Surface Rheology & Liquid Film Dynamics

+ Microfluidics applications

Benoit Scheid

TIPs – Transfers, Interfaces and Processes
Université Libre de Bruxelles

bscheid@ulb.ac.be

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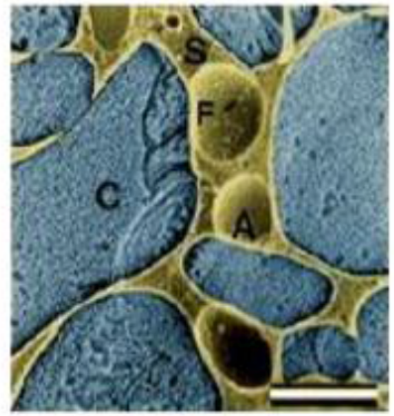
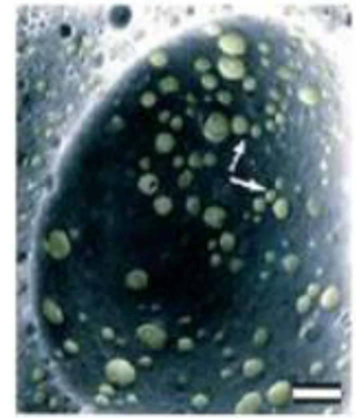
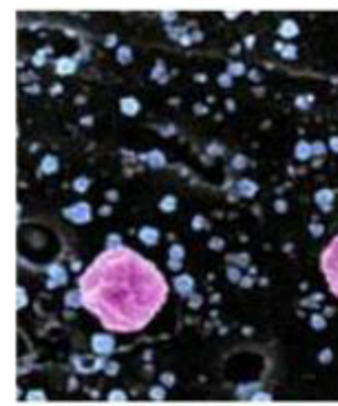
Surface rheology: motivation

- Interfaces between two immiscible fluids are made more stable by "particles"
- Fat globules in ice cream
- Asphaltenes in crude oil
- Proteins in food products







- Goff, D.; http://www.foodsci.uoguelph.ca/dairyedu/icmilos2.html (ice cream)
- www.itopf.com/fate.html (oil spill emulsion)
- McManus, W.; http://bioweb.usu.edu/emlab/Galleries/foods/casein_micelles_in_milk.html (casein)

[G. G. Fuller, Stanford University, seminar on surface rheology]

Surface rheology: motivation

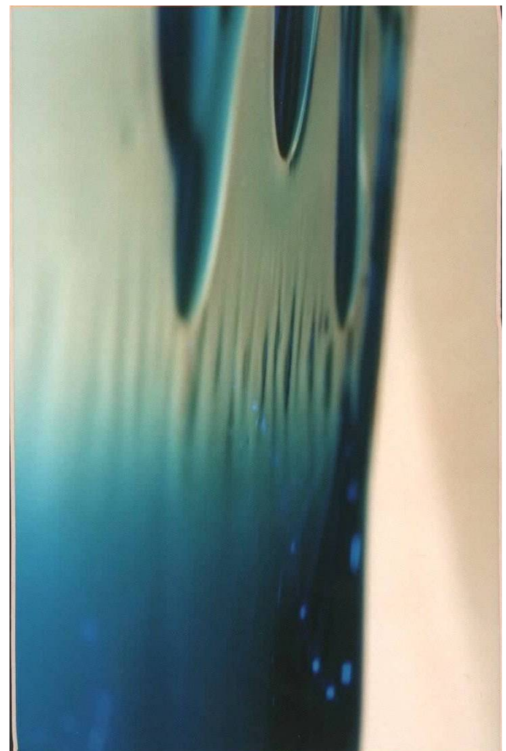
- Interfacial rheology is the main reason for which surfactants are essential in
  - Food
  - Pharmaceuticals
  - Cosmetics
  - Paints
  - Oil recovery
  - Detergency
  - Multiphase reactions and separations
  - Water remediation
  - Fire-fighting foams
  - …
  - But also in Biology: i.e. lung surfactants

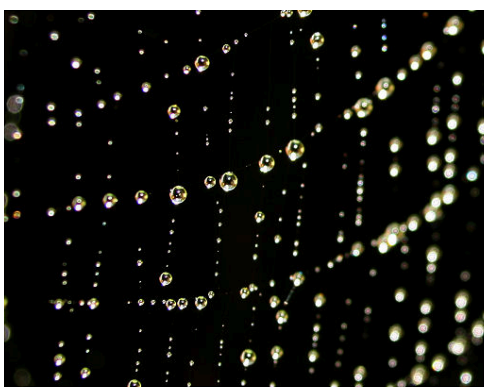
Even in “clean” system, impurities act as surface-active agent!!!

Surface rheology: background

- Surface tension: daily observations

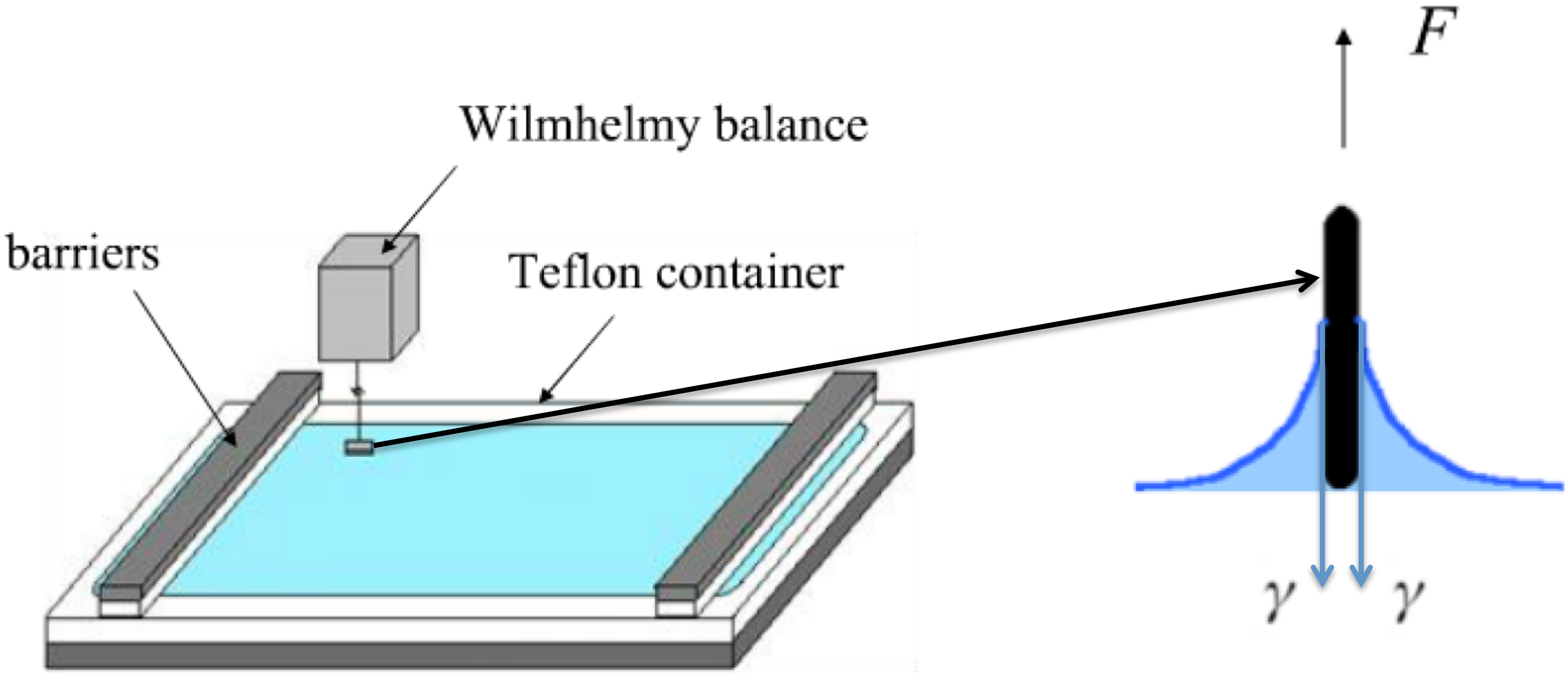






Surface rheology: background

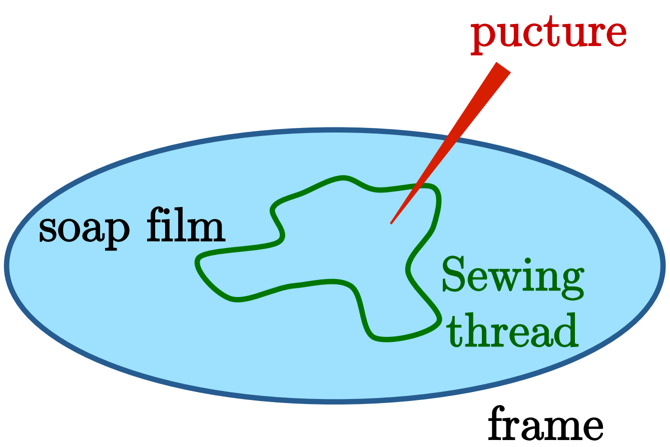
- Surface tension: measurement



$$\gamma = \frac{F}{L}; \; L \text{ is the perimeter}$$

Surface rheology: background

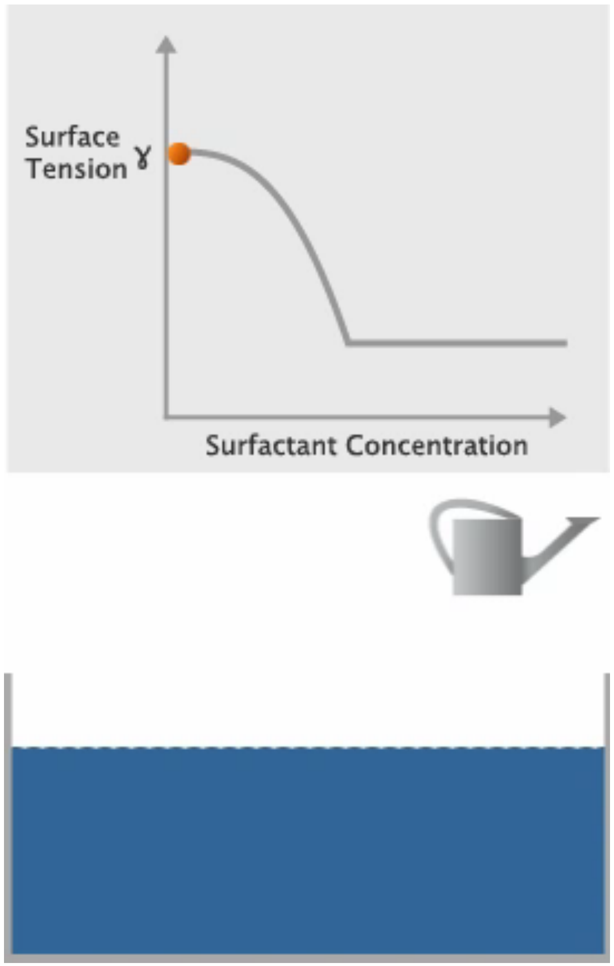
- Surface tension: concept

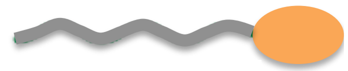


QUIZZ:
(1) The loop grows
(2) The loop shrinks
(3) Nothing changes

Surface rheology: background

Surface tension and soluble surfactants





Gibbs monolayer

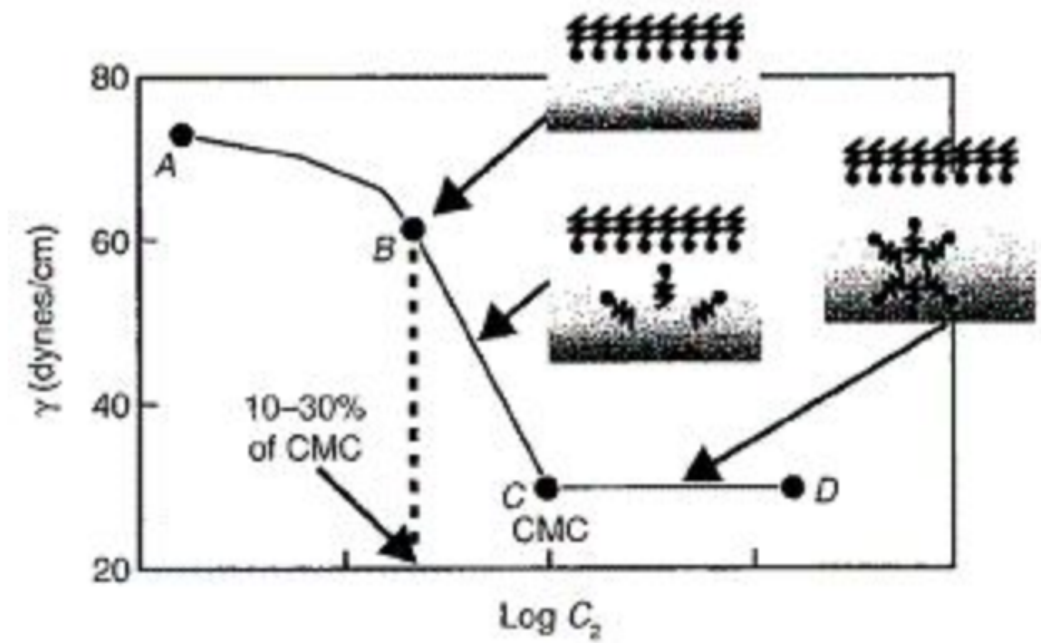


Fig. 16–13. Decrease in the surface tension of water when a strait-chain amphiphile is added. Key: CMC = critical micelle concentration. (Replotted from H. Schott, J. Pharm. Sci. 69, 852, 1980.)

[MFM, Homsy et al., 2007}

Surface rheology: background

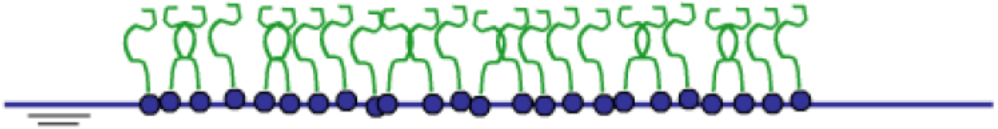
Surface tension and insoluble surfactants

Insoluble Monolayers: Langmuir Films

- There are molecules that are able to spread on the surface of liquids but are insoluble. These are referred to a *Langmuir* monolayers

- These molecules are *amphiphilic* and contain hydrophilic portions attached to hydrophobic pieces.

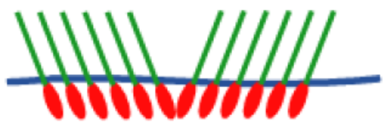
- The hydrophobic portion must be large enough to render the molecule insoluble in the subphase. The hydrophilic part must have a strong affinity to water and anchor the molecule to the surface.



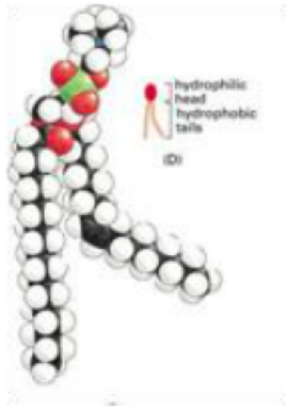
Surface rheology: background

Surface tension and insoluble surfactants

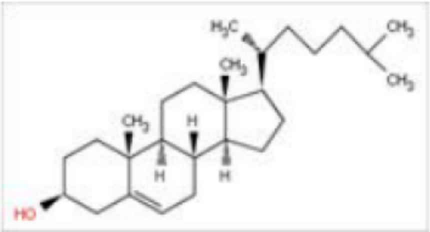
Insoluble Monolayers - Examples



fatty acids/alcohols

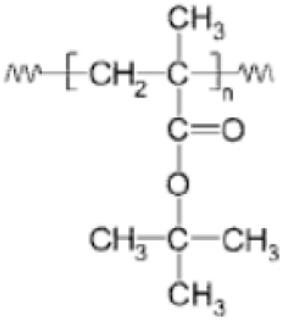


phospholipids



cholesterol

Polymers (poly tert butyl methacrylate)



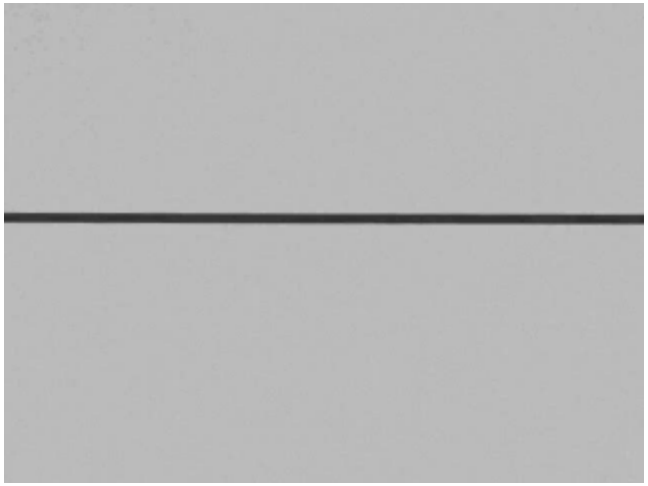
Liquid film dynamics: background

Interfacial phenomena and instabilities

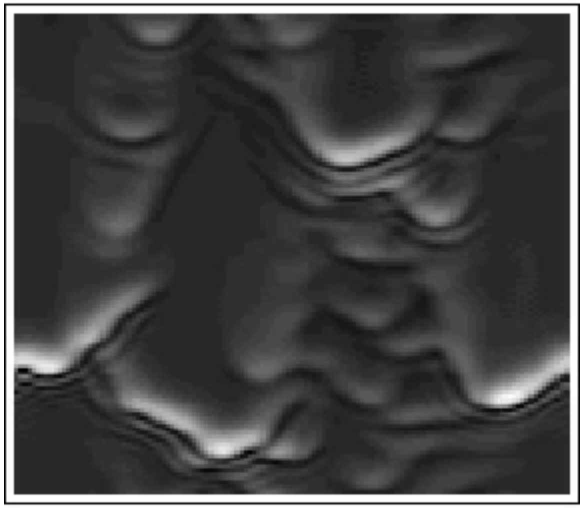
vidéo

Rayleigh-Taylor

Rayleigh-Plateau



Kapitza



<u>Suspended films</u>

Driving force: gravity

(condensed or painted films on a ceiling)

<u>Fiber coating</u>

Driving force: capillarity

(hairs, capillaries)

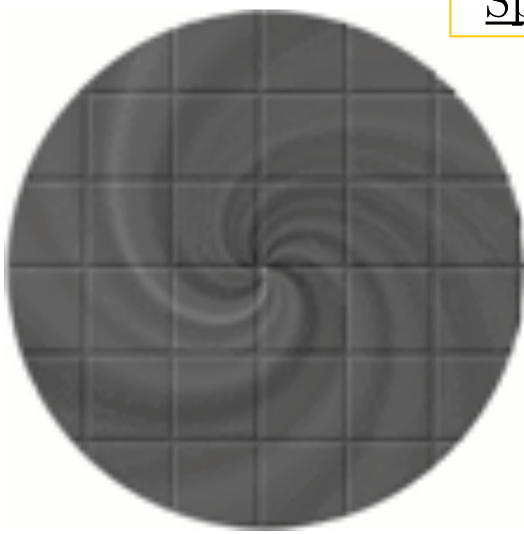
<u>Falling films</u>

Driving force: inertia

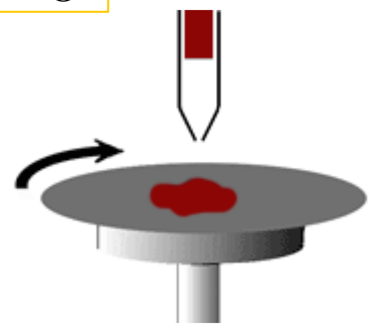
(rain on a windshield)
(cooling electronic device)
(evaporators)

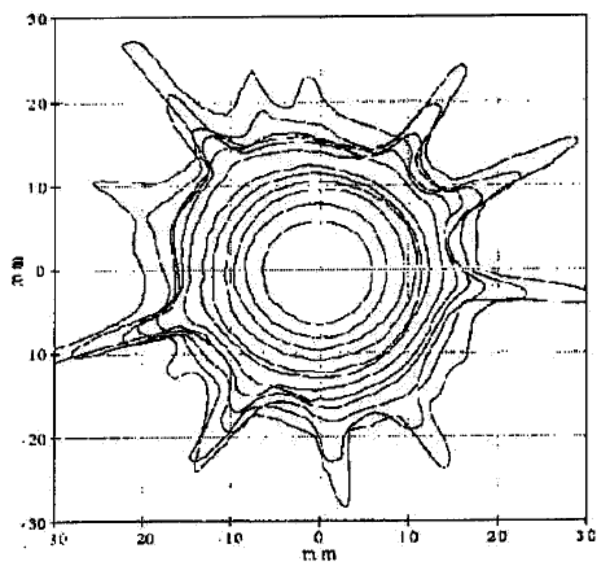
Liquid film dynamics: background

Partial wetting inducing rivulet instabilities



Spin coating

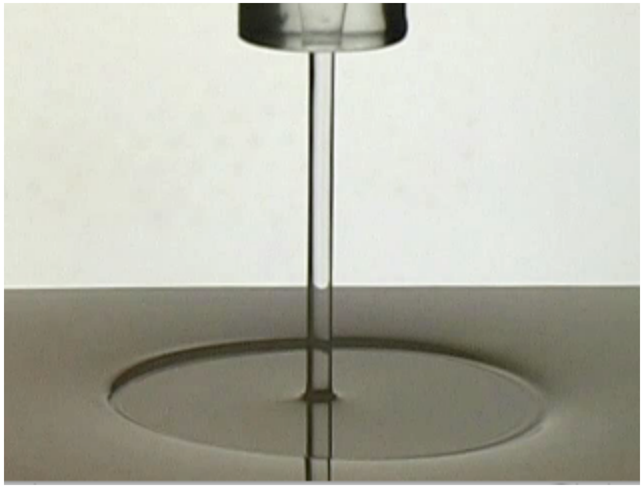




Painting

Liquid film dynamics: background

Other examples



Hydraulic jump

Splashing

Motivations of this lecture

- Interfacial phenomena dominate systems with at least one small dimensions
  - Liquid films
  - Microfluidics
- In almost all liquid films and microfluidic problems, surfactants (or impurities) are present!
  - Need for a comprehensive theoretical framework that combines surface rheology and film dynamics
    - Boussinesq-Scriven constitutive equation
    - Lubrication approximation

    → Model of reduce dimensionality (highly nonlinear but solve faster)

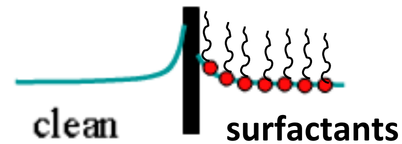
Outline

- Surface Rheology
  - Complex interface
    - Surface viscosity
    - Surface elasticity
    - Interfacial boundary condition
- Liquid Film Dynamics
  - Shear vs. extensional flow
  - Soap film vs. dip coating
    - Experiments with surface elasticity
    - Experiments with surface viscosity
- Applications to Microfluidics

Characterization of complex interfaces

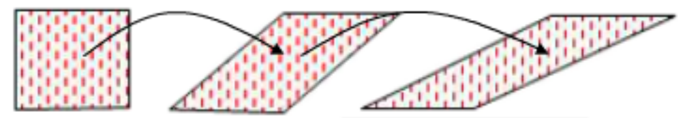
γ : surface tension - energy per unit area

$\Pi = \gamma_{clean} - \gamma_{surf}$: surface pressure

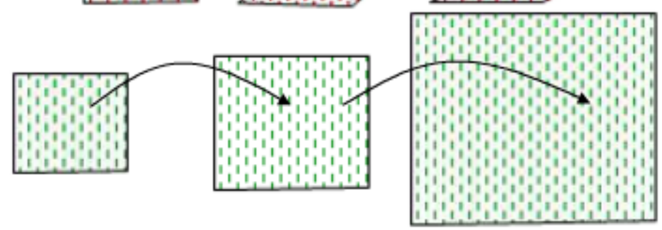


viscous

ε : surface shear viscosity



κ : dilational viscosity



elastic

~~G^s : surface shear modulus, $\sigma^s = G^s \gamma^s$ (γ^s - shear strain)~~

E : surface dilational modulus,

$$\sigma^s = E\varepsilon \; (\varepsilon \text{ - elongational strain})$$

[G. G. Fuller, Stanford University, seminar on surface rheology]

Constitutive Equation for a Newtonian fluid/fluid interface

Linear Boussinesq-Scriven surface fluid model

[Boussinesq, 1913; Scriven, 1960; Slattery, Sagis & Oh, 2007]

compressible fluid bulk

$$\mathbf{T} = -P\mathbf{I} + \boldsymbol{\sigma}$$

$$\boldsymbol{\sigma} = (\kappa_b - \frac{2}{3}\mu)(\nabla \cdot \mathbf{u})\mathbf{I} + 2\mu\mathbf{D}$$

$$\mathbf{D} = \frac{1}{2}\left[(\nabla\mathbf{u}) + (\nabla\mathbf{u})^T\right]$$

Bulk coefficient of viscosity: $\kappa_b \geq 0$

Bulk shear viscosity: $\mu \geq 0$

Usually $\kappa_b >> \mu$

[Leal, 2007]

Stokes hypothesis: Isotropic and Newtonian fluid (valid for Mach $\ll$ 1)

$$\kappa_b = 0$$

Quizz: In practical applications, liquids are incompressible: $\nabla \cdot \mathbf{u} = 0$

What about $\nabla_s \cdot \mathbf{u}_s = 0$?

compressible fluid surface

$$\mathbf{T}_s = \gamma\mathbf{I}_s + \boldsymbol{\sigma}_s$$

$$\boldsymbol{\sigma}_s = (\kappa - \varepsilon)(\nabla_s \cdot \mathbf{u}_s)\mathbf{I}_s + 2\varepsilon\mathbf{D}_s$$

$$\mathbf{D}_s = \frac{1}{2}\left[(\nabla_s\mathbf{u}_s)\cdot\mathbf{I}_s + \mathbf{I}_s\cdot(\nabla_s\mathbf{u}_s)^T\right]$$

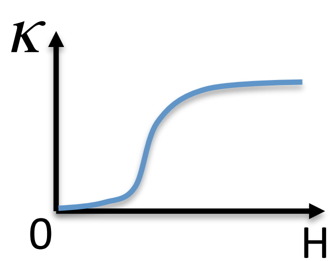
Surface dilatational viscosity: $\kappa \geq 0$

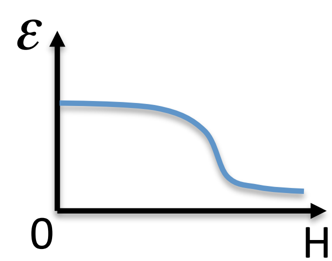
Surface shear viscosity: $\varepsilon \geq 0$

Usually $\kappa >> \varepsilon$

Can the Stokes hypothesis be valid for a fluid surface (at low frequency)?

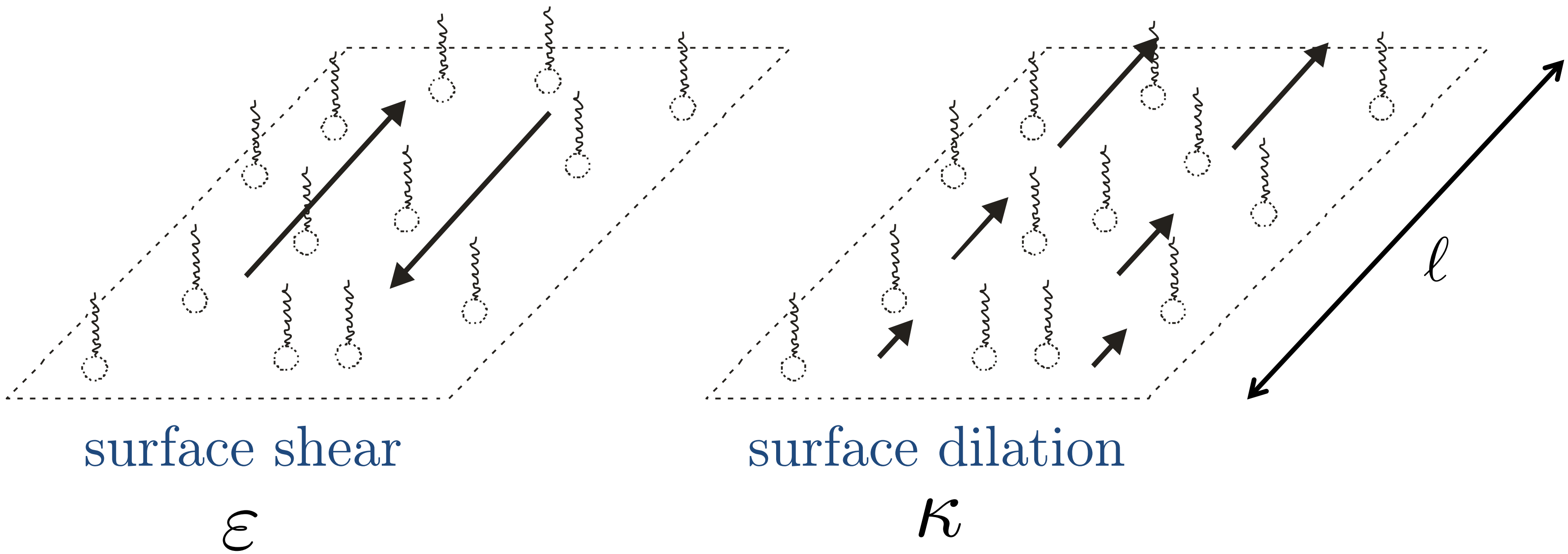
$$\kappa = 0 \ ?$$





Surface viscosity

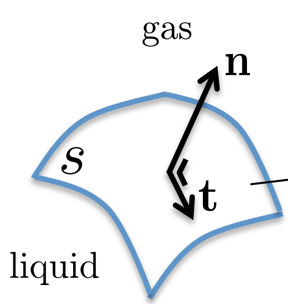
Viscous dissipation associated with shearing/dilating a "populated" interface



Planar interface: $\mu^* = \varepsilon + \kappa \sim 10^{-6} - 10^{-3}\,\mathrm{Pa.s.m}$

Boussinesq number: $Bq = \dfrac{\mu^*}{\mu\,\ell}$

Boundary conditions at a liquid-gas interface



H : surface curvature
γ : surface tension
κ : surface dilatational viscosity
ε : surface shear viscosity
$\mathbf{u}_s$: surface velocity
Γ : surface concentration

$$\nabla_s \cdot \mathbf{I}_s = 2H\mathbf{n}$$
$$H = -\frac{1}{2}\nabla_s \cdot \mathbf{n}$$

1) Jump momentum balance:

$$[\![\mathbf{T}]\!]_g^l \cdot \mathbf{n} = \nabla_s \cdot \mathbf{T}_s$$

$$(\mathbf{T}_s = \gamma \mathbf{I}_s + \boldsymbol{\sigma}_s)$$

$$[\![\mathbf{T}]\!]_g^l \cdot \mathbf{n} = 2\gamma H \mathbf{n} + \nabla_s \gamma + \nabla_s \cdot \boldsymbol{\sigma}_s$$

Stress from the liquid phase | Laplace pressure | Elasticity (Marangoni) stress | Surface viscous stress

Boussinesq-Scriven model

$$\boldsymbol{\sigma}_s = (\kappa - \varepsilon)(\nabla_s \cdot \mathbf{u}_s)\mathbf{I}_s + 2\varepsilon \mathbf{D}_s$$

$$\boxed{\begin{aligned} \kappa &= \mathrm{c^{st}} \\ \varepsilon &= \mathrm{c^{st}} \end{aligned}}$$

Quizz: What is the static limit?

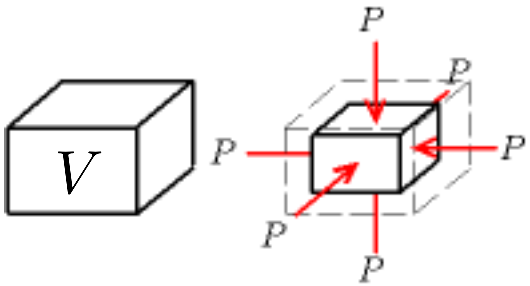
2) Jump mass balance:

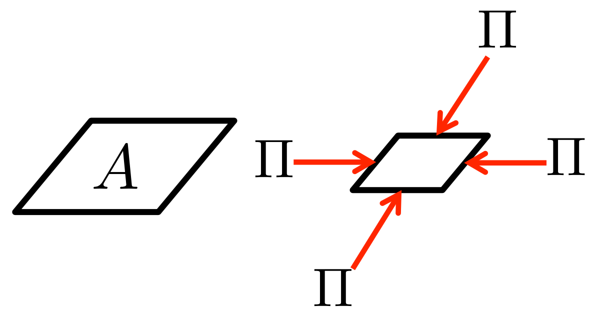
$$\partial_t \Gamma + \nabla_s \cdot (\Gamma \mathbf{u}_s) = D_s \nabla_s^2 \Gamma + \mathbf{j}$$

[Stone, 1989]

Quizz: What is the insoluble limit?

Surface elasticity

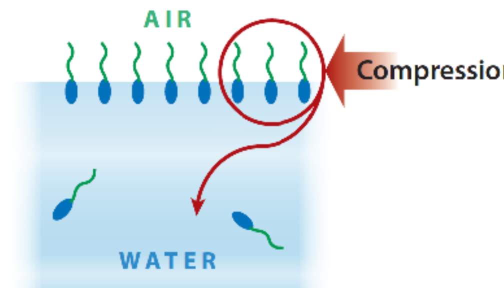




$$\frac{1}{E_{\text{bulk}}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\frac{1}{E} = -\frac{1}{A}\left(\frac{\partial A}{\partial \Pi}\right)_T$$

$$\Pi = \gamma_{\text{clean}} - \gamma$$



[Langevin, 2014]

$$\boxed{E = A\frac{\partial \gamma}{\partial A}}$$

Insoluble surfactant

Soluble surfactant

$$E = -\Gamma\frac{\partial \gamma}{\partial \Gamma}$$

$$E \simeq E_{\text{insol}} \equiv -\Gamma\frac{\partial \gamma}{\partial \Gamma}$$

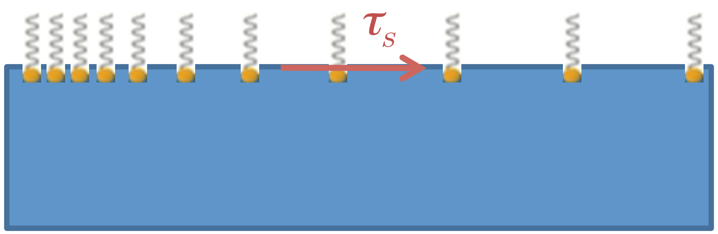
For "slow" sorption kinetics !

$$\boxed{\nabla_s \gamma = \frac{\partial \gamma}{\partial \Gamma}\nabla_s \Gamma = -\frac{E}{\Gamma}\nabla_s \Gamma}$$

Surface tension gradient

– Always generates a flow along the interface

$\gamma_1 < \gamma_2$



Thermocapillary effect

$$\tau_s : \nabla_s \gamma = \underbrace{\frac{\partial \gamma}{\partial T}}_{<0} \nabla_s T$$

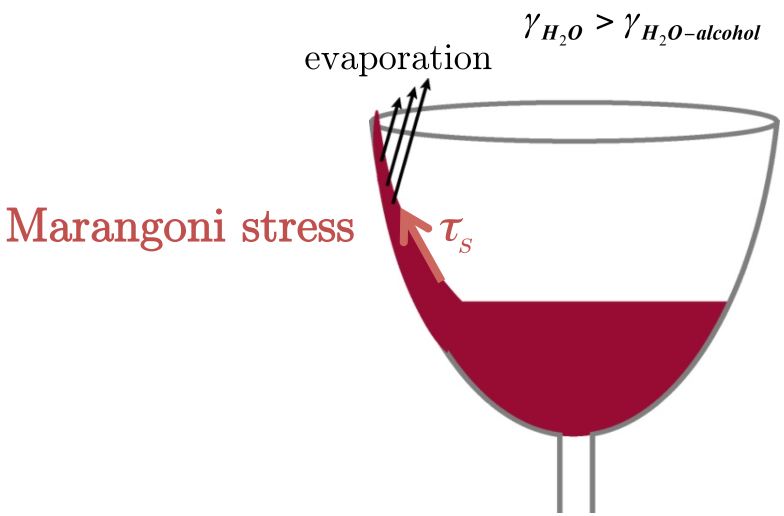
Soluto-capillary effect

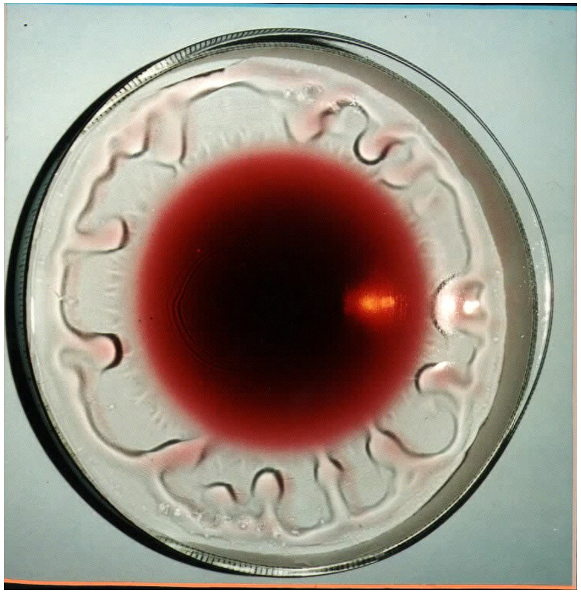
$$\tau_s : \nabla_s \gamma = \frac{\partial \gamma}{\partial \Gamma} \nabla_s \Gamma = -\frac{E}{\Gamma} \nabla_s \Gamma$$

Marangoni effect

Marangoni effect

- Surface tension gradient
  - James Thomson, older brother of Lord Kelvin (William Thomson) in 1855:
    - 'On certain curious motions observable at the surfaces of wine and other alcoholic liquors'
  - Tears of wine





[Images: John Bush, MIT]

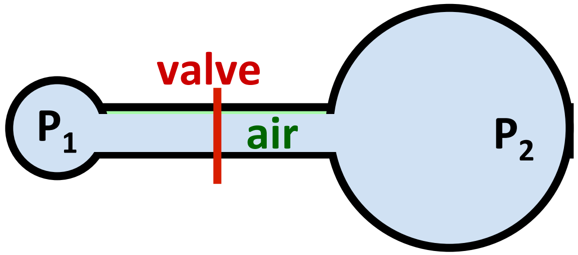
Carlo Marangoni
(1840-1925)

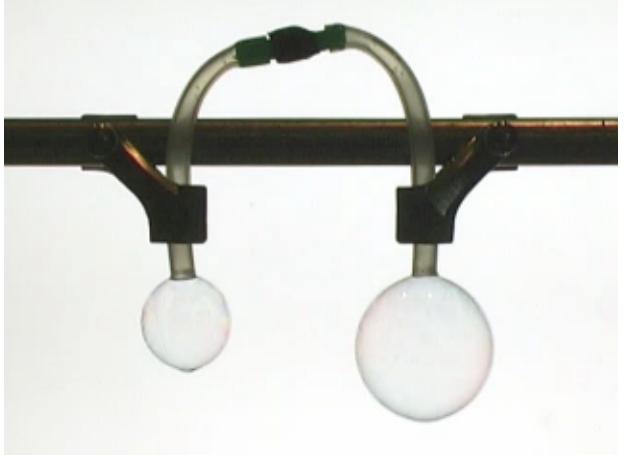
  - Studied by Marangoni at the end of 19^{th} century

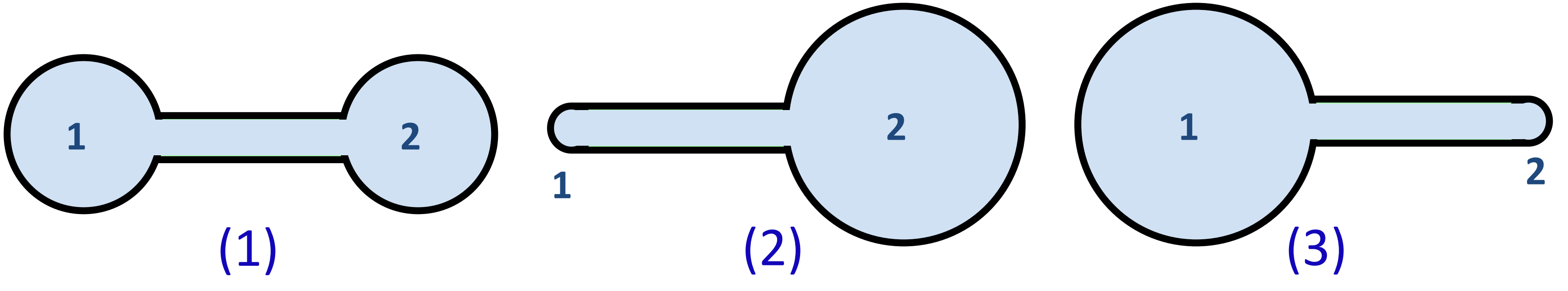
Quizz: Laplace pressure

- Two soap bubbles are connected by a closed valve.
  What happens when the valve is open?

  (Hint: fluids flow from high to low pressure)

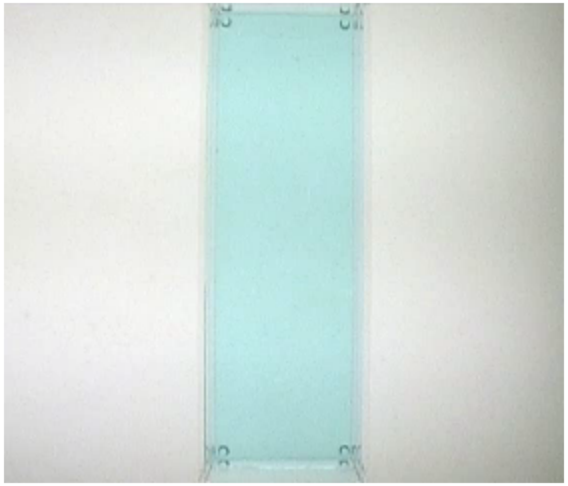


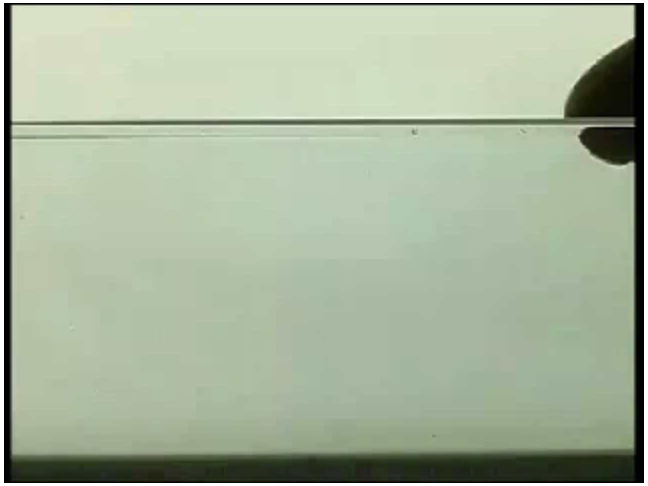




Quizz: Marangoni effect

Soluto-capillary effect

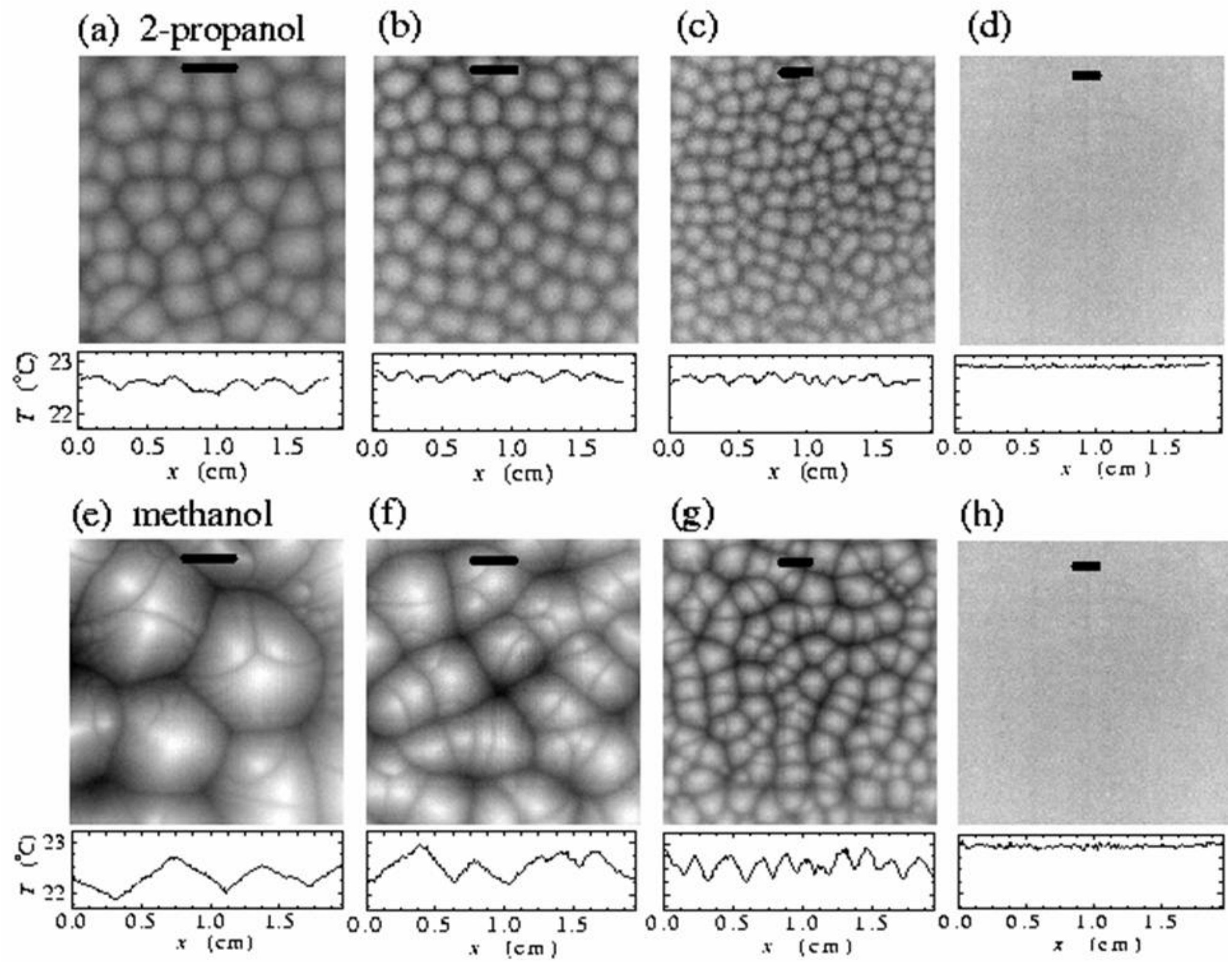




Thermocapillary effect

[MFM, Homsy et al., 2007}

Marangoni instability: drying of liquid films



ex: orange peal in drying

Outline

- Surface Rheology
  - Complex interface
    - Surface viscosity
    - Surface elasticity
  - Surface boundary conditions
- Liquid Film Dynamics
  - Shear vs. extensional flow
  - Soap film vs. dip coating
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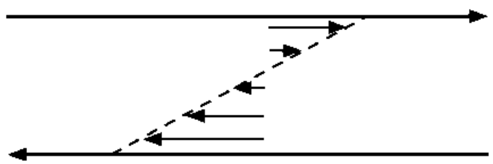
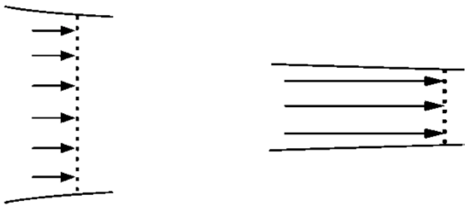
- Applications to Microfluidics

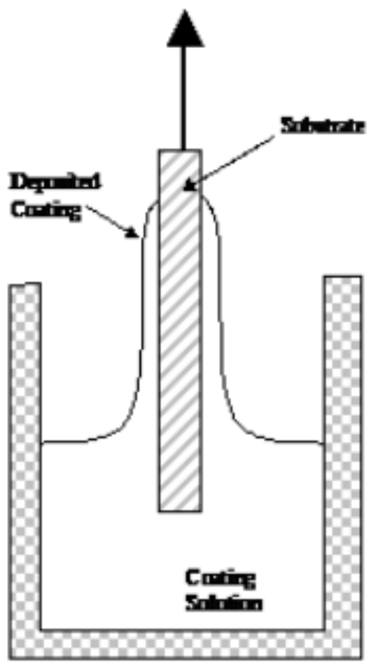
Classification of liquid film flows

Shear flow vs. Extensional flow

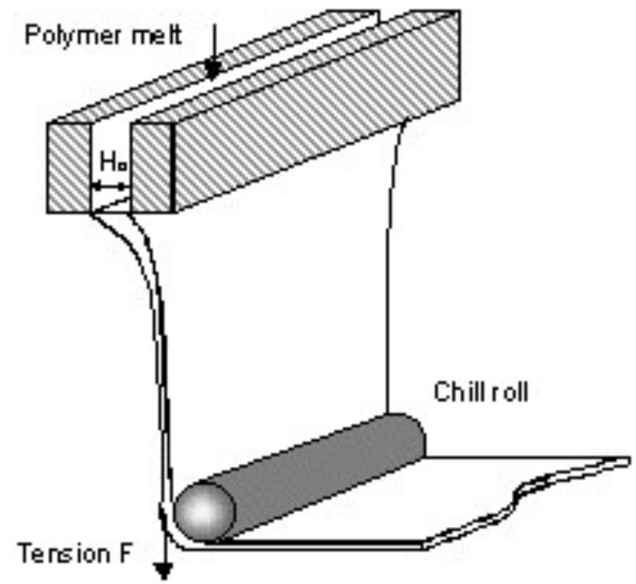




Ex: Dip coating

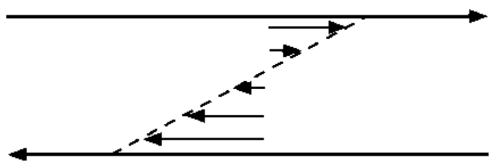


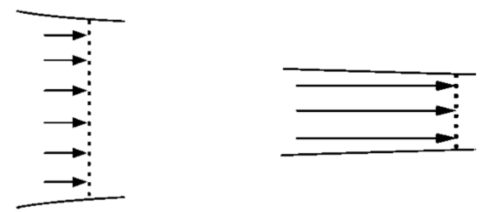
Ex: Film casting



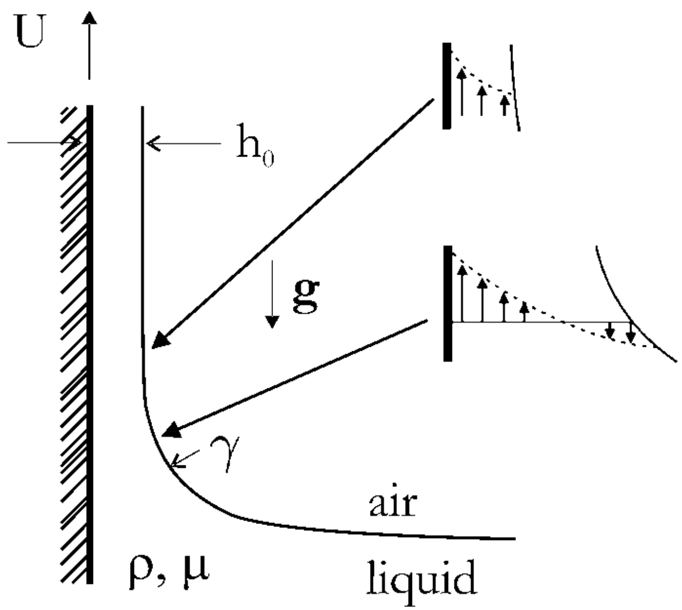
Classification of liquid film flows

Shear flow vs. Extensional flow

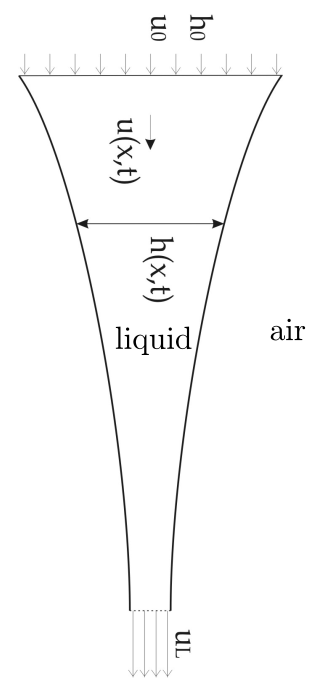




Ex: Dip coating

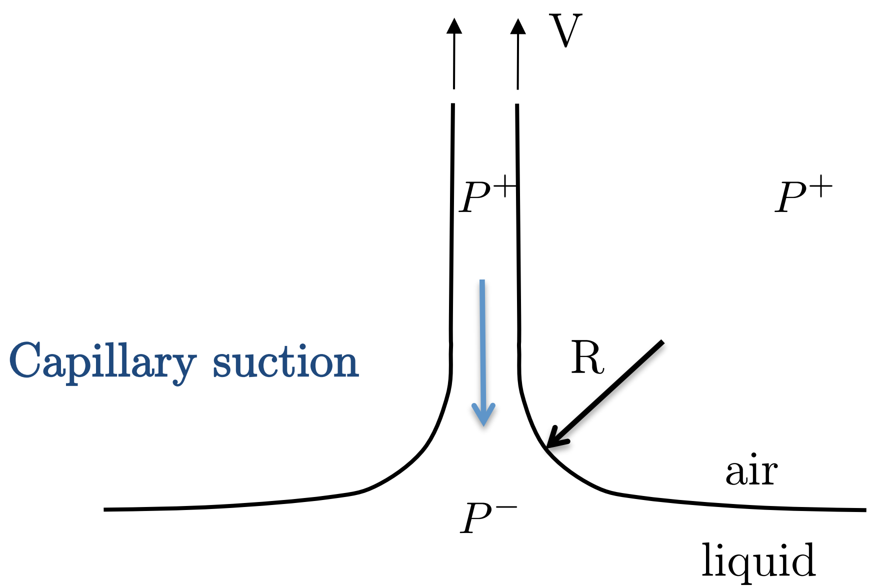


Ex: Film casting



Quizz: Making a film of pure viscous liquid

Where is the pressure minimum?
Is this stable?



Laplace pressure

$$P^+ - P^- = \frac{\gamma}{R}$$

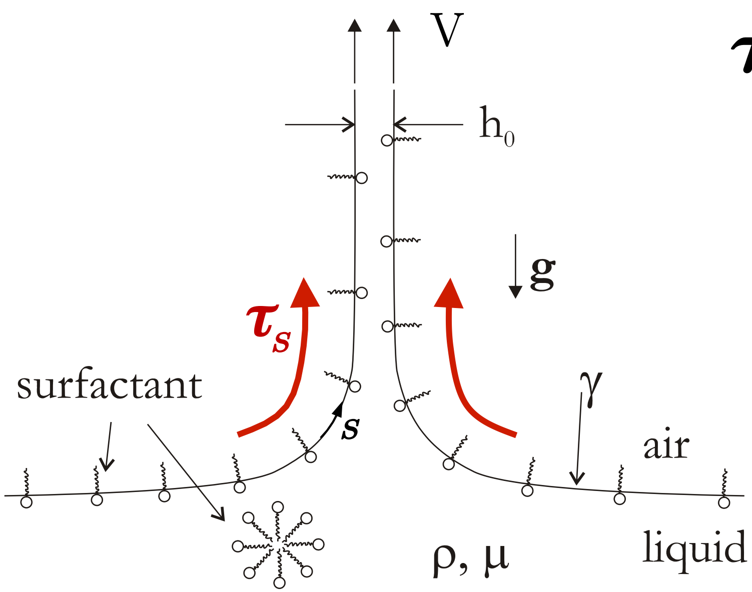
Quizz: Making a soap film

Pulling stable films need strong interfacial stress

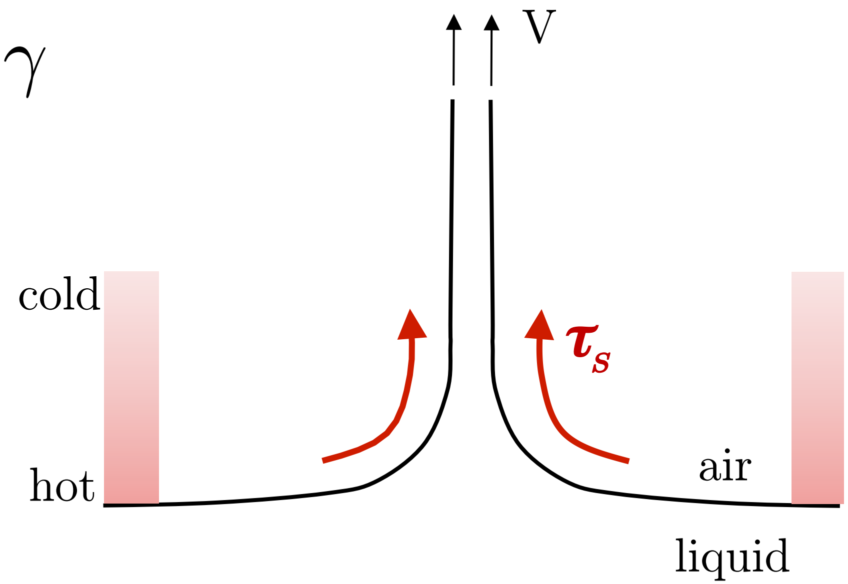
Surface
(Marangoni)
elasticity

$$\boldsymbol{\tau}_s = \nabla_s \gamma$$

soap film



Film of pure material?



What means strong? → "shear" distinguished limit

$$Ca = \frac{\mu V}{\gamma} \ll 1 \qquad M = \frac{\Delta\gamma}{\mu V} \gg 1$$

Outline

- Surface Rheology
  - Complex interface
    - Surface viscosity
    - Surface elasticity
  - Surface boundary conditions
- Liquid Film Dynamics
  - Shear vs. extensional flow
  - Soap film vs. dip coating
    - Experiments with surface elasticity
    - Experiments with surface viscosity
- Applications to Microfluidics

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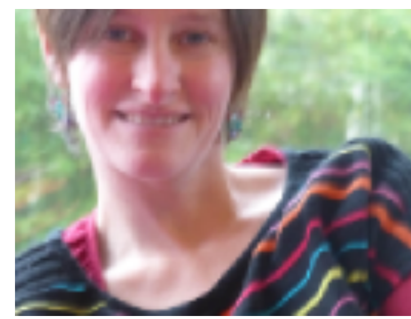
Surfactant-induced rigidity of interfaces: a unified approach to free and dip-coated films

Lorène Champougny,[a] Benoit Scheid,[b] Frédéric Restagno,[a] Jan Vermant[c] and Emmanuelle Rio*[a]

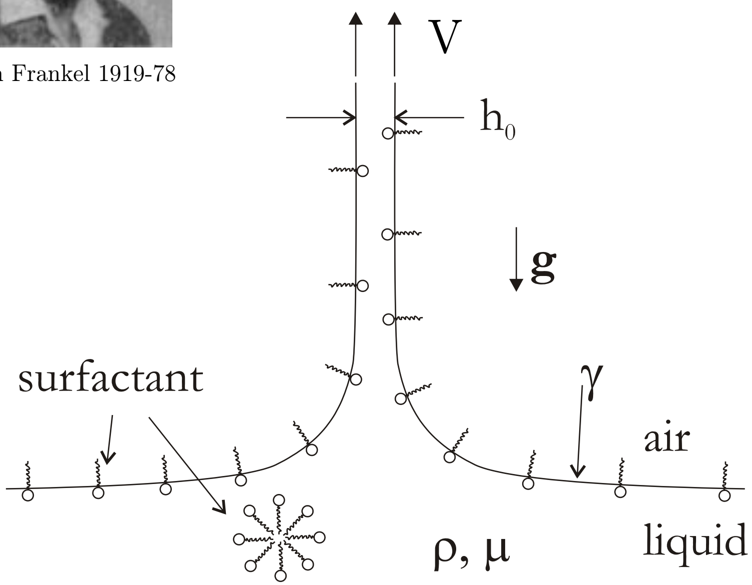


Soap films vs. dip coating

Frankel, 1962

Stan Frankel 1919-78

soap film



$$\boxed{h_0/\ell_c = 1.88\ \mathrm{Ca}^{2/3}}$$

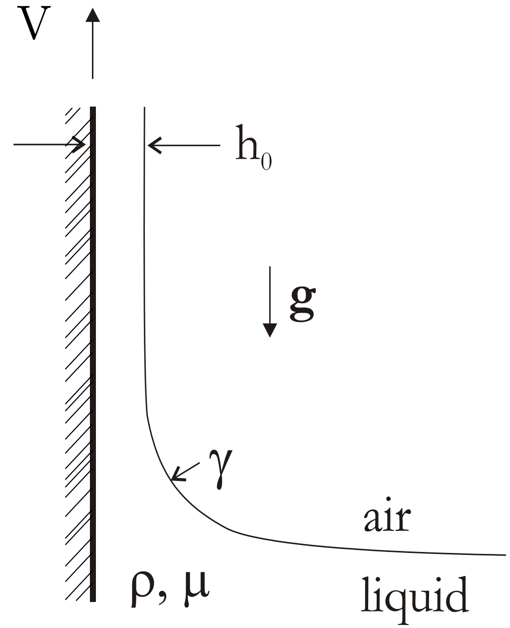
Is this always true?

$$Ca = \frac{\mu V}{\gamma}$$

$$\ell_c = \sqrt{\frac{\gamma}{\rho g}}$$

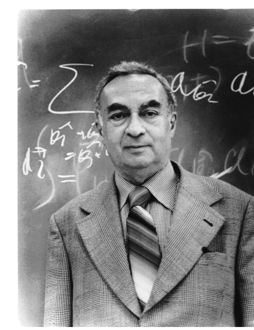
Landau-Levich-Derjaguin (LLD), 1942-1943

dip coating

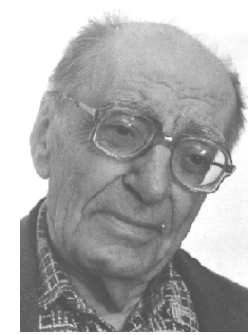


$$\boxed{h_0/\ell_c = 0.94\ \mathrm{Ca}^{2/3}}$$

Lev Landau 1908-68



Benjamin Levich 1917-87



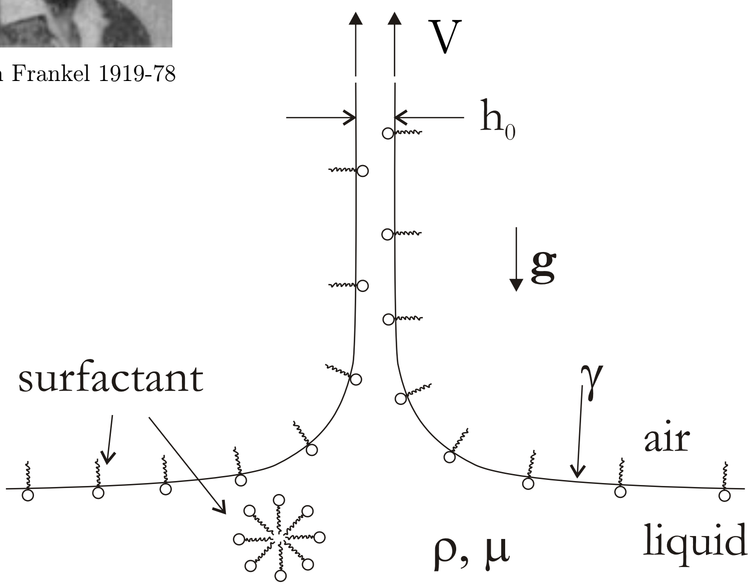
Boris Derjaguin 1902-94

Soap films vs. dip coating

<u>Frankel, 1962</u>

Stan Frankel 1919-78

soap film

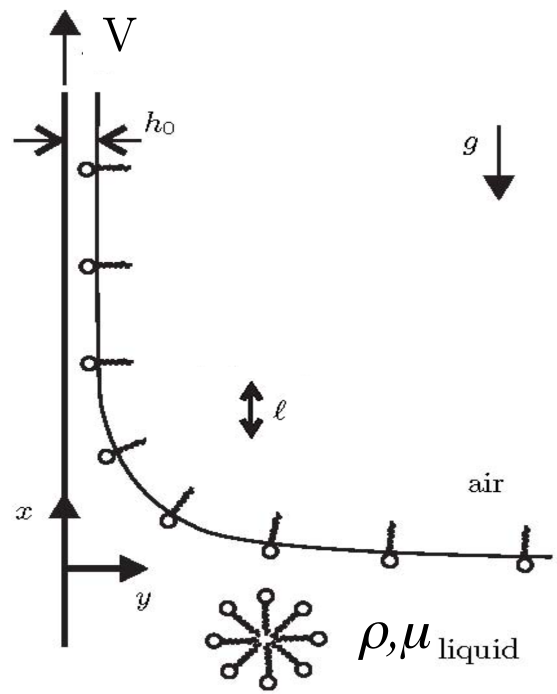


$$\boxed{h_0/\ell_c = 1.88\ \mathrm{Ca}^{2/3}}$$

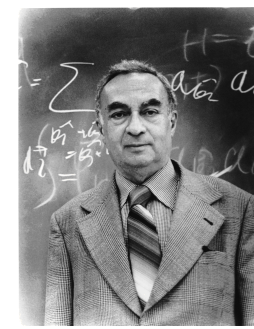
Is this always true?

<u>Landau-Levich-Derjaguin (LLD), 1942-1943</u>

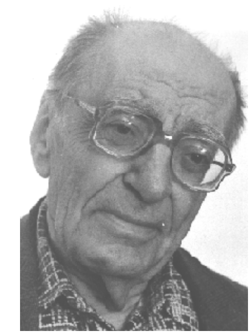
dip coating



Lev Landau 1908-68



Benjamin Levich 1917-87



Boris Derjaguin 1902-94

$$Ca = \frac{\mu V}{\gamma}$$

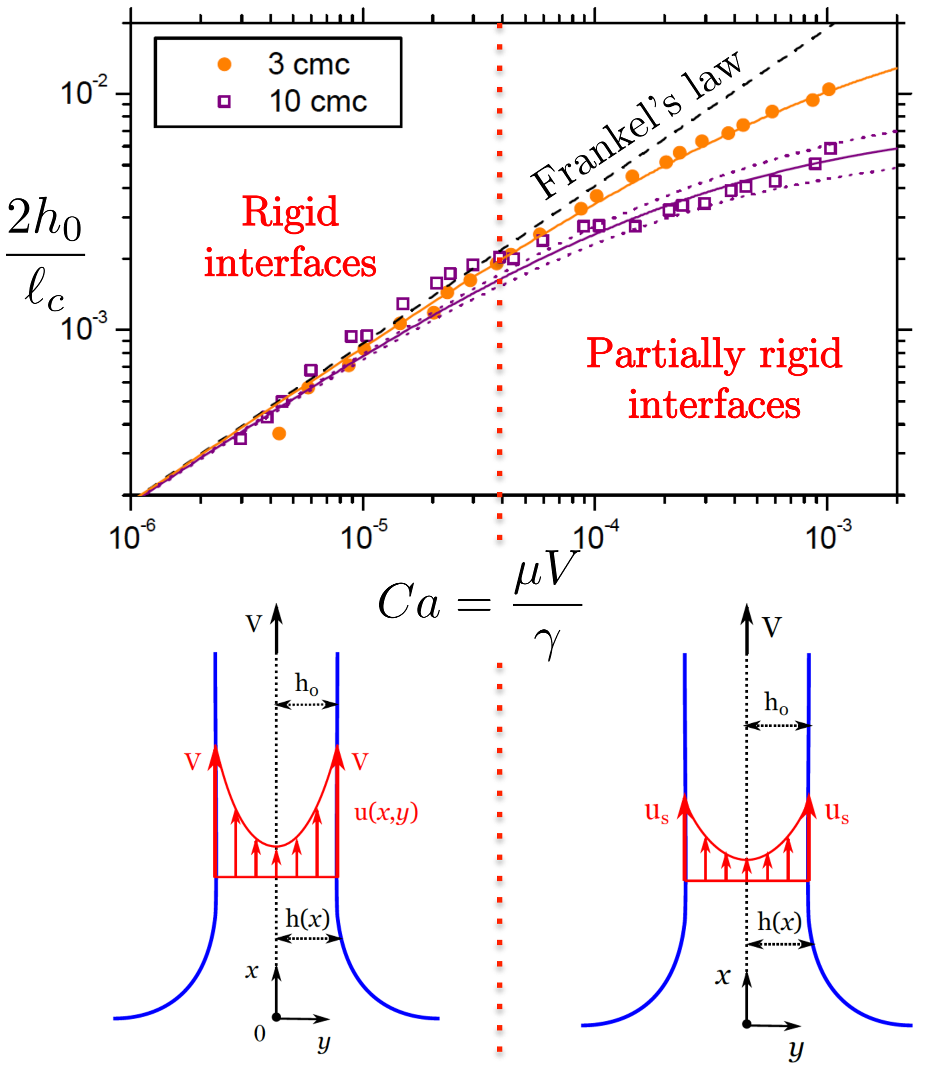
$$\ell_c = \sqrt{\frac{\gamma}{\rho\, g}}$$

$$\boxed{h_0/\ell_c = 0.94\ \mathrm{Ca}^{2/3}}$$

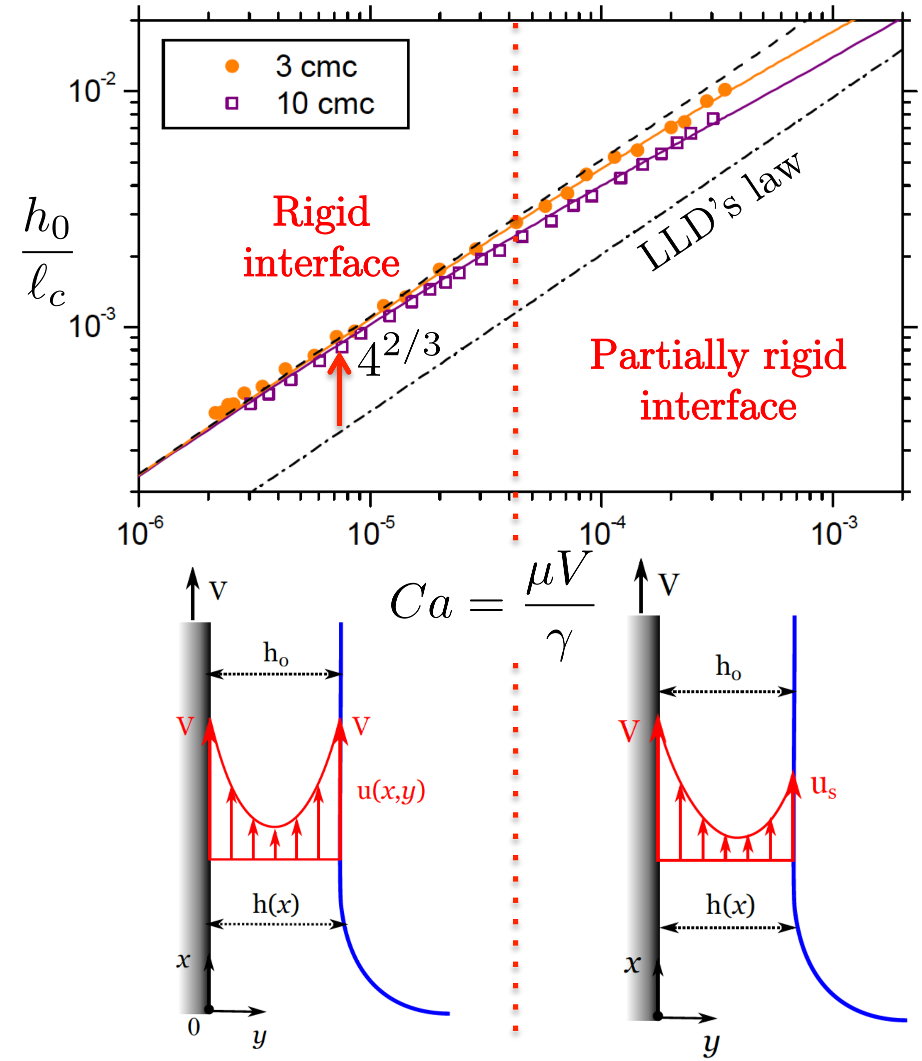
?

Experiments with $C_{12}E_6$

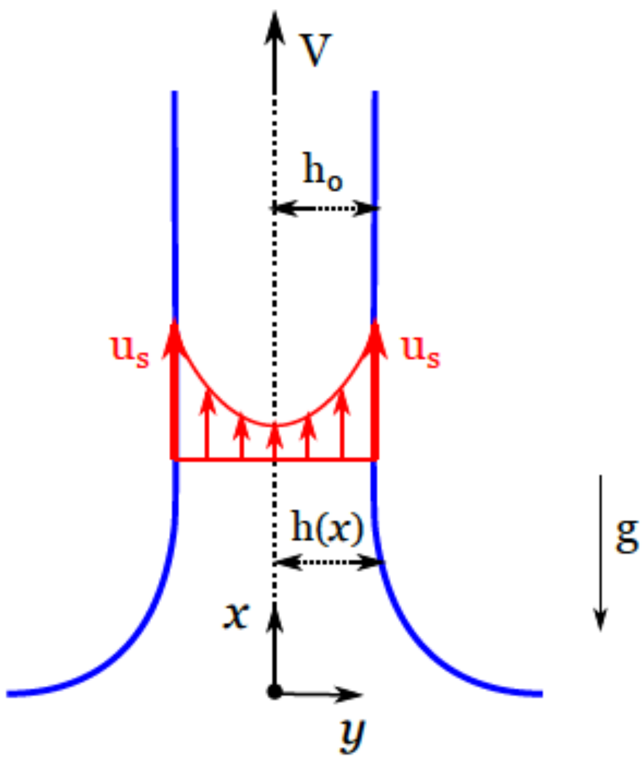
soap film [Saulnier et al., 2011]



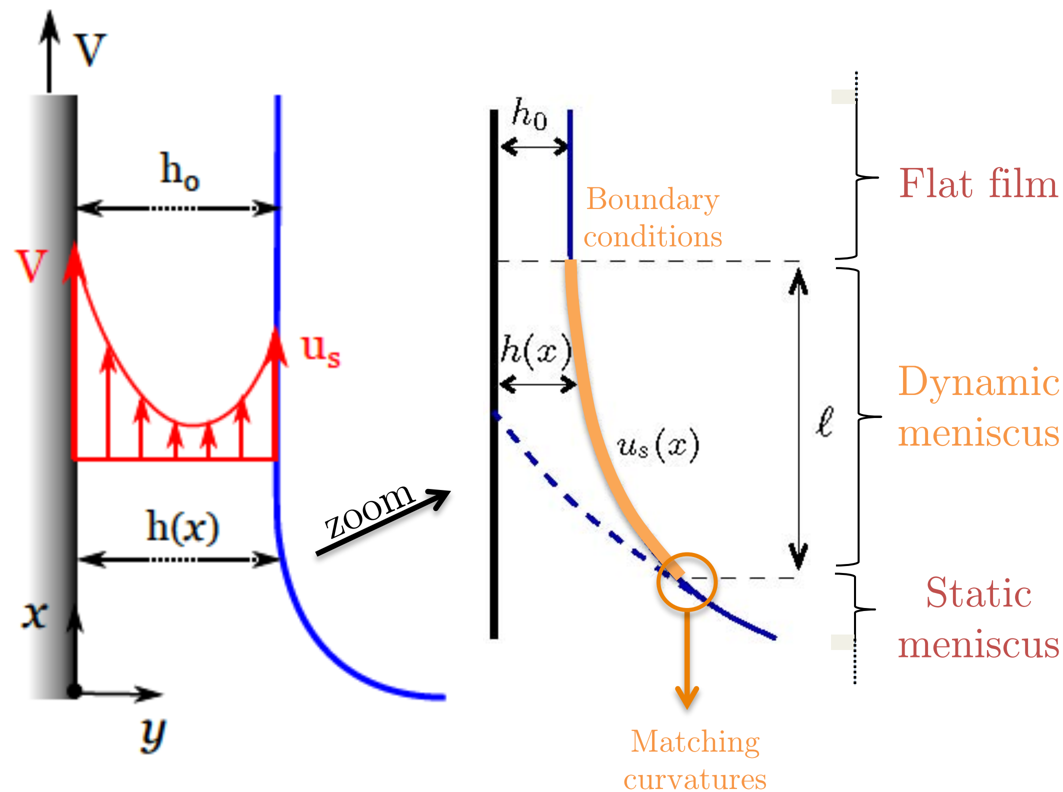
dip coating [Delacotte et al., 2012]



Modeling films with partially rigid interfaces



soap film

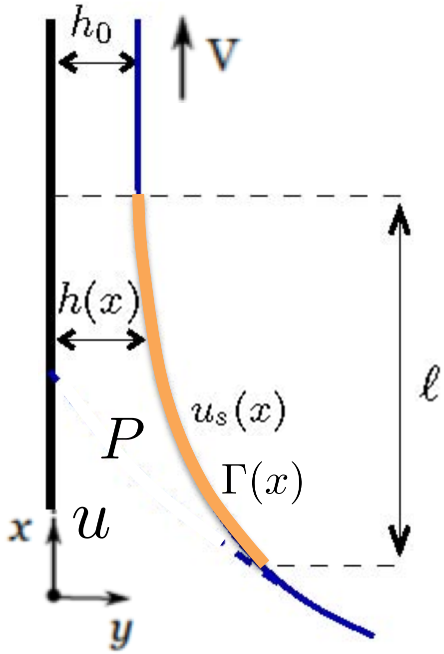


Dip coating

$$\partial_{xx} h = \frac{\sqrt{2}}{\ell_c} \qquad \text{for} \quad x \to -\infty$$

Lubrication approximation

$$\partial_x h \sim \frac{h_0}{\ell} \ll 1$$



Modeling the dynamic meniscus in stationary regime

Lubrication approximation

Mass balance: $h\bar{u} = h_0 V$

Momentum balance (Stokes): $\partial_x P = \mu \partial_{yy} u$

$\partial_y P = 0$

Jump momentum balance: $P - P_g = \gamma \partial_{xx} h$

$$\mu \partial_y u|_h = -\frac{E}{\Gamma}\partial_x \Gamma + (\kappa + \varepsilon)\partial_{xx} u_s$$

(Insoluble) surfactant conservation: $\partial_x(\Gamma u_s) = 0$

Quizz: Find the Landau-Levich-Derjaguin scaling law, i.e. $h_0/l_c \sim Ca^{2/3}$

Hint: the interface is stress-free for a pure liquid

At the wall: soap film : $\partial_y u|_0 = 0$ dip coating : $u|_0 = V$

Dimensionless equations

$$y \to h_0 y, \quad h \to h_0 h, \quad x \to \ell x, \quad \gamma \to \gamma_0, \quad u_s \to V u_s, \quad \Gamma \to \Gamma_0 \Gamma$$

$$\partial_{xxx} h = Ca \frac{\ell^3}{h_0^3} \partial_{yy} u \longrightarrow \ell = h_0 Ca^{-1/3}$$

$$Ca = \frac{\mu V}{\gamma_0}$$

$$Ma = \frac{E}{\gamma_0} \ll 1$$

soap film

$$h''' = 3 \frac{(1 - u_s h)}{h^3}$$

$$u_s' = -3\Lambda \frac{u_s}{h^2}(1 - u_s h),$$

$$\Gamma' = -\frac{\Gamma}{u_s} u_s',$$

$$\boxed{\Lambda = \frac{\mathrm{Ma}}{\mathrm{Ca}^{2/3}}}$$

Dip coating

$$h''' = 6 \frac{[2 - (1 + u_s)h]}{h^3}$$

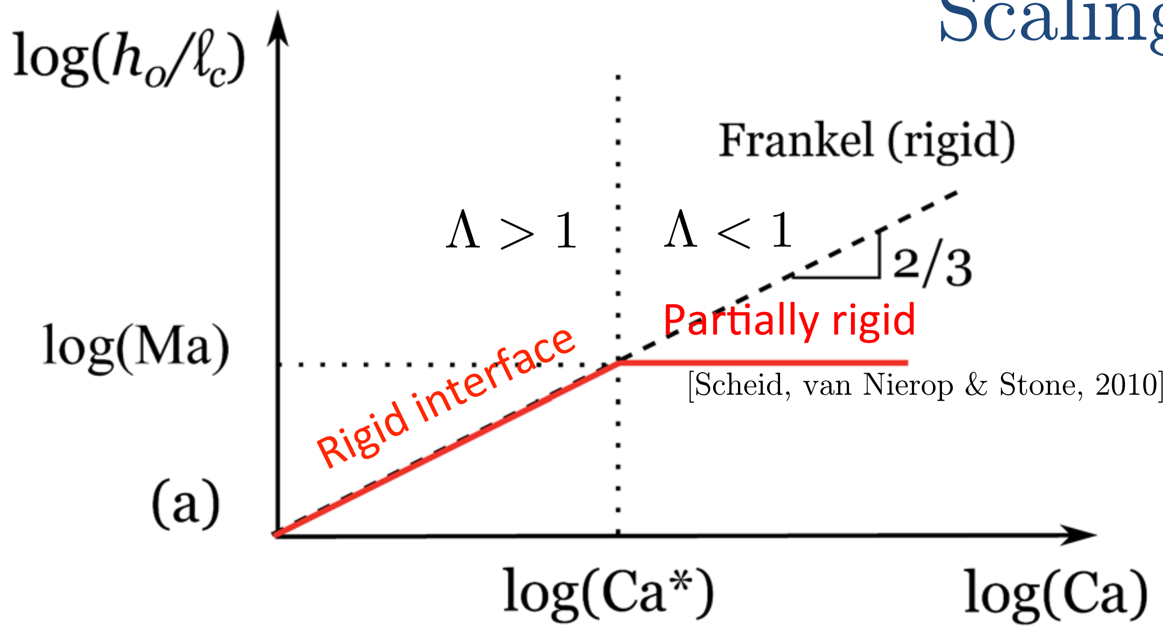
$$u_s' = -2\Lambda \frac{u_s}{h^2}[3 - (1 + 2u_s)h]$$

$$\Gamma' = -\frac{\Gamma}{u_s} u_s',$$

B.C.: $h(\infty) = 1, \quad h'(\infty) = 0, \quad h''(\infty) = 0, \quad u_s(\infty) = 1, \quad \Gamma(-\infty) = 1$

Matching condition: $\dfrac{h_0}{\ell_c} = \dfrac{h''(-\infty)}{\sqrt{2}} \mathrm{Ca}^{2/3}$

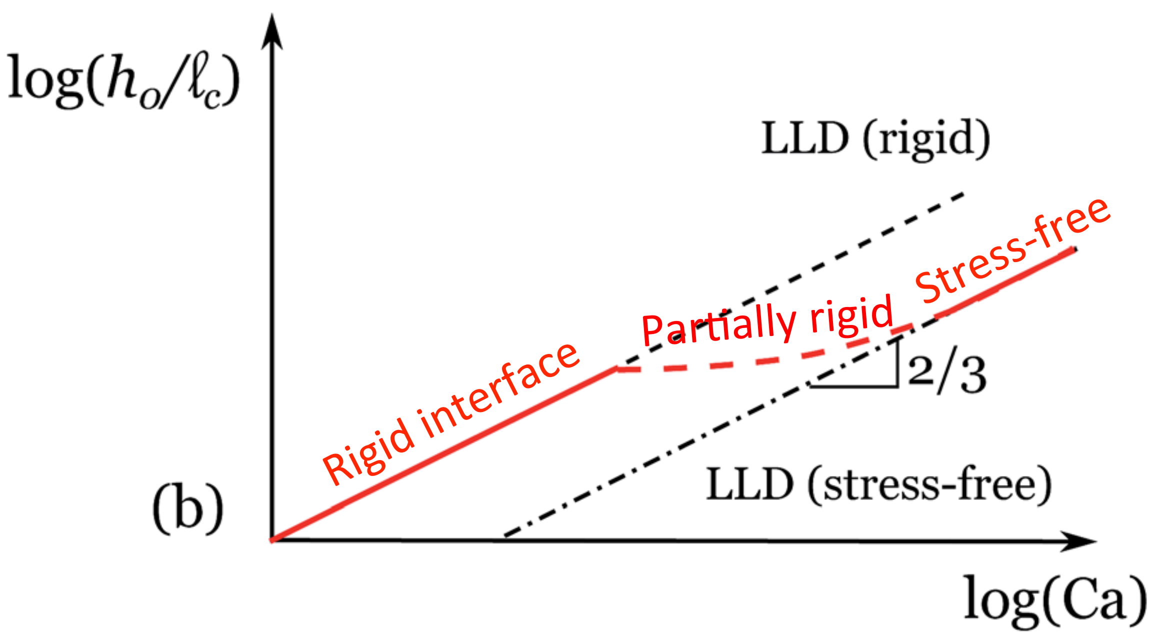
Scaling arguments



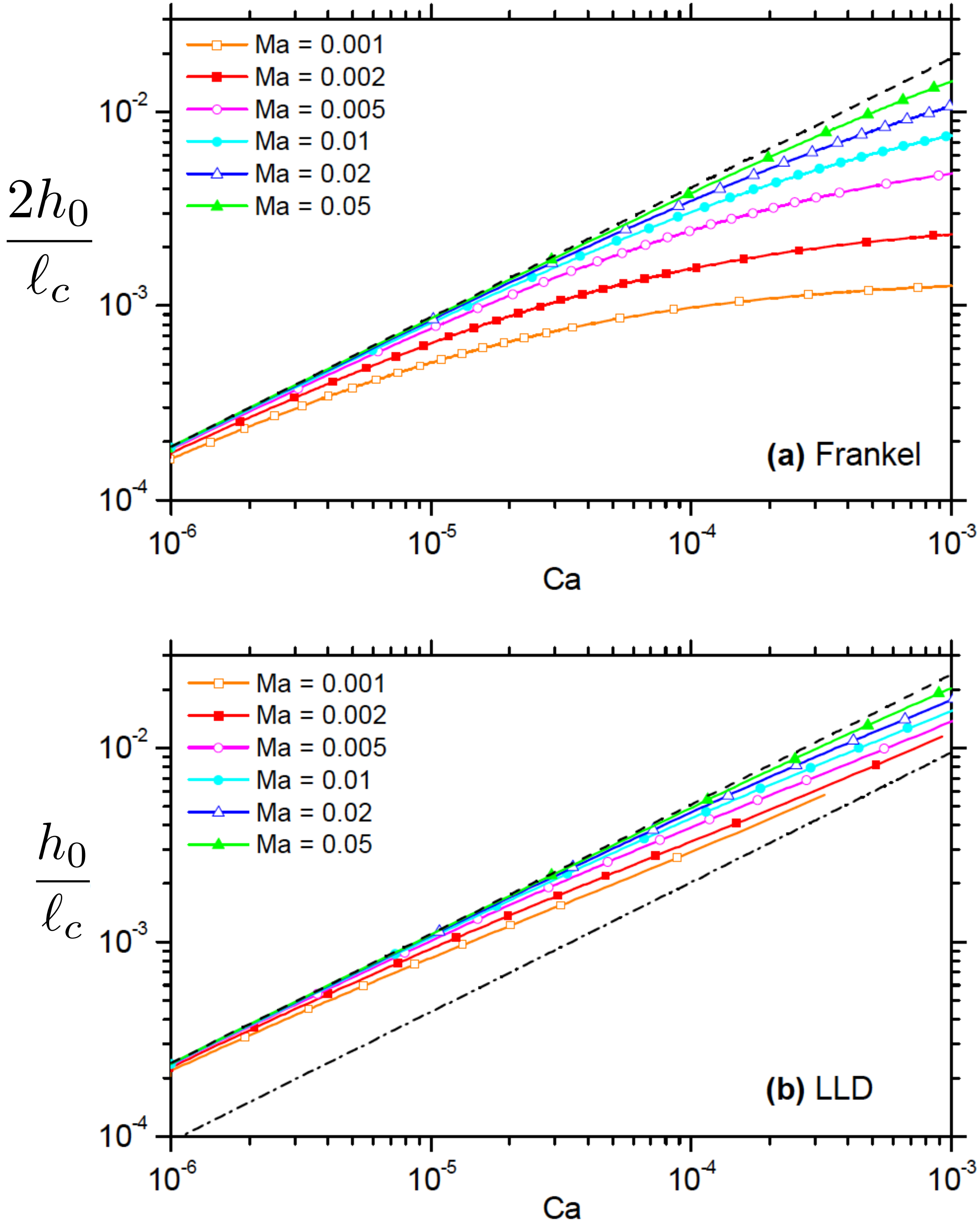
Rigidity parameter

$$\Lambda = \frac{\mathrm{Ma}}{\mathrm{Ca}^{2/3}} = 1$$

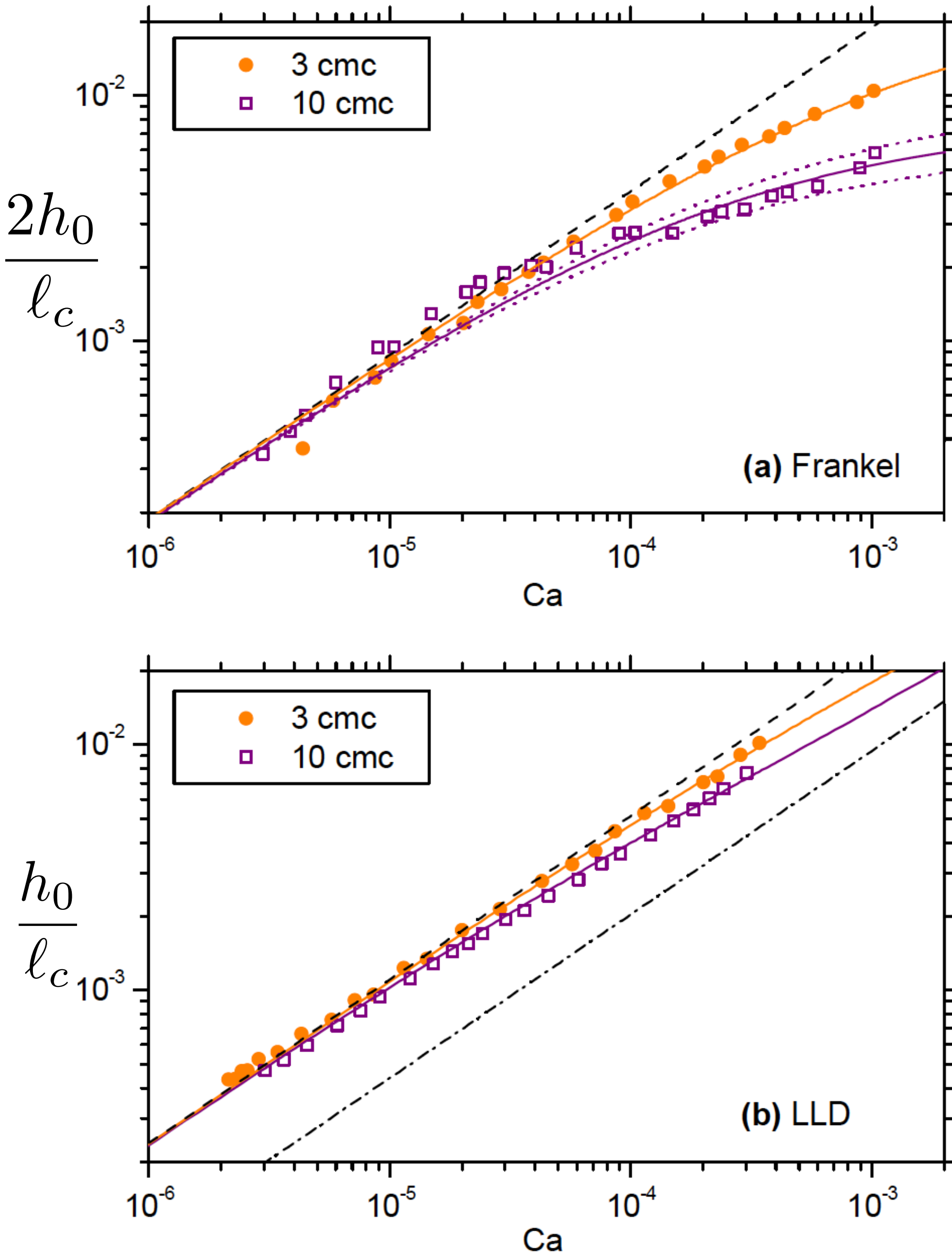
$$\mathrm{Ca}^* \sim \mathrm{Ma}^{3/2}.$$



The “rigidity” of the interface is not an intrinsic property of a surfactant solution



Theoretical curves

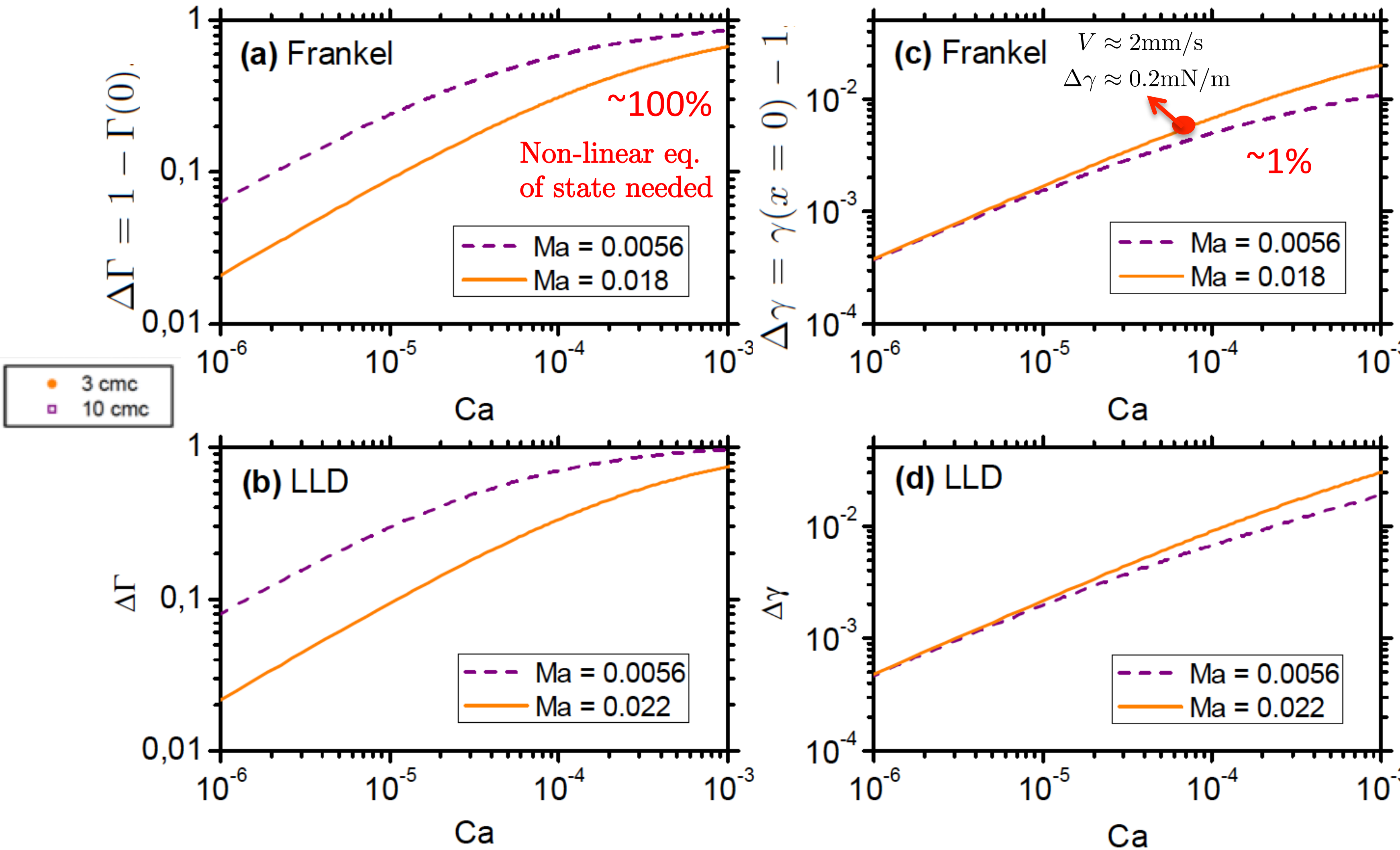


Fitting with constant E

$C_{12}E_6$		3 cmc	10 cmc
Frankel	$\mathrm{Ma} \times 10^3$	18^{+8}_{-2}	$5.6^{+1.4}_{-1.2}$
	E (mN/m)	$0.62^{+0.28}_{-0.07}$	$0.19^{+0.05}_{-0.04}$
LLD	$\mathrm{Ma} \times 10^3$	22^{+8}_{-7}	$5.6^{+1.4}_{-2.1}$
	E (mN/m)	$0.71^{+0.26}_{-0.23}$	$0.18^{+0.05}_{-0.07}$

What is the relative variation of surface tension along the film?

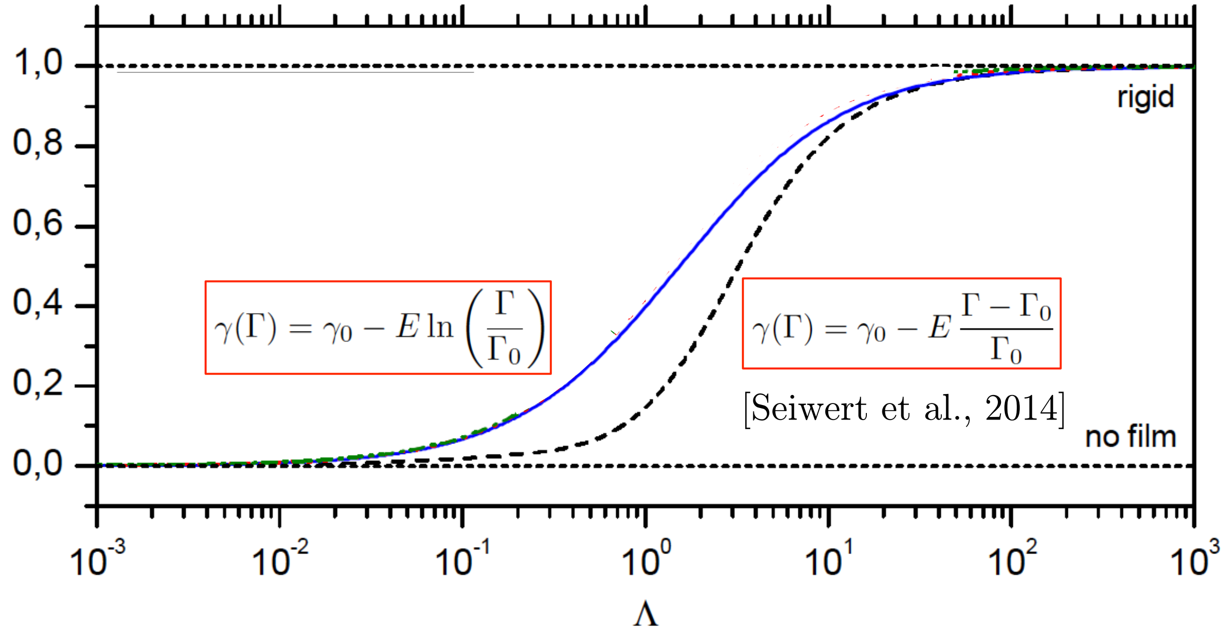
$$E = -\Gamma \frac{\partial \gamma}{\partial \Gamma} \longrightarrow \gamma(\Gamma) = \gamma_0 - E \ln\left(\frac{\Gamma}{\Gamma_0}\right) \longrightarrow \boxed{\gamma(\Gamma) = 1 - \mathrm{Ma}\ln(\Gamma)}$$



Linear versus nonlinear equation of state

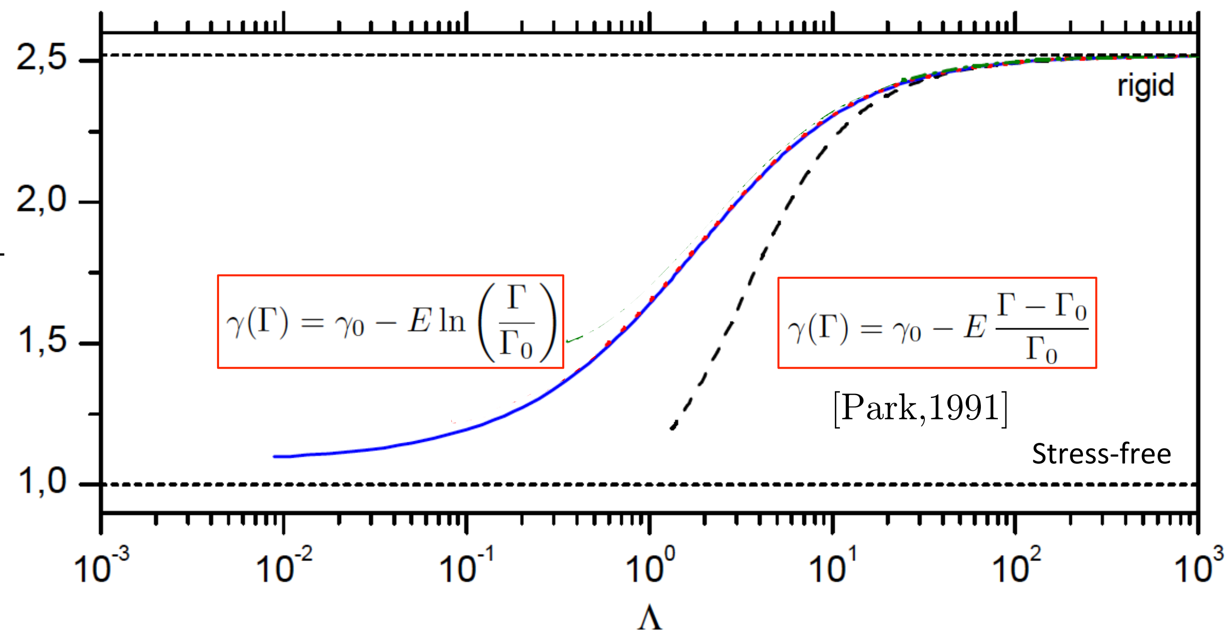
Frankel:

$$\alpha_{\mathrm{Fr}} = \frac{h}{h_{\mathrm{Fr}}}$$

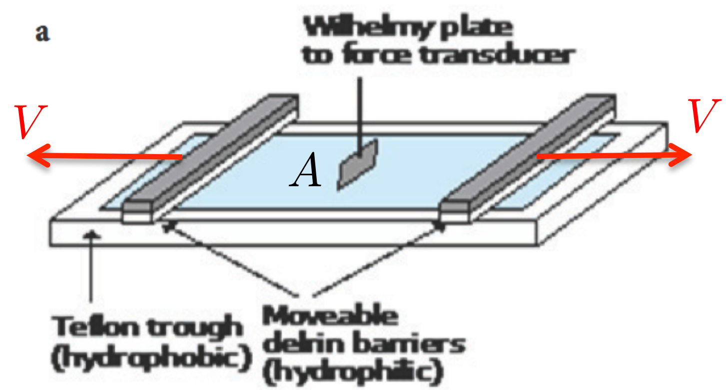


LLD:

$$\alpha_{\mathrm{LLD}} = \frac{h}{h_{\mathrm{LLD}}}$$

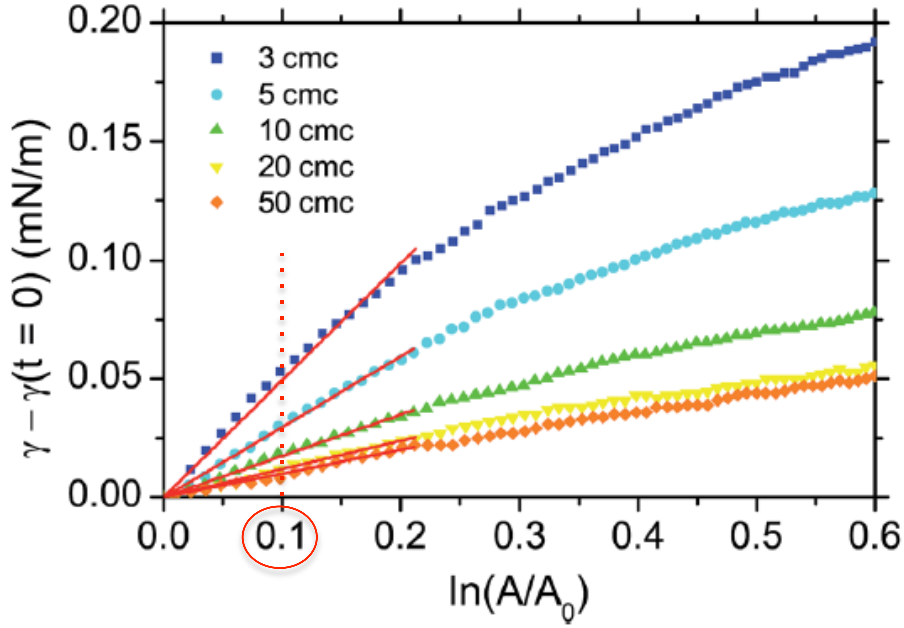


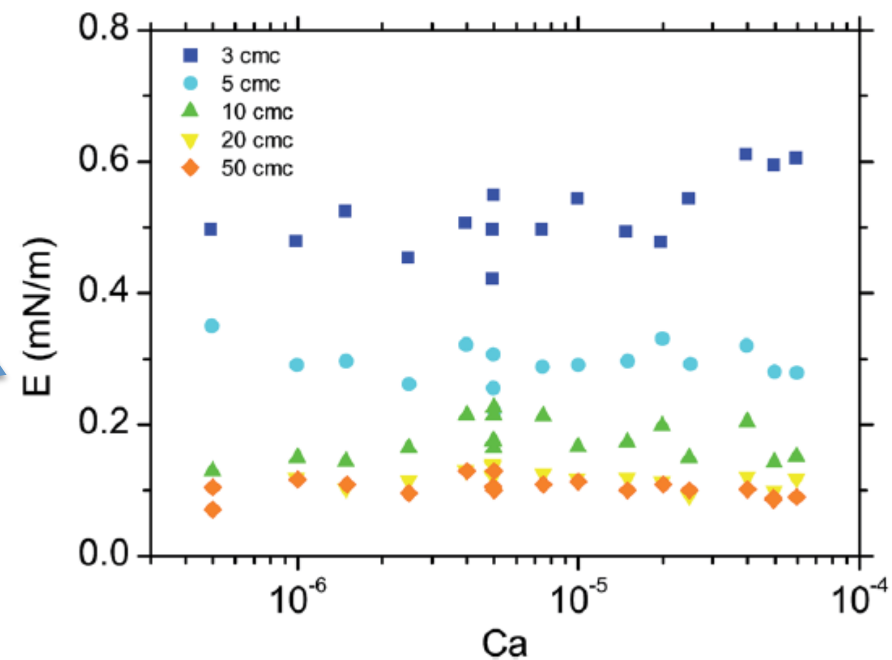
Independent measurement of surface elasticity!



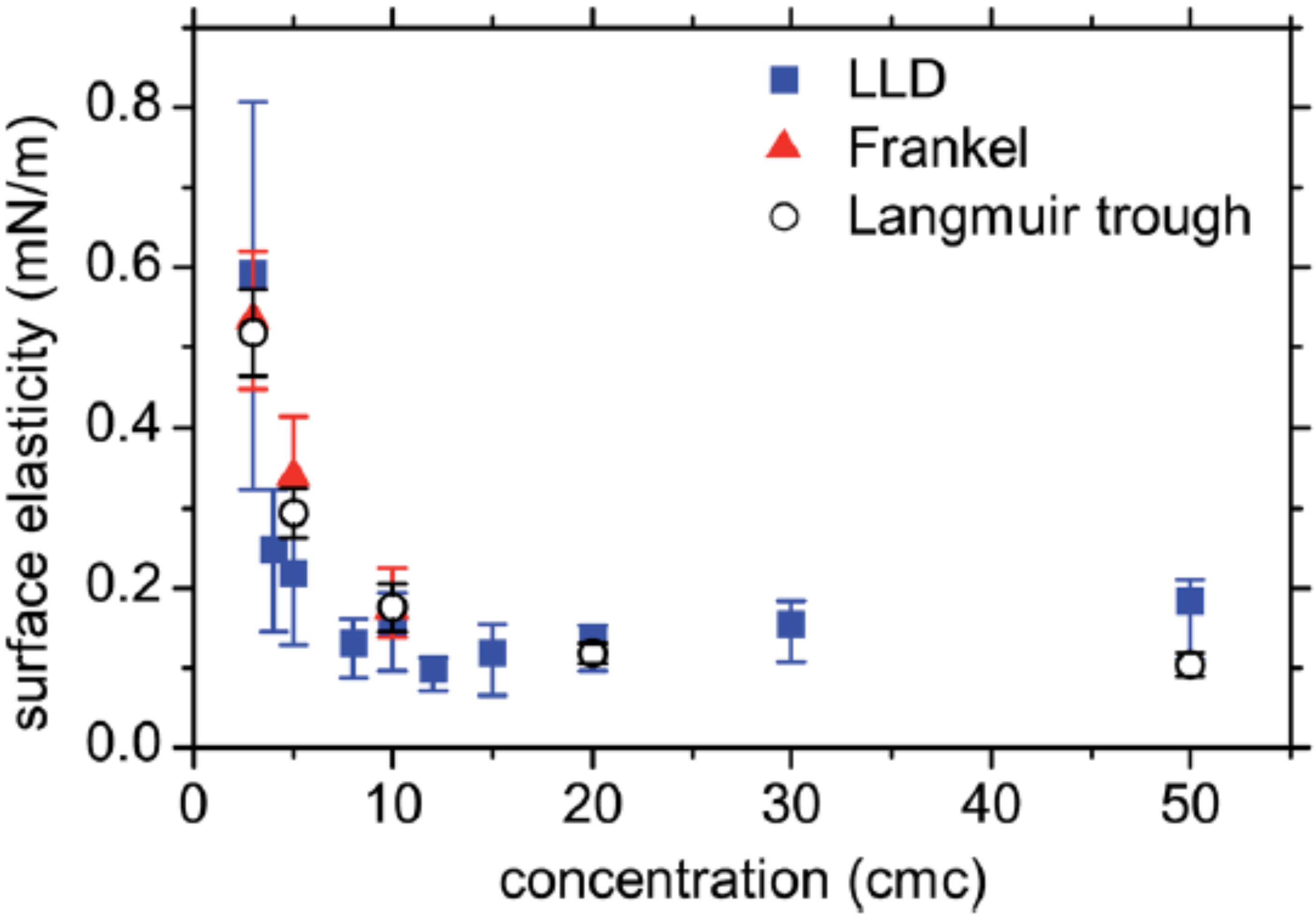
$$\boxed{E = A\frac{\partial \gamma}{\partial A}}$$

$$\gamma - \gamma(t=0) = E \ln\left(\frac{A}{A_0}\right)$$





All results for $C_{12}E_6$



No influence of confinement: slow adsorption, out-of-equilibrium

Conclusions on surface elasticity

– Experimental/theoretical unification of two independent settings: Dip-coating and soap films

- Rigidity parameter: a system parameter!

$$\Lambda = \frac{\mathrm{Ma}}{\mathrm{Ca}^{2/3}}.$$

- Constant surface elasticity for soluble surfactant with 'slow' adsorption kinetics

$$E \simeq E_{\mathrm{insol}} \equiv -\Gamma \frac{\partial \gamma}{\partial \Gamma}$$

- Nonlinear equation of state

$$\gamma(\Gamma) = \gamma_0 - E \ln\left(\frac{\Gamma}{\Gamma_0}\right)$$

Outline

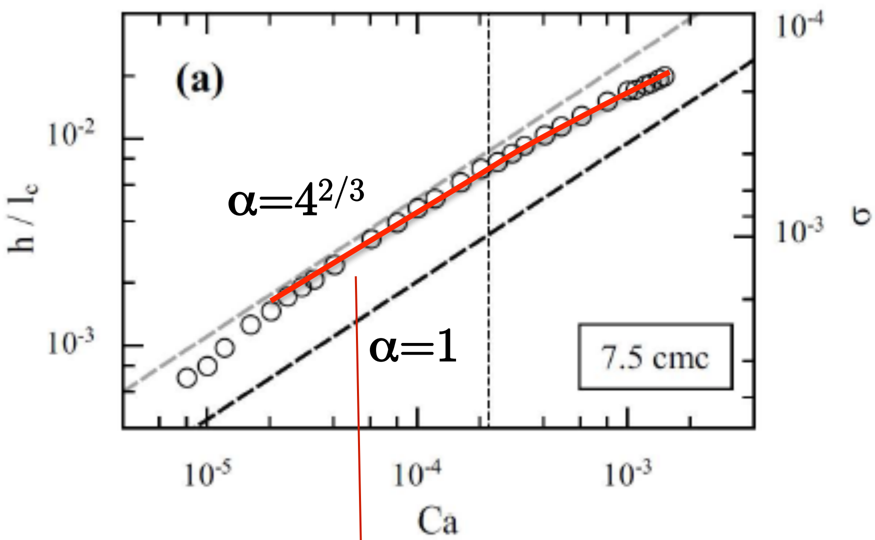
- Surface Rheology
  - Complex interface
    - Surface viscosity
    - Surface elasticity
  - Surface boundary conditions
- Liquid Film Dynamics
  - Shear vs. extensional flow
  - Soap film vs. dip coating
    - Experiments with surface elasticity
    - Experiments with surface viscosity
- Applications to Microfluidics

Dip-coating experiments

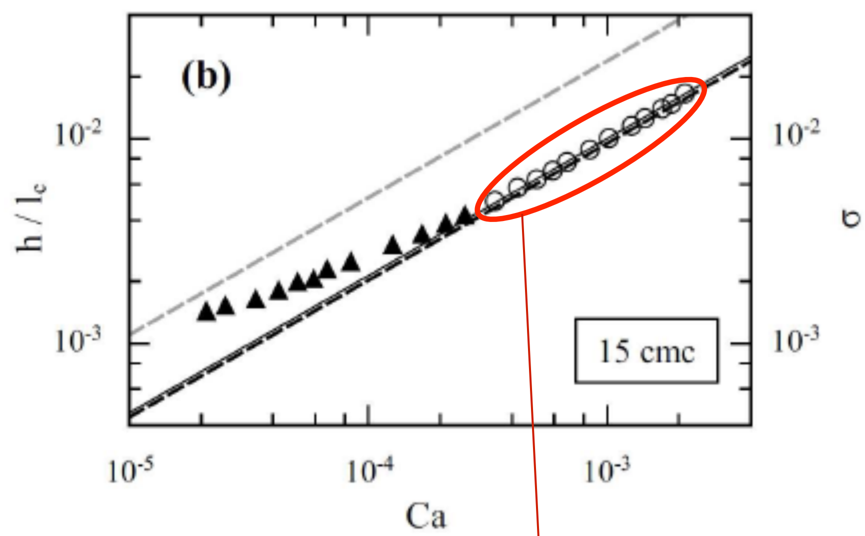
[Delacotte *et al.*, Langmuir, 2012]

surfactant: DeTAB or decyl trimethyl ammonium bromide

$$\boxed{h_0/\ell_c = 0.9458\,\alpha\,Ca^{2/3}}$$



Purely elastic interface



Purely viscous interface ?

Lubrication Model

In the dynamic meniscus

$$\mu\partial_{yy}u + \gamma\partial_{xxx}h = 0$$

shear viscous forces

surface tension forces

$$\mu\partial_y u\big|_{y=h} = \mu^*\partial_{xx}u_s$$

shear stress

surface viscosity stress

$(\mu^* = \kappa + \varepsilon)$

$$H = h/h_0$$

$$U = u_s/u_0$$

$$X = x/\ell$$

$$\ell = h_0\, Ca^{-1/3}$$

$$\boxed{H''' = \frac{12}{H^3} - \frac{6+6U}{H^2}}$$

$$\boxed{\beta\, U'' = -\frac{6}{H^2} + \frac{2+4U}{H}}$$

$$\beta = Bq\, Ca^{2/3}\, \ell_c/h_0 \qquad Bq = \frac{\mu^*}{\mu\ell_c}$$

Flat film b.c.: $H, U \to 1$ and $H', H'', U' \to 0$ as $X \to \infty$

Matching conditions: $H''(-\infty) = \sqrt{2}\,(h_0/\ell_c)\, Ca^{-2/3}$ $\qquad U(-\infty) = \mathrm{c}^{st}$

Curvature of the dynamic meniscus

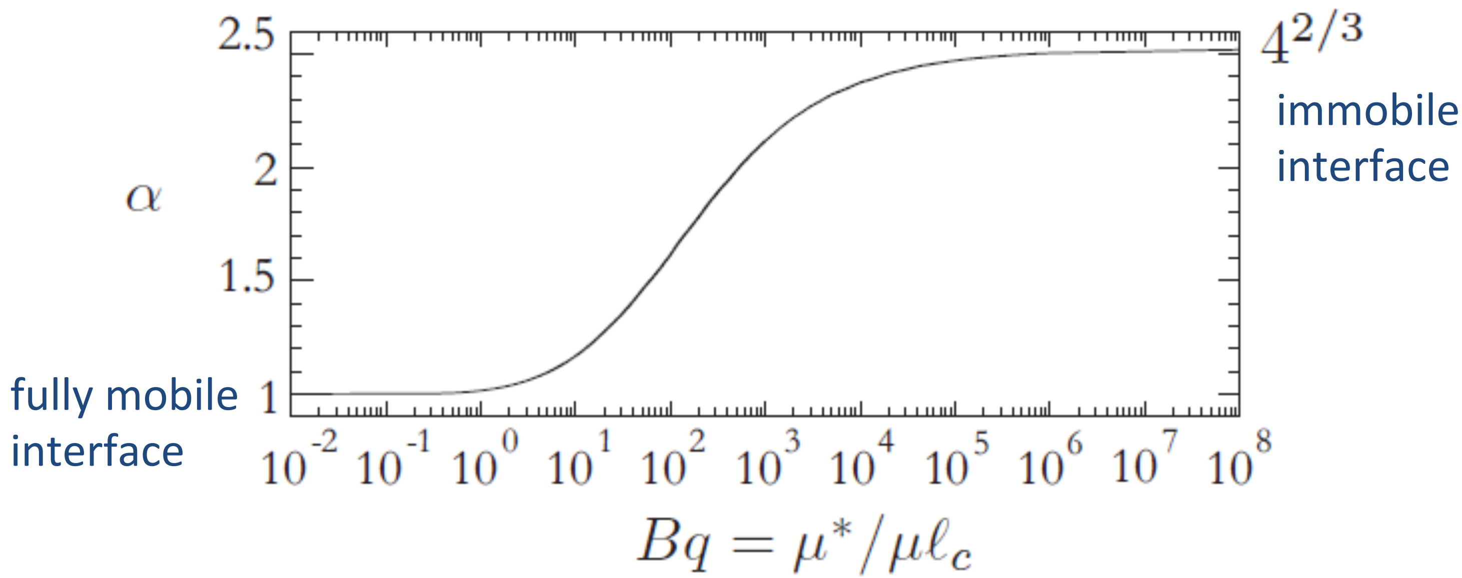
Curvature of the static meniscus

Matching constant surface velocity

Results

Liquid film dynamics and surface viscosity

Thickening factor : $\boxed{h_0/\ell_c = 0.9458\,\alpha\,Ca^{2/3}}$



More viscous the interface, thicker the film!

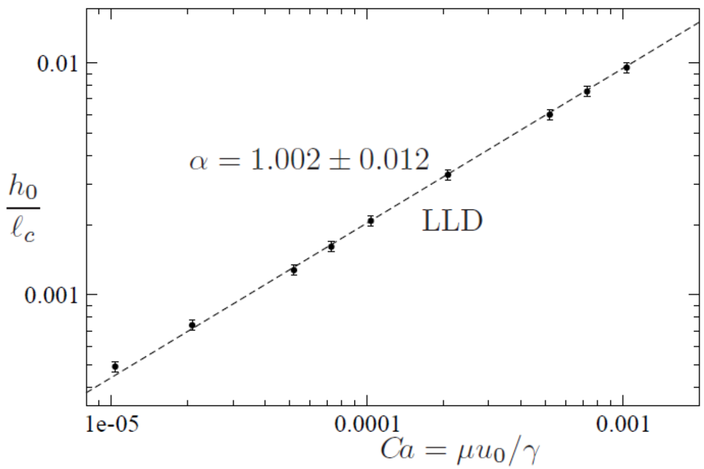
Experiments

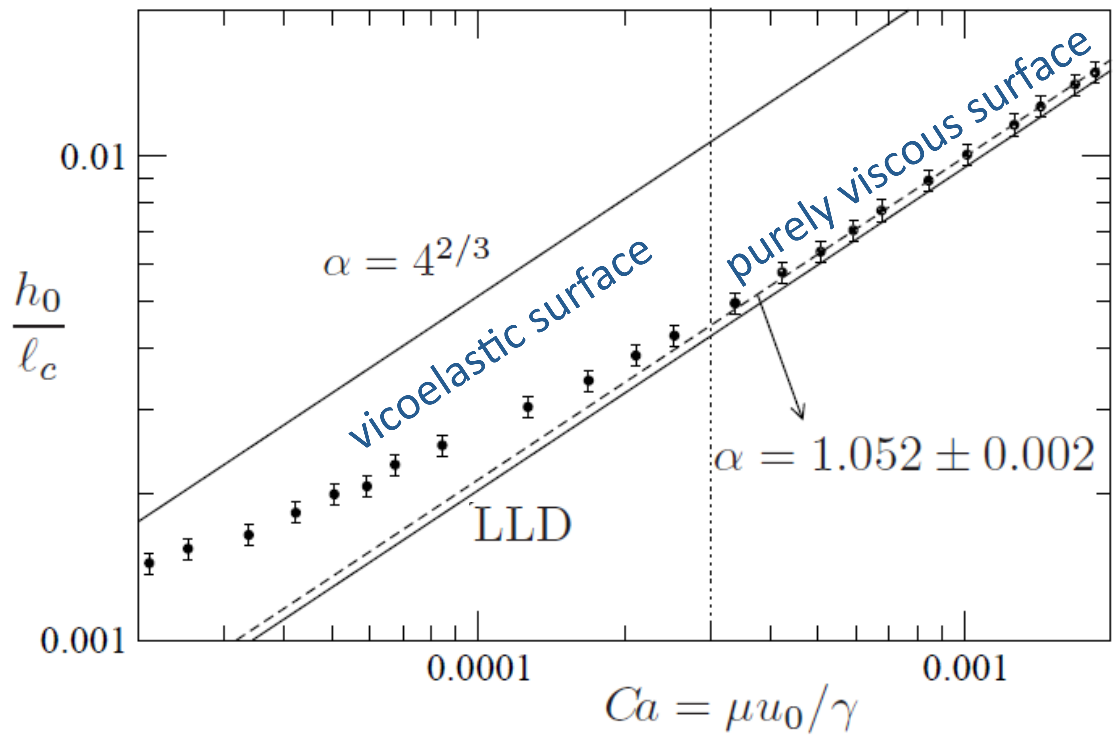
Liquid film dynamics and surface viscosity

$$\boxed{\alpha = h_0 / h_0^{(LLD)}}$$

With surfactant (DeTAB 15cmc)

No surfactant





Conditions for observing this weak constant thickening at large Ca:

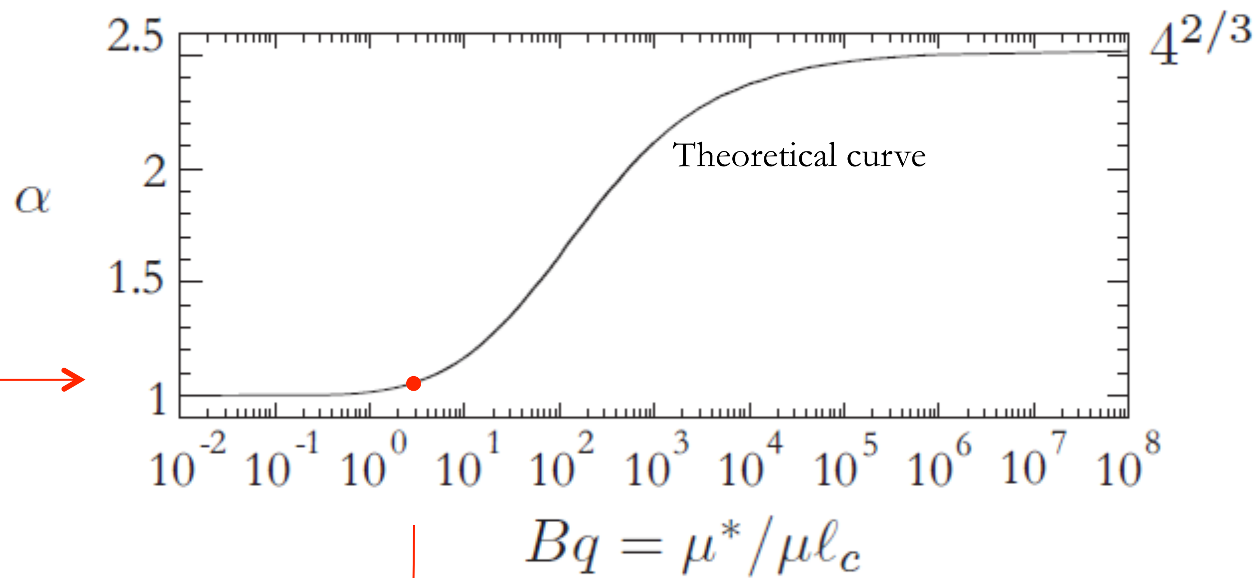
$Ca^{1/3} \ll 1$	$\tau_a \ll \tau_s$	$\sigma = \Gamma_0 / c h_0 \ll 0.01$
no gravity	adsorption / stretching	large reservoir of surfactants

Results

Thickening factor :

From experiment

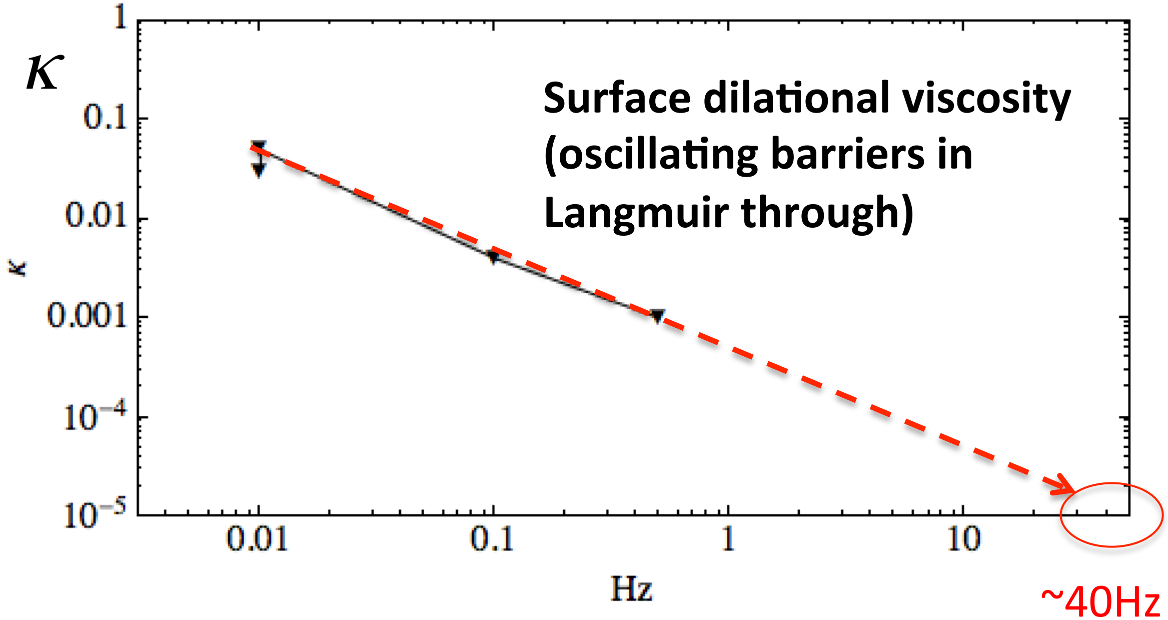
$\alpha = 1.052$ →



From the model

$\boxed{\mu^* \approx 2\times10^{-5}\,\text{Pa.s.m}}$ → **Surface rheometer?**

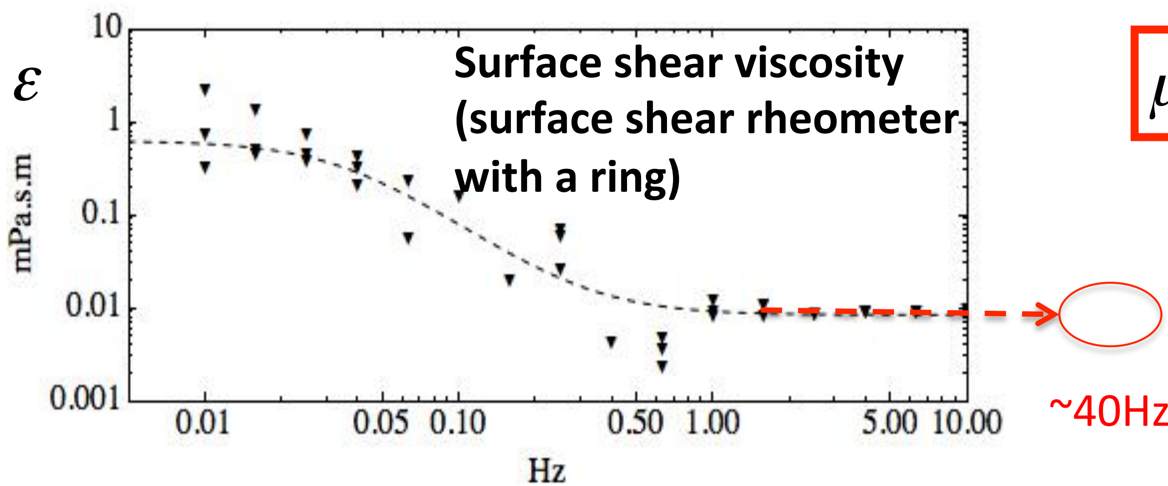
Independent measurements



KUL: Jan Vermant,
Tom Verwijlen

**With surfactant
(DeTAB 15cmc)**

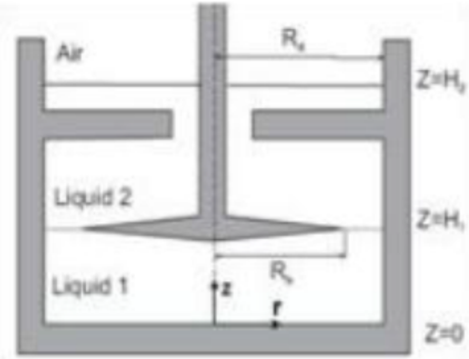
$$\kappa \approx 10^{-5}\,\mathrm{Pa\,s\,m}$$



$$\boxed{\mu^* = \kappa + \varepsilon \approx 2\times 10^{-5}\,\mathrm{Pa\,s\,m}}$$

$$\varepsilon \approx 10^{-5}\,\mathrm{Pa\,s\,m}$$

Measuring surface shear viscosity



Bicone

Visco-(elasticity)
Lowest sensitivity

Interfacial rheometry

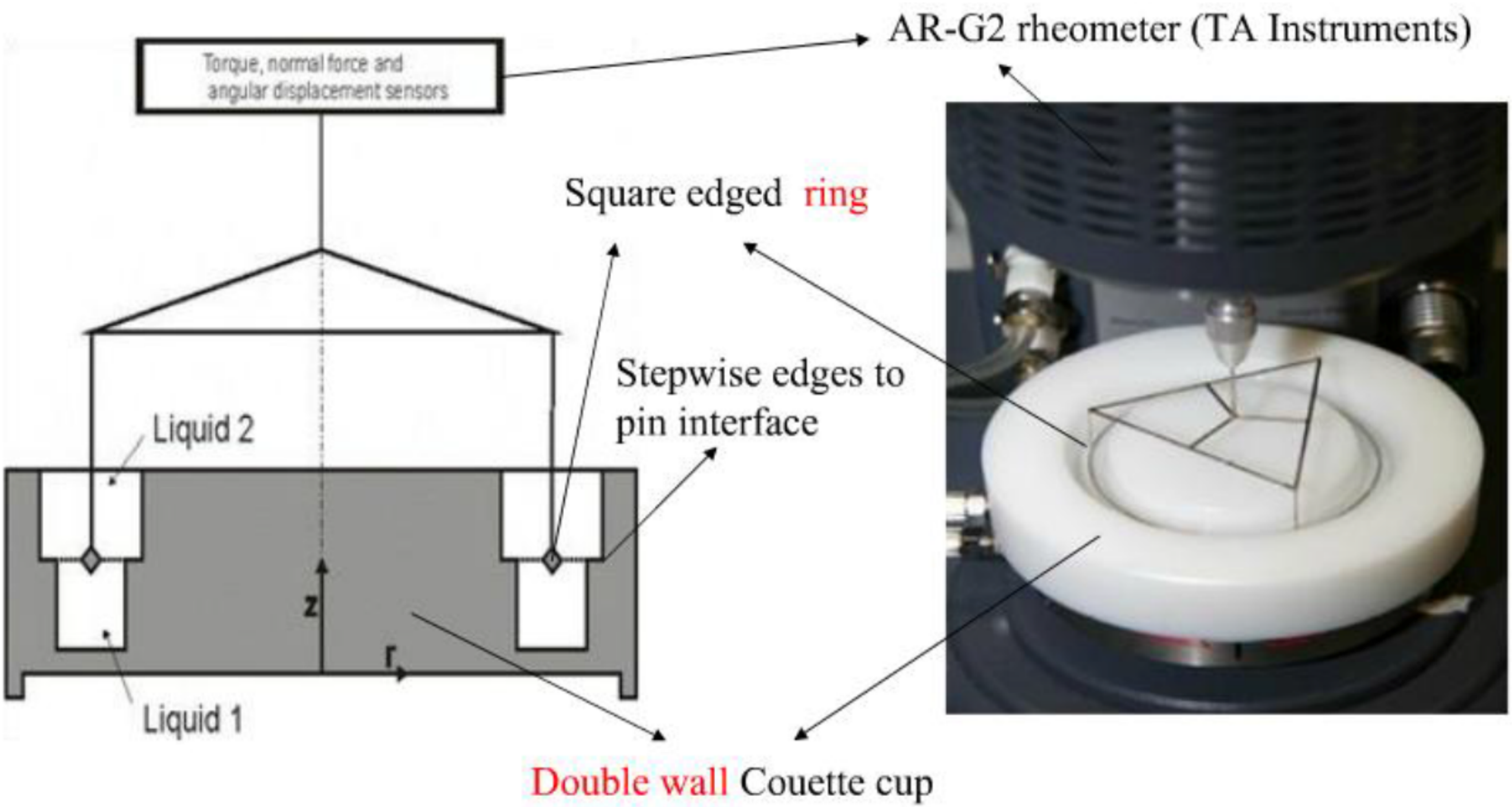
Double wall-ring

Increased sensitivity
Visco-(elasticity)

Magnetic needle rheometer

Most sensitive
Difficult

Double wall-ring



[1]Vandebril S, Franck A, Fuller GG , Moldenaers P, Vermant J(2009) Analysis of a double wall-ring geometry to study interfacial shear rheology. In preparation

[2]Franck A, Vermant J, Moldenaers P, Fuller GG (2007) System and method for interfacial rheometry; US –Patent applied No:60/970,115

Conclusions on surface shear viscosity

- “Plenty of room” for surface rheology using film dynamics
  - Discriminate between various surface properties
    - Various time scales (adsorption, diffusion, electrostatic,⋯)
  - Coherence between two independent settings
    - Dip-coating and soap films
  - Rationalization of experimental data
    - Effective surface elasticity
    - Surface viscosity in planar geometry
      - But coupled!
      - Need for other (curvilinear) geometries (antibubbles!)

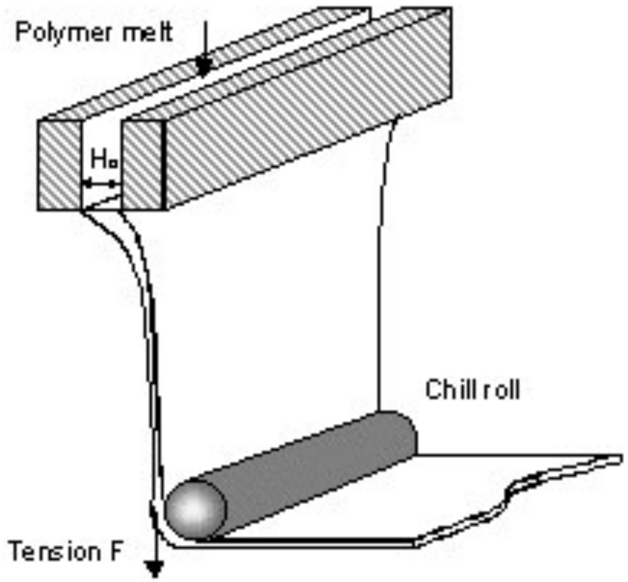
Workshop: COMSOL

PDE: Partial Diff. Eq.
ODE: Ordinary Diff. Eq.
ADE: Algebraic Diff. Eq.

- Tool: Comsol Multiphysics 5.0
  - PDE solver
    - Also solves ODE and ADE
  - Multiphysics (combines as many equations as needed)
  - Finite Element Method
    - Integral (or weak) formulation
    - Moving boundary (deformed Mesh)
      - Arbitrary Lagrangian Eulerian (ALE)
  - All-in-one: Drawing, Meshing, Solving, Postprocessing

Background: polymer processing

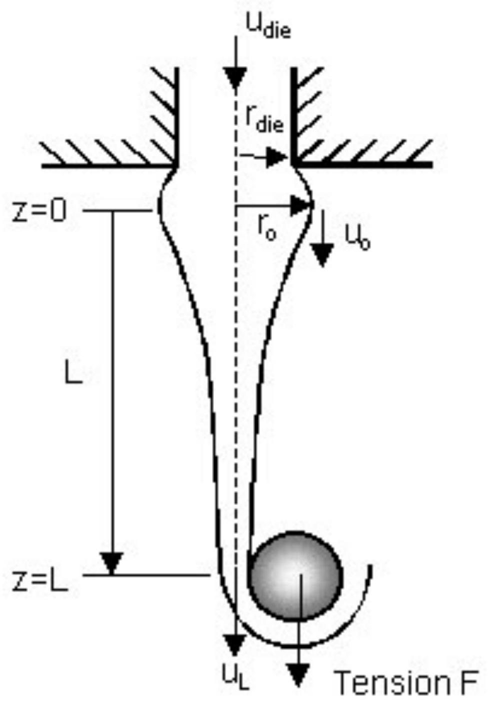
- Film casting



Control parameter:

$$\boxed{Dr = \frac{\text{take - up velocity}}{\text{inlet velocity}}}$$

- Fiber spinning



J.R.A. Pearson, *Mechanics of Polymer Processing* (Elsevier Applied Science Publishers, 1985)

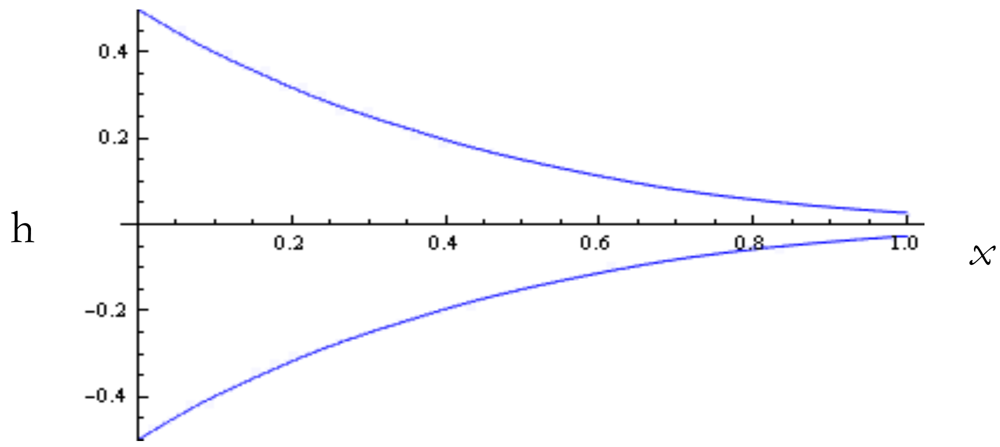
Quizz: extensional or shear flow?

Stretching sheet or fiber
Draw resonance instability

$$\boxed{\begin{aligned} \partial_t h + \partial_x(hu) &= 0 \\ \partial_x\left(h\partial_x u\right) &= 0 \end{aligned}}$$

$$\left\{ \begin{array}{lcl} h(0,t) & = & 1 \\ u(0,t) & = & 1 \\ u(1,t) & = & D_r \end{array} \right.$$ (Draw ratio)

Fiber: h → *a*



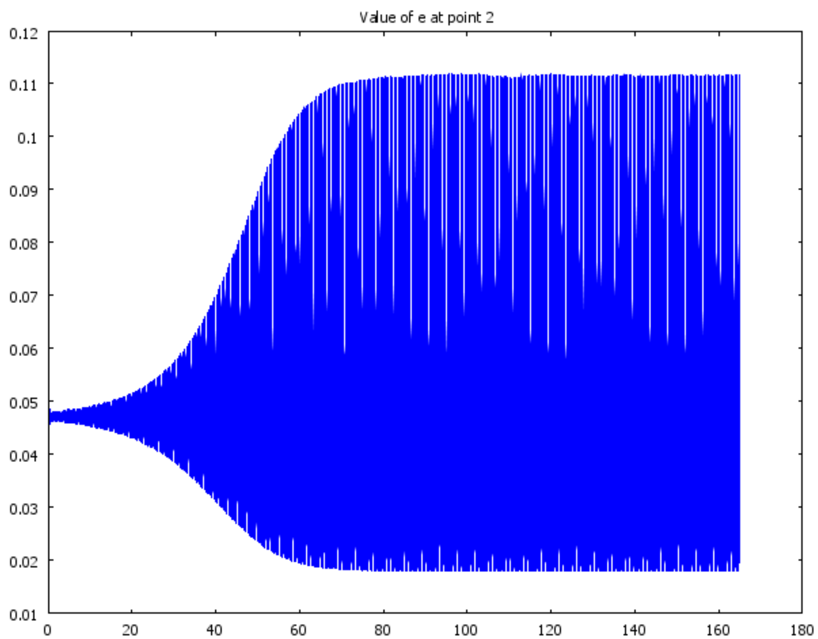
Threshold: Dr_c= 20.218 [Denn, 1971 - Yeow, 1974]

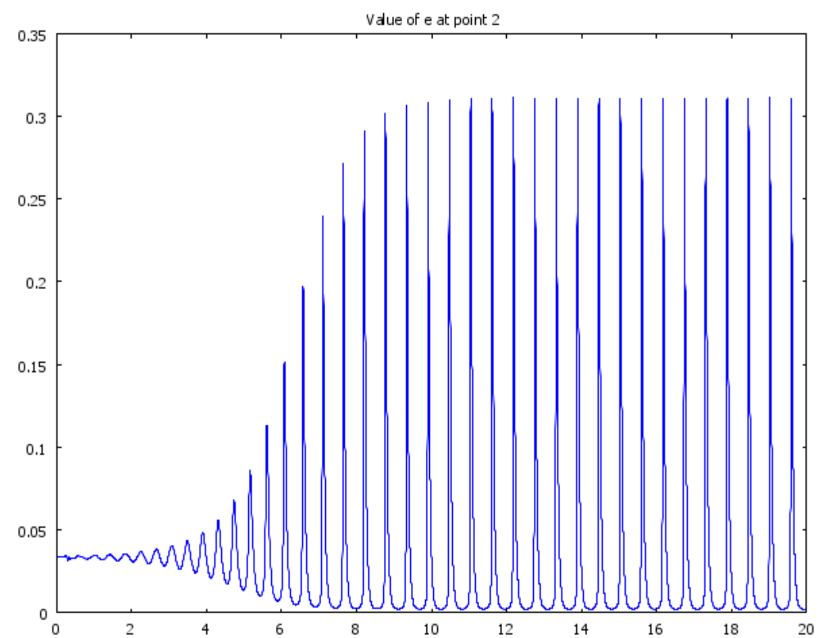
- Spatially uniform tension f(t)
  → Feedback mechanism between the two ends
  → Sustain oscillations of the thickness h(x,t) for Dr > Dr_c

Nonlinear regime (Comsol)

$\boxed{Dr = 21.2}$

$\boxed{Dr = 30}$





Exercise 1: Stretching sheet in Comsol

- Geometry: interval for x $\in [0,1]$
- PDE general form and BC:

$$\boxed{\begin{array}{l} e = h \\ \nabla = \partial_x \end{array}}$$

$$\boxed{\begin{array}{r} e_t + \nabla(eu) = 0 \\ \nabla(eu_x) = 0 \end{array}} \qquad \boxed{\begin{array}{l} e(0,t) = 1 \\ u(0,t) = 1 \\ u(1,t) = D \end{array}}$$

  - set the correct flux condition (flux/source) at x=1: $\boxed{-\mathbf{n}\cdot\Gamma = -eu}$
- Stationary solution: Solutions for a given value of D that can be compared to the analytical solutions for $q = eu = 1$: $\boxed{e_s = D^{-x} \quad \text{and} \quad u_s = D^{x}}$
  - Initial values: $\boxed{e = u = 1}$
  - If it is not satisfying, refine the mesh
  - Play with the control parameter D (you can use parametric sweep)
- Time-dependent solution (a thickness perturbation should be introduced)
  - Initial values: $\boxed{e = D^{-1.1x} \quad \text{and} \quad u = D^{x}}$
  - Look for time interval of 5 by step of 0.1
  - Look at the behavior of the system for $D <> D_c$ where $D_c = 20.218$
  - Plot the value of e at x=1 versus time.
  - If the system is damped even for $D > D_c$, it shouldn't and it means you probably have to decrease the relative and absolute tolerances.

Exercise 2: Inertia and gravity effects

Read the paper and reproduce the stationary and the time-dependent results

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INTERNATIONAL JOURNAL OF SOLIDS and STRUCTURES

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Effect of inertia and gravity on the draw resonance in high-speed film casting of Newtonian fluids

Fang Cao [a], Roger E. Khayat [a,*], J.E. Puskas [b]

[a] Department of Mechanical and Materials Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9
[b] Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9

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Exercice 2 (con't)

$$\boxed{\begin{aligned} e(0,t) &= 1 \\ u(0,t) &= 1 \\ u(1,t) &= D \end{aligned}}$$

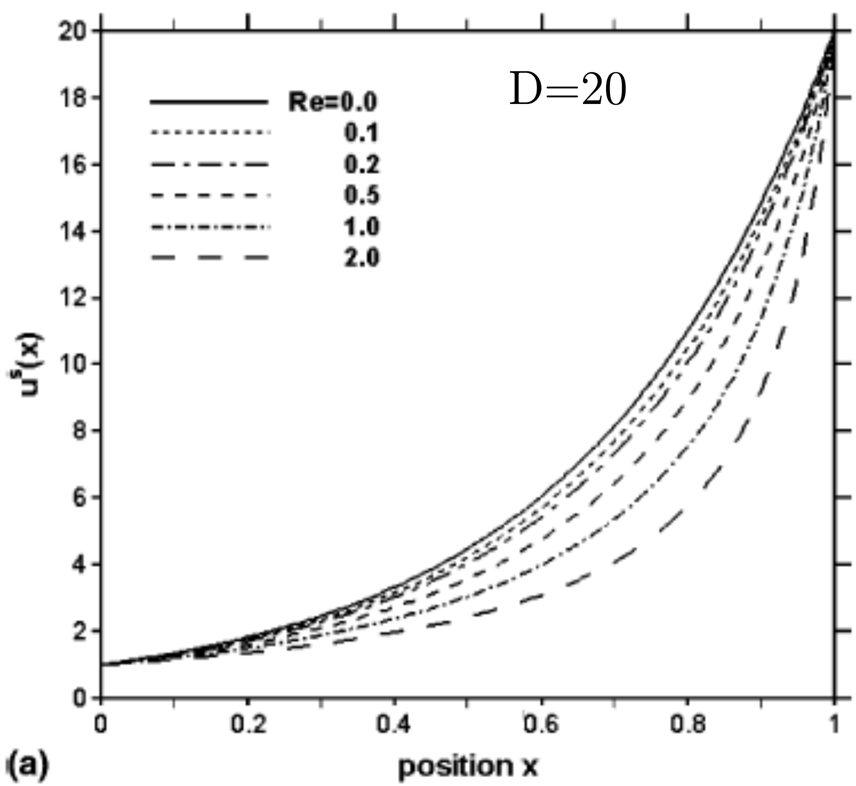
$$\frac{Re}{4} h\left(u_t + uu_x - \frac{1}{Fr}\right) = (hu_x)_x$$

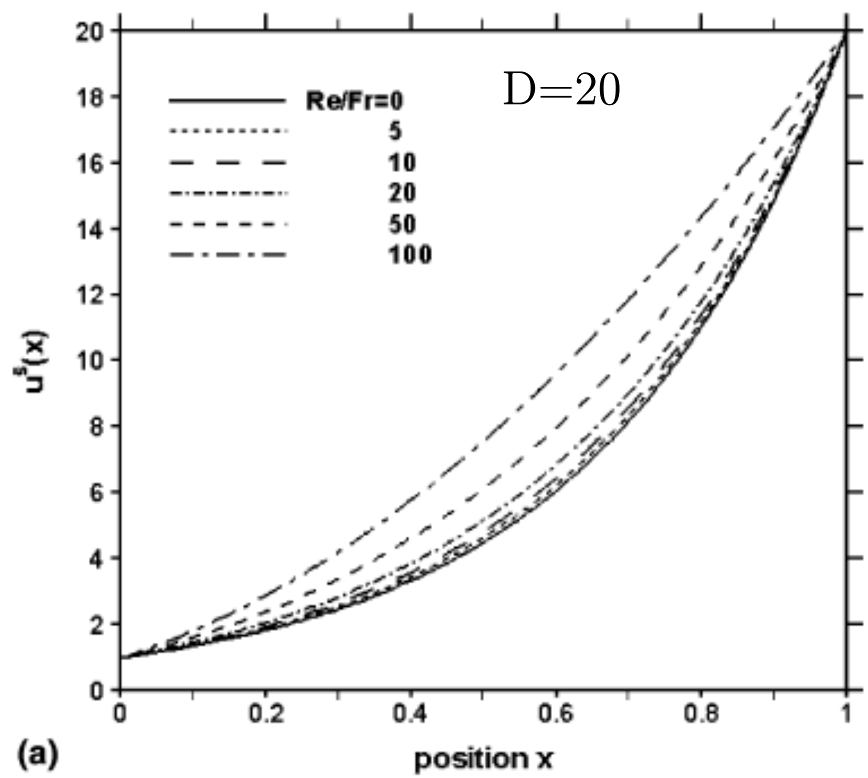
$$Re = \frac{\rho U_0 L}{\mu}, \quad Fr = \frac{U_0^2}{gL};$$

$$\boxed{e_t + \nabla(eu) = 0}$$

$$\boxed{\left[-\frac{R}{4} e\right] u_t + \nabla(e u_x) = \frac{e}{4}\left(R u u_x - G\right)}$$

d_a $\qquad$ $\boldsymbol{\Gamma}$ $\qquad$ F





Exercise 3: “Honey” sheet

- Viscous sheet stretching due to gravity (i.e. its own weight)

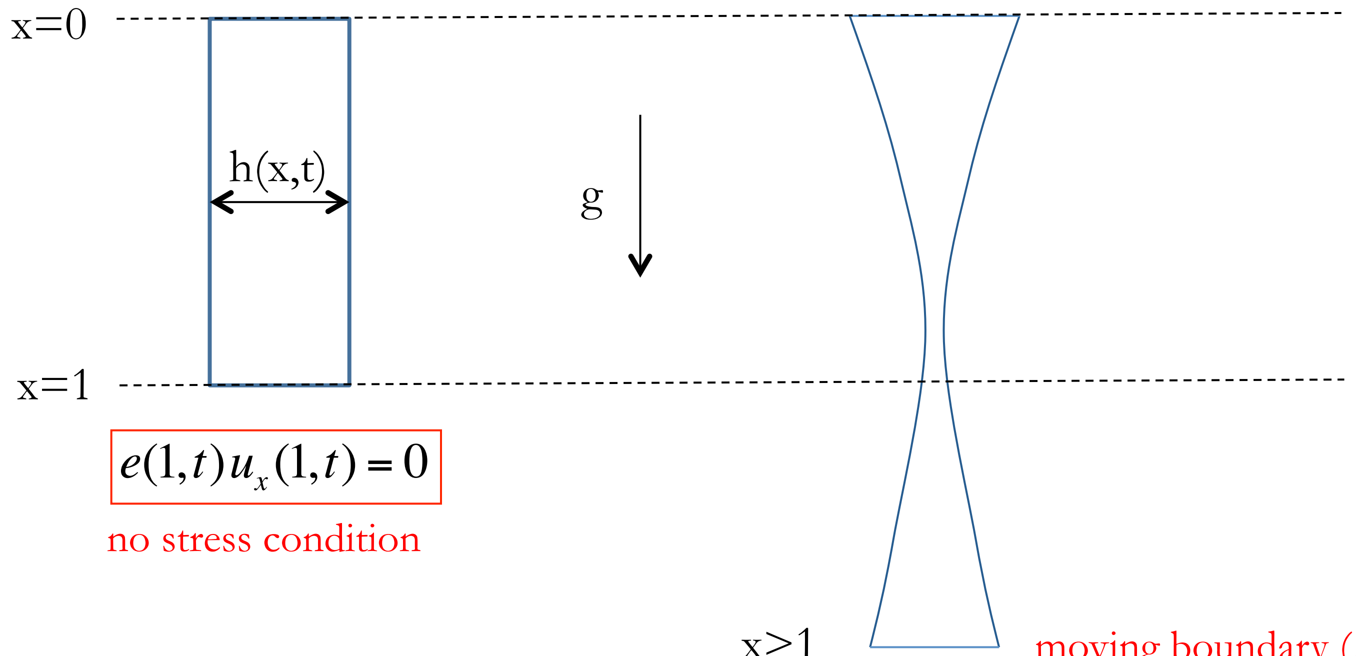
$$e_t + \nabla(eu) = 0$$

$$\nabla(eu_x) = -\frac{G}{4}e$$

gravity number

$$G = \frac{R}{F} = \frac{\rho g L^2}{\mu u_0}$$

$$e(0,t) = 1$$
$$u(0,t) = 1$$



$$e(1,t)u_x(1,t) = 0$$

no stress condition

moving boundary (ALE)

Master equation including surface rheology (1D)

Mass balance

$$\partial_t h + \partial_x (hu) = 0$$

Stress balance

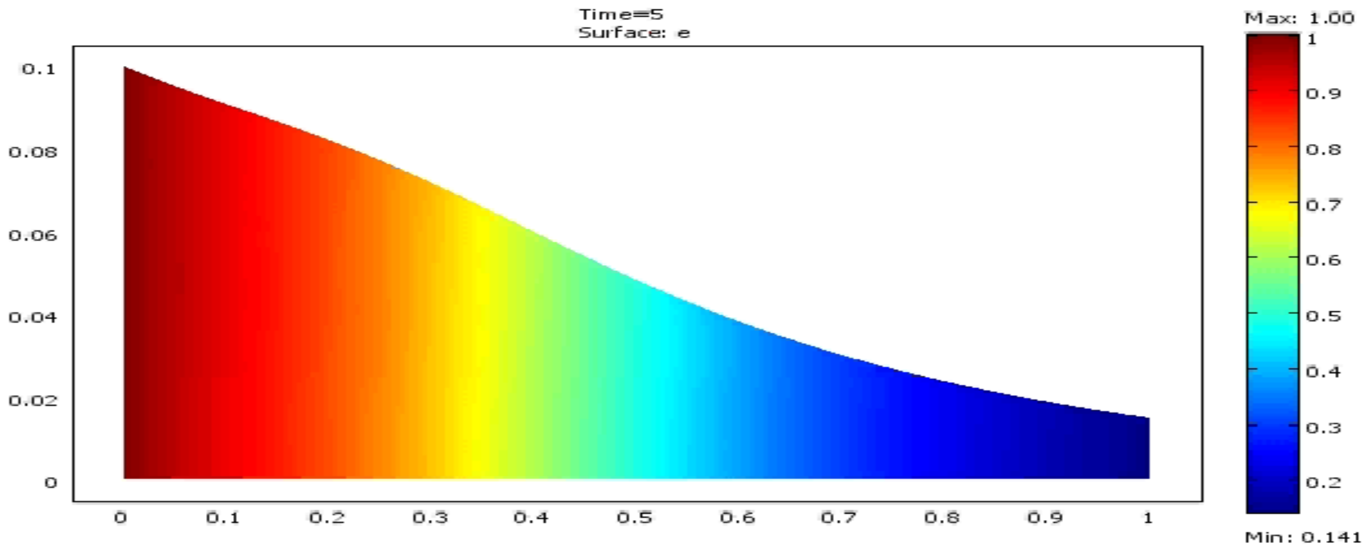
$$\underbrace{\rho h \left(\partial_t u + u \partial_x u\right)}_{\text{inertia}} = \underbrace{4\mu\partial_x \left(h\partial_x u\right)}_{\substack{\text{extensional}\\ \text{viscosity}}} + \underbrace{2\frac{E}{\Gamma}\partial_x \Gamma}_{\substack{\text{surface}\\ \text{elasticity}}} + \underbrace{2(\kappa+\varepsilon)\partial_{xx} u}_{\substack{\text{surface}\\ \text{viscosity}}} + \underbrace{\frac{\gamma}{2} h \partial_{xxx} h}_{\substack{\text{surface}\\ \text{tension}}} - \underbrace{\rho g h}_{\text{gravity}}$$

Transport equation for insoluble surfactant at the interface

$$\partial_t \Gamma + \partial_x (\Gamma u) = D_{\mathrm{s}} \partial_{xx} \Gamma$$

2D stretching sheet

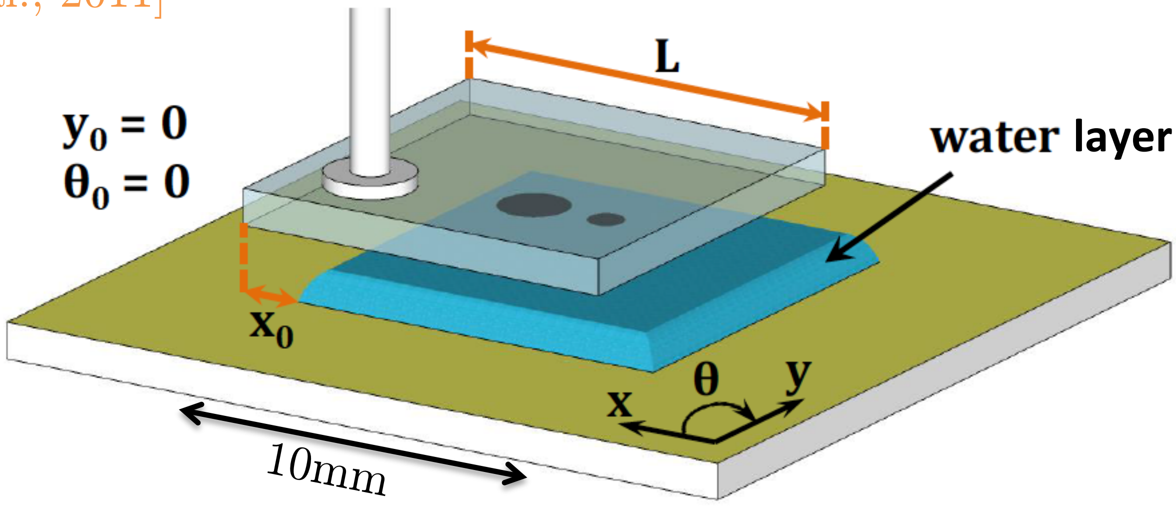
- Solved with COMSOL
  - moving mesh/boundaries (ALE method)
  - oscillation of half the width :

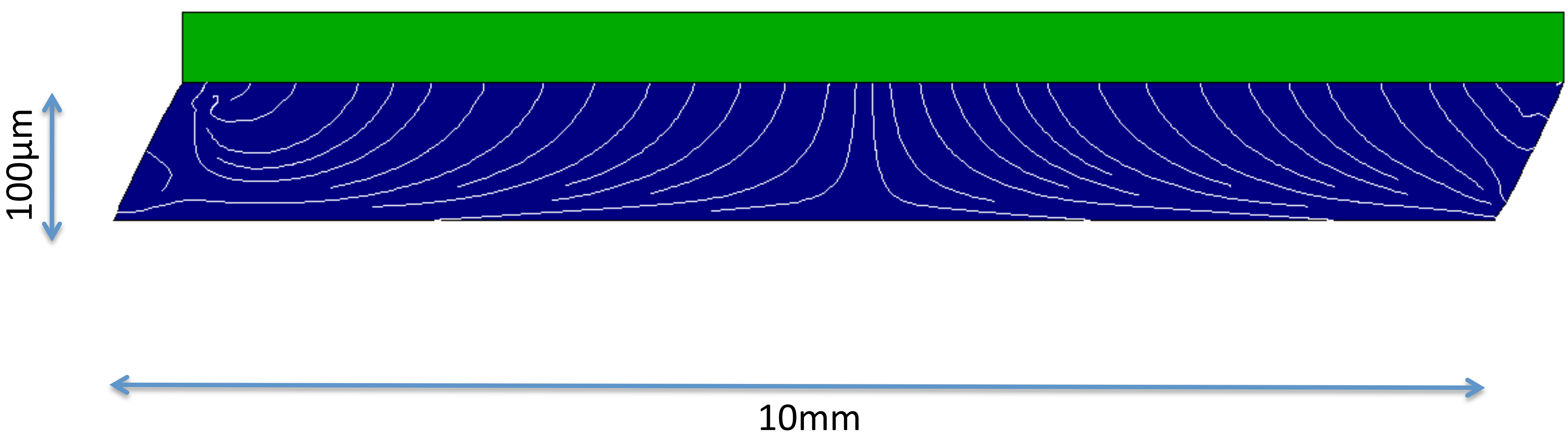


[Scheid et al., 2009]

Self-alignment

[Arutinov et al., 2011]





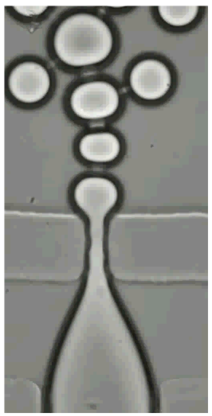
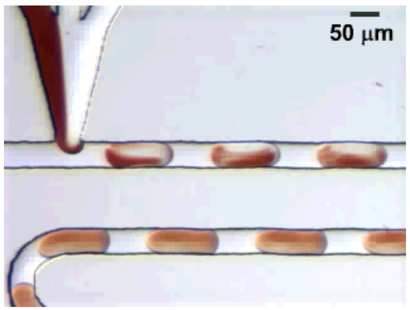
Outline

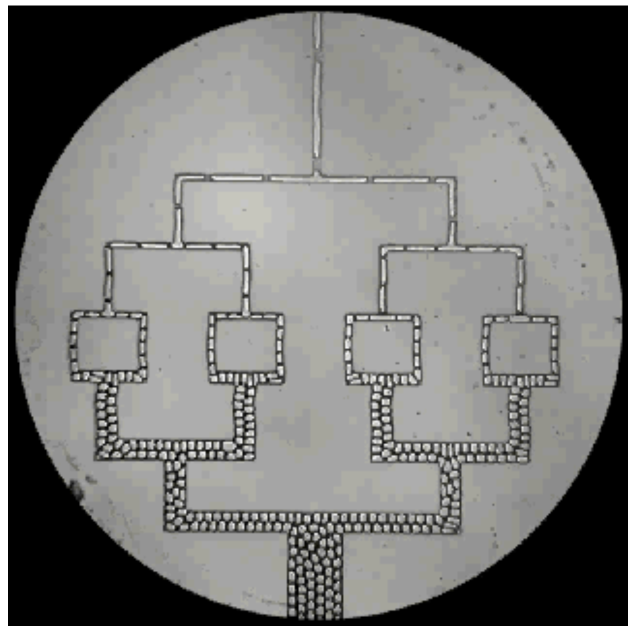
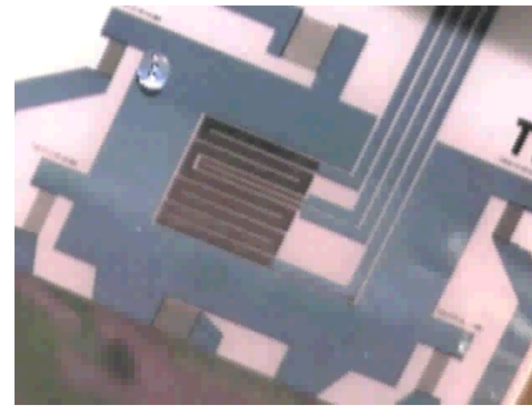
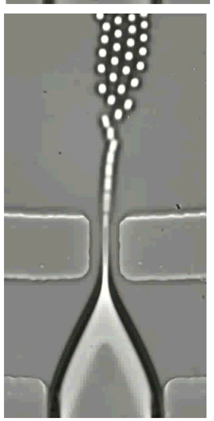
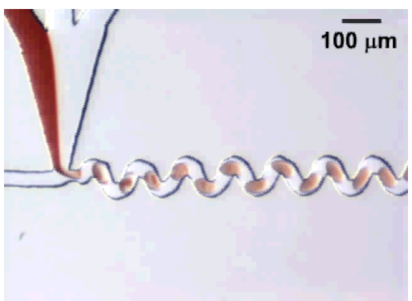
- Surface Rheology
  - Complex interface
    - Surface viscosity
    - Surface elasticity
  - Surface boundary conditions
- Liquid Film Dynamics
  - Shear vs. extensional flow
  - Soap film vs. dip coating
    - Experiments with surface elasticity
    - Experiments with surface viscosity
- Applications to Microfluidics

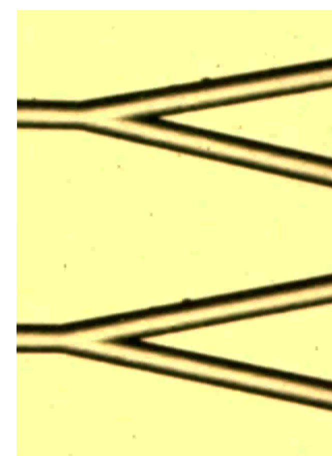
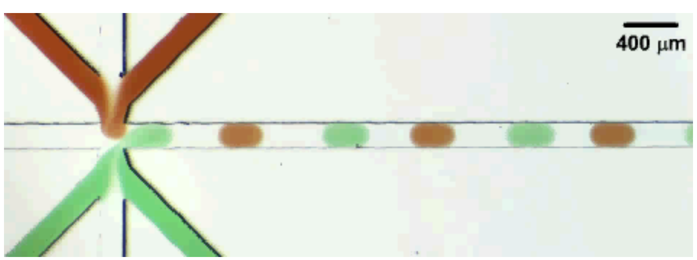
Droplet-based Microfluidics

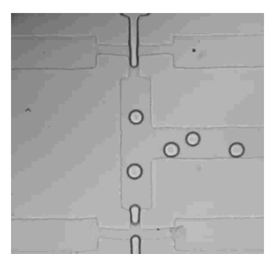
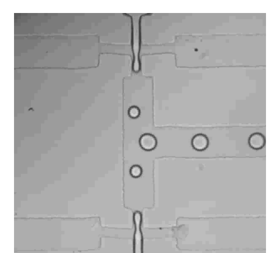
- Droplet = microreacteur $\rightarrow$ 10kHz
- Sum of basic operations $\rightarrow$ lab-on-a-chip

Make » Fill » Mix » Split » Combine » Drive » Sort

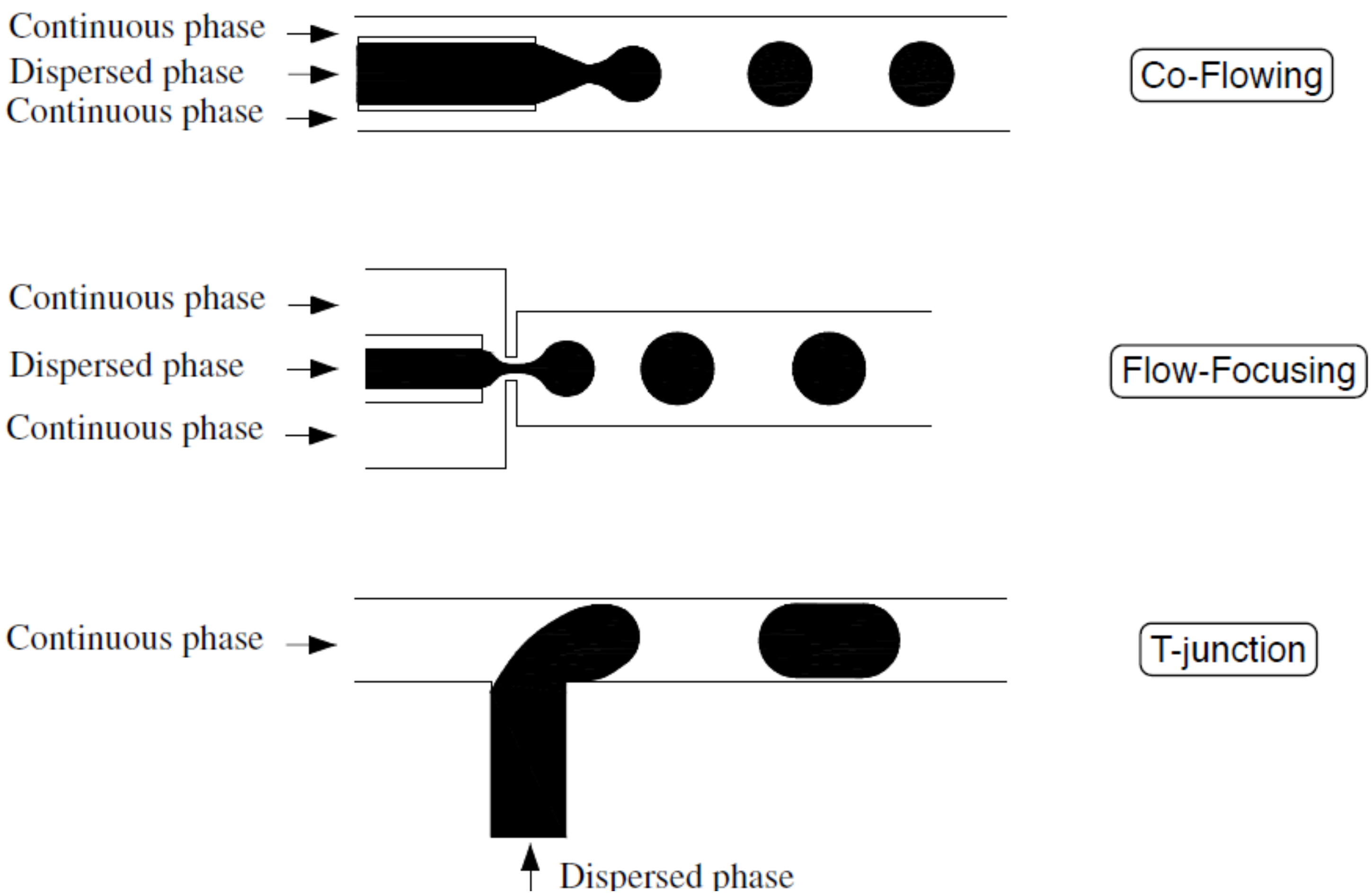



Important role of surfactants in microfluidics !!!

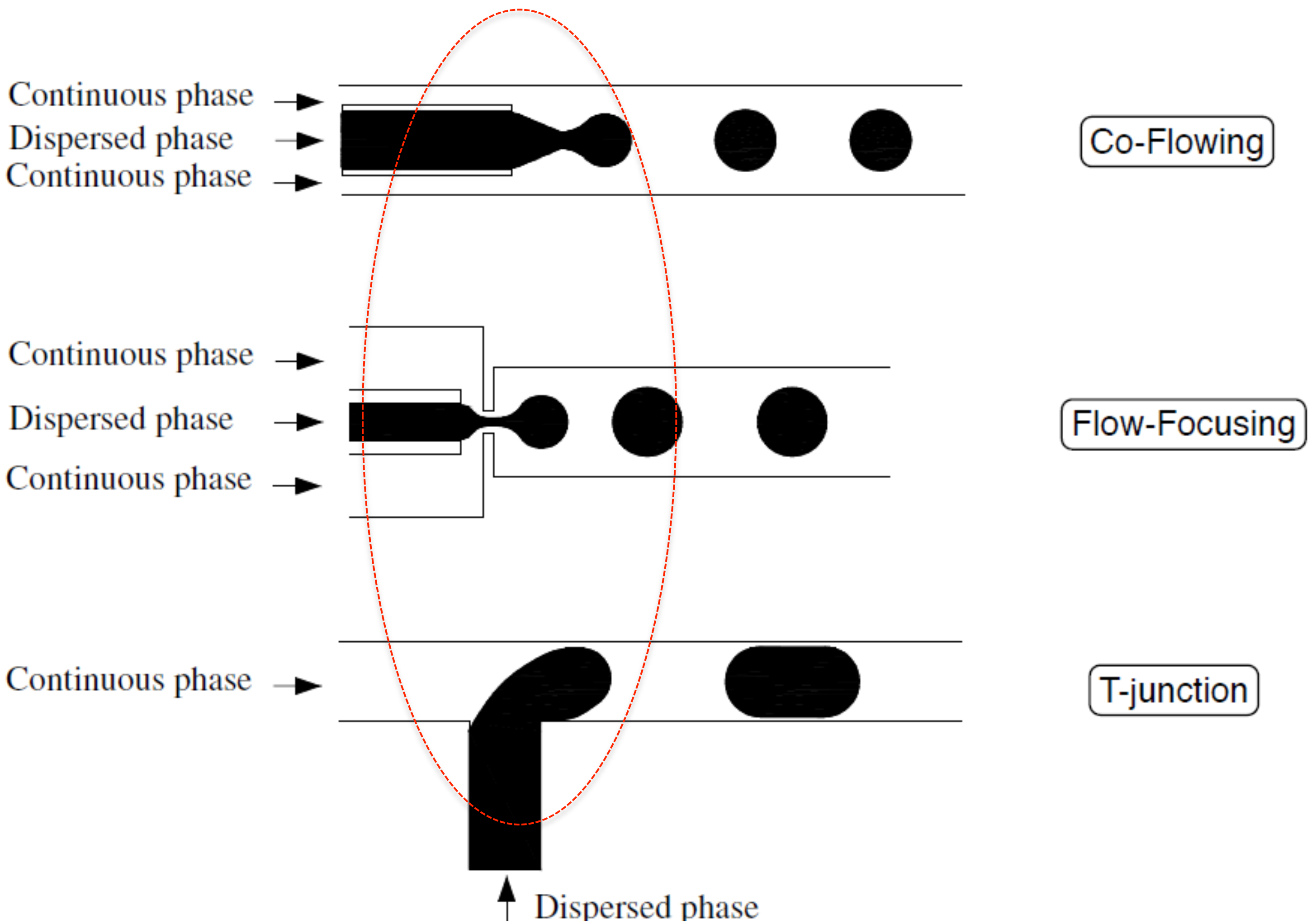
Multiphase Microfluidics

1. Generation 2. Displacement



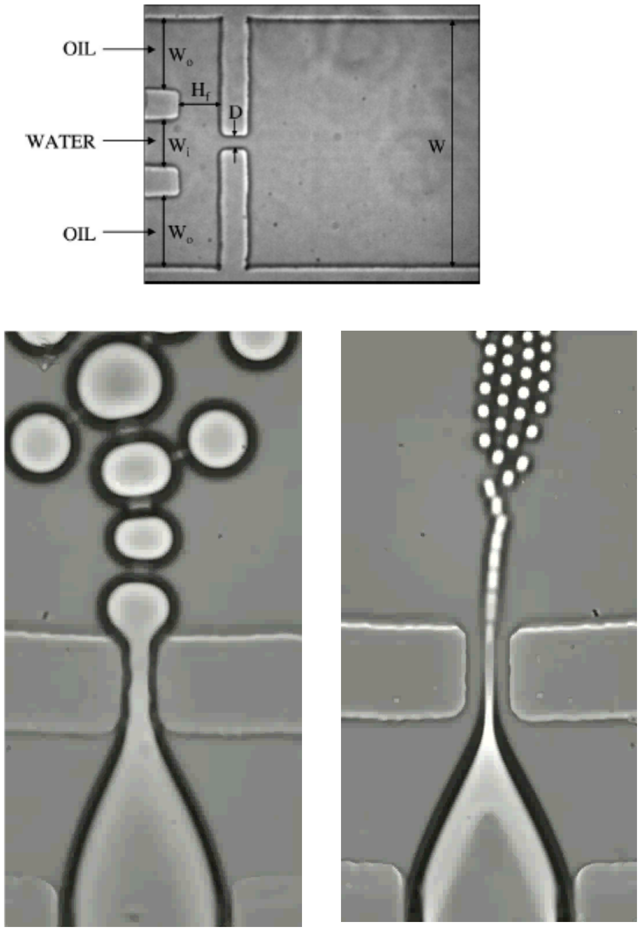
Multiphase Microfluidics

1. Generation   2. Displacement

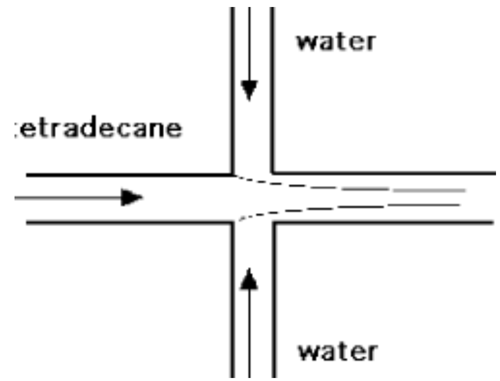


1. Droplet generation in microchannels

Monodispersed droplets can be formed
with immiscible fluids in microchannels



[Anna et al., 2006]

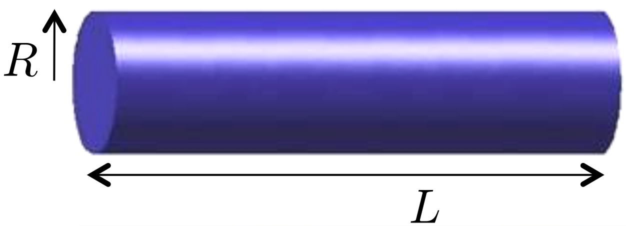


movie

Typical values

- Droplet speed: 10 μm/s – 1 cm/s
- Droplet volume: 1 pL – 1 μL (10 μm - 1 mm)
- Droplet frequency: 1 – 1000 Hz

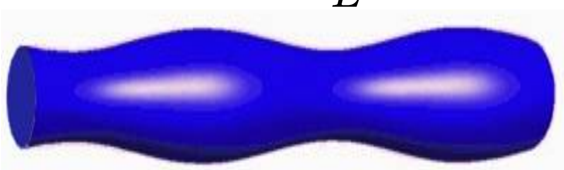
Rayleigh-Plateau instability (Simplified explanation)



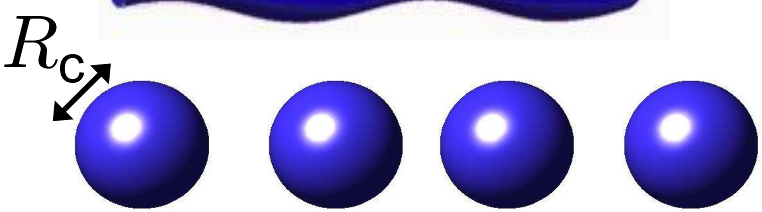
Liquid volume V,
Surface tension γ

Surface energy for a cylindre ?

$$E_s = 2\pi R L \gamma = 2V\gamma/R$$



← destabilisation ⇒ dynamical problem



Surface energy for a sphere ?

$$E_s = 4\pi N R_c^2 \gamma = 3V\gamma/R_c$$

If $R_c > 3R/2$ ⇒ the droplets are energetically favourable

⇒ **surface tension is responsible for the formation of droplets (or bubbles) in microfluidics**

1. Droplet/bubble generation in microchannels

$\Rightarrow$ Surface tension is responsible for droplet formation BUT$\cdots$:

A. Confinement

B. Geometry and Hydrodynamic (viscosities, flow rates, ...)

C. Walls and wetting properties

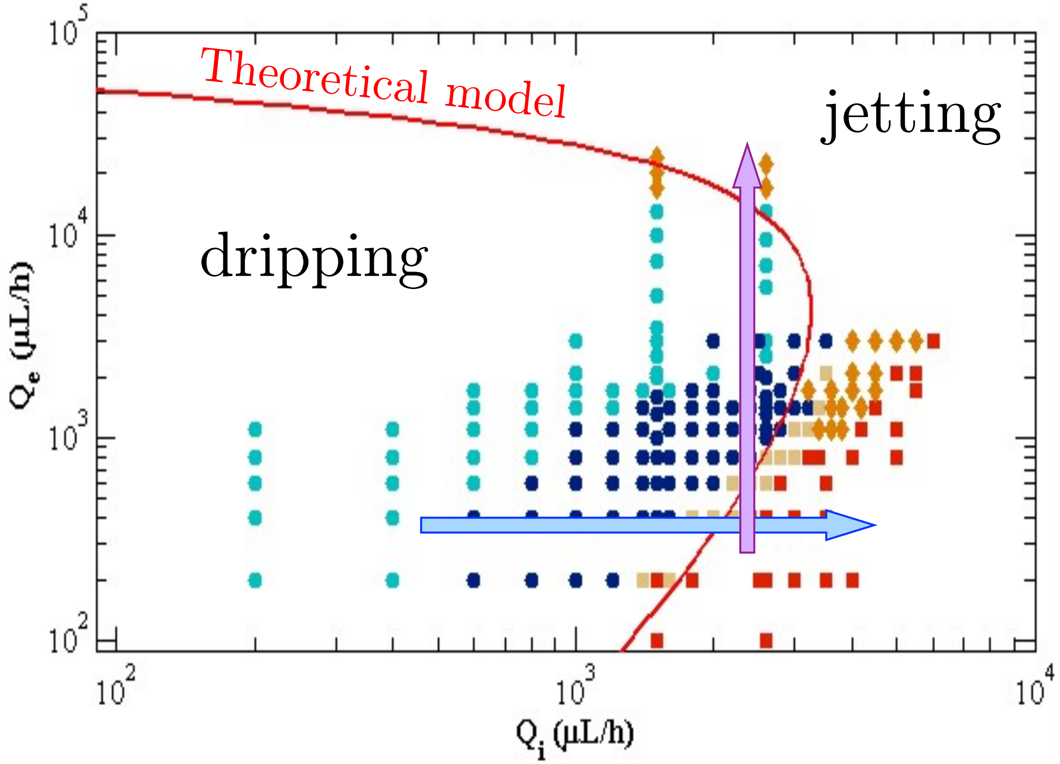
D. Surfactants

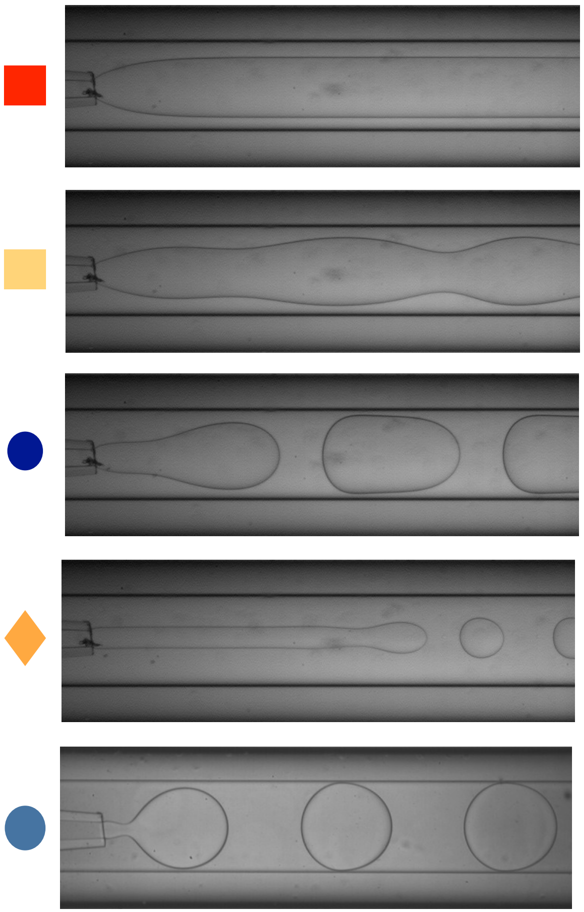
$\Rightarrow$ There is no simple and accurate theory today that can predict the complexity of the observed phenomena

A. Role of confinement

Guillot *et al.* Phys. Rev. Lett. 2007

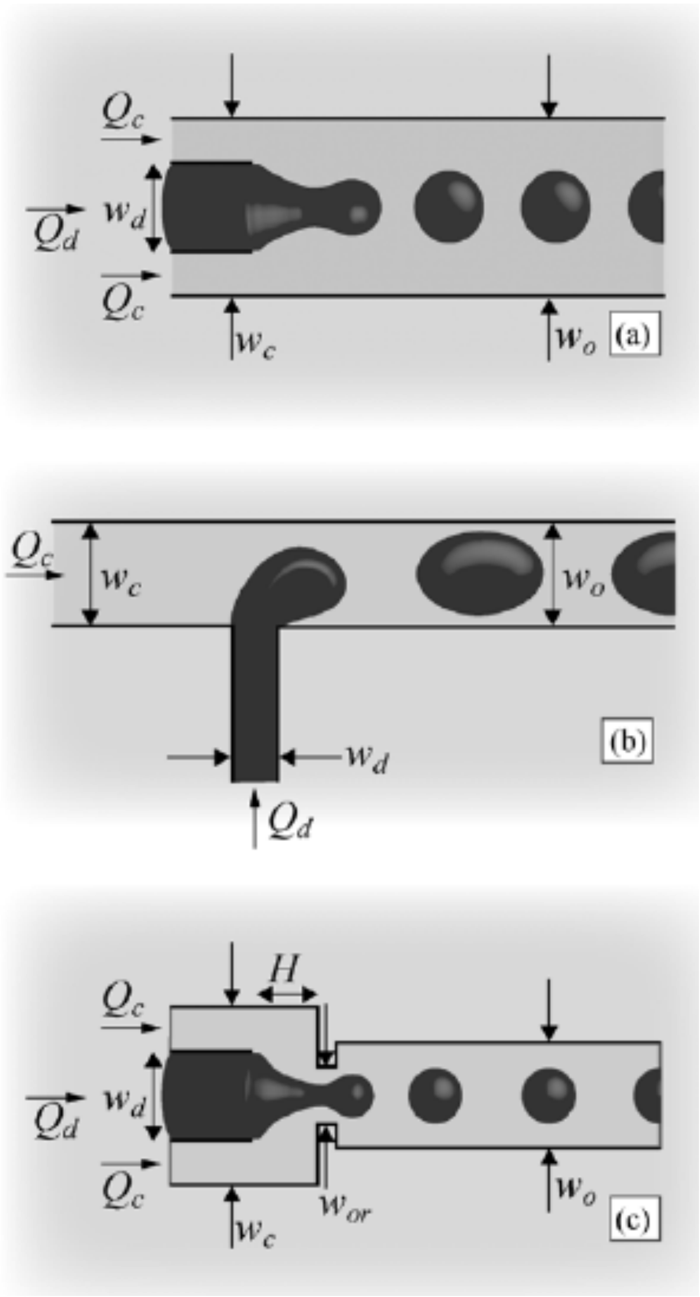
Silicon oil, Q_e
Water + glycerol, Q_i





Active research: how the threshold absolute/convective is modified by surface viscosity

B. Role of geometry and hydrodynamics



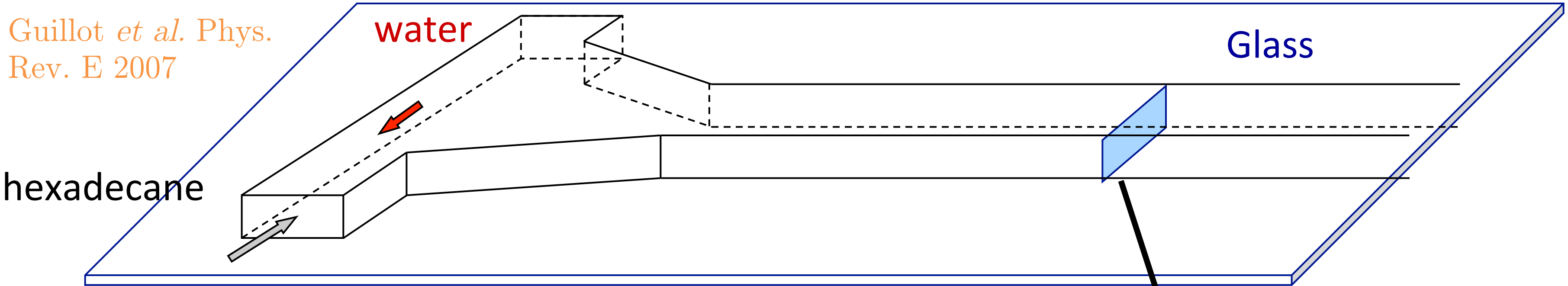
Christopher & Anna, J. Phys. D: Appl. Phys. 40 (2007) R319–R336

Flow parameters: Q_c , Q_d

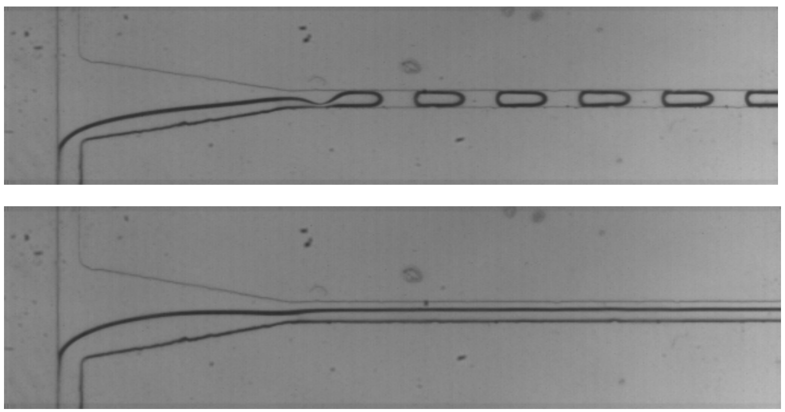
Geometrical parameters: w_c , w_d , w_0

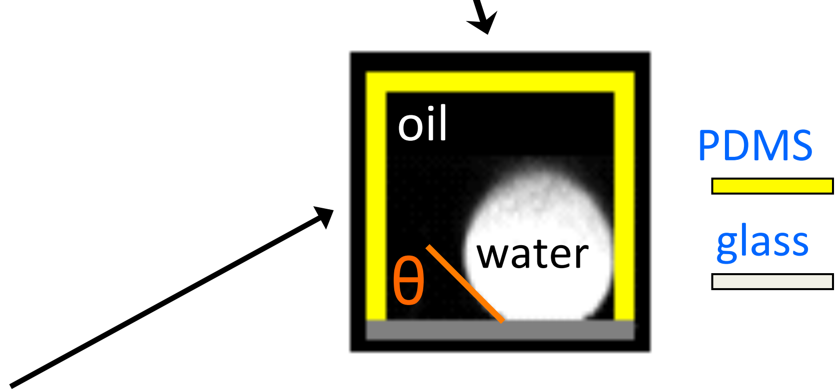
C. Role of wetting properties

Guillot *et al.* Phys. Rev. E 2007



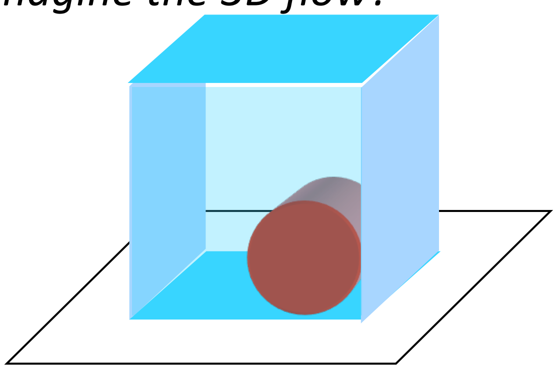
Different regimes for different flow rates :





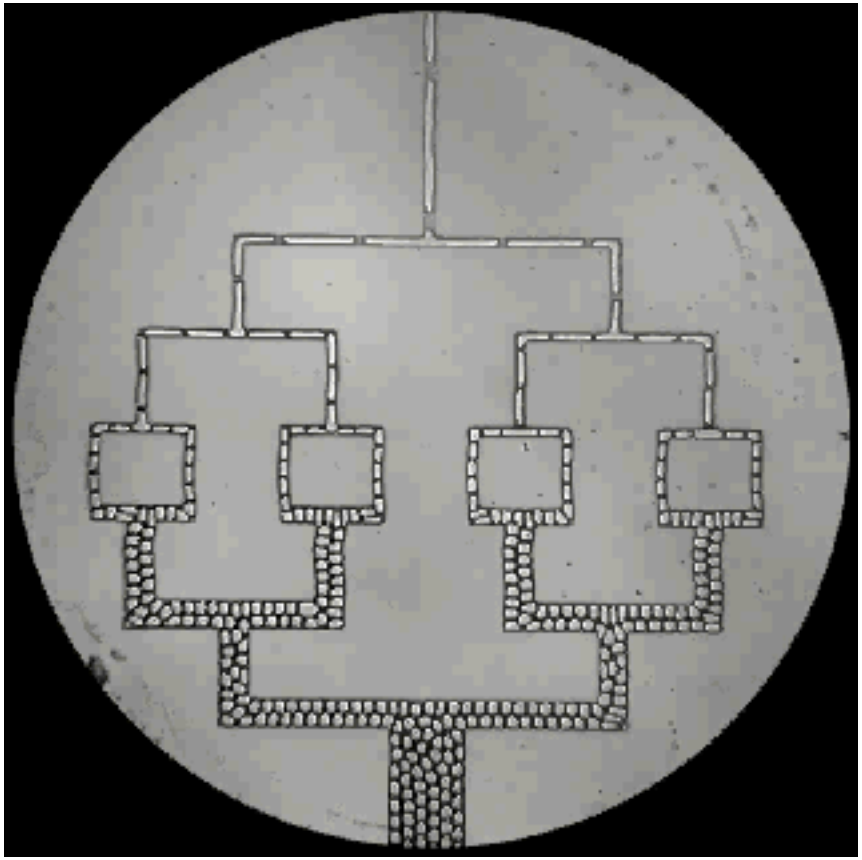
Water wets glass but not PDMS

Imagine the 3D flow?

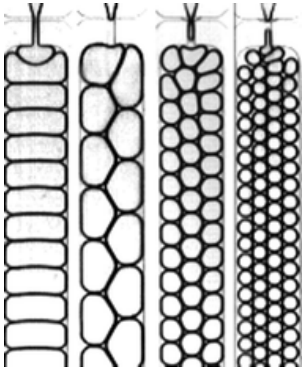


- Hydrophobic channels (e.g. PDMS):
  -> Water droplet in oil
- Hydrophilic channels (e.g. glass)
  -> oil droplet in water

D. Role of surfactants



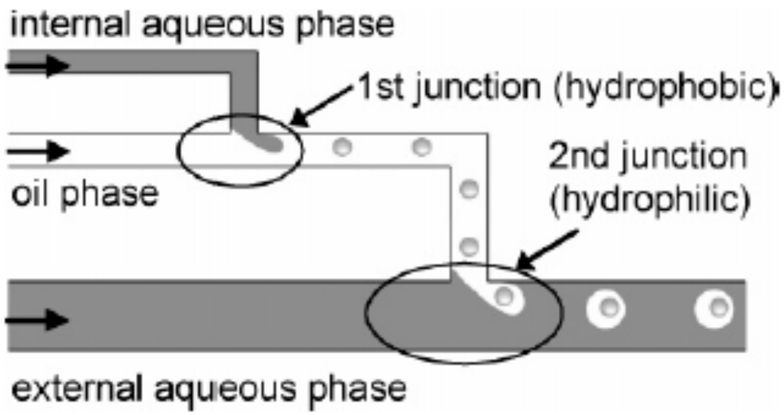
Surfactants used to avoid coalescence

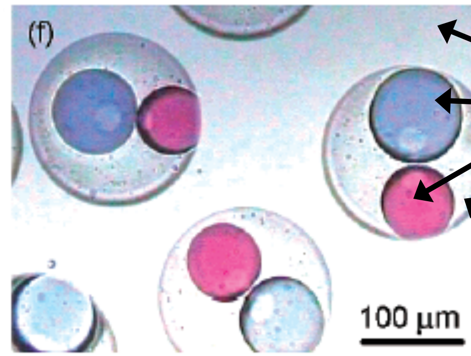


Application:
- high-throughput screening
- 2D foam

All effects combined: double emuslion

silanisation of glass to make it hydrophobic



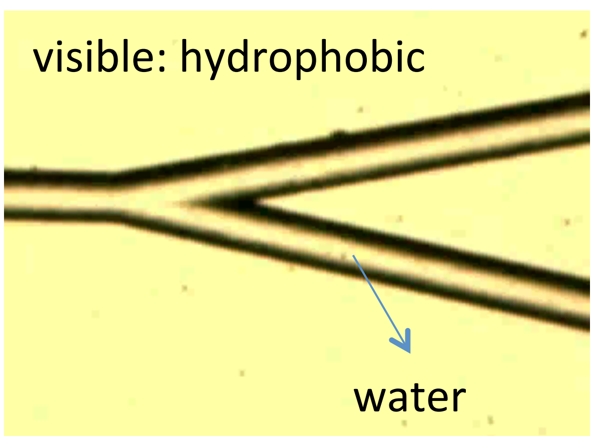


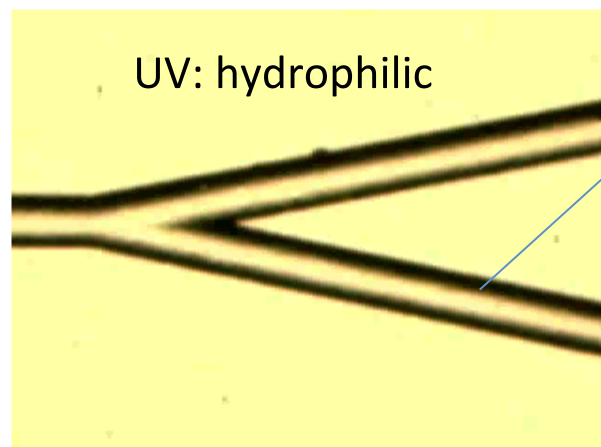
solution aqueuse

goutte organique

Okushima *et al.* Langmuir 2004

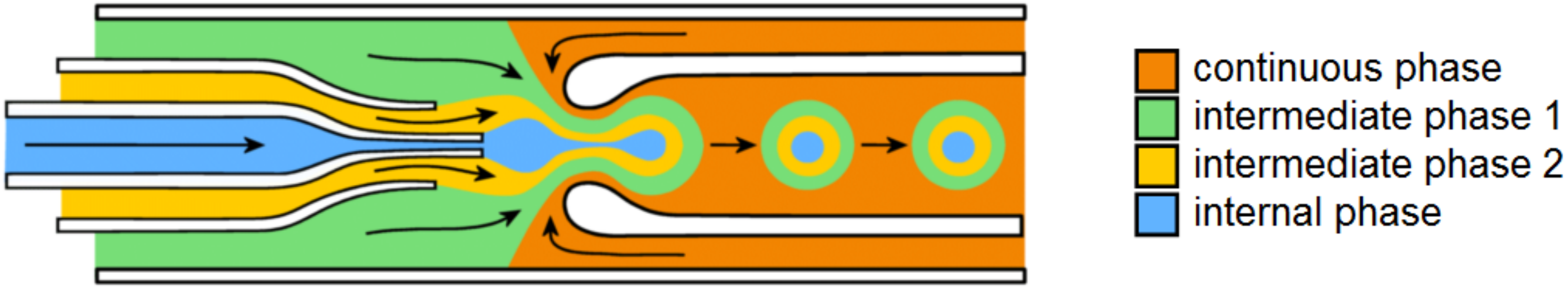
oil
(hexane)

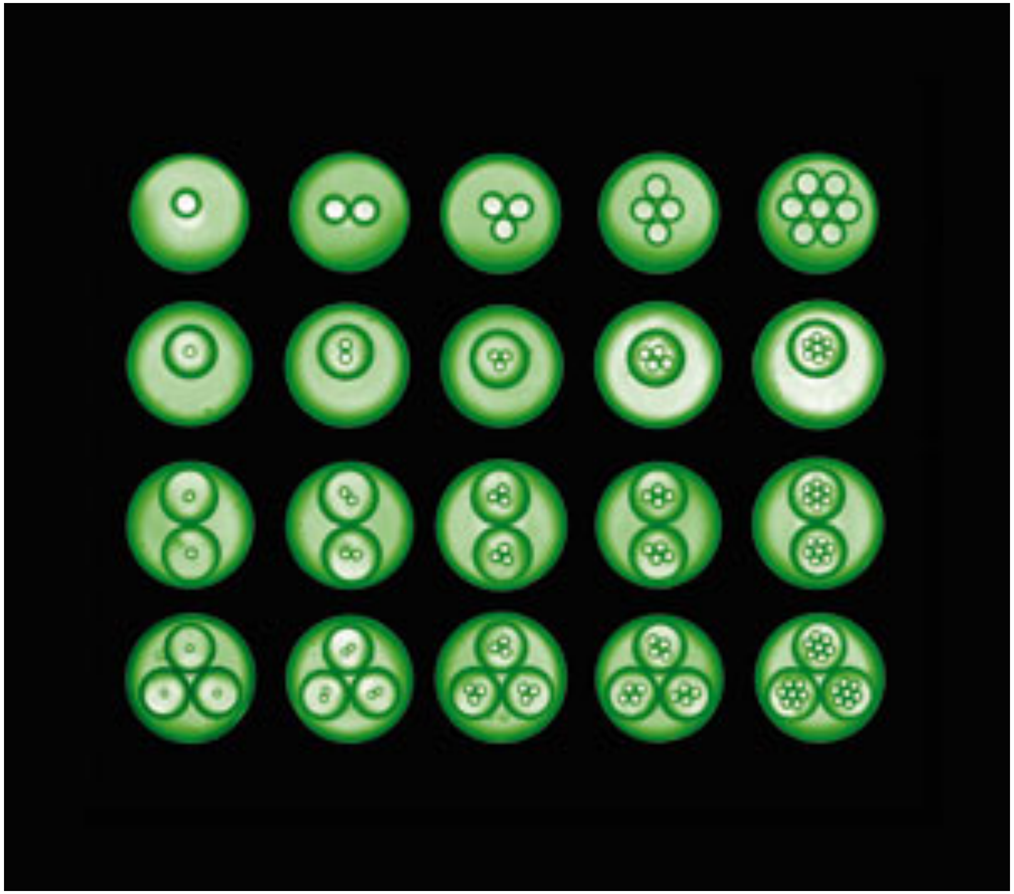




Molecules adsorbed on the walls, whose conformation change with the light

All effects combined: Multiple emuslion



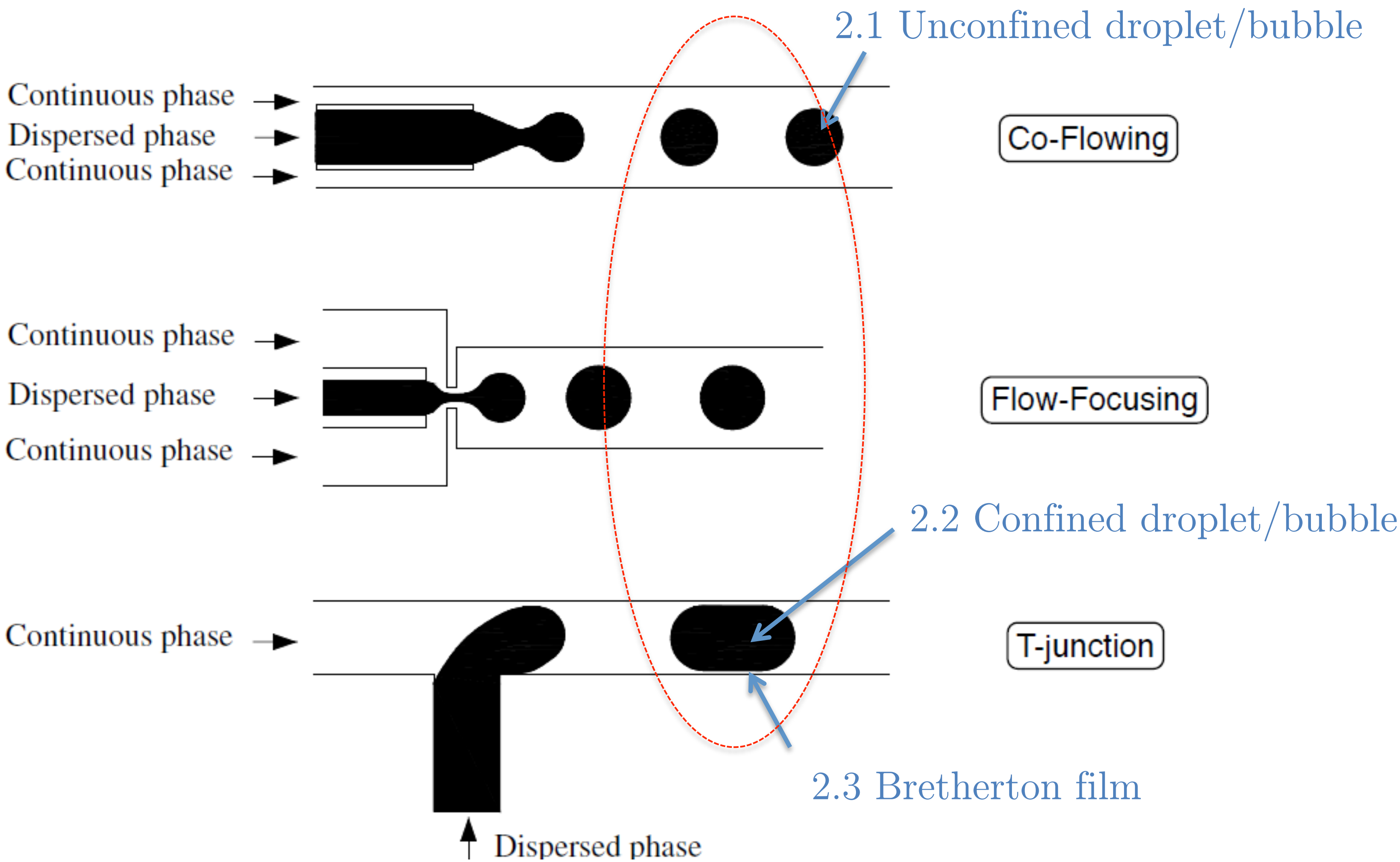


Application: microencapsulation

Weitz group

Multiphase Microfluidics

1. Generation 2. Displacement

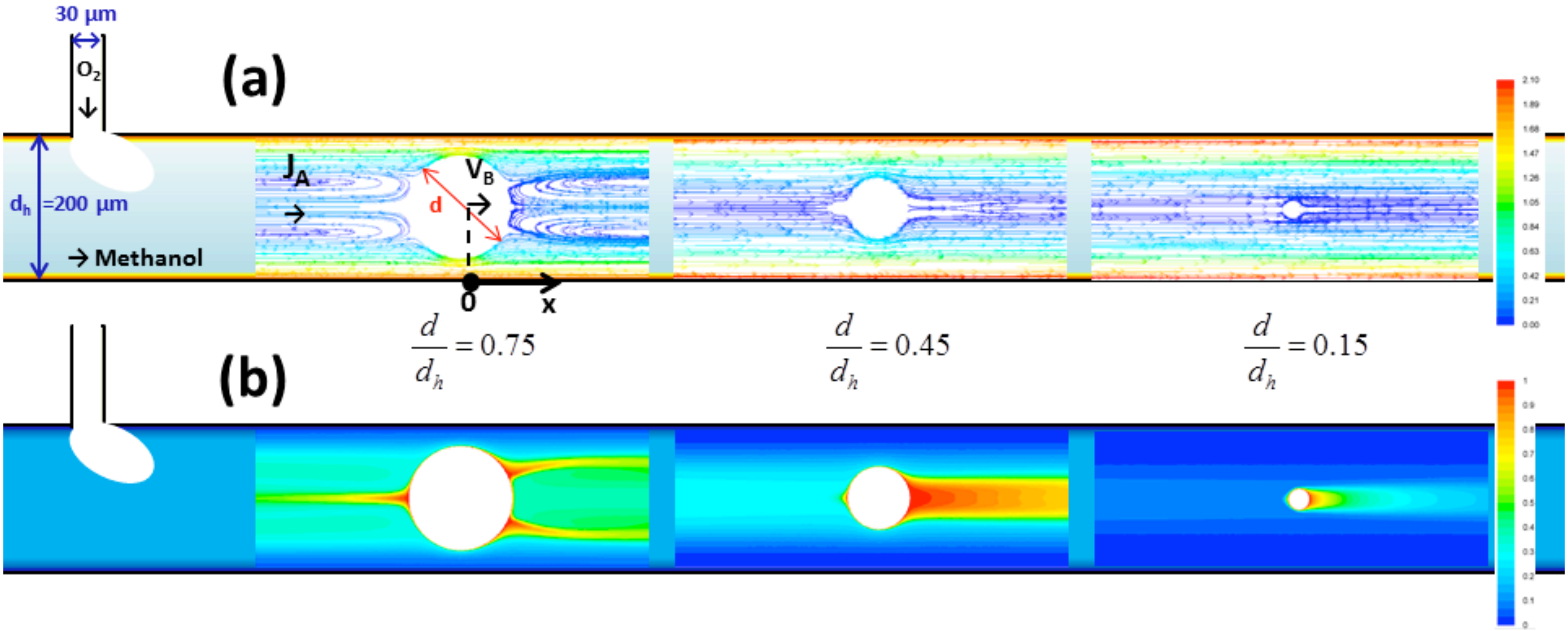


2. Bubble displacement in microchannels

2.1 Unconfined bubbles

Gas/liquid absorption: local approach for bubbly flow

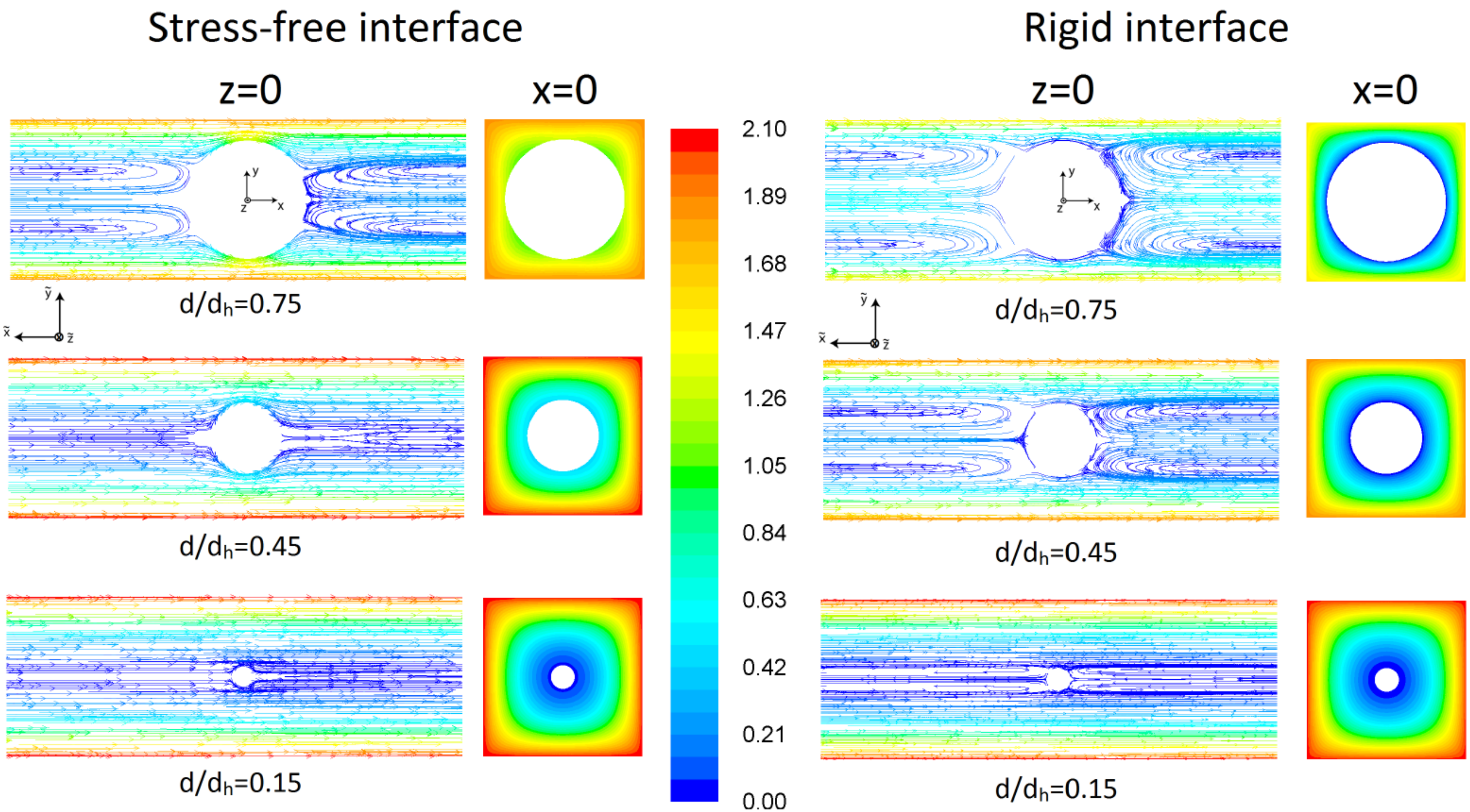
[Mikaelian, Haut, Scheid, Microfluidics & Nonofluidics 2015]



2. Bubble displacement in square microchannels

Importance of boundary conditions on the flow structure

[Mikaelian, Haut, Scheid, Microfluidics & Nonofluidics 2015]

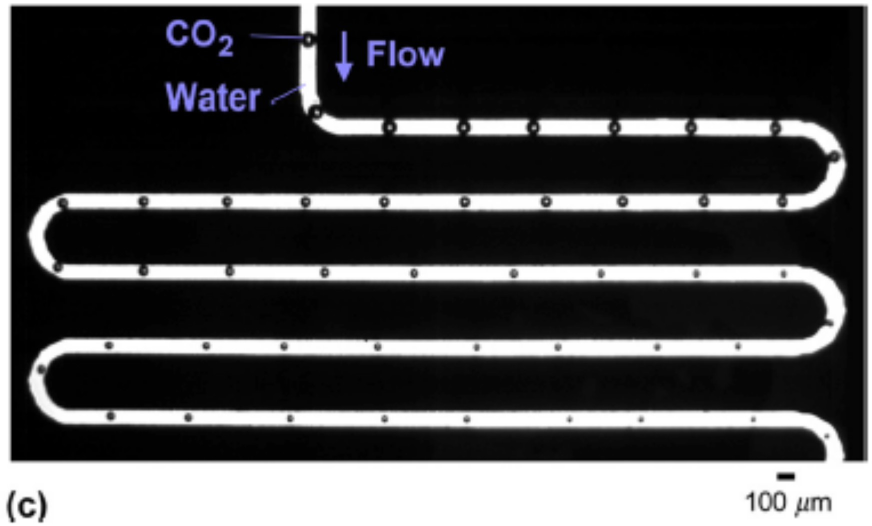


$$\boxed{\frac{V_B}{J_A} = 1 + 1.1\exp\left[-\left(\frac{d}{d_h}\right)^5\right]}$$

$$\boxed{\frac{V_B}{J_A} = 1 + 1.1\exp\left[-1.5\left(\frac{d}{d_h}\right)^{9/4}\right]}$$

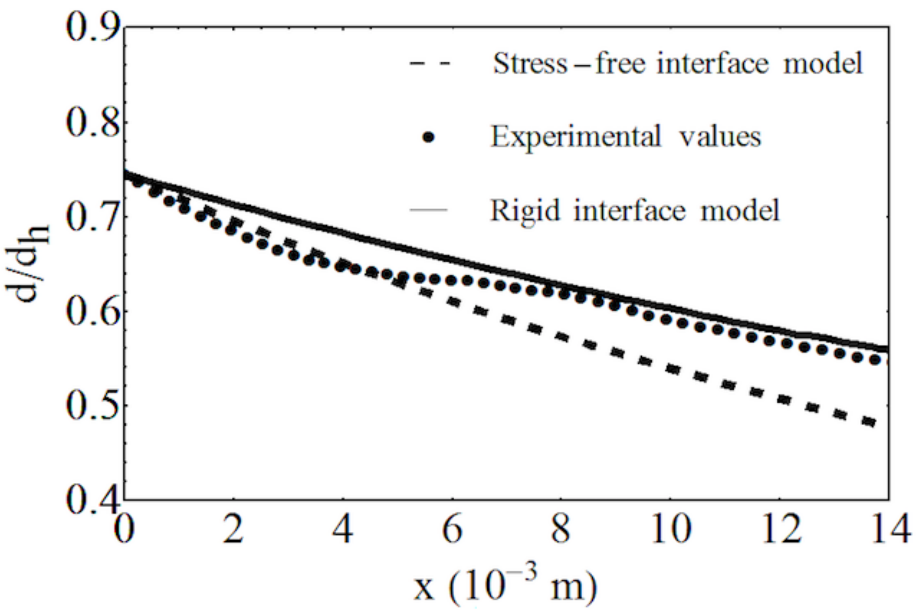
2. Bubble dissolution in square microchannels

Experiment:

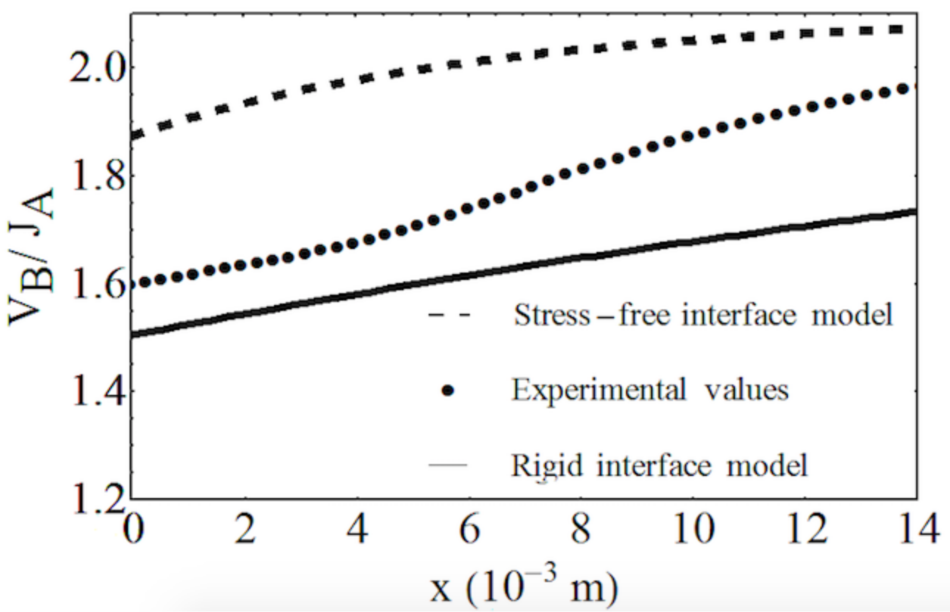


[Cubaud et al., 2012]

Bubble diameter along the microchannel



Bubble velocity along the microchannel

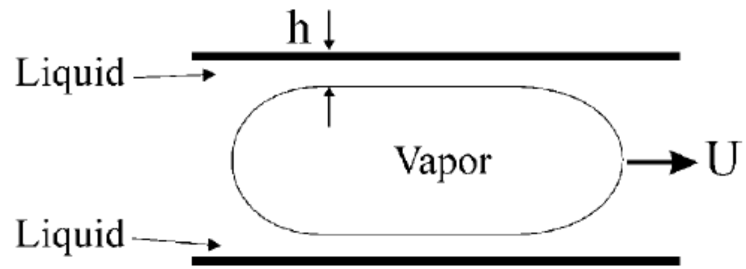


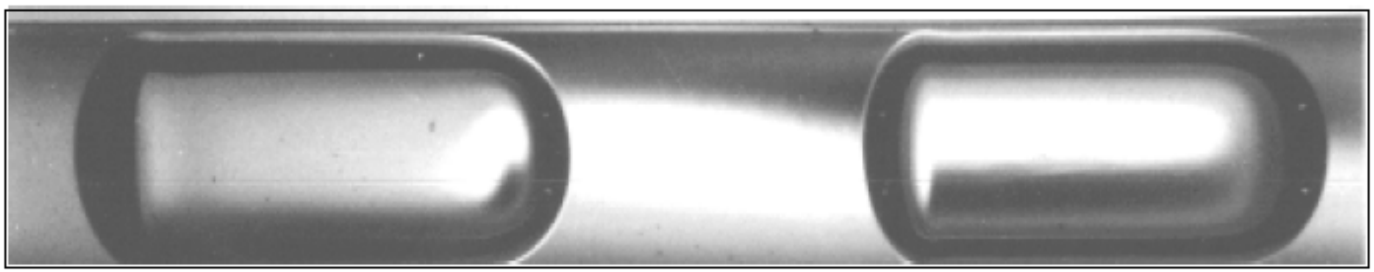
[Mikaelian, Haut, Scheid, Microfluidics & Nonofluidics 2015]

2. Bubble displacement in microchannels

2.2 Confined bubbles

[Bretherton,1961]





velocity vector field

velocity streamlines

[Günther *et al.*, Lab. Chip 2004]

2. Bubble displacement in microchannels

2.3 Bretherton problem

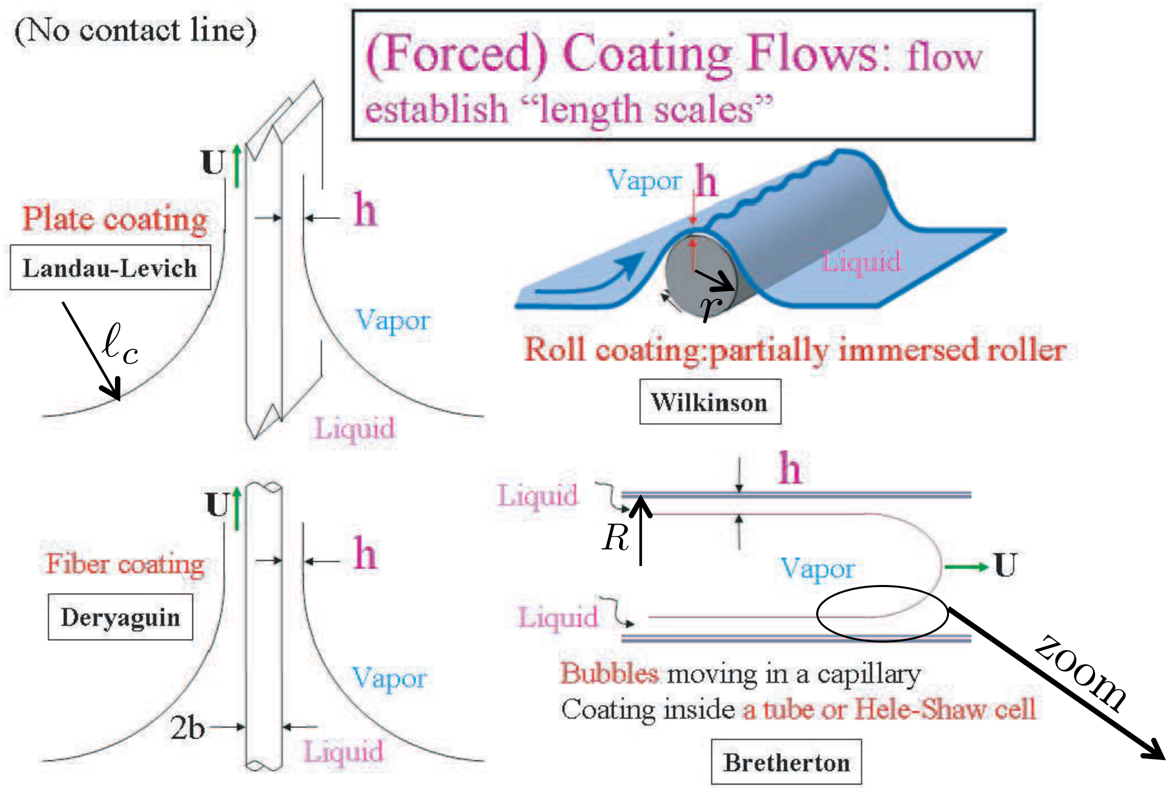
Landau-Levich-Derjaguin: Universal solution

$$\boxed{\frac{h}{\ell_{\text{men}}} \approx \left(\frac{\mu U}{\gamma}\right)^{2/3}}$$

[Stone, 2010]

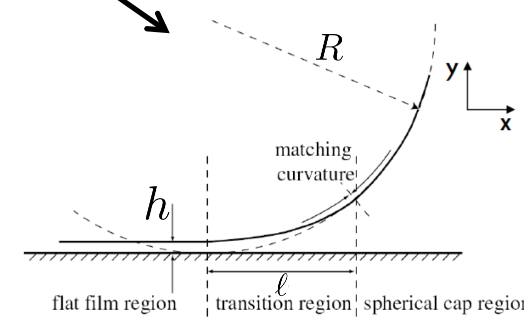
$\ell_{\text{men}} \approx \ell_c$

$\ell_{\text{men}} \approx b$



$\ell_{\text{men}} \approx r$

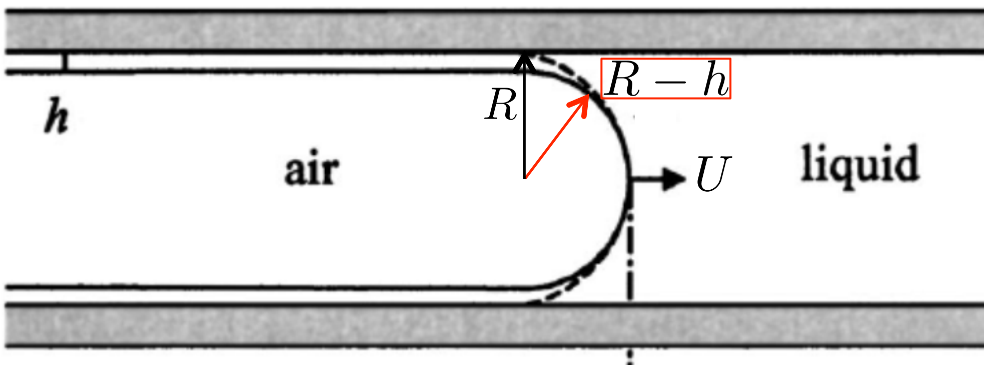
$\ell_{\text{men}} \approx R$



2. Bubble displacement in microchannels

Correction to the radius of curvature

$$\boxed{\frac{h}{\ell_{\text{men}}} \approx \left(\frac{\mu U}{\gamma}\right)^{2/3} = Ca^{2/3}}$$



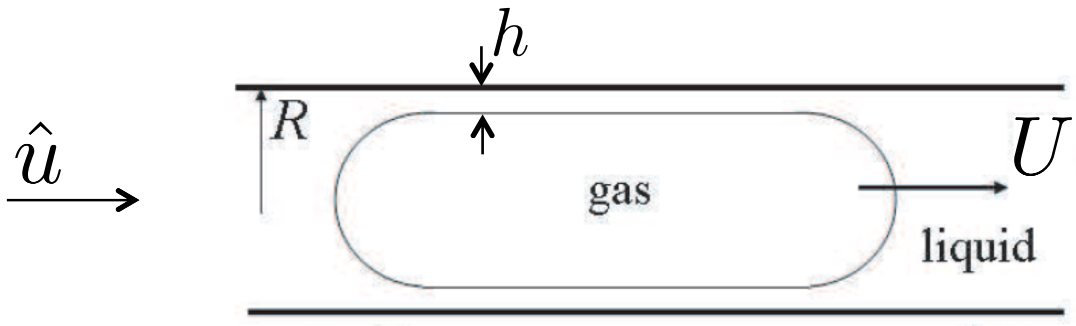
$$\ell_{\text{men}} = R \xrightarrow{\text{correction}} \boxed{\ell_{\text{men}} = R - h}$$

$$\frac{h}{R} \approx Ca^{2/3} \qquad \boxed{\frac{h}{R} \approx \frac{Ca^{2/3}}{1 + Ca^{2/3}}}$$

Thick film increases curvature !!! → h < R

2. Droplet/bubble displacement in microchannels

At what speed travels a confined bubble ?



[Stone, 2010]

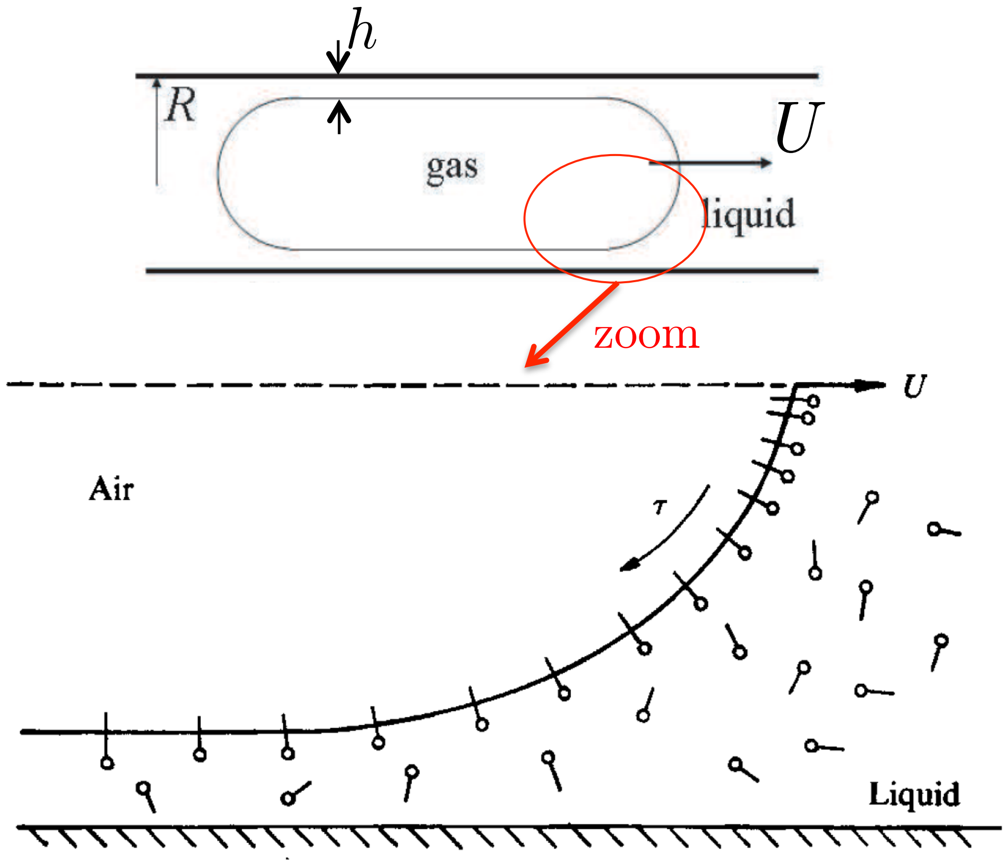
Mass balance in the frame of reference of the bubble:

$$(\hat{u} - U)\pi R^2 = -2\pi R h U$$

$$\frac{U - \hat{u}}{U} = \frac{2h}{R} \propto \left(\frac{\mu U}{\gamma}\right)^{2/3}$$

2. Bubble displacement in microchannels

Effect of surfactants



[Ratulowski and Chang, 1990]

The presence of surfactant can "rigidify" the interface as in the LLD problem

Conclusions

- Importance of surfactants in microfluidics
  - Generation of droplets/bubbles
  - Displacement of droplets/bubbles
- Confined droplets/bubbles
  - Lubrication film near the walls
    - Bretherton // Landau-Levich-Derjaguin
- Role of surface rheology
  - Surface elasticity → rigidity
  - Nothing has been done so far on surface viscosity effects in microfluidics !!!

Thank you for your attention

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