Elasticity mediated long range attraction of particles

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Self Assembly of Particles

- Nanoscale-particle assembly via Molecular Interactions

Hydrogen Bonding, Van der Waals interactions, etc

- Externally directed self assembly

Electric, Magnetic fields– particles are polarized

- Assembly induced by – *combination of fields*

Capillary interactions,

Nicolson, M. M. **1949**, Gifford & Scriven **1971**, Bowden, Terfort, Carbeck, Whitesides Science **1997**.

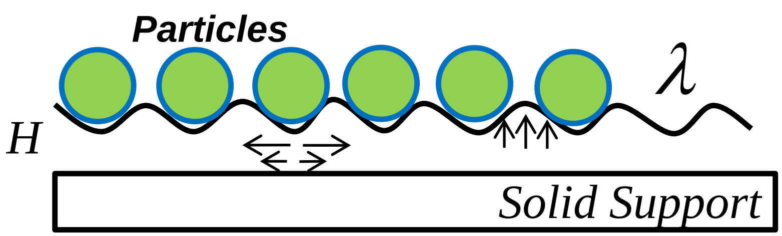
Assembly in Liquid crystals

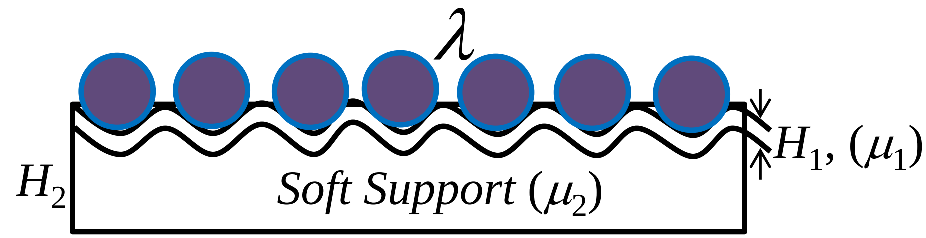
Poulin, Stark, Lubensky, Weitz *Science* **1997.** Cavallaro, Gharbi, Beller, Čopar, Shi, Baumgart, Yang, Kamien, Stebe, *PNAS* **2013**

Directed Self Assembly- Role of Elasticity ?

Elastic Films ?

Elastic Half Space ?





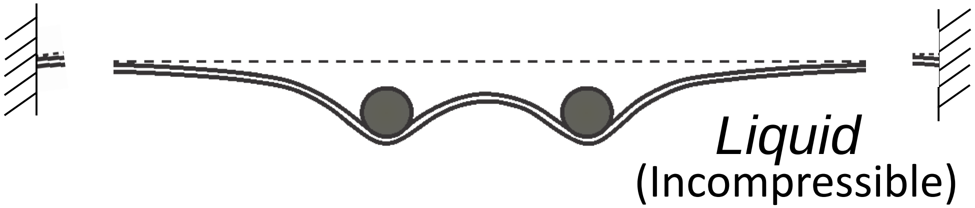
Small Scale: Van der Waals forces → **Large Scale: Gravitational Forces**

Role of Adhesion and Friction

Monch and Herminghaus, EPL, **53**, 2001.
Ghatak and Chaudhury, Langmuir, **19**, 2003.

Systems used to study Self Assembly of Particles

Attraction of:
I. Cylinders on elastic film

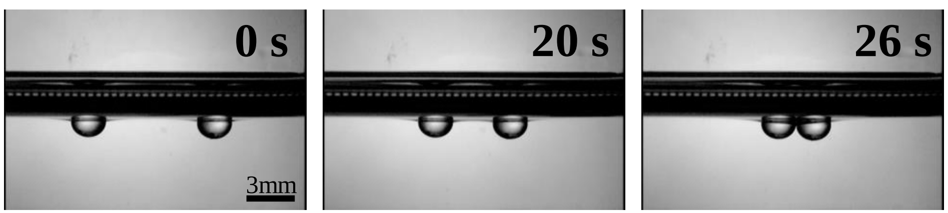


Elastic Bond No.

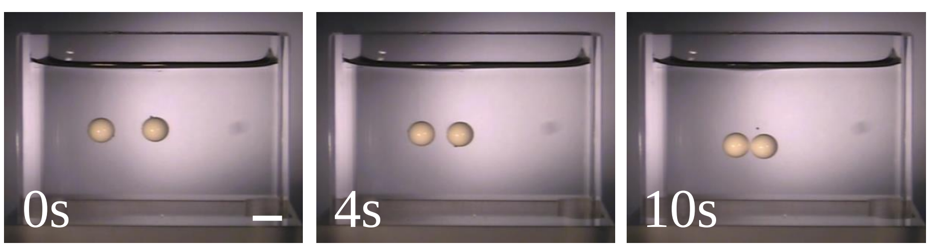
Case I.

$$EBo = \left(\frac{\Delta\rho^{3}}{\rho_{liq}^{2}} \frac{R^{2} g}{\mu H} \right)$$

II. Spheres on Gel Surface



III. Spheres inside Gel



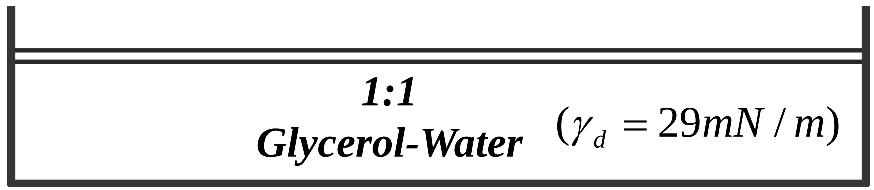
Elastic Bond No.

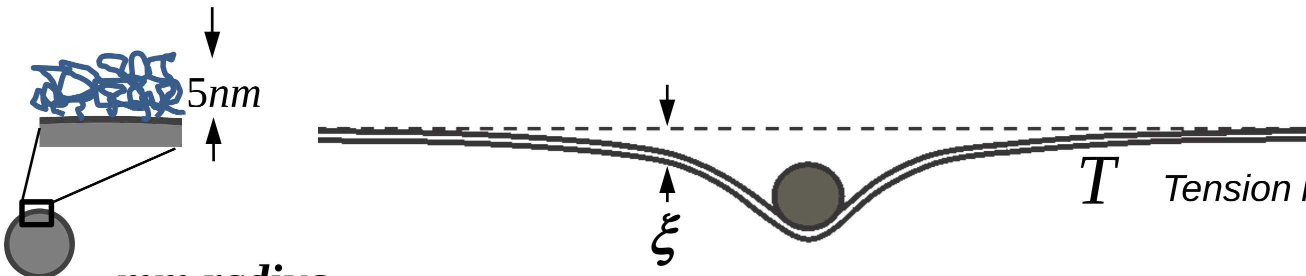
For Gels
II., III.

$$EBo = \frac{\Delta\rho R g}{\mu}$$

Chakrabarti, A.; Chaudhury, M. K *Langmuir* **2014**, *30*, 4684.
Chakrabarti, A.; Chaudhury, M. K *Langmuir* **2013**, *29*, 15543.

Thin Elastic Film supported on a Pool of Liquid





$$U_T = \frac{L}{2}\left[\int_0^{\infty} \rho g \xi^2 dx + T\int_0^{\infty}\left(\frac{d\xi}{dx}\right)^2 dx\right]$$

Gravitational Free Energy of Liquid — Elastic Energy of the Stretched Film

Functional Minimization:

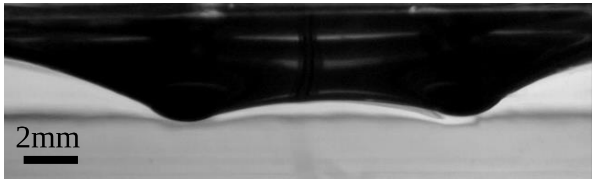
$\delta U_T / \delta \xi = 0$

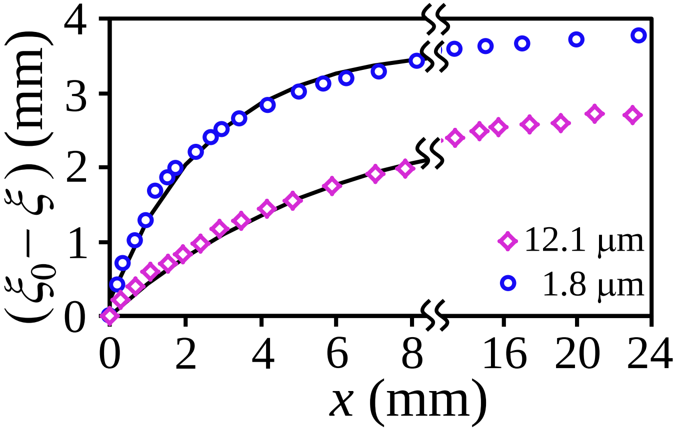
$$\xi = \xi_0 e^{-\alpha x}$$

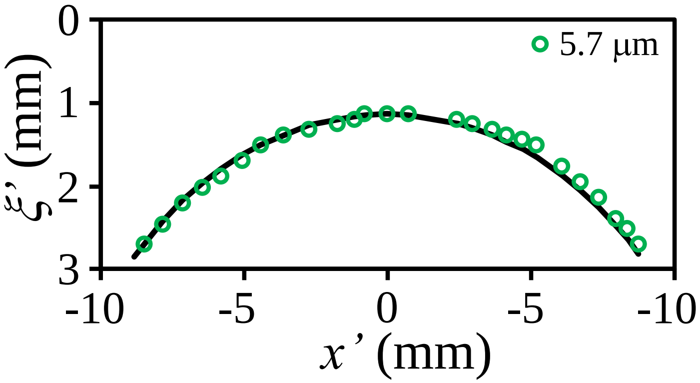
Decay Length

$$\alpha^{-1} = \sqrt{(T_E + \gamma)/\rho g}$$

Experimental Investigation of Decay Length α^{-1}





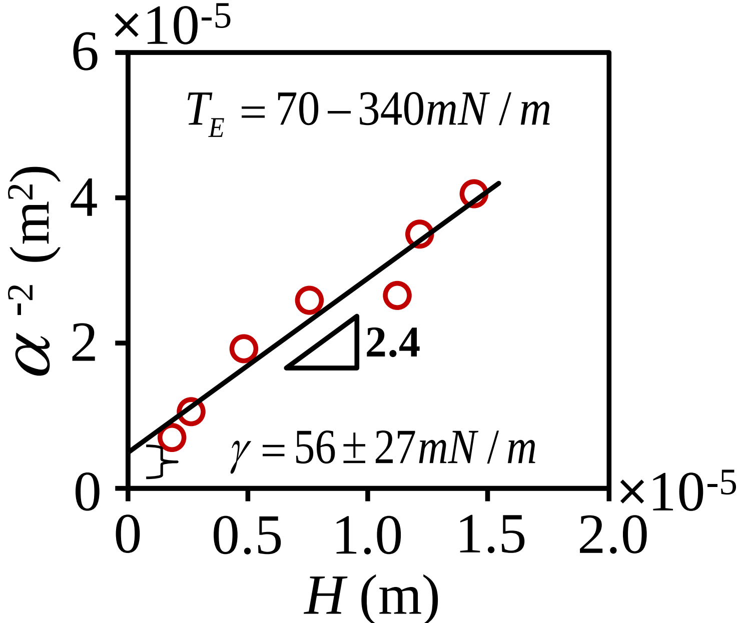


$$\xi' = \xi'_0 \frac{\cosh(\alpha x)}{\cosh(\alpha \ell / 2)}$$

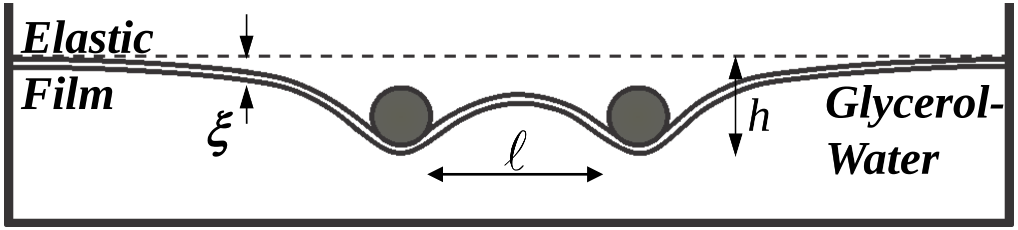
$$(\xi_0 - \xi) = \xi_0 (1 - e^{-\alpha x})$$

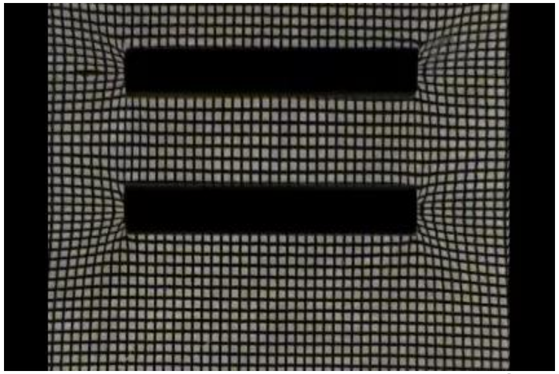
Decay Length

$$\alpha^{-1} = \sqrt{(T_E + \gamma)/\rho g}$$



Estimation of Energy of Attraction





$$U_T^E = -2m^* gh + L\left[\int_0^\infty \rho g \xi^2 dx + T\int_0^\infty \left(\frac{d\xi}{dx}\right)^2 dx\right] + L\left[\int_{-\ell/2}^{+\ell/2} \frac{\rho g \xi'^2}{2} dx' + \frac{T}{2}\int_{-\ell/2}^{+\ell/2}\left(\frac{d\xi'}{dx}\right)^2 dx'\right]$$

Gravitational Energy of Particles on Film

Gravitational Free Energy of Displaced Liquid

Elastic Energy of the Stretched Film

G.E. and E.E for Intermediate Profile

Vertical Stability:

$$\partial U_T / \partial \xi_0 = 0,$$

$$\xi_o(\ell) \approx h(\ell)$$

Total Energy, U_T

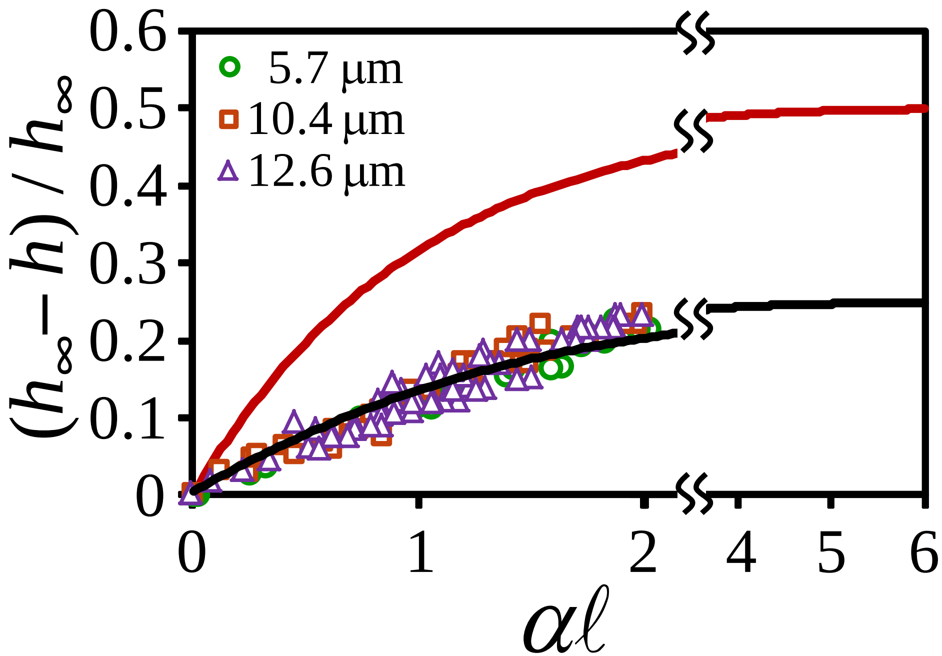
Implicit $-m^* g \xi_0(\ell)$

Explicit $-\frac{\xi_0^2 \rho g L}{\alpha}\left(1 + \frac{\sinh(\alpha\ell)}{2\cosh^2(\alpha\ell/2)}\right)$

L : *Length of cylinder*

α^{-1} : *Decay Length*

Role of Adhesion Hysteresis



Adhesion Hysteresis ΔW

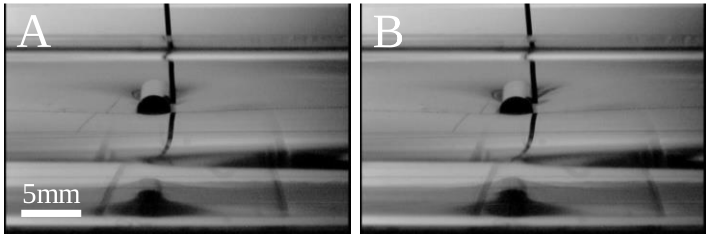
$$\Delta W = 135 mJ / m^2$$

$$(\Delta W)\ell L = m^* g(h_\infty - h_\infty')$$

$$\frac{h_\infty - h(\ell)}{h_\infty} = \frac{\sinh(\alpha\ell)}{C_1 \cosh^2(\alpha\ell/2) + \sinh(\alpha\ell)}$$

Difference in energy of CLOSING and OPENING a crack

Forced rolling against a spring to estimate the hysteresis:

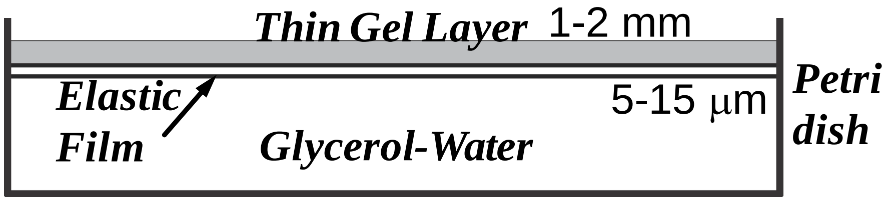


$$\Delta W = F / L \rightarrow \Delta W = 100 mJ / m^2$$

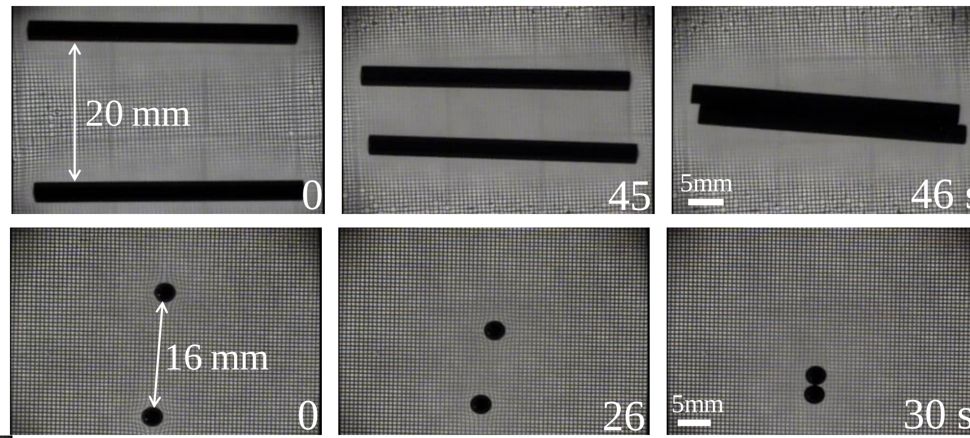
Kendall, K. *Wear* **1975**, *33*, 351-358.

She, H.; Chaudhury, M. K. *Langmuir* **2000**, *16*, 622-625.

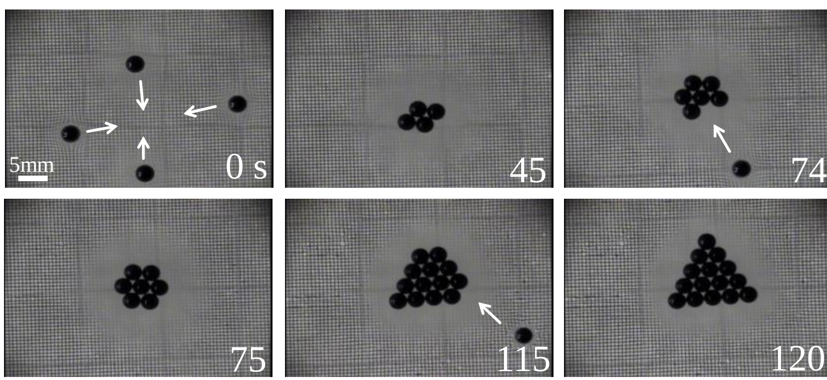
Reducing Adhesion Hysteresis with Hydrogel layer on Elastic Film



Longer range of attraction

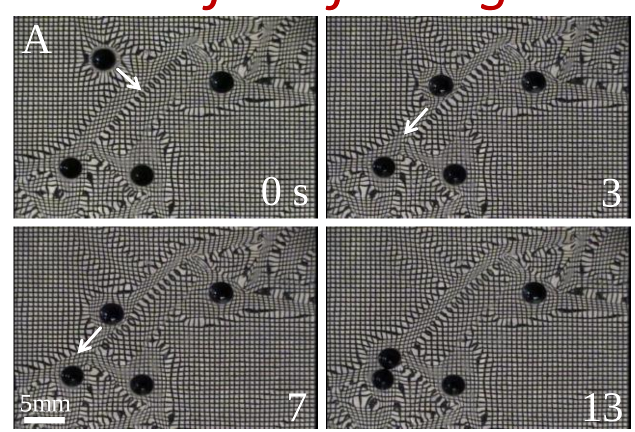


Low friction of Gel + Flexibility of Elastic film

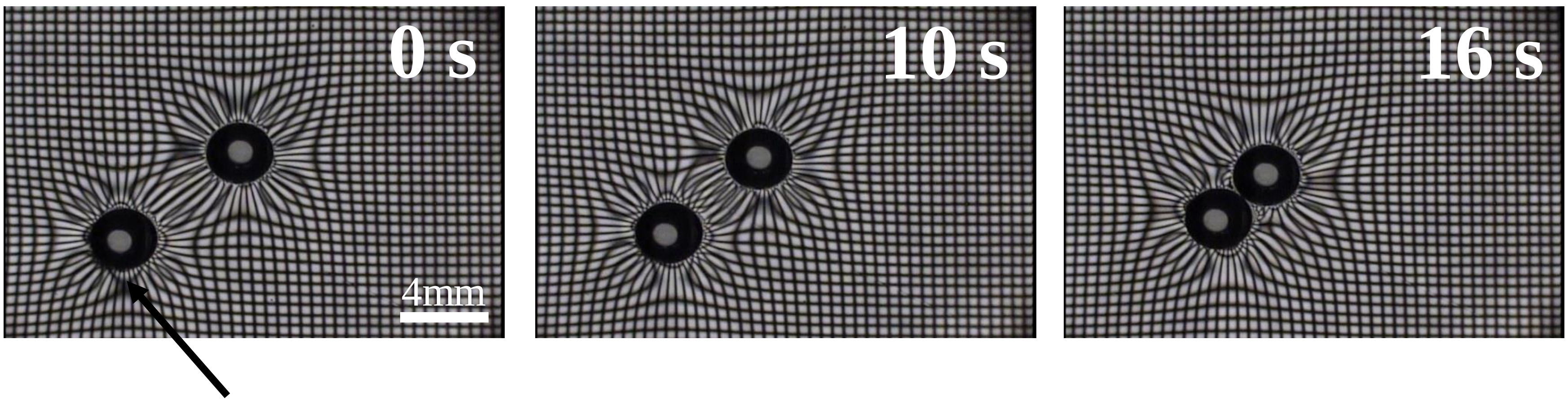


Self Assembly

Guided interaction with Surface folding

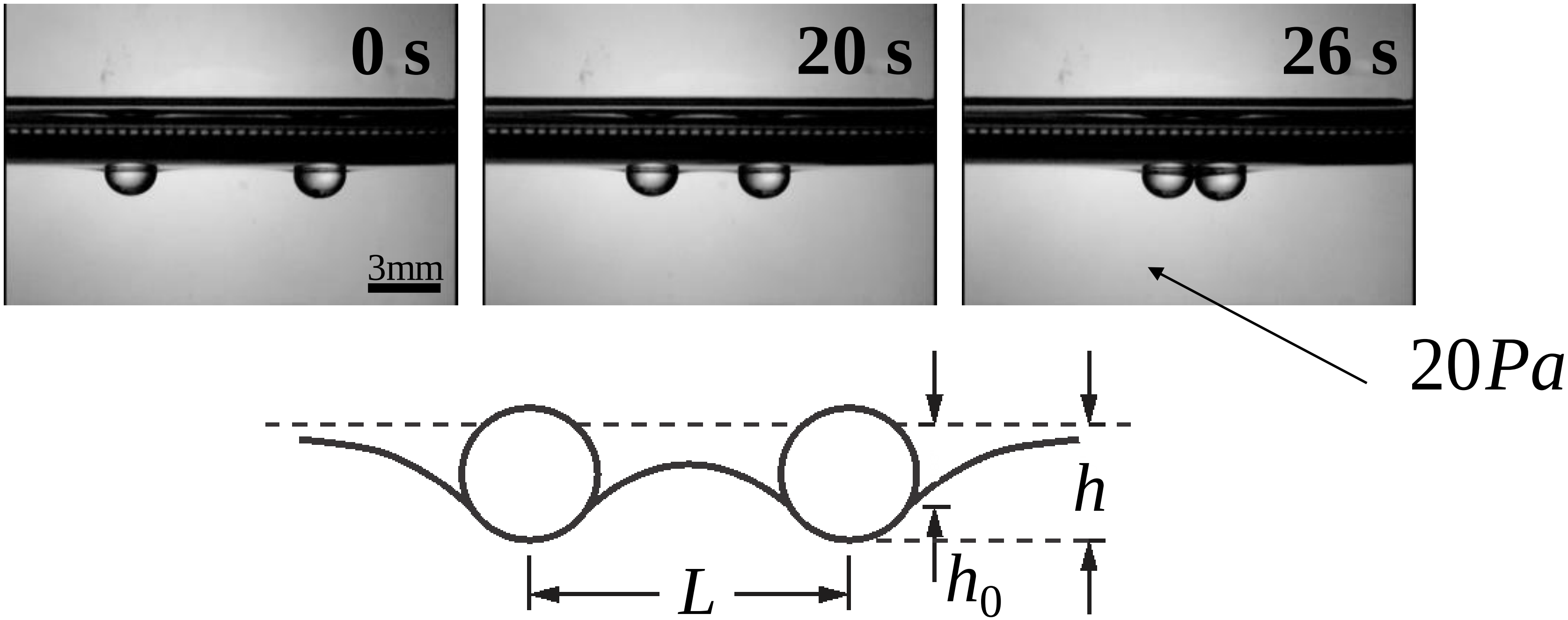


Particles on the Surface of GEL (10-50 Pa) ?



Hydrophobic Glass Particles ~mm range

Scaling Theory *for Elastocapillary Attraction of Particles on Soft Gels*



Change in Gravitational Potential Energy

Implicit

$$m^* g \Delta h$$

Explicit

$$m^* g h_o K_o (L / L_c^*)$$

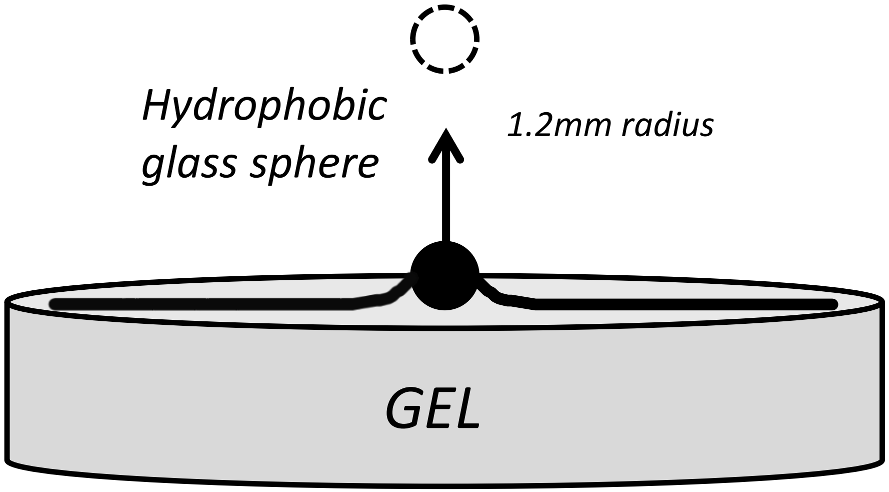
Nicolson's Superposition Principle

$$\frac{\Delta h}{h_o} \approx K_o (L / L_c^*)$$

L_c^* *Decay Length for Gels*

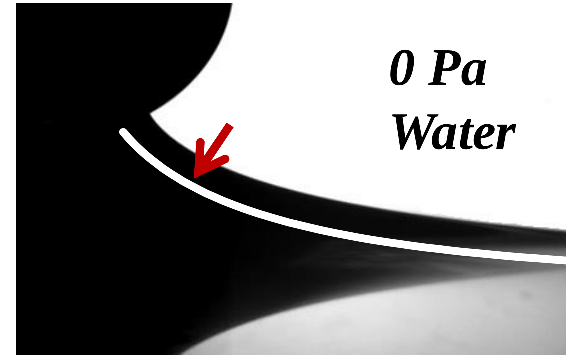
Nicolson, M. M. *Proc. Cambridge Philos. Soc.* **1949**, *45*, 288−295

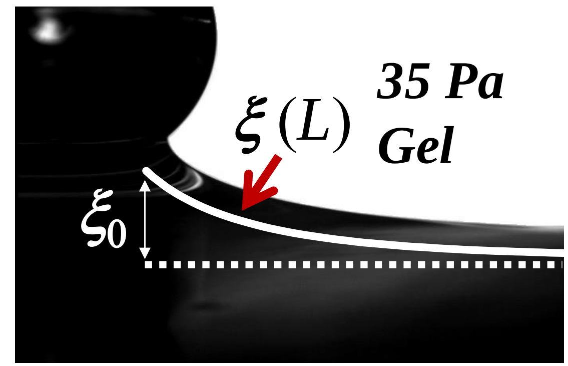
Elastocapillary Decay Length L_c^* for Soft Gels

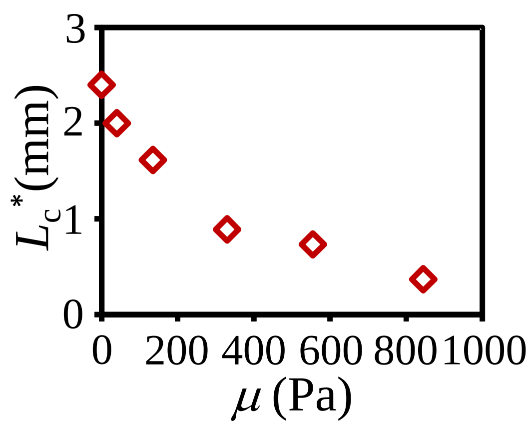


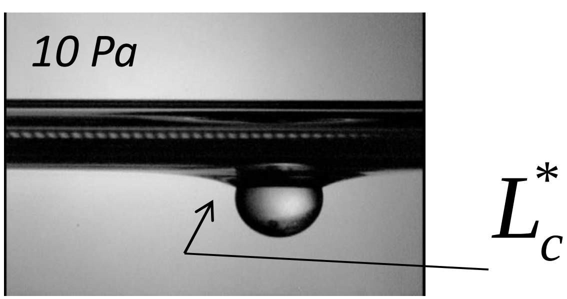
Modified
Bessel
function

$$\xi(L) = \xi_0 K_0(L / L_c^*)$$



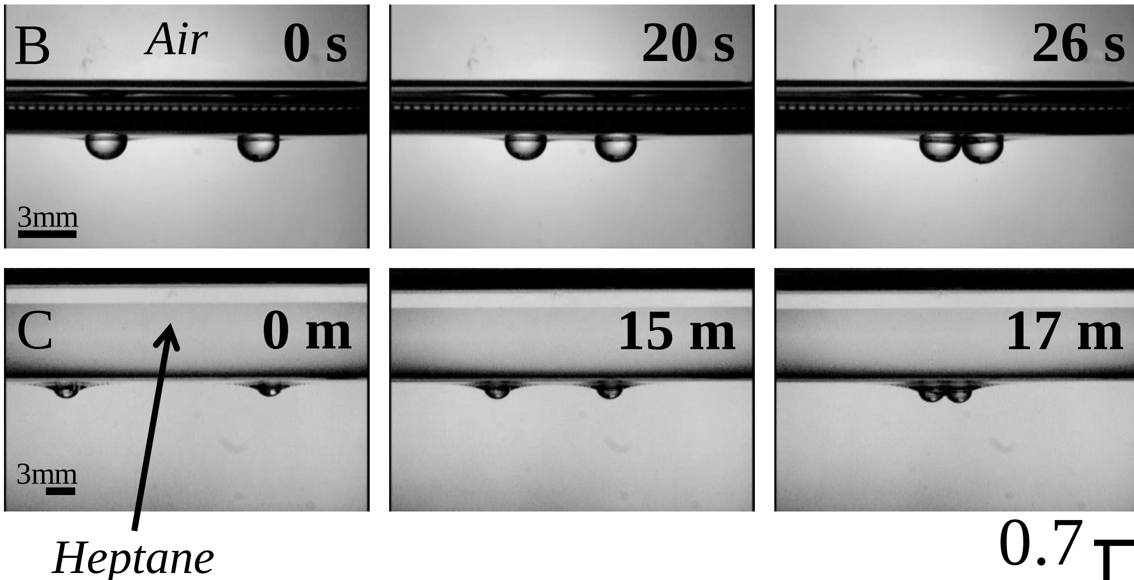




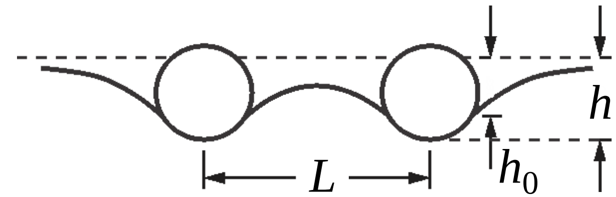


Decay Length of Gel
Can also be determined

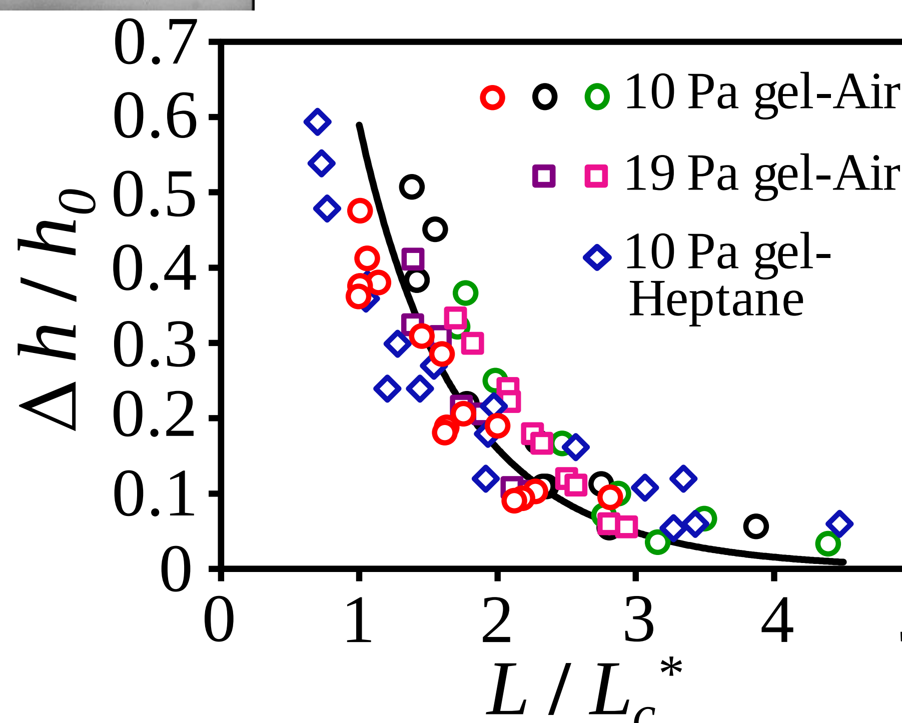
Elastocapillary Attraction of Particles on the Surface of Soft Gels



Schematic showing how the analysis was done



$$\frac{\Delta h}{h_o} \sim K_o(L / L_c^*)$$



Linear Kinematic Friction in Spheres moving on the surface of Gels

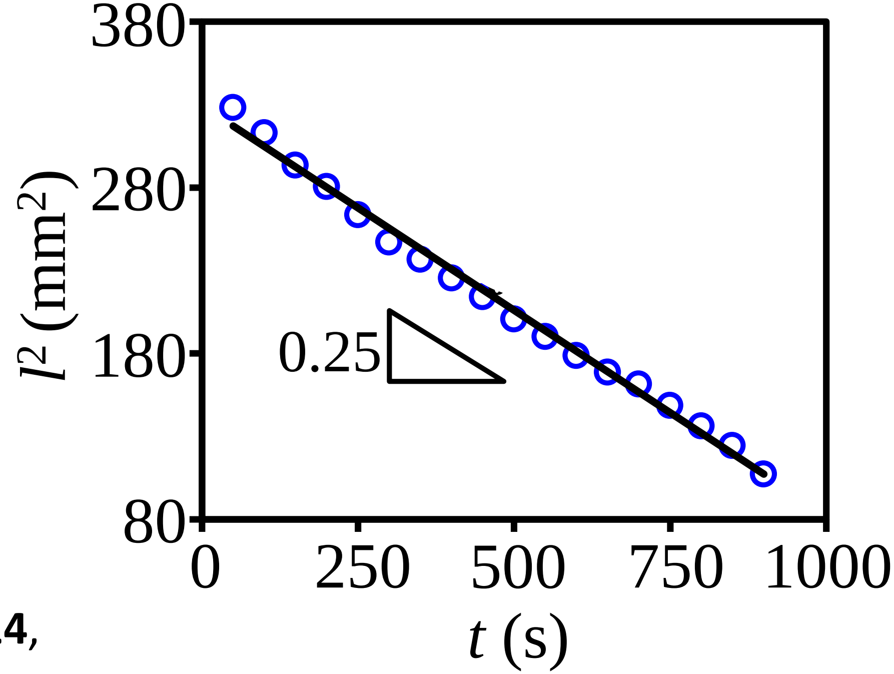
$$\bar{U} \sim m^* g h_0 K_0(\ell / L_c^*)$$

Attractive Force: $\sim -\dfrac{m^* g h_0}{\ell}$

Frictional Force: $\sim \xi \dfrac{d\ell}{dt}$

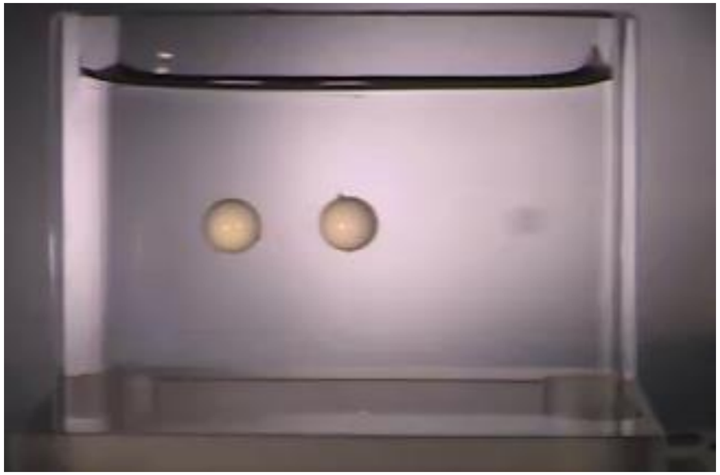
$$\ell^2 \sim t$$

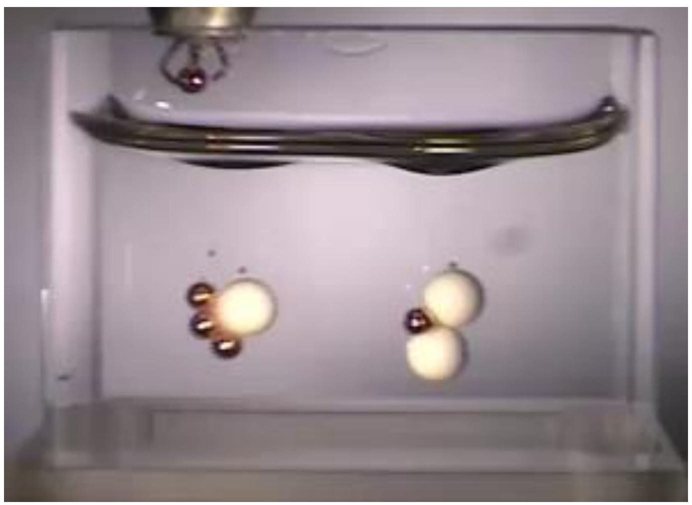
Diffusive collapse

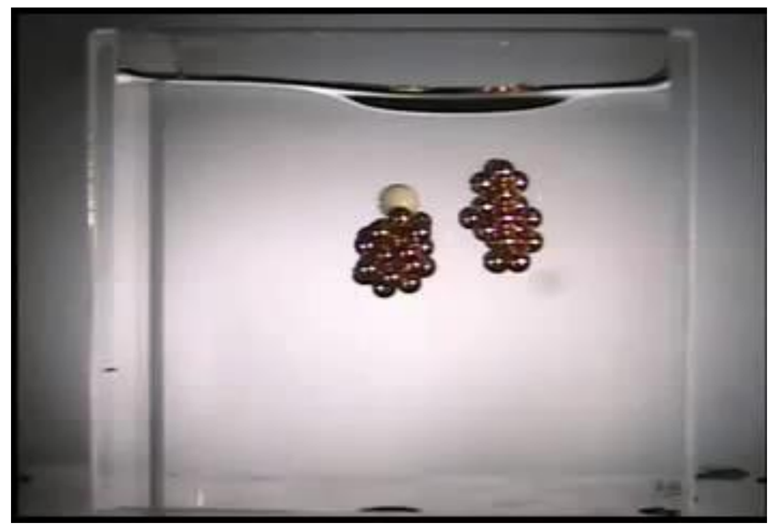


Chakrabarti, A.; Chaudhury, M. K *Langmuir* **2014**, *30*, 4684.

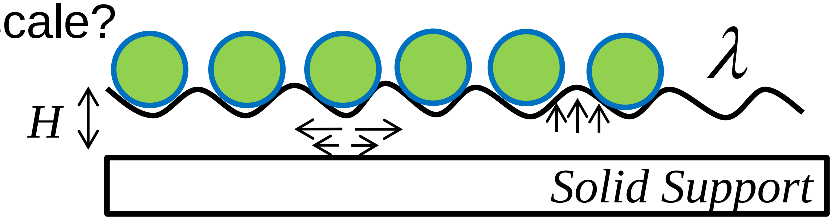
Self Assembly of particles inside Gel







At Nanoscale?



Gravitational Forces

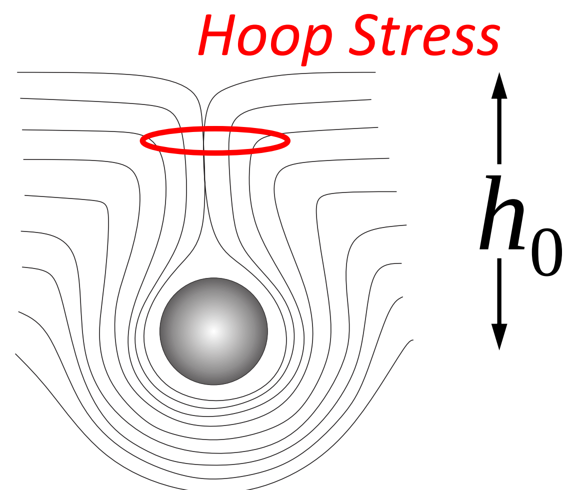
↓

Van der Waals forces,
Externally Applied Forces
Electric field, Magnetic field

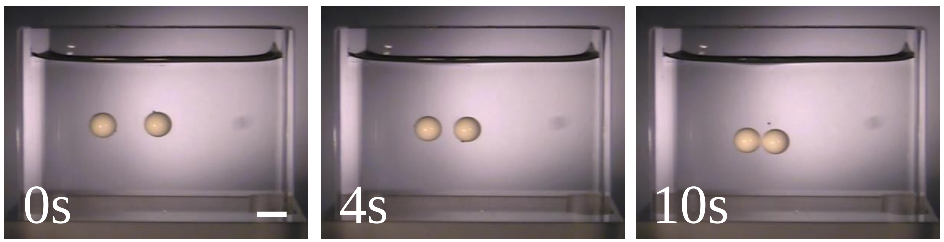
BACKUP SLIDES

Attraction and Self Assembly of Particles inside a Soft Gel

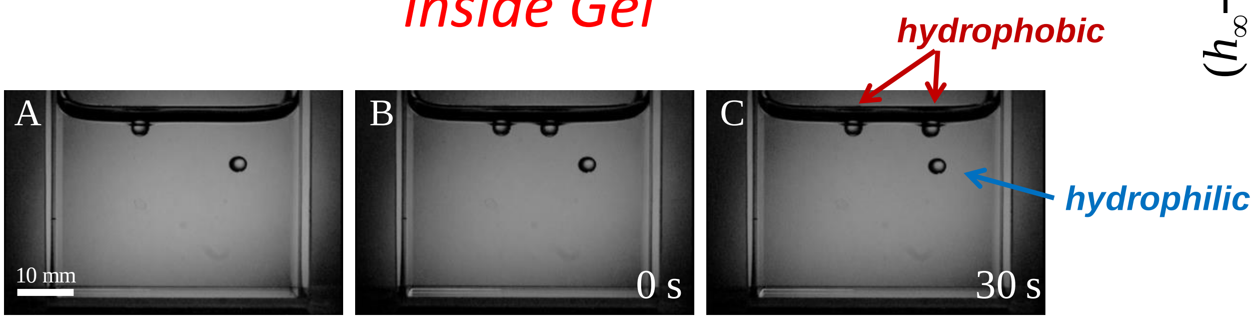
Podgorski, T.; Belmonte, A. *J. Fluid Mech.* **2002**, 460, 337−348
Graham, M. D. *Phys. Fluids* **2003** *15*(6), 1702-1710
(for similar phenomenon in viscoelastic liquid)

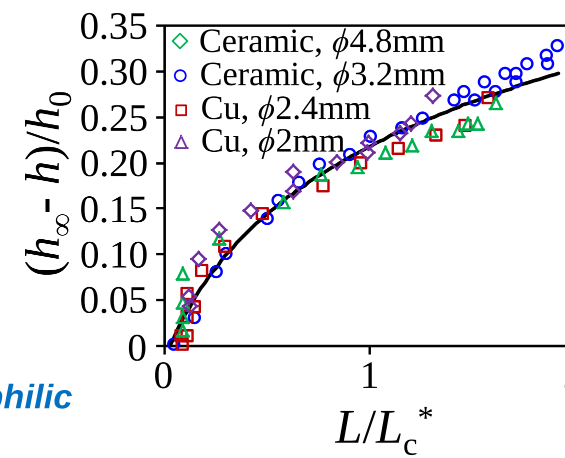


Excessive Stretching in the Gel



Lot more energy stored when Particle is inside Gel





$$L_c^* = \sqrt{(\mu h_0/\rho g)}$$

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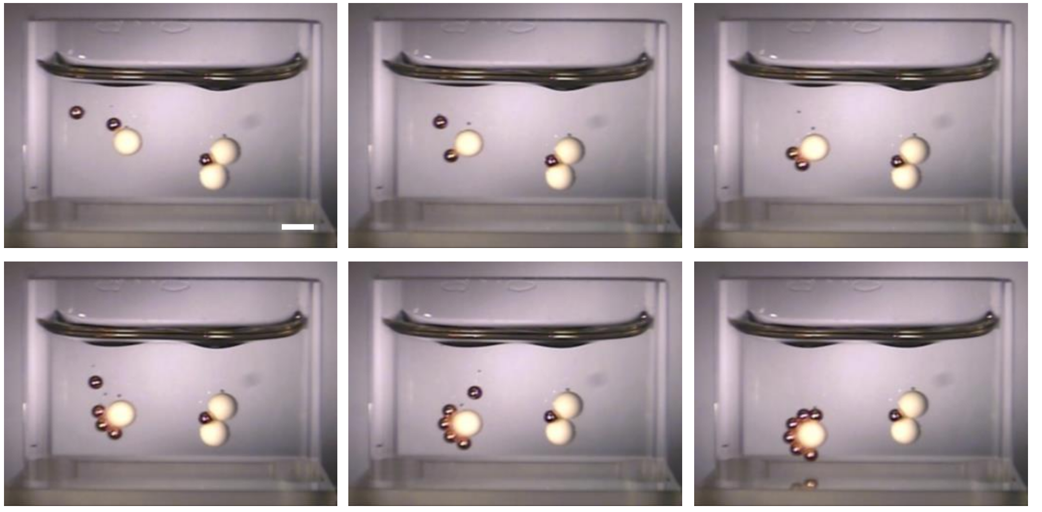
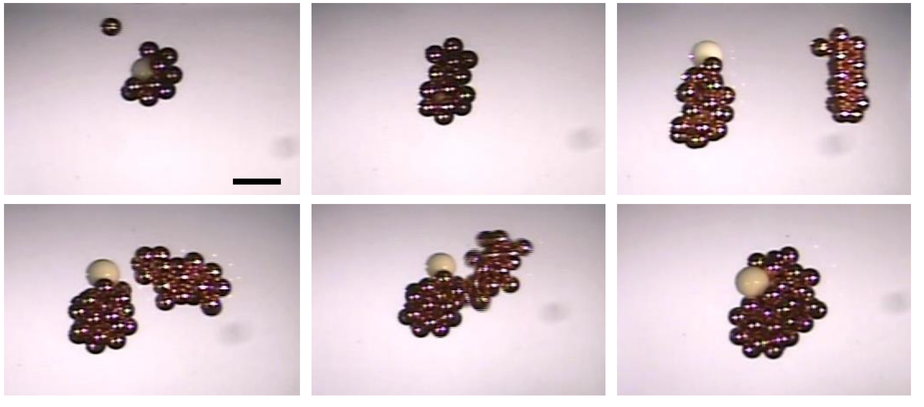
Cooperative Effects of Surface Tension, Elasticity, and Gravity

Self Organization inside Gels





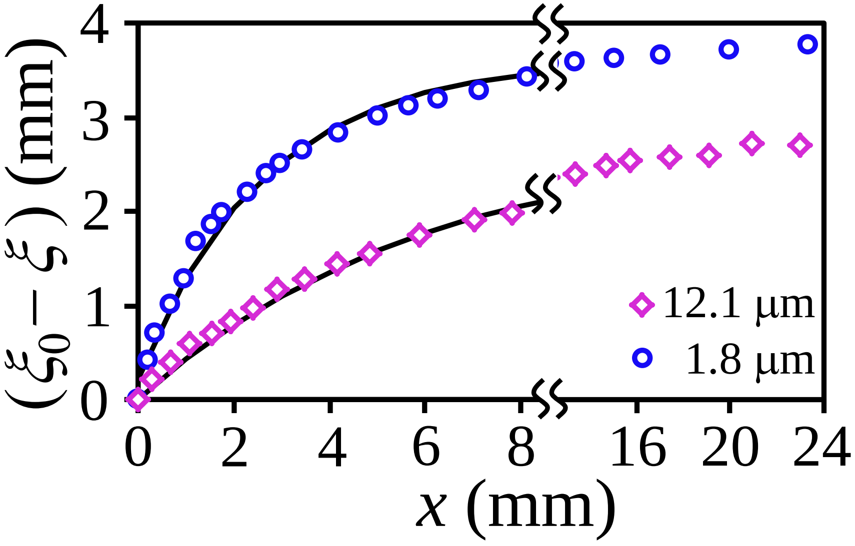
When a film undergoes both bending and stretching,

$$D\xi_{xxxx} - T\xi_{xx} + pg\xi = 0$$

Periodic solution with exponential decay

Ratio of Bending to Stretching,

$$(1/\varepsilon)(H\alpha)^2 \approx 10^{-5}$$

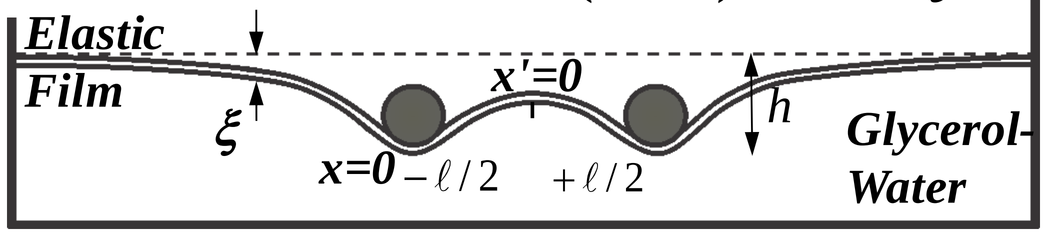


$$(\xi_0 - \xi) = \xi_0(1 - e^{-\alpha x})$$

Estimation of Energy of Attraction

$$\xi' = \xi'_0 \frac{\cosh(\alpha x)}{\cosh(\alpha\ell/2)}$$

$$\xi = \xi_0 e^{-\alpha x}$$



$$U = -2m^* gh + L\left[\int_0^\infty \rho g \xi^2 dx + T\int_0^\infty \left(\frac{d\xi}{dx}\right)^2 dx\right] + L\left[\int_{-l/2}^{+l/2} \frac{\rho g \xi'^2}{2} dx' + \frac{T}{2}\int_{-l/2}^{+l/2}\left(\frac{d\xi'}{dx}\right)^2 dx'\right]$$

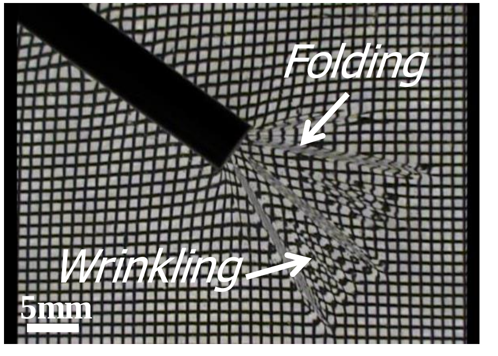
$$U_T = -2m^* g\xi_0 + \frac{\rho g \xi_0^2 L}{\alpha}\left(1 + \frac{\sinh(\alpha\ell)}{2\cosh^2(\alpha\ell/2)}\right)$$

$$\partial U / \partial \xi_0 = 0, \quad m^* g = \frac{\xi_o \rho g L}{\alpha}\left(1 + \frac{\sinh(\alpha\ell)}{2\cosh^2(\alpha\ell/2)}\right)$$

Assumption:

$$\xi_0 \approx h(\ell)$$

$$U_T = -m^* g \xi_0$$



$$\xi_o \approx h$$

$$\frac{h_\infty - h(\ell)}{h_\infty} = \frac{\sinh(\alpha\ell)}{2\cosh^2(\alpha\ell/2) + \sinh(\alpha\ell)}$$

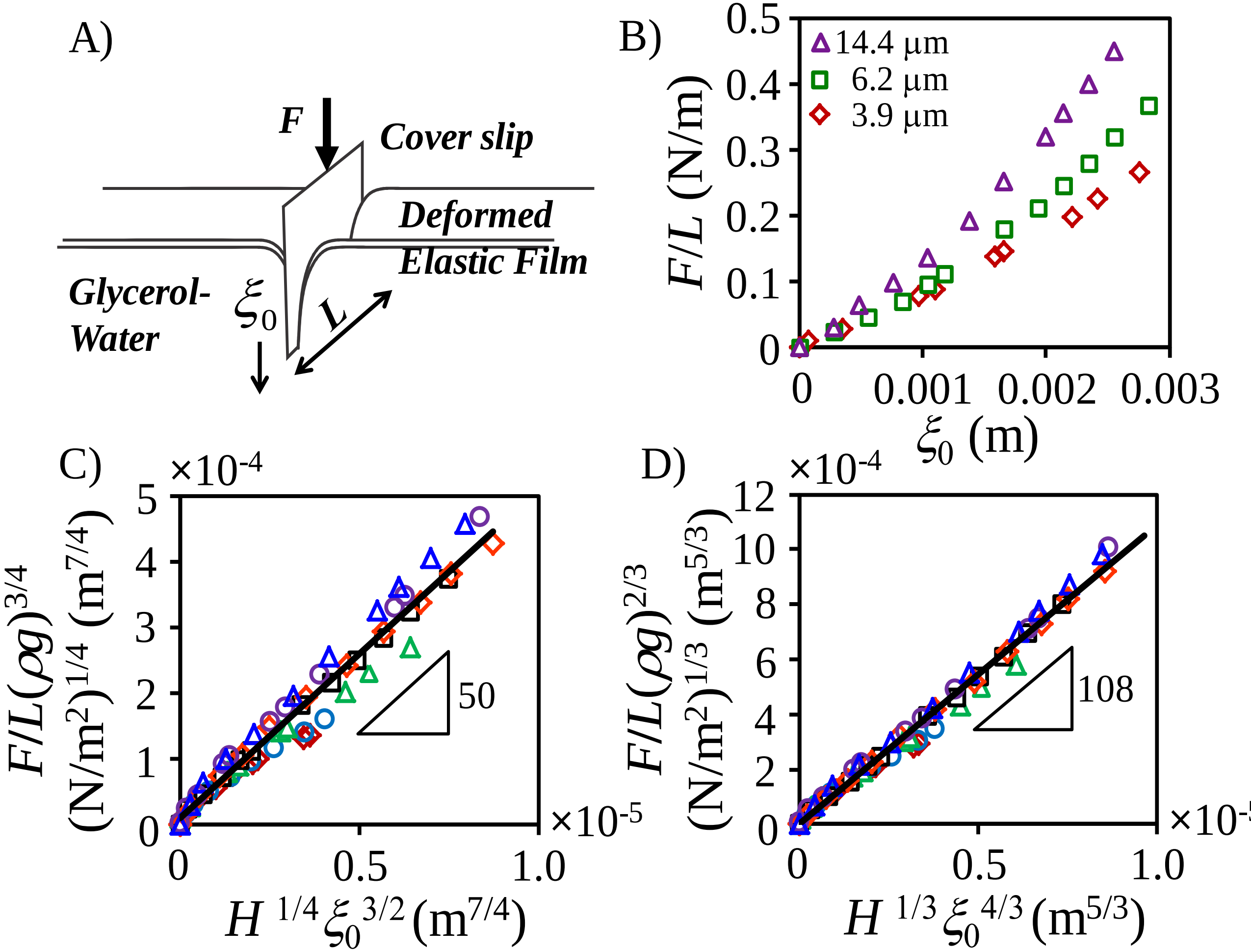
Estimation of Elastic Modulus of the Thin Film

$$U_f = L\int \rho g \xi^2 dx + TL\int \left(\frac{d\xi}{dx}\right)^2 dx$$

$$F = -\partial U_f / \partial \xi_0 \longrightarrow \frac{F}{L} = -\frac{2\rho g}{\alpha}\xi_0$$

Strain in the film,

$$\varepsilon \approx (\xi_0 \alpha)^n$$



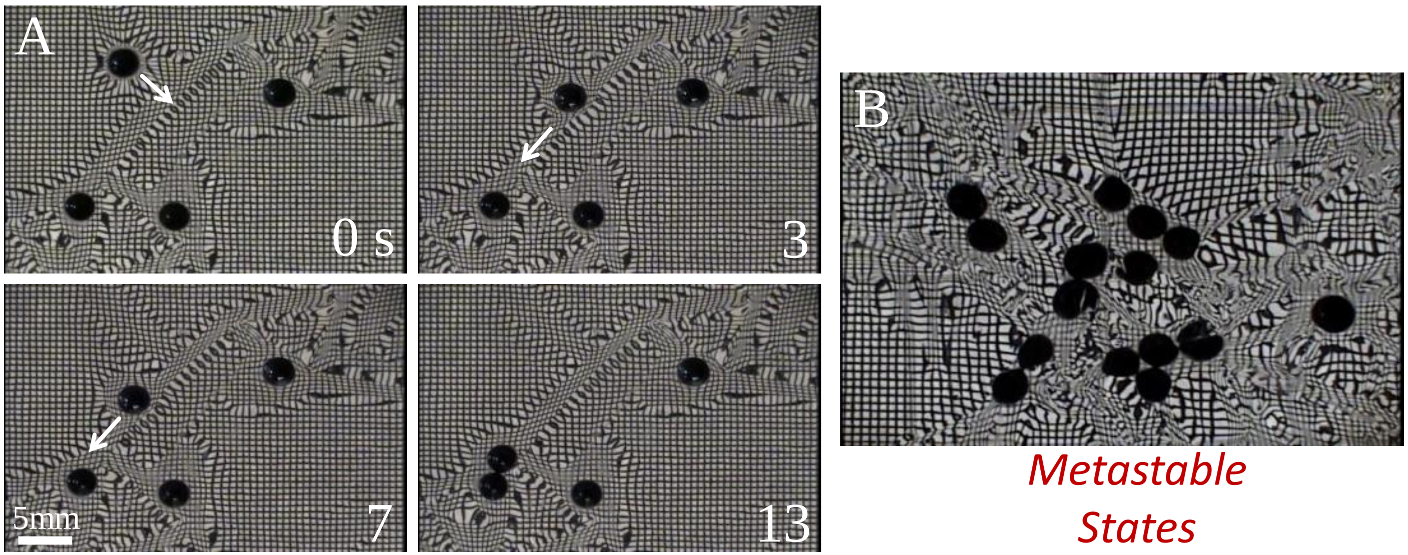
n=2

$$\frac{F}{L} \propto (\rho g)^{3/4}(EH)^{1/4}\xi_0^{3/2}$$

n=1

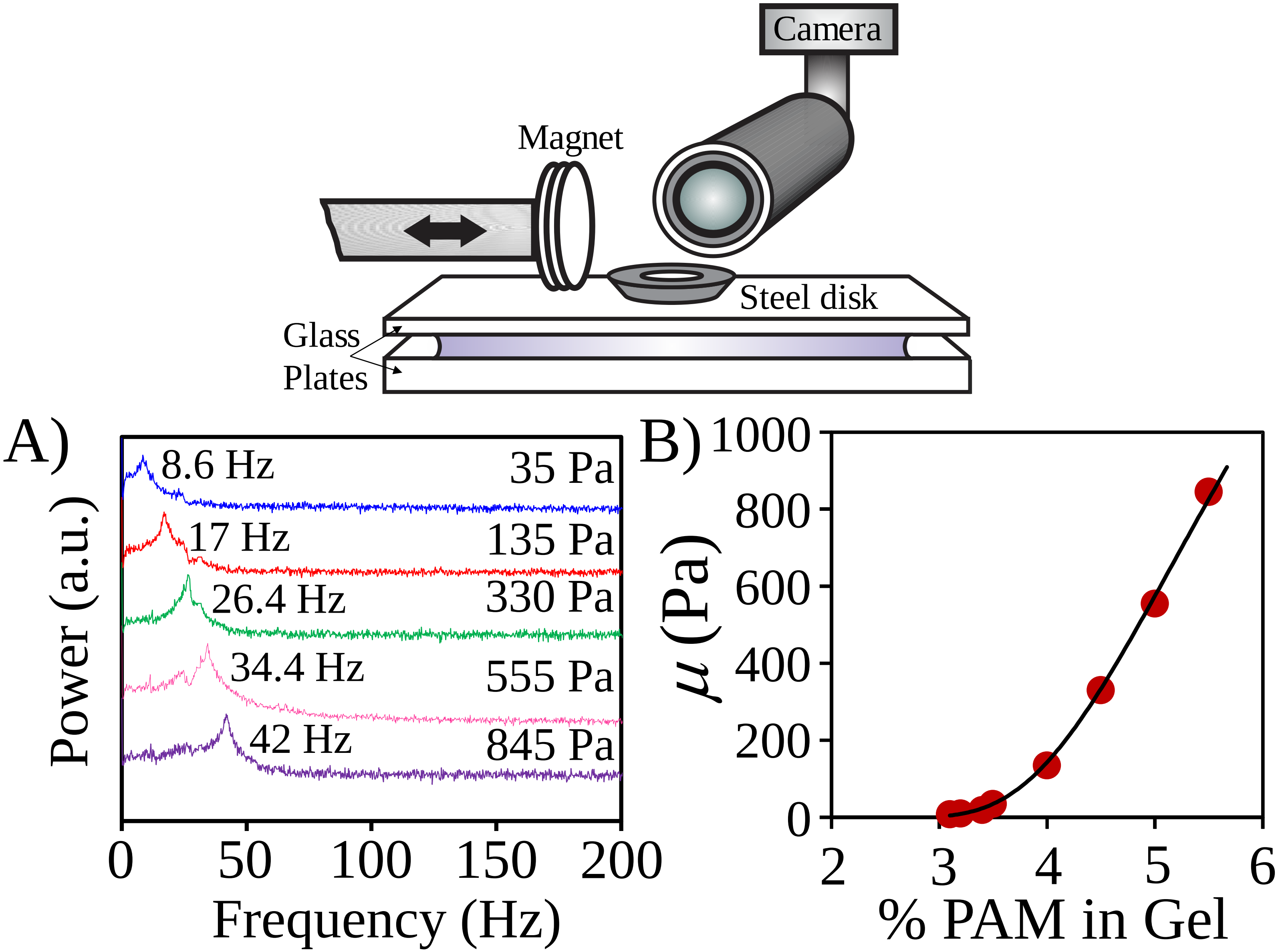
$$\frac{F}{L} \propto (\rho g)^{2/3}(EH)^{1/3}\xi_0^{4/3}$$

Folding Instabilities guiding Particle Interaction

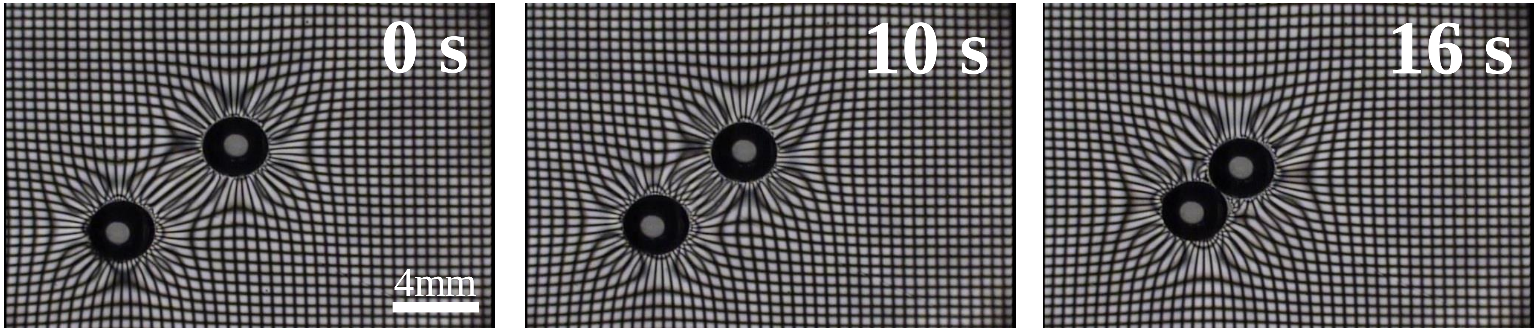


Metastable States

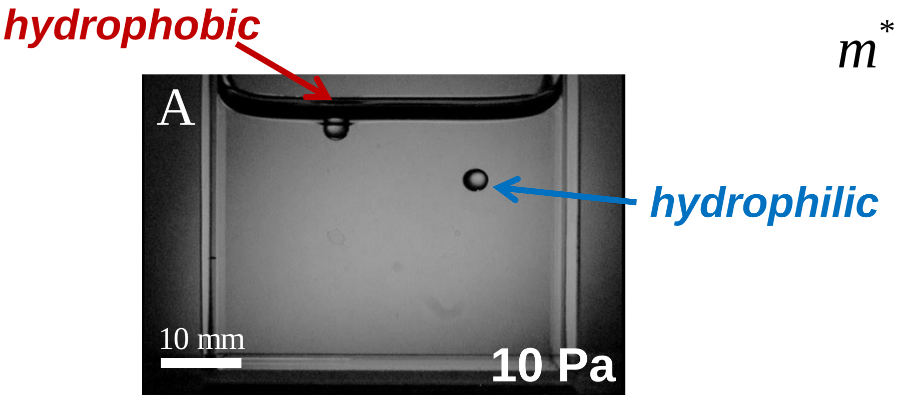
Measurement of the Shear Moduli μ of Gel



Bulk Hydrogel– What happens to the Particles on the surface of GEL (10-50 Pa) ?



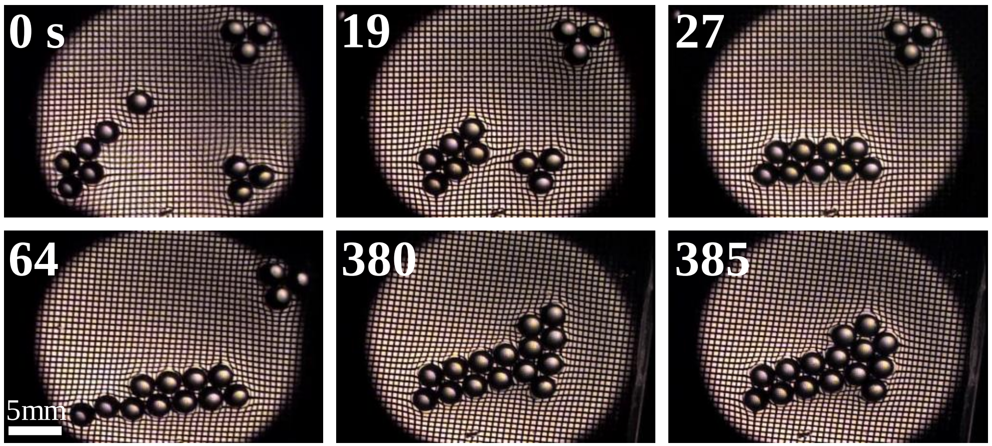
Surface Chemistry Matters



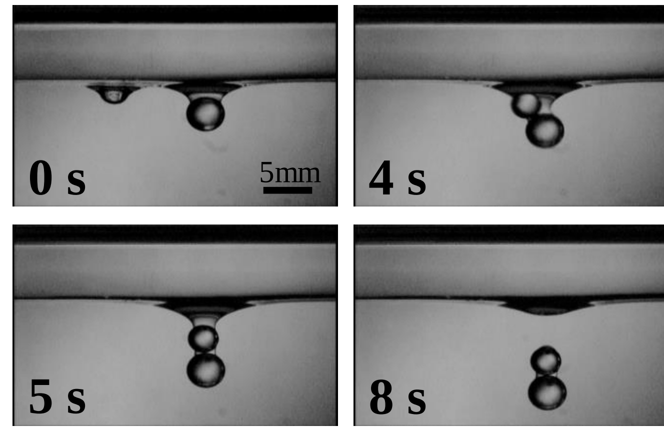
$$m^{*} g \Delta h \approx \Delta \gamma A_{contact}$$

Elastocapillary Force Mediated Attractions in Different Scenarios

Particle Self Assembly at the Gel Surface



Tubulation and Engulfment at Gel-Heptane Interface



Stress Patterning in Gel to Guide Attractions on Surface