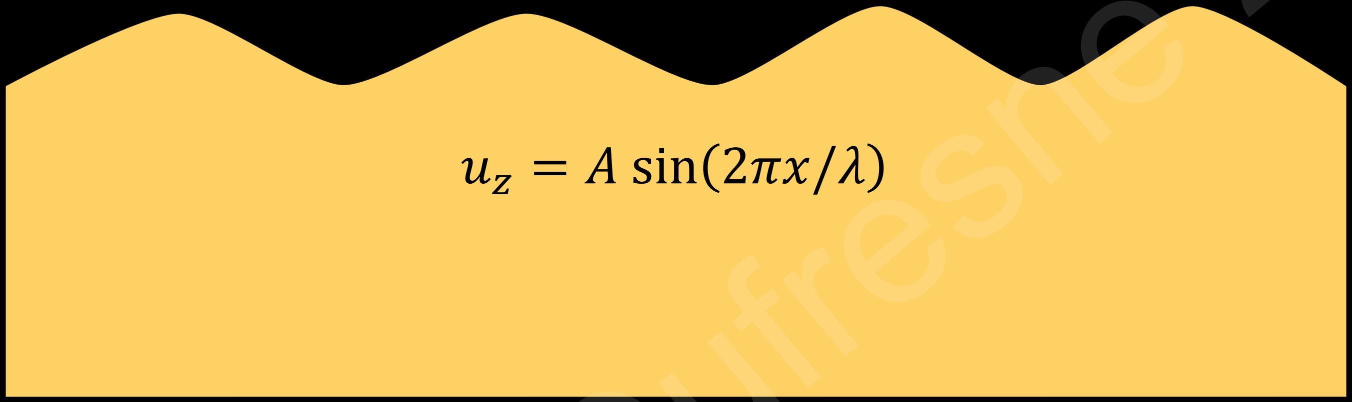


$$u_z = A \sin(2\pi x/\lambda)$$

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

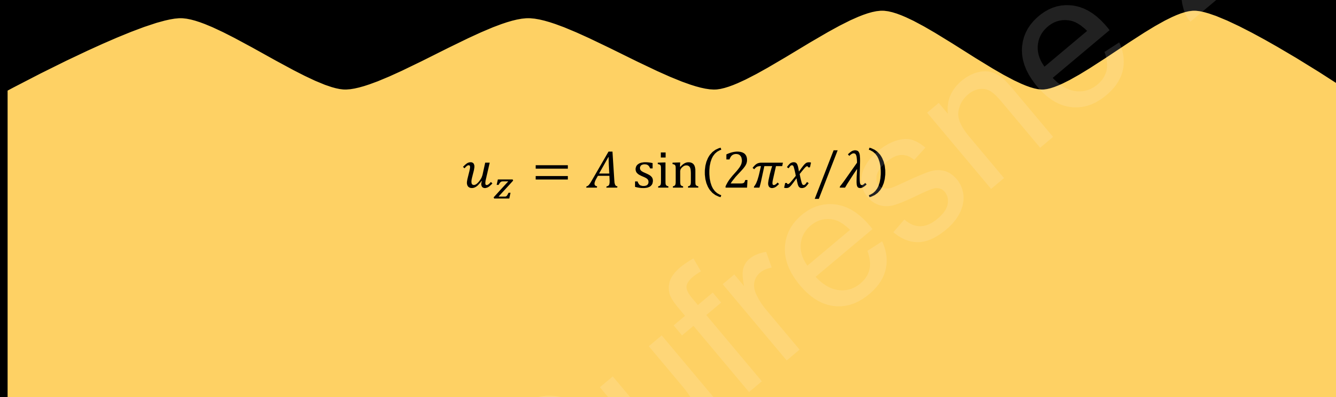


Elastic restoring force: $\sigma_E = \varepsilon E \sim AE/\lambda$

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

Υ: solid surface tension

Balance of Elasticity and Capillarity Defines a Length scale



$$\frac{\sigma_E}{\sigma_\Upsilon} \sim \frac{\lambda}{\Upsilon/E}$$

$$l = \Upsilon/E$$

Elastocapillary Length

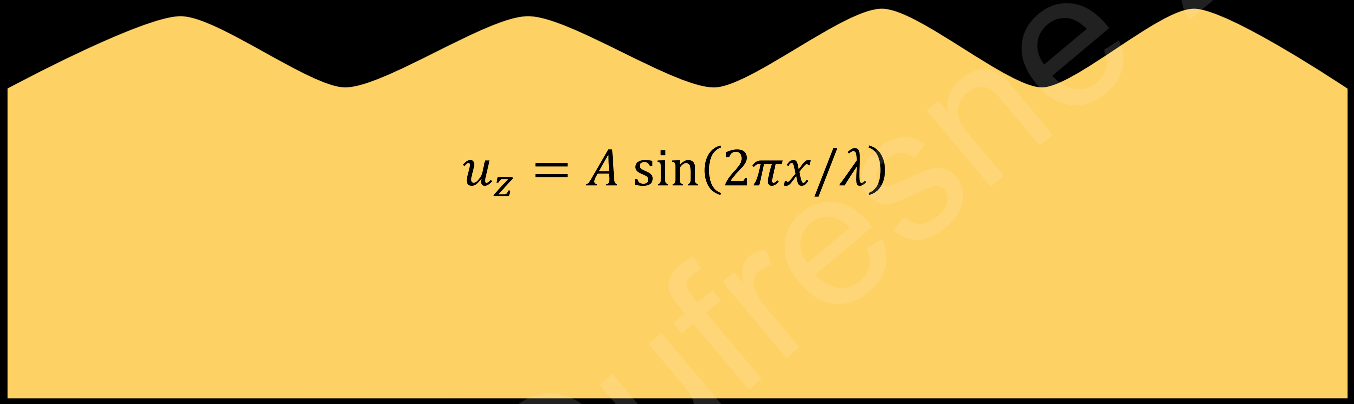
$$\lambda \gg \Upsilon/E$$

Elasticity Dominates

$$\lambda \ll \Upsilon/E$$

Surface Tension Dominates

Capillarity Dominates at Short Length Scales on Soft Materials



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

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

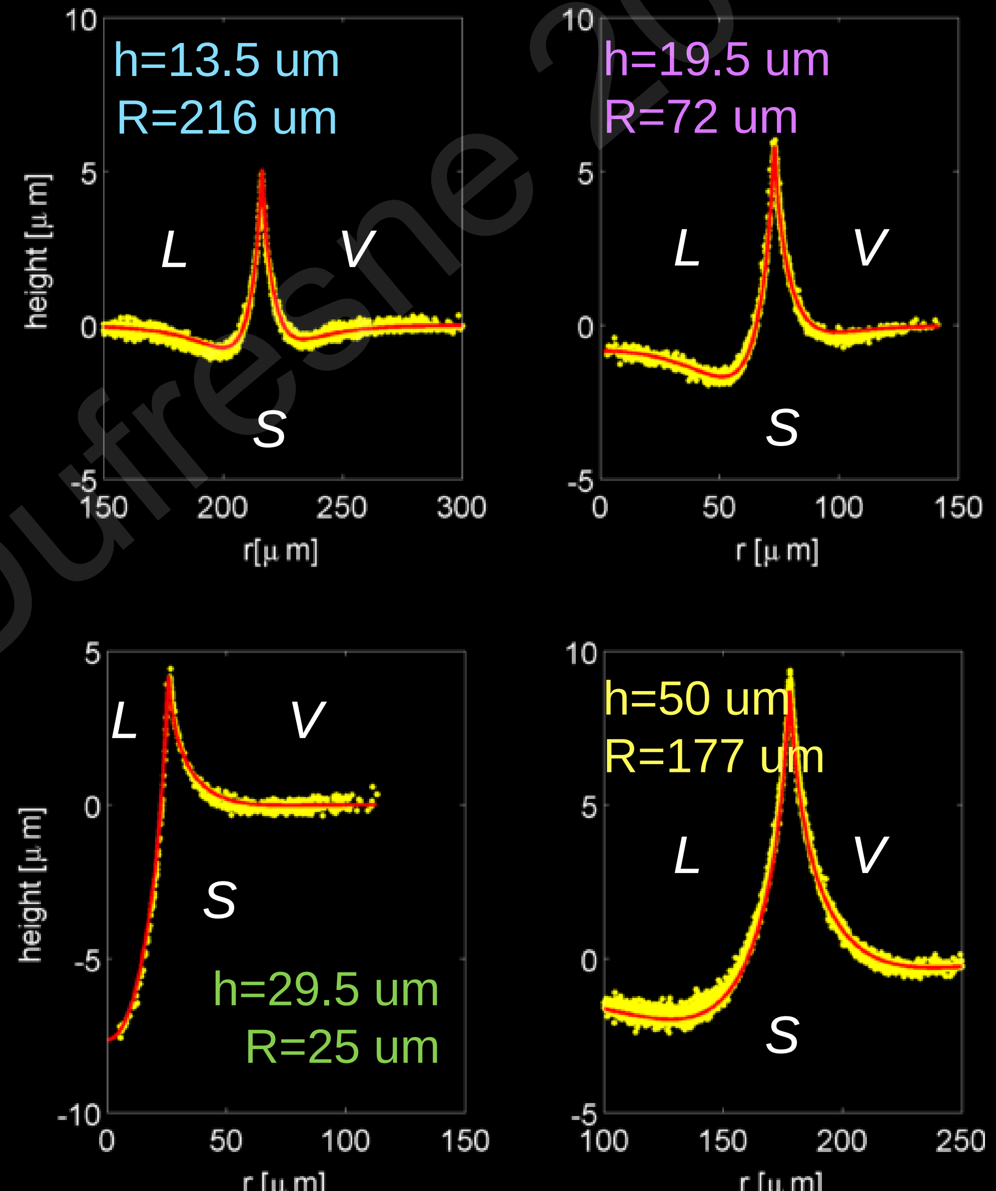
$\Upsilon/E = 10\ \mathrm{nm}\ \text{for } E = 3\ \mathrm{MPa}$

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

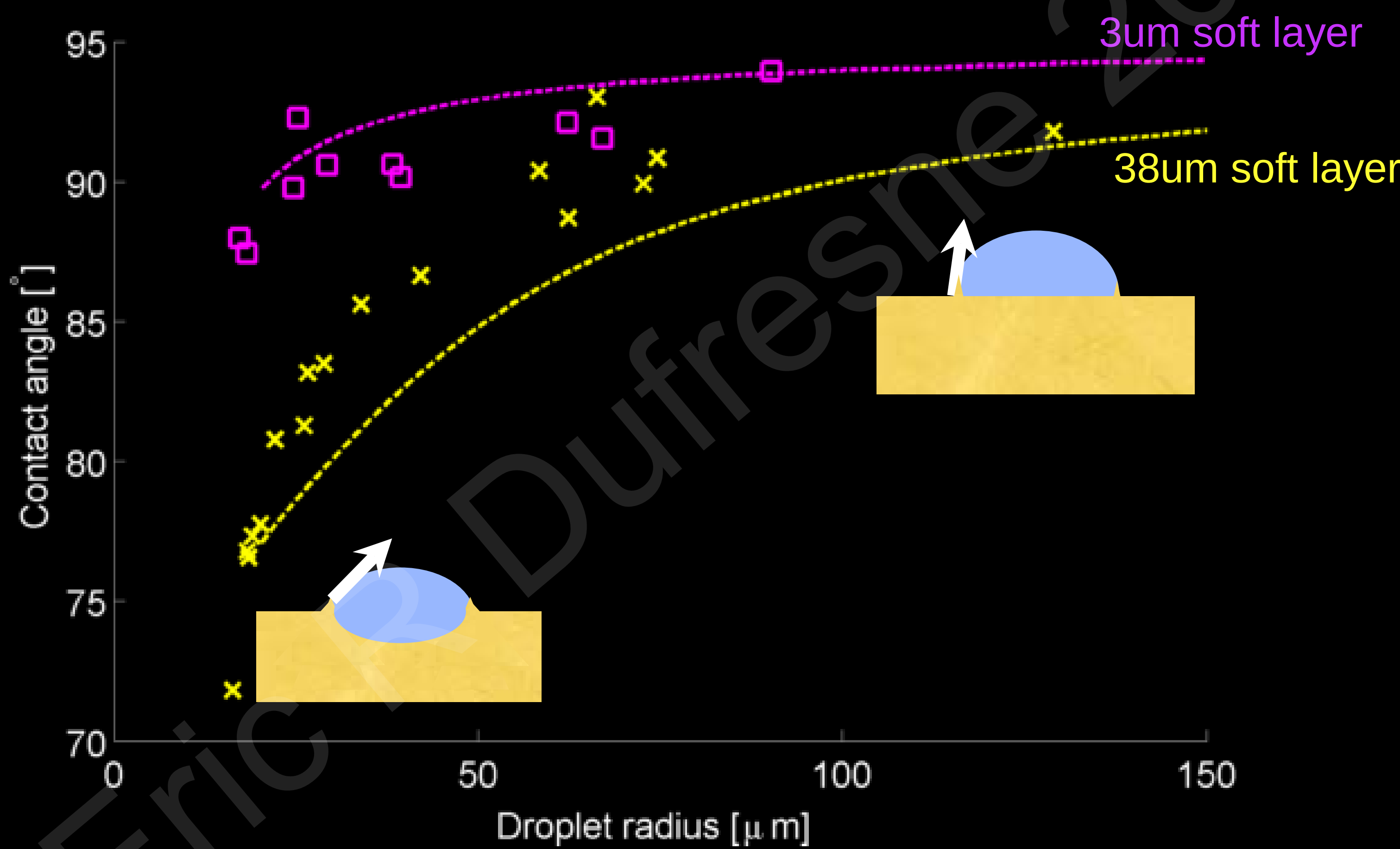
Linear Elasticity Plus Solid Surface Tension Captures Profiles

Sharp features near contact line are controlled by surface tension.

Far-field determined by elasticity



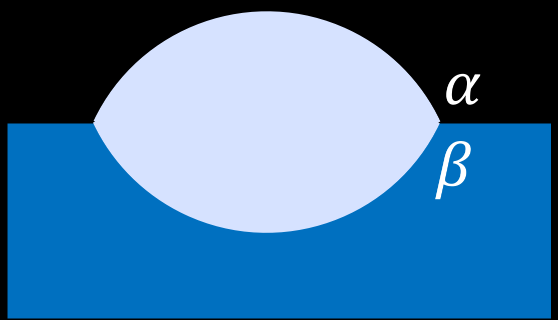
Linear Elasticity Plus Solid Surface Tension Predicts Change in Apparent Contact Angle



Glycerol drops on silicone (E=3kPa)

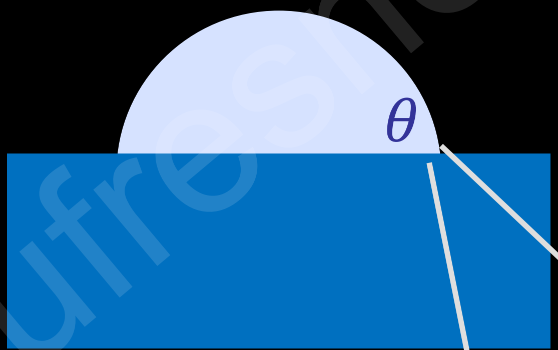
Wetting on Deformable Solids

Neumann
(liquid on liquid)

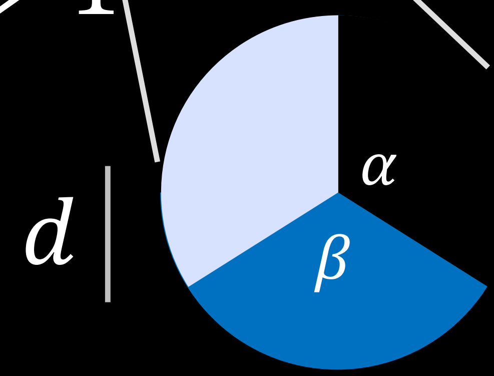


$$\Upsilon/ER \ll 1$$

Young-Dupre
(liquid on rigid solid)



$$\Upsilon/ER \gg 1$$



$$\Upsilon/Ed \gg 1$$

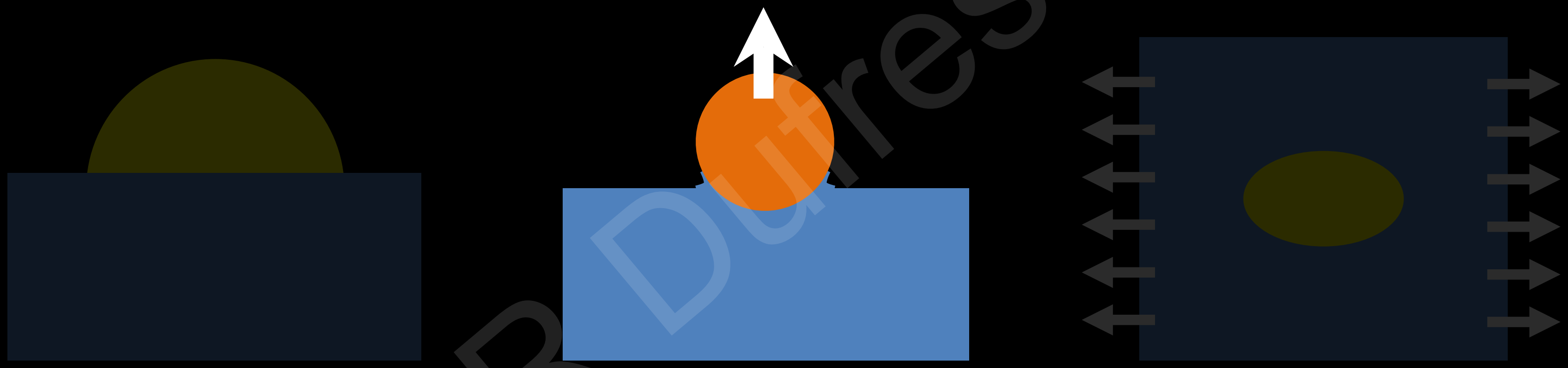
Theory and preliminary expts:
Jerison *et al Physical Review Letters* 2011
Style *et al Soft Matter* 2012

Breakdown of Young-Dupre
Style *et al Physical Review Letters* 2013

Drop movement
Style et al PNAS 2013

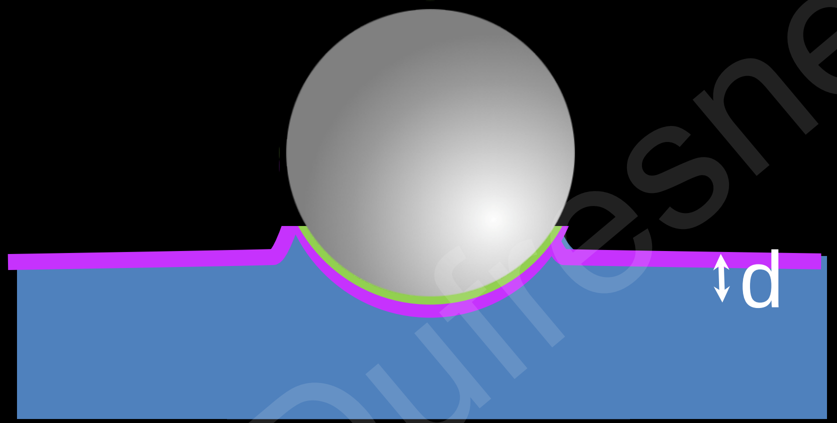
Three Foundational Theories of Interfacial Mechanics

Young-Dupre (18XX) *JKR (1971)* *Eshelby (1957)*



wetting | adhesion | composites, fracture, dislocations

Johnson, Kendall & Roberts (1971) – 'JKR'

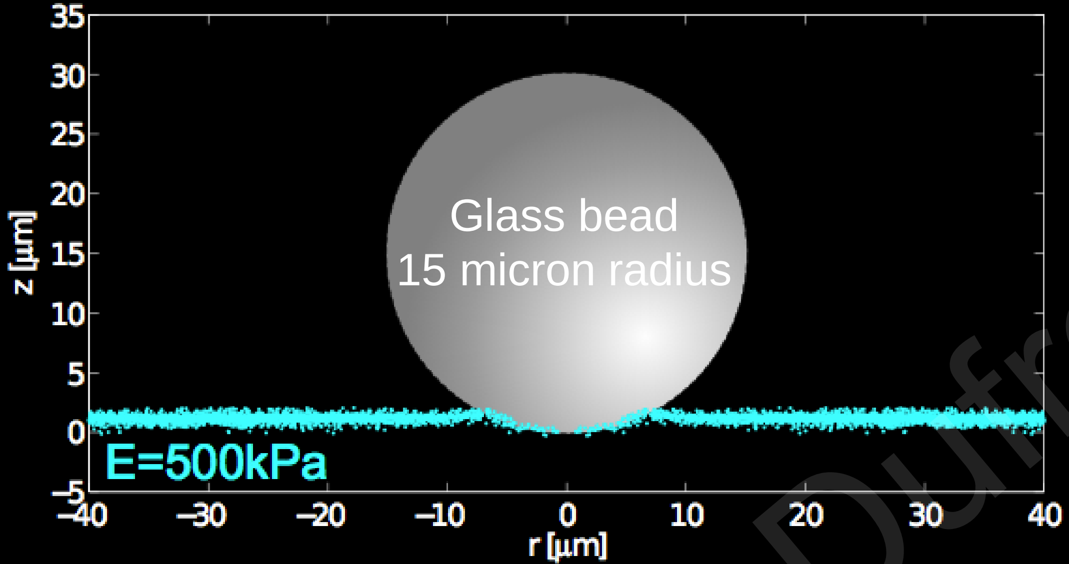


Adhesion Energy, $W = \gamma_{sp} - \gamma_{sv} - \gamma_{pv}$

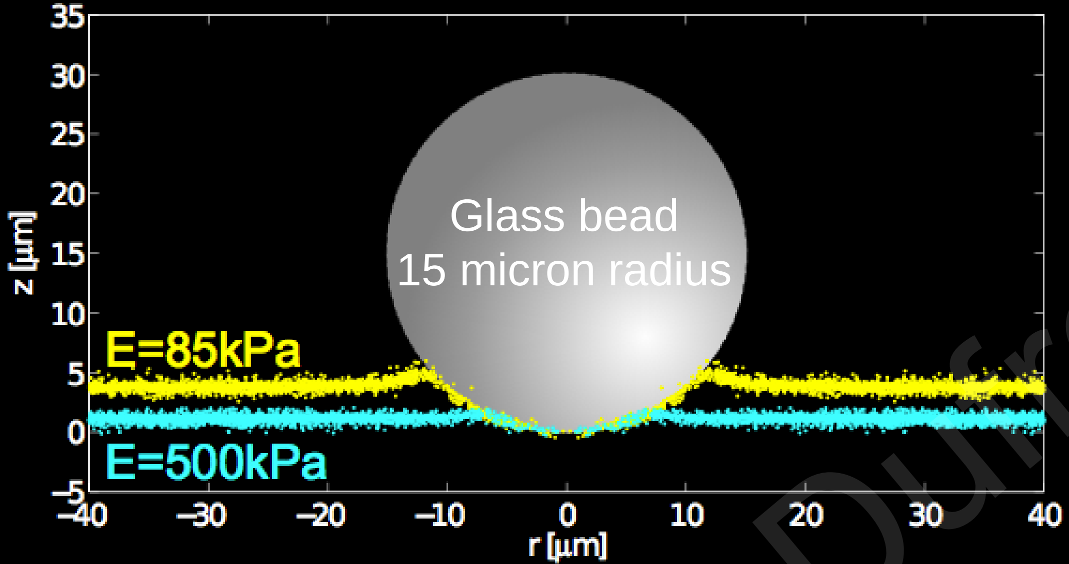
Substrate Elasticity, E

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

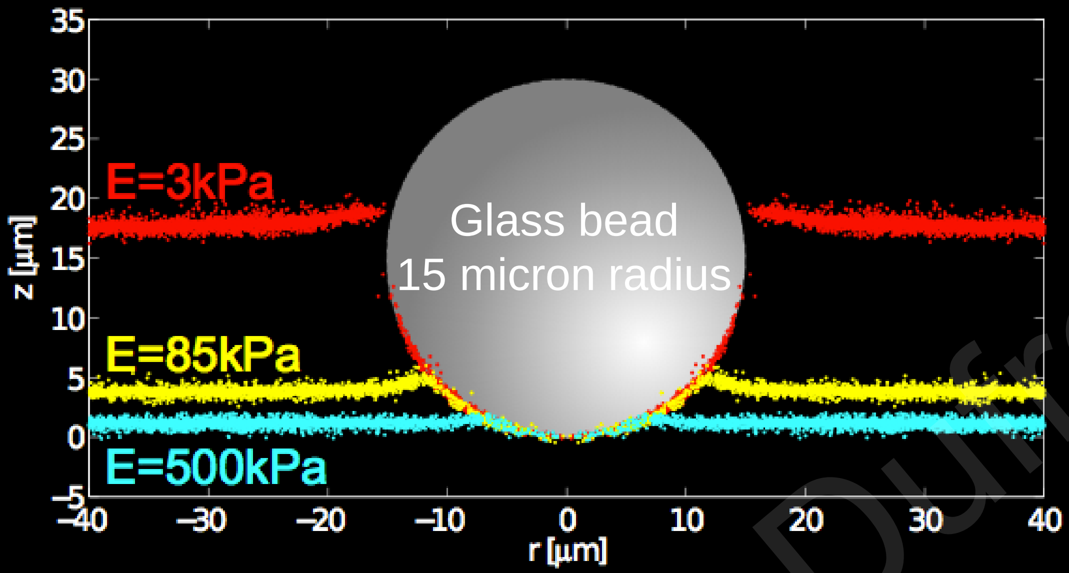
Zero-force indentation for different stiffness substrates



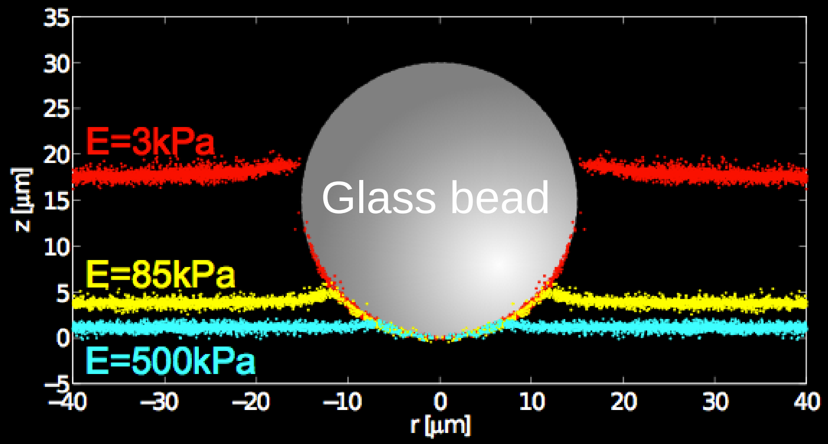
Zero-force indentation for different stiffness substrates

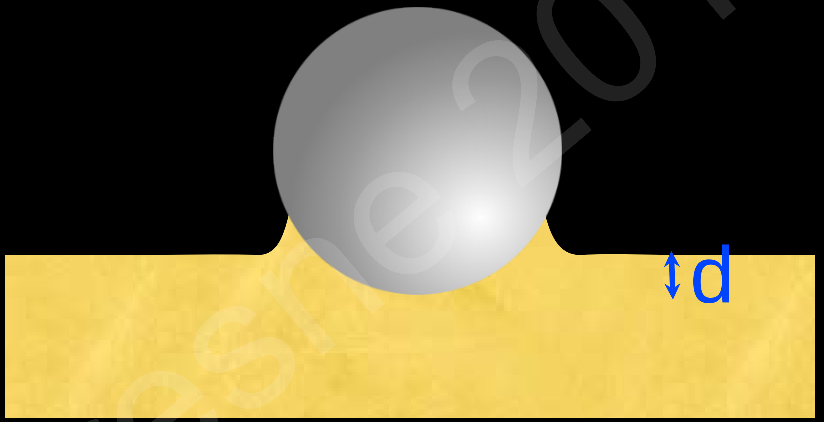


Zero-force indentation for different stiffness substrates

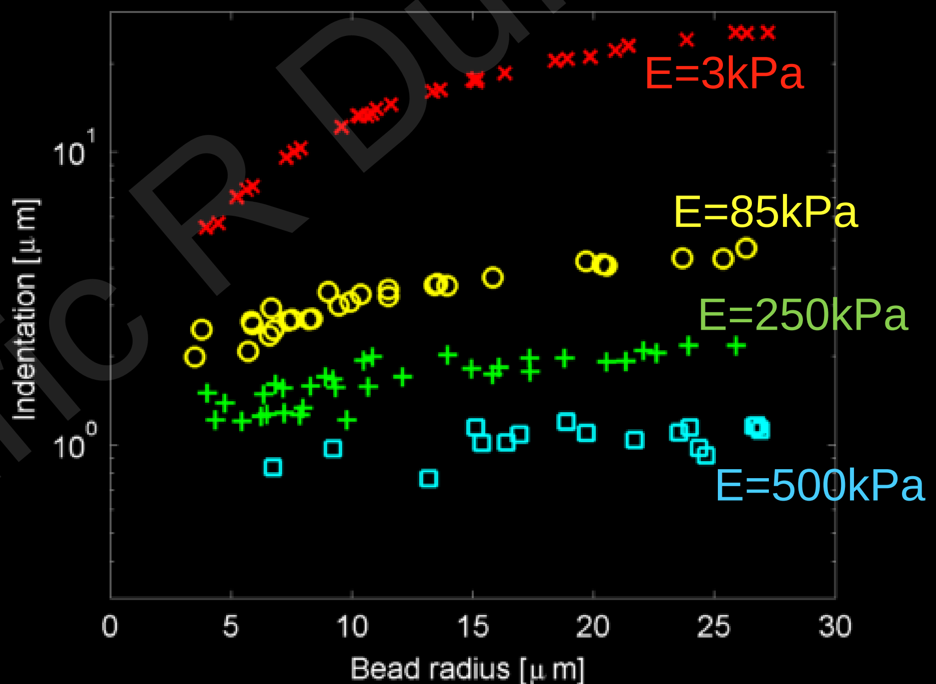


Zero-force indentation for different stiffness substrates



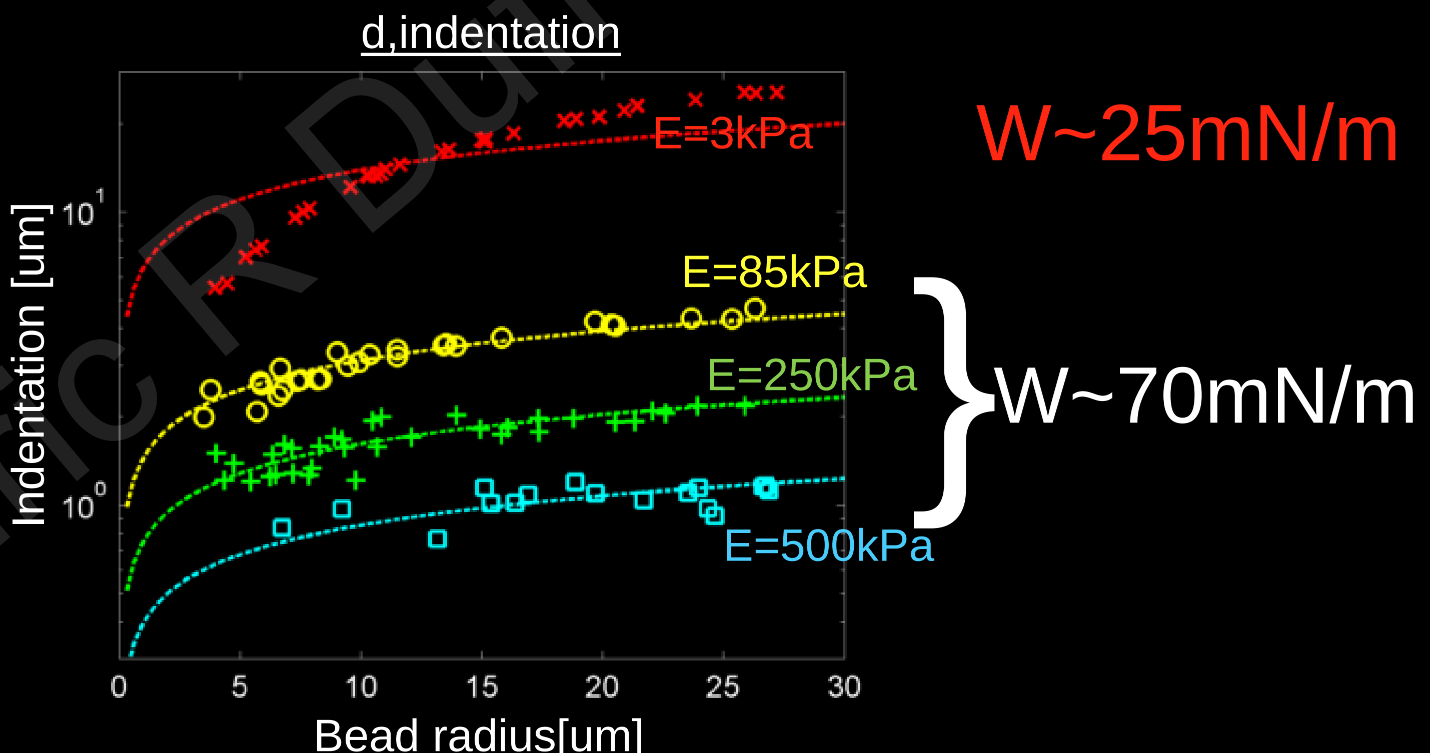


d, indentation



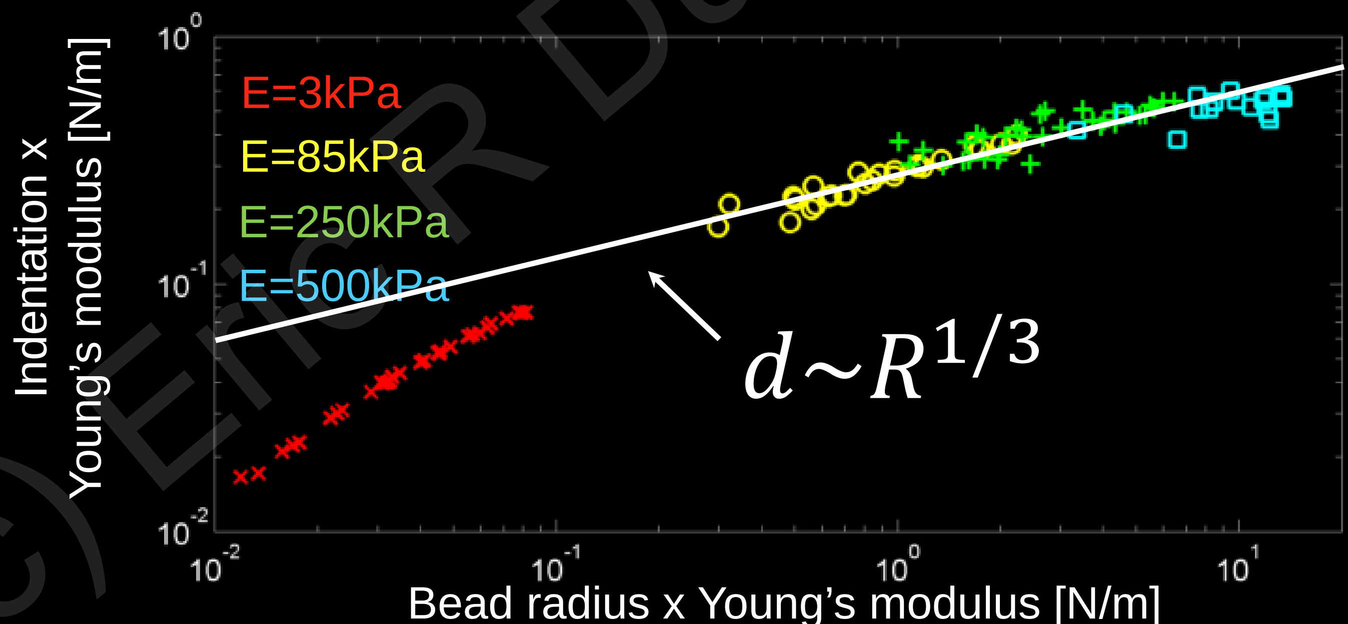
Comparing results with JKR

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

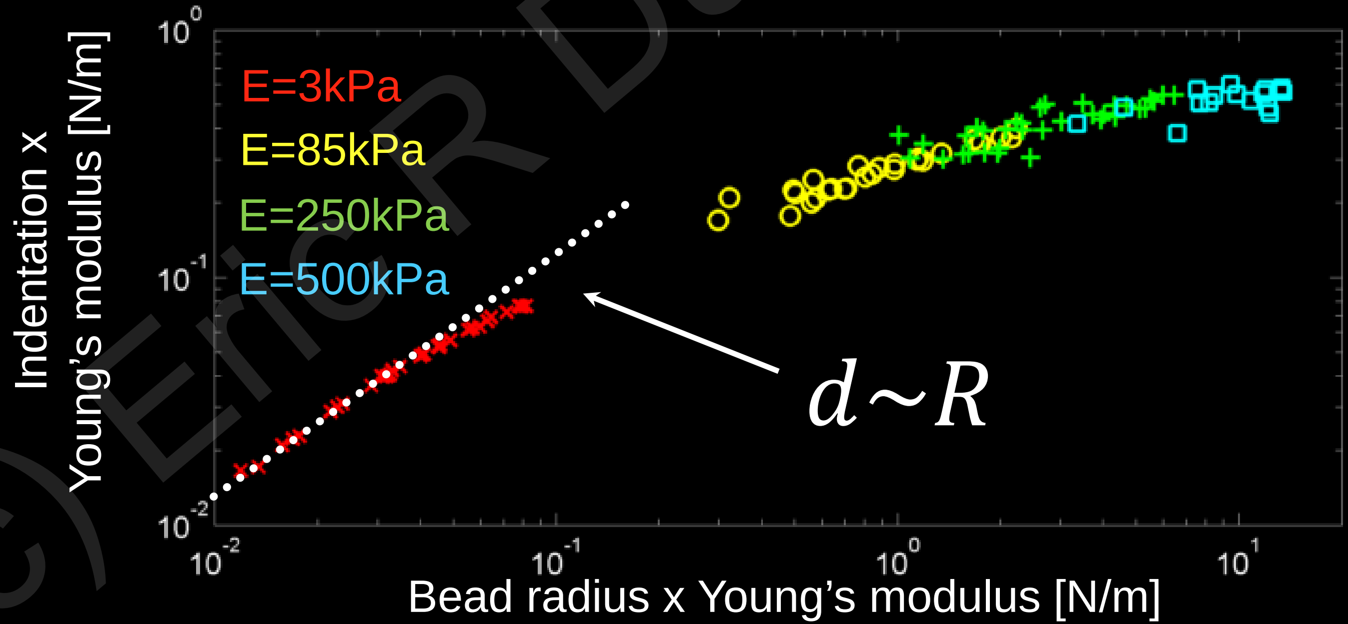


JKR collapses the data, but scaling changes for small particles and soft surfaces

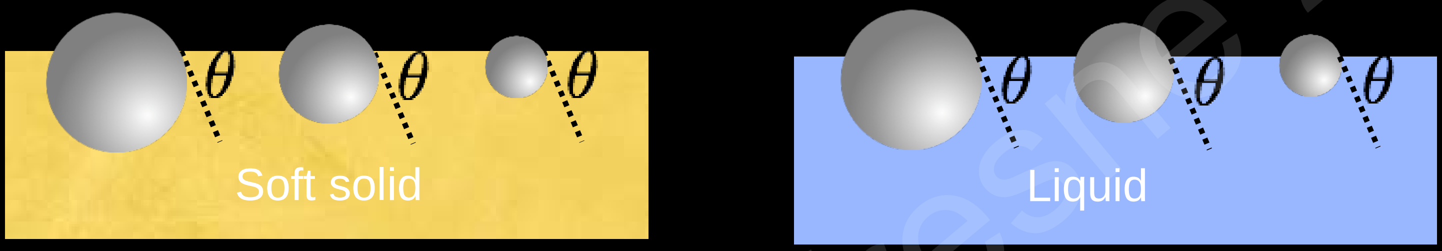
JKR: $$dE = \left(\frac{\sqrt{3}W(1-\nu^2)}{2}\right)^{2/3}(RE)^{1/3}$$



Indentation proportional to bead radius for small beads



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



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

For small particles at zero force, the indentation depth is given by Young-Dupre, just like a colloidal particle on a fluid interface

Style *et al Nature Communications (2013)*
Jensen *et al …preprint to appear soon on arXiv*

JKR plus surface tension fits data

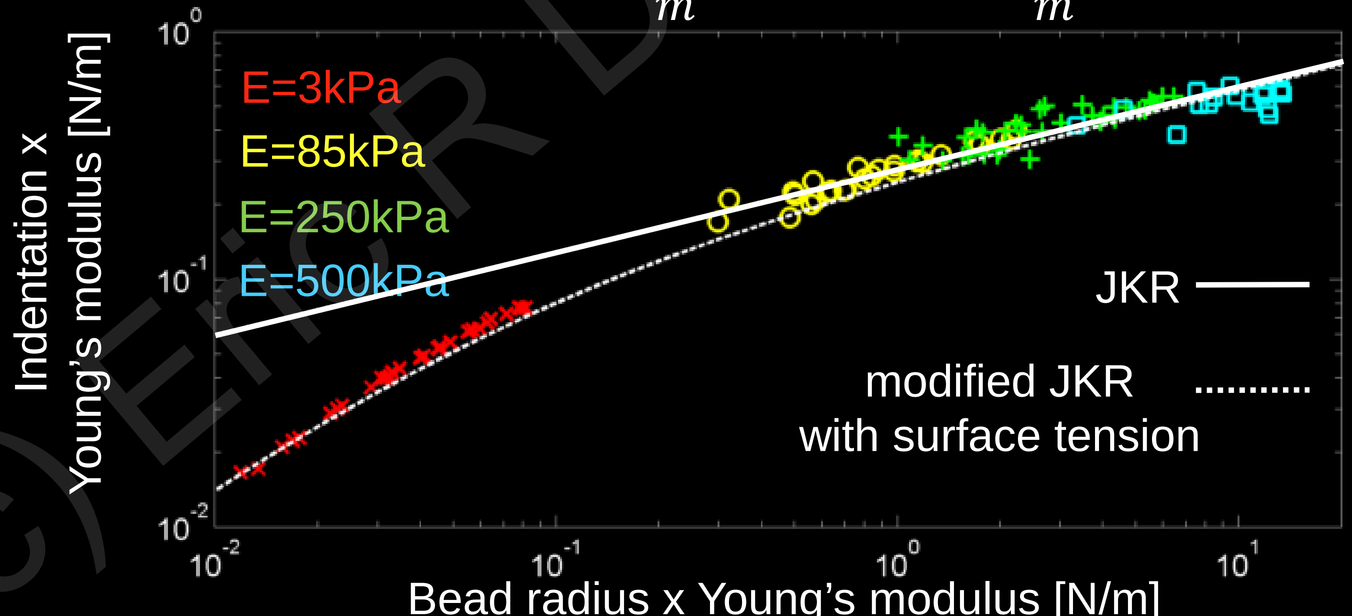
Minimize total energy (a la Carillo/Raphael/Dobrynin 2010):

Elastic energy + Adhesion Energy + Surface Tension

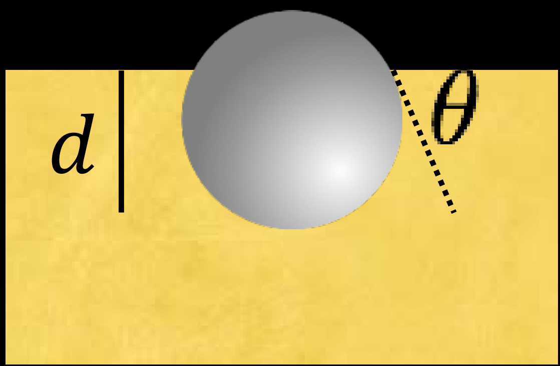
(from JKR)

$\Upsilon_{sv} \Delta A$

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



In the limit of small beads, our scaling predicts…



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

equivalently…

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

'Smells' like Young-Dupre

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

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

Young-Dupre with soft substrate in the place of the liquid

Adhesion Summary

- For large particles, $\Upsilon/ER \ll 1$, the classic balance of surface energy and elasticity by JKR accurately describes contact mechanics of soft substrate
- For small particles, $\Upsilon/ER \gg 1$, the indentation depth is given by Young-Dupre, just like a colloidal particle on a fluid interface.

- Again, surface tension swamps elasticity for $\Upsilon/ER \gg 1$

Style *et al Nature Communications (2013)*

Latest coming to the *arXiv* next week!

Three Foundational Theories of Interfacial Mechanics

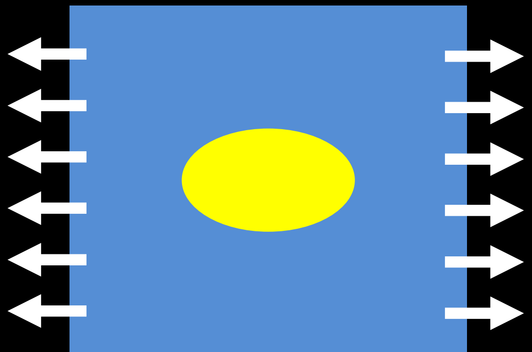
Young-Dupre (18XX)

wetting

JKR (1971)

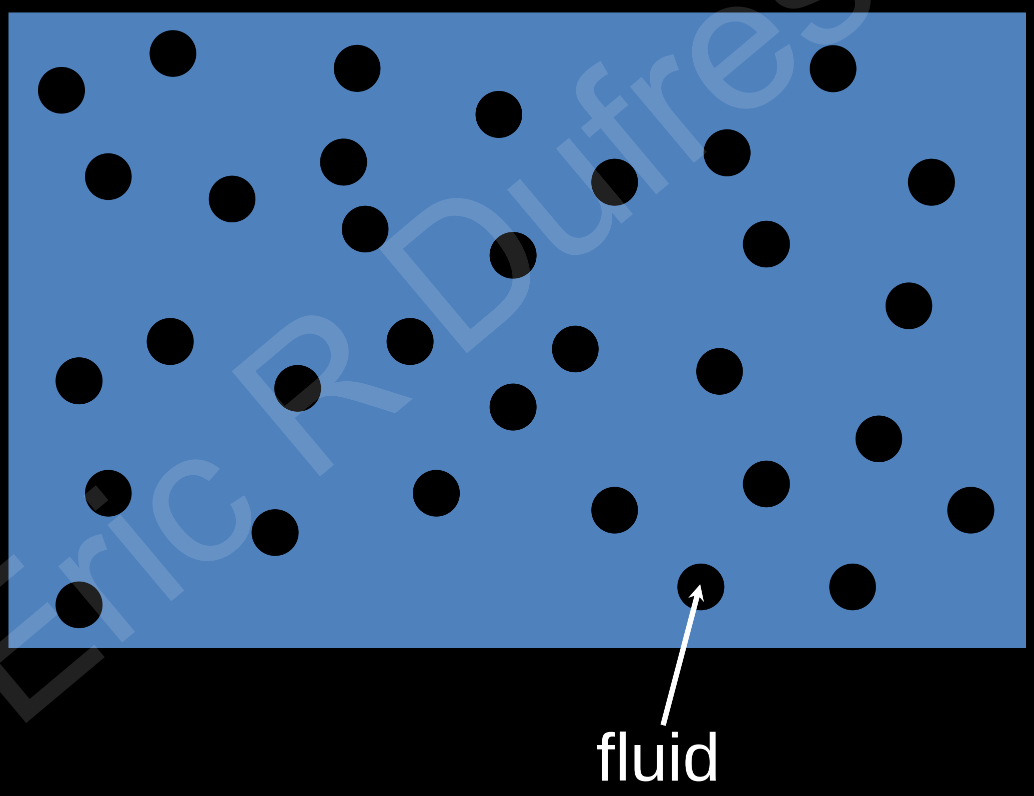
adhesion

Eshelby (1957)



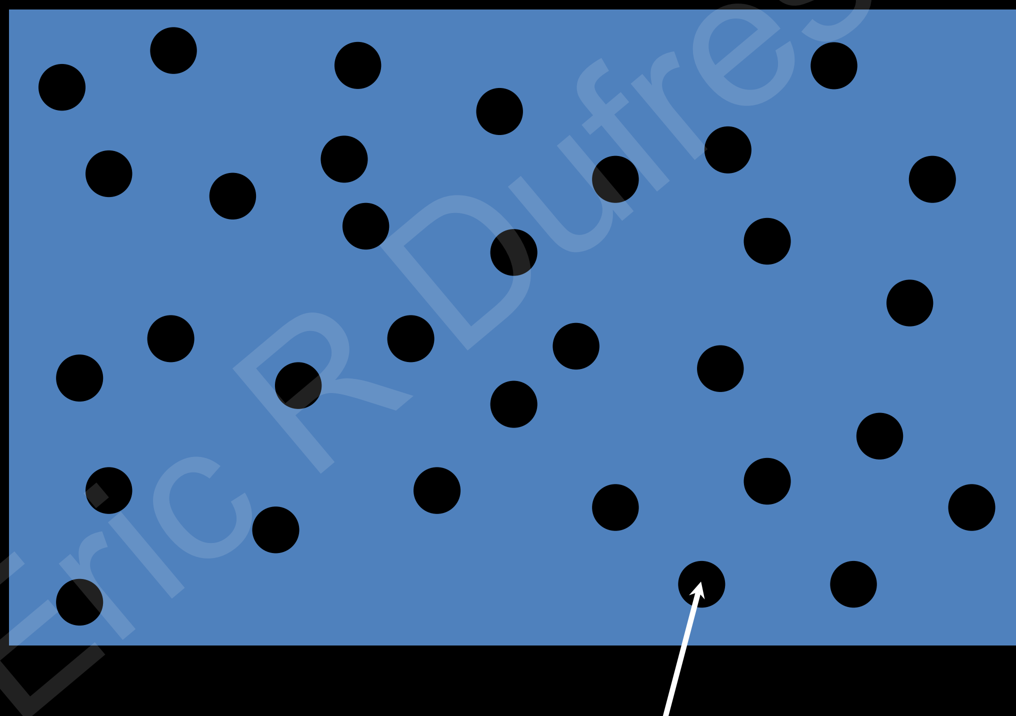
composites,
fracture,
dislocations


solid


fluid

0% 5% 10% 15% 20% v/v

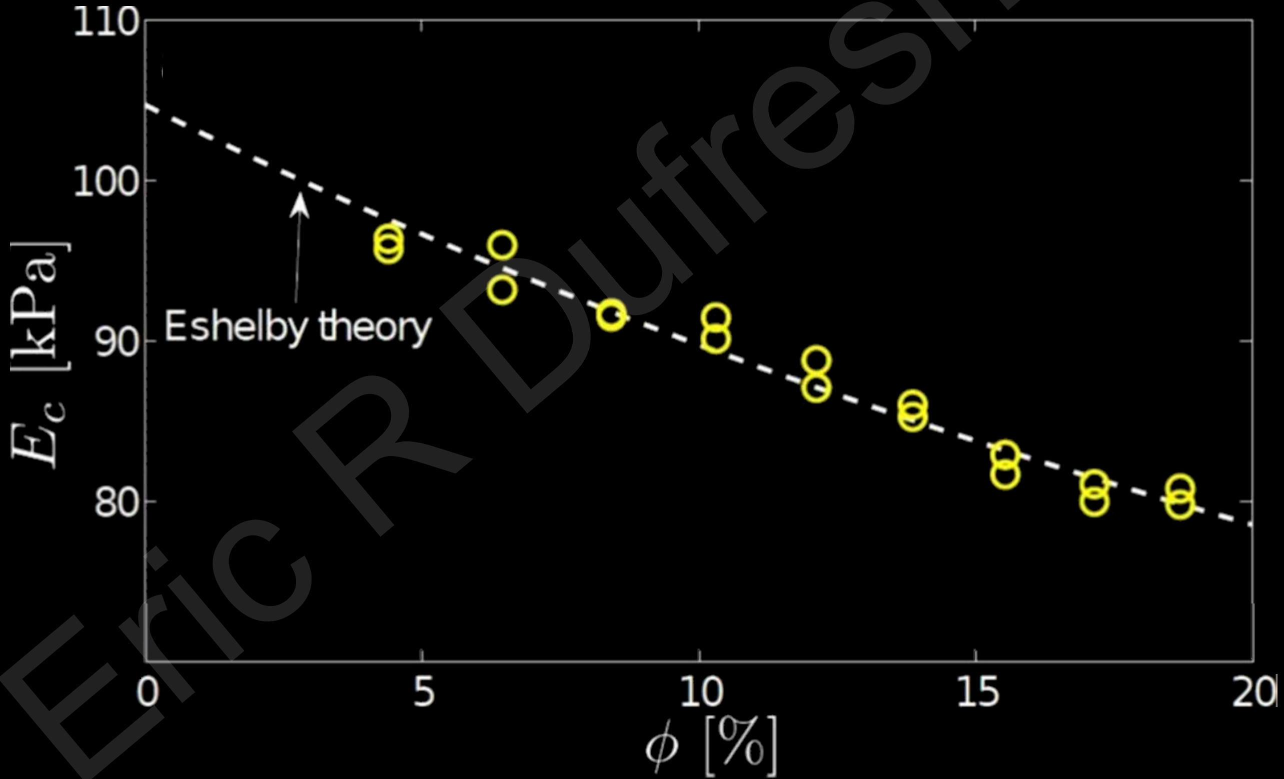
micron scale glycerol droplets in PDMS



fluid

Micron-scale glycerol droplets soften 100KPa PDMS

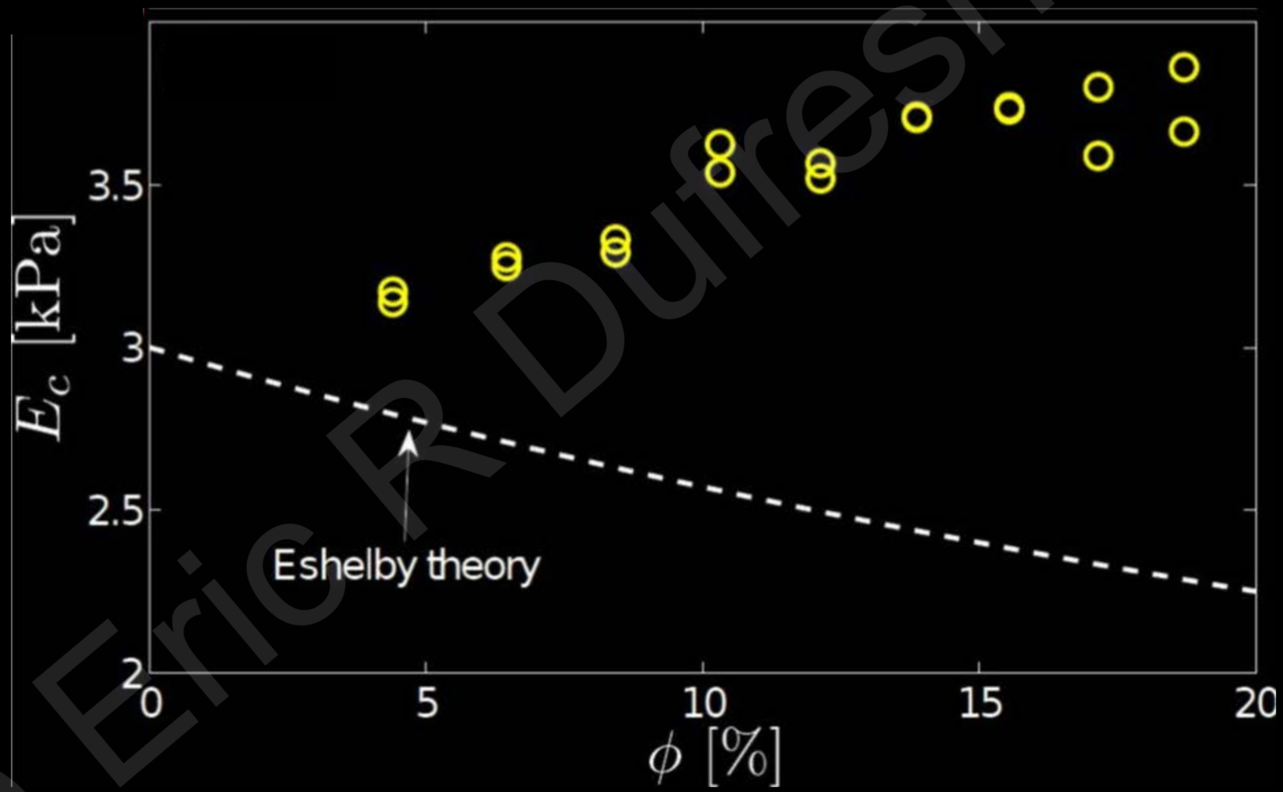
Composite Stiffness



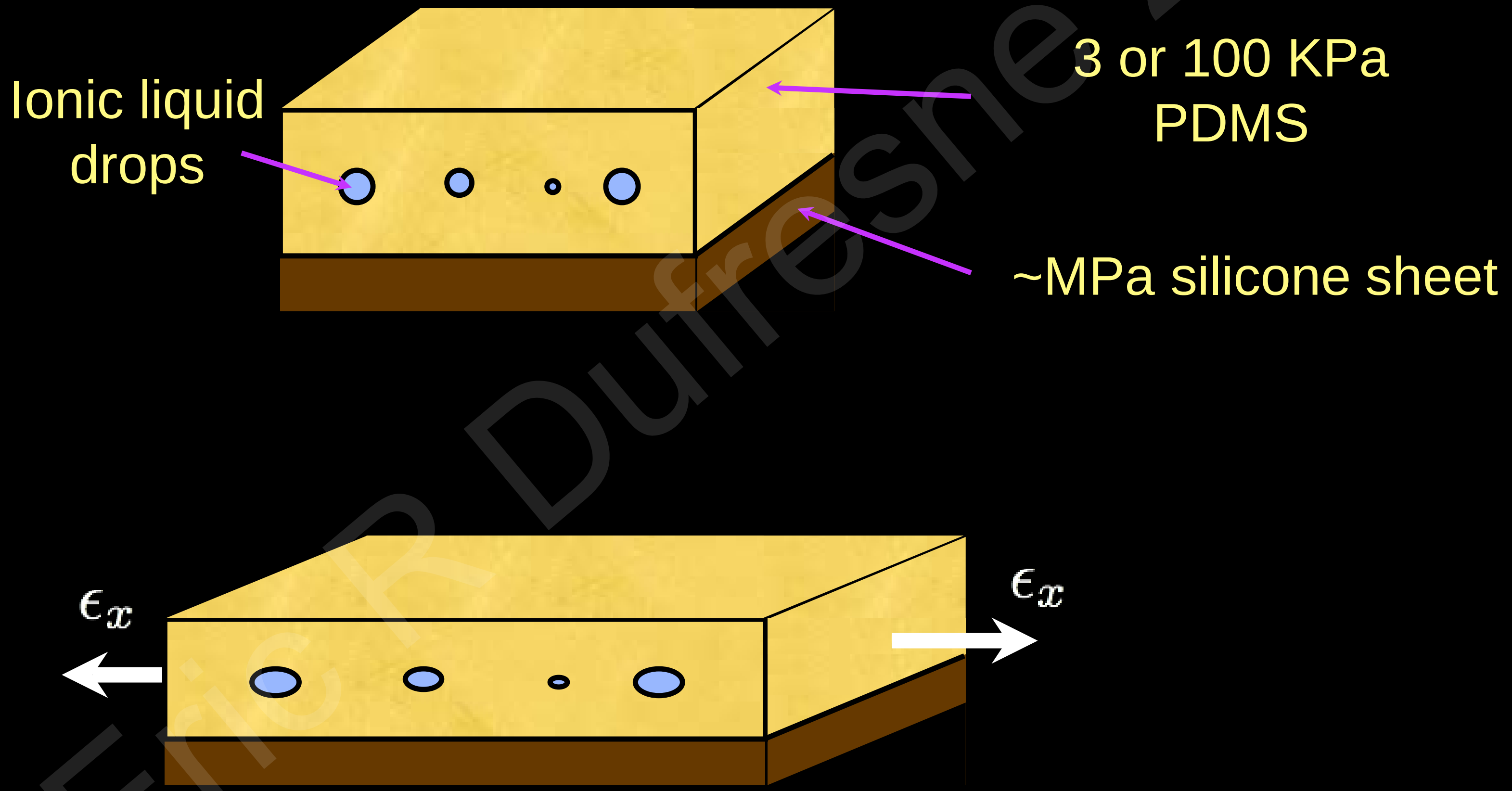
Increasing glycerol ⟶

Micron-scale glycerol droplets stiffen 3 KPa PDMS

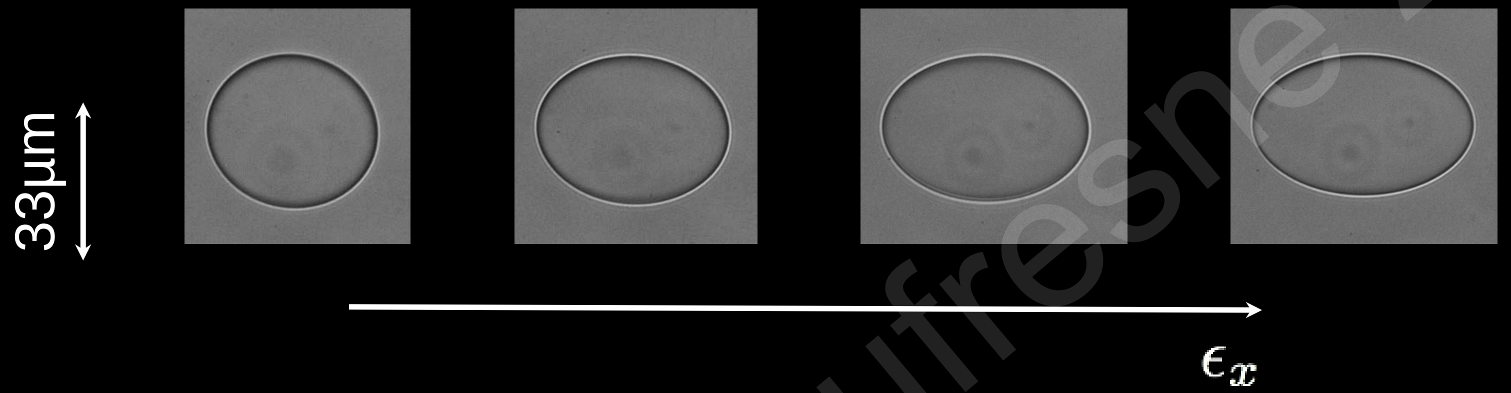
→ *Elastic theory works for stiff matrices, but not for soft!*

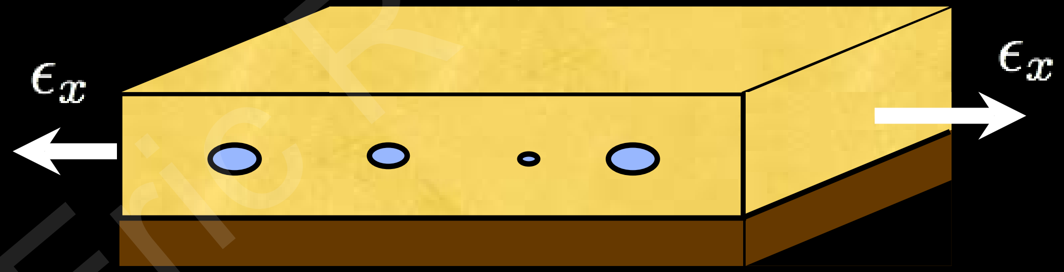


Visualizing single inclusions

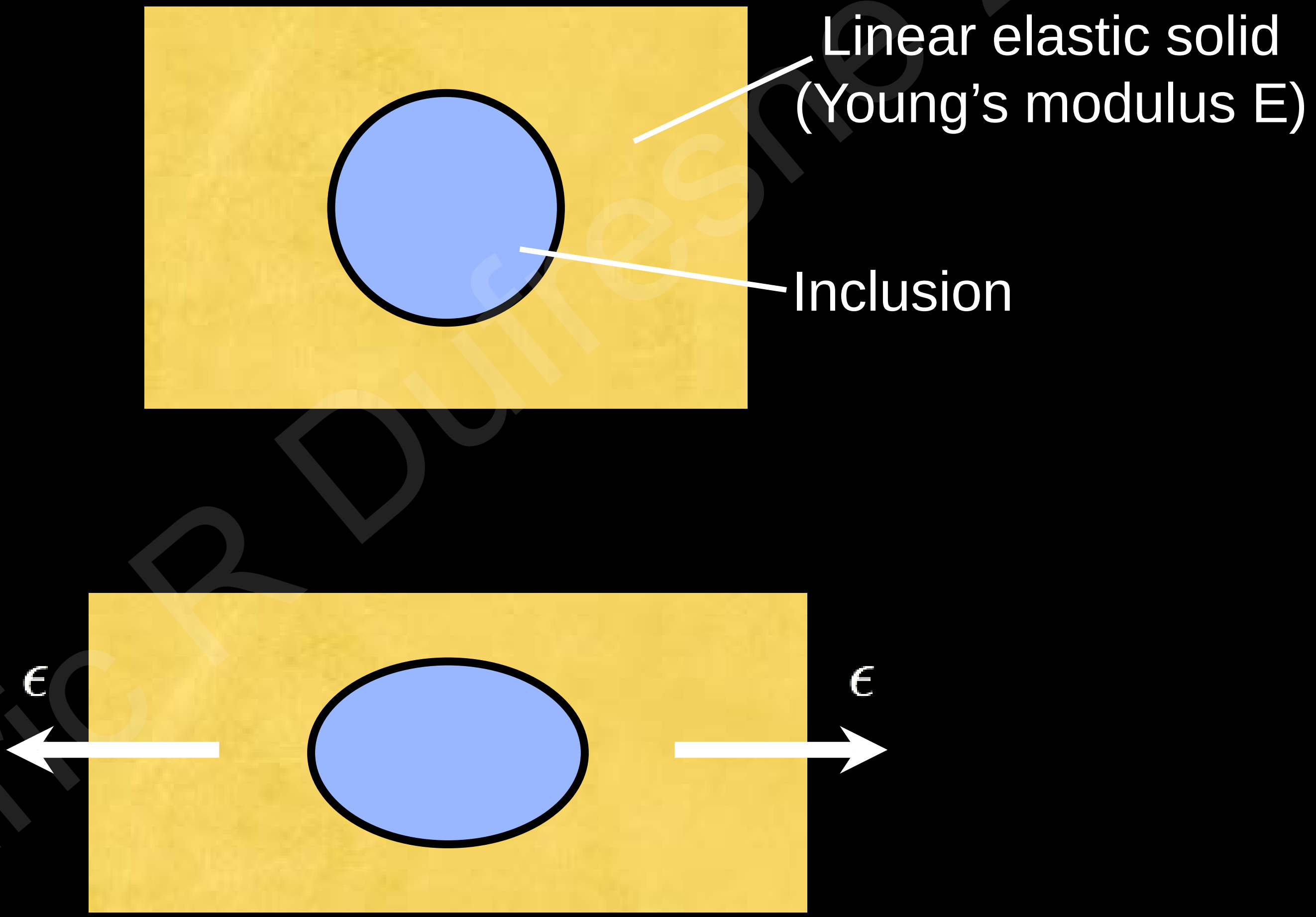


Visualizing single inclusions



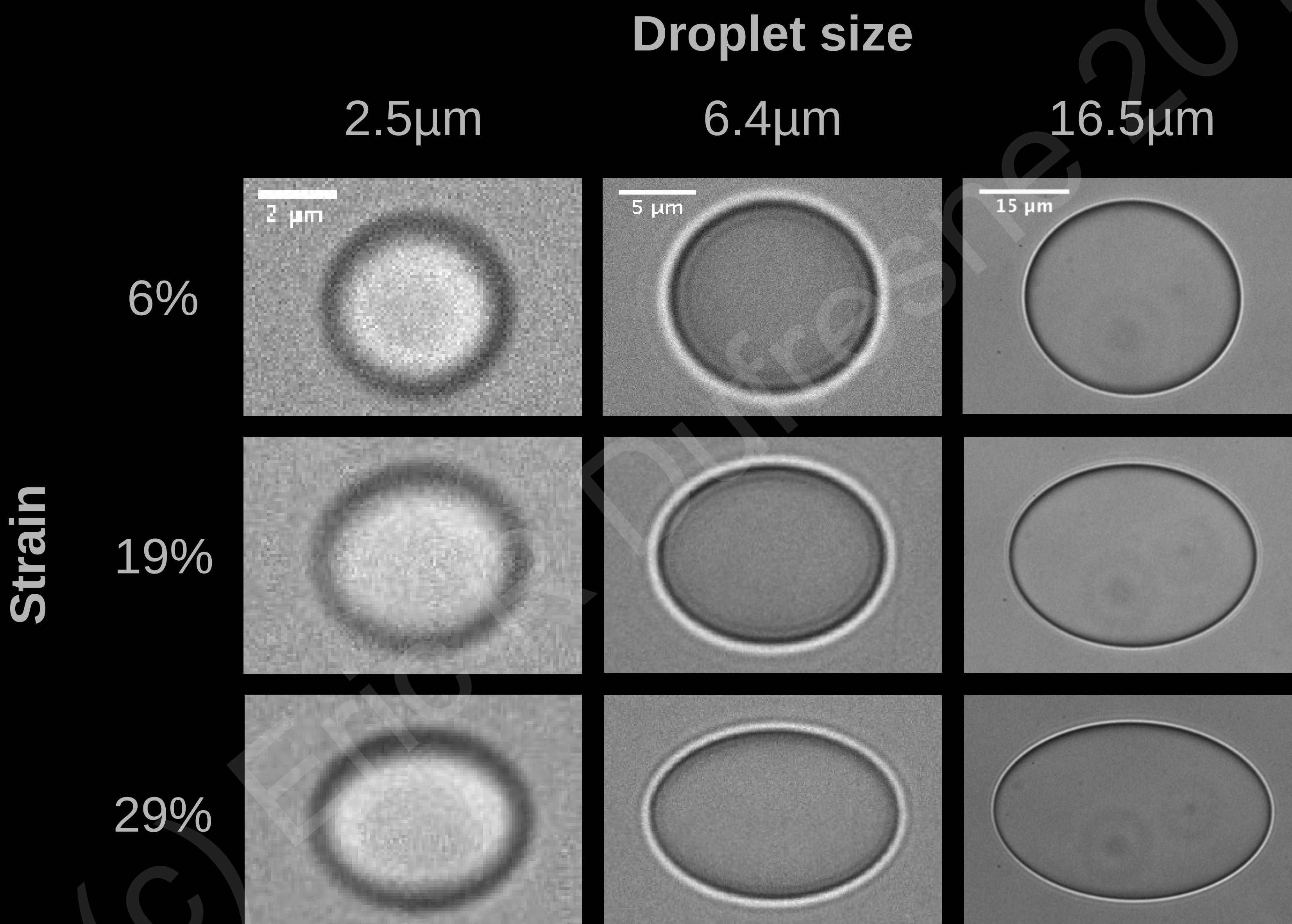


Elastic theory says drop shape should depend on strain… not size or stiffness

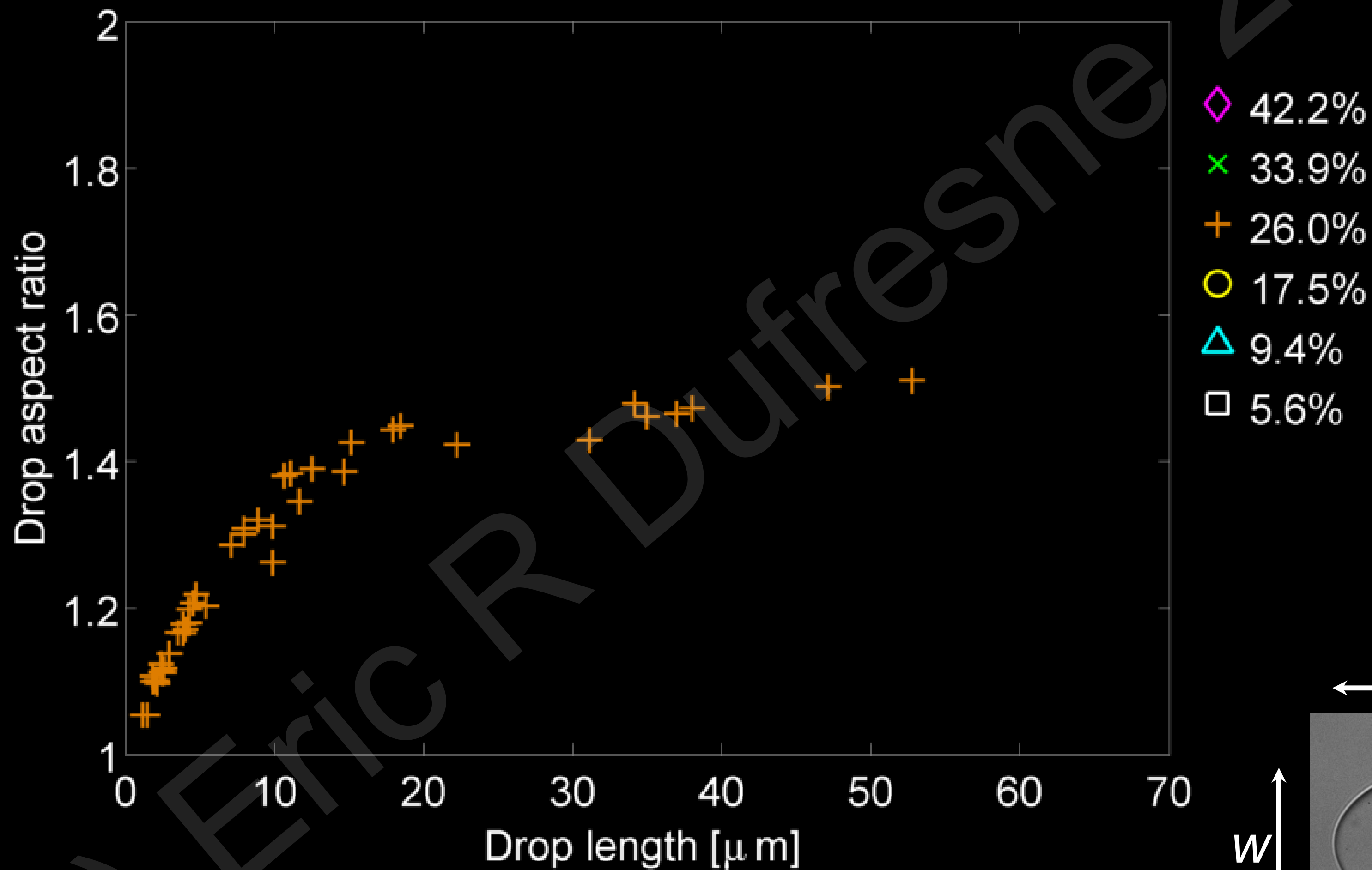


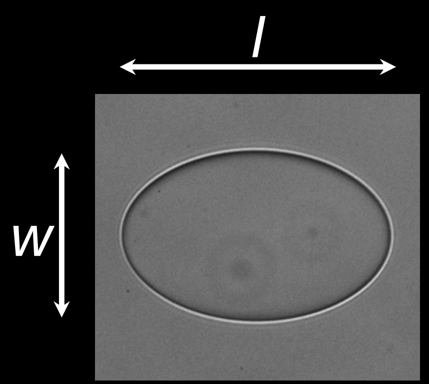
(Eshelby, 1957)

Bigger droplets deform more than little ones

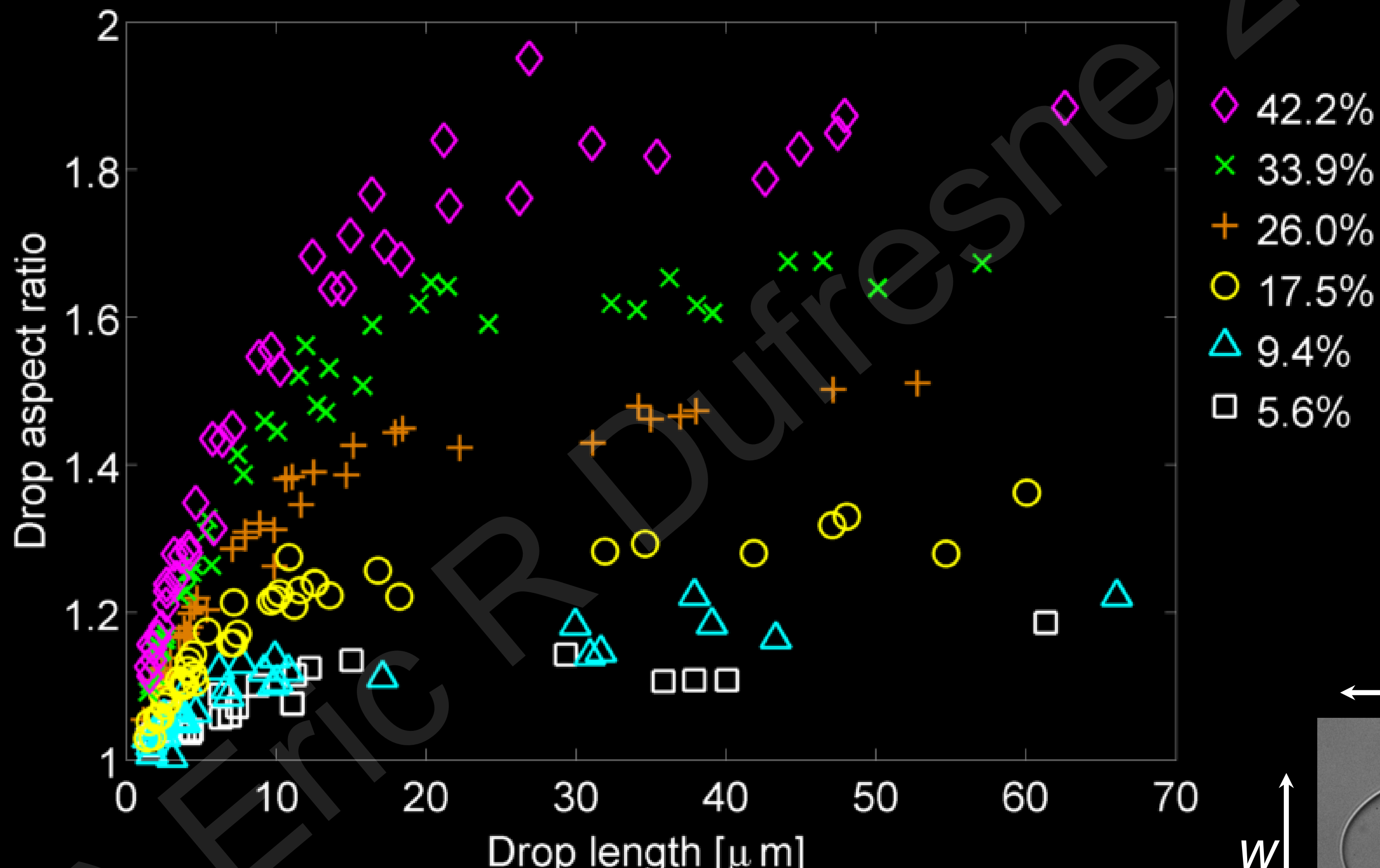


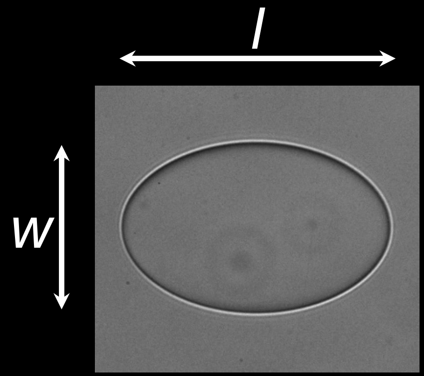
Scale-dependent deformation





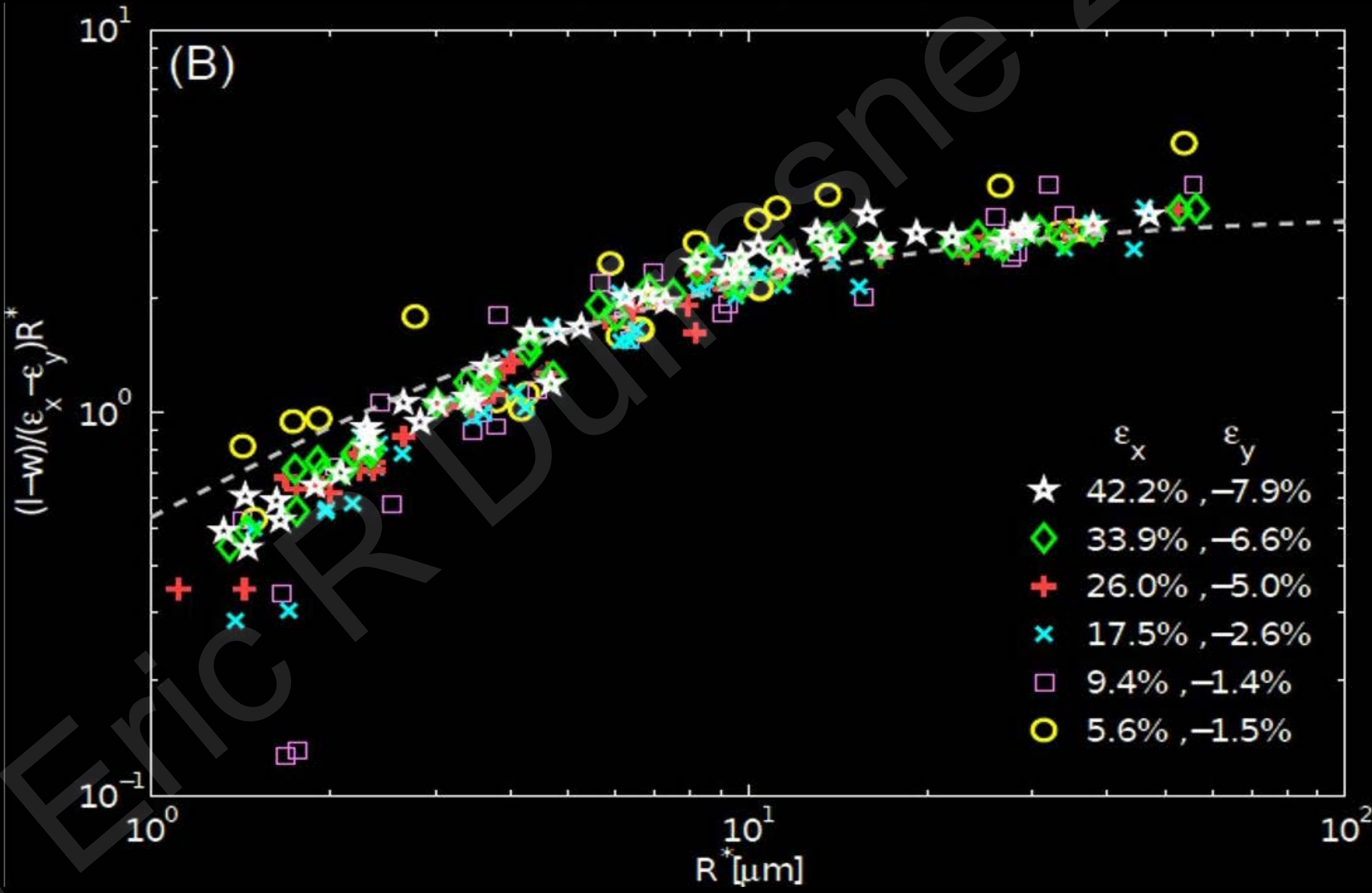
Scale-dependent deformation





Far-field strain collapses droplet strain…
…and a length scale emerges!

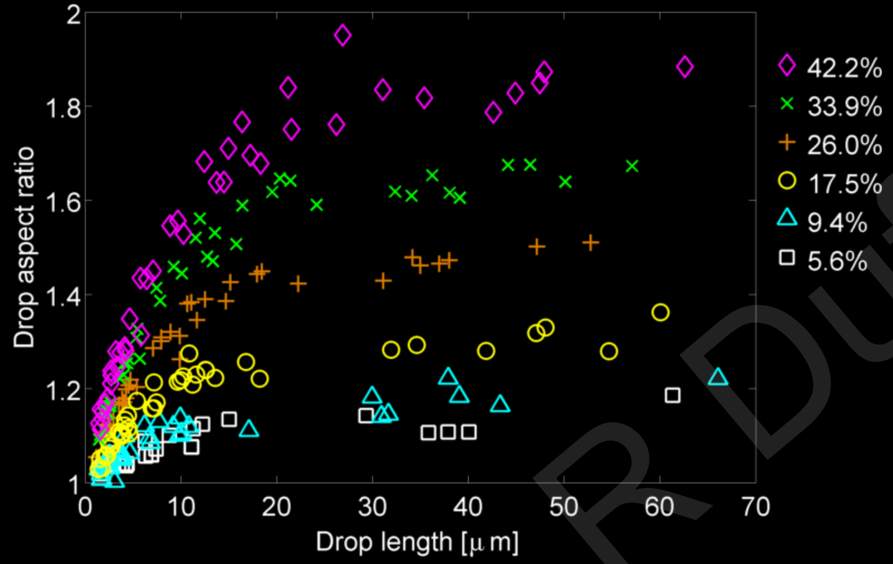
Micro strain/
Macro strain



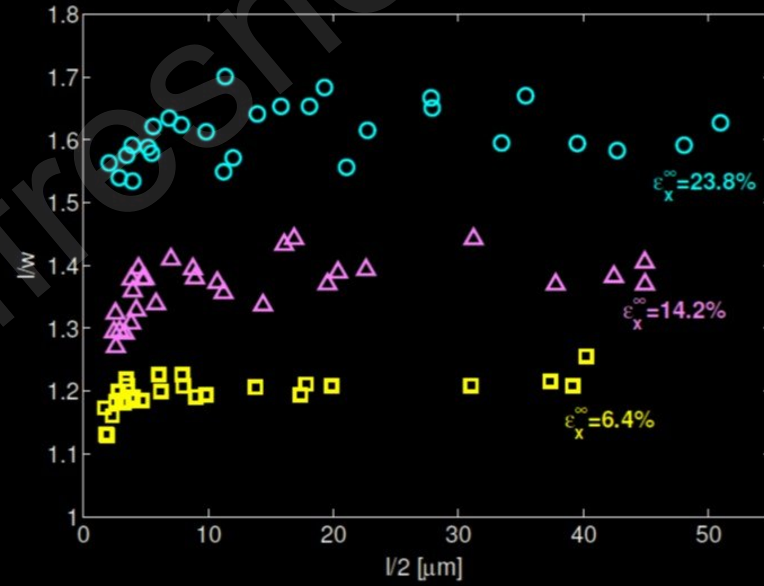
Droplet Size

Microscopic response depends on size and stiffness

E = 3 KPa

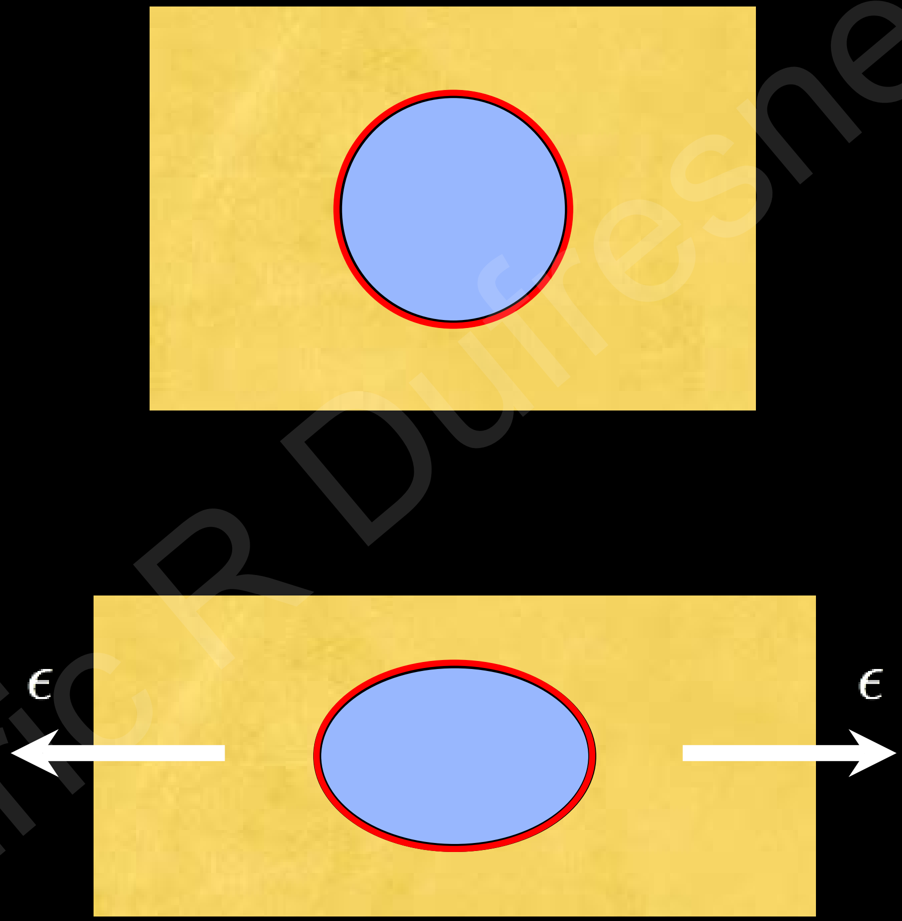


E = 100 KPa

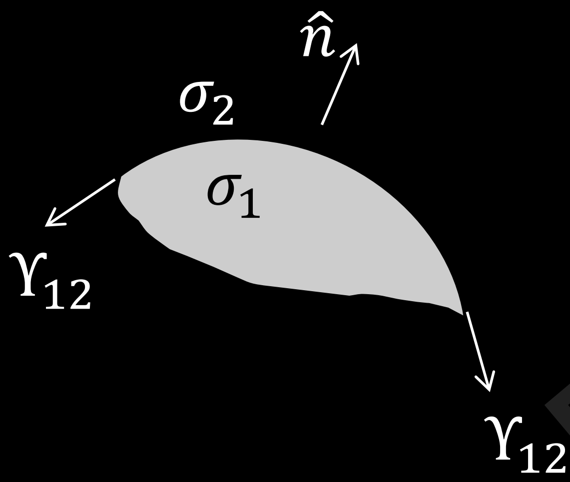


Elastic theory says this response should be ***independent*** of size and stiffness

Classic elastic theories ignore the interface



More generally, surface tension creates a normal-stress jump across curved interfaces



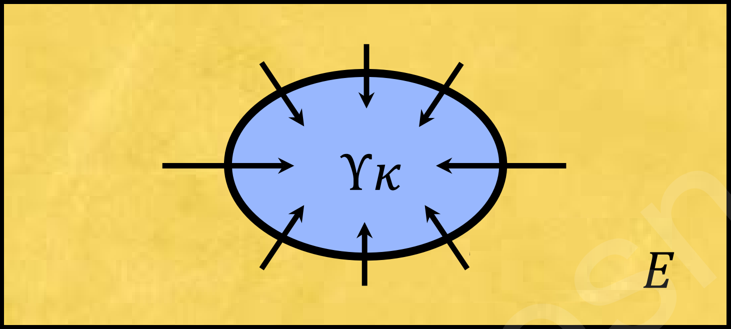
Generalized Young-Laplace:

$$(\sigma_2 - \sigma_1) \cdot \hat{n} = \Upsilon_{12} \kappa \hat{n}$$

total curvature: $\kappa = \partial_i n_i$

surface tension, Υ_{12}:
i.e. surface stress assumed to be isotropic

Surface tension can drive elastic deformation



$$\Upsilon\kappa \sim \varepsilon E$$

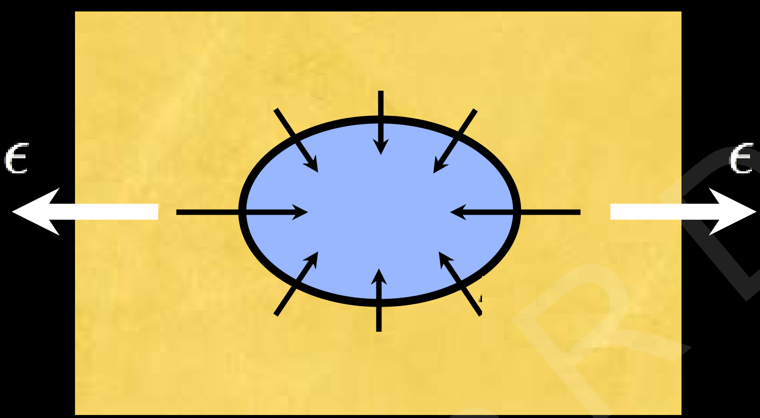
$$\varepsilon \sim \kappa\, \Upsilon / E$$

material property

Microscopic response to macroscopic strain

$\kappa\Upsilon/E \ll 1$

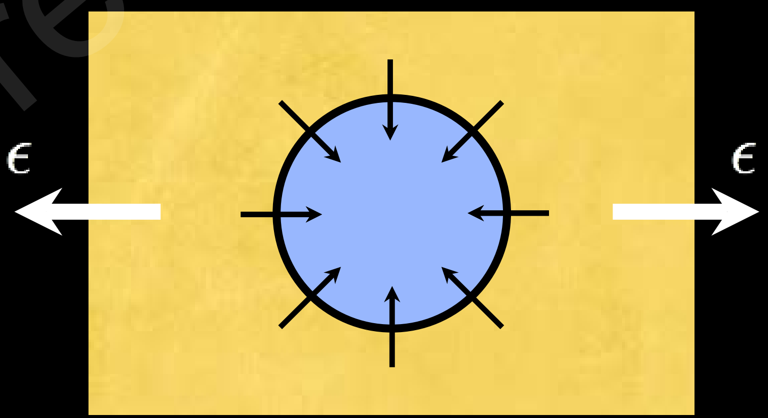
$\Upsilon/ER \ll 1$



bulk elasticity dominates

$\kappa\Upsilon/E \gg 1$

$\Upsilon/ER \gg 1$

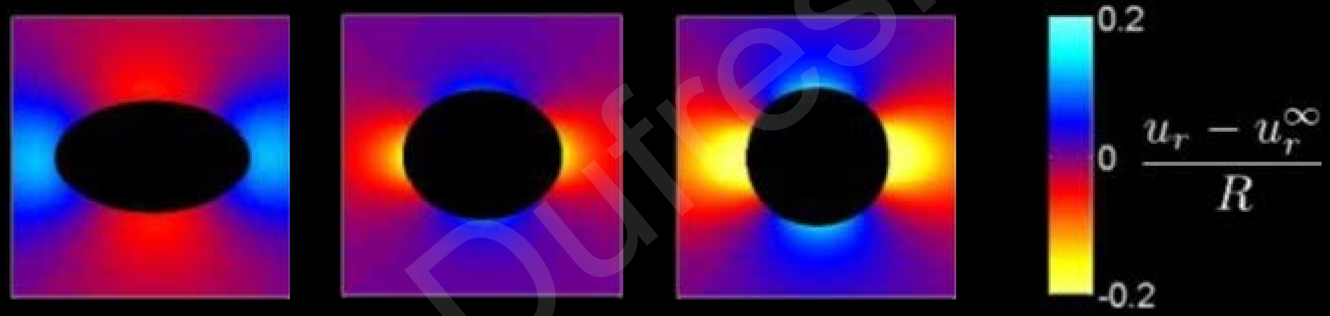


surface tension dominates

Eshelby with Surface Tension (analytic)

strain independent surface tension, no shear stress at the interface

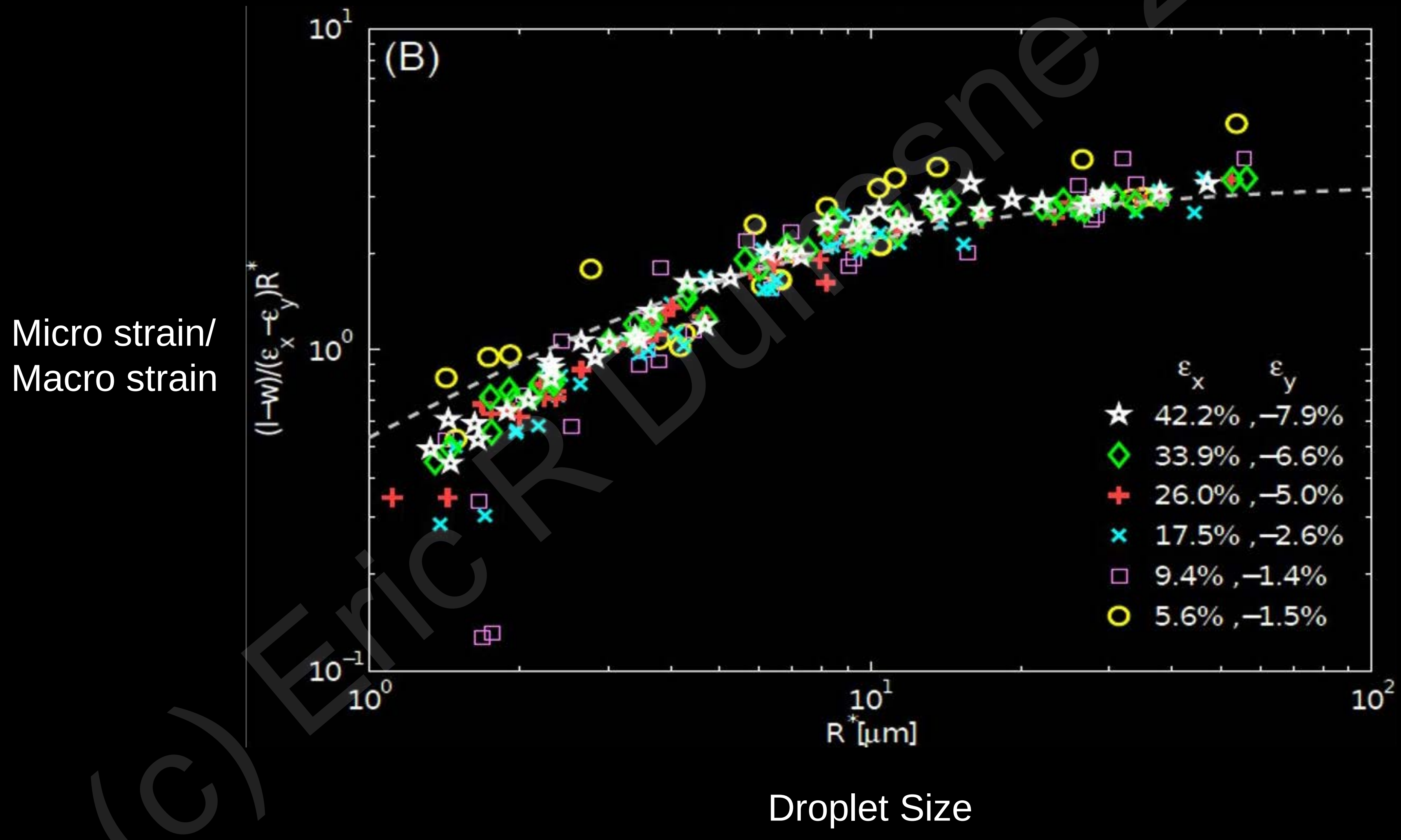
macroscopic strain 0.3



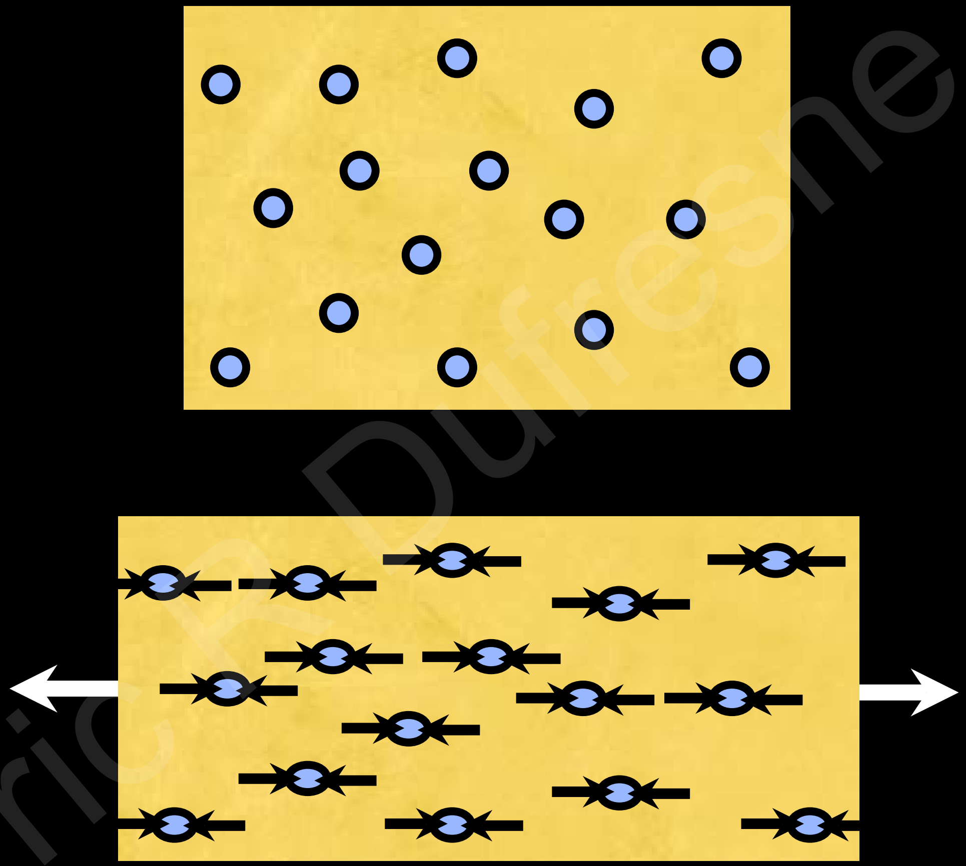
$\Upsilon/ER = 0.1$ $\Upsilon/ER = 1$ $\Upsilon/ER = 10$

Increasing surface tension

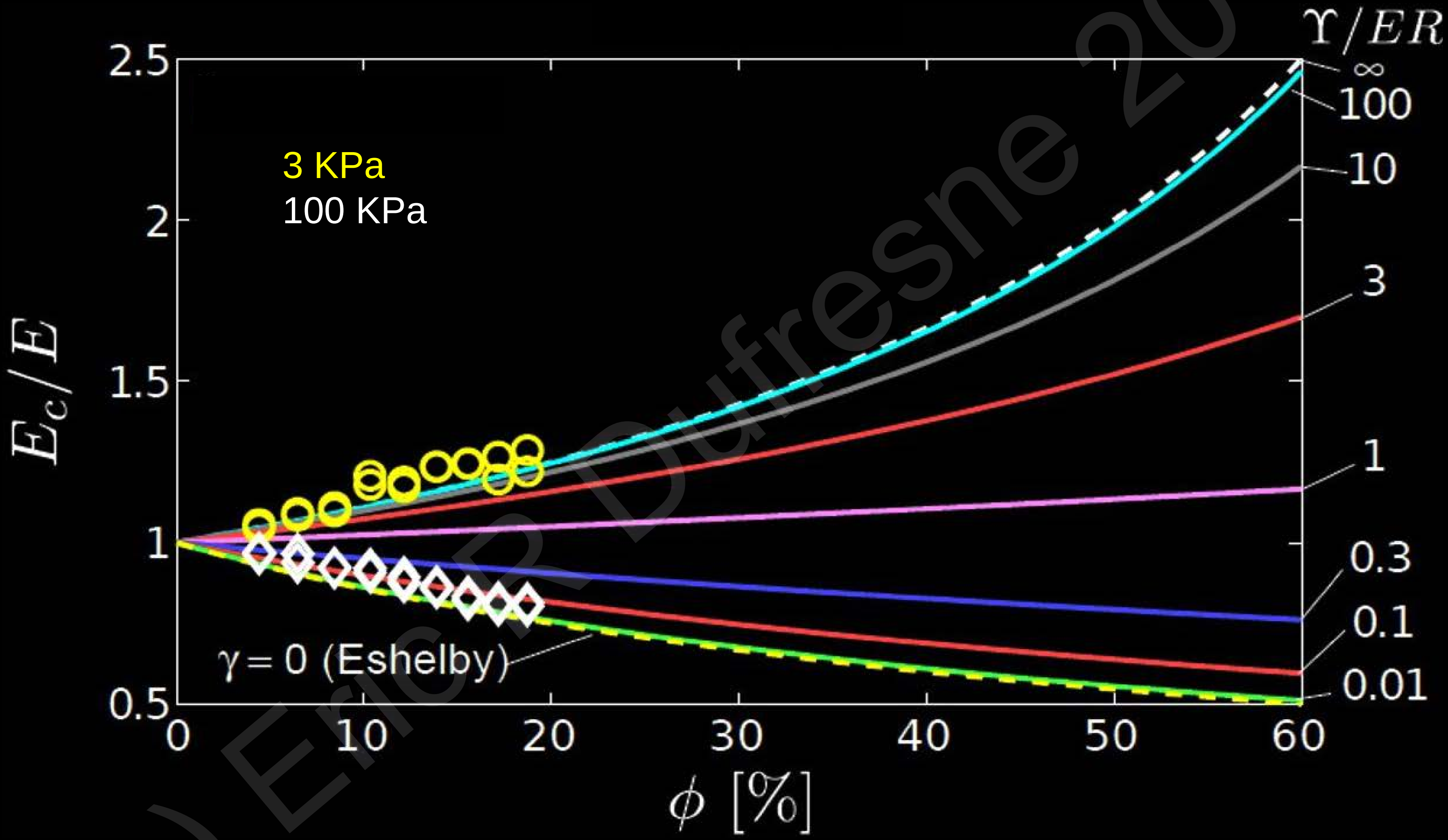
Linear elastic theory with surface tension captures single droplet trend



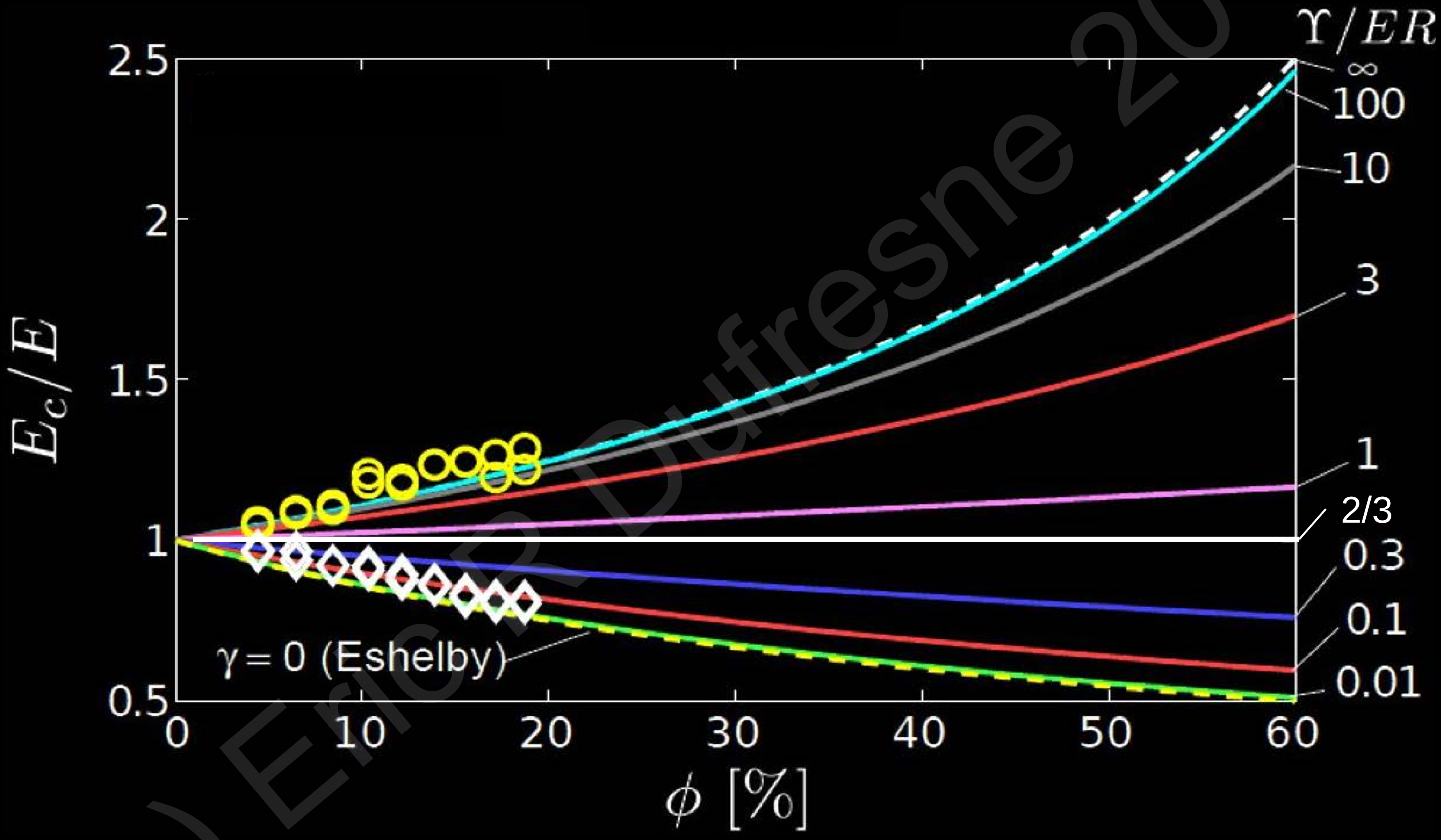
Surface tension 'pulls back' when the bulk solid attempts to deform embedded droplets



Composite Stiffness Dilute Limit (Eshelby Method)



Composite Stiffness Dilute Limit (Eshelby Method)

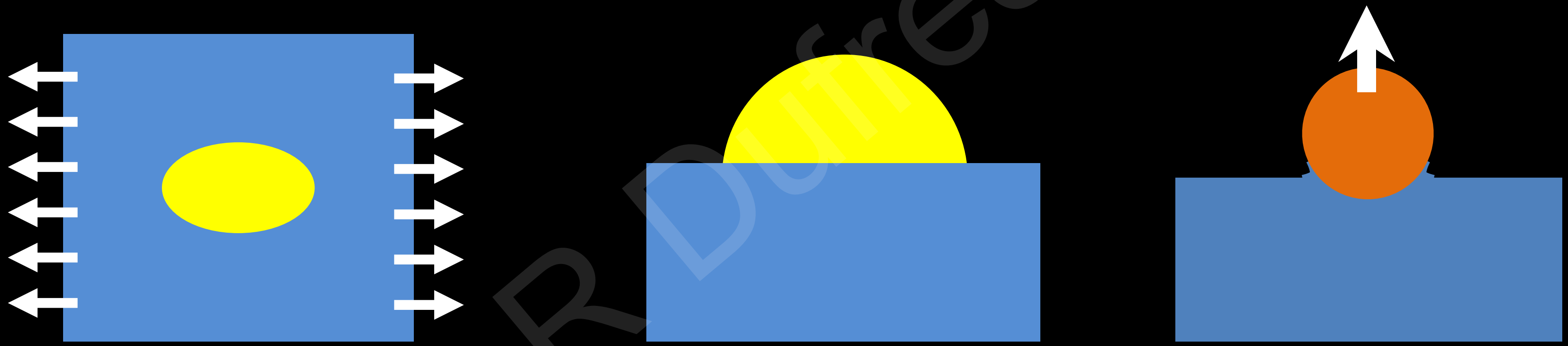


Inclusions in Soft Solids

- When liquid inclusions are smaller than Υ/E, surface tension dominates bulk elastic response
- In this limit, fluid inclusions *stiffen* soft solids
- Need to revisit applications of Eshelby, *e.g.* fracture mechanics
- More generally, surface tension dominates elastic response when $\kappa\Upsilon/E \gg 1$
- References:
  - *Experiment:* Style *et al Nature Physics* 2015
  - *Theory:* Style *et al Soft Matter* 2015

The Big Picture

Classic theories of solid mechanics fail when $\kappa\Upsilon/E \gtrsim 1$



Soft solids can behave very differently than stiff ones.

Implications for cellular biomechanics…

Many solid mechanics problems need to be revisited…