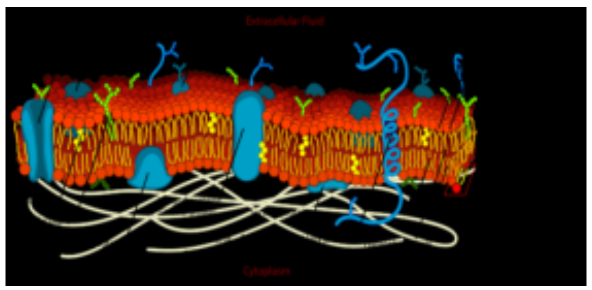
ISSP soft matter 2010

Interfacial microrheology of phospholipid monolayers at the air/water Interface

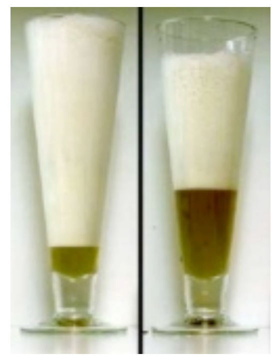
Siyoung Choi
K. Kim, J. Zasadzinski, T. Squires
University of California, Santa Barbara

Motivation

Science → Engineering



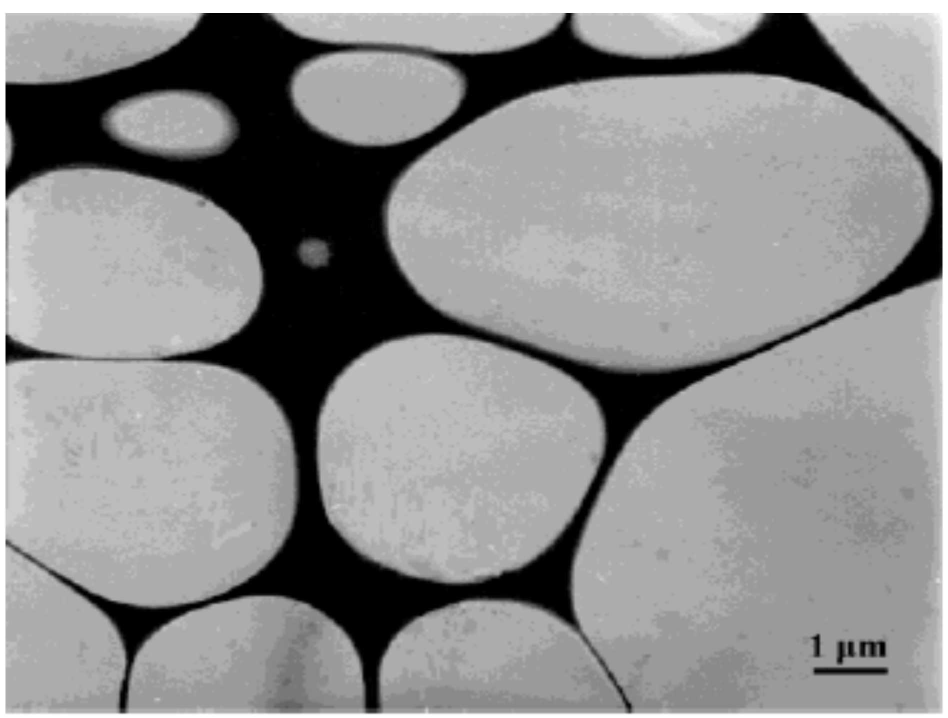
Cell membrane



Foams

Shampoo, detergents, etc.

Coating Process

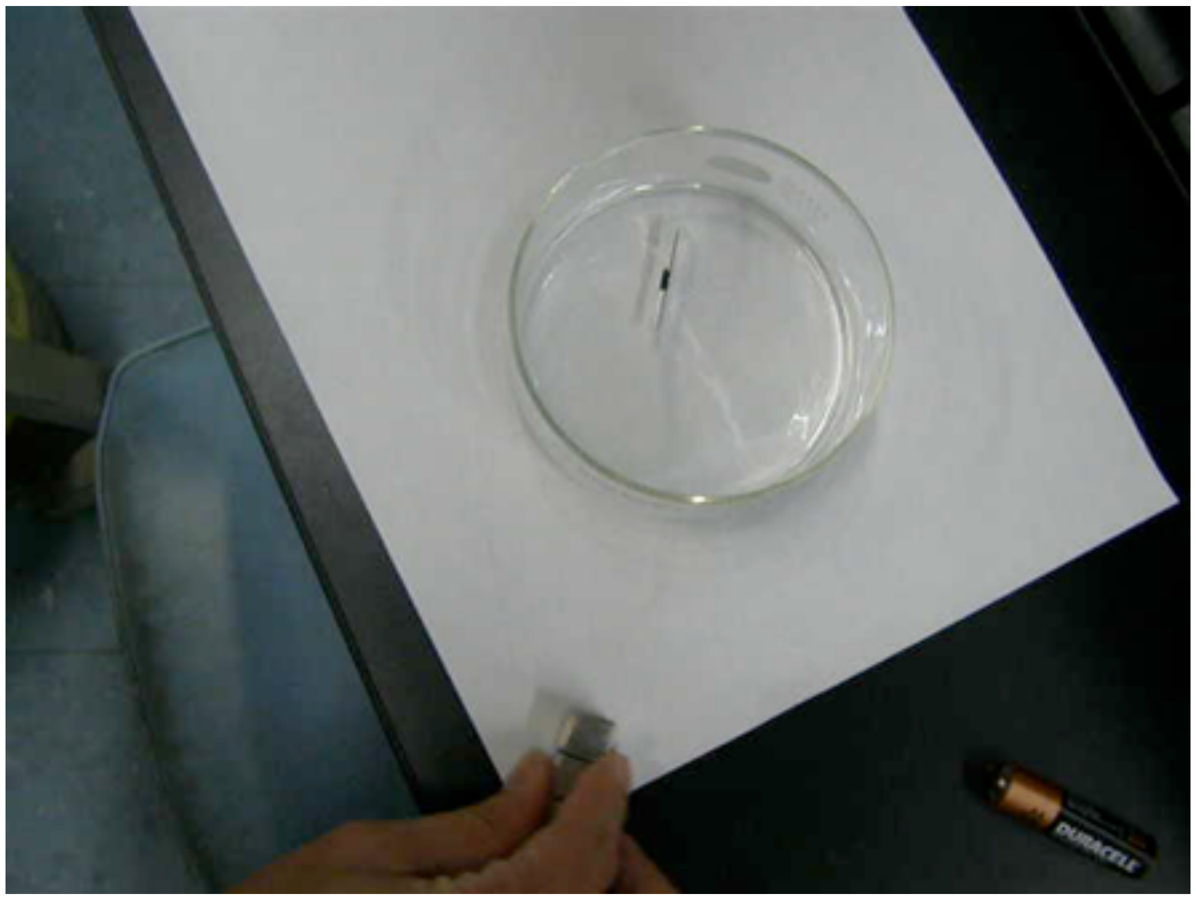


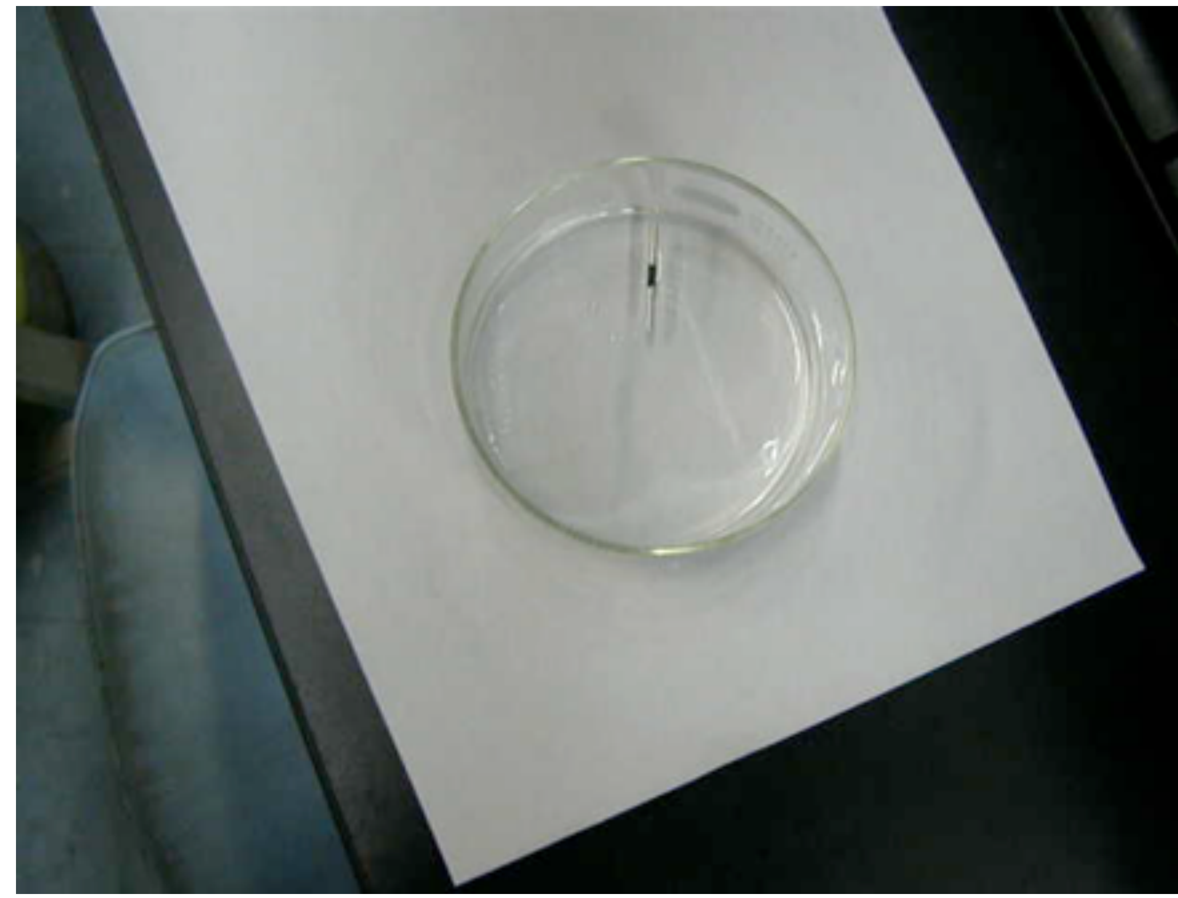
High Internal Phase Emulsion(PS-P2VP)
Kramer group (2003)

Lung surfactants
Zasadzinski group (2003)

Interfacial viscoelasticity

A magnetic needle at the air/water Interface





Interfacial viscoelasticity

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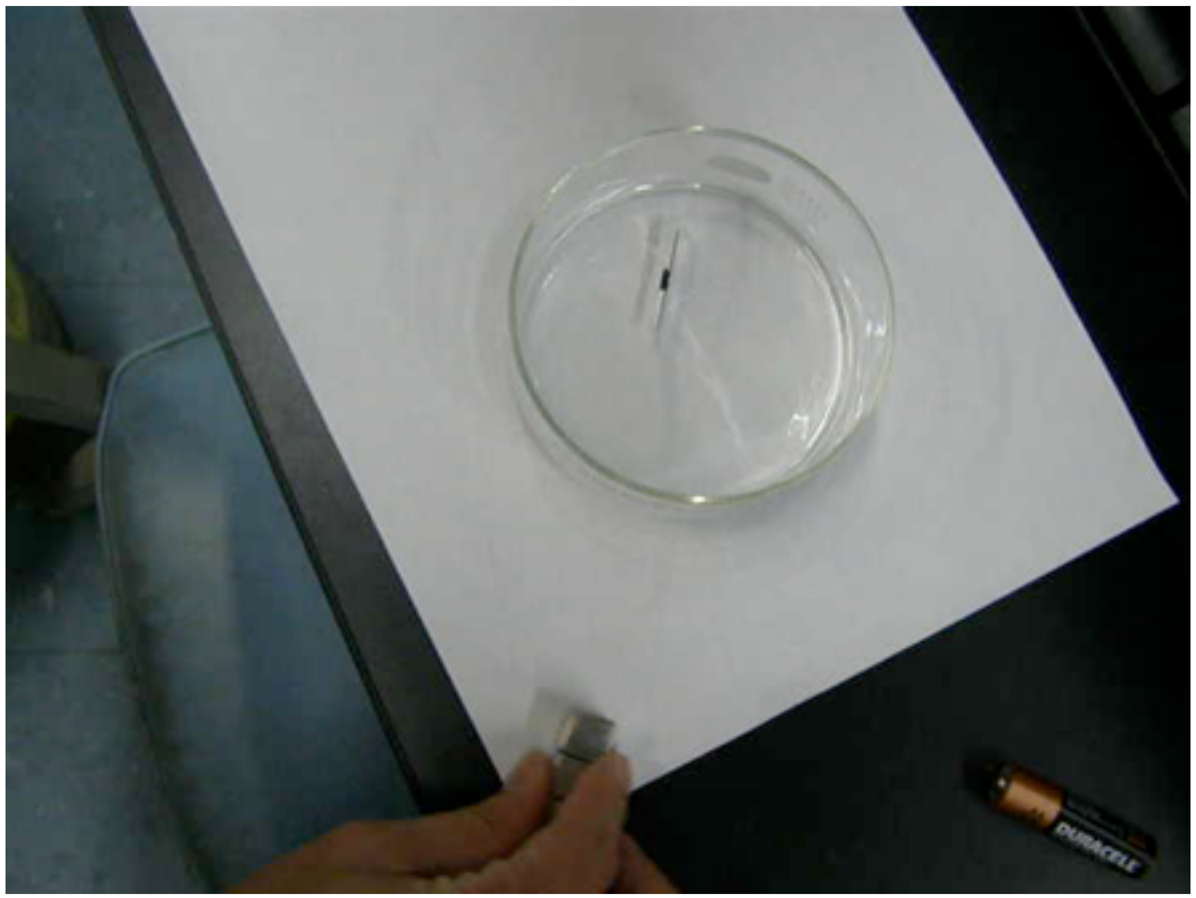
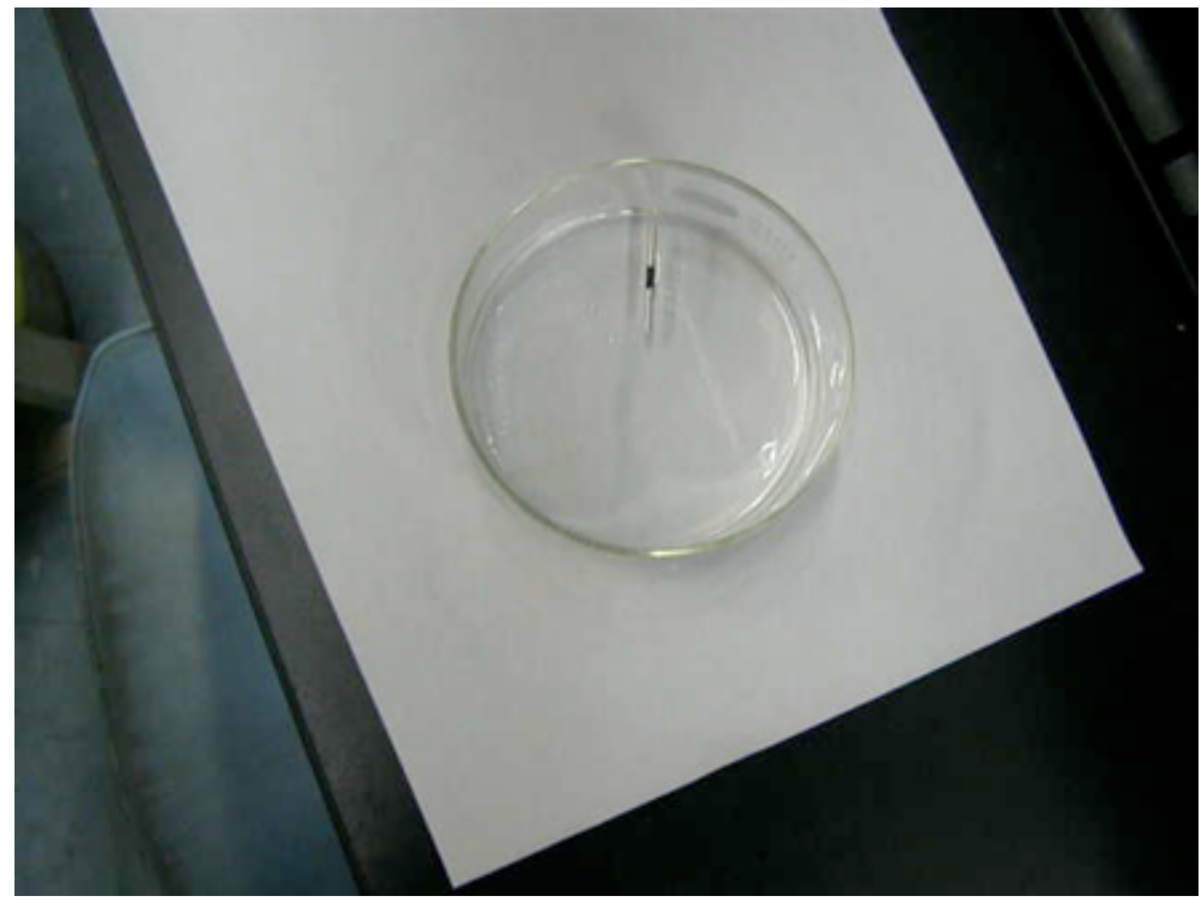




A few drops of water-insoluble surfactants

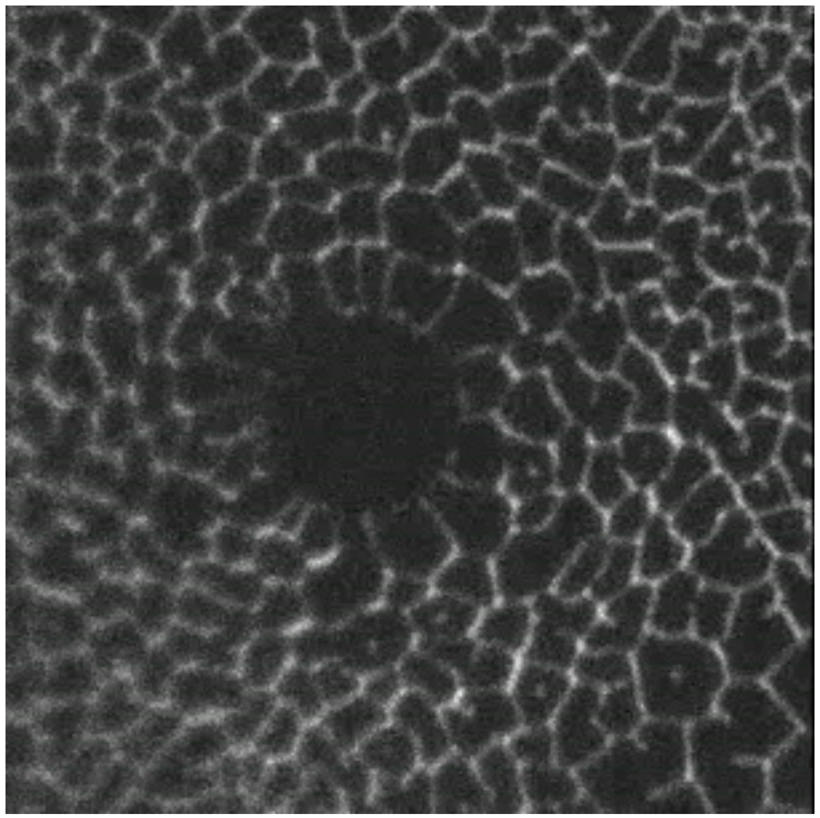
Systems we are working on

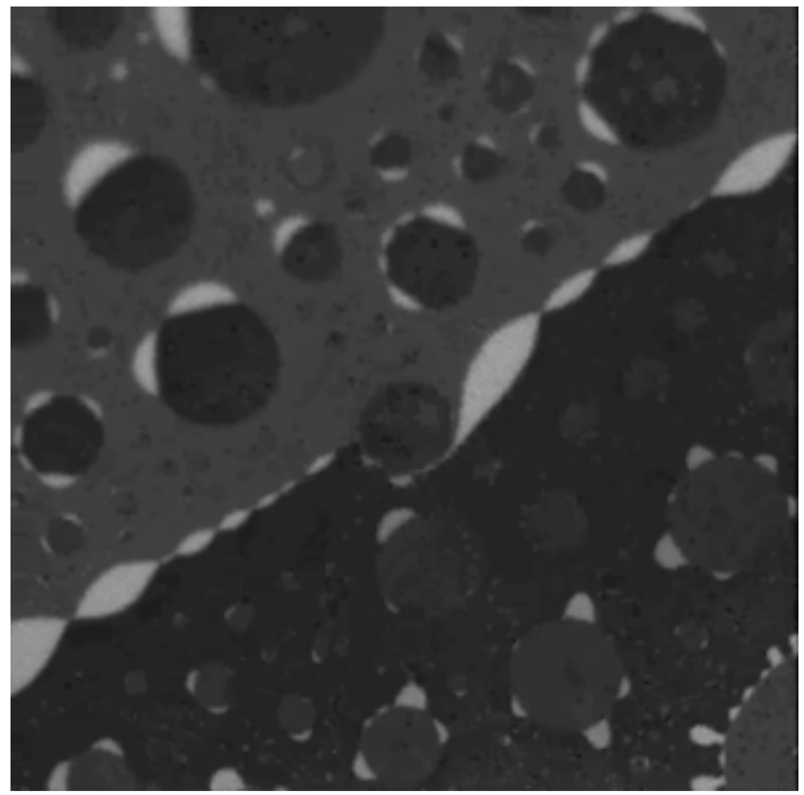
DPPC
(phospholipid)

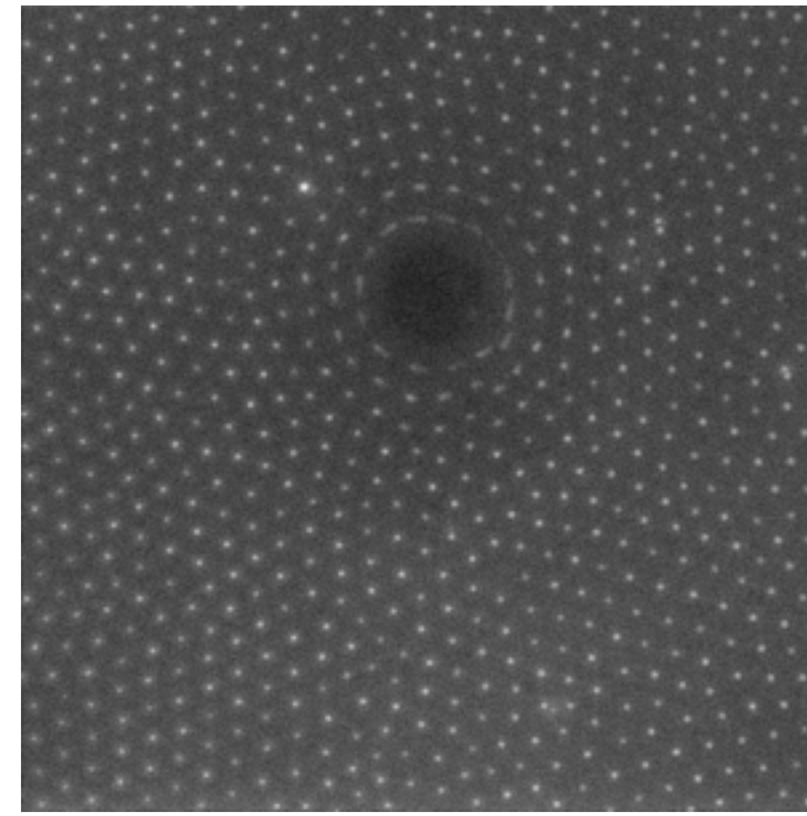
DPPC +Chol
(60:40)

Colloidal crystal
at the oil/water
interface

Systems we are working on







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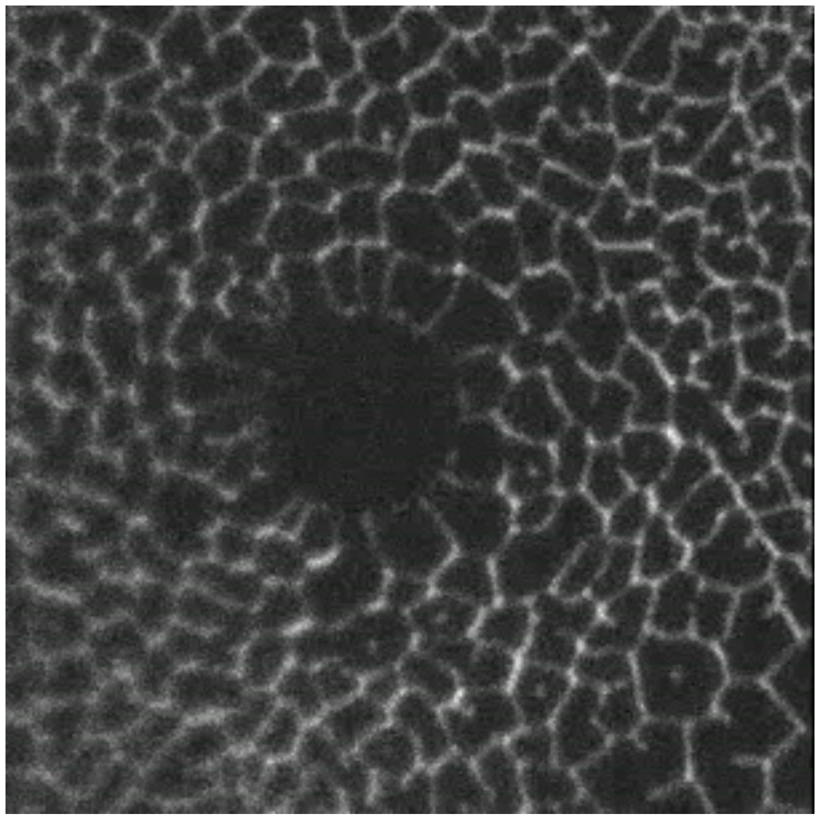

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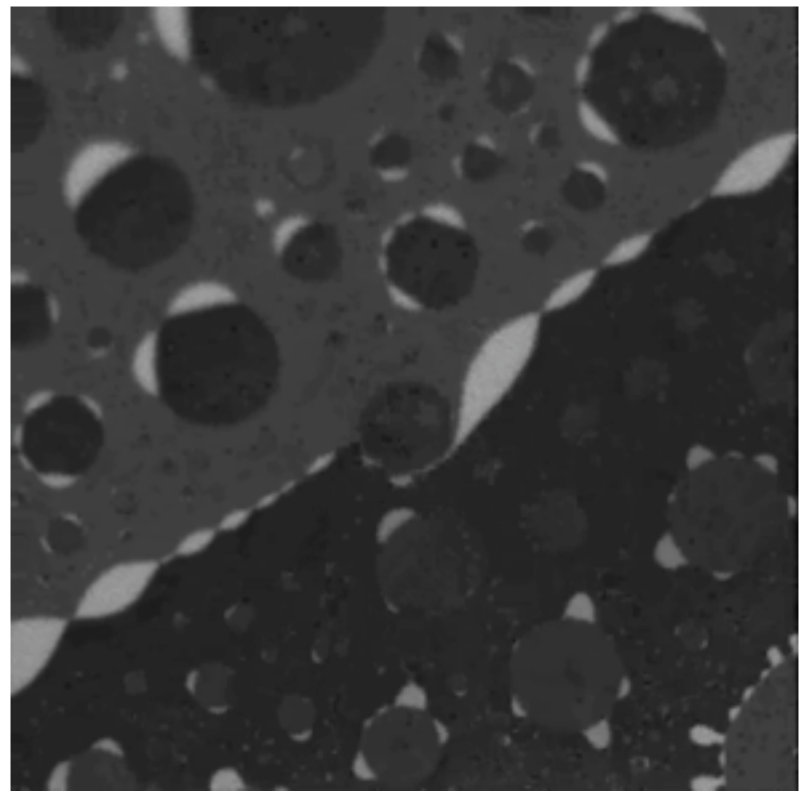

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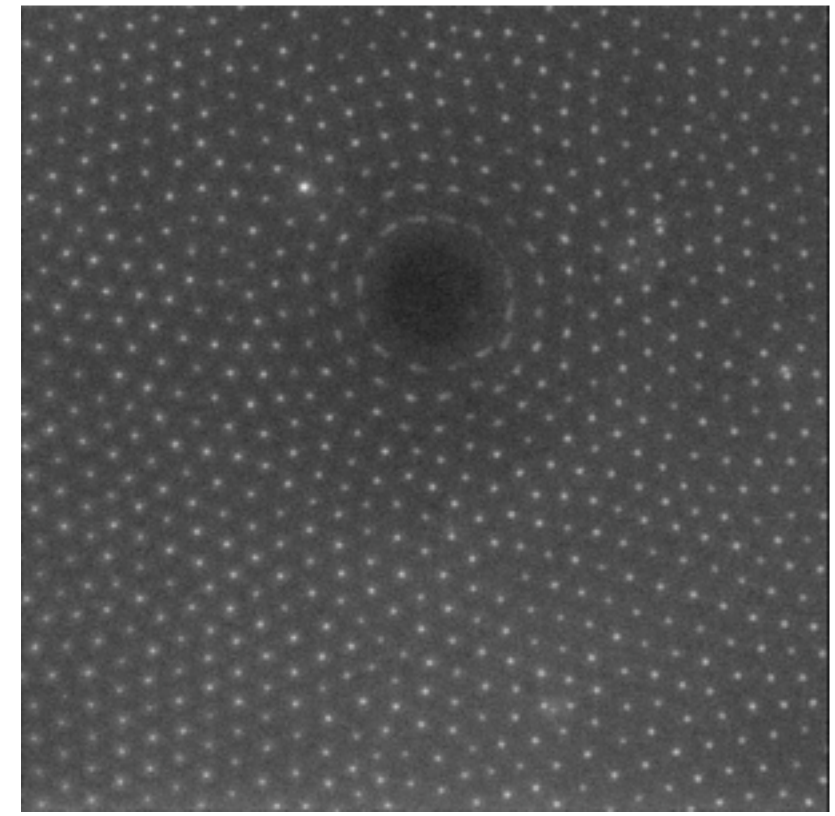

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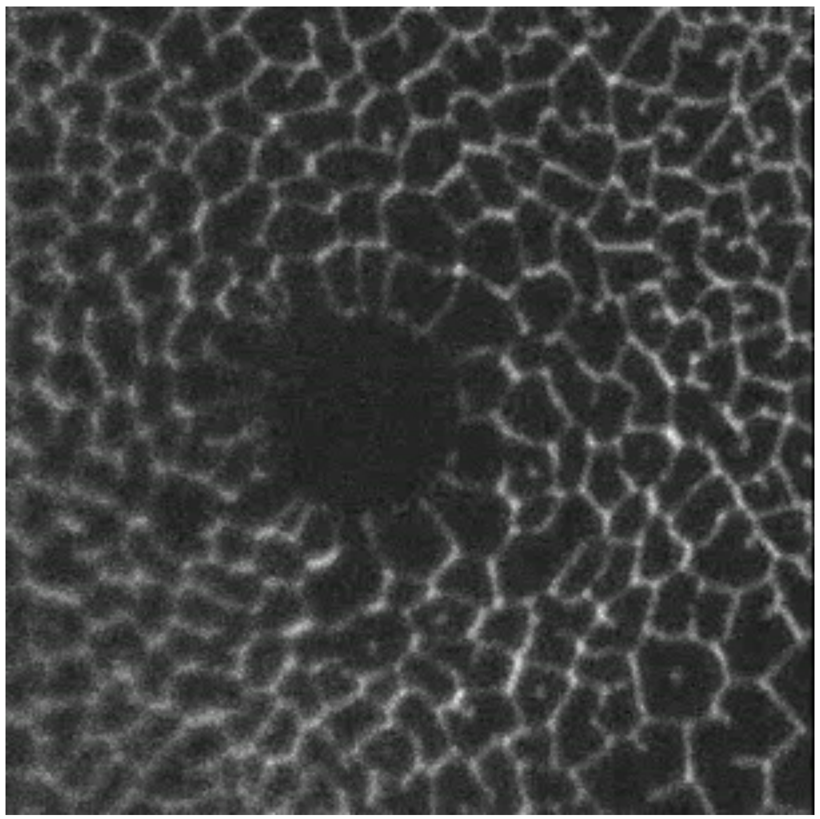

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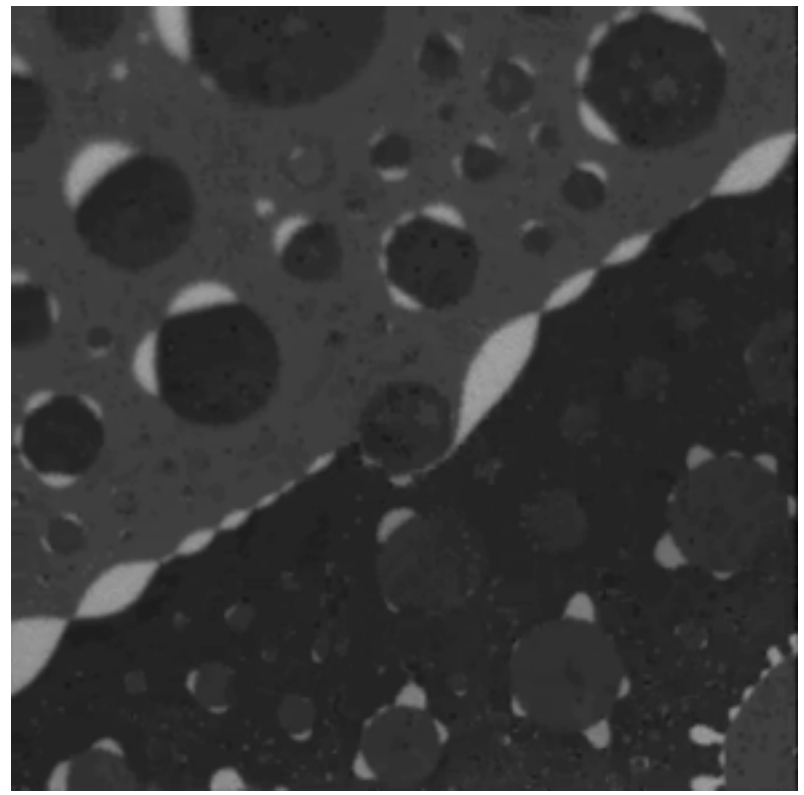

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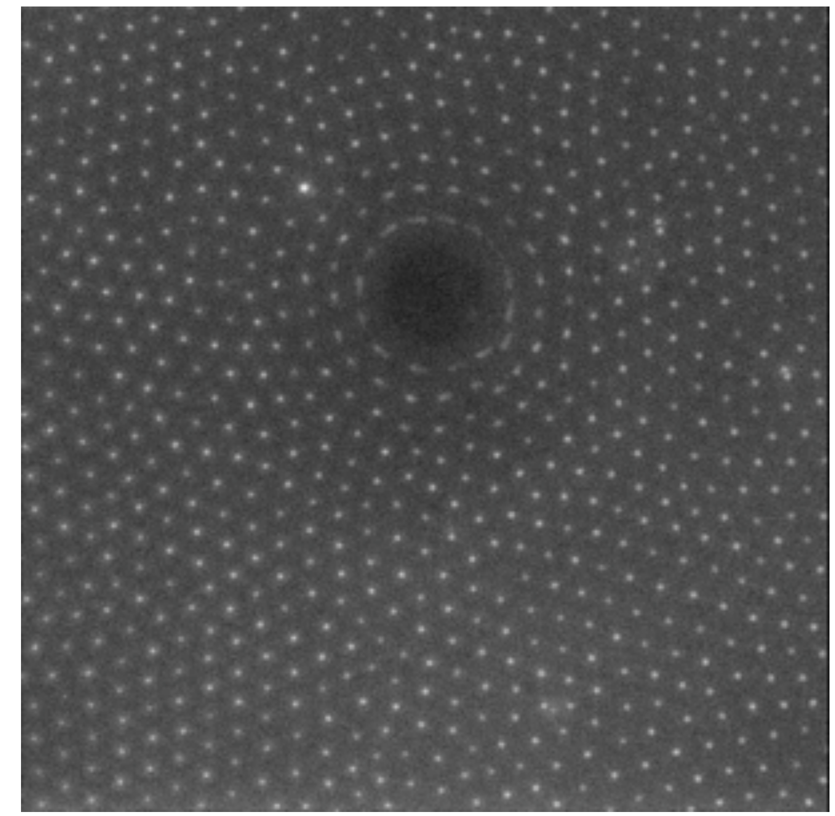
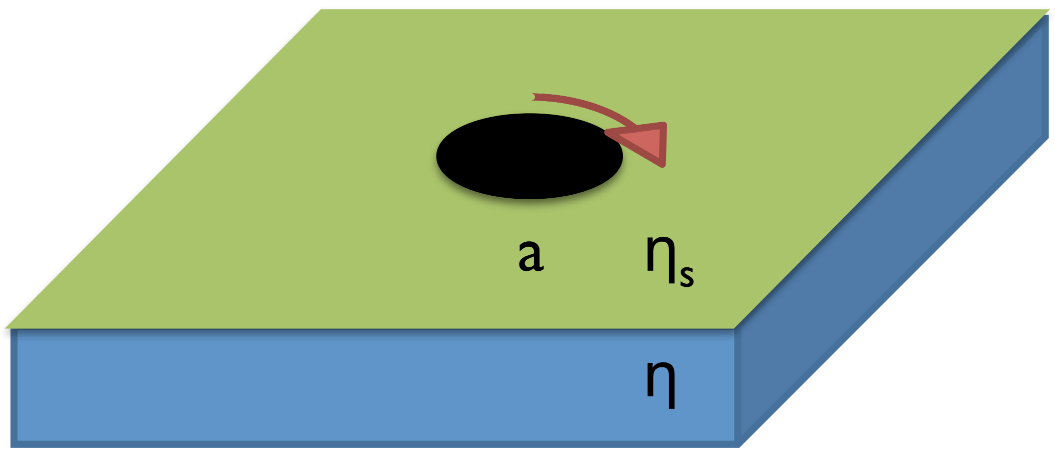


Colloidal crystal
at the oil/water
interface

Viscometry of 2D interfaces



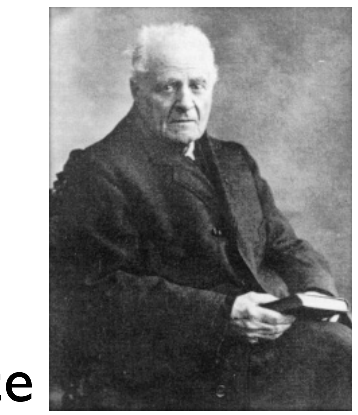
η_s : surface viscosity

η : subphase viscosity

a : disk radius

P : Contact perimeter to 2D surface

A : Contact Area to bulk phase



$$\mathrm{Bo} = \frac{\text{surface drag}}{\text{bulk drag}} = \frac{\eta_s \nabla u P}{\eta \nabla u A} \approx \frac{\eta_s}{\eta a}$$

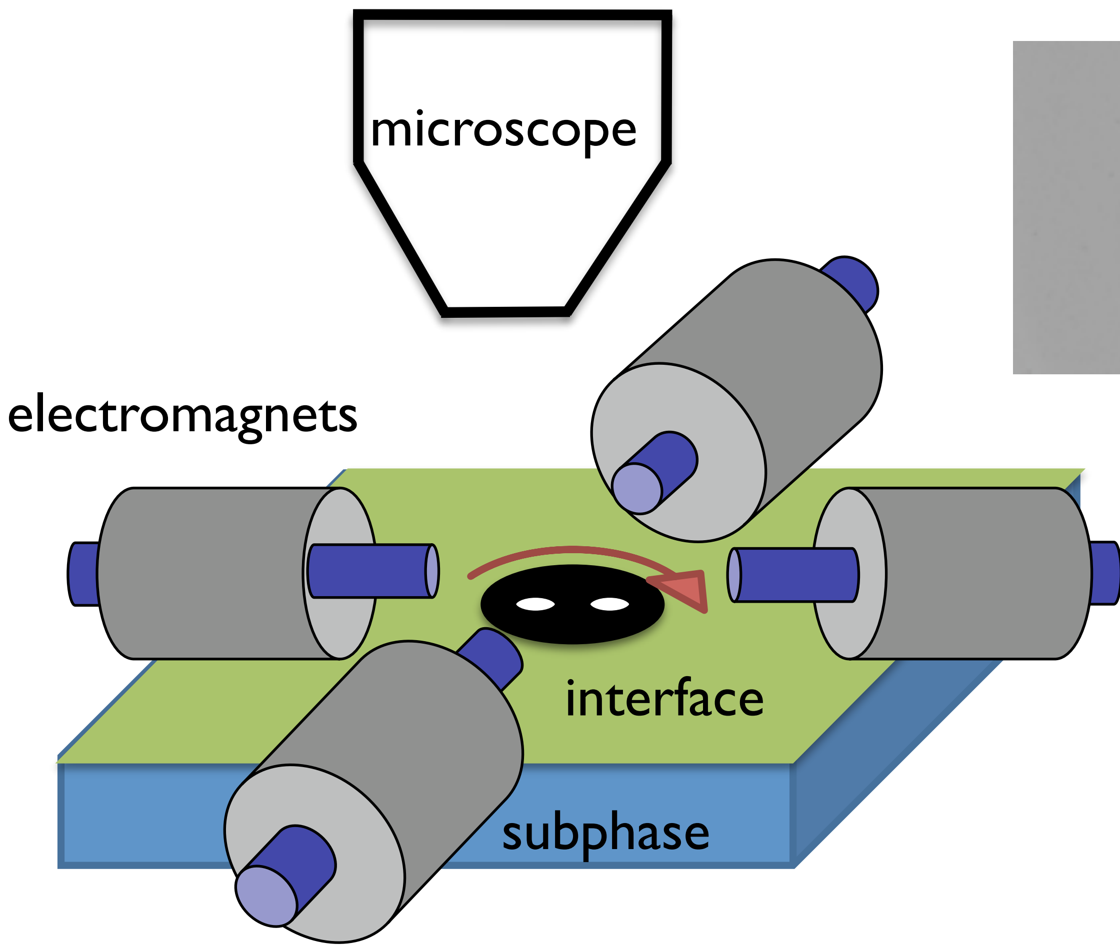
"Boussinesq Number"

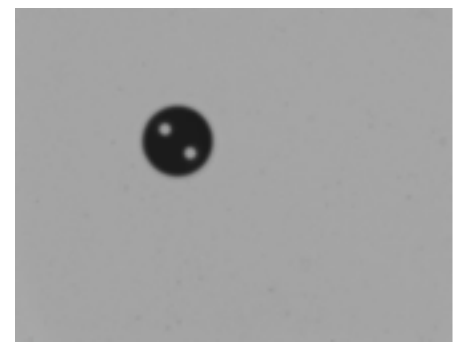
High perimeter/area ratio: higher sensitivity

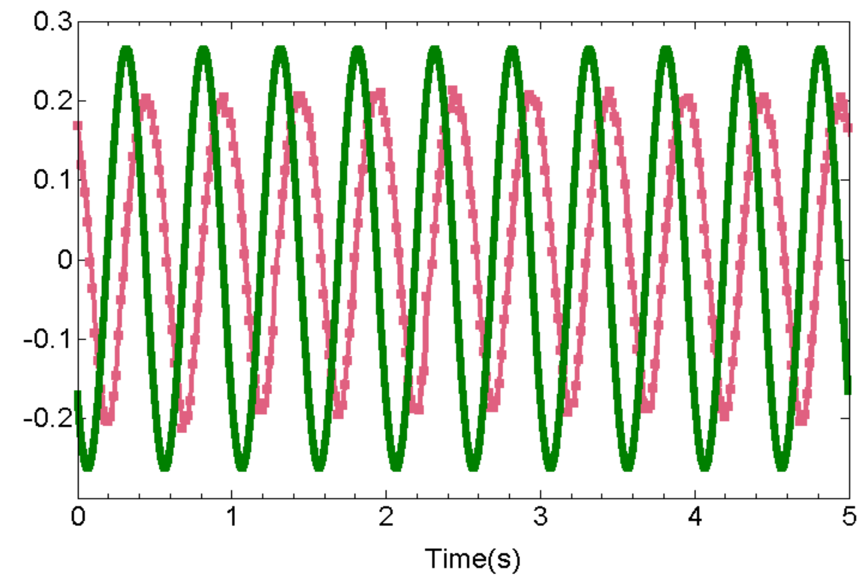
High aspect ratio (e.g. needles - Brooks, Fuller, Vermant, Fischer, Zasadzinski, ...)
Small probes (microrheology - Weeks, Sickert & Rondelez, Fischer, Dai, ...

General Experimental Procedure

Camera → Image analysis → Angular strain(t) (Red)







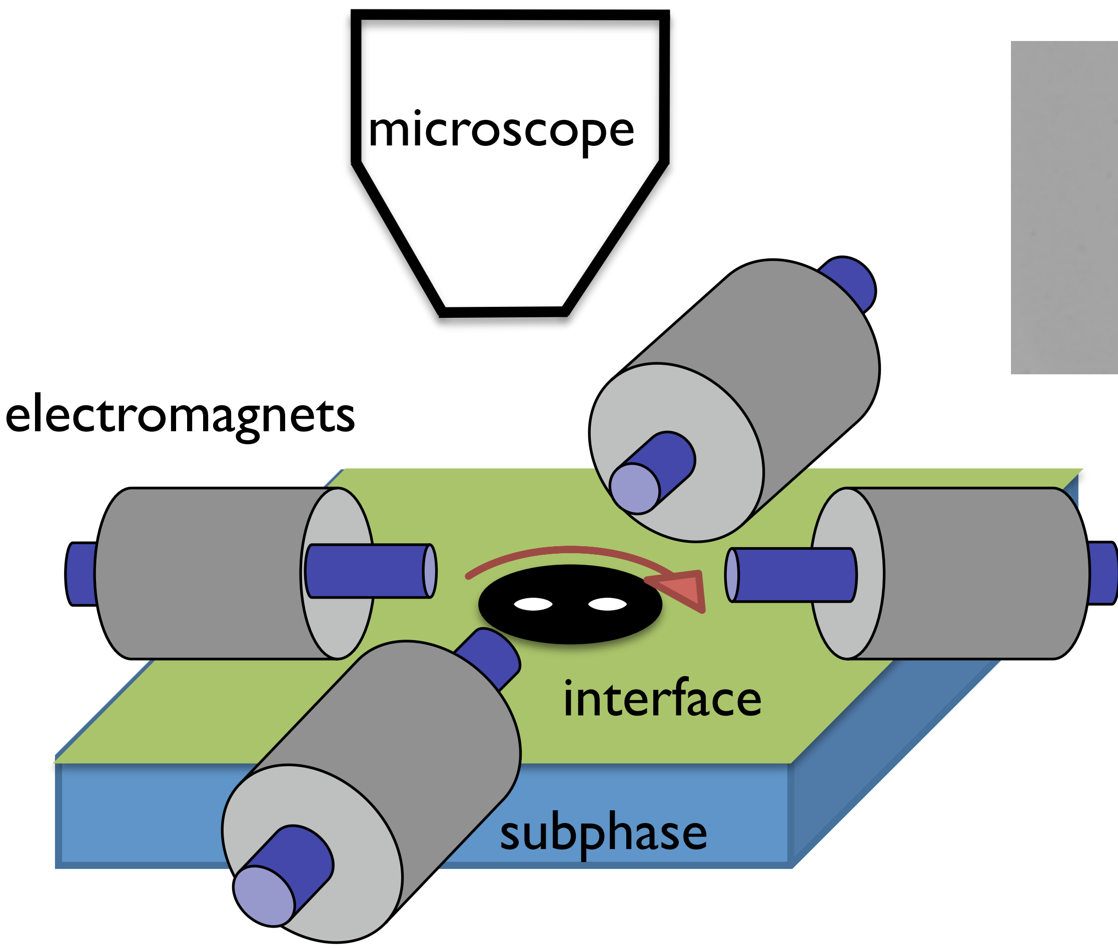
Applied Torque ~ Stress
Rotational displacement ~ Strain

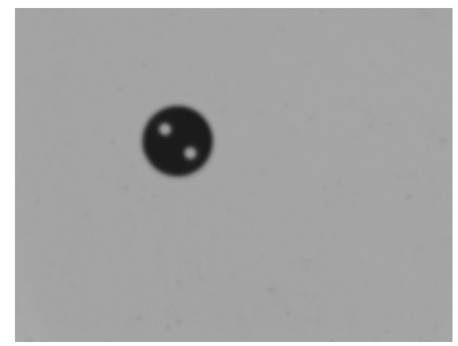
DATA acquisition board → Magnetic torque(t) (Green)

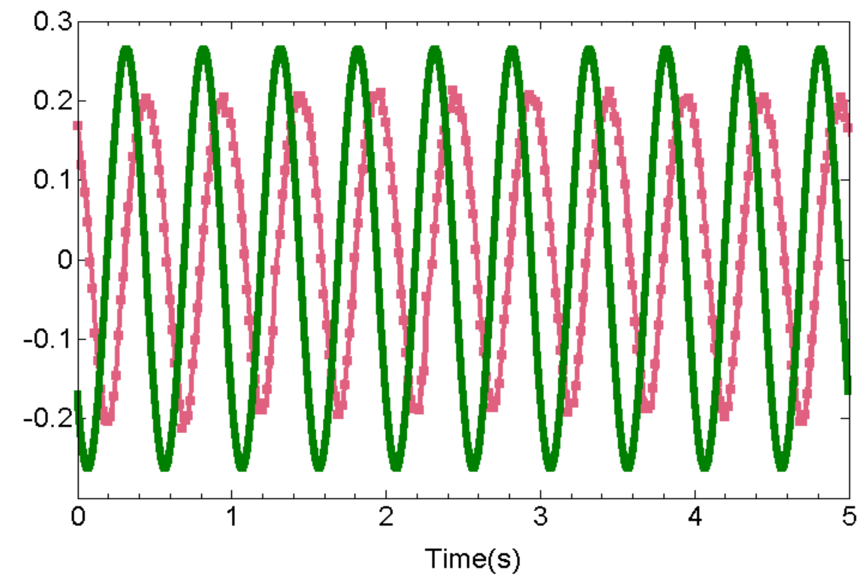
Imposed oscillatory magnetic field → Can compute viscoelasticity(G’, G”)

General Experimental Procedure

Camera → Image analysis → Angular strain(t) (Red)







Applied Torque ~ Stress

Rotational displacement ~ Strain

DATA acquisition board → Magnetic torque(t) (Green)

Imposed constant stress → Can measure Creep compliance--J(t)

Janus ferromagnetic microprobes

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requirements

- Small, yet visible
- Ferromagnetic
- Amphiphilic

Janus ferromagnetic microprobes

Photolithography

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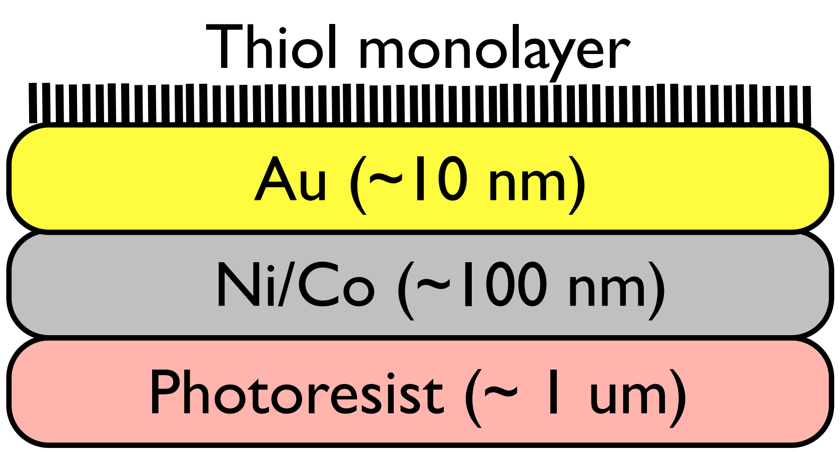

Janus ferromagnetic microprobes

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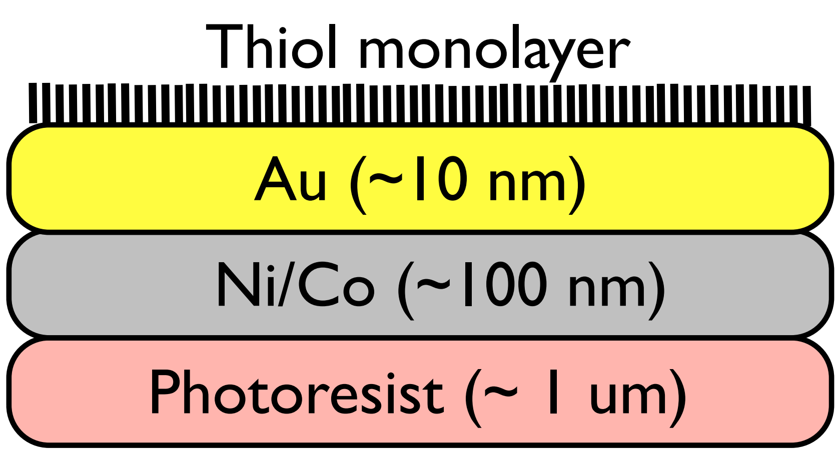
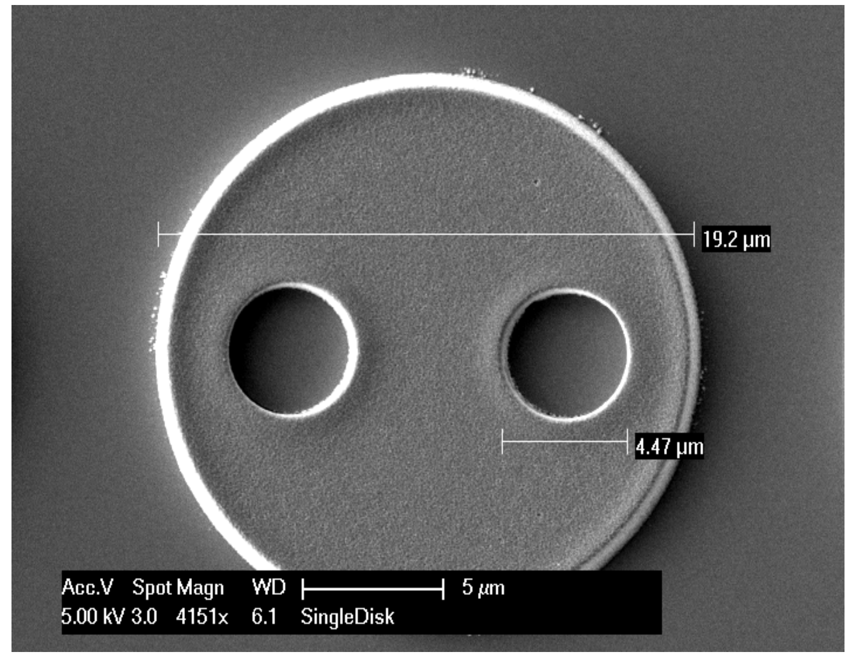
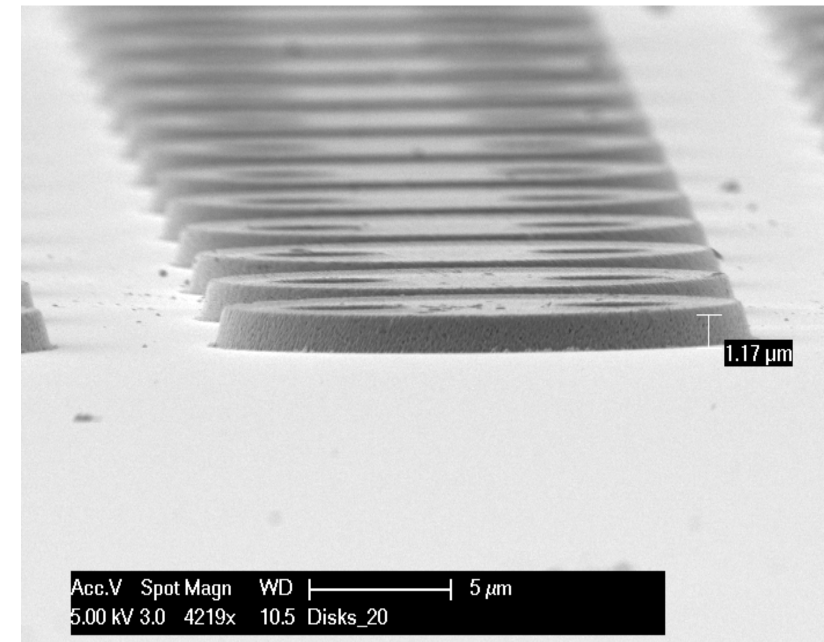
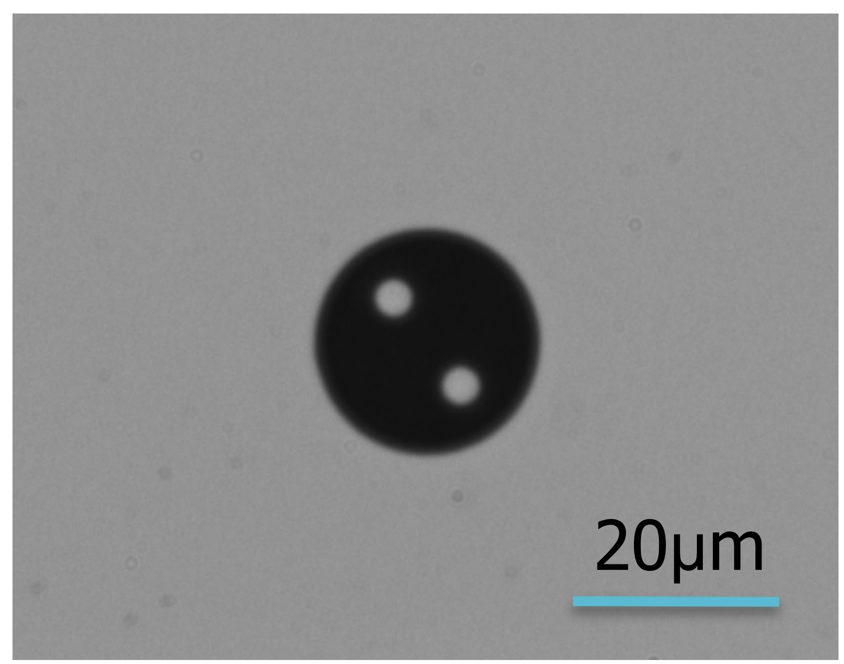




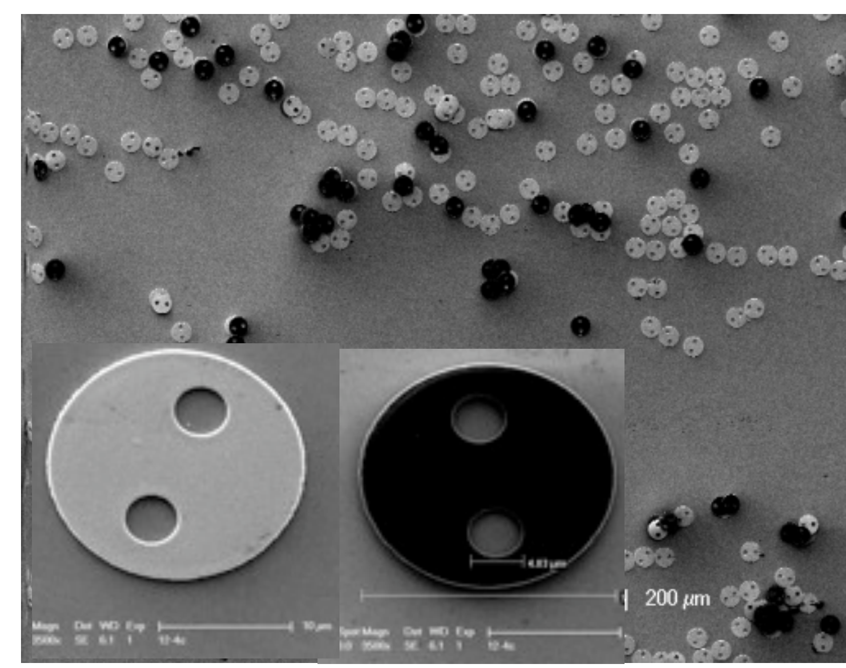
20µm diameter



1 µm tall



bright field image



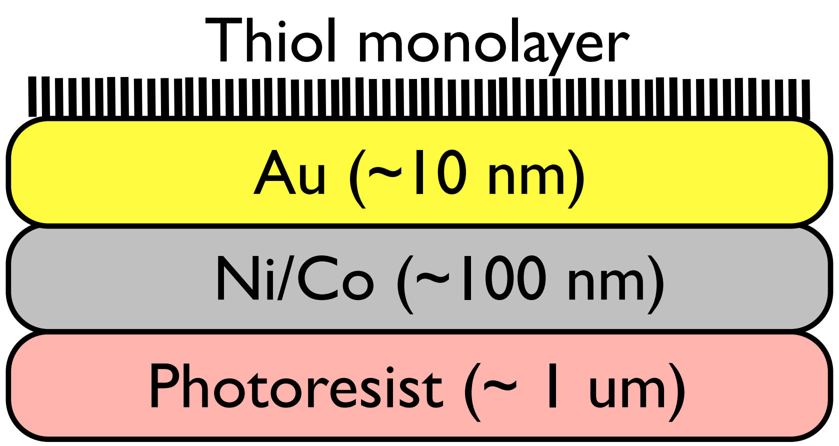
Amphiphilic - Janus

Janus ferromagnetic microprobes

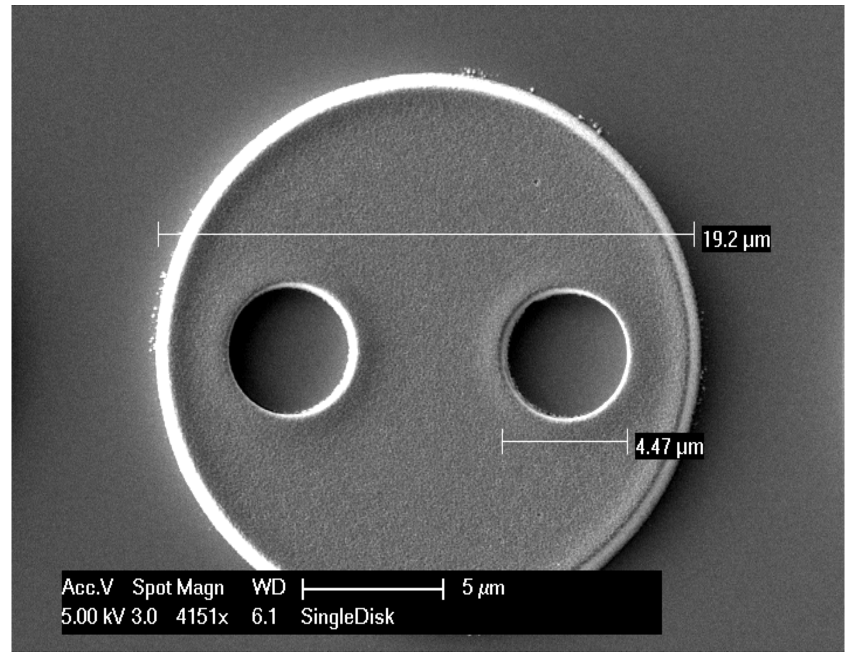
Photolithography

requirements

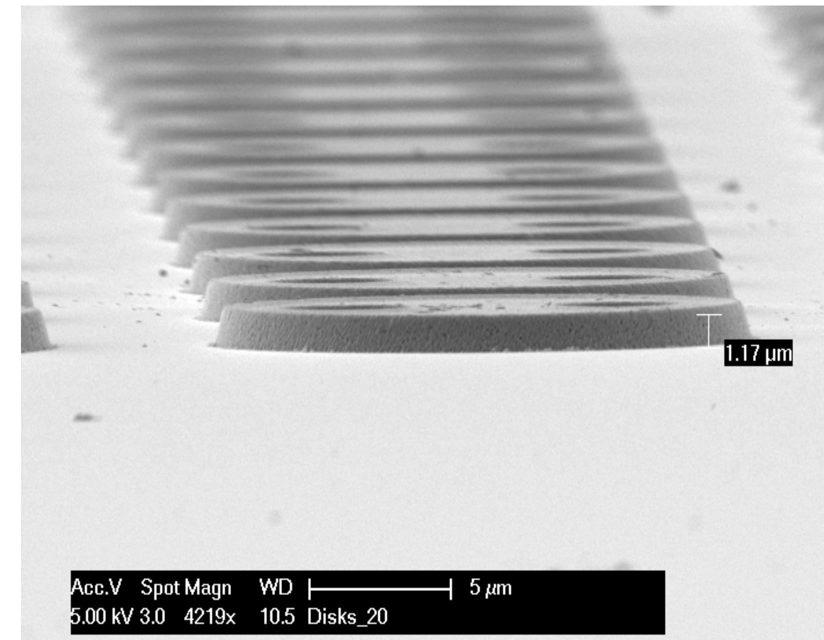
- Small, yet visible
- Ferromagnetic
- Amphiphilic



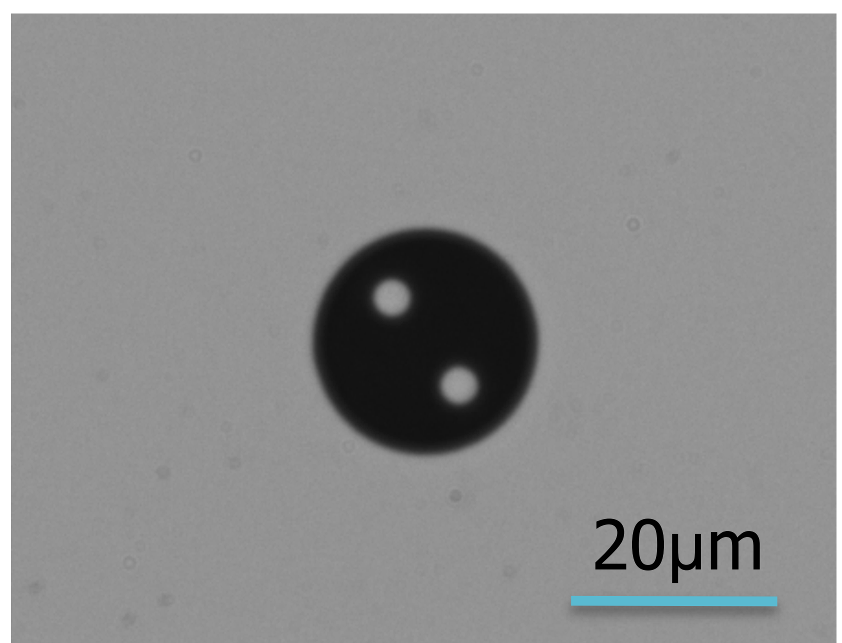
Control over
Size, Shape,
Magnetic and Surface properties



20µm diameter



1µm tall



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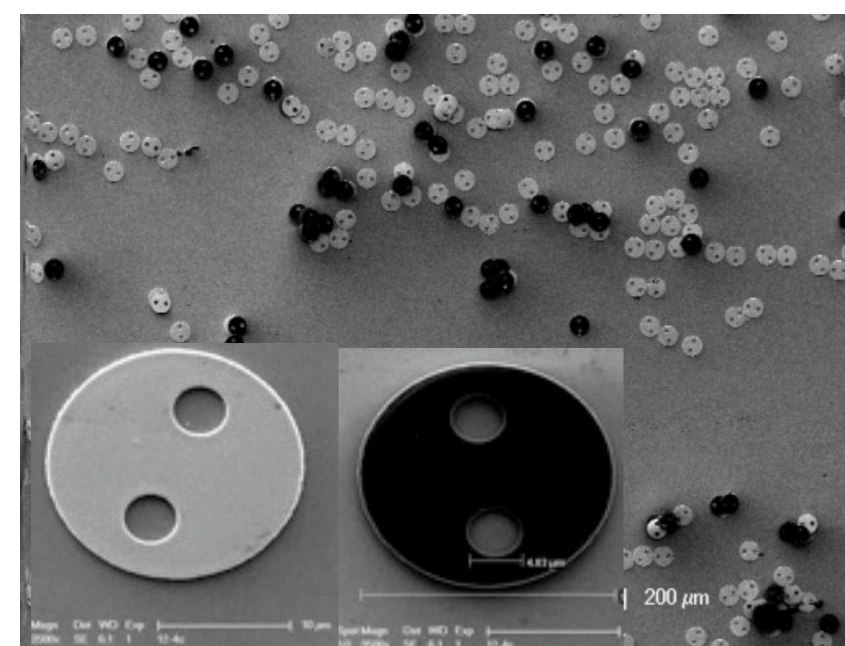


Amphiphilic - Janus

How the disk responds

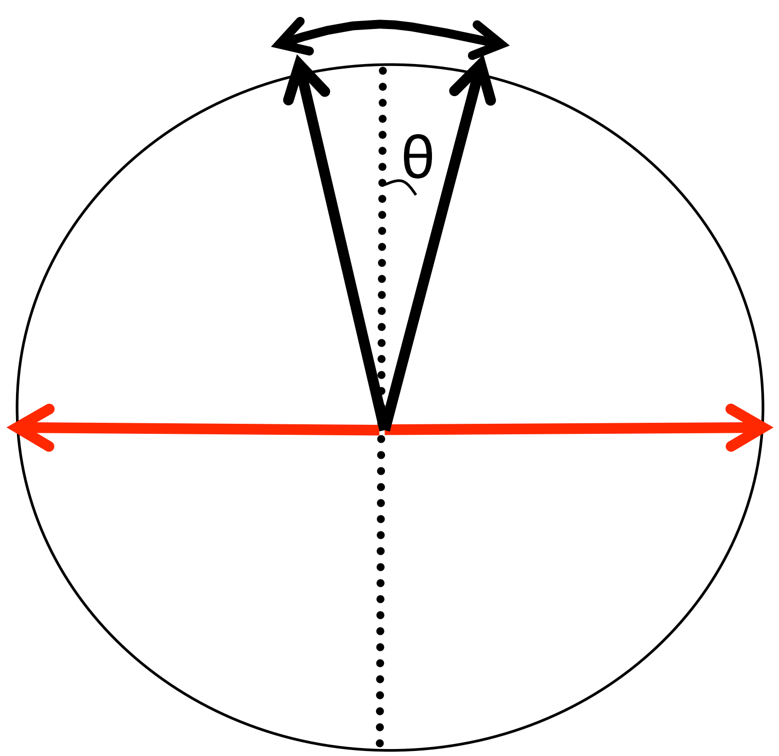
$$I\ddot{\theta} + \zeta\dot{\vartheta} + k\theta = m \times B$$

$\omega < 10^6$

Rotational drag — Rotational elastic constant — Torque

$$= mB\sin(\phi - \theta)$$

$$\approx mB$$



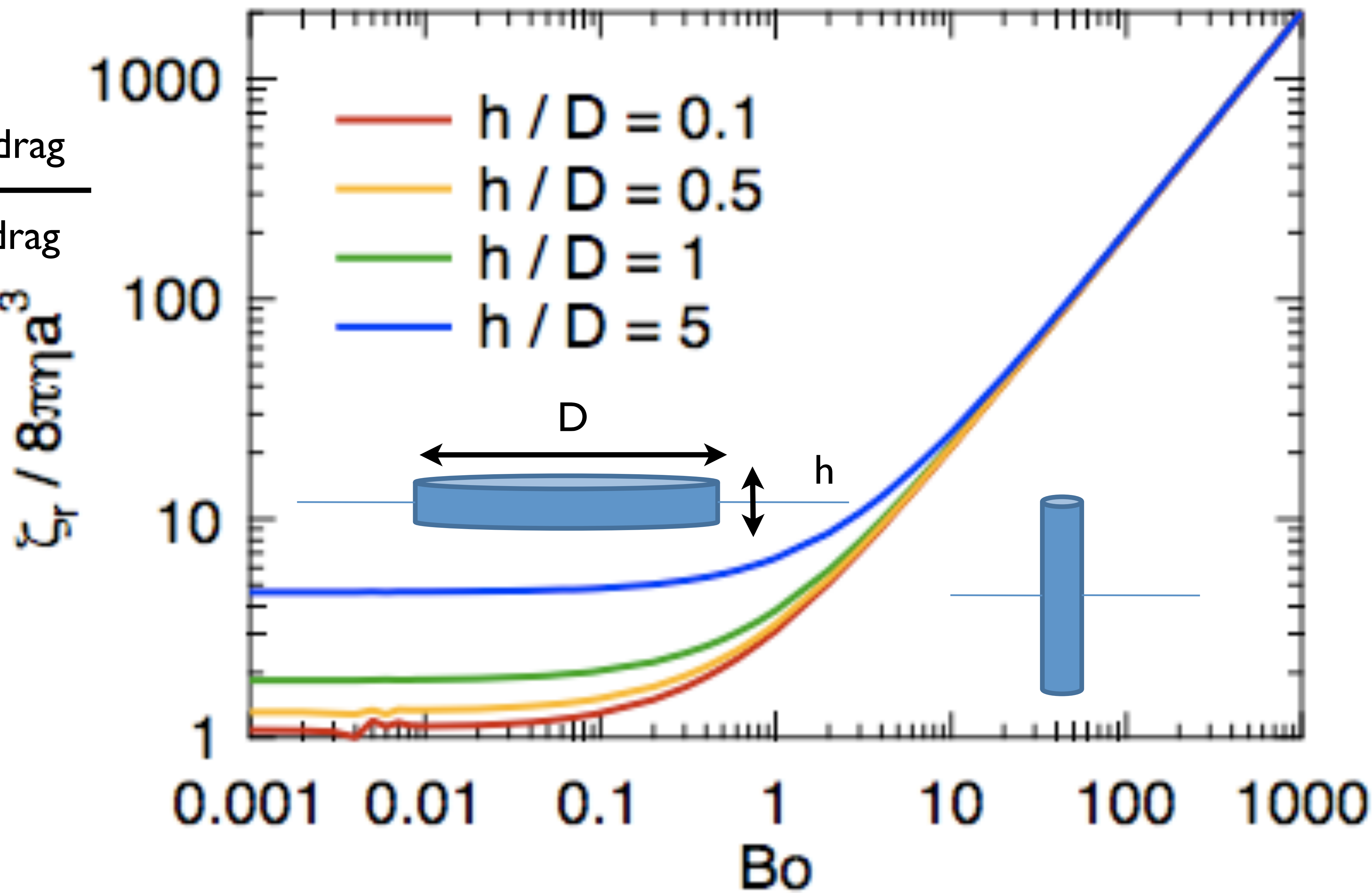
— Oscillatory Magnetic Field
— Angular displacement

m : magnetic moment
B : magnetic field
ϕ : angle for magnetic field
θ : angle for magnetic moment
ς : drag coefficient
k : spring constant

From field vs. orientation:
recover ς(~viscosity) and κ (~elasticity)

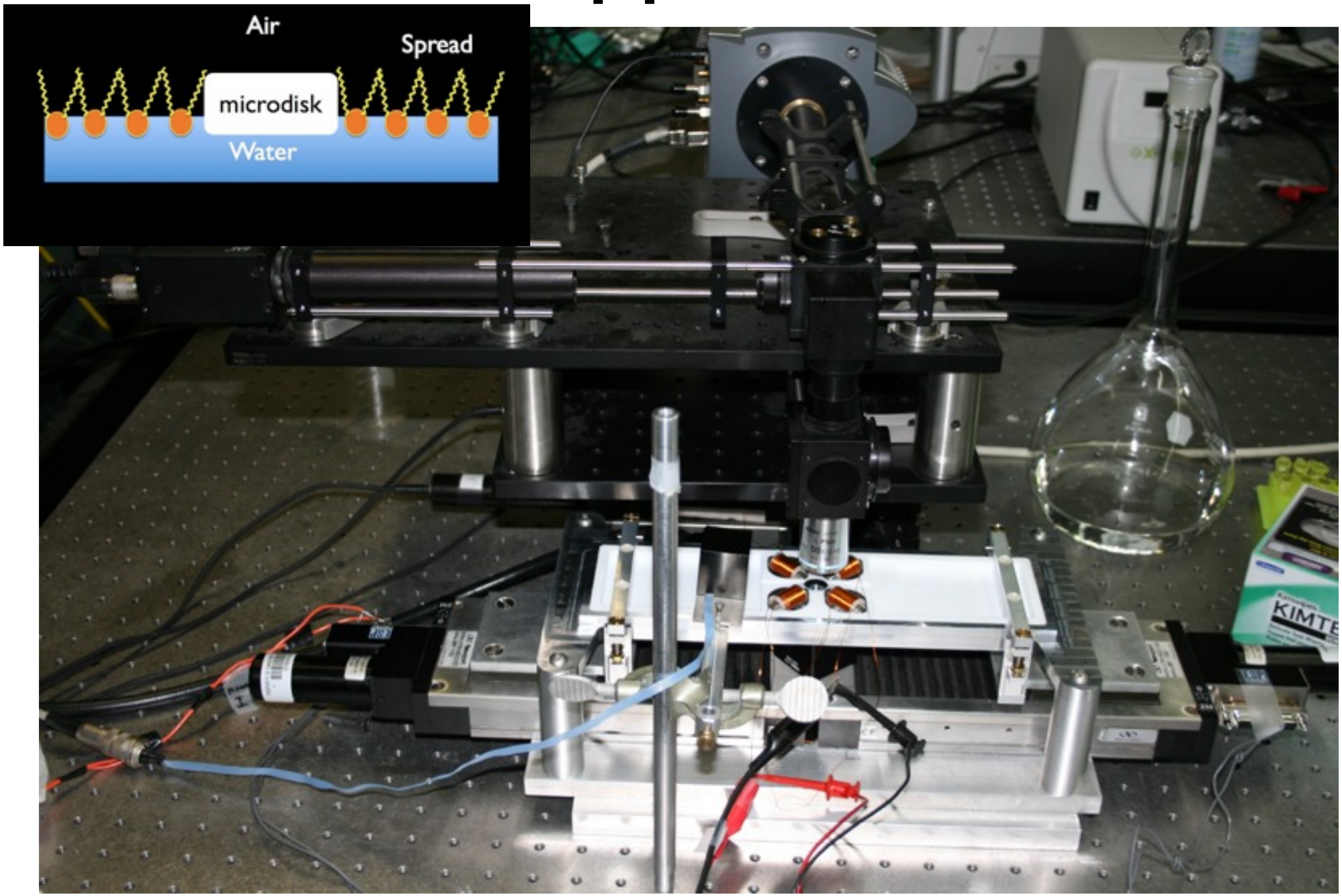
Surface drag of the probe

$$\frac{\text{Total drag}}{\text{Bulk drag}}$$



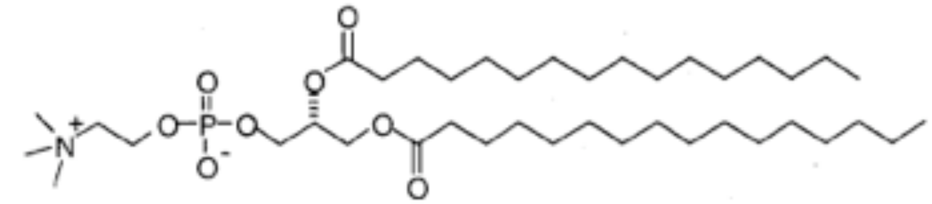
$$\text{Bo} = \frac{\eta s\text{(surface viscosity)}}{\eta\text{(bulk viscosity)}a}$$

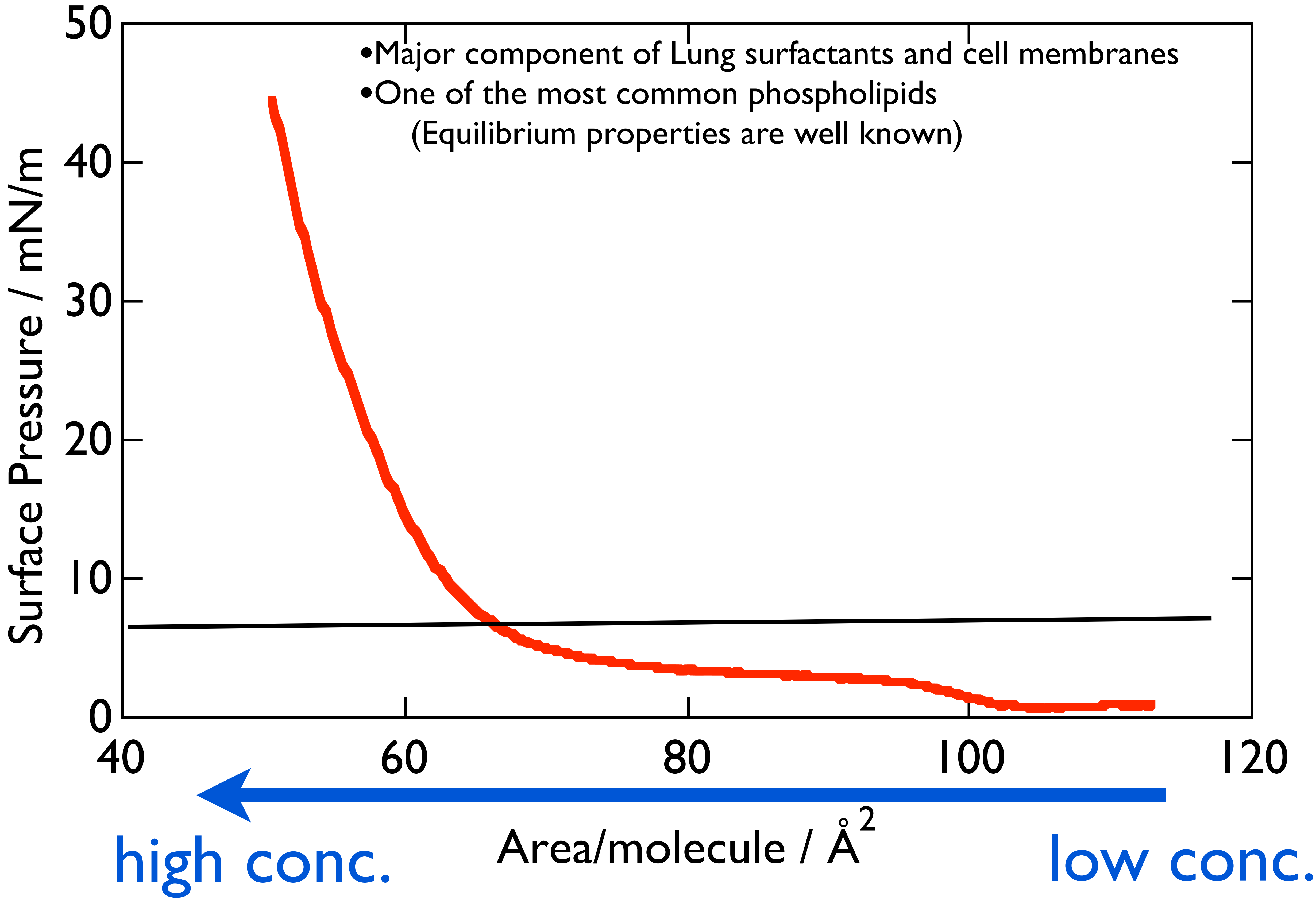
Apparatus



Allows interfacial visualization *during* measurement

DPPC and its isotherm





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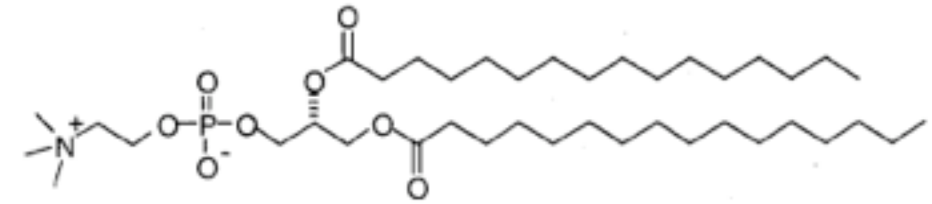

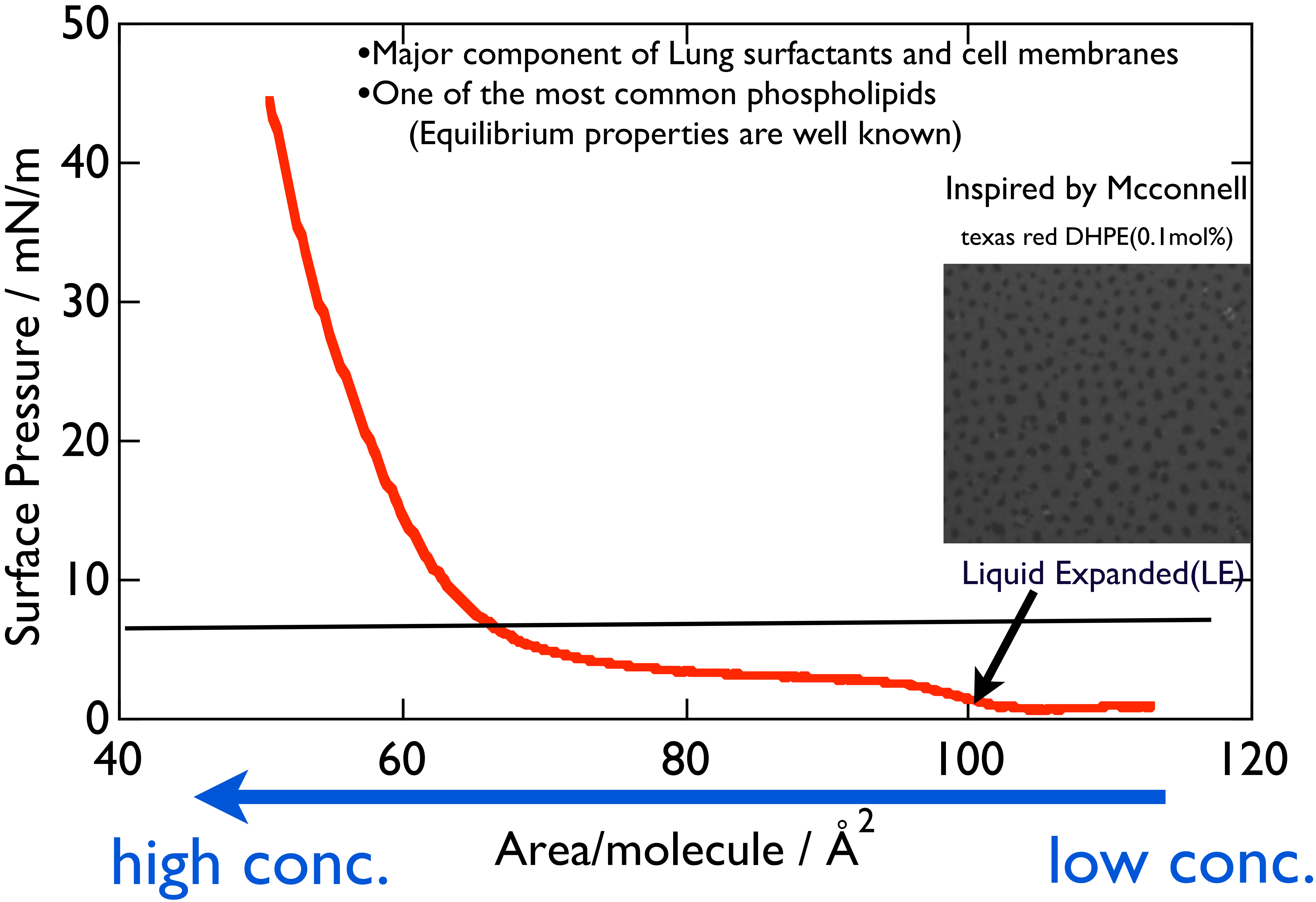

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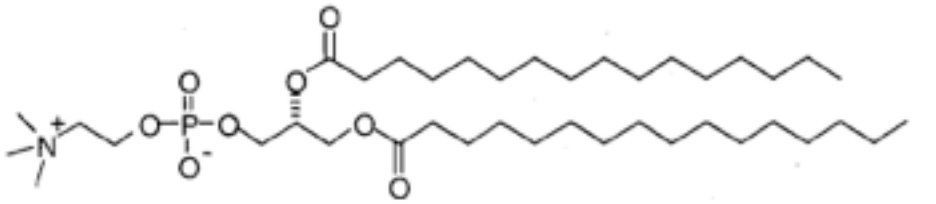

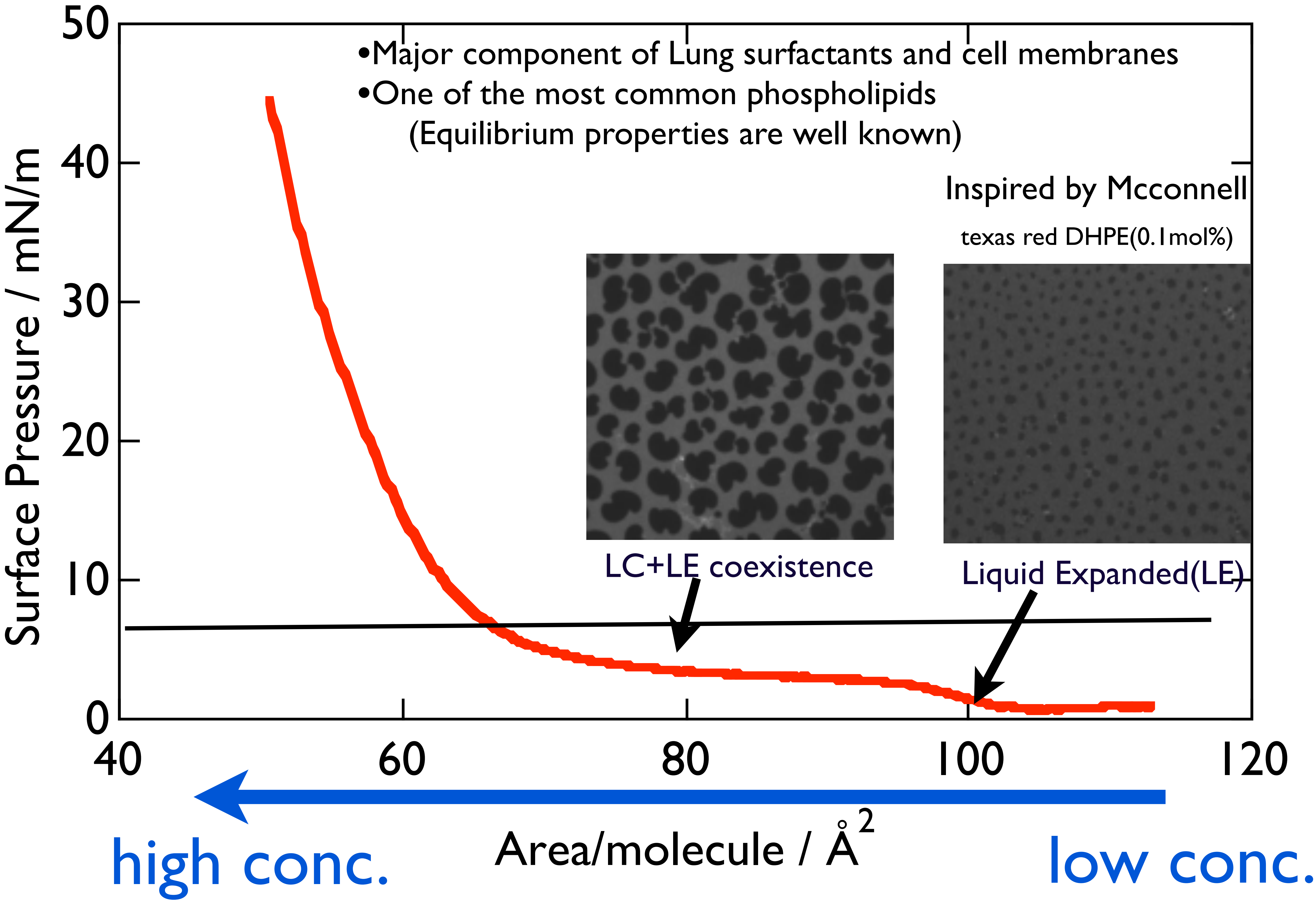

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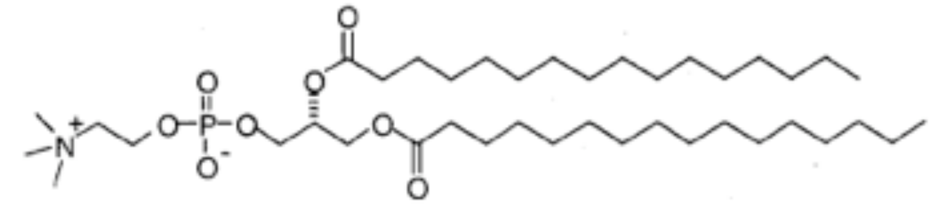

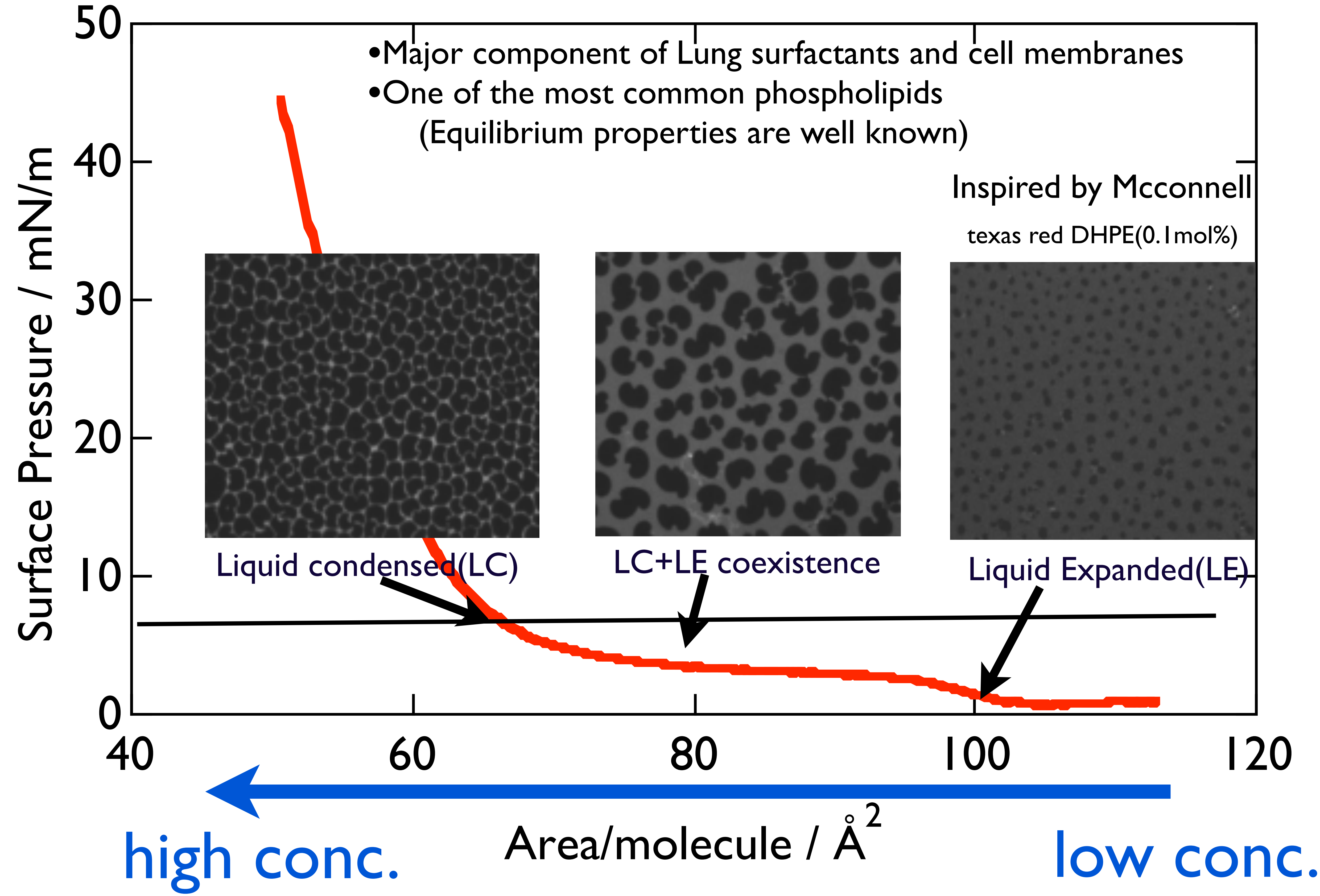

Linear viscoelasticity of LC phase

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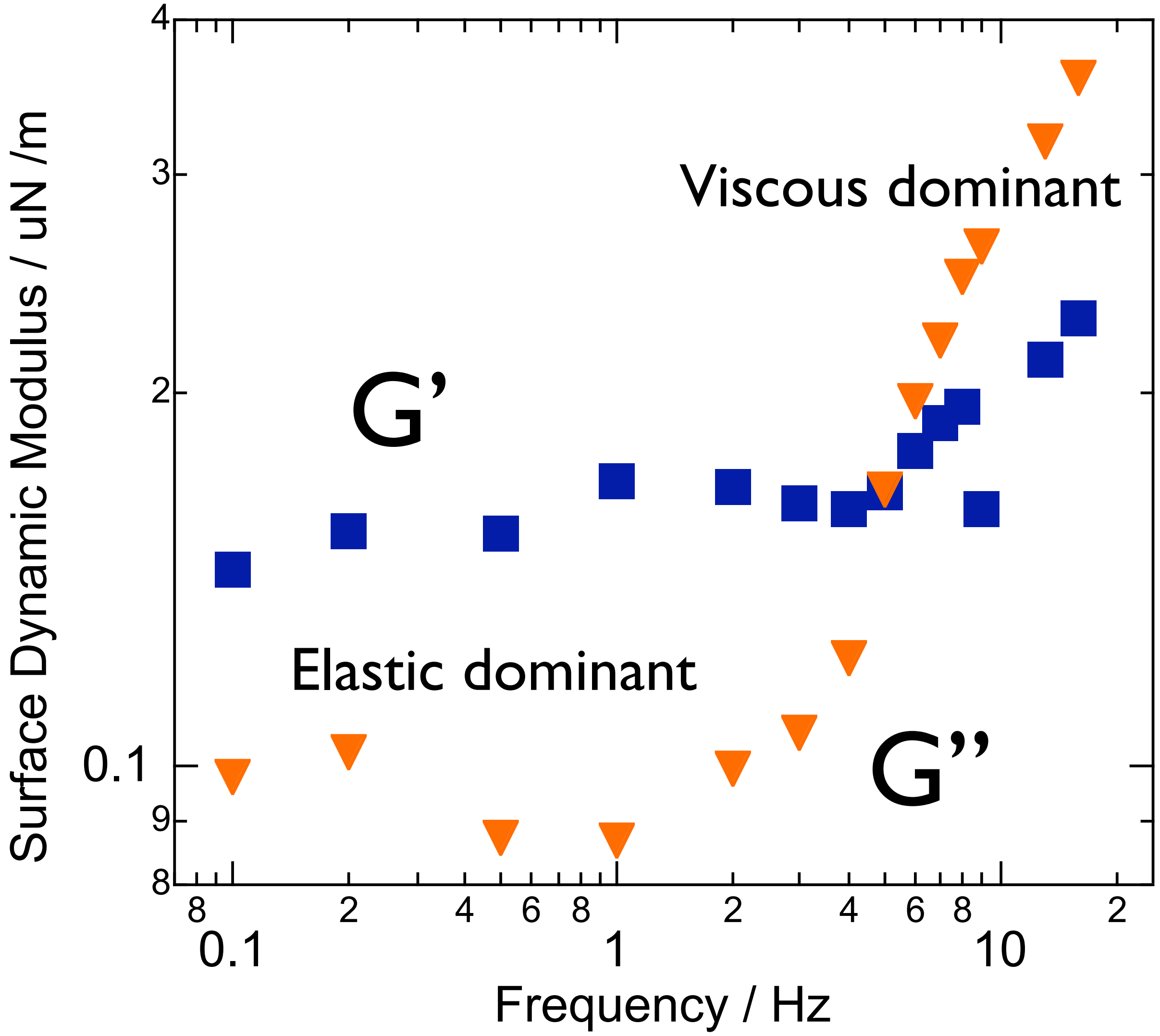
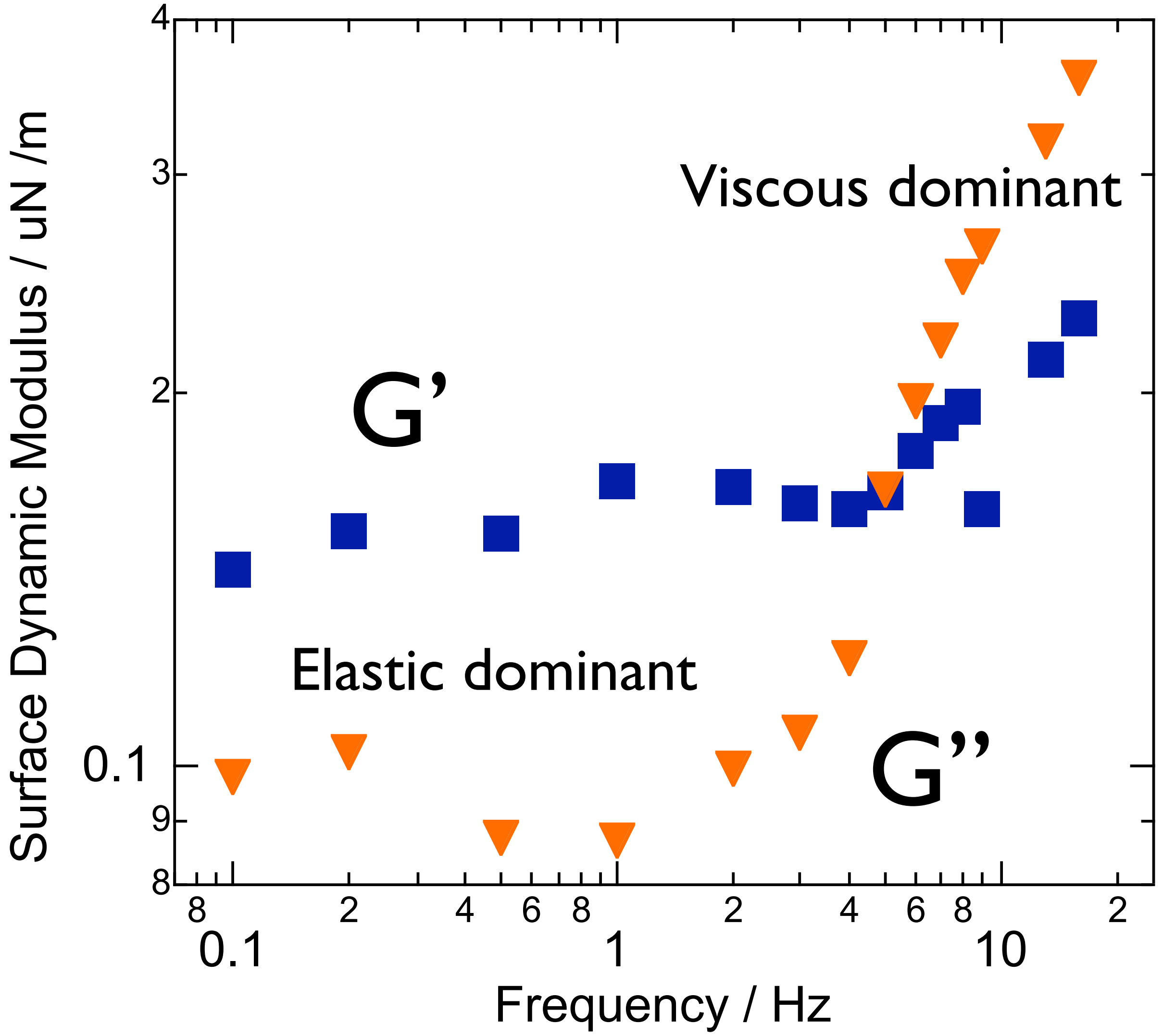


Slow dynamics

- does not flow for 10 sec

Linear viscoelasticity of LC phase



Slow dynamics

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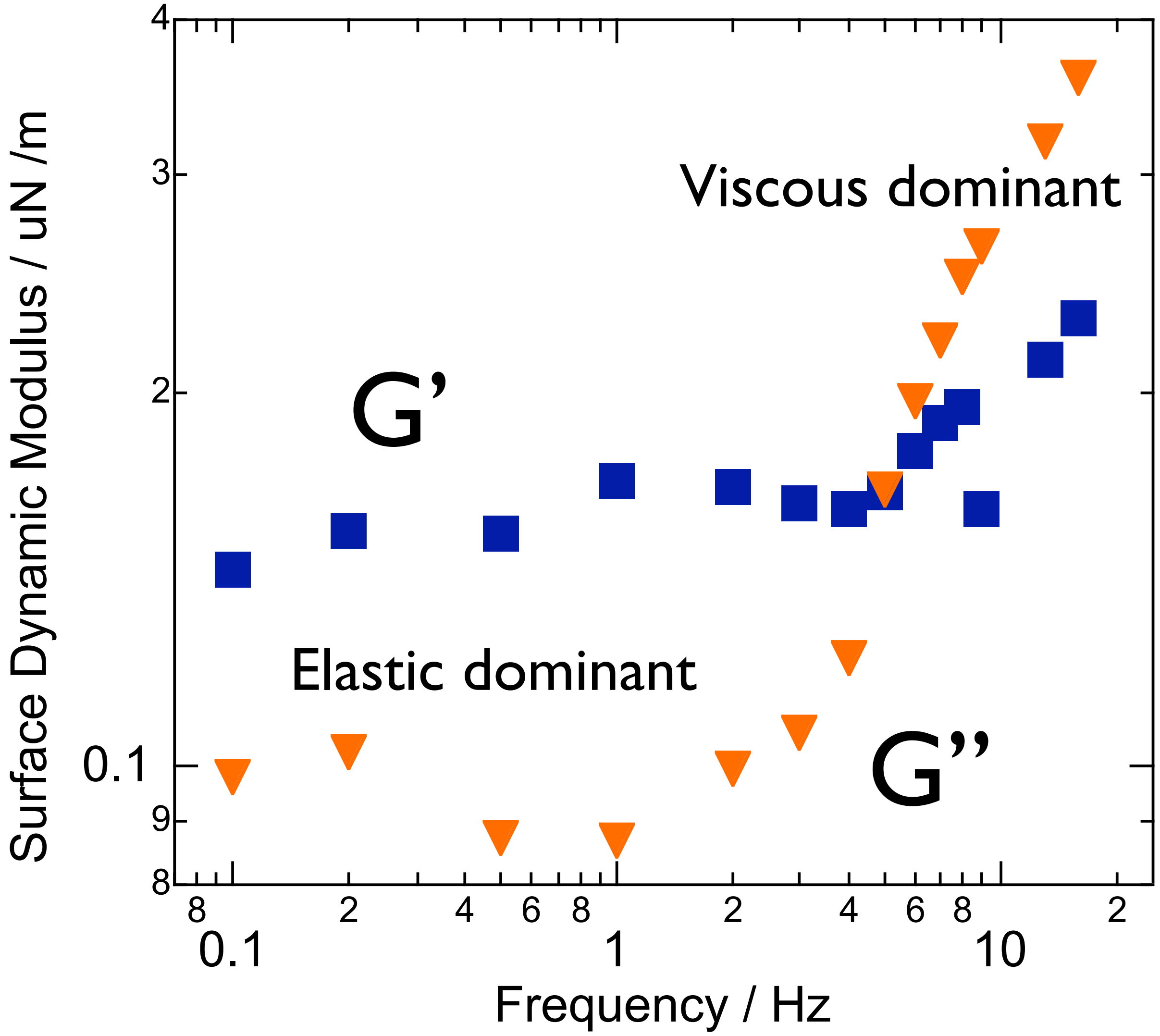
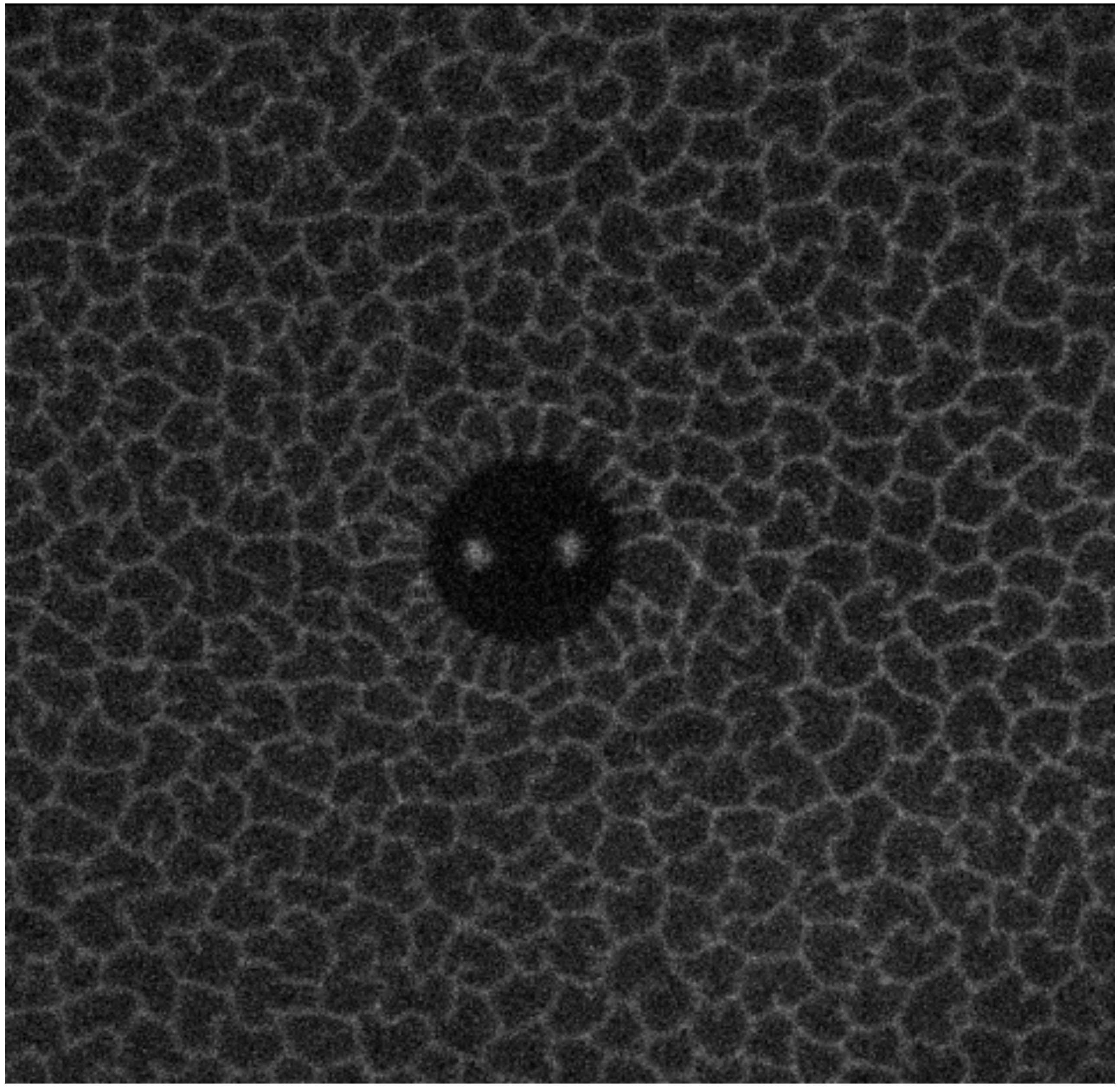
Incredibly long relaxation time for 2 nm thick film

Linear viscoelasticity of LC phase





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Elasticity - domain deformation

Viscosity - Slipping domains

Incredibly long relaxation time for 2 nm thick film

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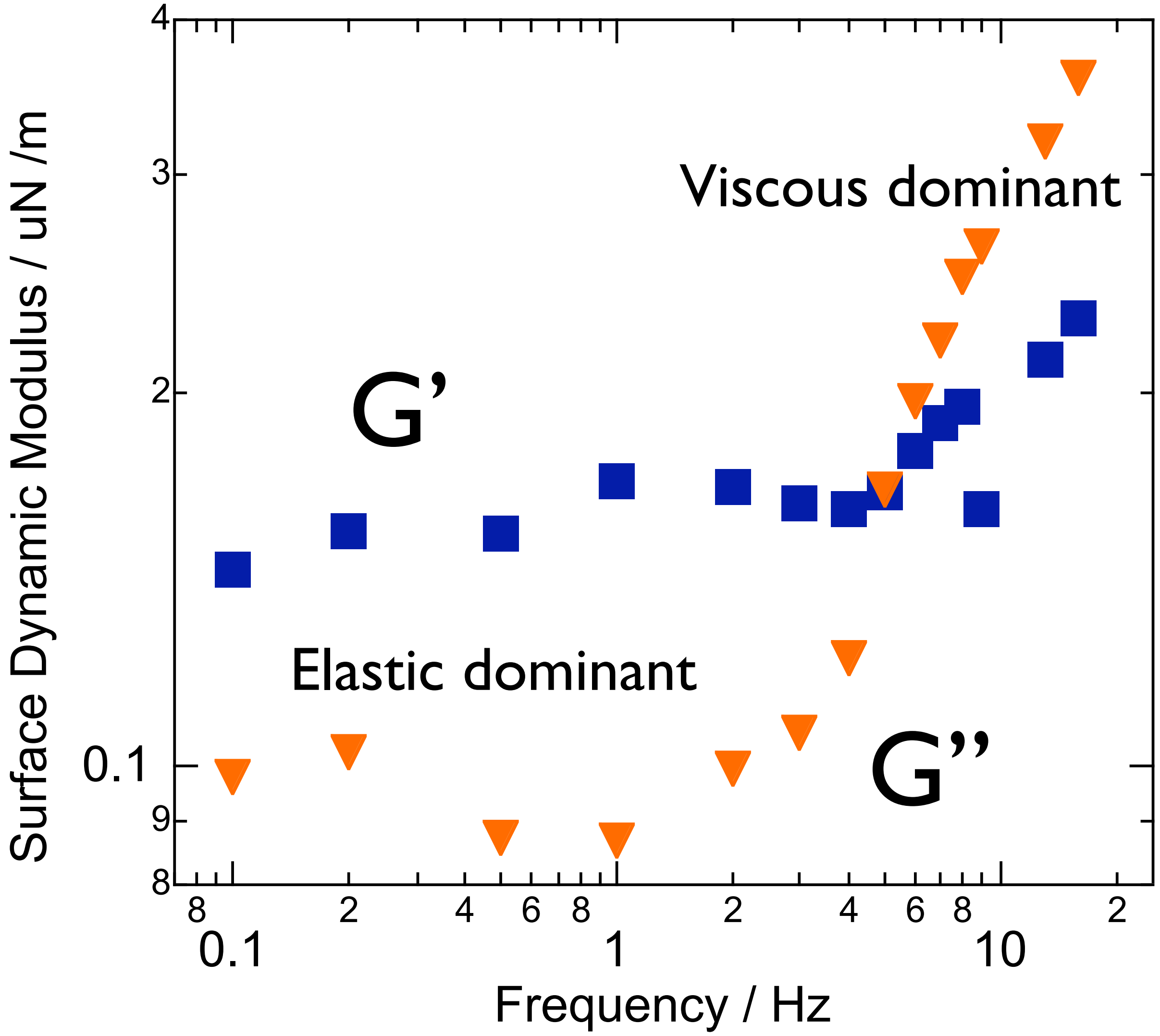

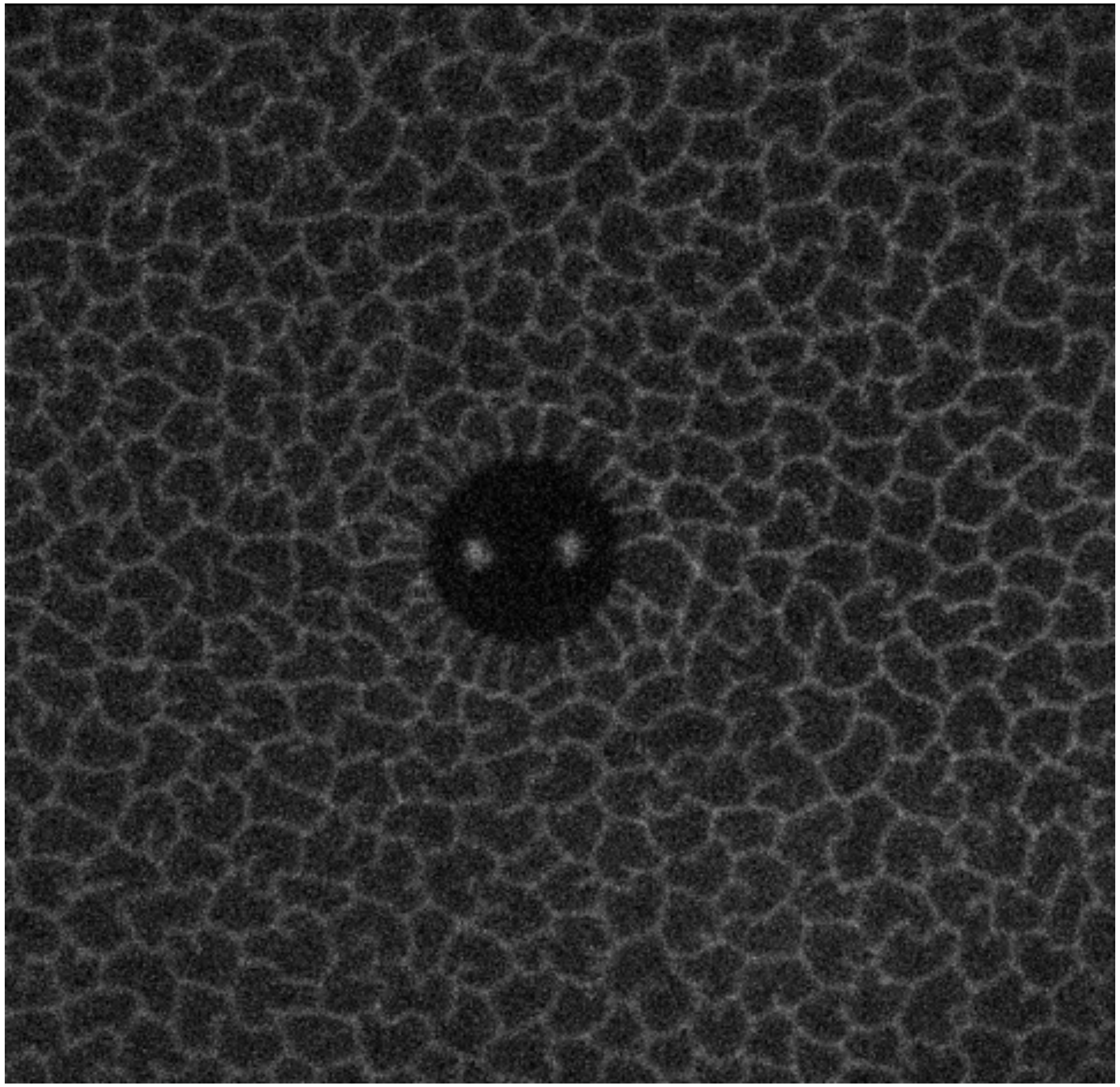

Slow dynamics

- does not flow for 10 sec

Elasticity - domain deformation

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Incredibly long relaxation time for 2 nm thick film

Where does this G' come from?

$$G' \sim \frac{\gamma a}{a^2} \sim \frac{\gamma}{a}$$ From emulsion theory

$$\gamma \sim G' a \sim 10^{-7} (N / m) \times 10^{-5} (m) \sim 1 pN$$

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Molecular argument

$$\text{line tension} \sim \frac{\text{adhesive energy}}{\text{length}} \sim \frac{\text{kT}}{\text{1 nm}} \sim \boxed{\text{1 pN}}$$

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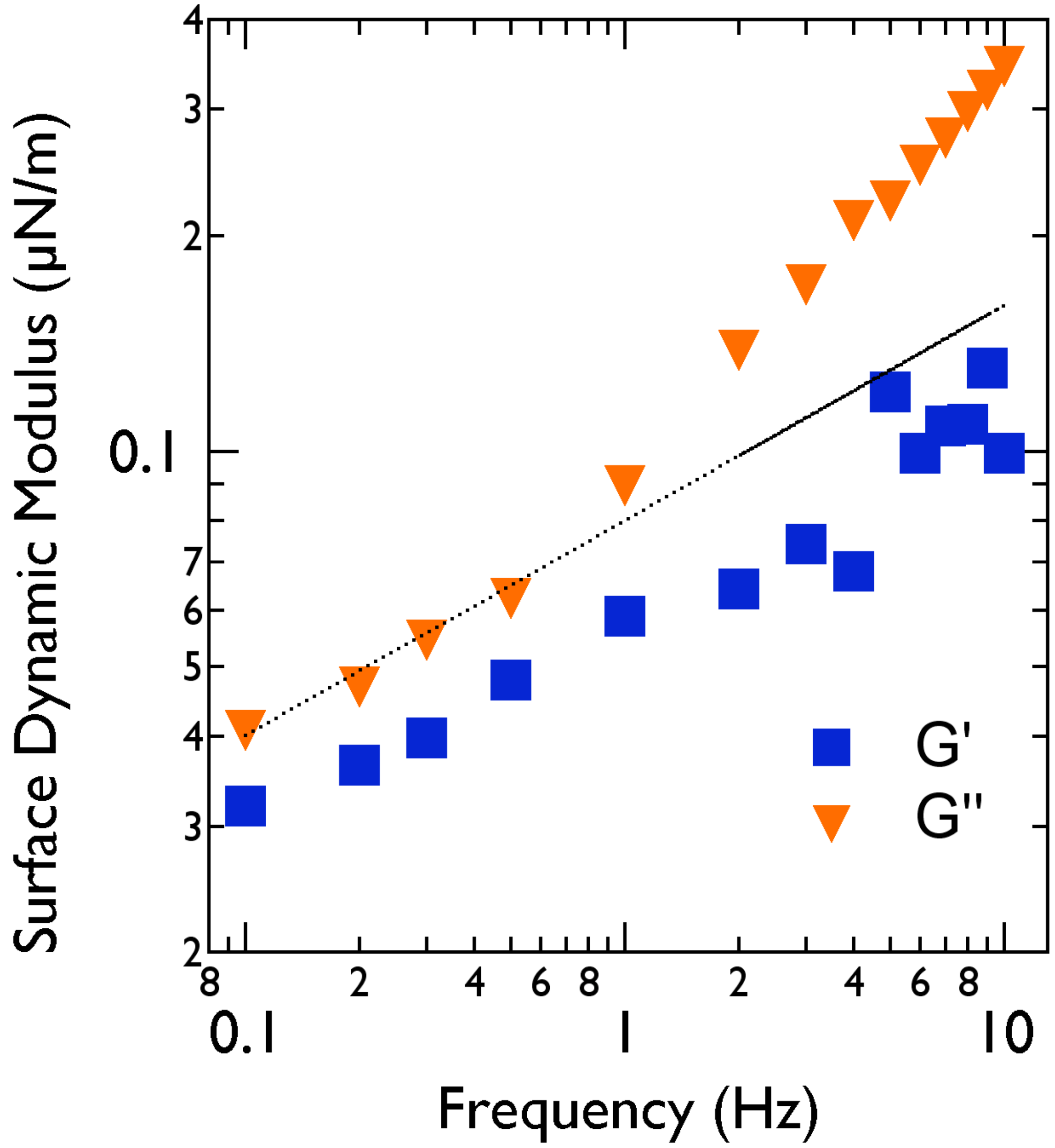
Molecular argument

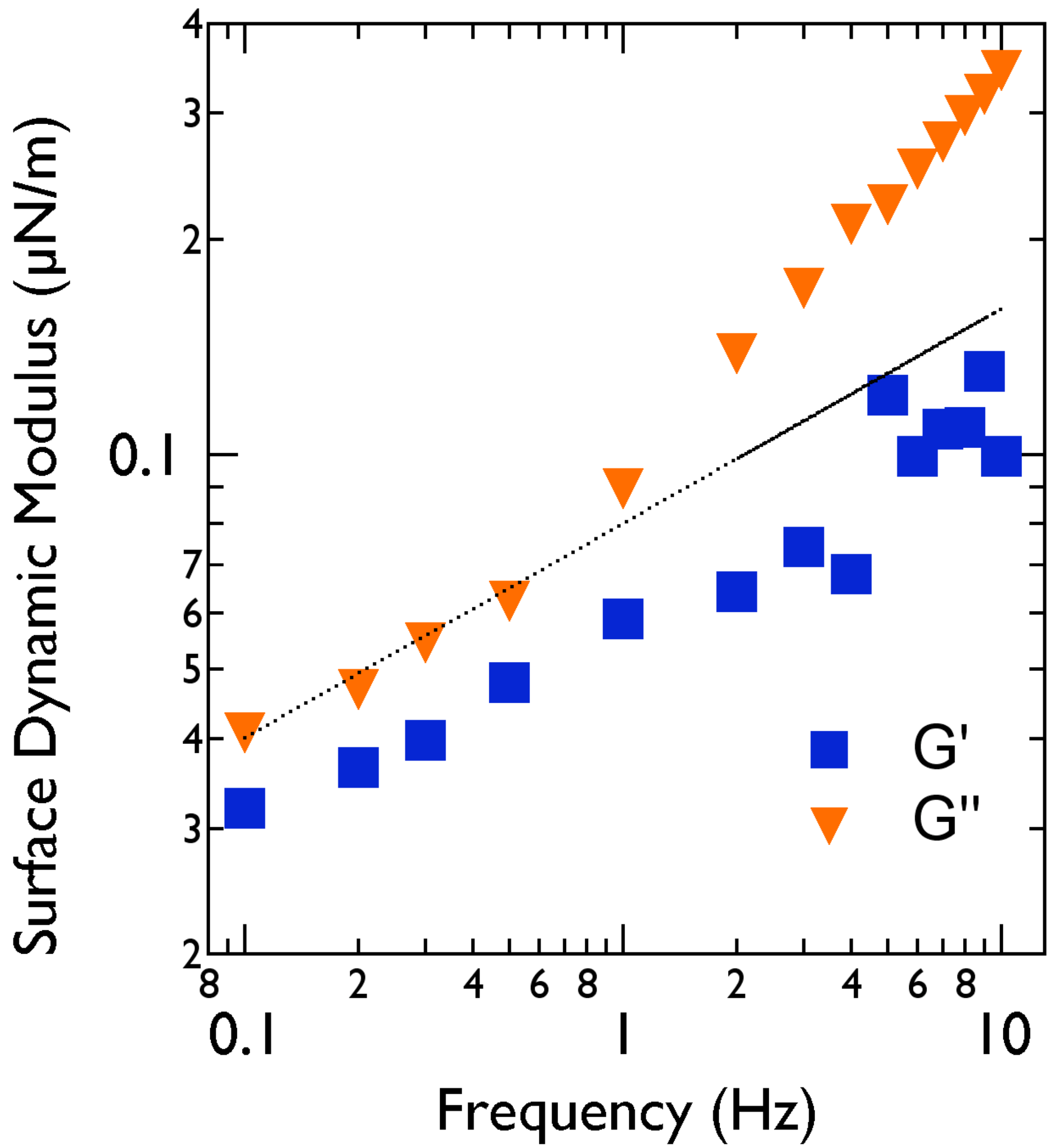
line tension $\sim \frac{\text{adhesive energy}}{\text{length}} \sim \frac{kT}{1\text{ nm}} \sim$ 1 pN

surface tension $\sim \frac{\text{adhesive energy}}{\text{area}} \sim \frac{kT}{1\text{ nm}^2} \sim$ 1 mN/m

Linear rheology after large shear

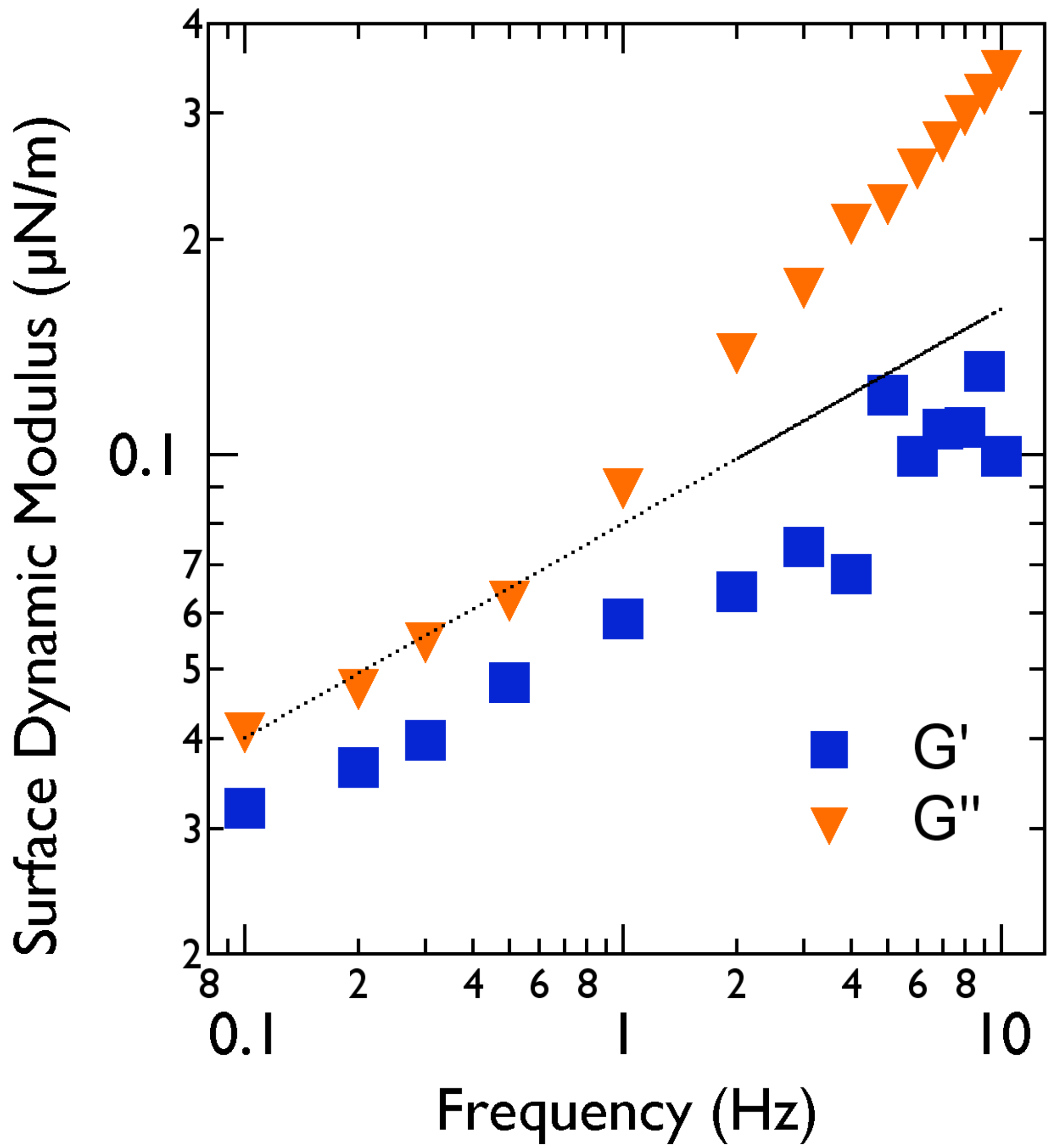


Linear rheology after large shear



Viscous dominant over frequencies

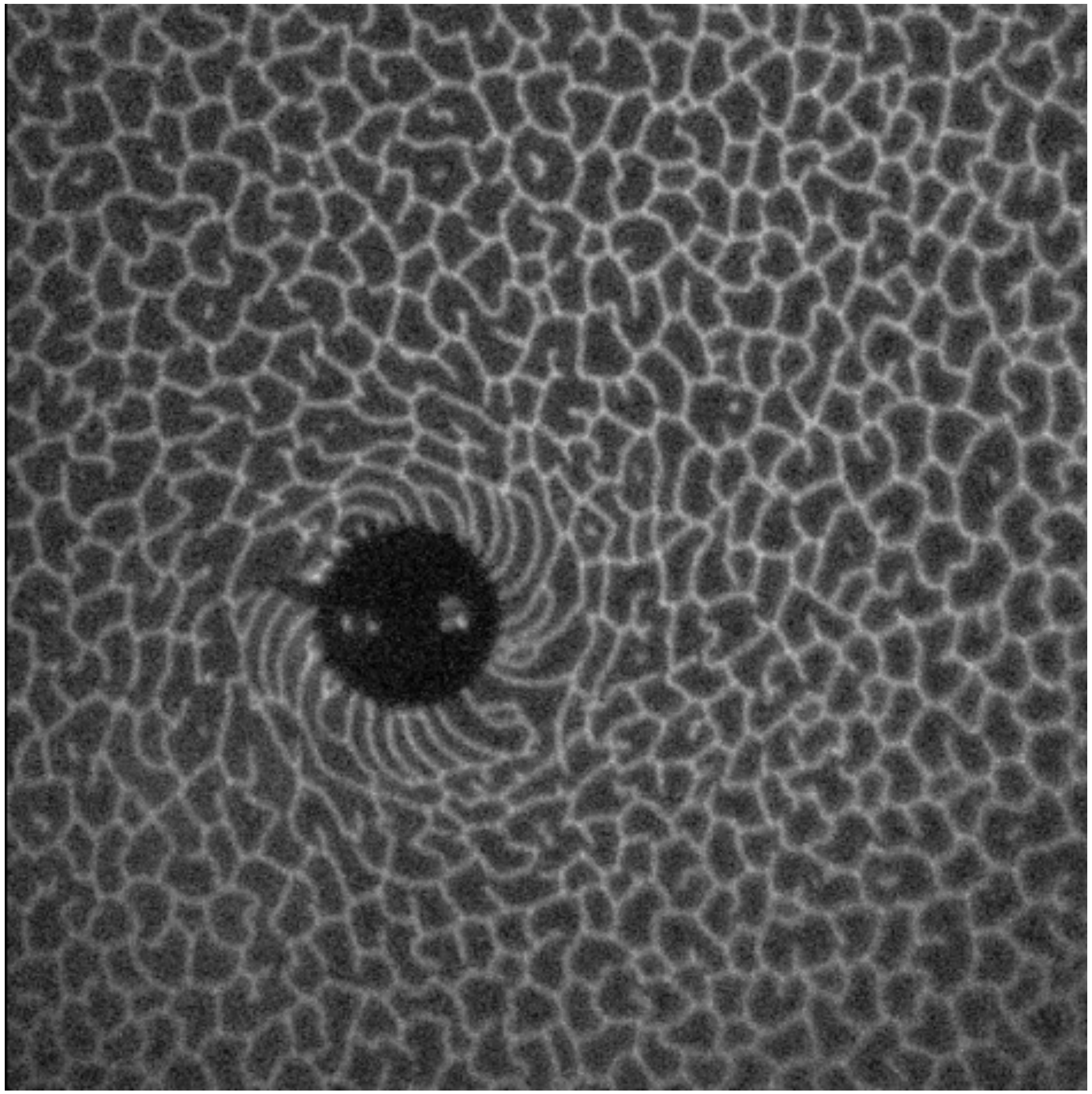
Linear rheology after large shear



Viscous dominant over frequencies

History dependent rheology

Visualization for large shear



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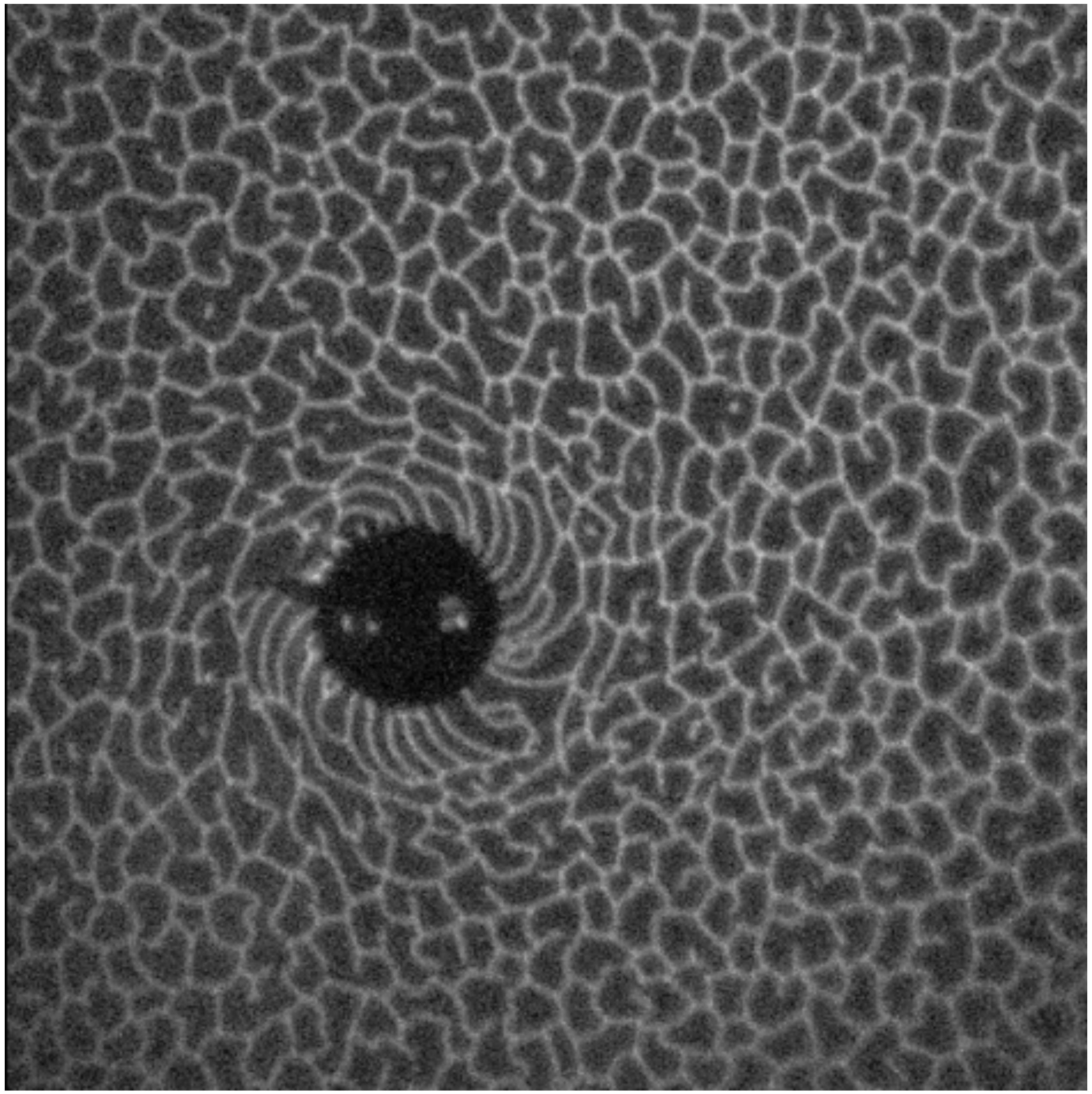
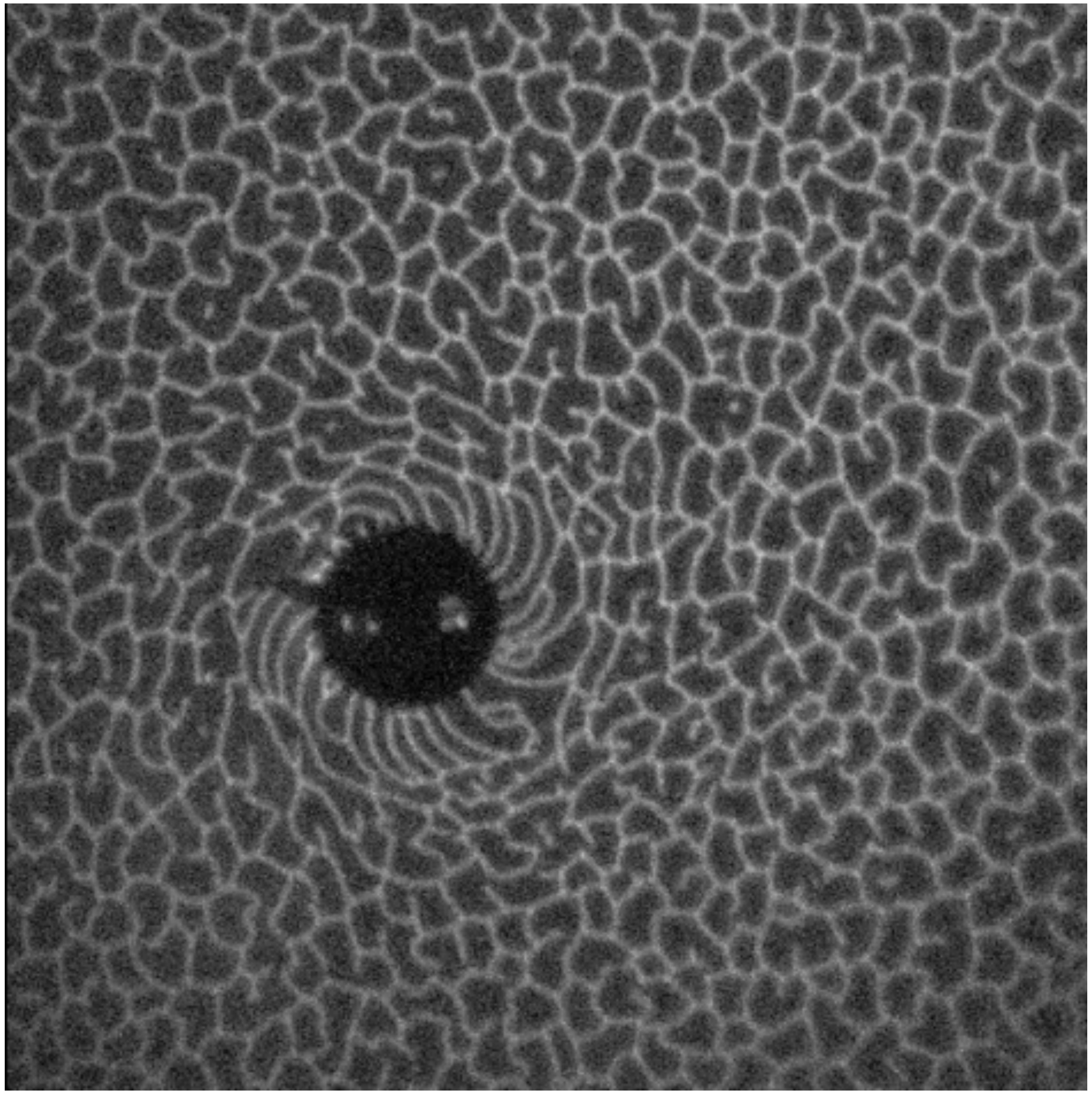


- Domain deformation
- Interface fractures(plastic)
- Slip-line forms

Visualization for large shear

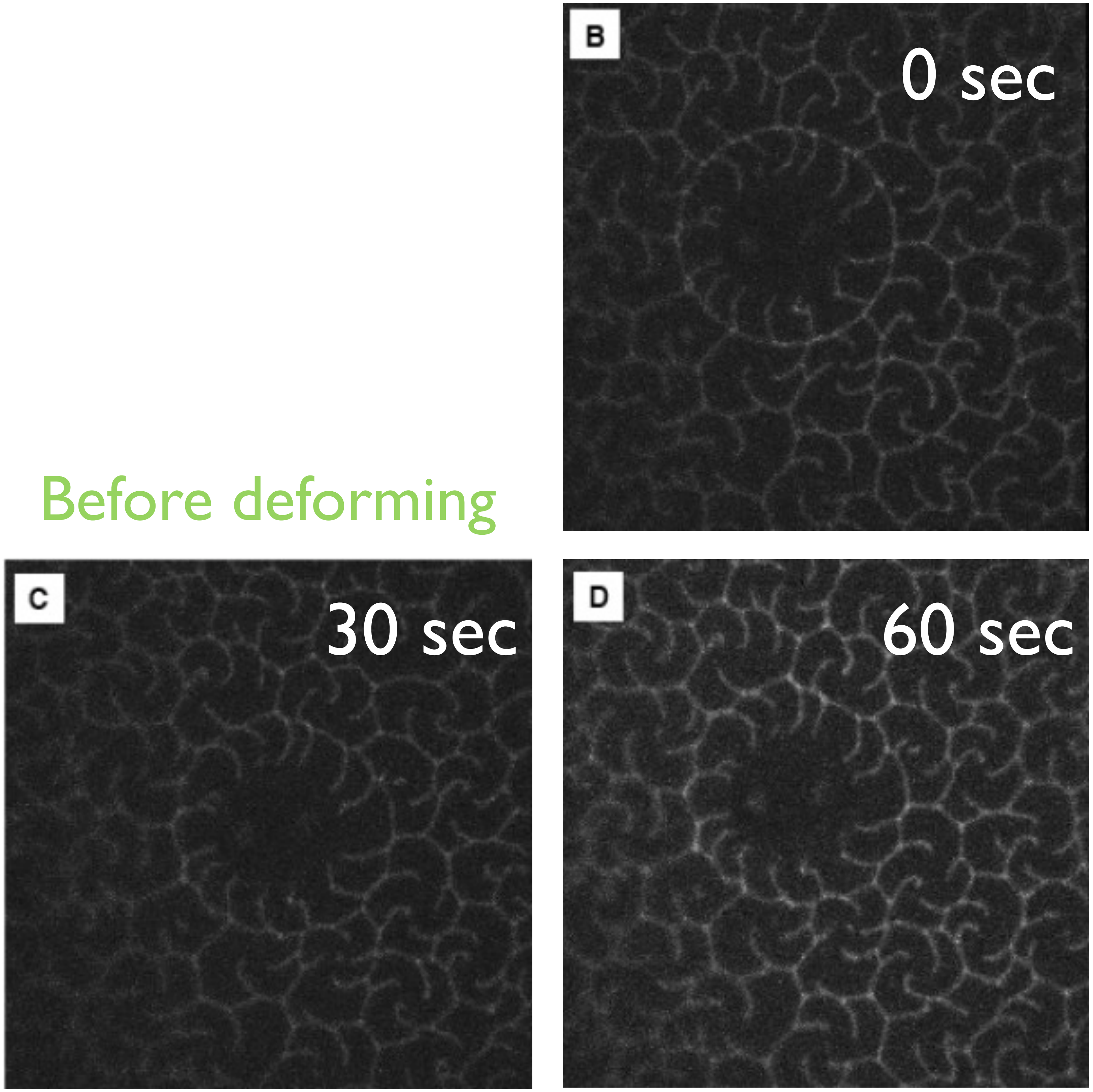


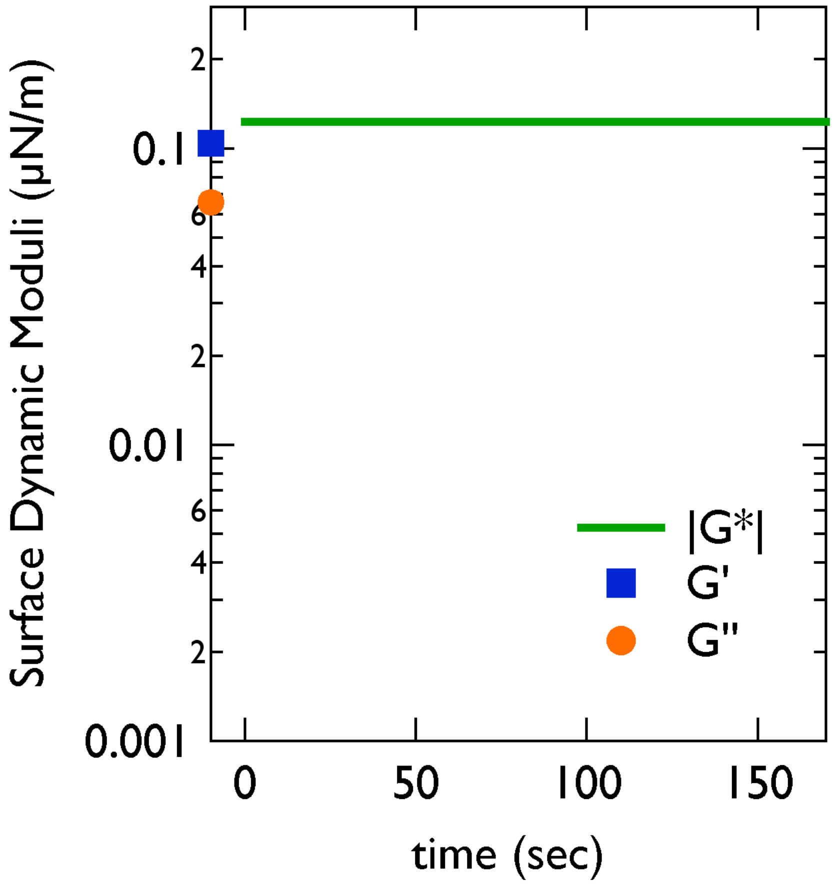
Does the interface heal?

- Domain deformation
- Interface fractures(plastic)
- Slip-line forms

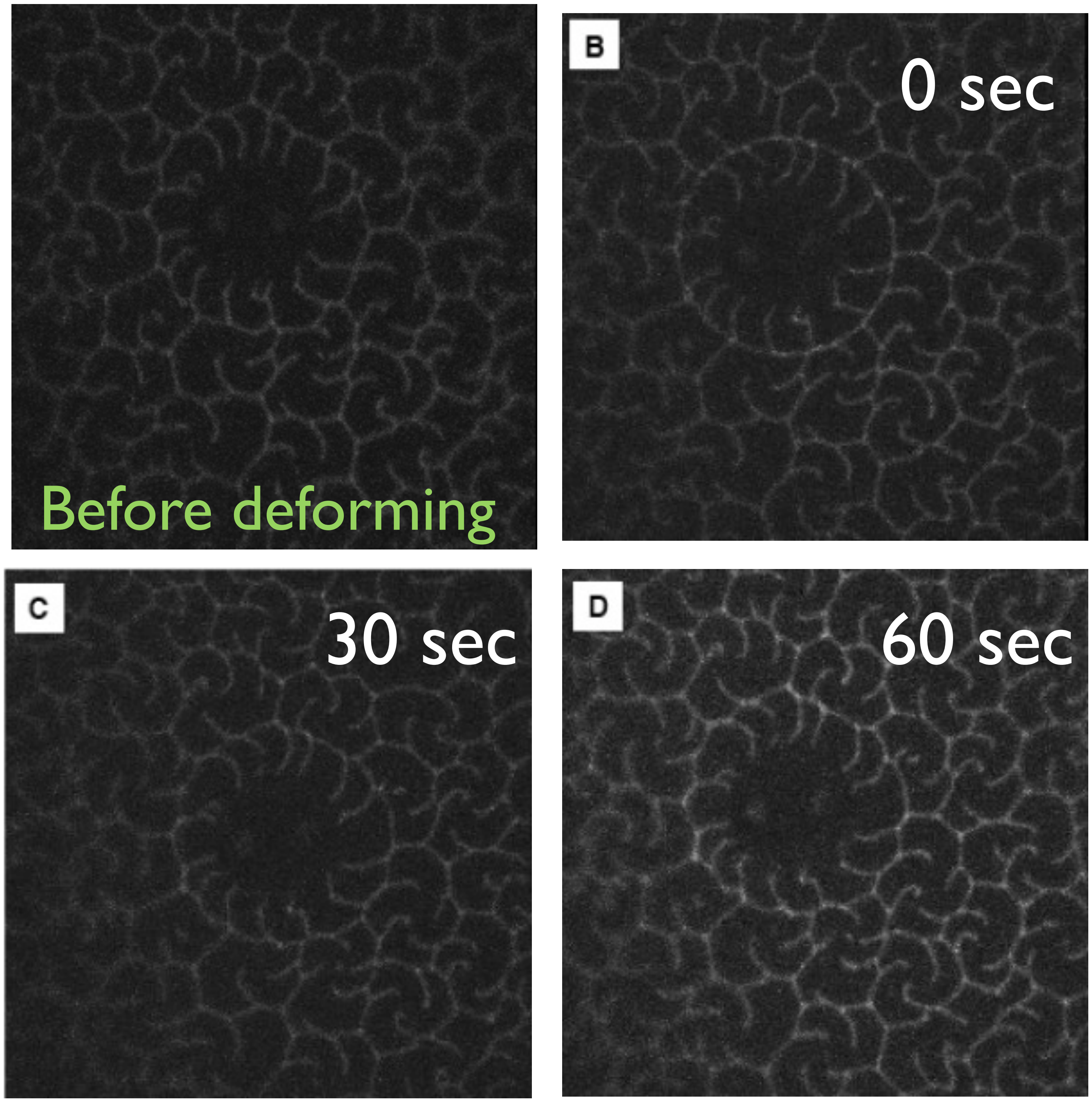
Complete healing of the deformed domains

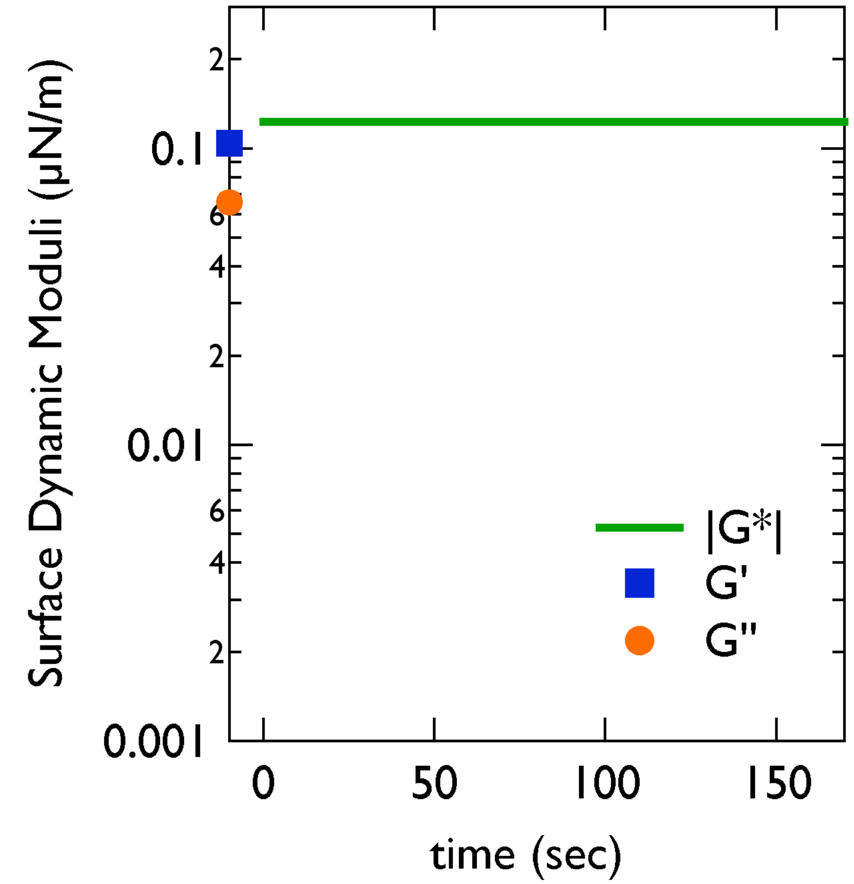
Before deforming



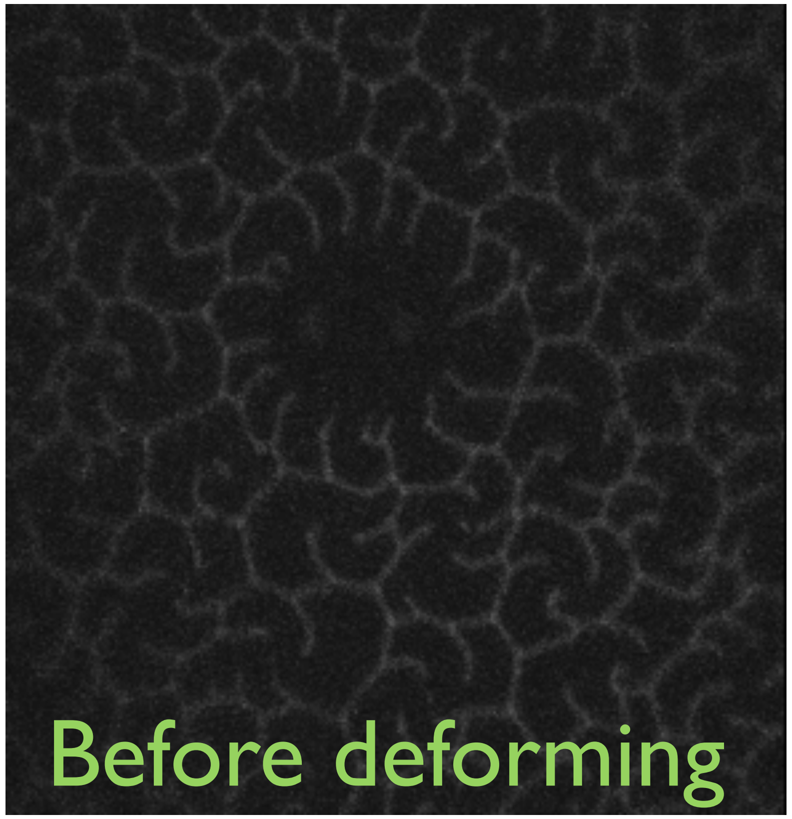


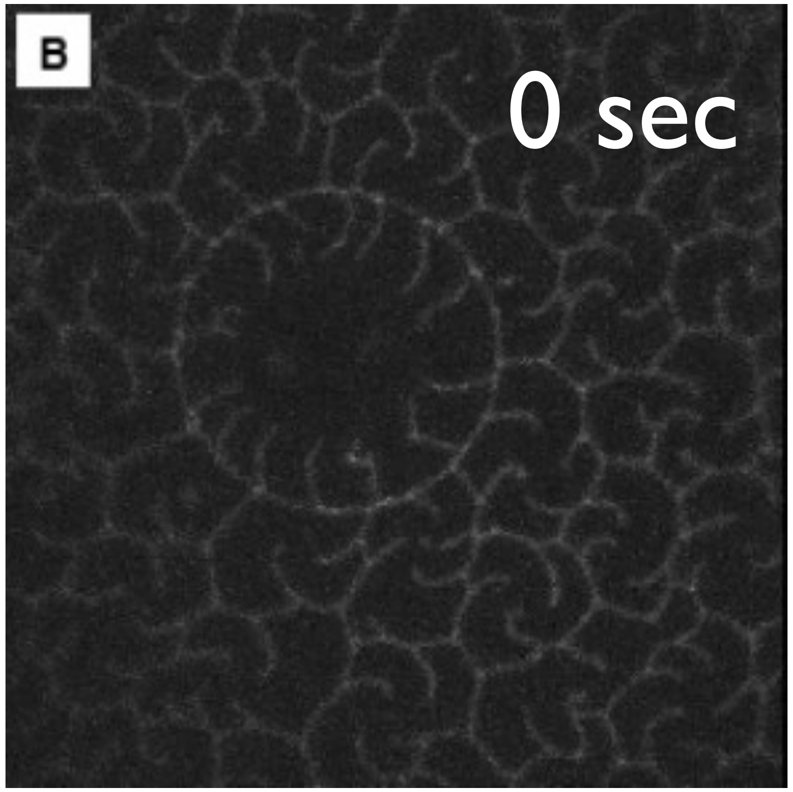
Complete healing of the deformed domains

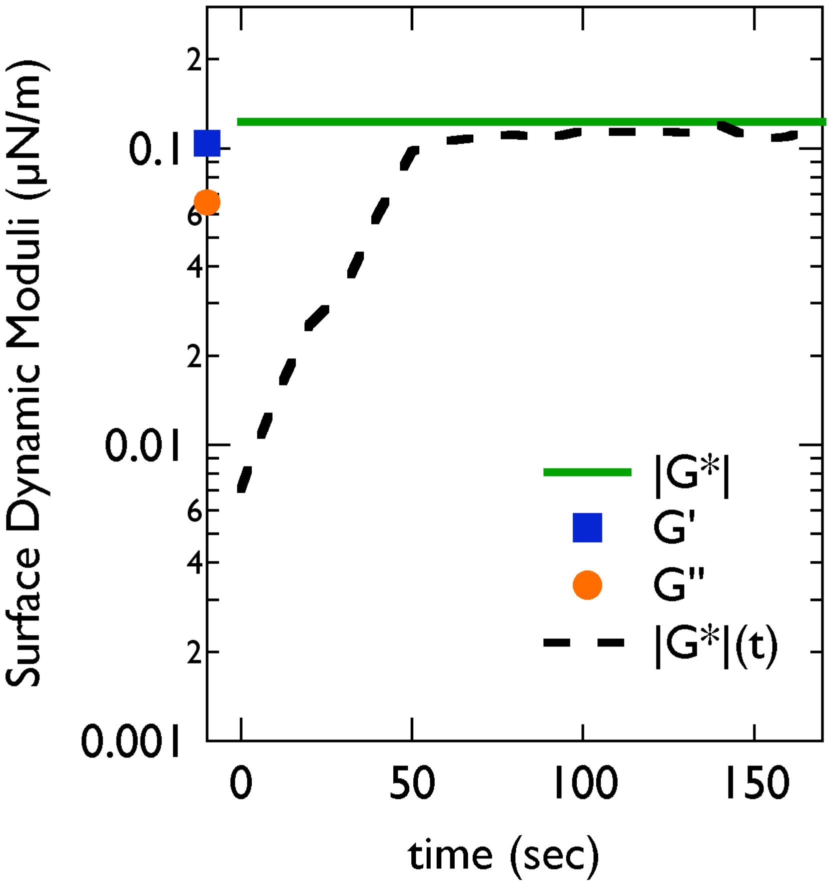


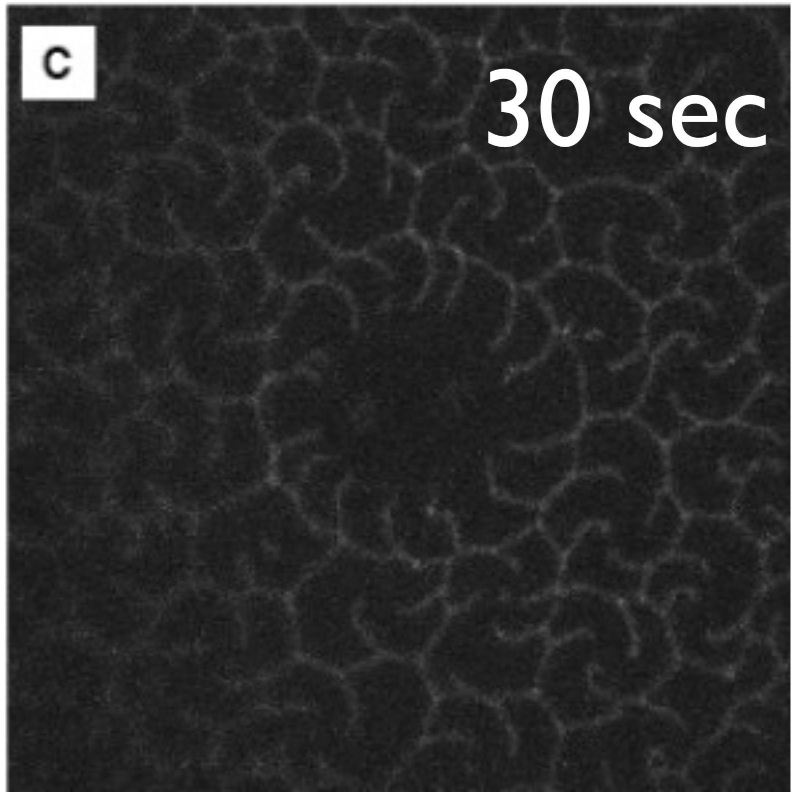


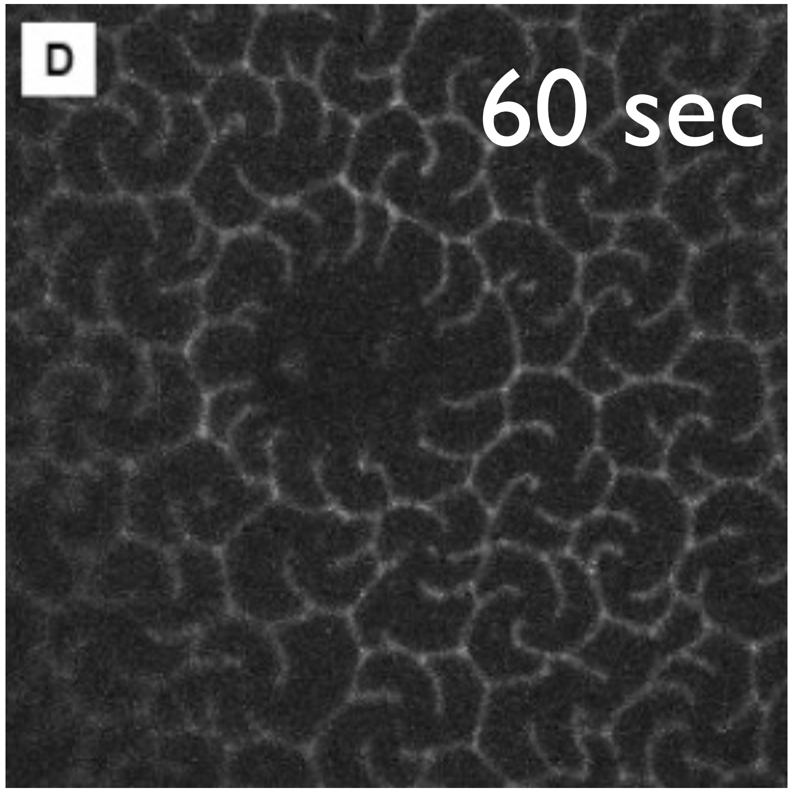
Complete healing of the deformed domains





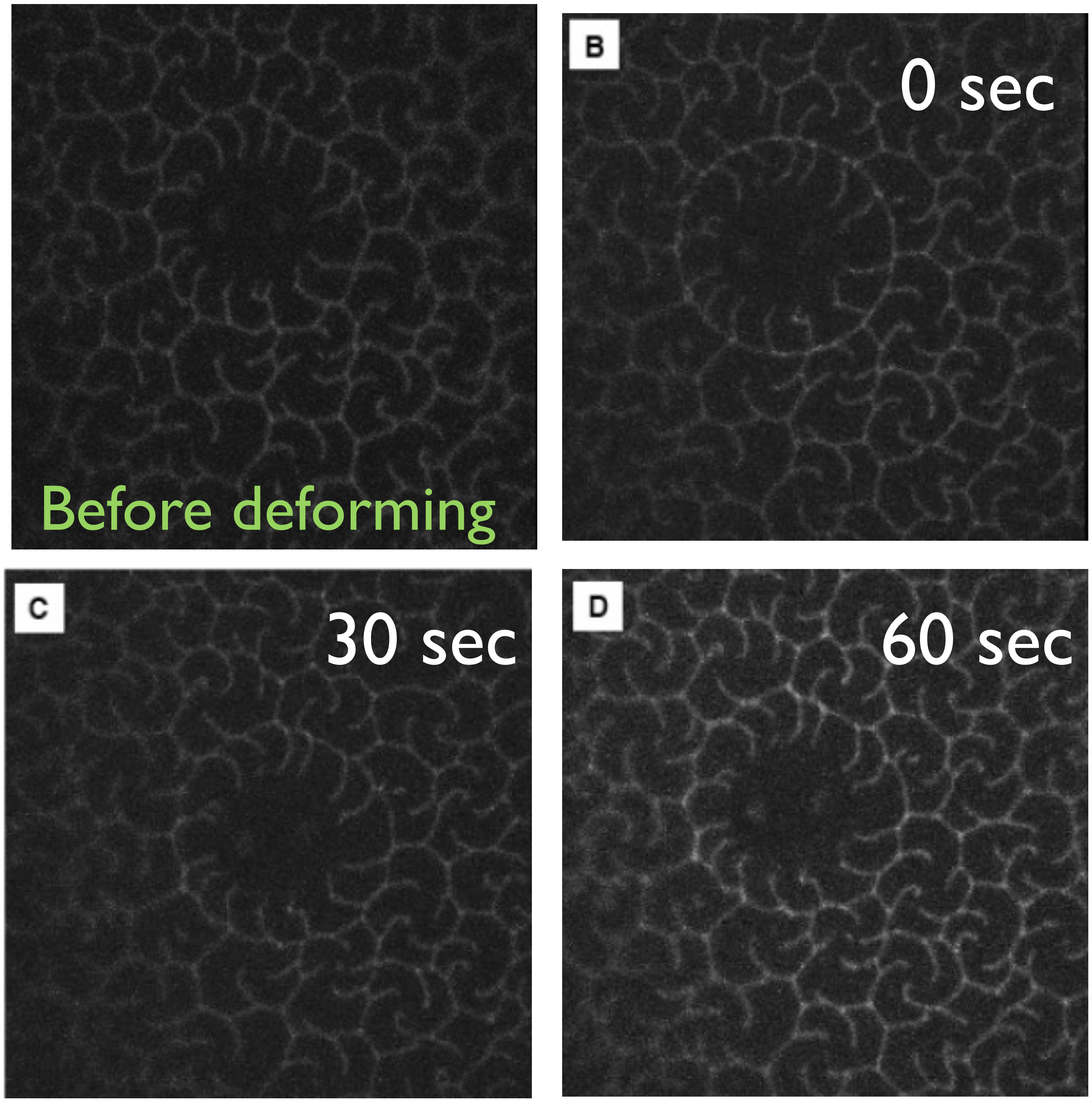


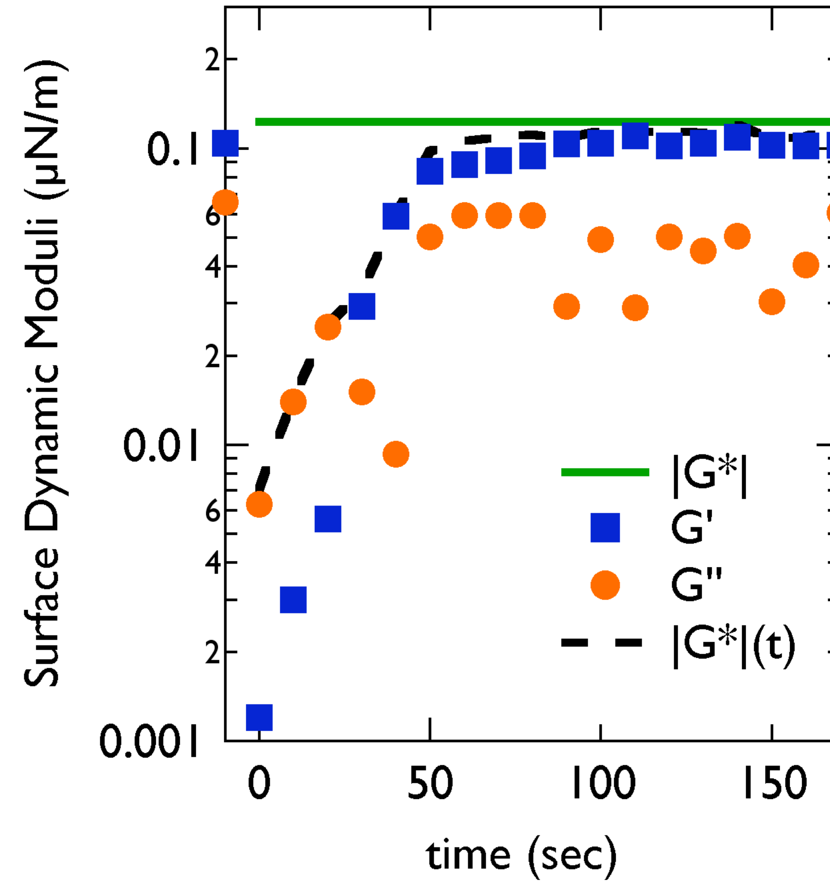




20 times smaller moduli after large stress

Complete healing of the deformed domains



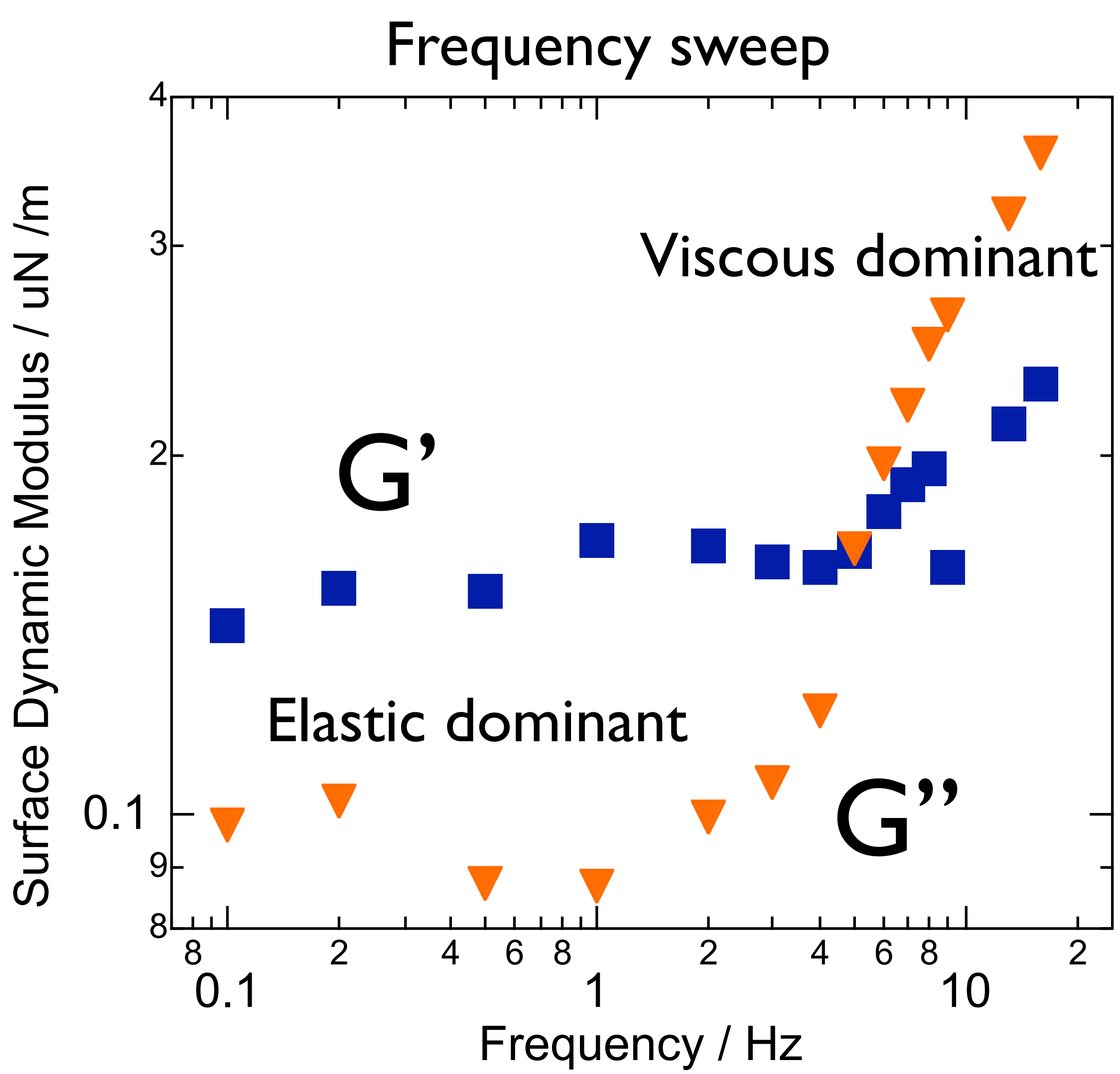


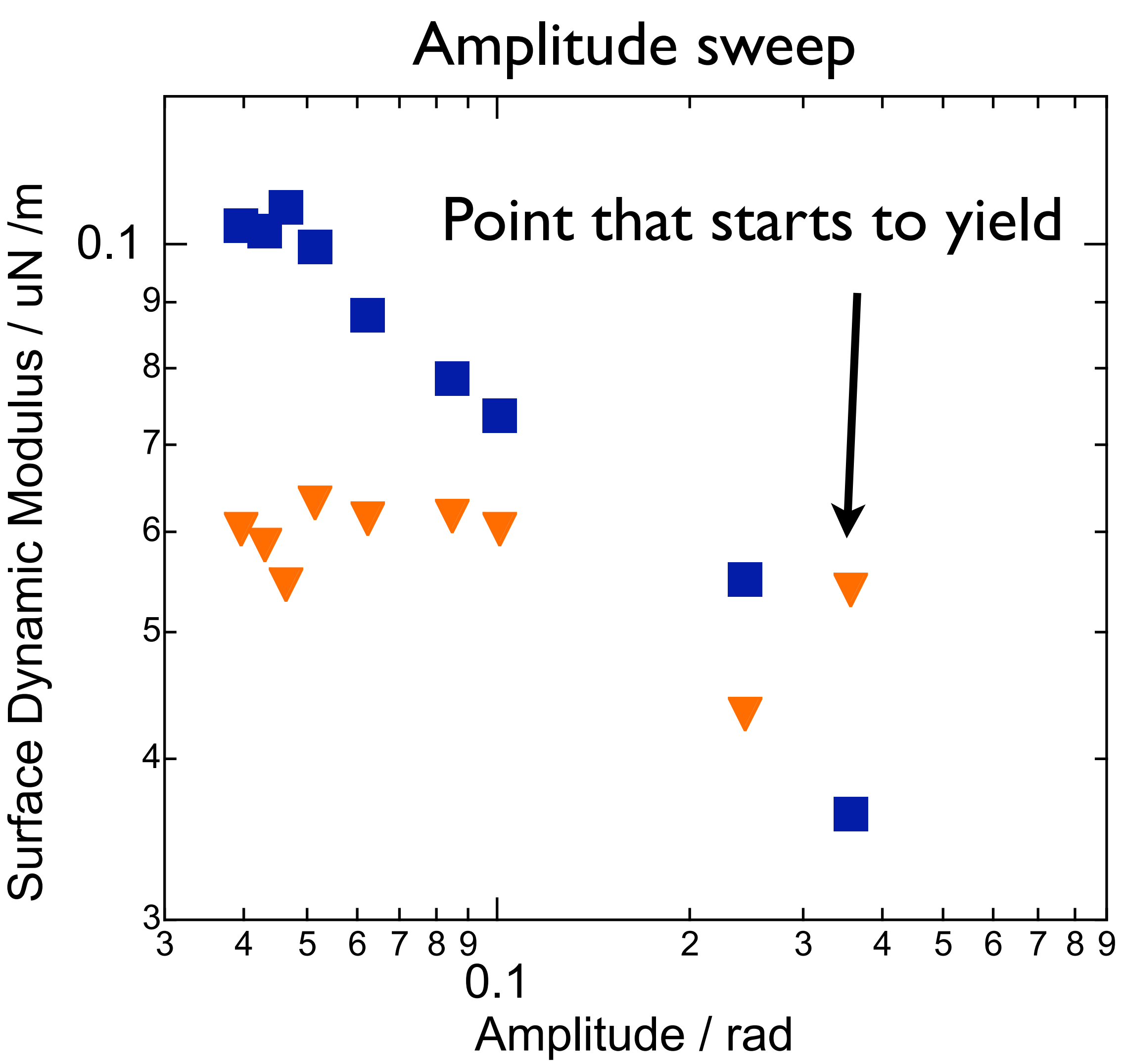
20 times smaller moduli after large stress

Viscous - Elastic transition

A few clues of yield stress

2 nm molecular Mayonnaise??





Steady rotation - yield stress

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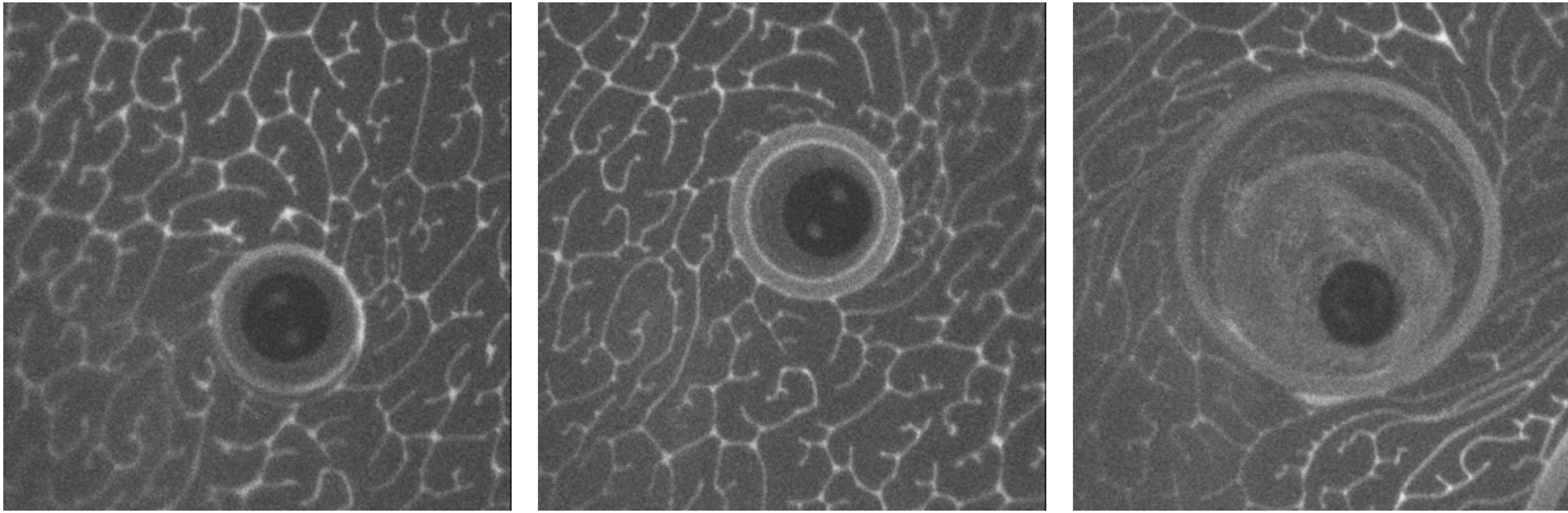
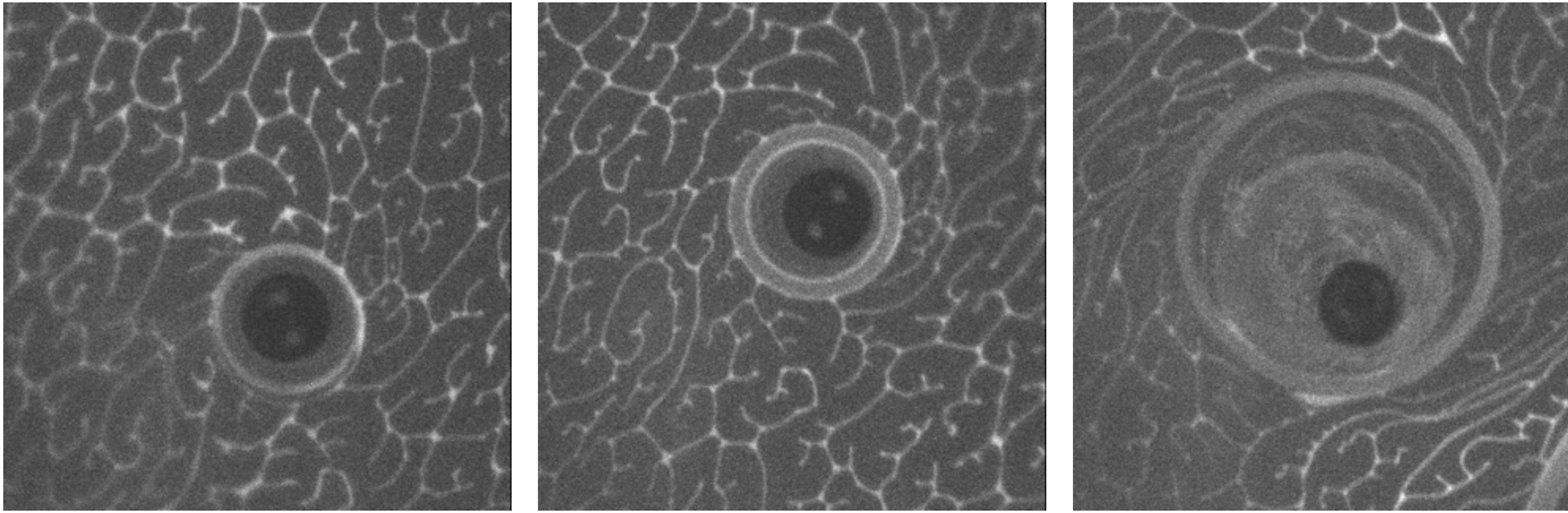


Steady rotation - yield stress



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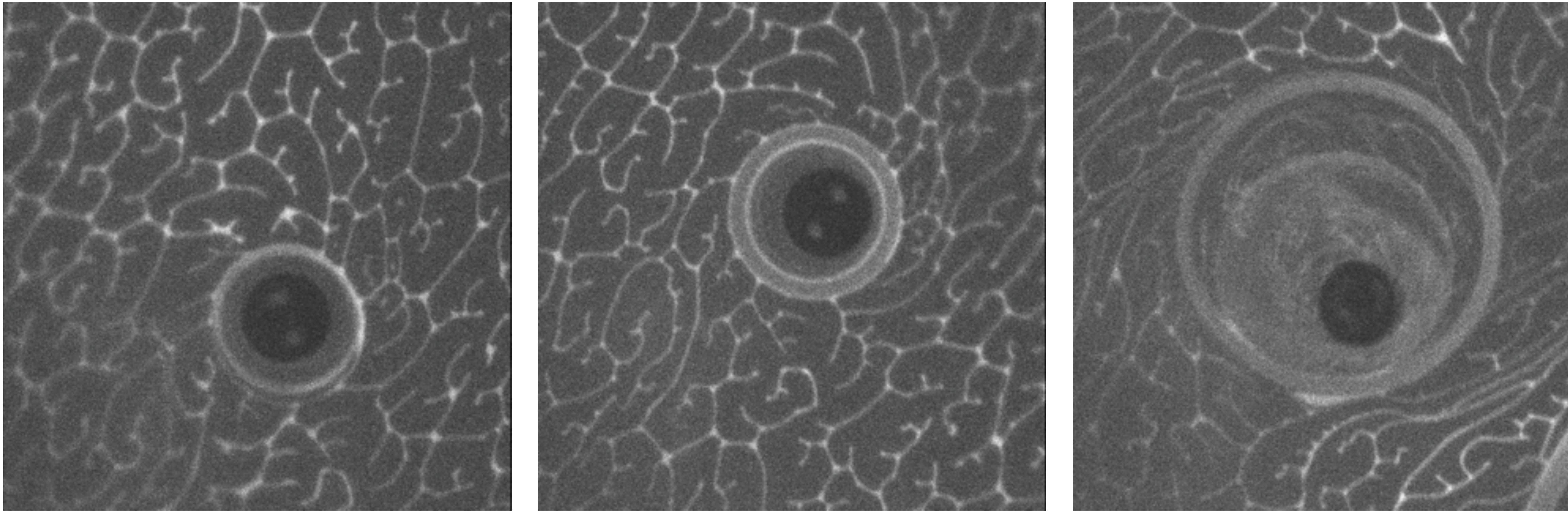

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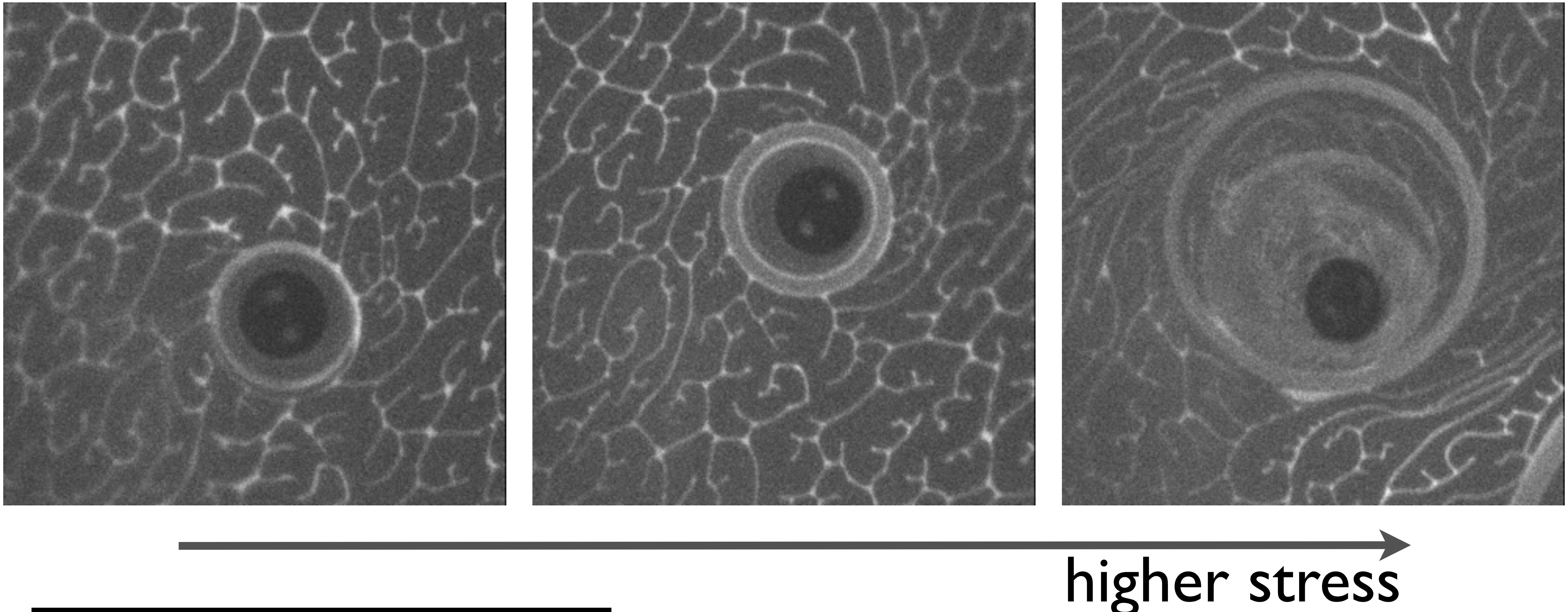


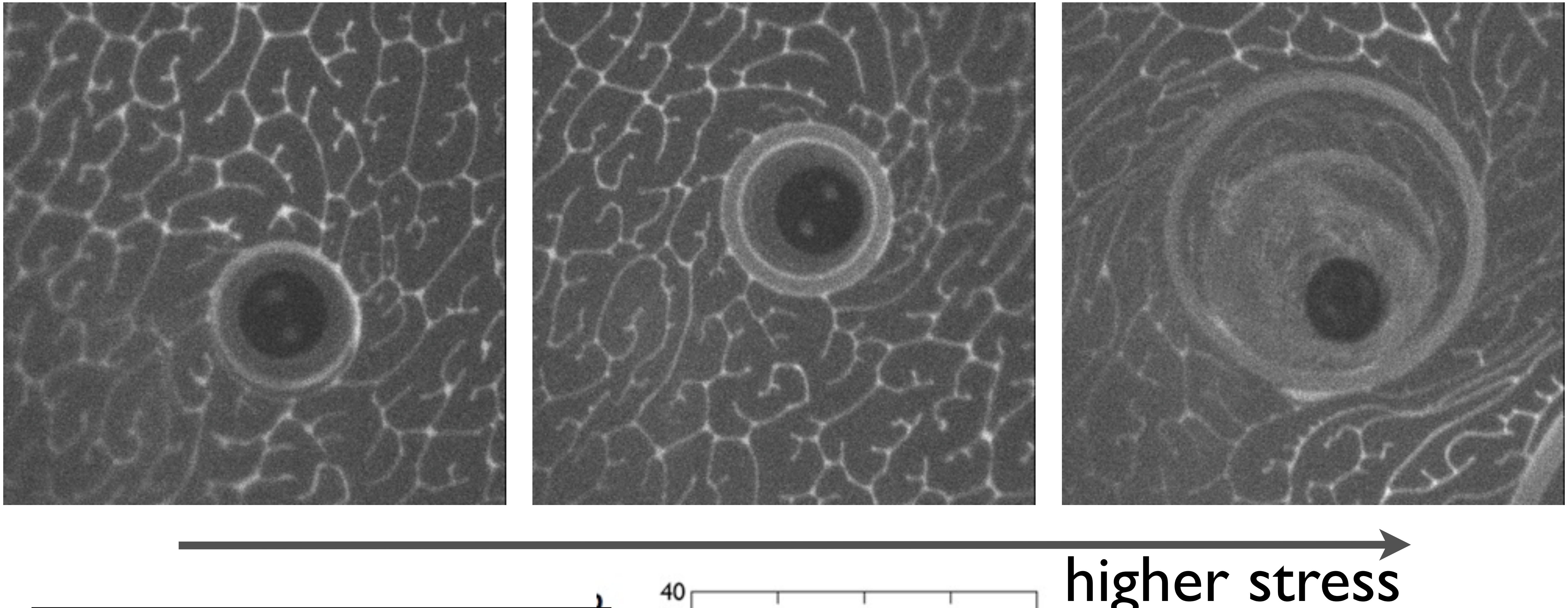
- **Evident yield stress**

$$\tau \sim \sigma_y r_c (2\pi r_c)$$

applied stress~ yield stress

$$\sigma_y \sim 10^{-8} N / m$$

Steady rotation - yield stress



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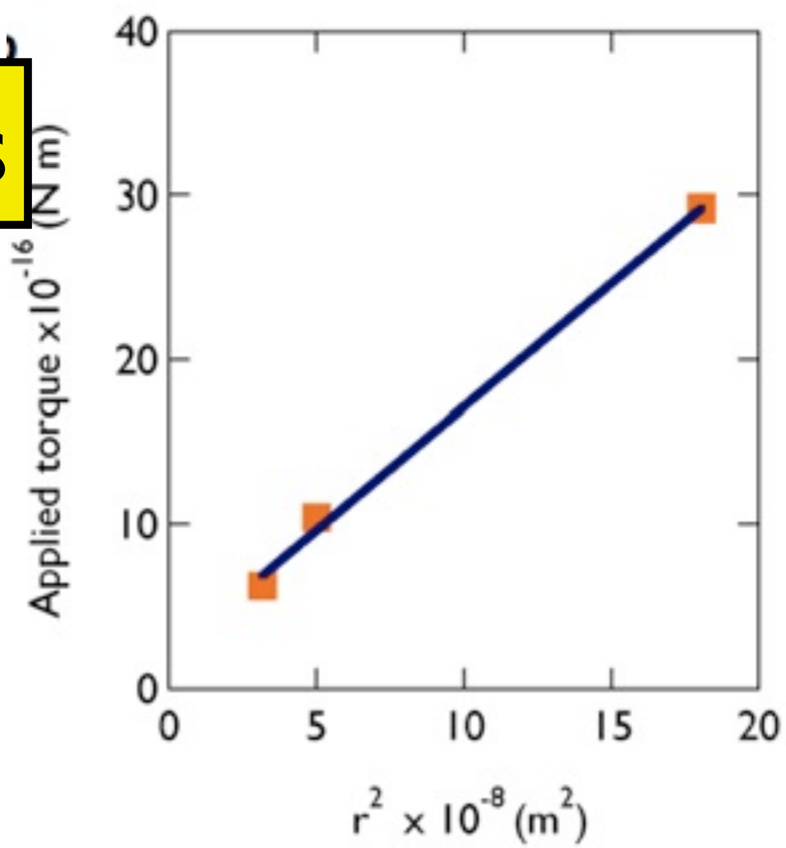
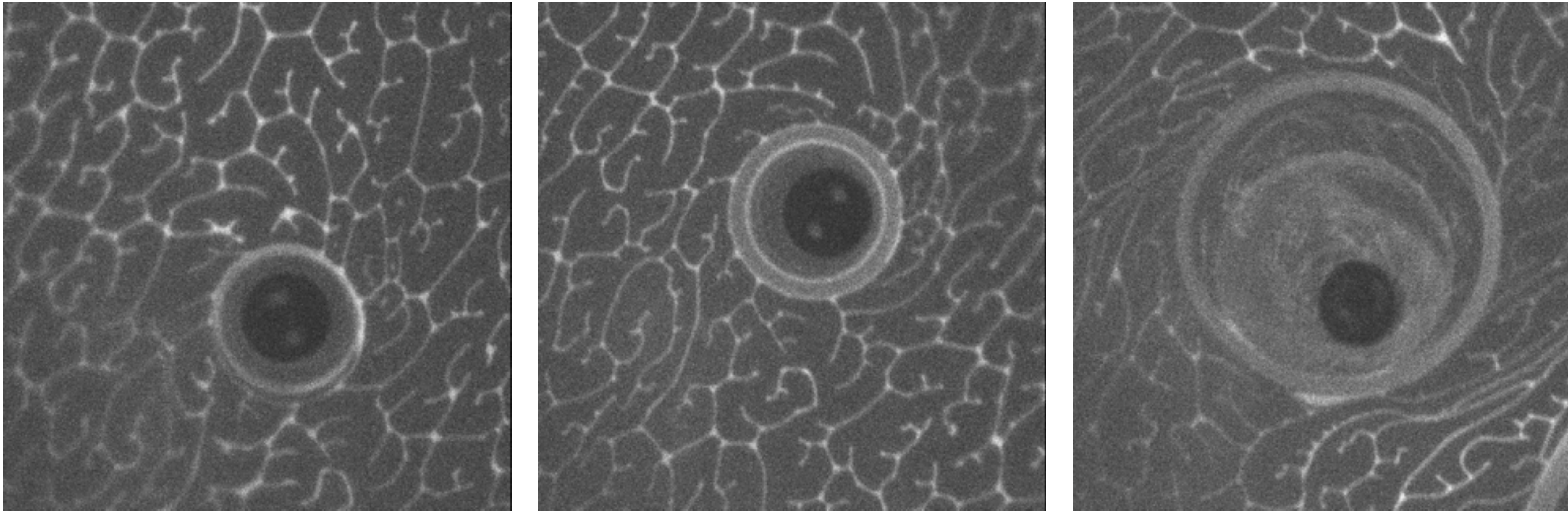


Steady rotation - yield stress



higher stress

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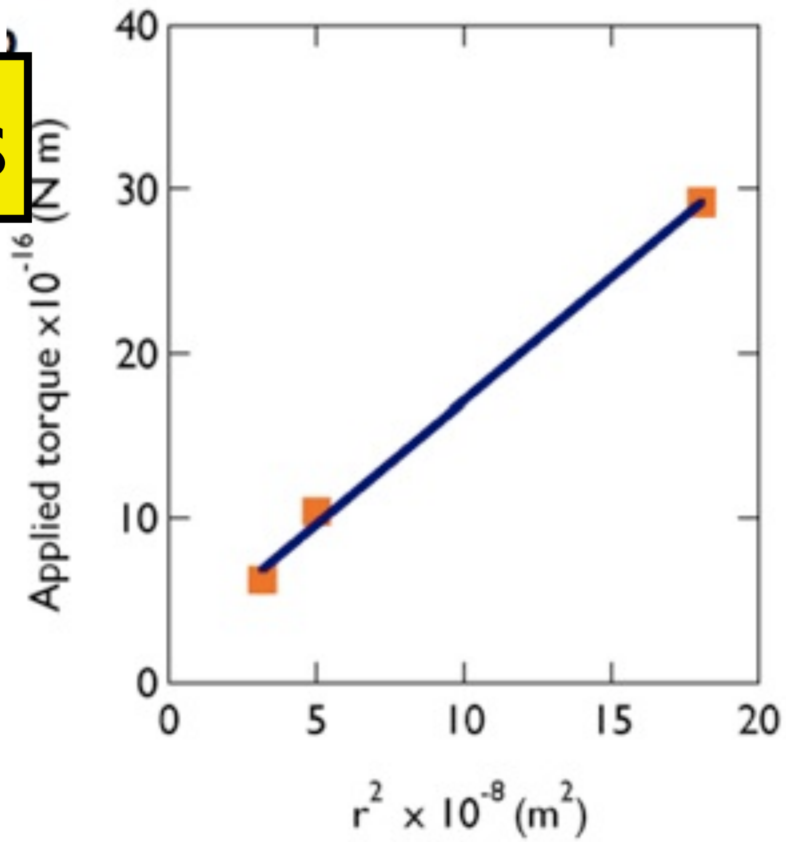
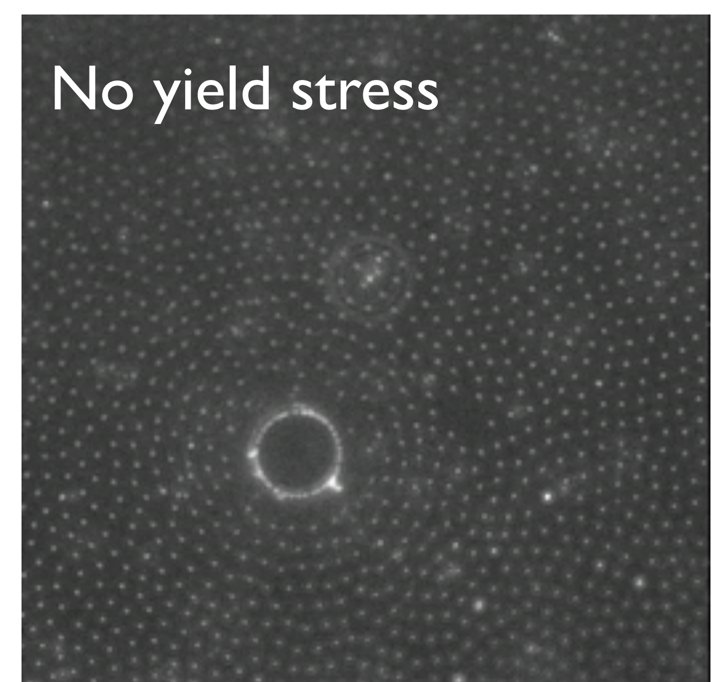
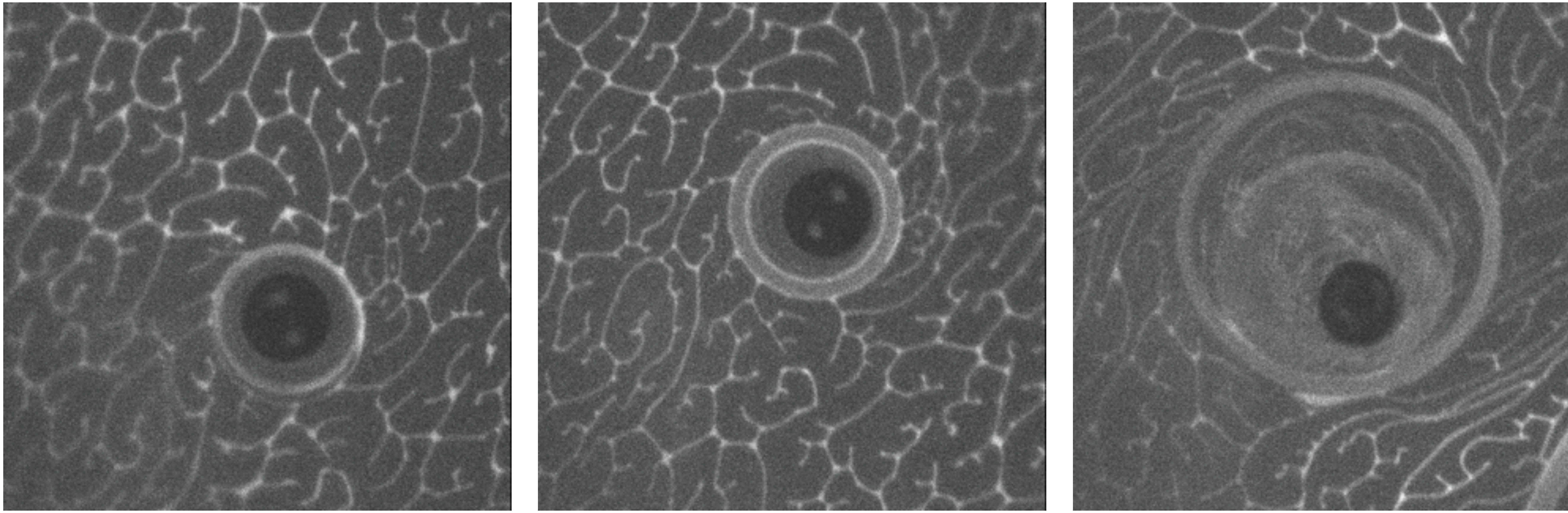




Steady rotation - yield stress



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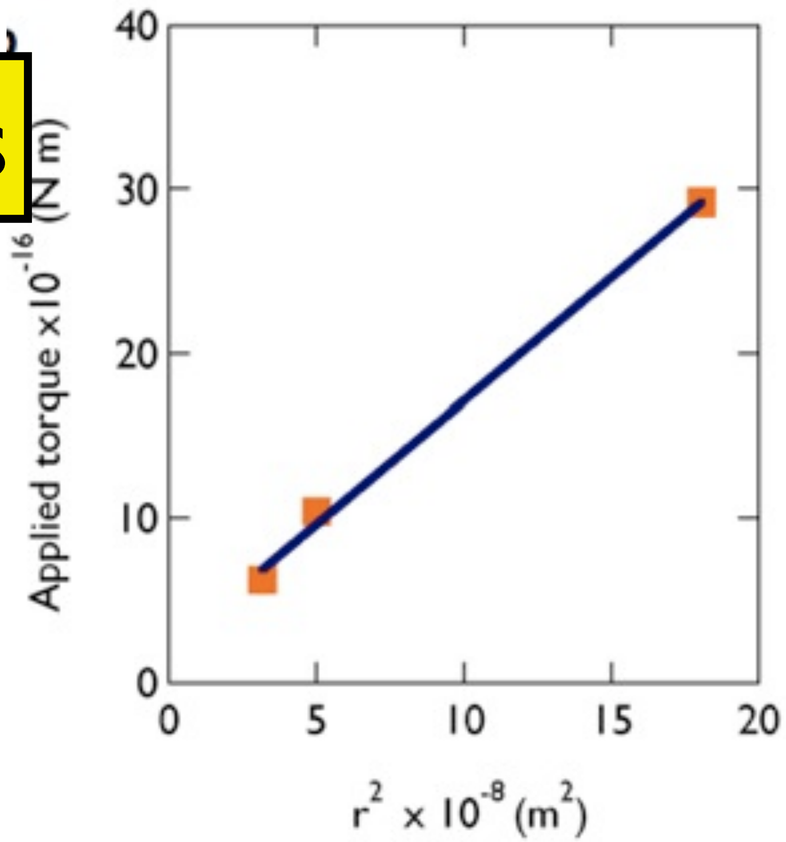
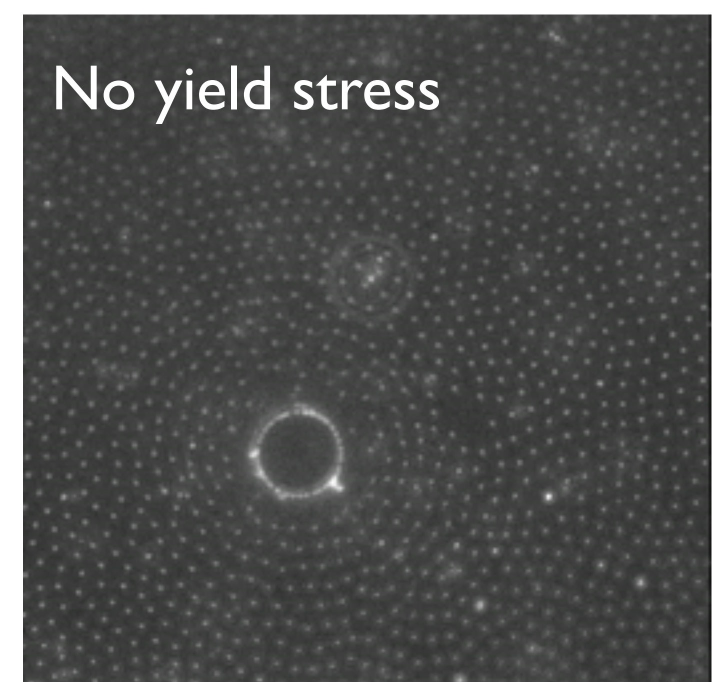
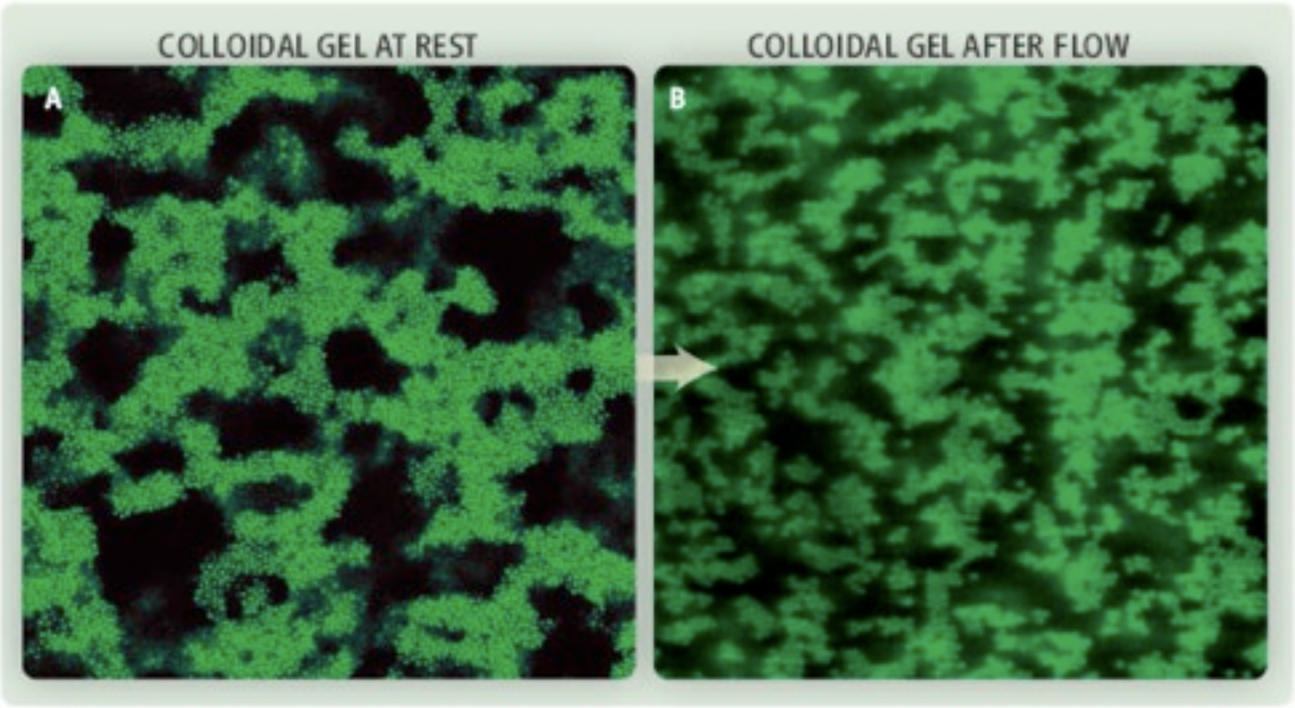


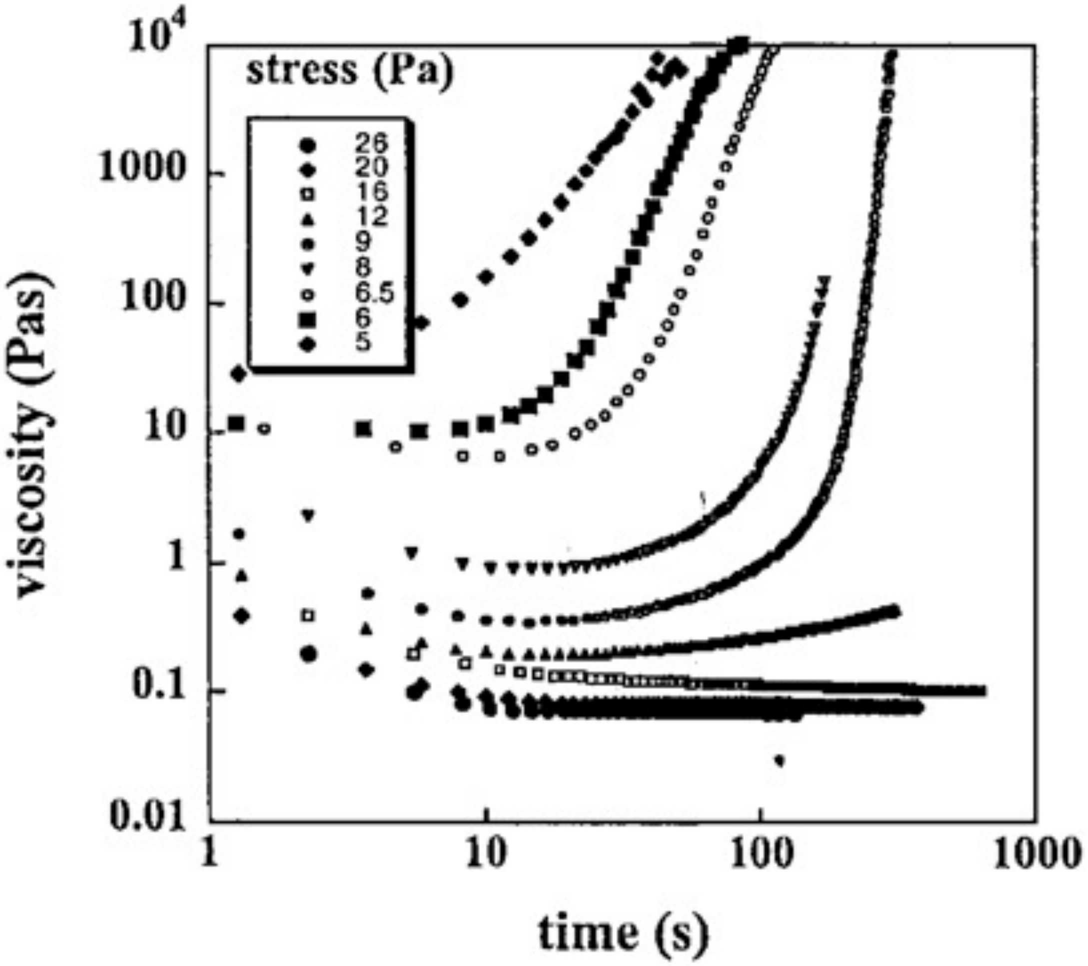


Yield stress

Thixotropic behavior

(time dependent viscosity)





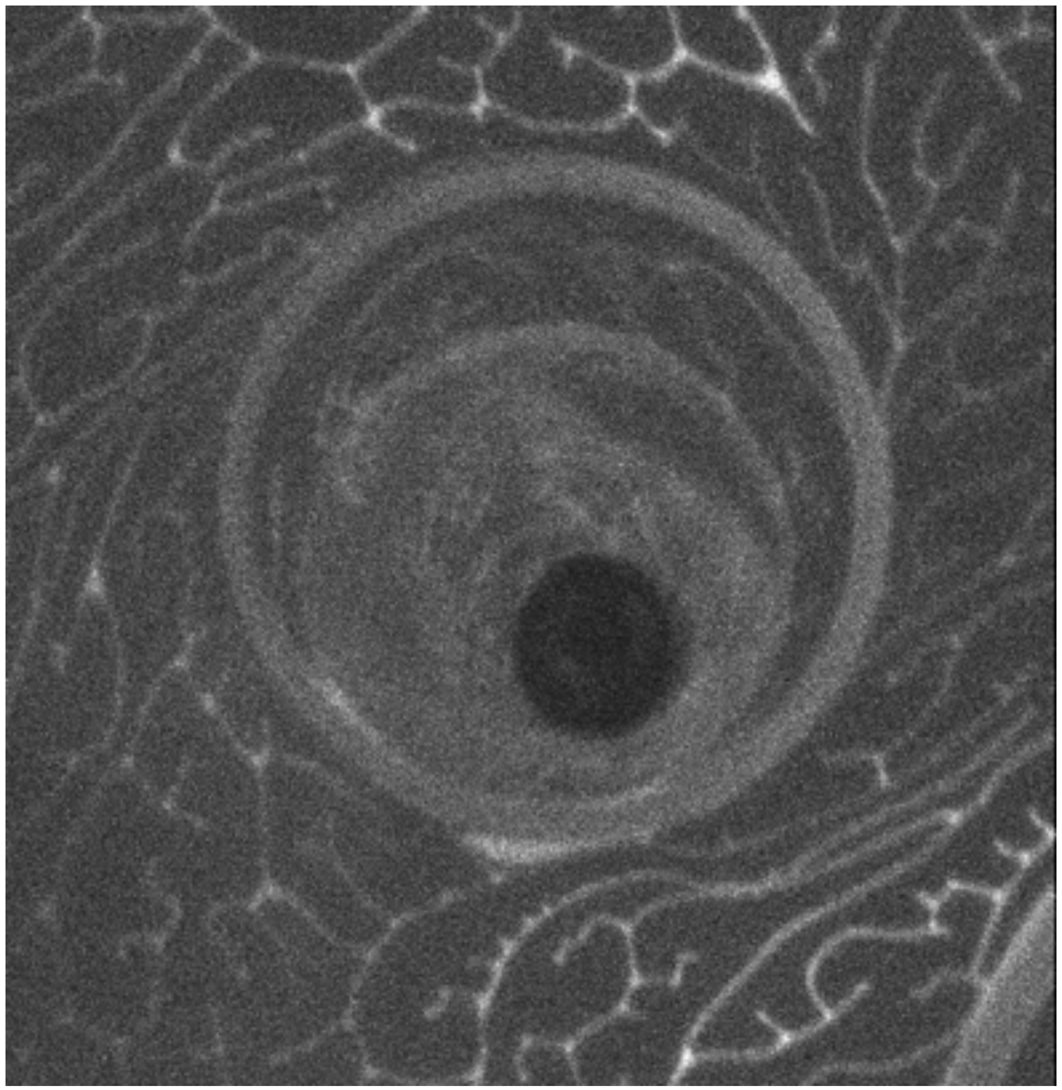
Theories and experiments by Daniel Bonn

Aging (system) vs Rejuvenation (applied stress)

Can we do analogous experiments after yielding the interface?

After ~ 5 minutes rotation
We turn off the field

After ~ 5 minutes rotation
We turn off the field



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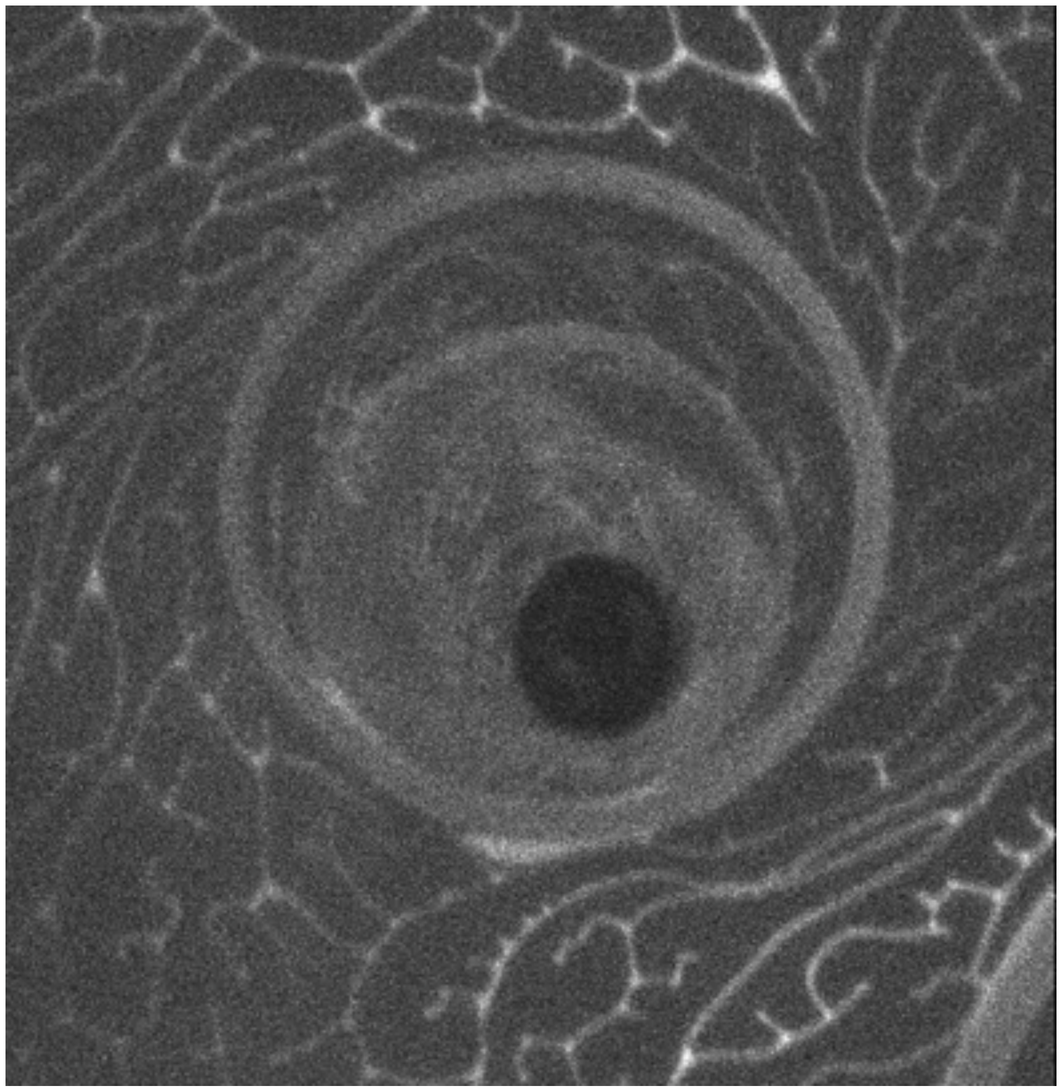

Field off

→

After ~ 5 minutes rotation
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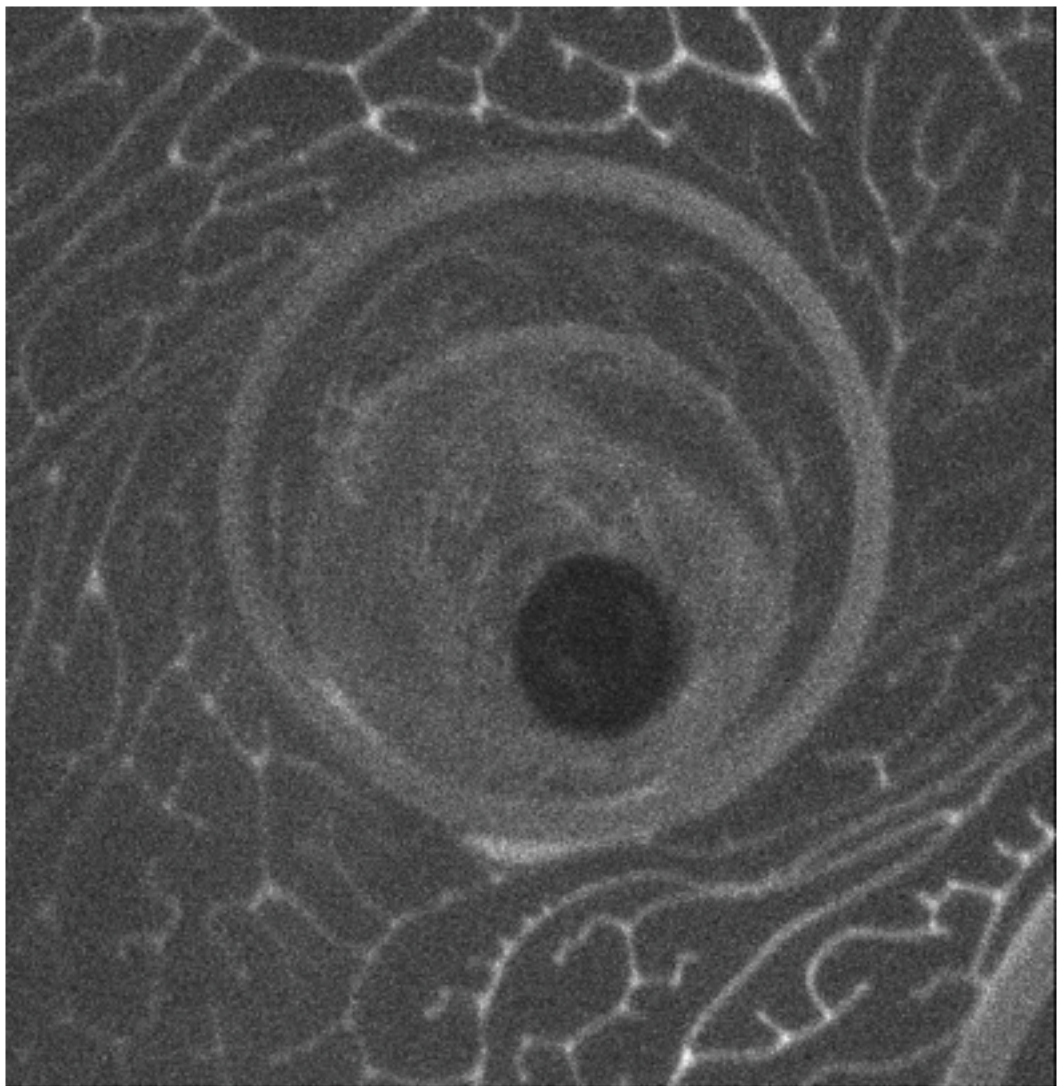
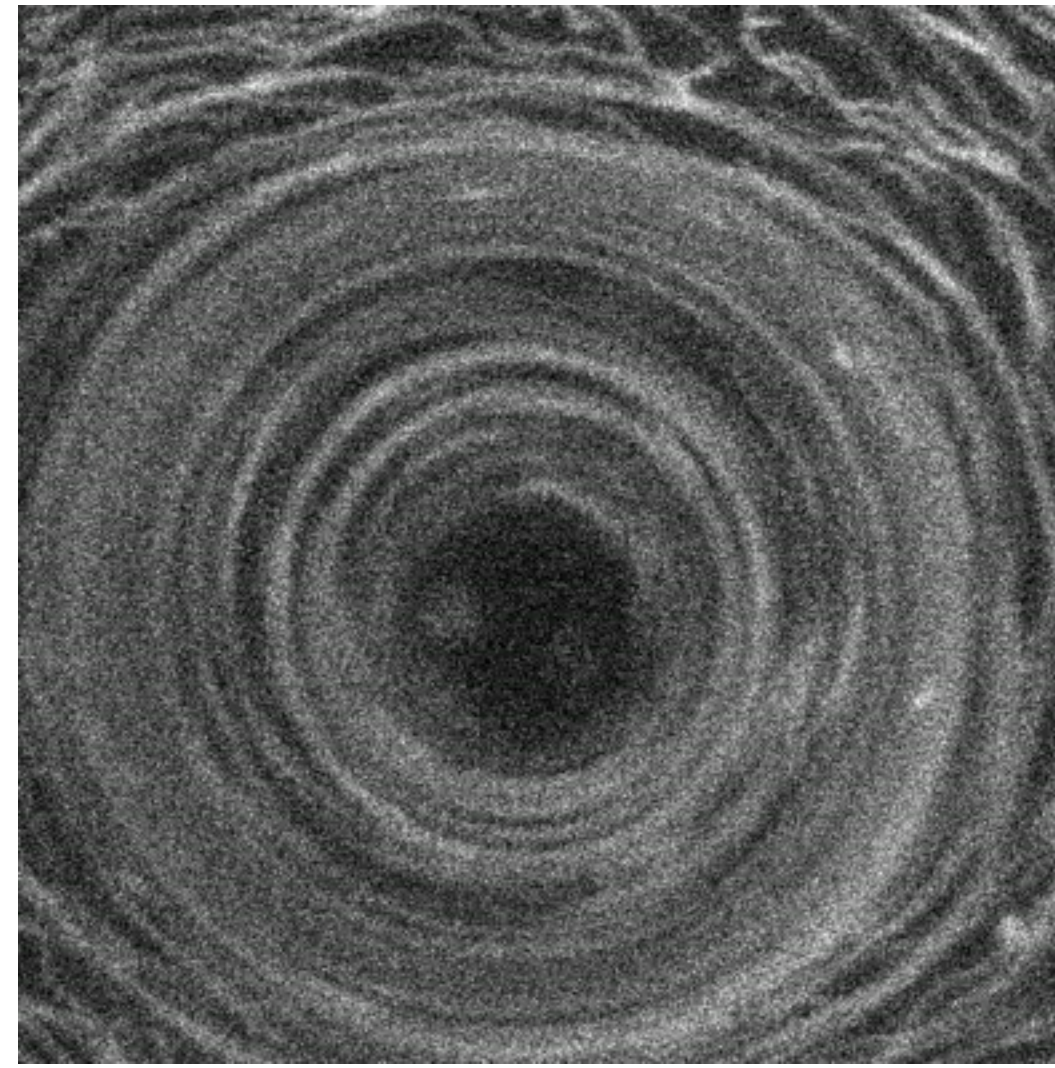


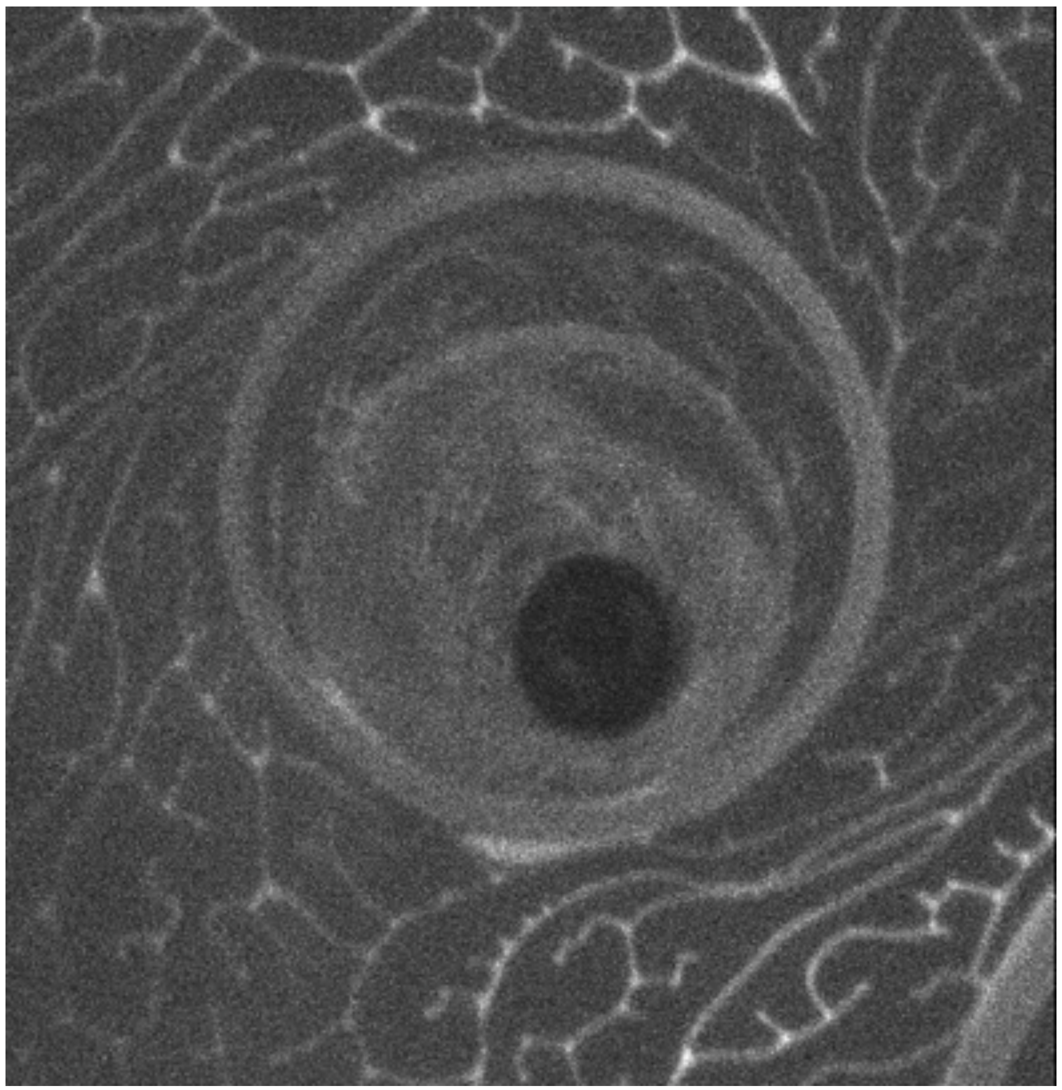
Field off



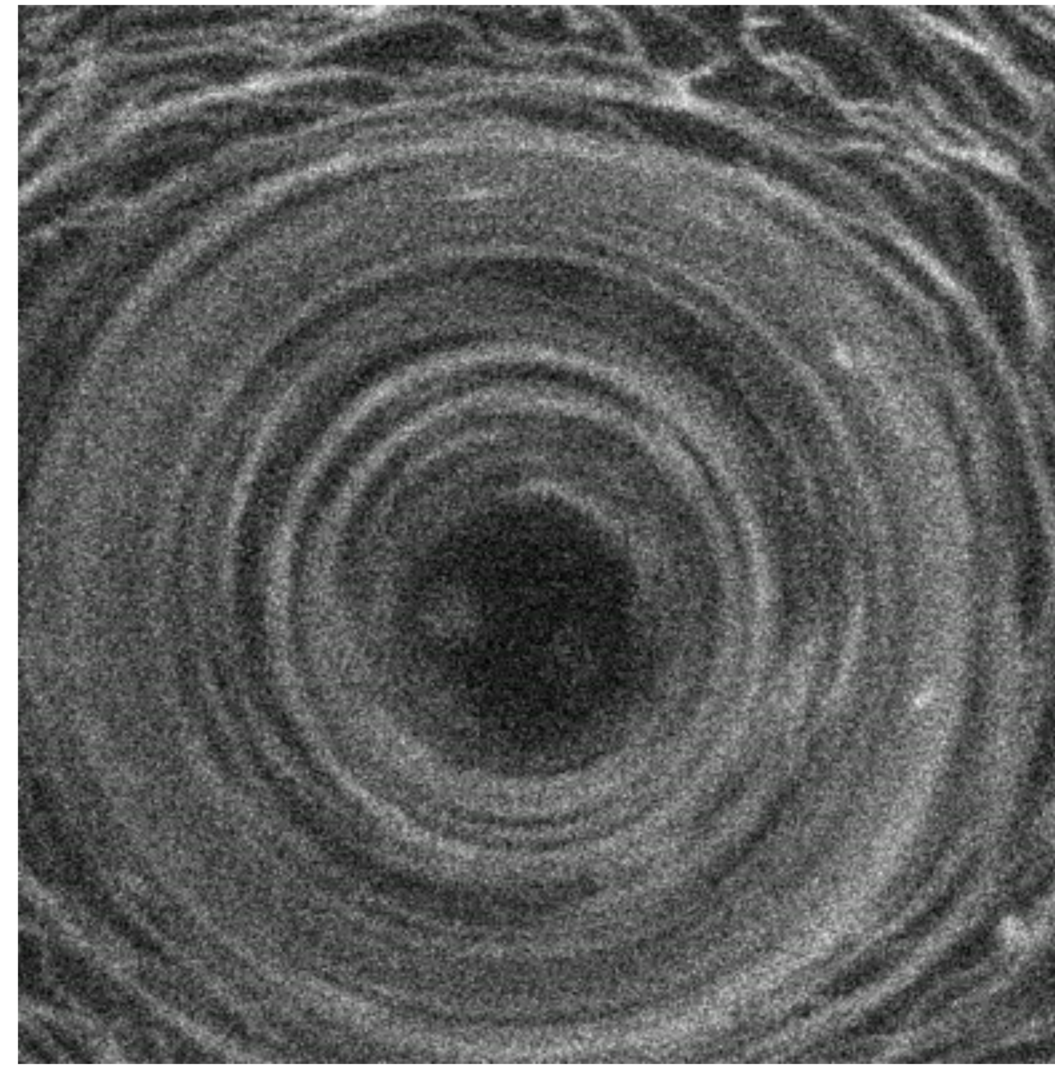
25x real time

Healing by unwinding

After ~ 5 minutes rotation
We turn off the field



Field off →



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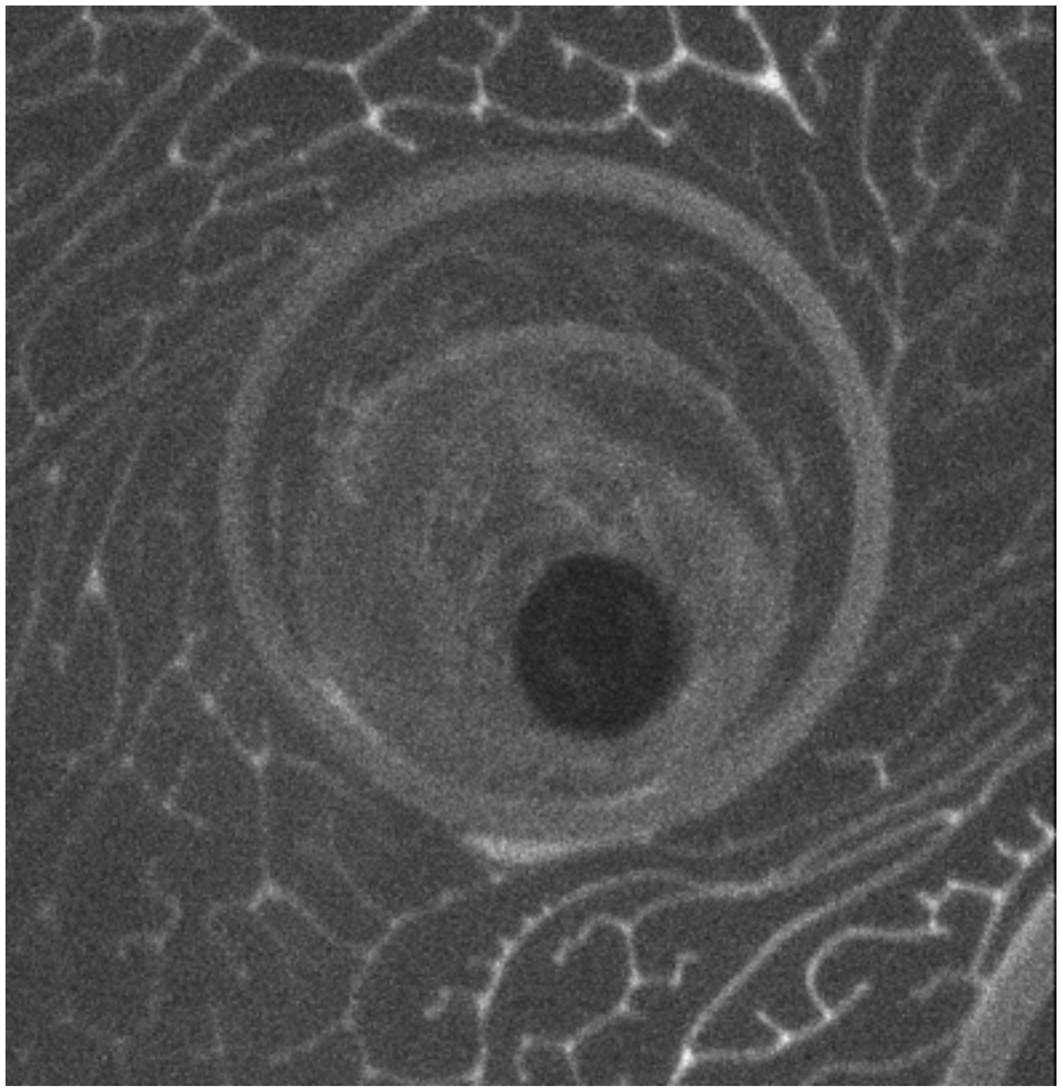
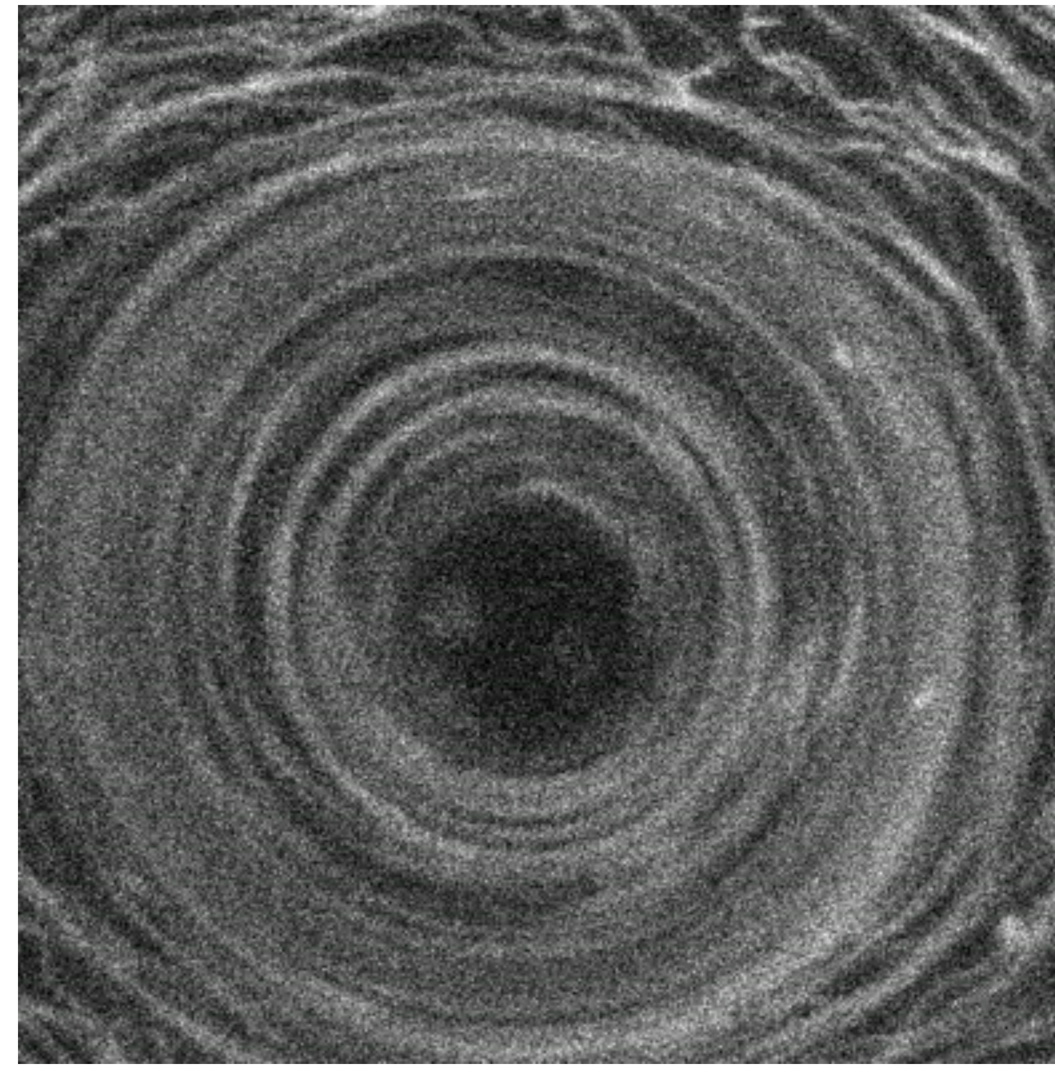


Field off →

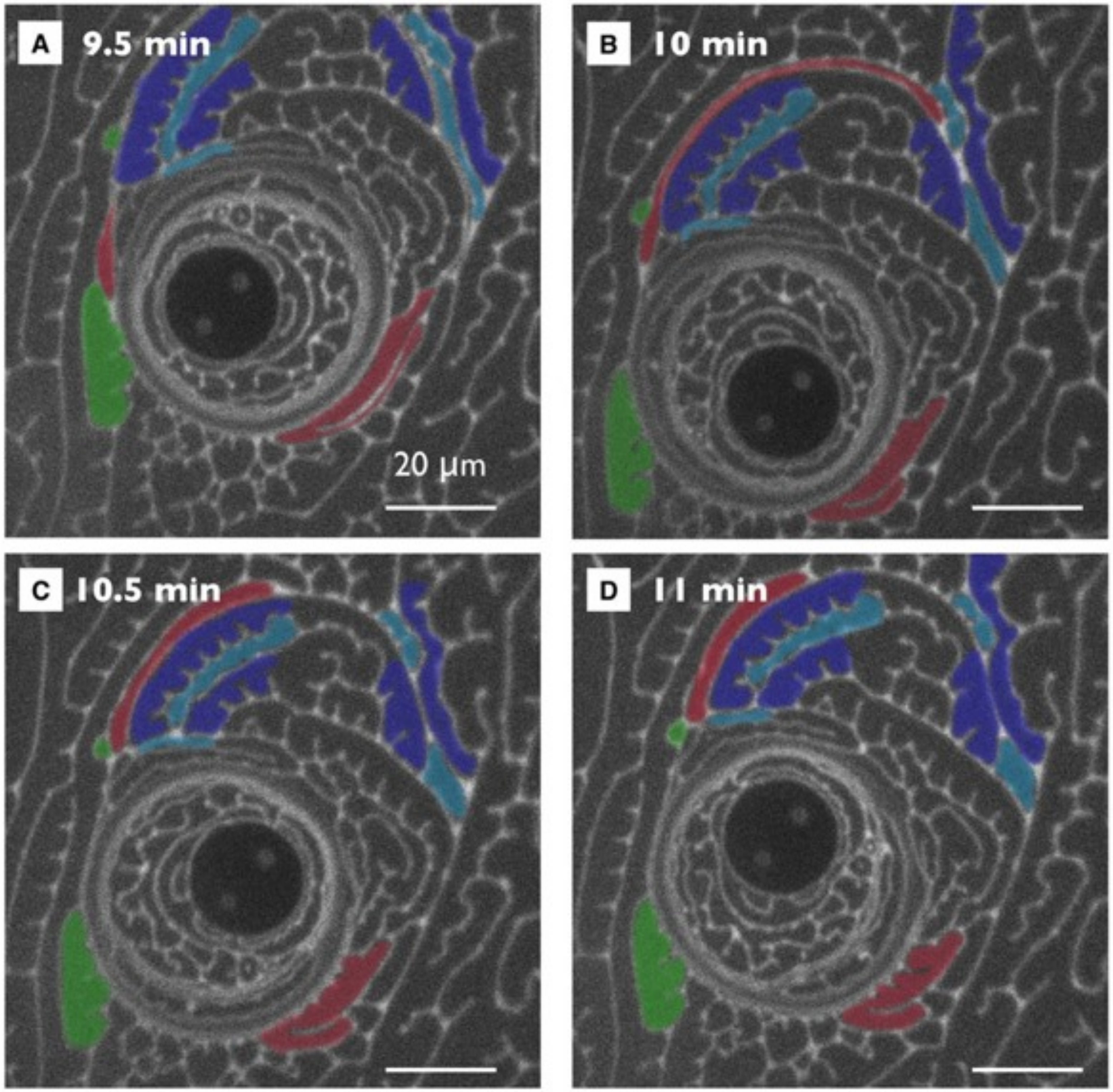


25x real time

Healing by unwinding

Strong memory
Slow recovery

Watching individual domains



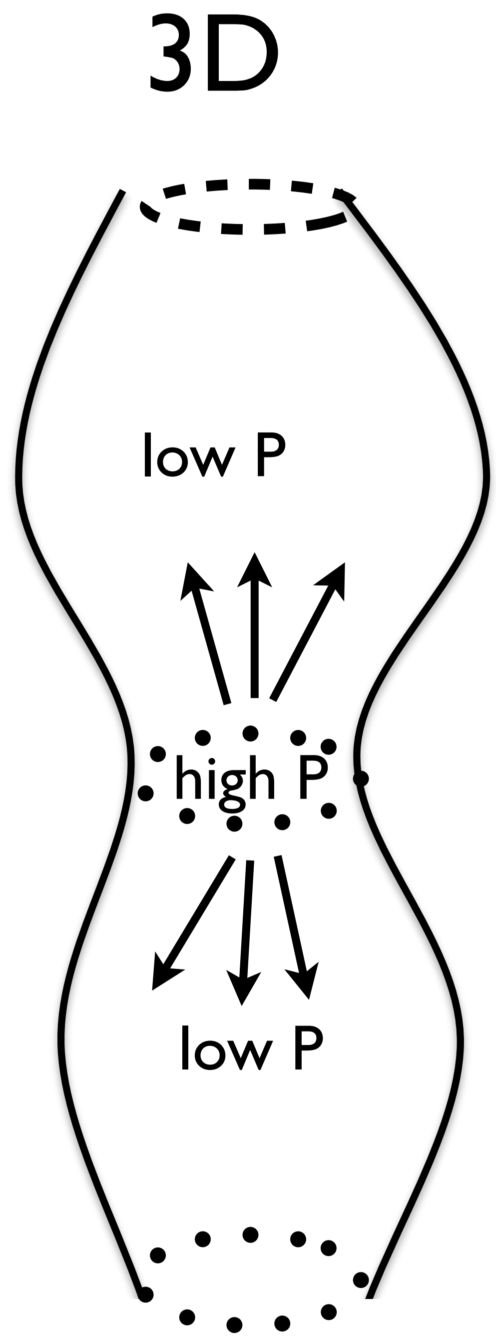
Blue - T1 transition

Red - recoiling

Green - change its neighbor

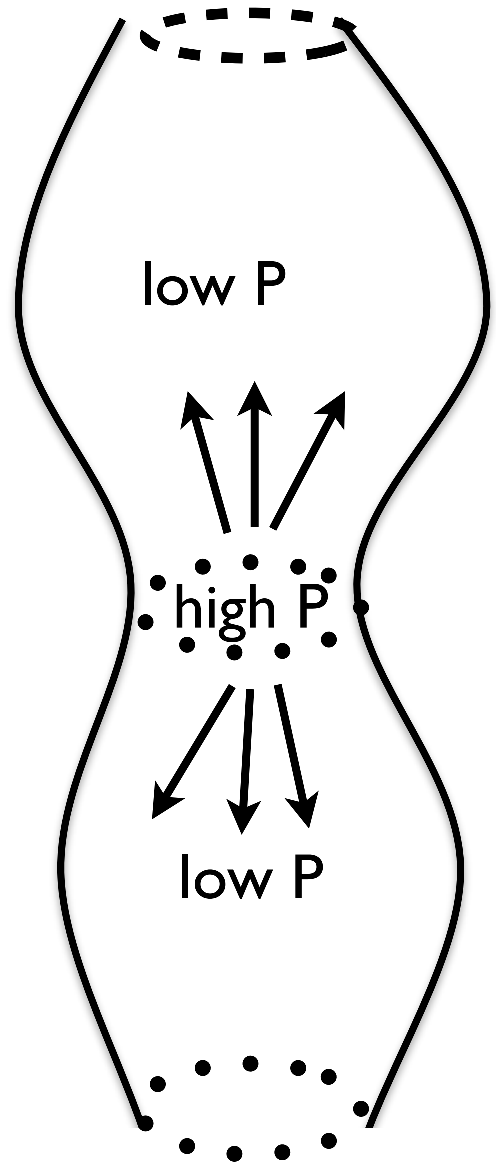
Domains don't melt - they stretch!

Rayleigh - Plateau instability

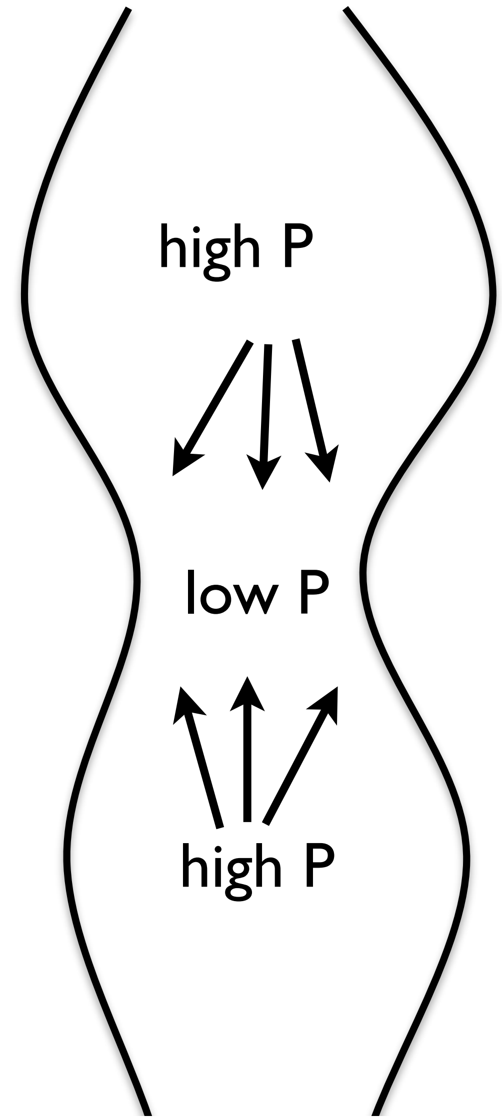


Rayleigh - Plateau instability

3D

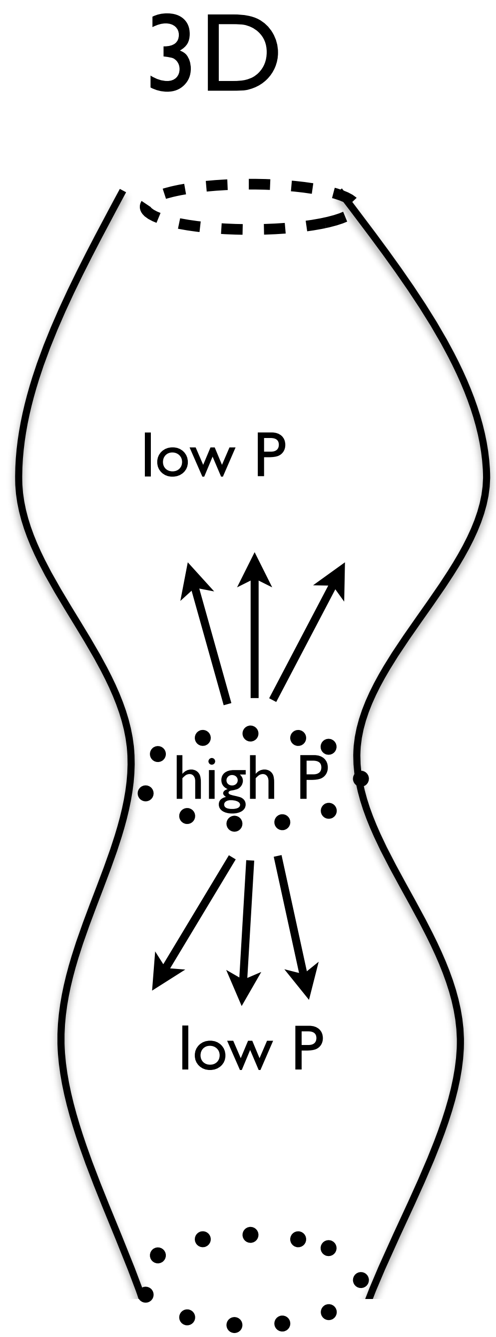


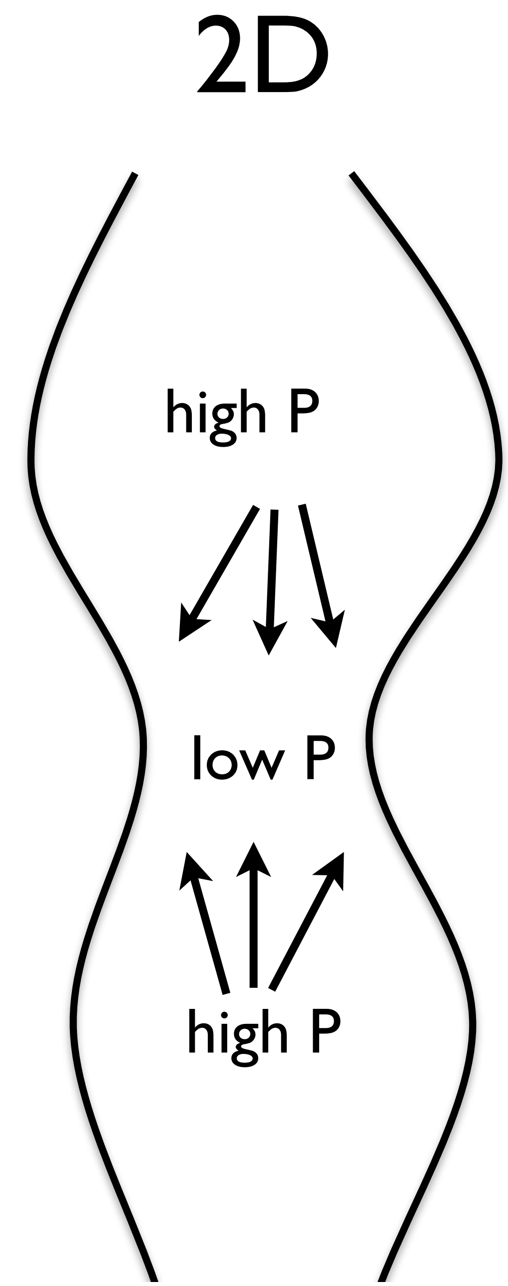
2D



Always stable without fluctuation or defects

Rayleigh - Plateau instability

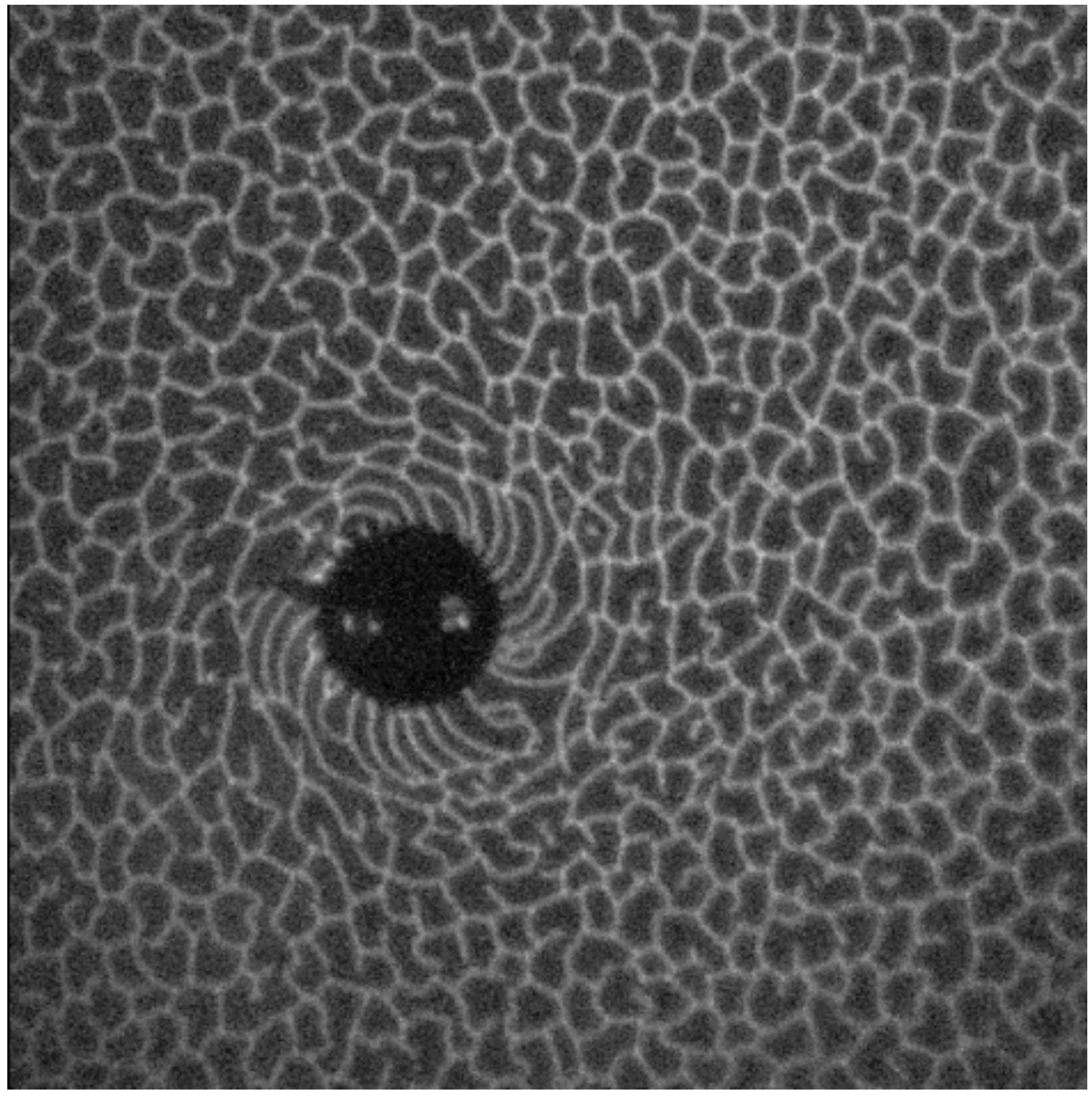




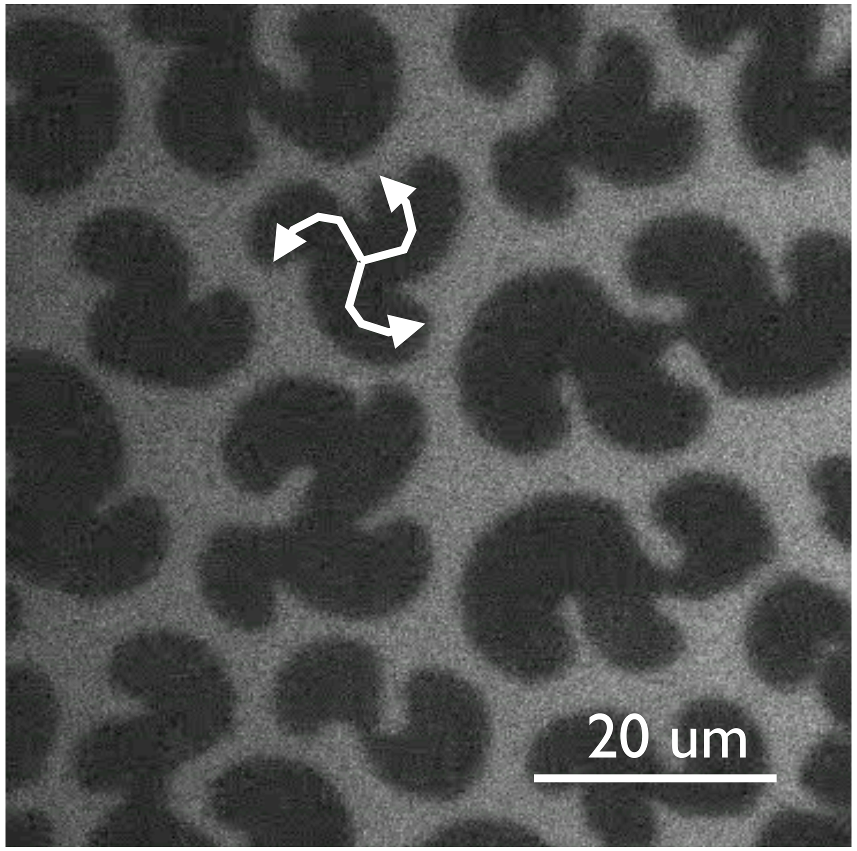
Always stable without fluctuation or defects

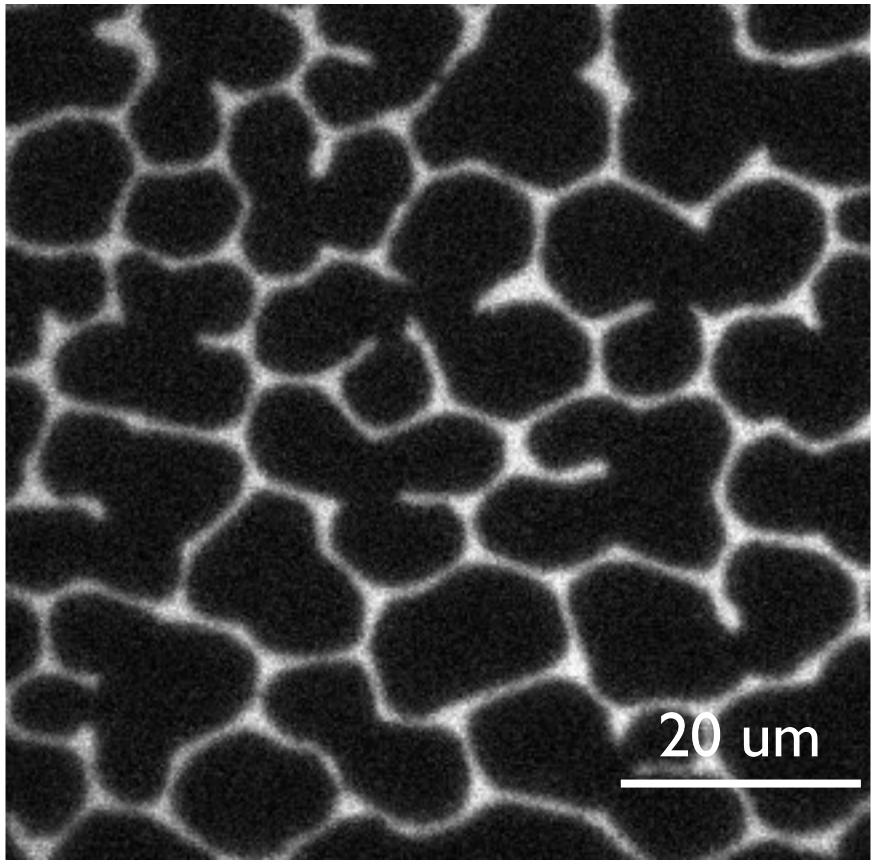
No Rayleigh-Plateau instability for 2D

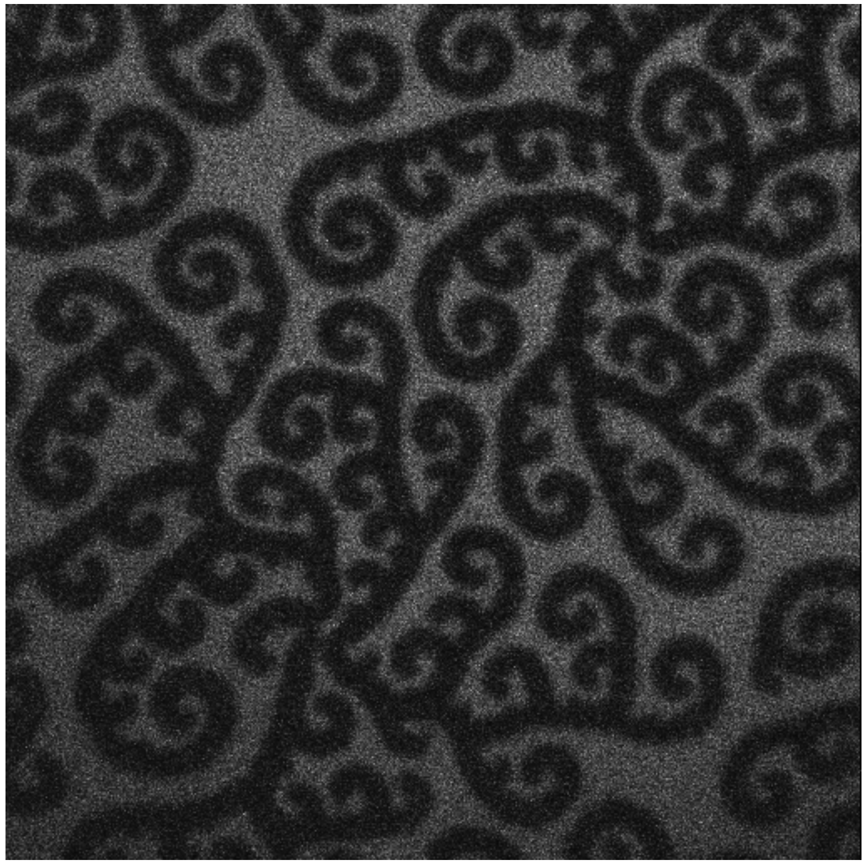
Asymmetric stress response

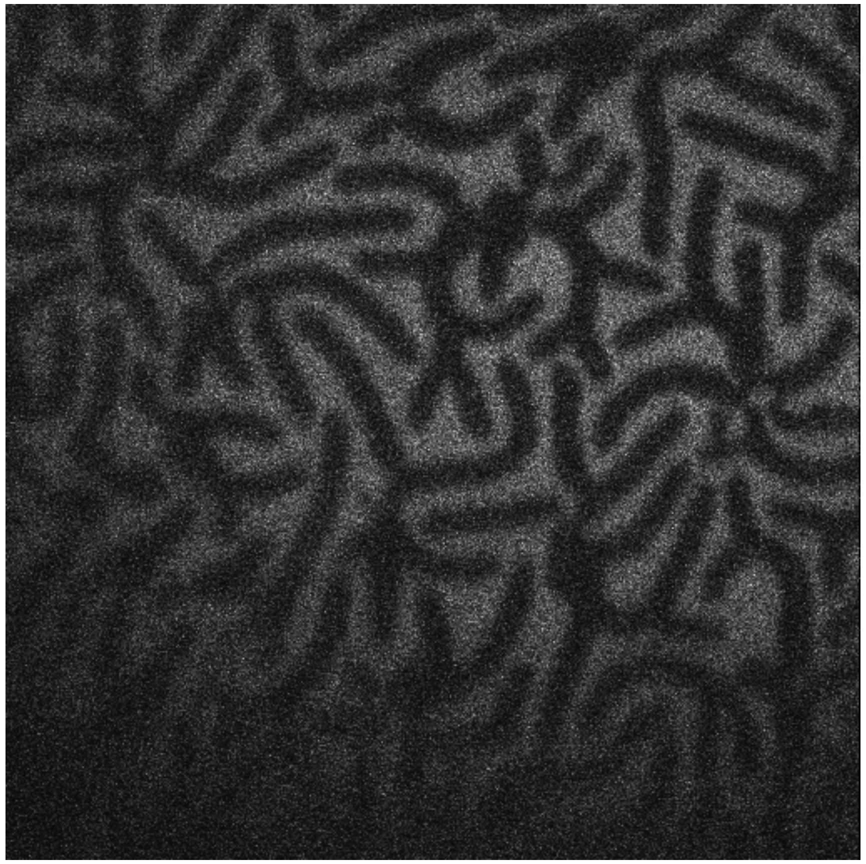


Chirality of DPPC



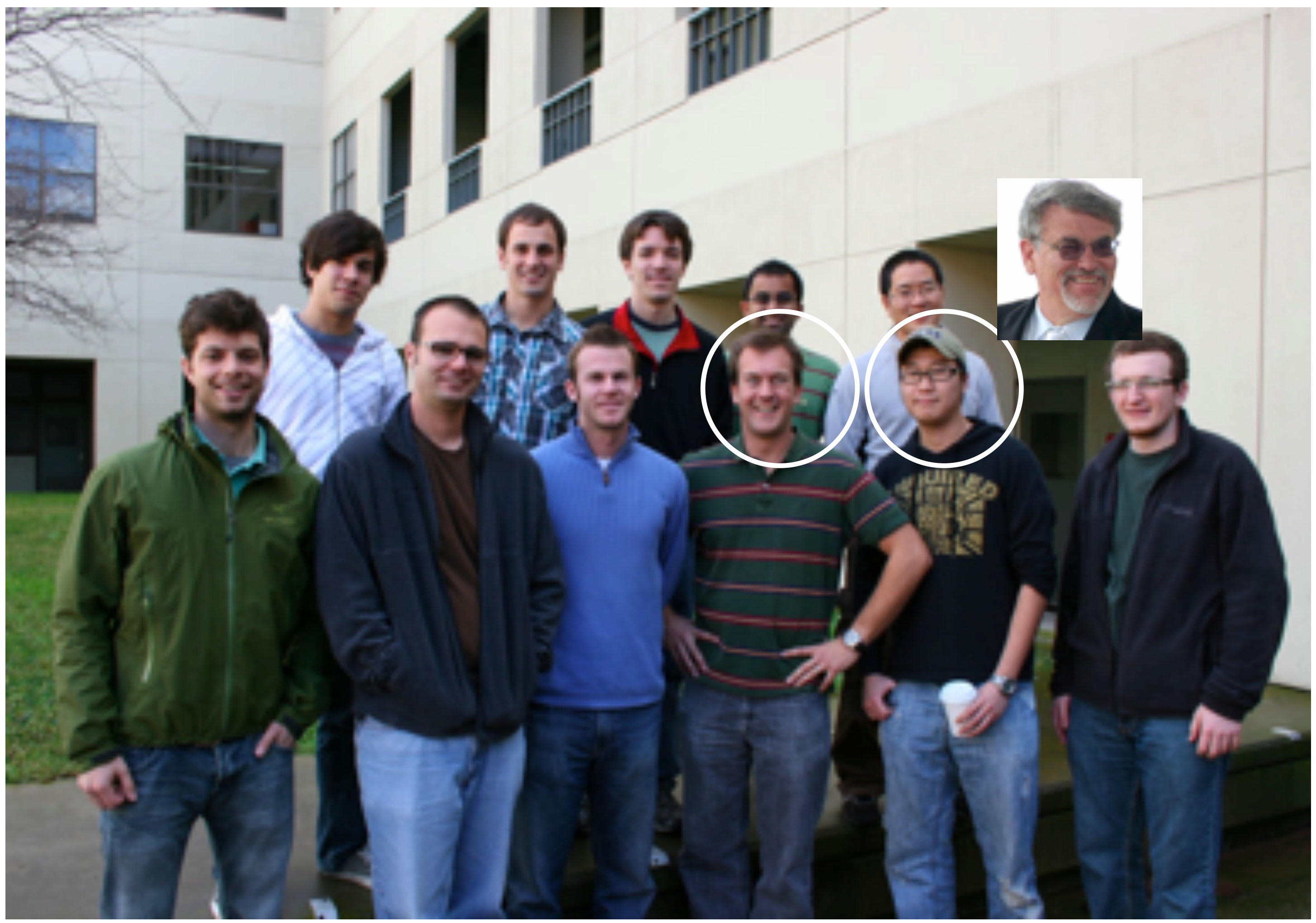






Conclusion

- Direct visualization of individual DPPC domains under stress
- Shear banding, yield stress, history dependence and aging
- 2D Soft glassy materials - 2D high internal phase emulsions



mrl NSF ACS PRF