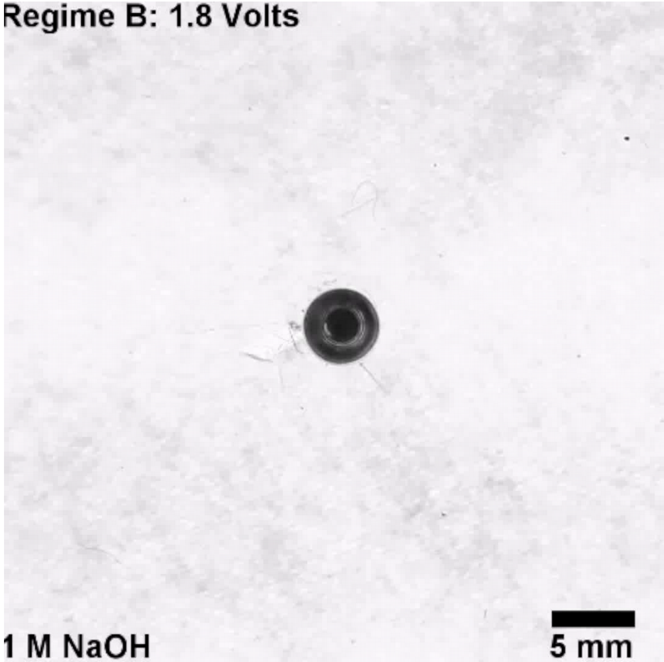
Starbursts and Flowers

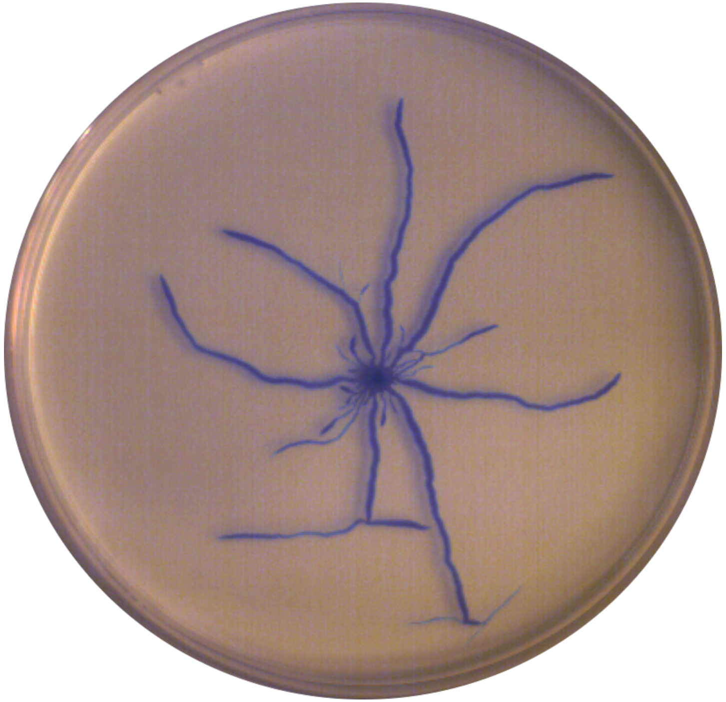
when spreading droplets break bad

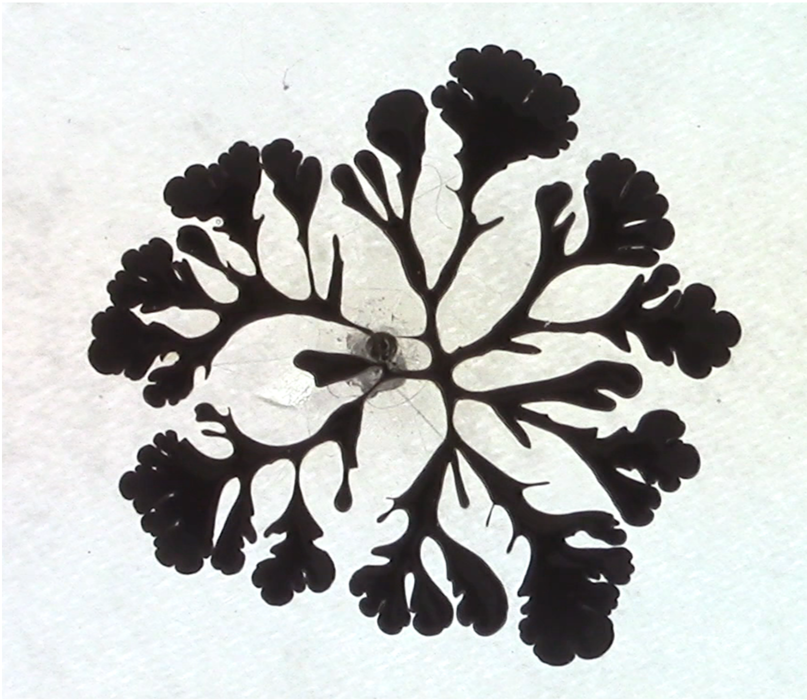


Karen Daniels
Department of Physics
NC STATE UNIVERSITY

Starbursts and Flowers

when spreading droplets break bad





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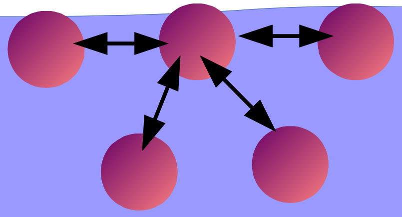
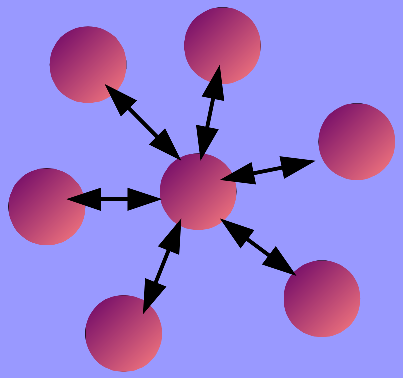
Why are droplets spherical?

Molecular Origins of Surface Tension



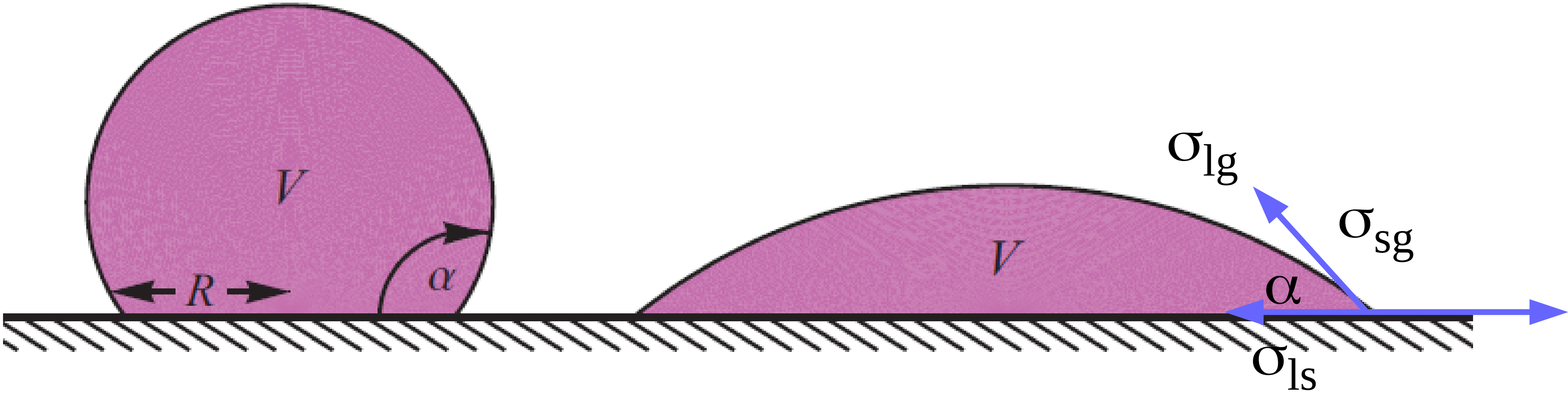
surface molecules:
fewer neighbors
higher potential energy
less preferred state



bulk molecules:
more neighbors
lower potential energy
preferred state

surface tension:
energy/(unit area) required
to increase the surface area

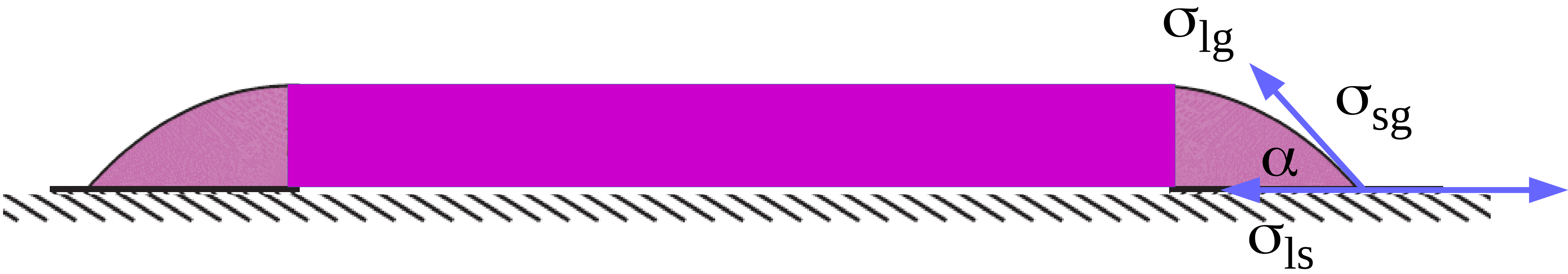
Droplets On Surfaces:
Young-Dupré Law sets the contact angle α



$$\sigma_{sg} - \sigma_{ls} = \sigma_{lg} \cos \alpha$$

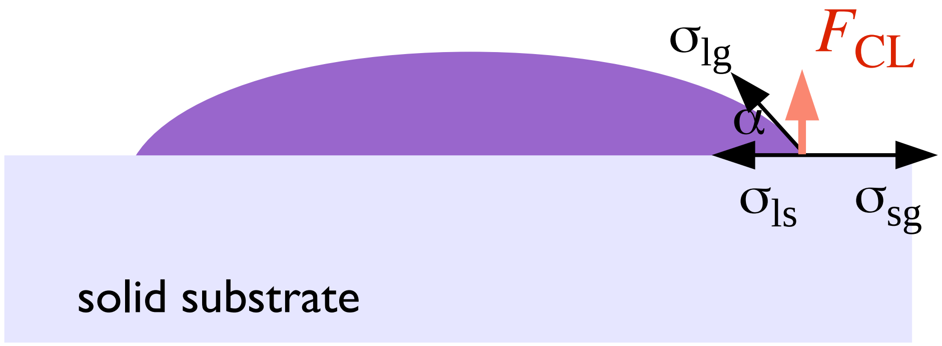
Bigger Droplets On Surfaces:

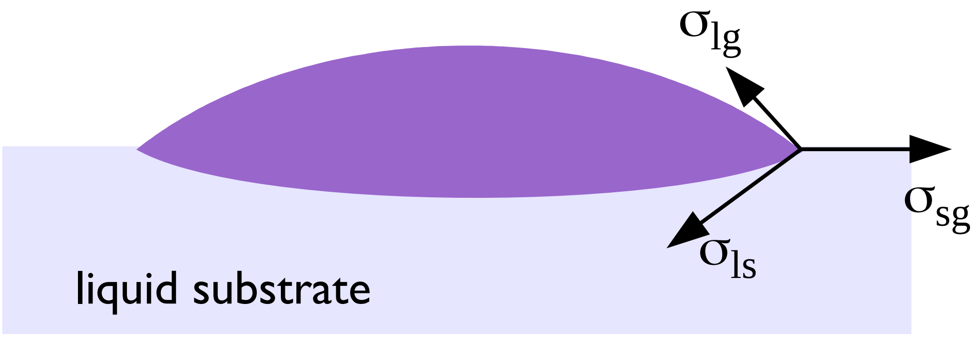
Young-Dupré Law still sets the contact angle α
but gravity moves the contacts further away



$$\sigma_{sg} - \sigma_{ls} = \sigma_{lg} \cos \alpha$$

Solid vs. Liquid Substrates





$$\sigma_{sg} - \sigma_{ls} = \sigma_{lg} \cos\alpha$$

⊥ unbalanced force

$F_{CL} = \sigma_{lg} \sin \alpha$

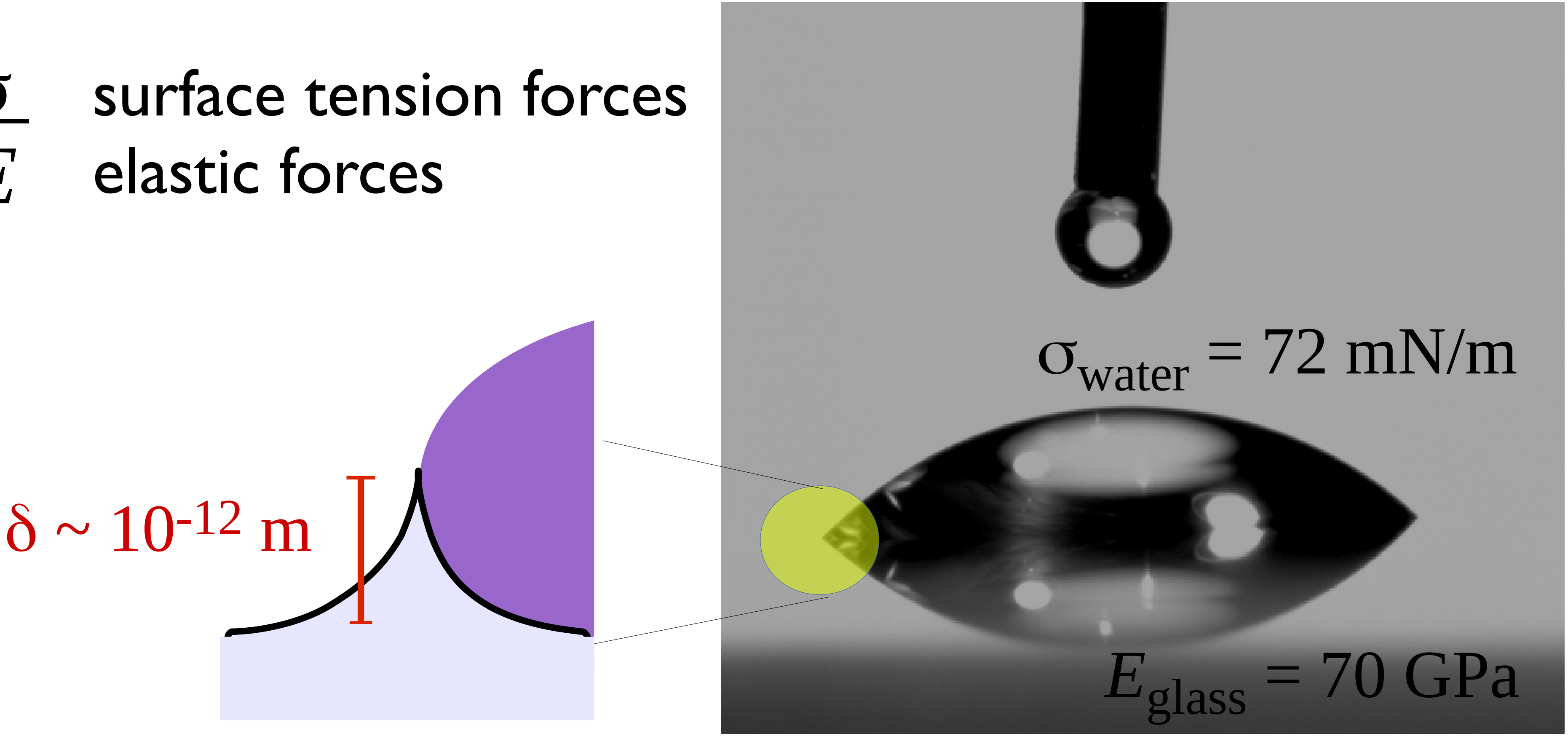
Young-Dupré

$$\vec{\sigma}_{sg} + \vec{\sigma}_{ls} + \vec{\sigma}_{lg} = 0$$

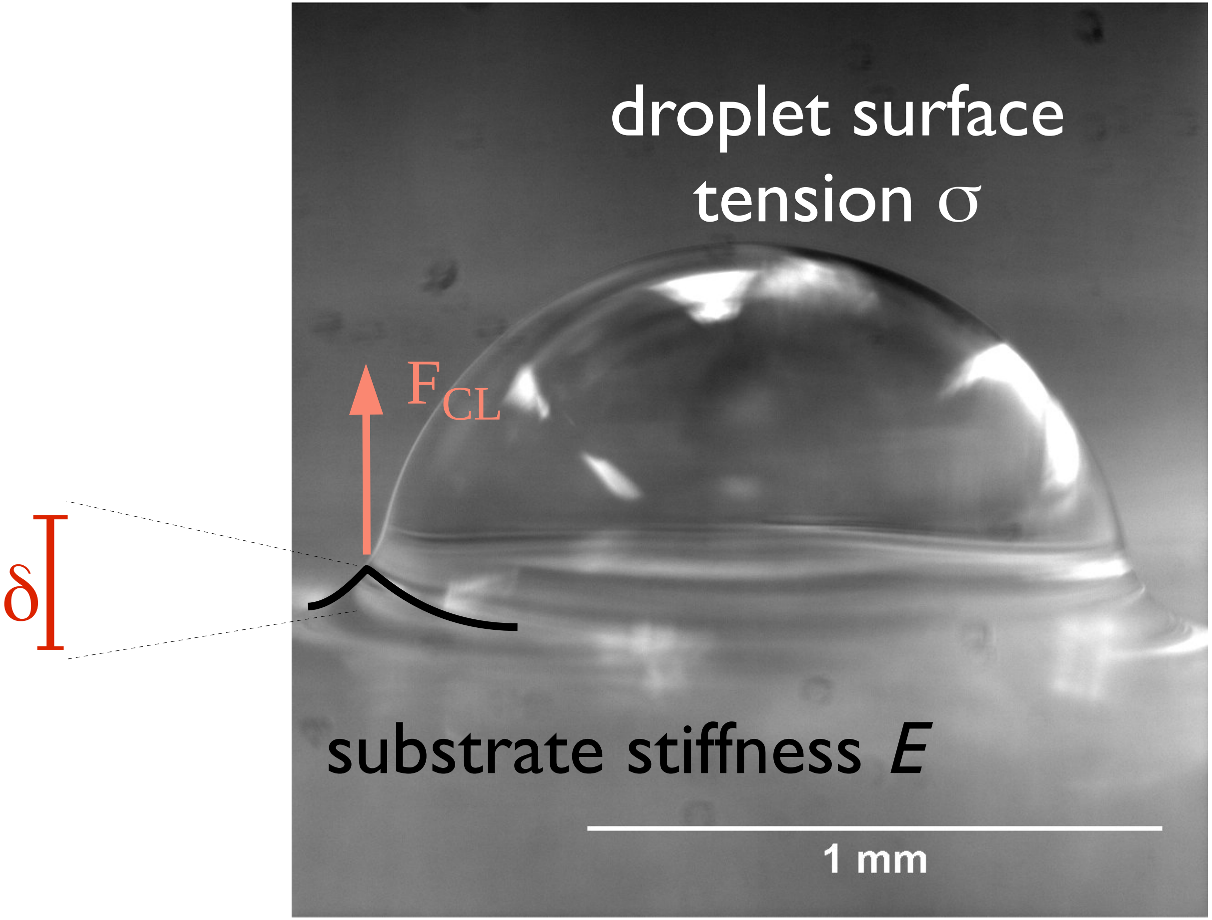
Neumann

Elastocapillary Length

$$\delta = \frac{\sigma}{E} \quad \frac{\text{surface tension forces}}{\text{elastic forces}}$$

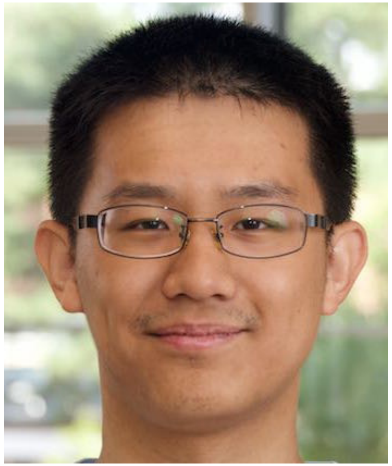


Droplets on Soft Materials



elastocapillary length

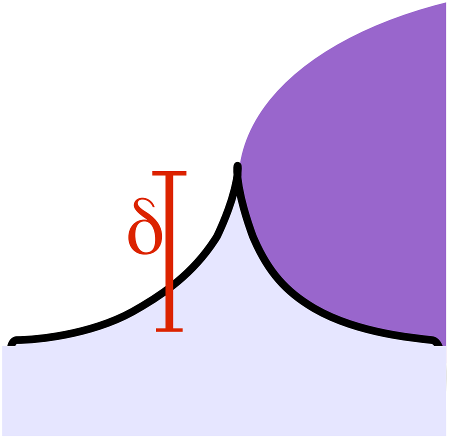
$$\delta = \frac{\sigma}{E}$$



Shih-Yuan Chen

Why did my pudding fracture?

$$\delta = \frac{\sigma}{E} \approx 1\,mm$$

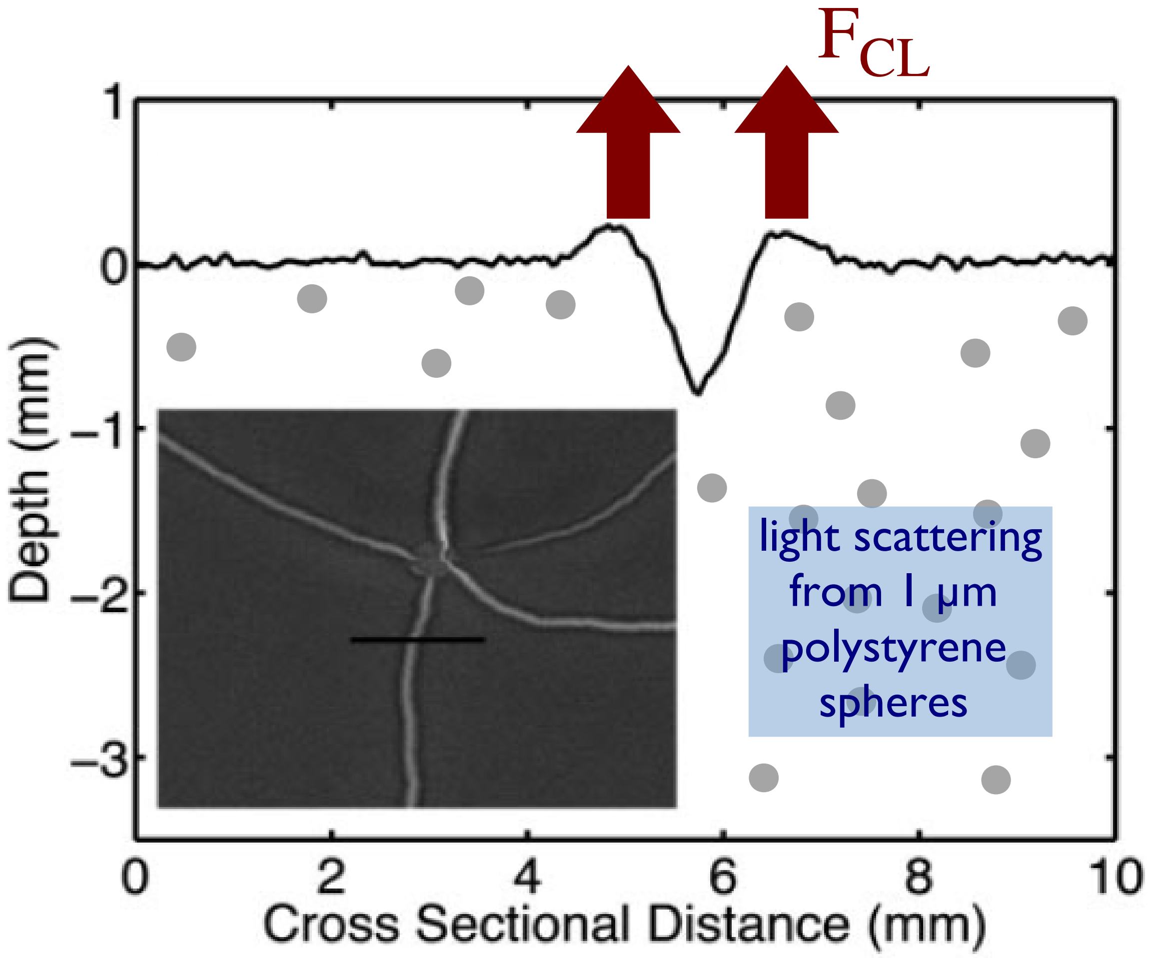


consider glass (70 GPa) instead of ultrasoft (30 Pa) substrate

⇓

40 Mini Coopers distributed on a ring of radius 1 mm

Measuring Surface Deformations

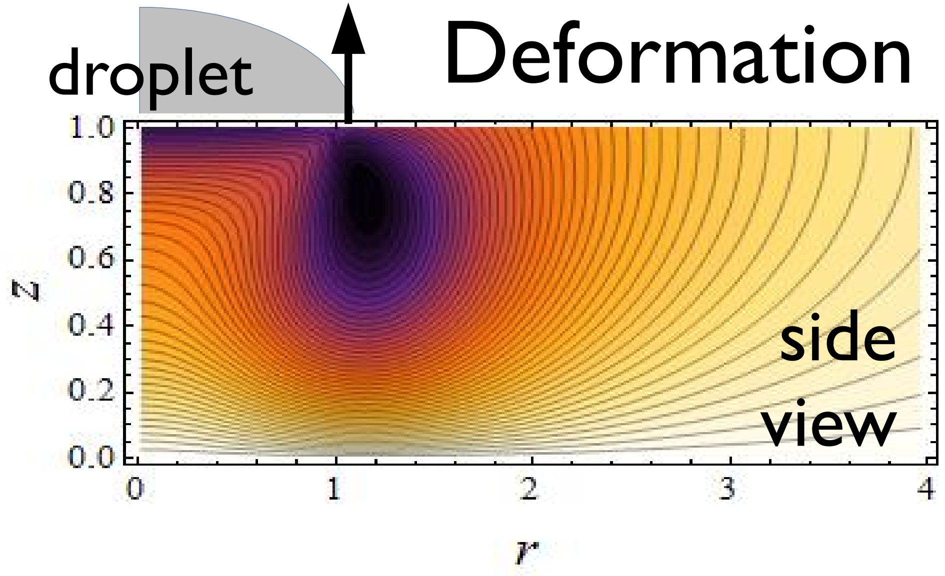


Paul Houseworth

Daniels, Mukhopadhyay, Houseworth, Behringer. *PRL* (2007)

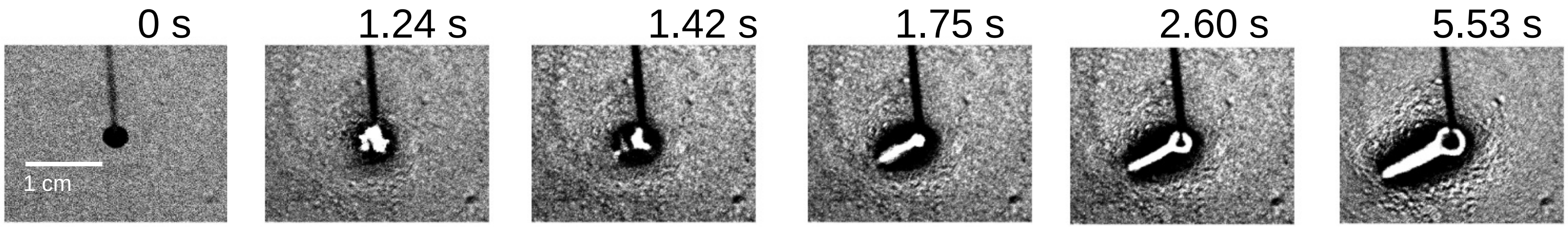
Understanding Elastocapillary Fracture

Deformation

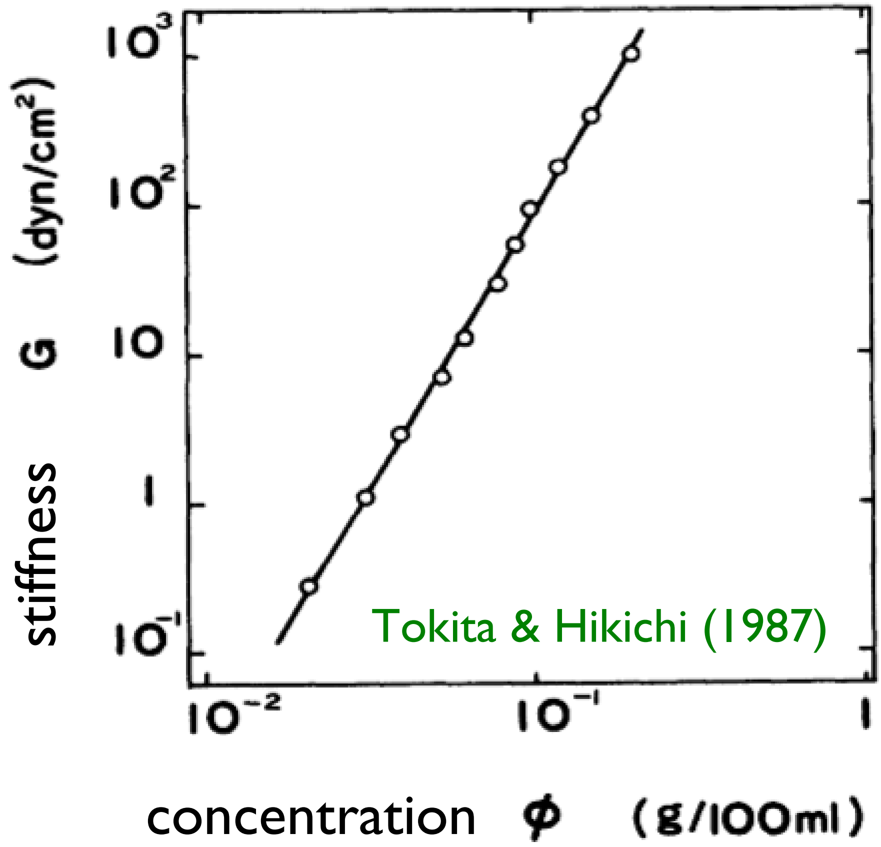


How many arms?

Initiation

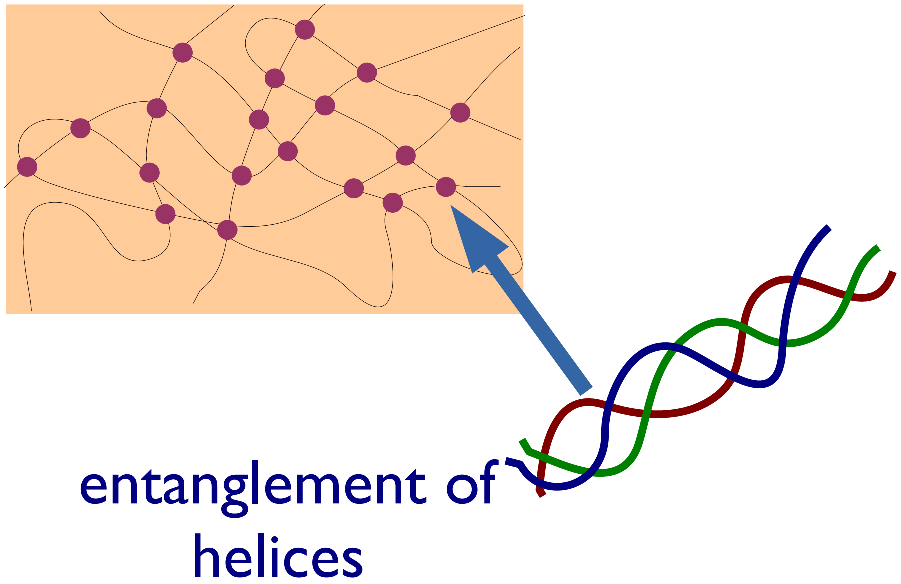


Substrate: Agar Gel

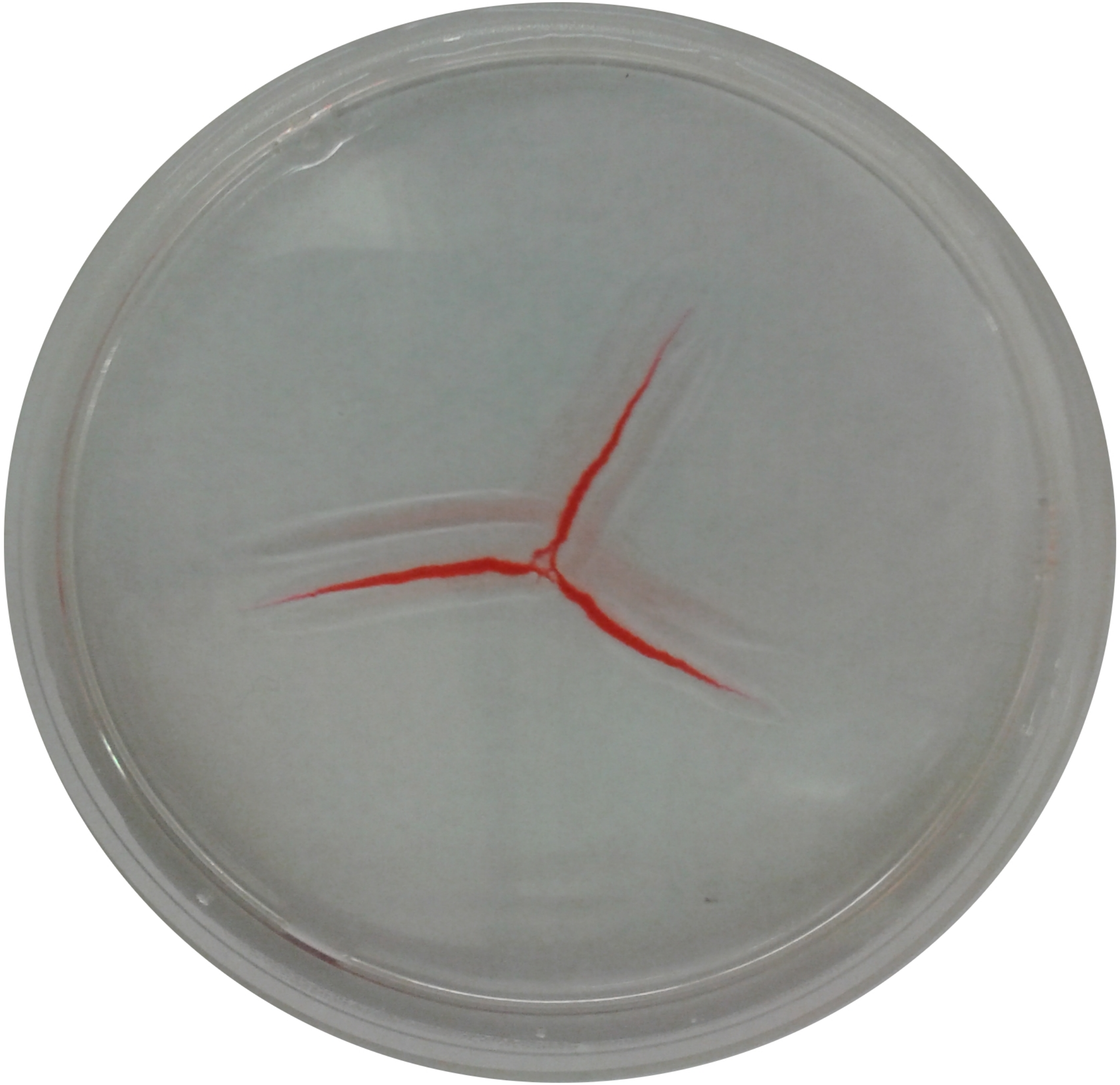


← tunable elasticity →

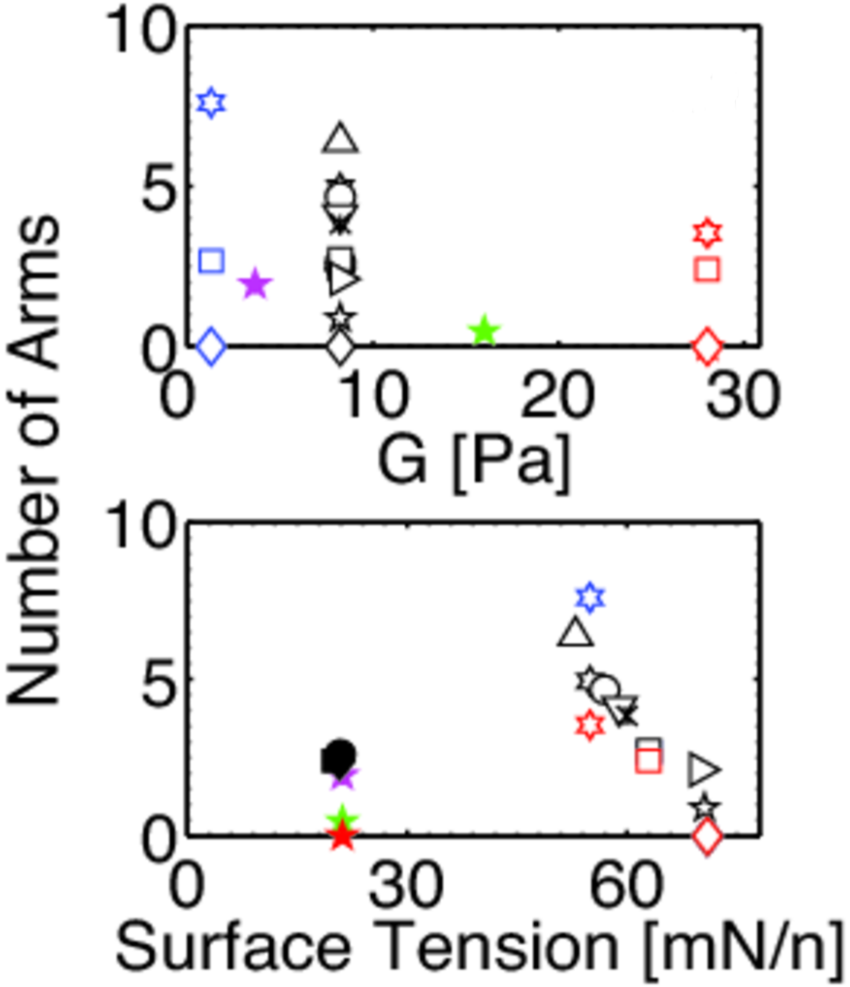
network of polysaccharide polymers cross-linked by reversible bonds



What sets the # of arms?



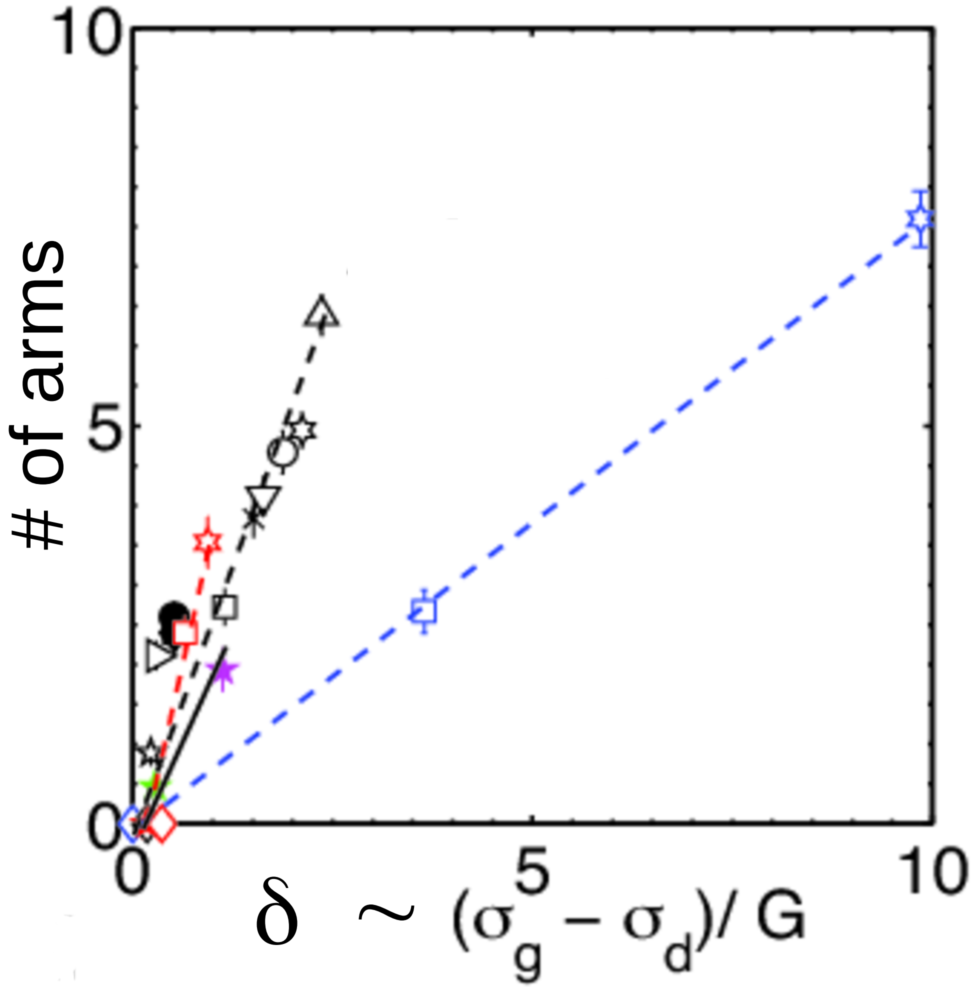
Experiments on # of Arms



- Color = gel stiffness
- Solid symbols = droplet is silicon oil
- Open symbols = droplet is Triton X-305 solution

Daniels, Mukhopadhyay, Houseworth, Behringer. *PRL* (2007)

Answer: Elastocapillary Length?



- Color = gel stiffness
- Solid symbols = droplet is silicon oil
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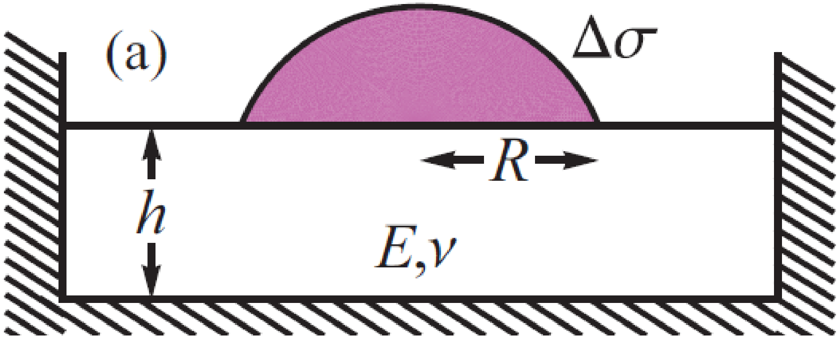
Daniels, Mukhopadhyay, Houseworth, Behringer. *PRL* (2007)

What forces act on the gel?

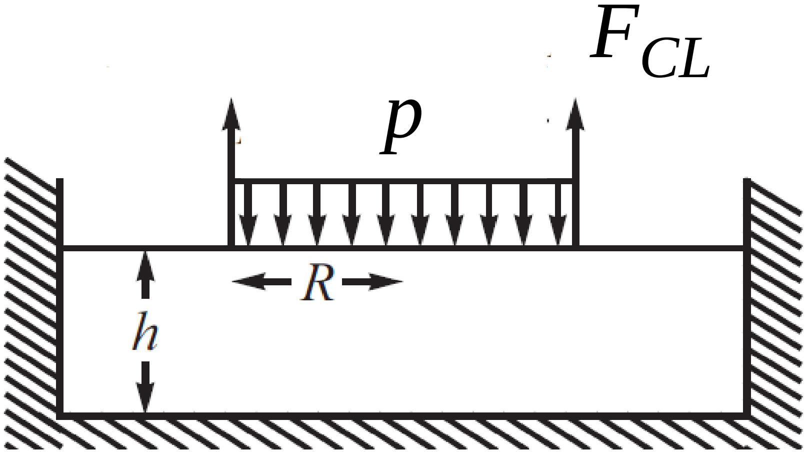
Michael Shearer

Josh Bostwick

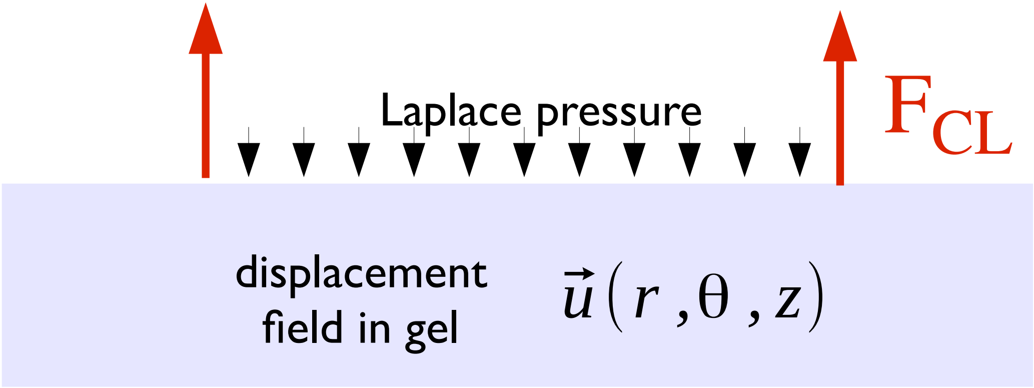


- contact line imposes upward force on gel: F_{CL}
- Laplace pressure of droplet pushes downward:

$$p = \frac{2\sigma_{lg}\sin\alpha}{R}$$



Continuum model of substrate



- **Linear elasticity:** $\boldsymbol{\varepsilon} = \frac{1}{2}\left(\nabla \vec{u} + (\nabla \vec{u})^T\right)$ strain

  Landau & Lifschitz $\nabla \cdot \boldsymbol{\sigma} = 0$ force balance

  $\boldsymbol{\sigma} = \boldsymbol{C} : \boldsymbol{\varepsilon}$ Hooke's Law

- **Equilibrium:** $(1-2\nu)\nabla^2 \vec{u} + \nabla(\nabla \cdot \vec{u}) = 0$

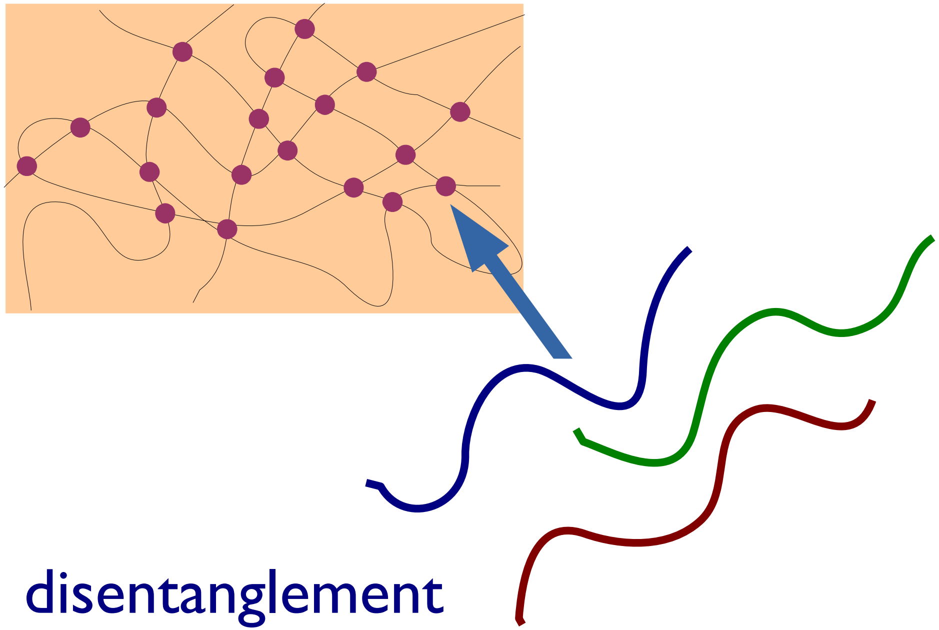
  Navier-Cauchy equation

Hoop strain sets failure criterion

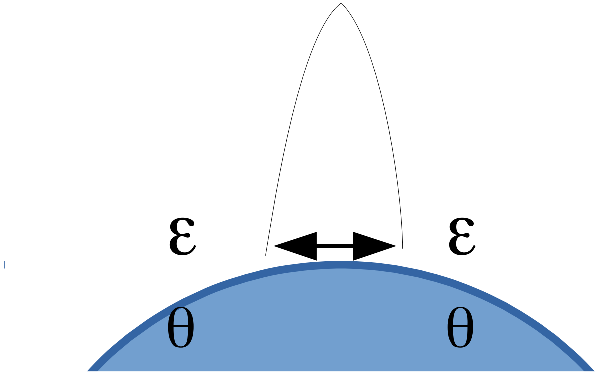
$$\sigma = \mathsf{C} : \varepsilon$$

large strains ⇒ failure

$\varepsilon_{\theta\theta}$ corresponds to Mode I



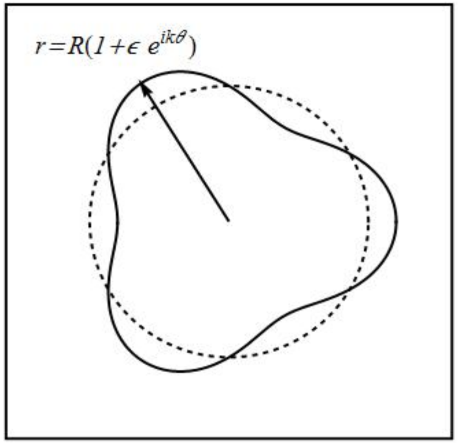
disentanglement of helices



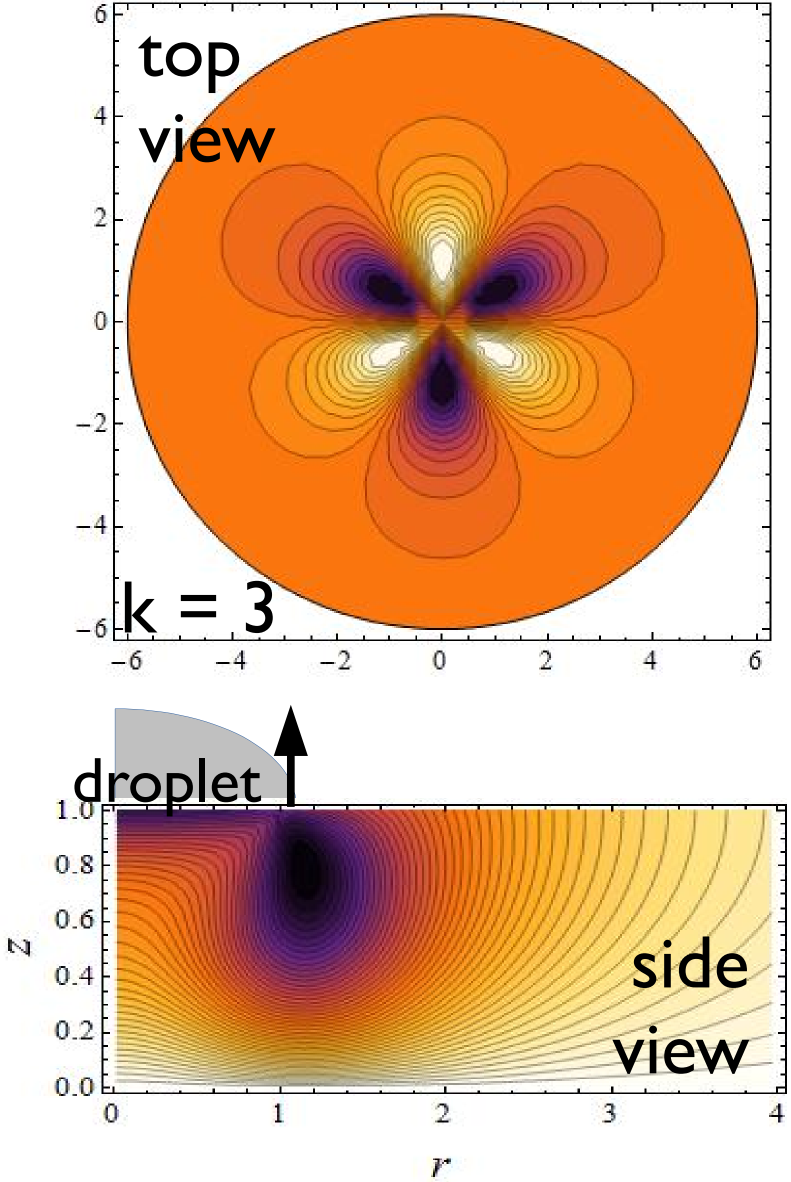
large hoop strain causes disentanglement, initiates fracture

Hoop strain field $\varepsilon_{\theta\theta}$

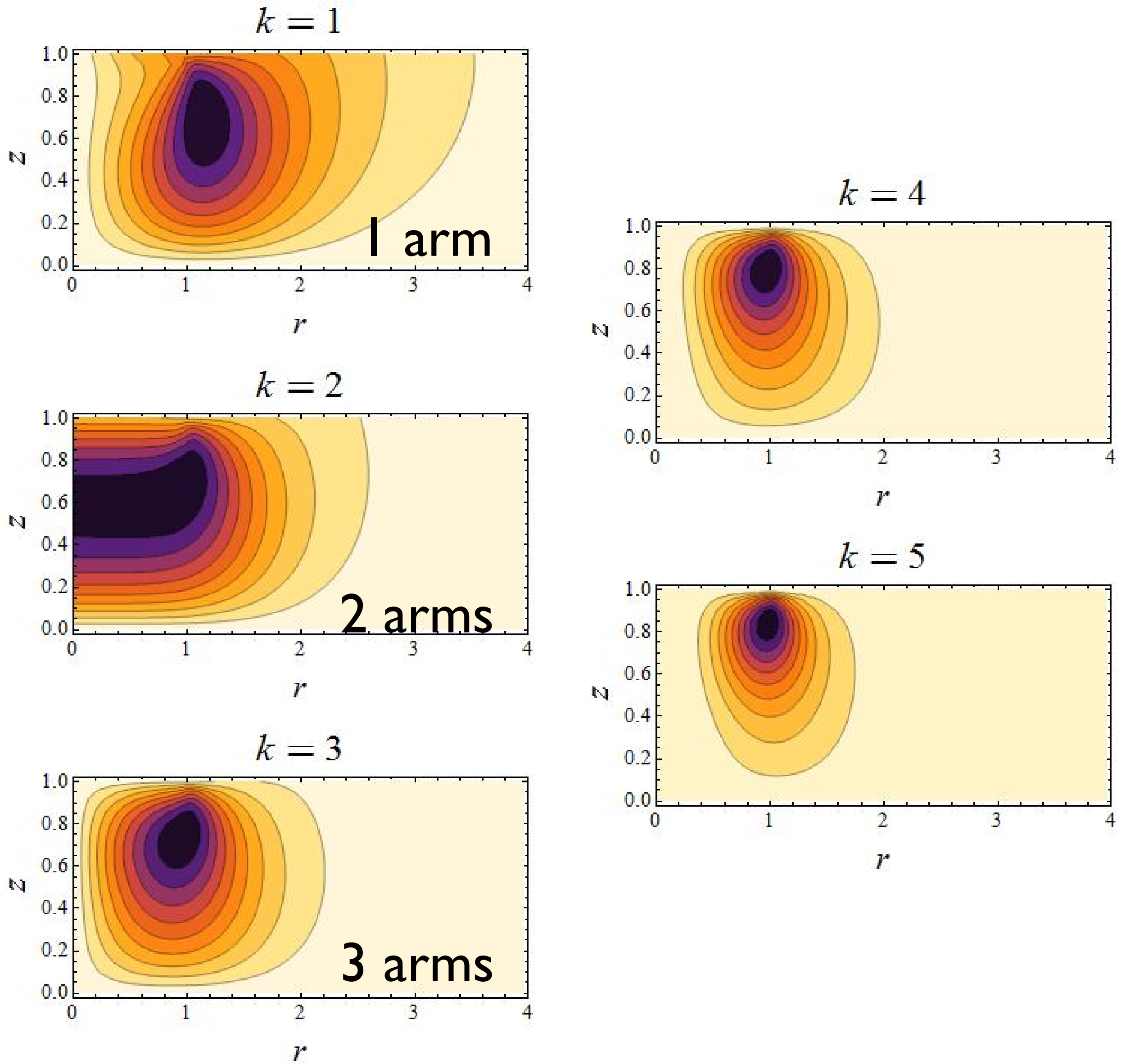
- solve elastic model for perturbed hoop strain field with k = 1, 2, 3, …



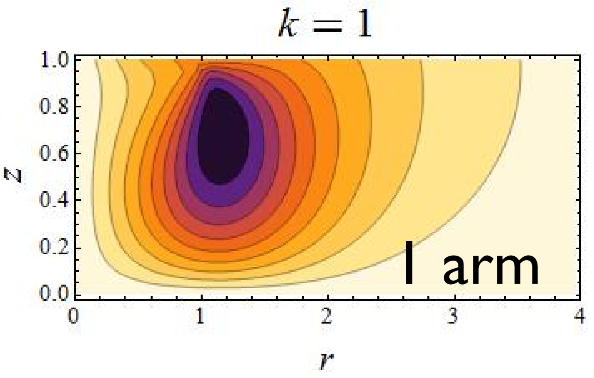
- observation: hoop strains are largest deep in the interior of the gel

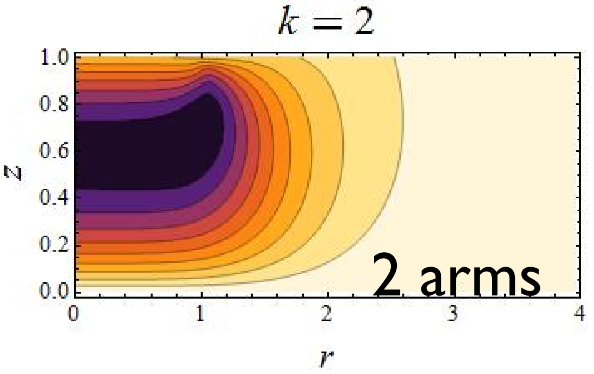


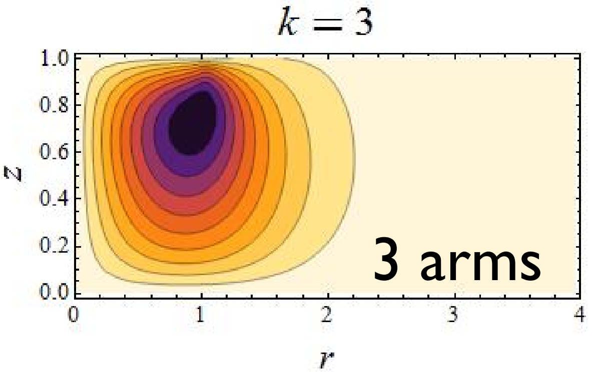
Bostwick, Daniels. *PRE* (2013)



Find the *k* with largest hoop strain

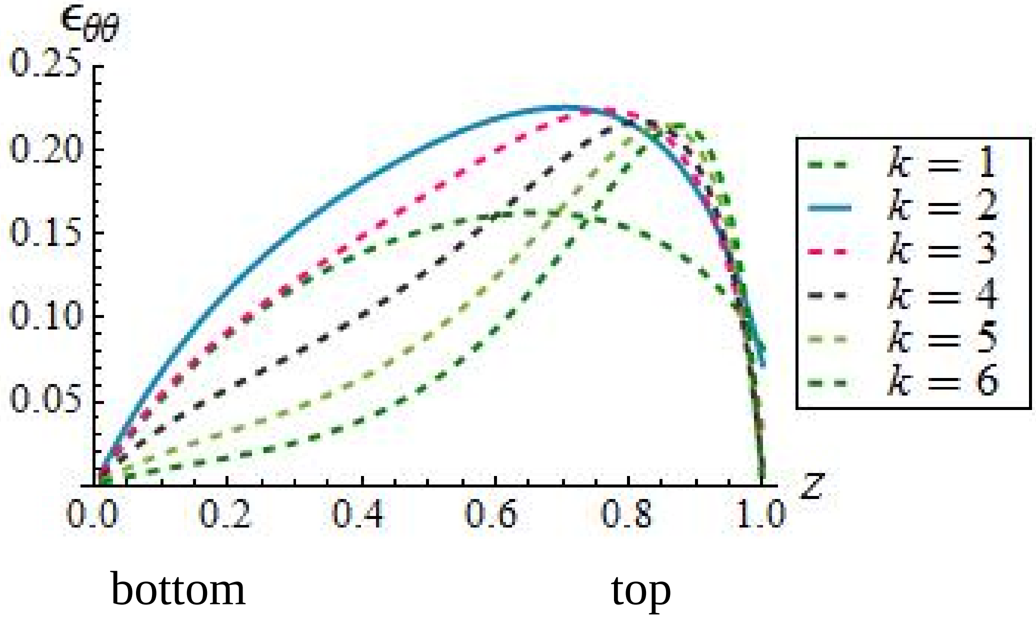






$R = 1$

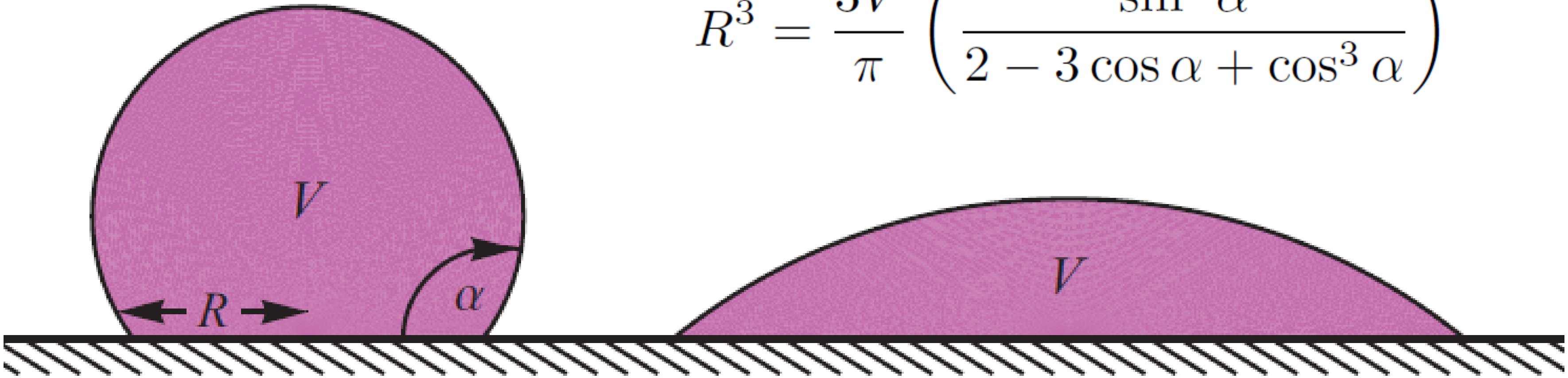
$k = 2$ largest



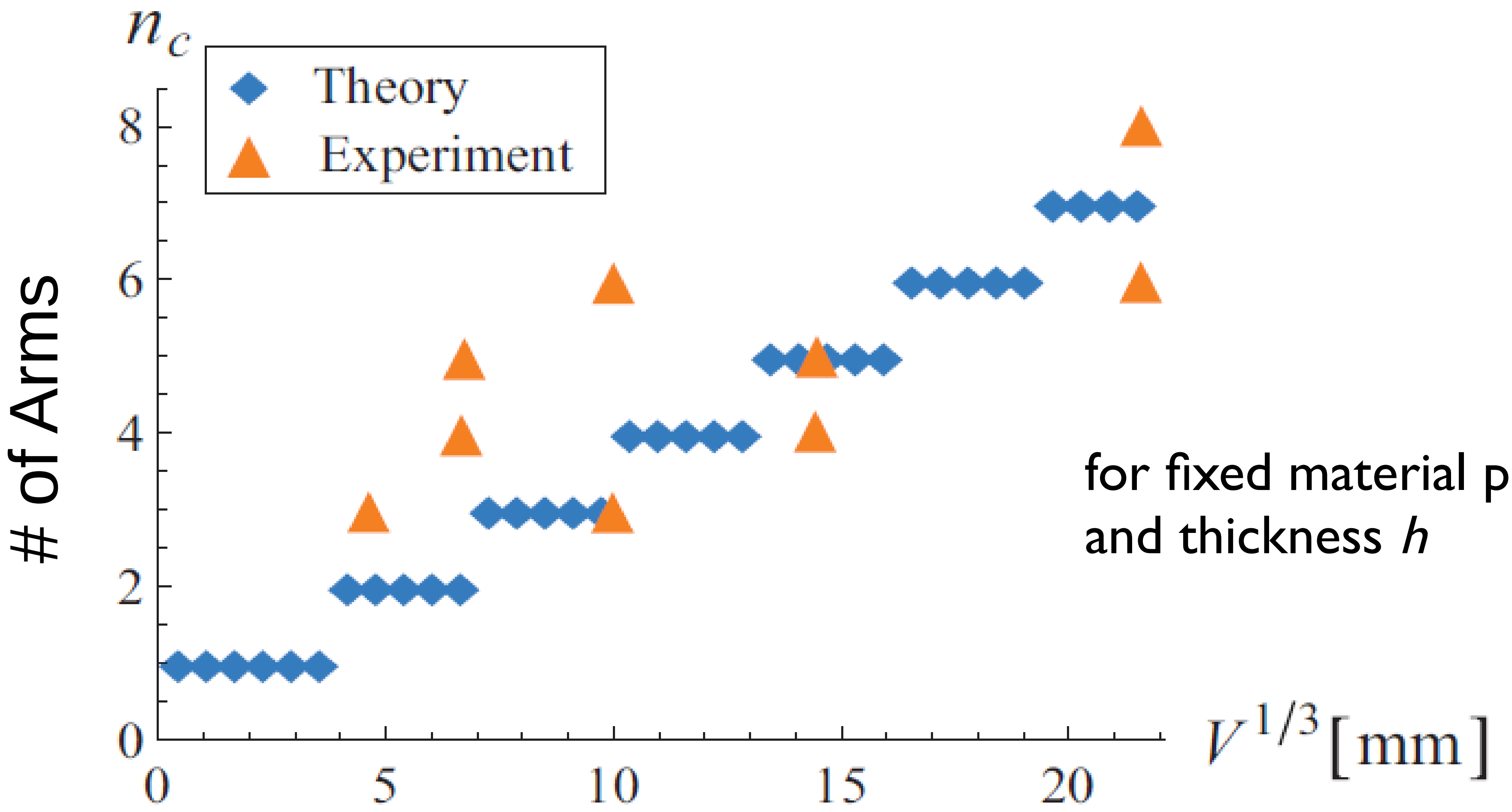
Comparing to Experiments

- vary droplet volume V for fixed surface tension (contact angle)
- for fixed volume V, vary surface tension → radius R of droplet depends on contact angle α

$$R^3 = \frac{3V}{\pi}\left(\frac{\sin^3\alpha}{2 - 3\cos\alpha + \cos^3\alpha}\right)$$

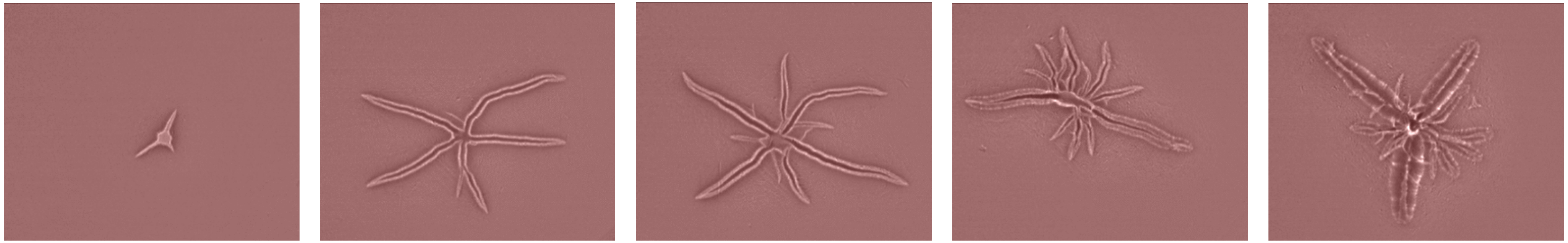


Bigger droplet ⇒ more arms

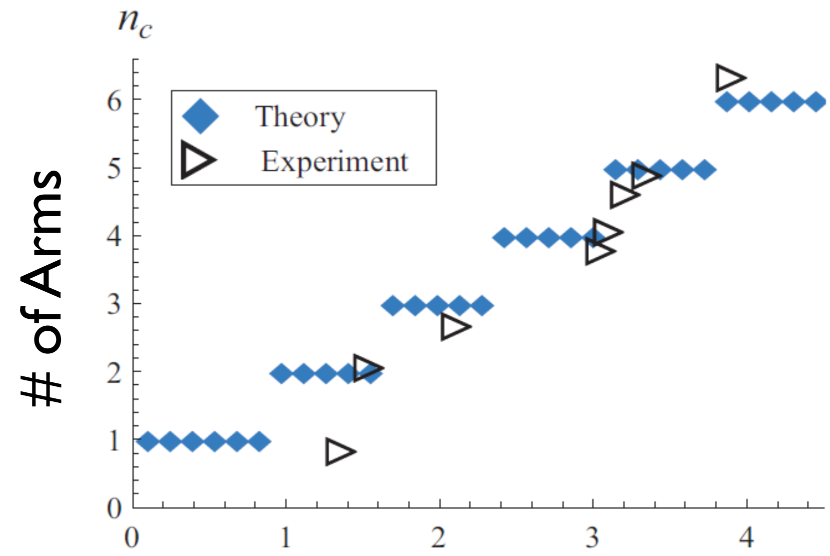


for fixed material properties and thickness h

Vary droplet surface tension

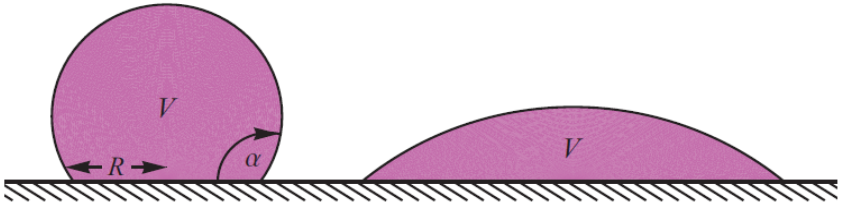


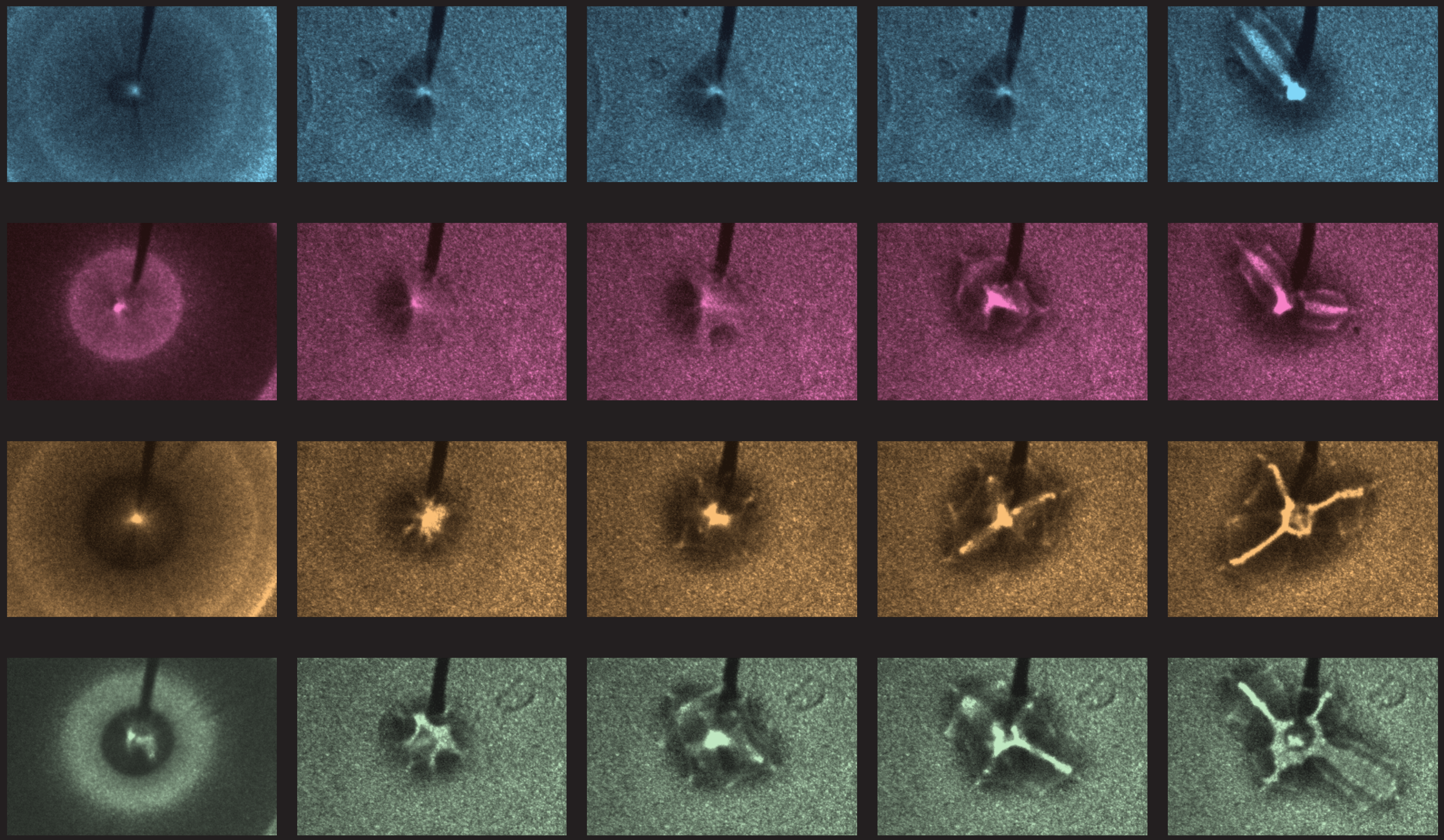
increase σ_{lg} $\Rightarrow$ increase R $\Rightarrow$ more arms



$$\Lambda \equiv \frac{R}{h}$$

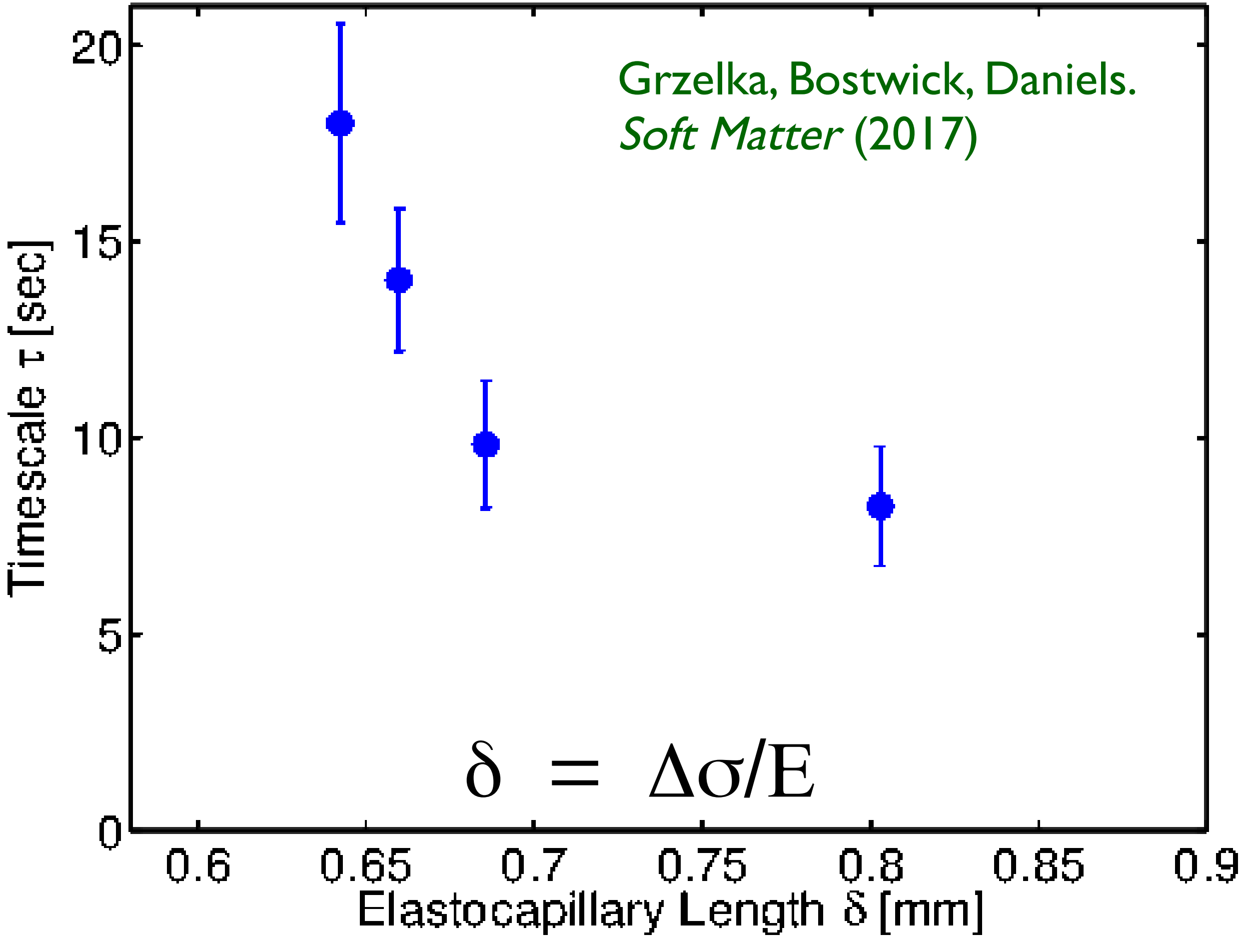
$$R^3 = \frac{3V}{\pi}\left(\frac{\sin^3\alpha}{2 - 3\cos\alpha + \cos^3\alpha}\right)$$





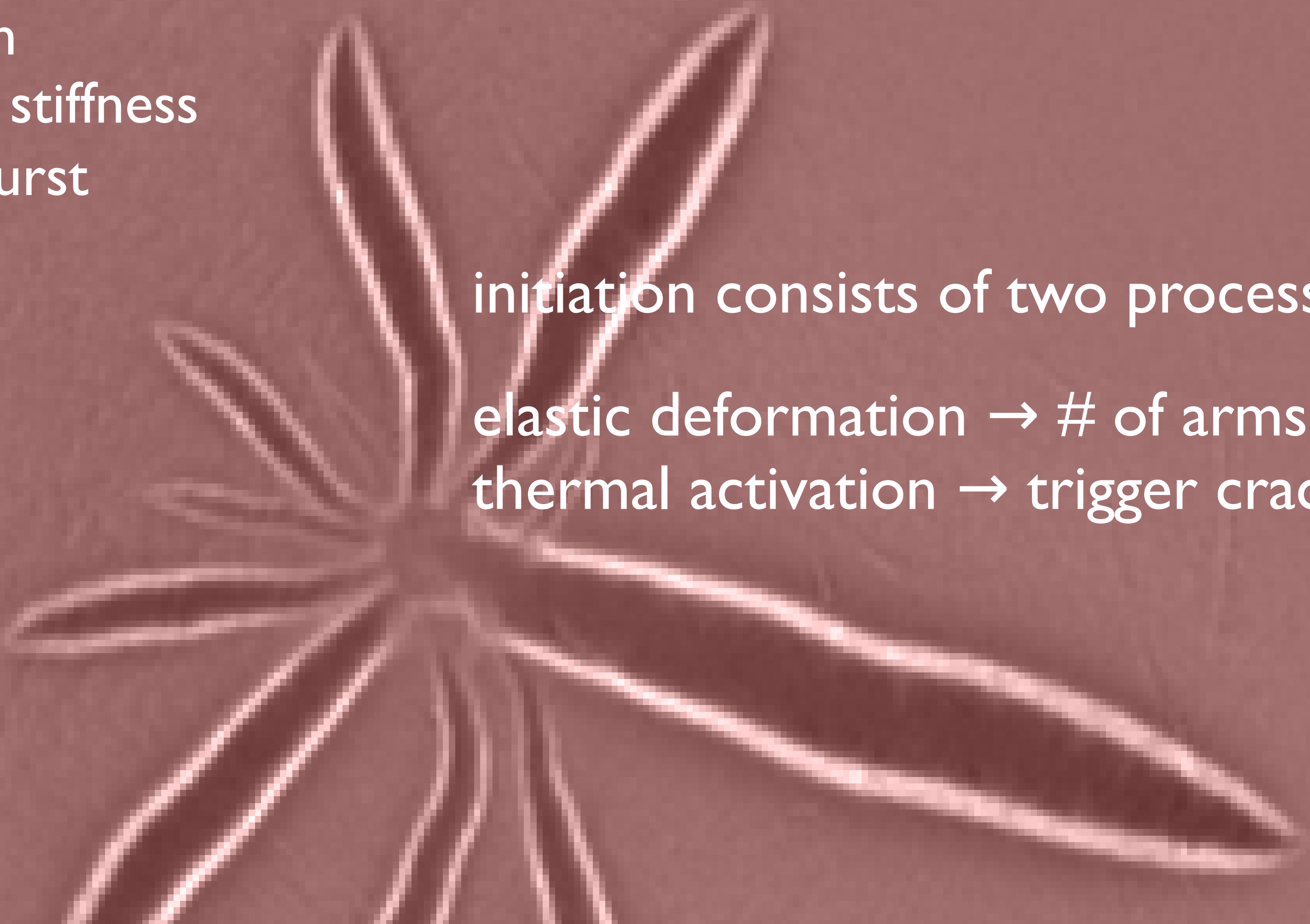
Grzelka, Bostwick, Daniels. *Soft Matter* (2017)

Elastocapillary length controls timescale



Marion Grzelka

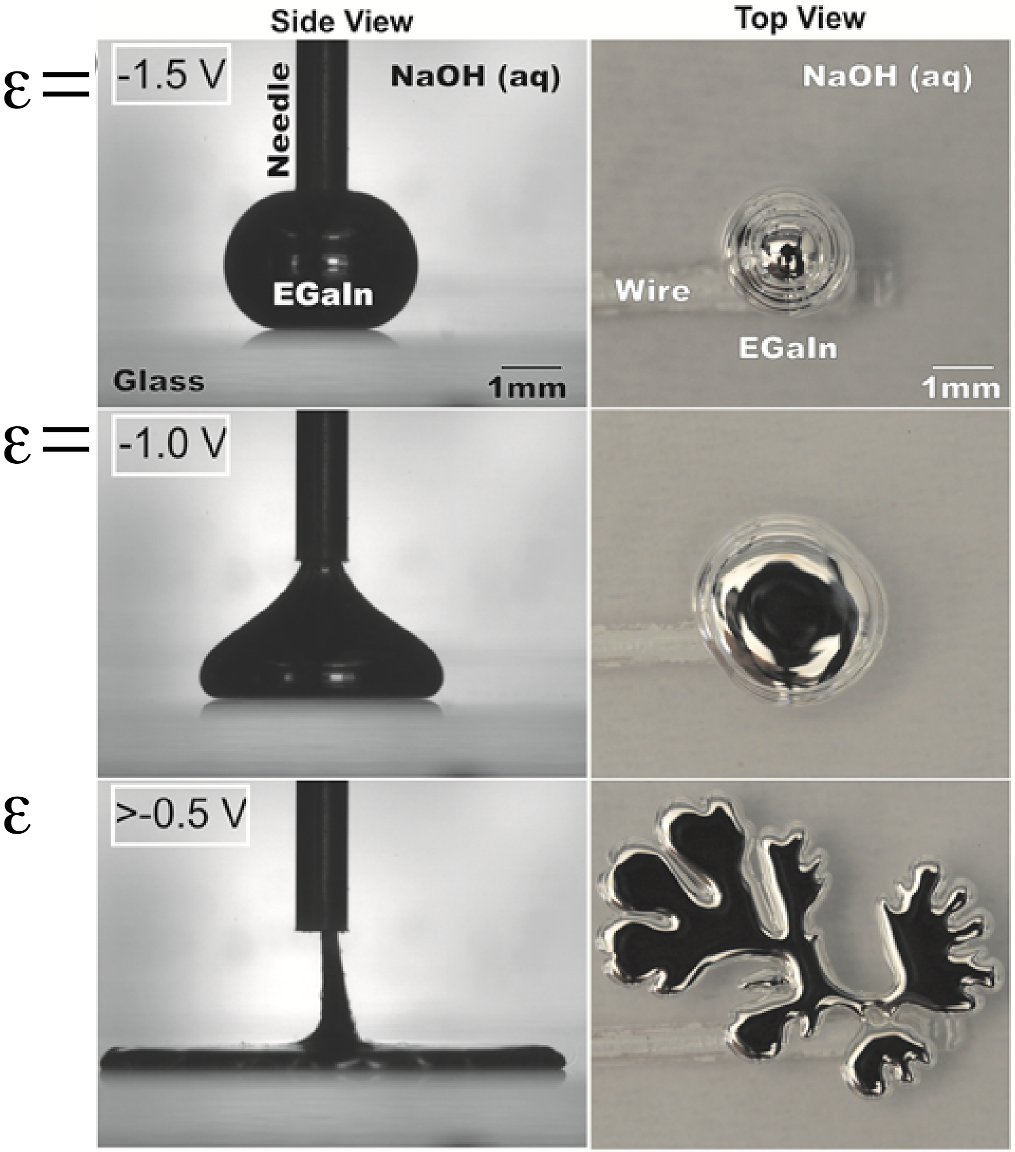
competition between surface tension difference and stiffness of gel → starburst morphology

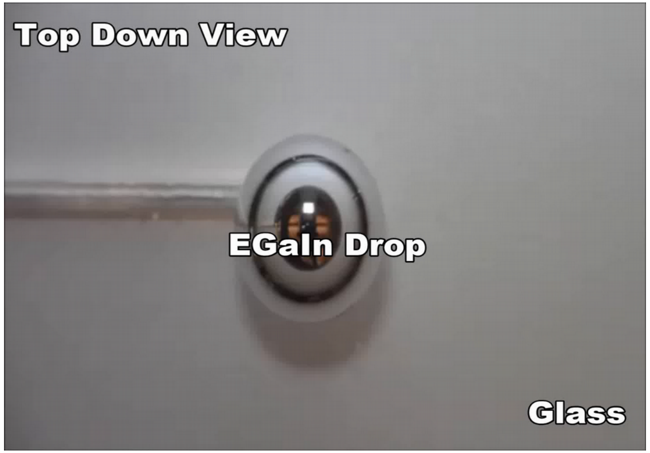


initiation consists of two processes:

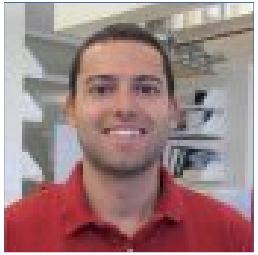
elastic deformation → # of arms
thermal activation → trigger crack

Khan, Eaker, Bowdon, Dickey. *PNAS.* (2014)
Eaker & Dickey. *Applied Physics Reviews* (2016)






Michael Dickey


Collin Eaker


Minyung Song

Surface Tensions

organics/alcohols: 20 mN/m

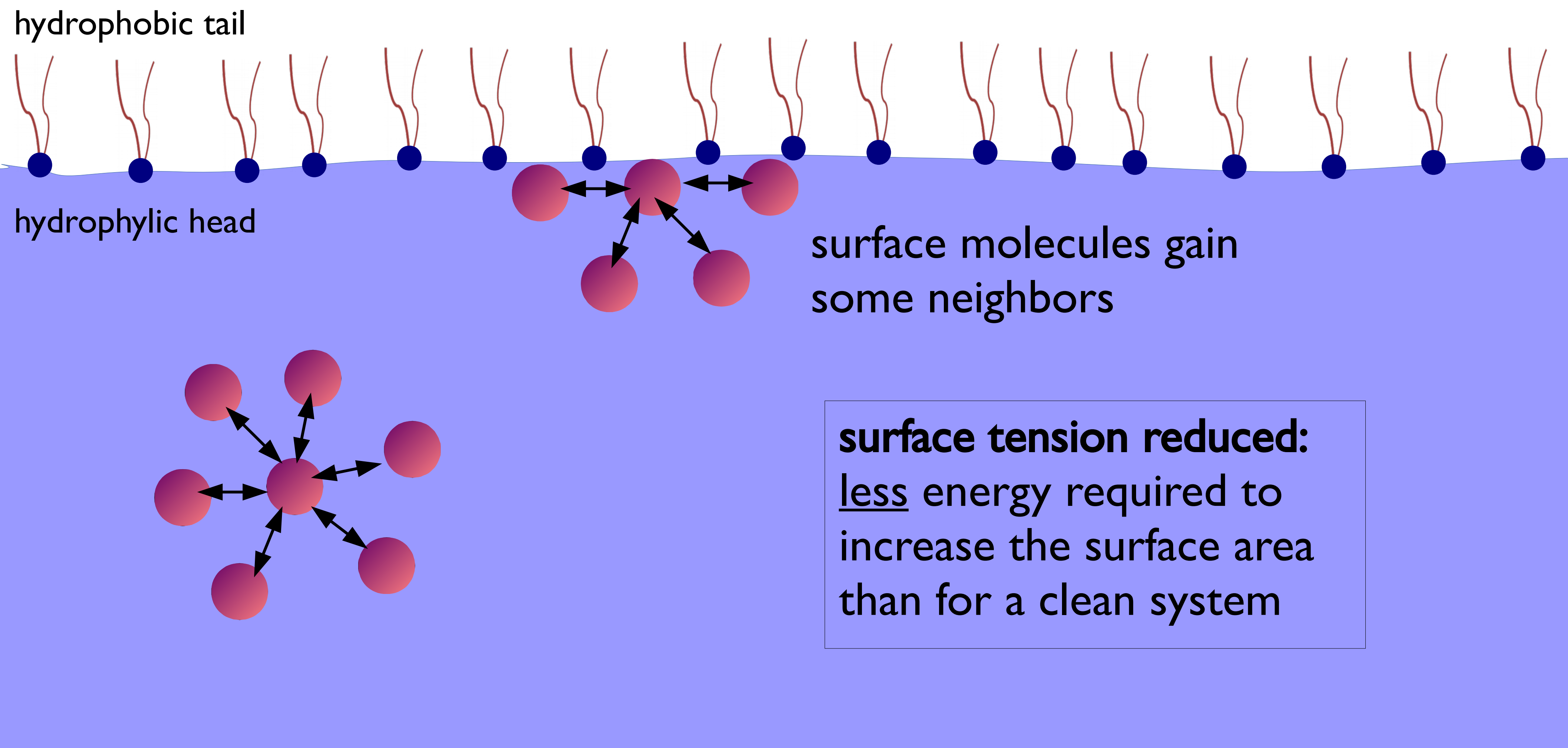
water: 70 mN/m

water + surfactant: 40 mN/m

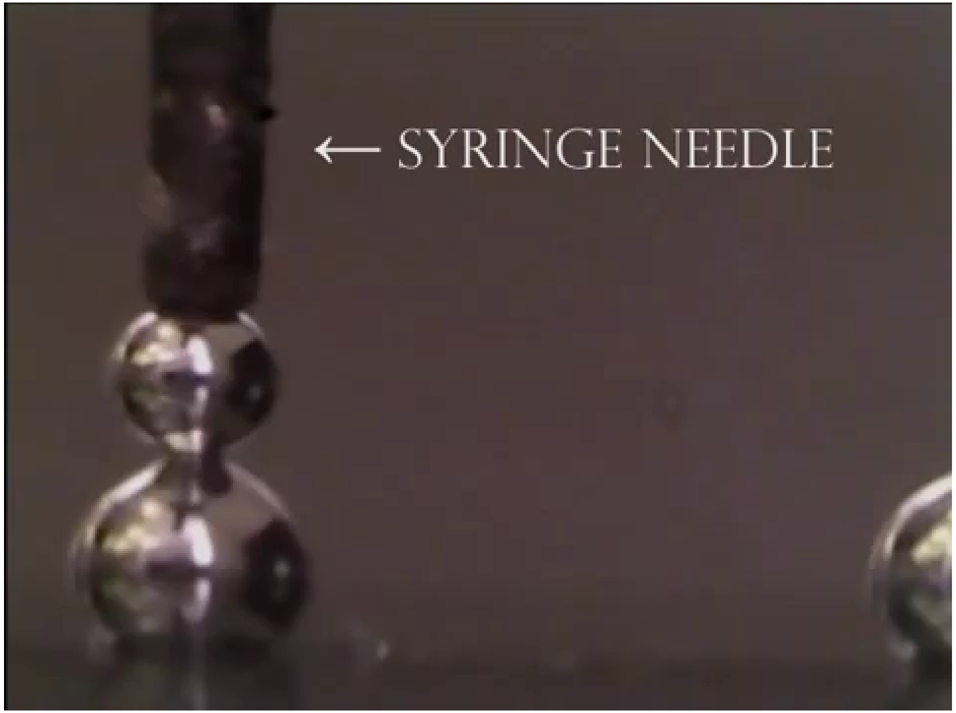
metals: 500 mN/m

metal + surfactant?

Surfactant = SURFace ACTive AgENT



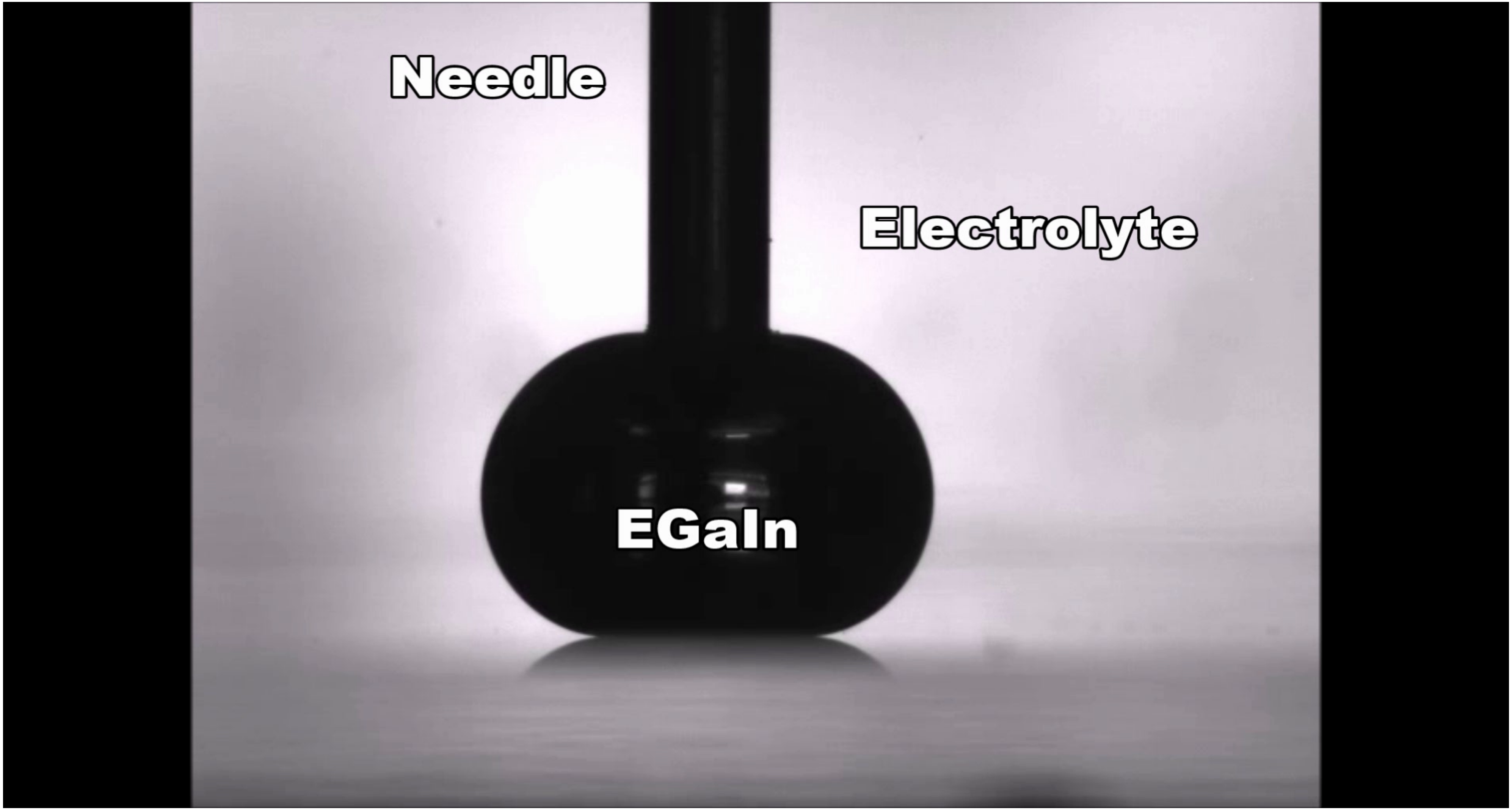
What is eGaIn?



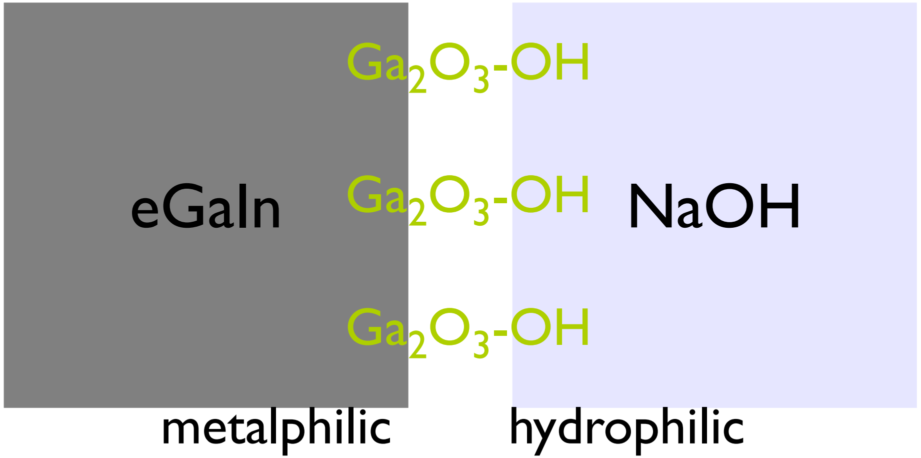
more at Michael Dickey's YouTube Channel
https://youtu.be/ql3pXn8-sHA

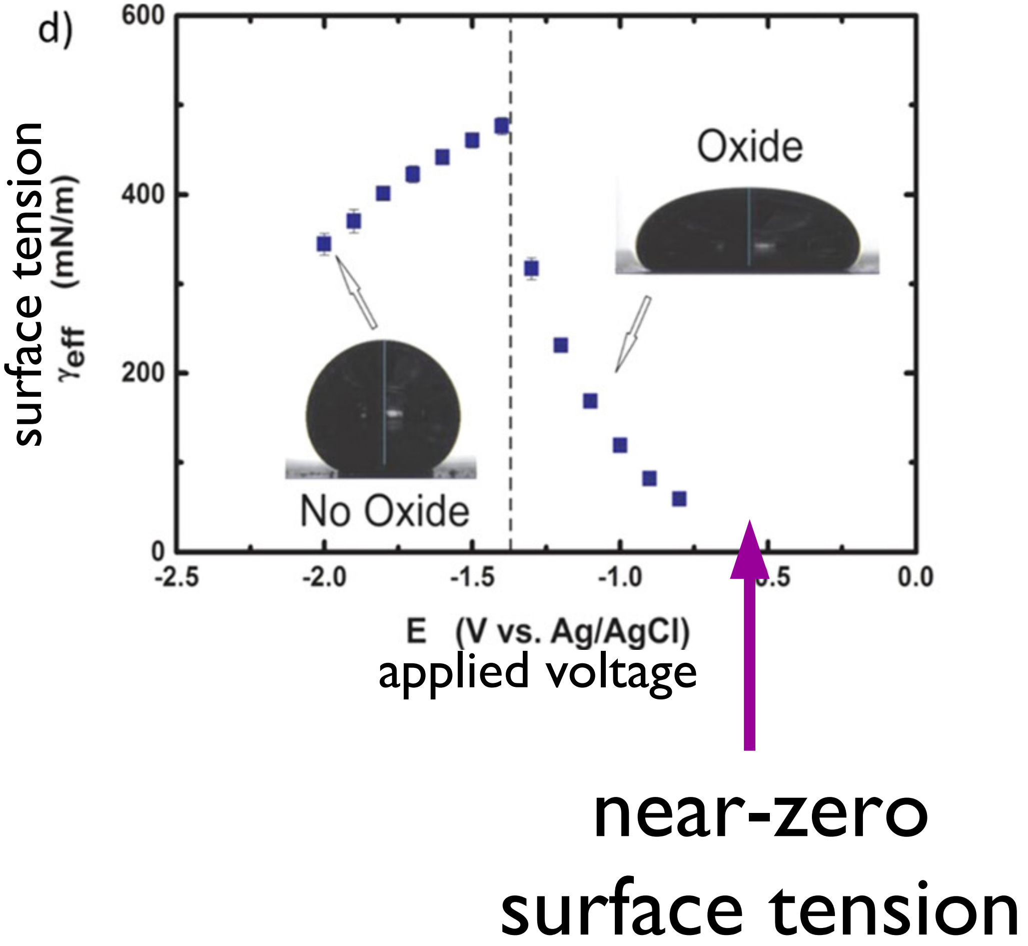
- eutectic gallium-indium (3:1 by weight)
- melts at 15 ºC
- oxide skin (Ga_2O_3) allows droplets to
  - hold their shape
  - ... but oxide dissolves in acid/ base


HCl 1M


Needle
Electrolyte
EGaIn

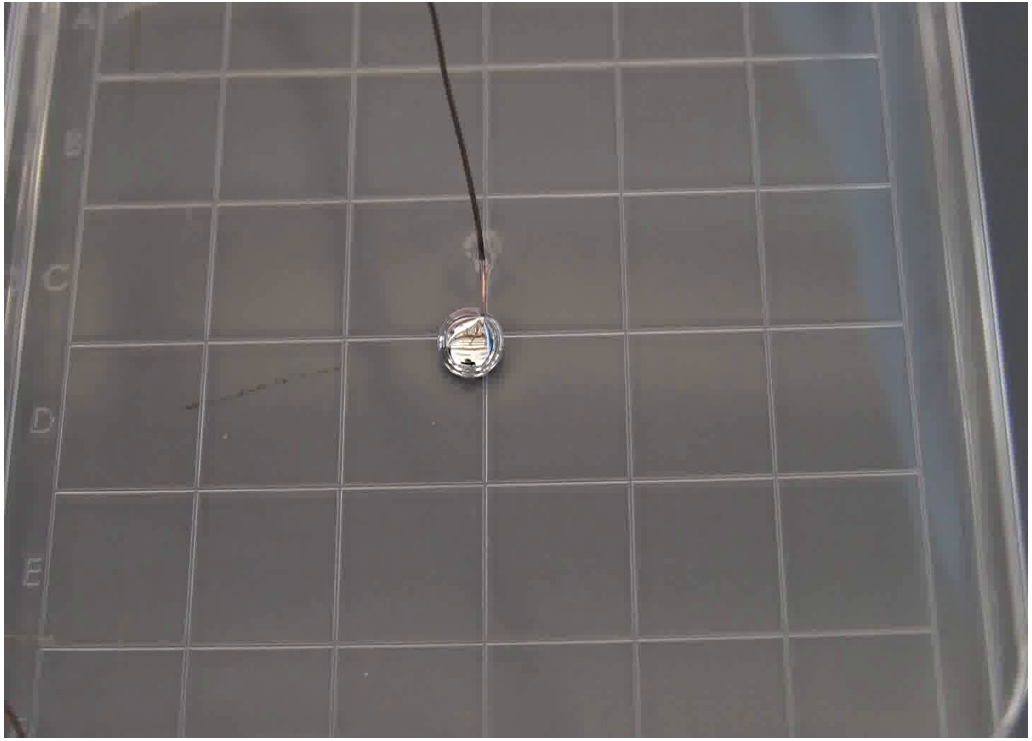
Oxides can act as surfactants

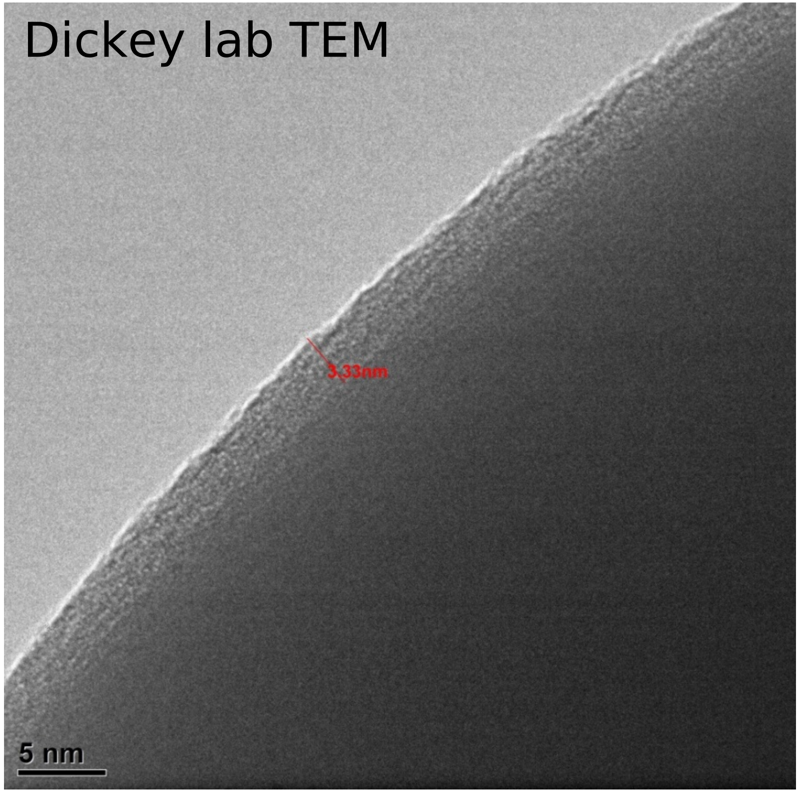


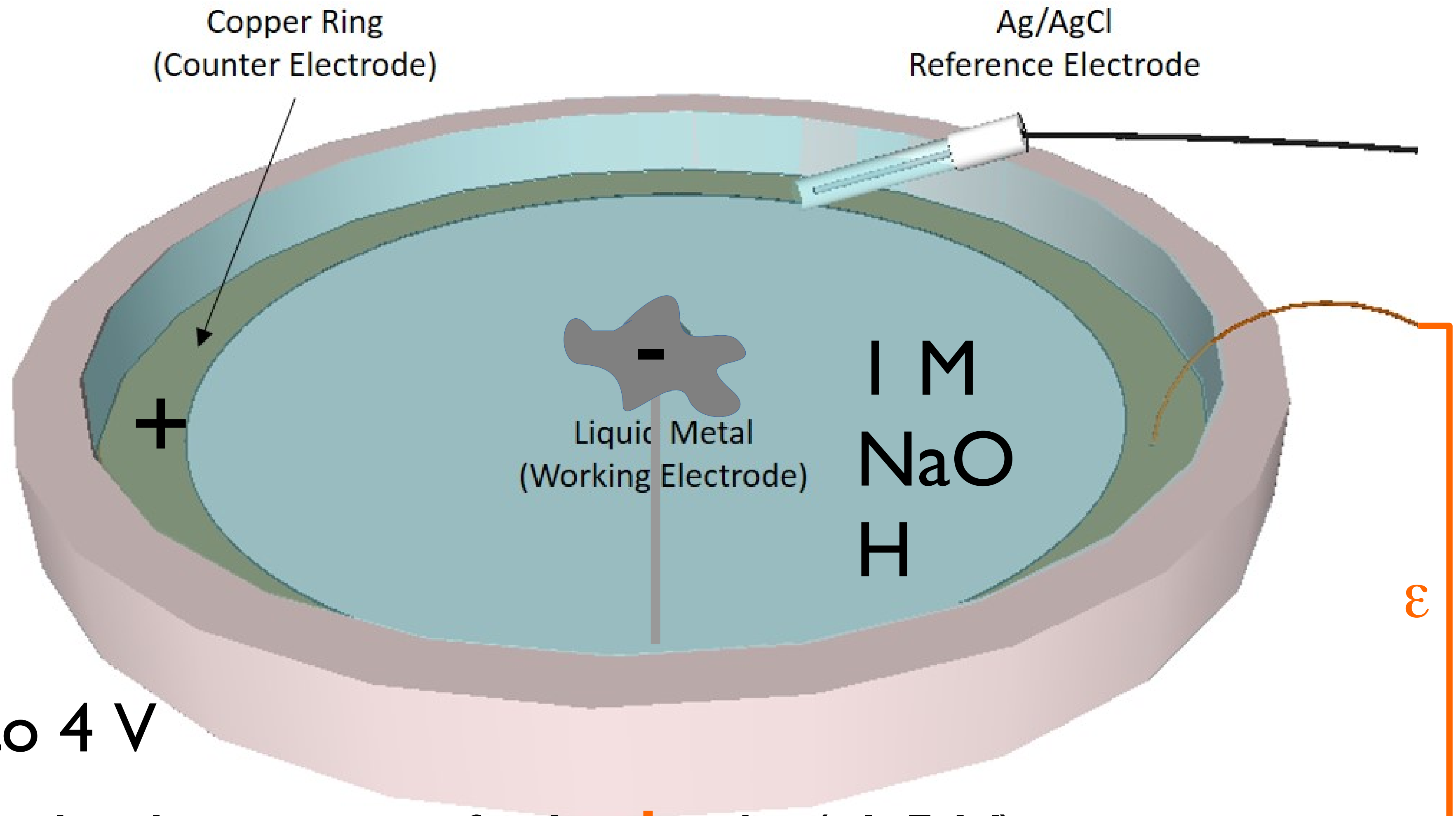


Khan, Eaker, Bowdon, Dickey. *PNAS.* (2014)

Formation of oxide: shiny → matte

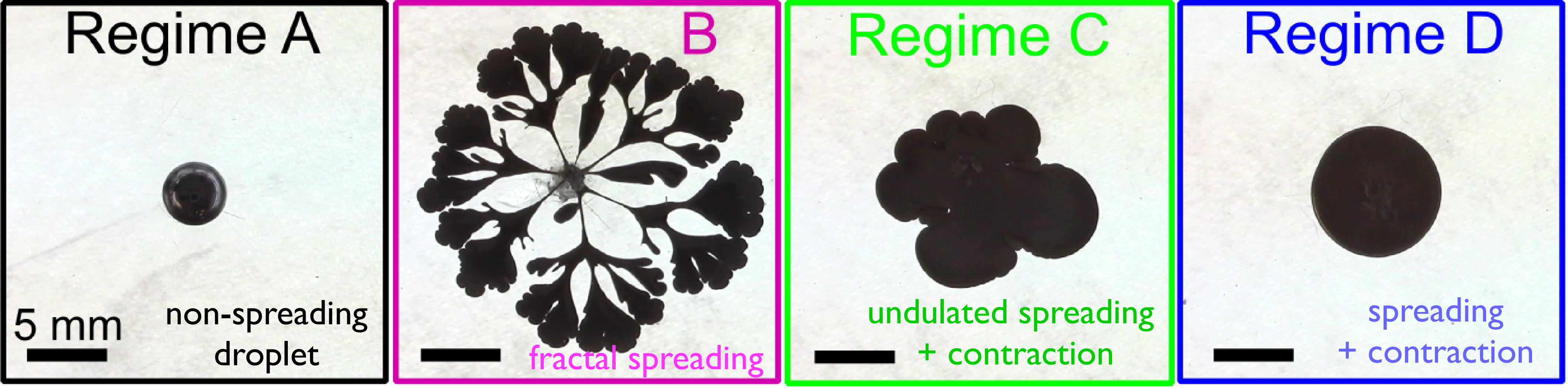


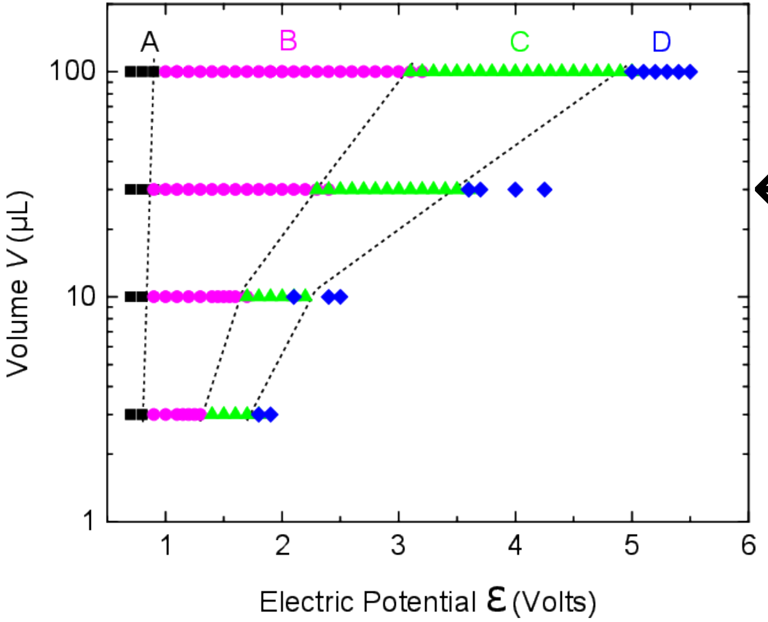




ε = -1 to 4 V

measured relative to ref. electrode (-1.5 V)



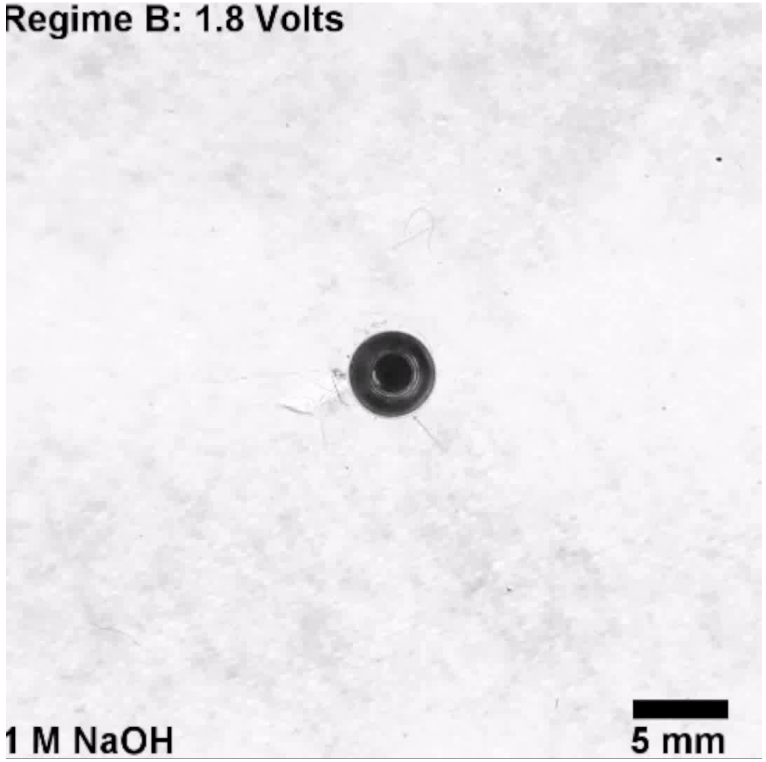


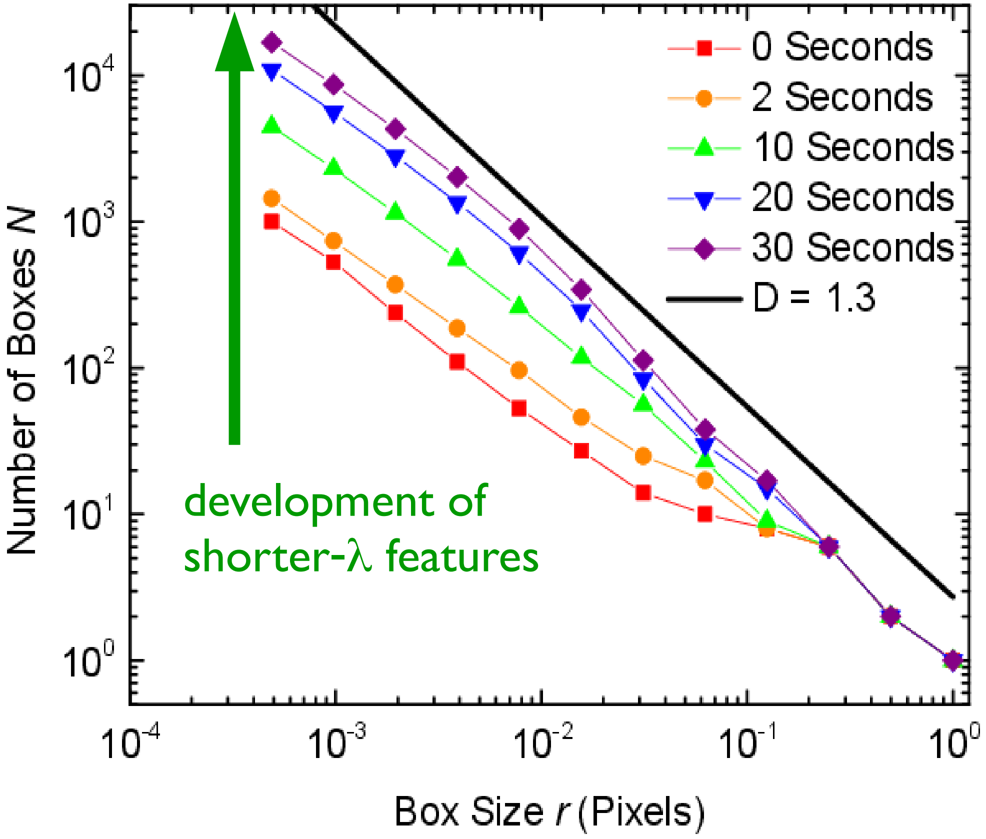
← V = 30 μL

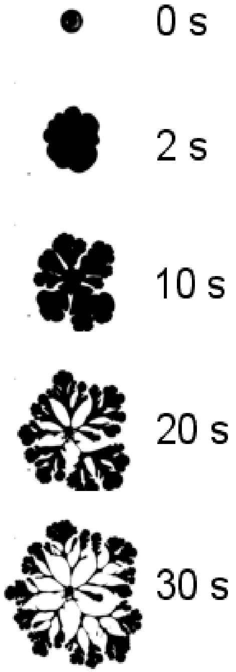
Eaker, Hight, O'Regan, Dickey, Daniels. *PRL* (2017)

Fractal Dimension

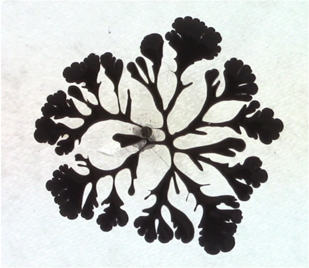
Hausdorff box-counting $$D = \lim_{r \to 0} \frac{\log N(r)}{\log(1/r)}$$



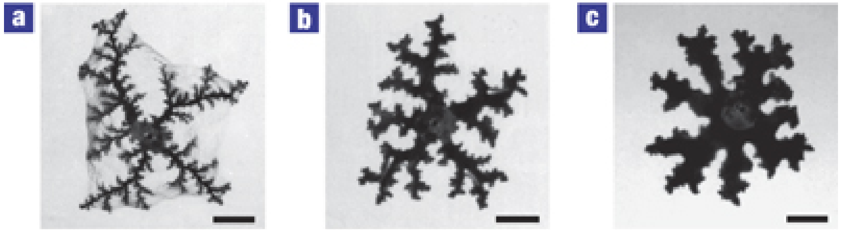




Viscous fingering?



- when a less viscous fluid displaces a more viscous one
- even works at zero surface tension



⇐ granular

Cheng et al. *Nature Physics* (2008)

⇓ miscible liquids

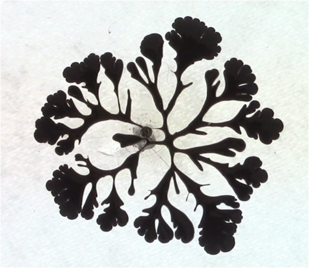
Bischofberger et al. *Nat. Comm* (2014)

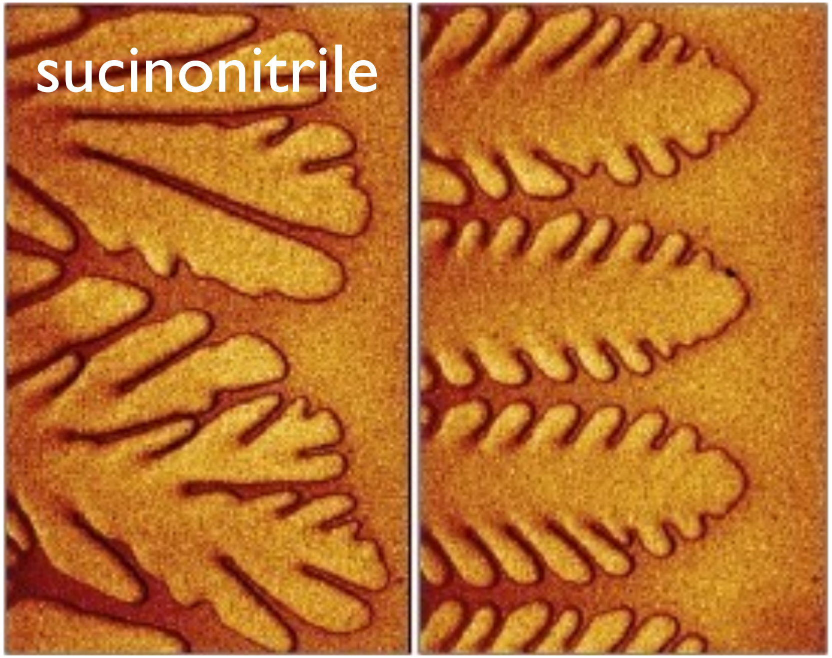
- … but viscosity of eGaIn is only 2x that of water
- … and D_{vf} = 1.7 is larger than observed D = 1.3

Directional solidification?

(a.k.a dendritic growth)

measured values: D_{DS} = 1.2 to 1.7

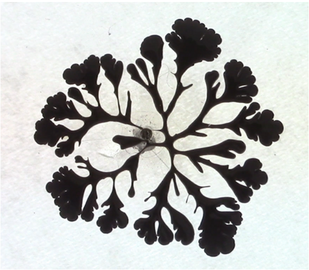


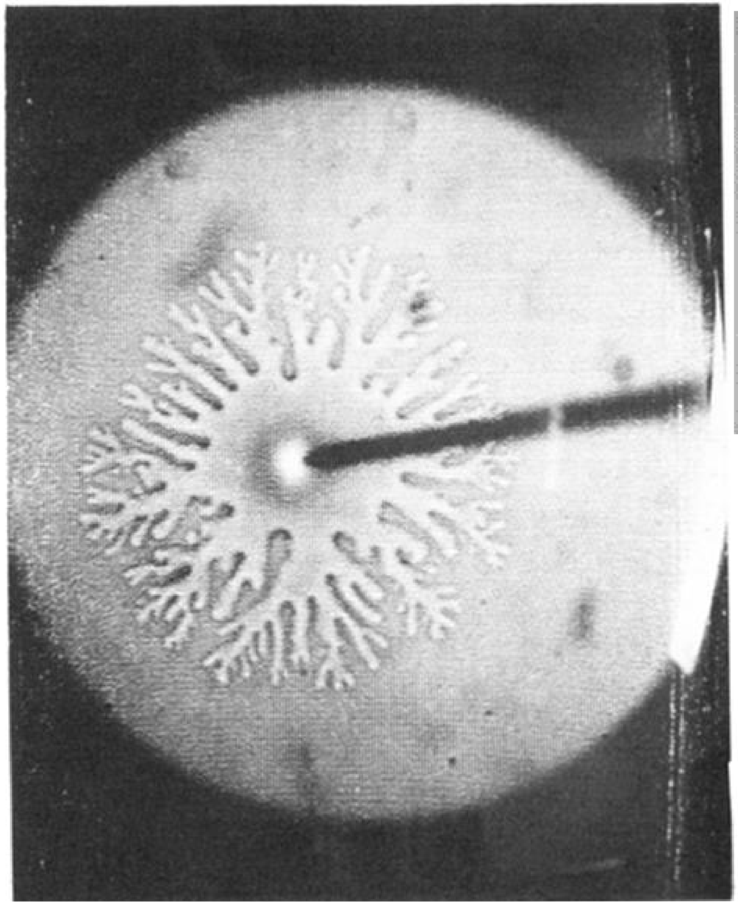


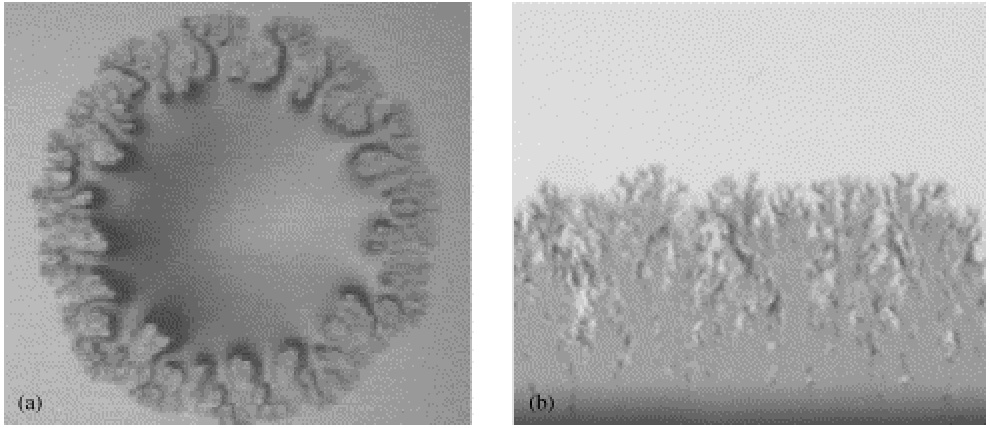
Utter, Ragnarsson, Bodenschatz.
PRL (2001)

Genau, Freedman, Ratke.
J. Crystal Growth (2013)

Surfactant-driven fingering?







⇑ $C_{12}E_n$ in ethylene glycol

Cachile, Albisua, Calvoa, Cazabat. *Physica A* (2003)

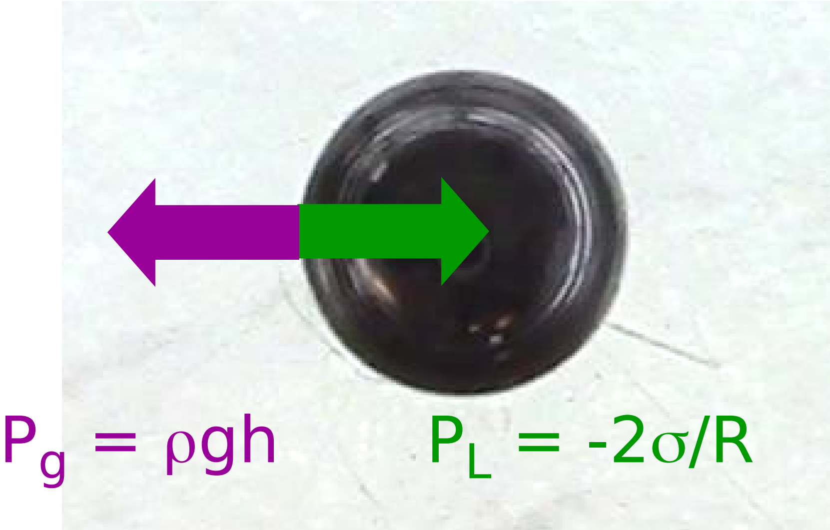
⇐ aqueous surfactant (AOT)

Troian, Wu, Safran. *PRL* (1989)

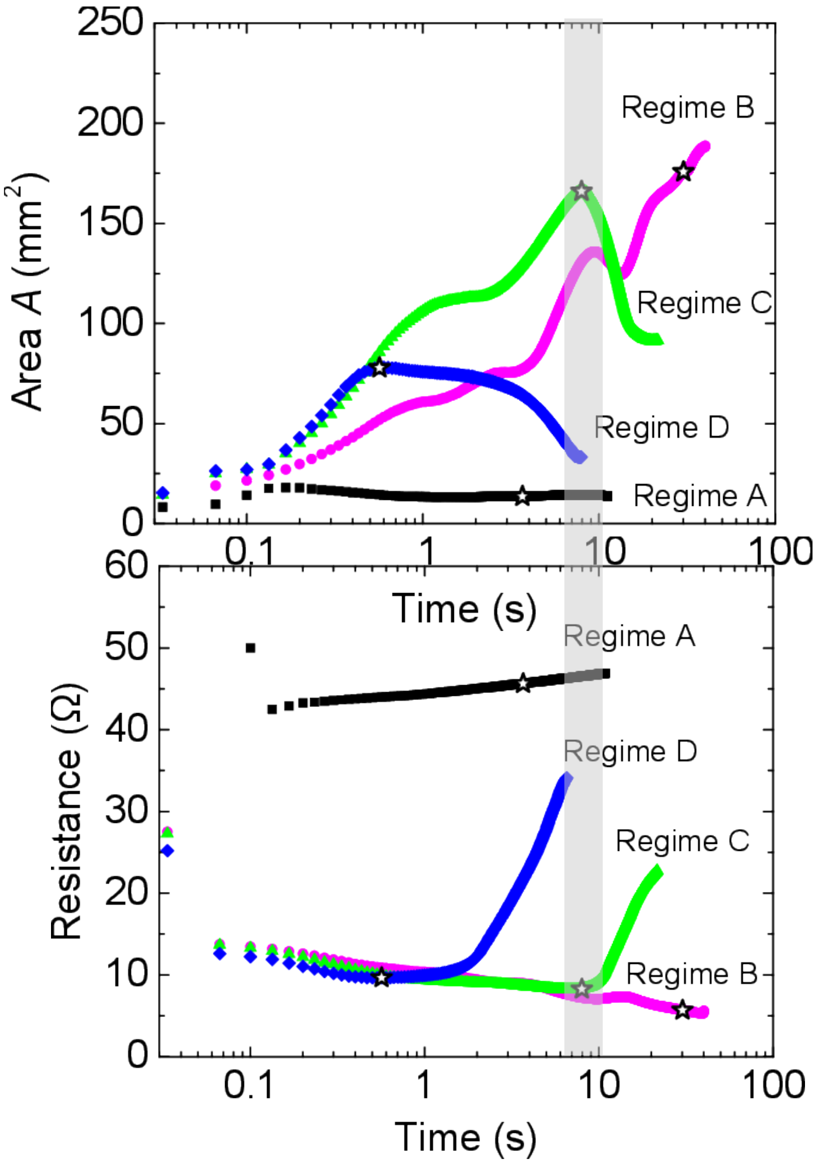
- caused by Marangoni effects (surface tension gradients)

low voltages: no spreading

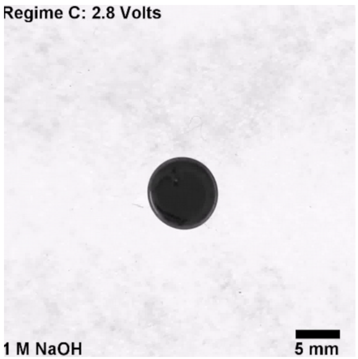
- oxide not visible (shiny surface) → high σ
- equilibrium: gravity and surface tension balance



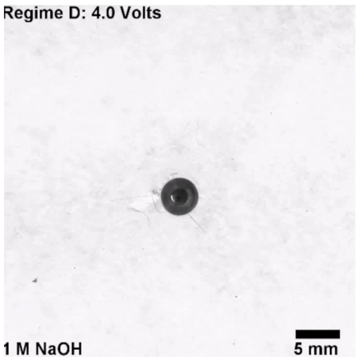
- as voltage ε increases above ~ 1 V → σ decreases → gravitational forces dominate → spreading



Regime C



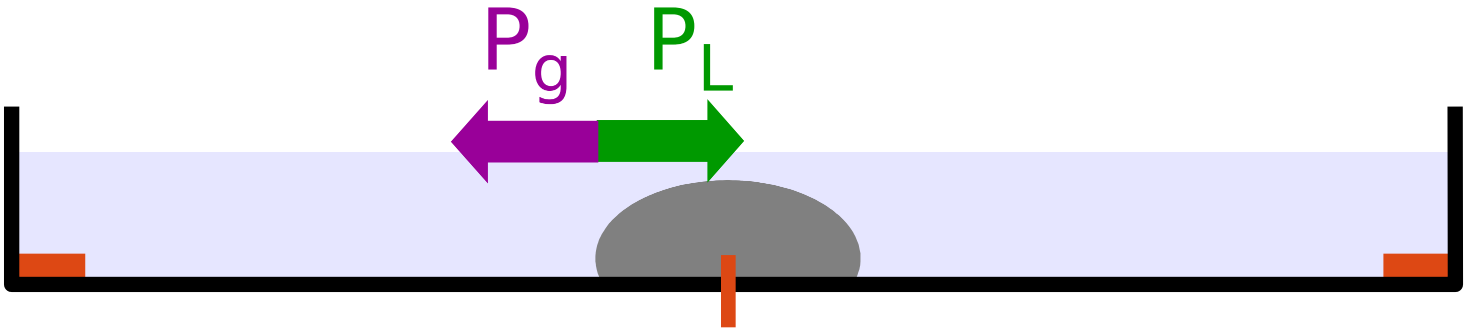
Regime D



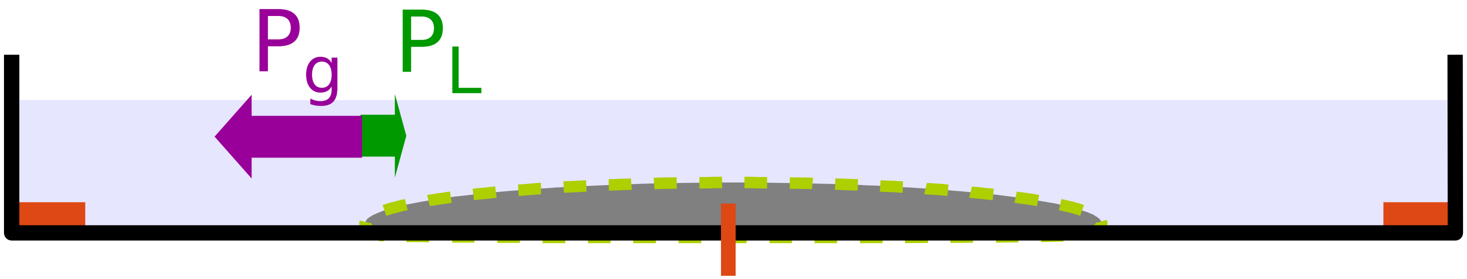
contraction associated with increase in electrical resistance

Eaker, Hight, O'Regan, Dickey, Daniels. *PRL* (2017)

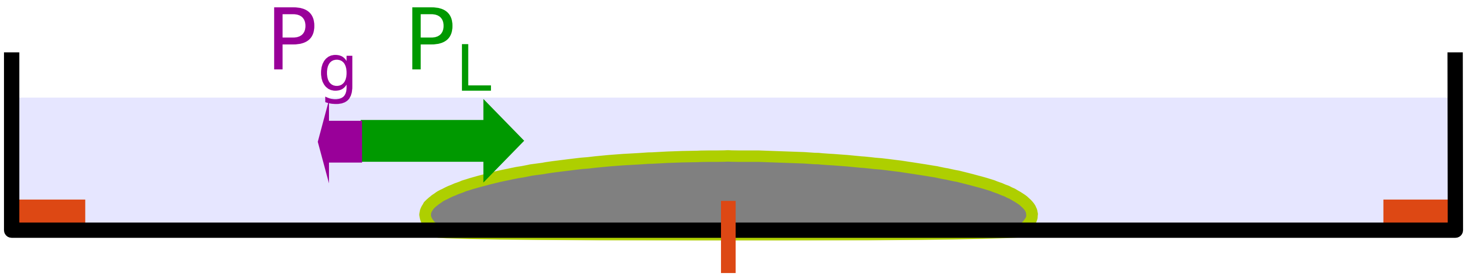
Regime A:
bare metal
$\sigma \sim 500$ mN/m

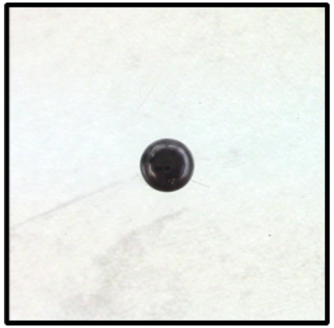


Regime B:
thin oxide surfactant
$\sigma_{eff} \rightarrow 0$



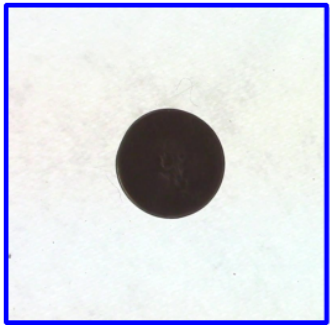
Regime C/D:
thick (stiff) oxide
oxidative stresses
due to ion insertion
$\sigma_{eff} > 30$ mN/m



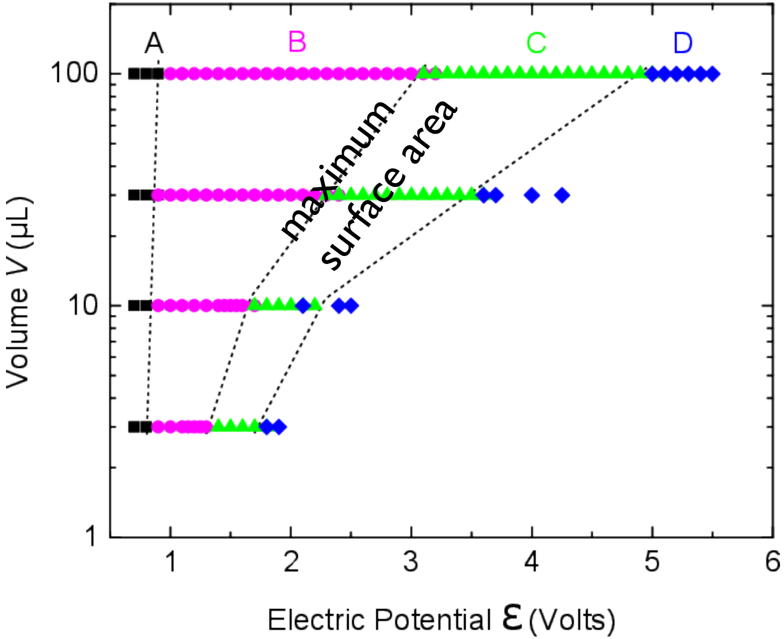


bare metal:
σ large

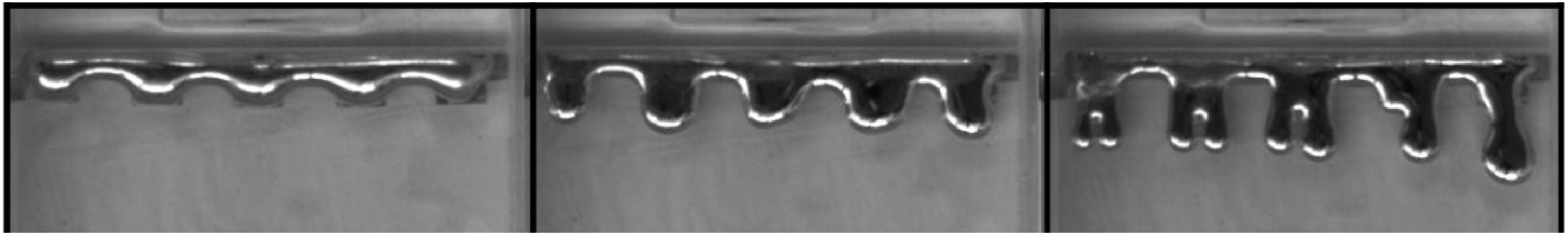
oxide surfactant
σ → 0

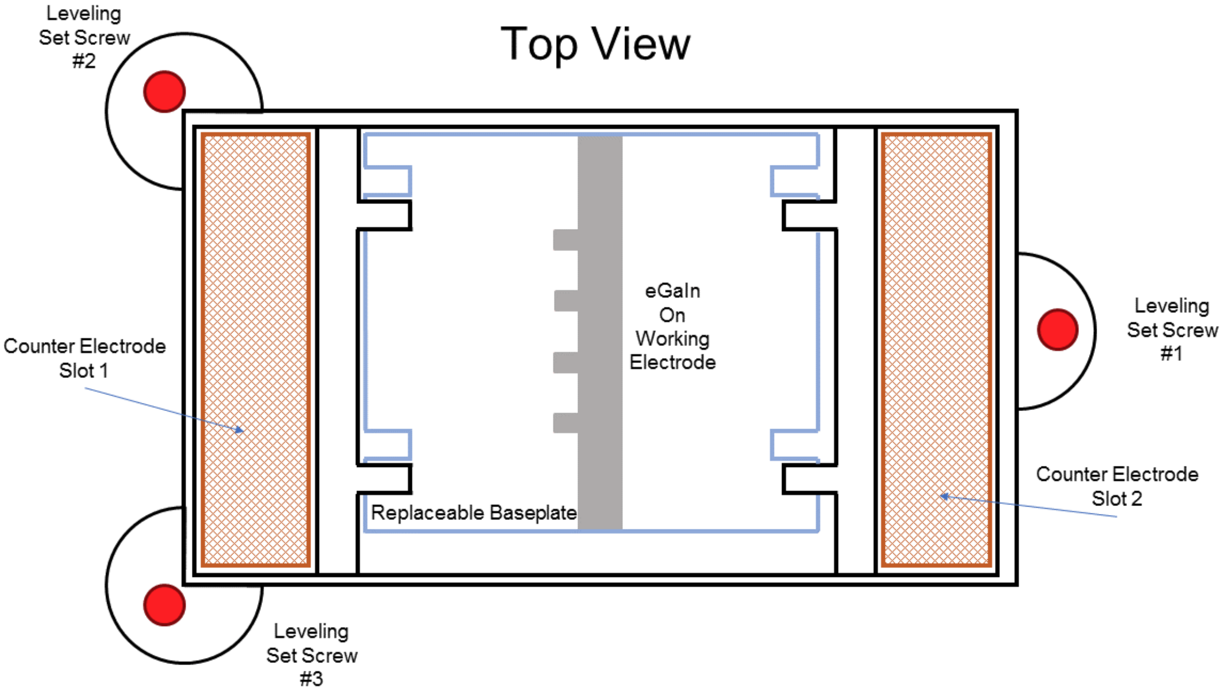


oxidative stress
(ion insertion)

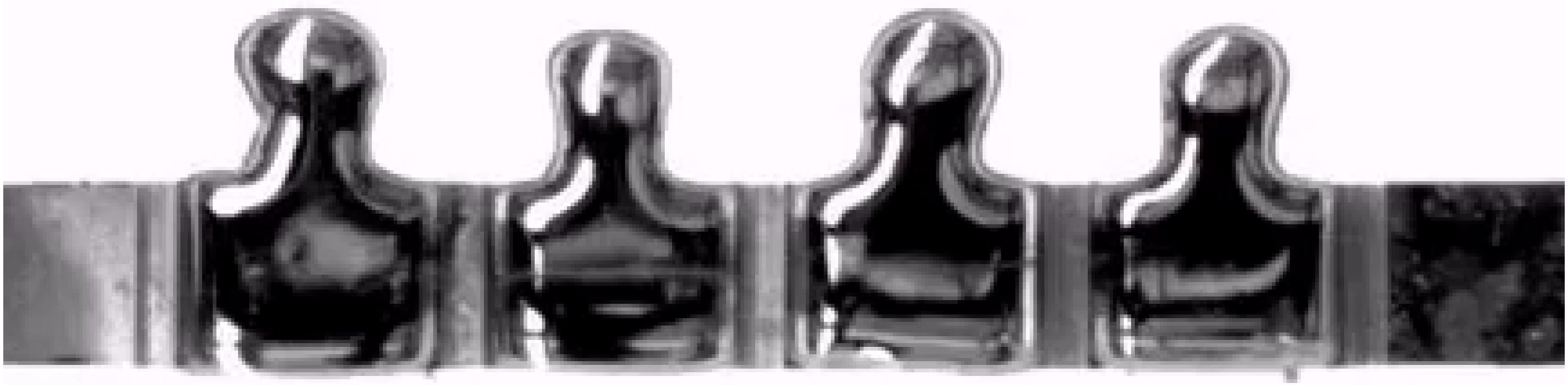


Testing the Marangoni-instability hypothesis

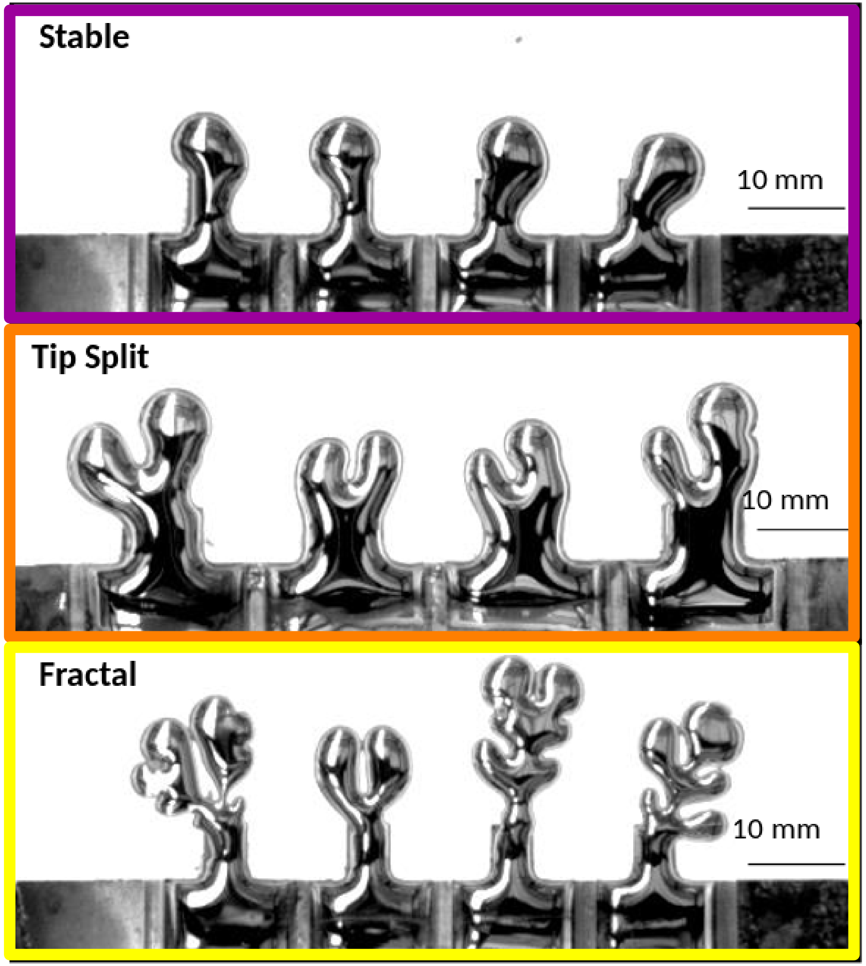


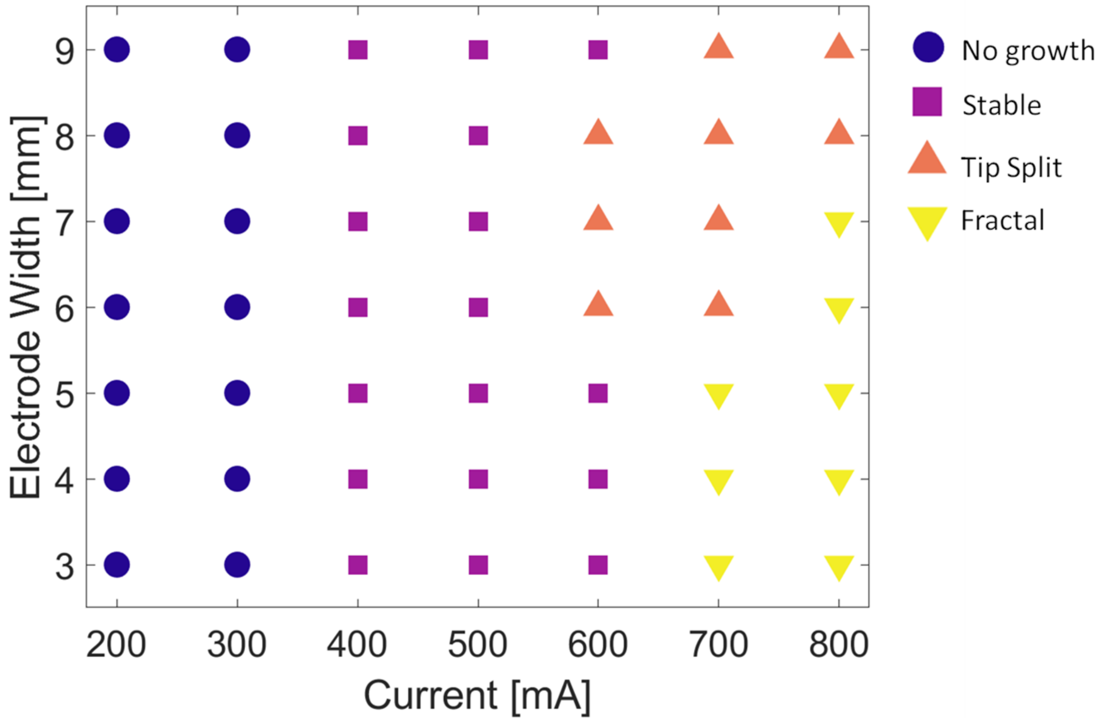


Keith Hillaire



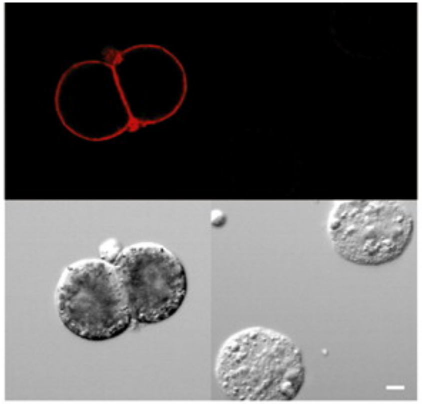
Phase Diagram



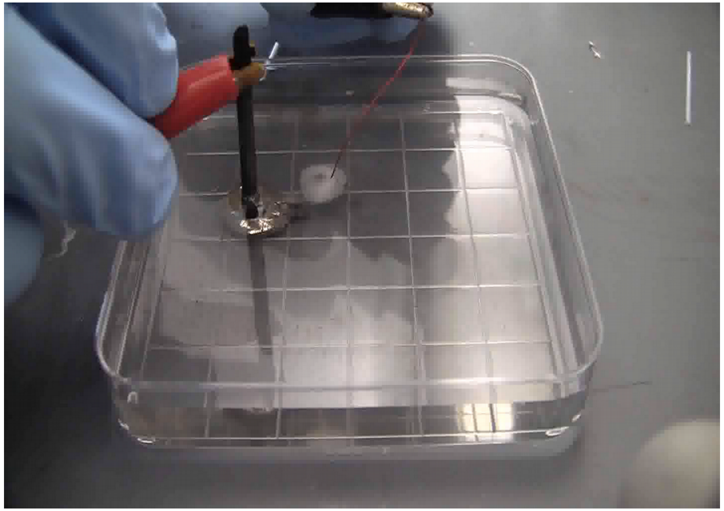


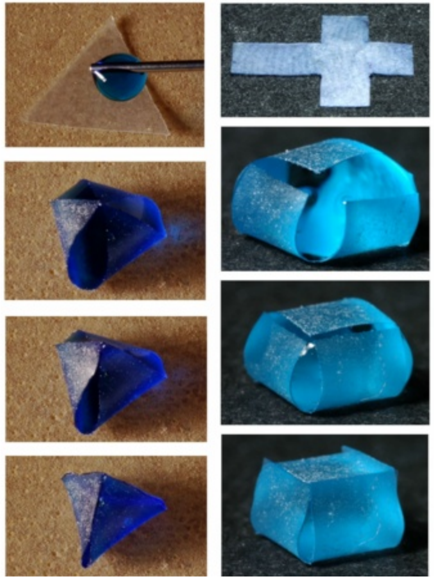
Deformation of Soft Materials

- biology: cell/tissue shape controlled by adhesion, elasticity and surface tension
- engineering: exploit interactions between elastic and capillary forces

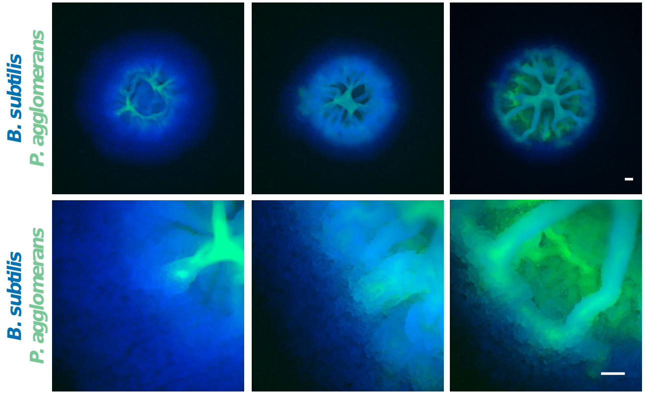


de Vries et al. *Development* (2004)

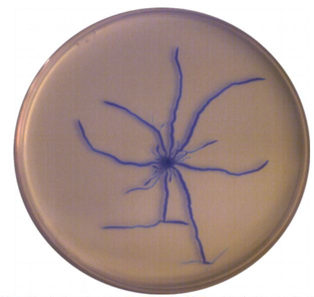
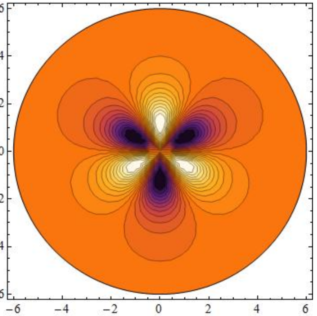


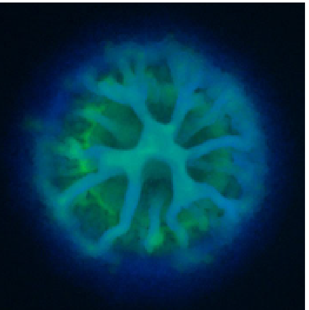


Bico, Roman (ESPCI)



Yannarell, Grandchamp, Chen, Daniels, Shank. *J. Bacteriology* (2019)

Conclusions

- fascinating dynamics as radial symmetries break during droplet spreading
- droplets on gels: competition between elasticity and surface tension controls fracture process
- passivating liquid metals: growth of oxide can reversibly stabilize or destabilize spreading

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