Stanford, February 28, 2006

# On Novel Marangoni Flows

Rouslan Krechetnikov

**California Institute of Technology**

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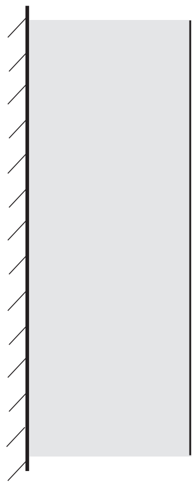

Thin films

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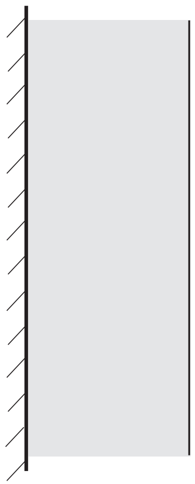

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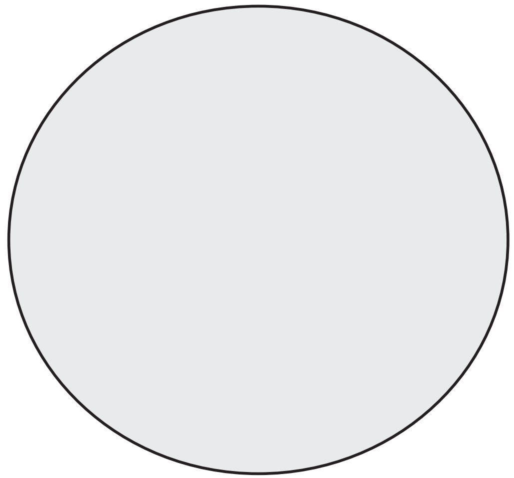

Drops/Bubbles

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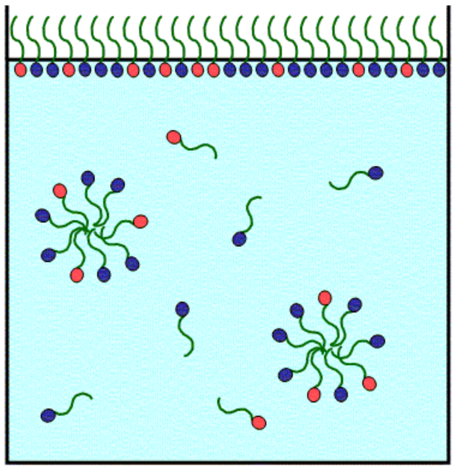

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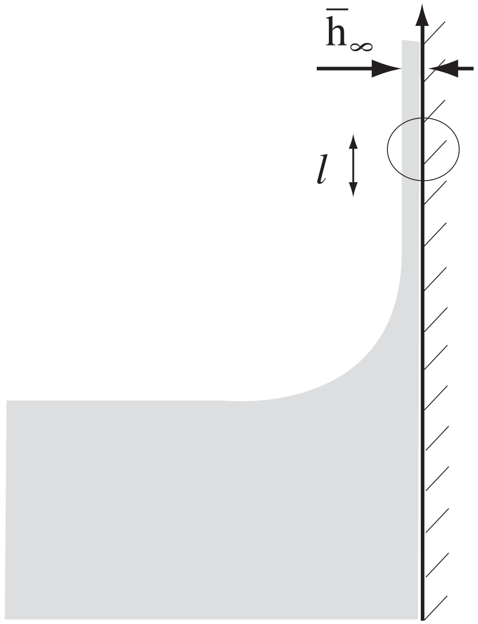


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- Conclusions

# What are the Marangoni effects[a]?

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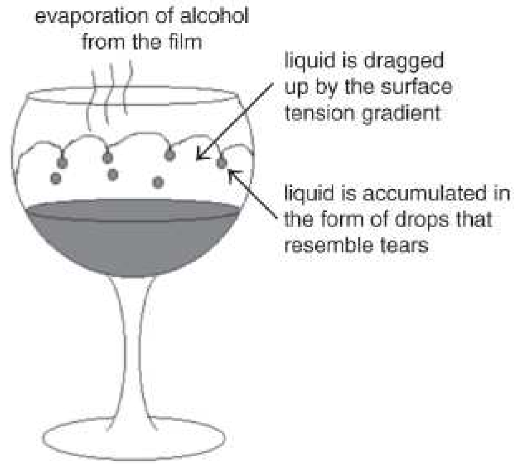


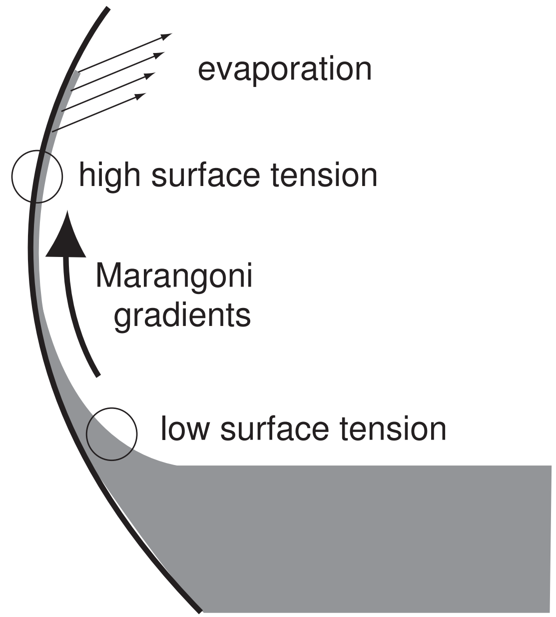


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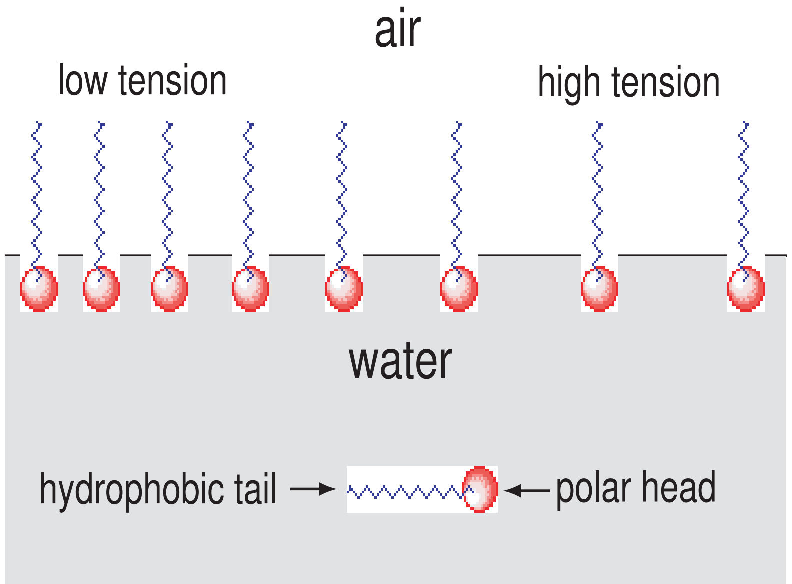
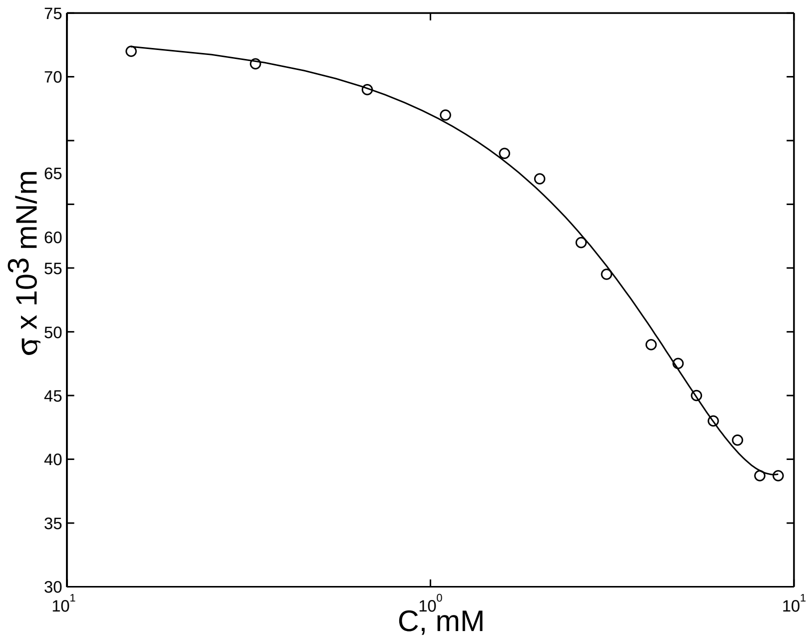
# Basic physics of surfactants

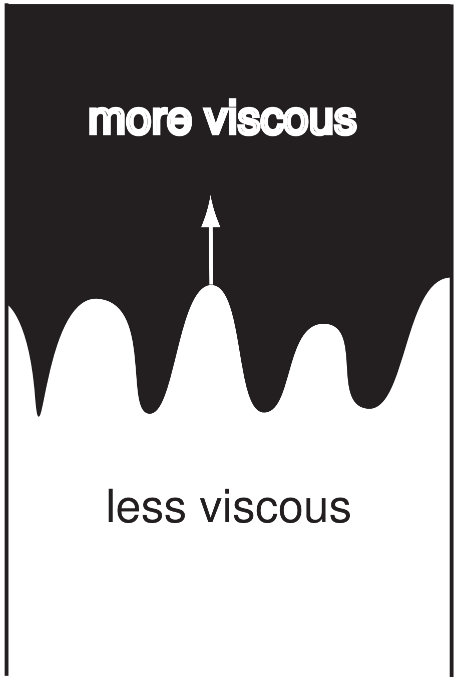


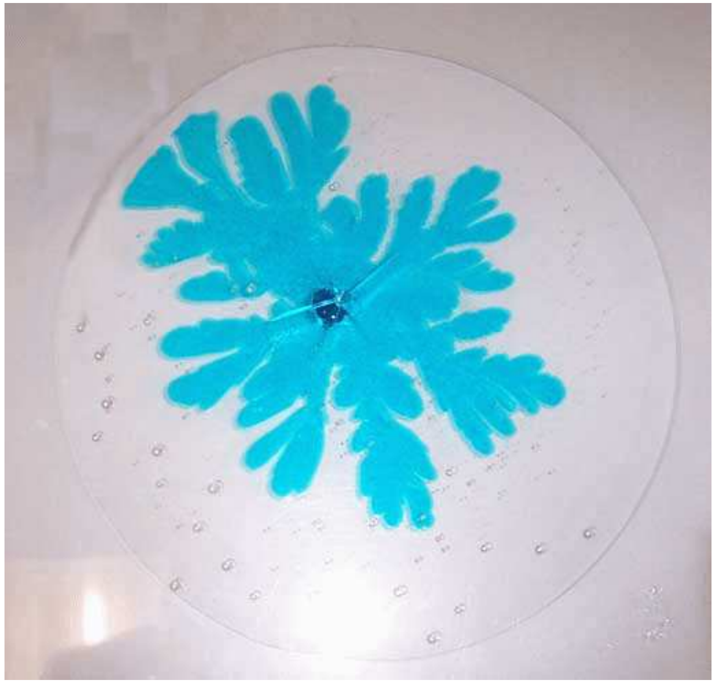

North American surfactant consumption in consumer products was 4.375 billion lbs last year, valued at $3.6 billion.

# Part I. Fingering in a Hele-Shaw cell

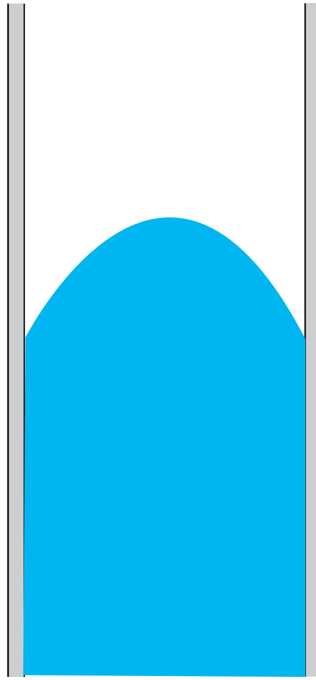
Saffman-Taylor instability[a]




Planar cell.



Circular cell.



Thin dimension.

Darcy's law: $\mathbf{u} = -\frac{b^2}{12\mu}\,\mathrm{grad}\,p, \quad \mathrm{div}\,\mathbf{u} = 0 \Longrightarrow$ 2D effect

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[a] Hill (1952), Saffman & Taylor (1958), Chuoke *et al.* (1959)

# Historical Prerequisites

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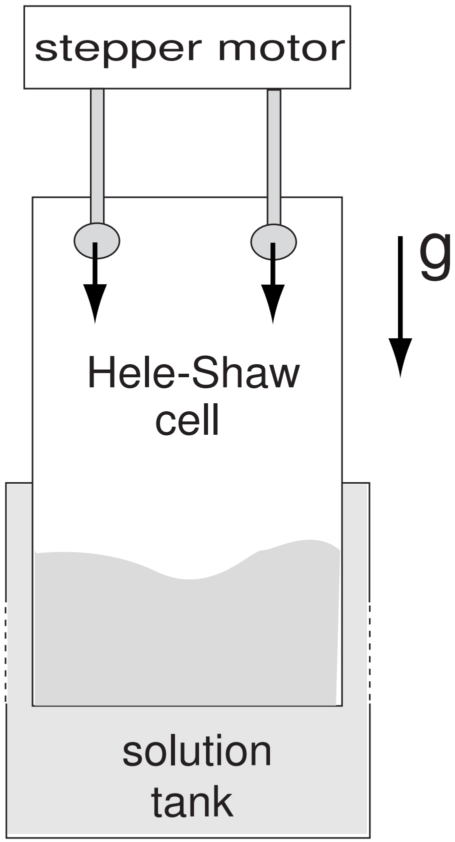


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- The **experiments** conducted by Chan & Liang (1997) have demonstrated that the *predictions of Guo et al. are not observable*. However, the presence of a *pre-existing wetting layer* allows surfactants to produce Reversed Saffman-Taylor (RST) instability.

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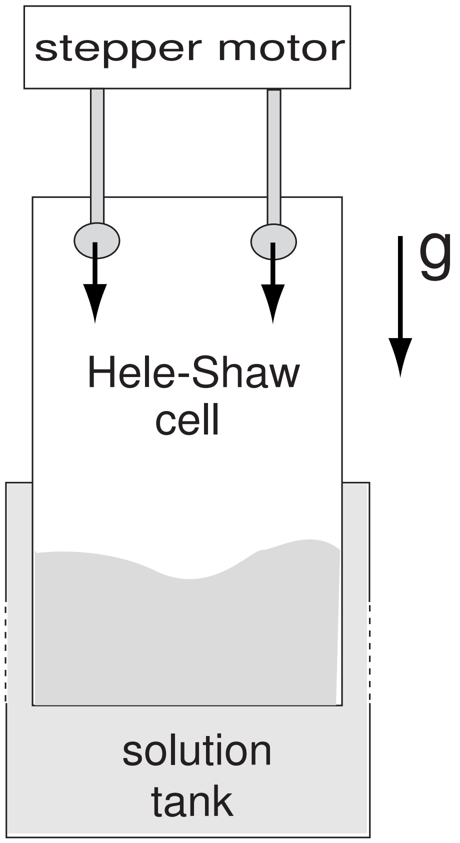


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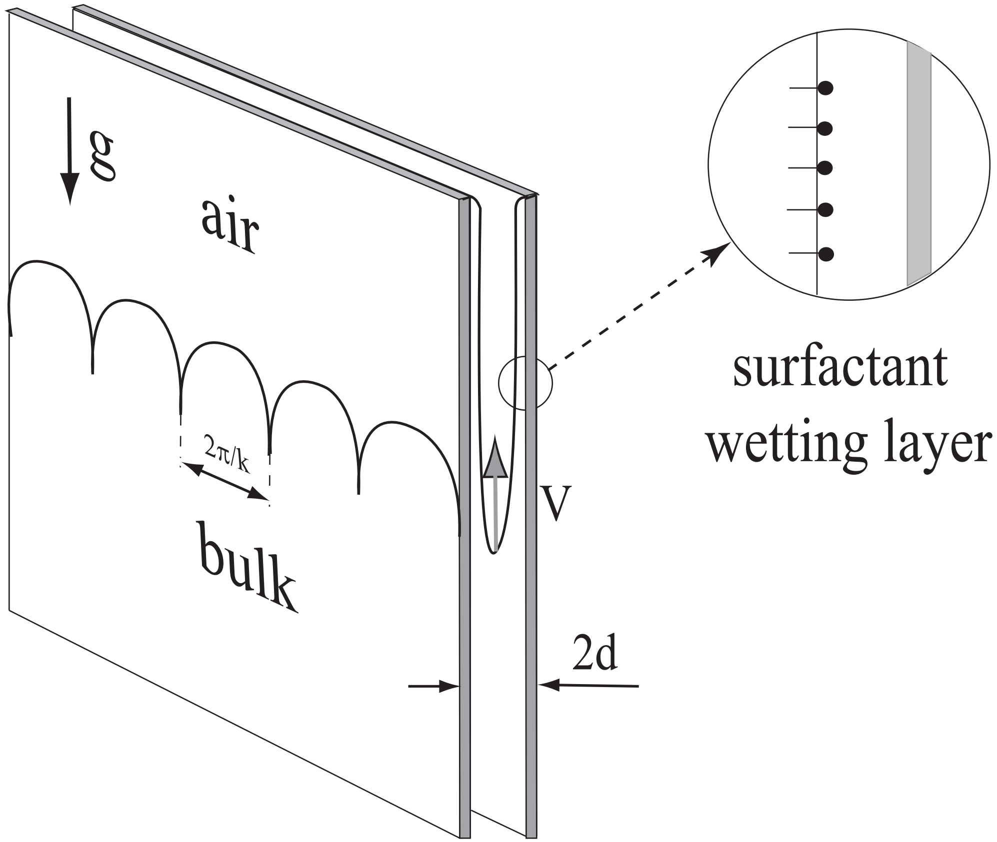
- Chan (2000) has proposed a **linear stability analysis** by considering another non-physical state equation for the surface tension – a linear dependence on the deformation of the interface.

# Surfactant-driven fingering[a]

Hele-Shaw cell




[a] Krechetnikov & Homsy, JFM (2004); Fernandez, Krechetnikov & Homsy, JFM (2005)

# Fingering pattern of RST instability


A Hele-Shaw cell with gap of width $300\ \mu m$ is driven at a speed of $3.8\ cm/s$ into a $4.0\ mM$ solution of SDS[a].

[a] Sodium Dodecyl Sulphate, which is widely used in soaps, detergents, *etc*.

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- predictive theory: criticality dependence on
  - the surfactant concentration and properties (material and kinetics)
  - the speed of interface
  - the substrate properties (wettability, smoothness)

# Processes in a "thin" dimension

Conditions at interface:

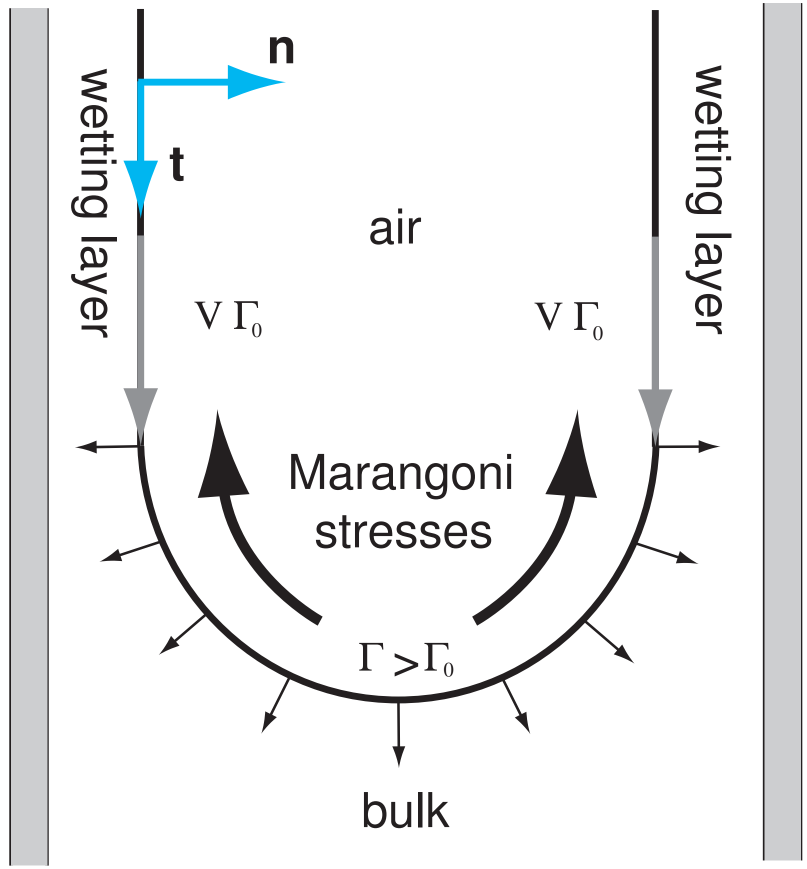
$$[\mathbf{t}\cdot\mathbf{T}\cdot\mathbf{n}]_1^2 = \mathbf{t}\cdot\nabla_s\sigma,$$

$$[\mathbf{n}\cdot\mathbf{T}\cdot\mathbf{n}]_1^2 = -\sigma\nabla\cdot\mathbf{n},$$

where $\mathbf{T} = -p\delta_{ij} + 2\mu e_{ij}$ is a stress tensor.

Surfactant transport dynamics:

$$\frac{d\Gamma}{dt} = k_a C\left(1 - \frac{\Gamma}{\Gamma_m}\right) - k_d\Gamma.$$



# The core of the problem

$$\text{the tangential BC}: \sigma_\gamma \frac{\partial \gamma}{\partial x} = Ca^{2/3} \frac{\partial^2 \Psi}{\partial y^2}, \; Ca = \frac{\mu V}{\sigma_0}.$$

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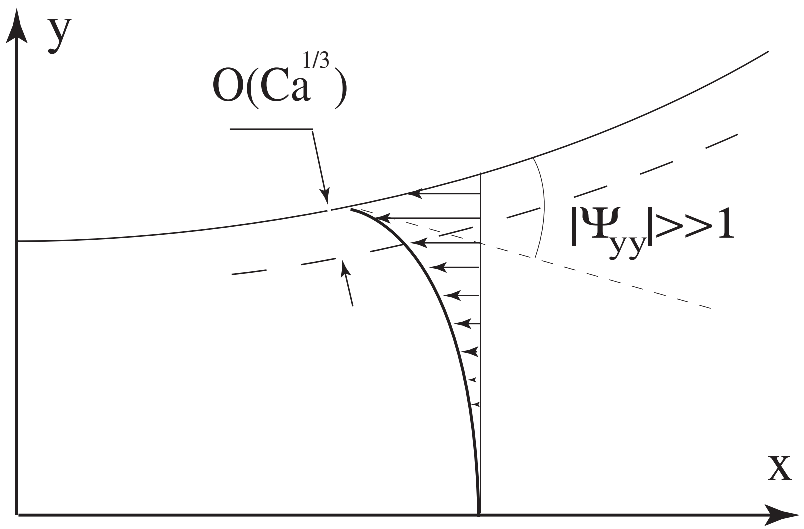
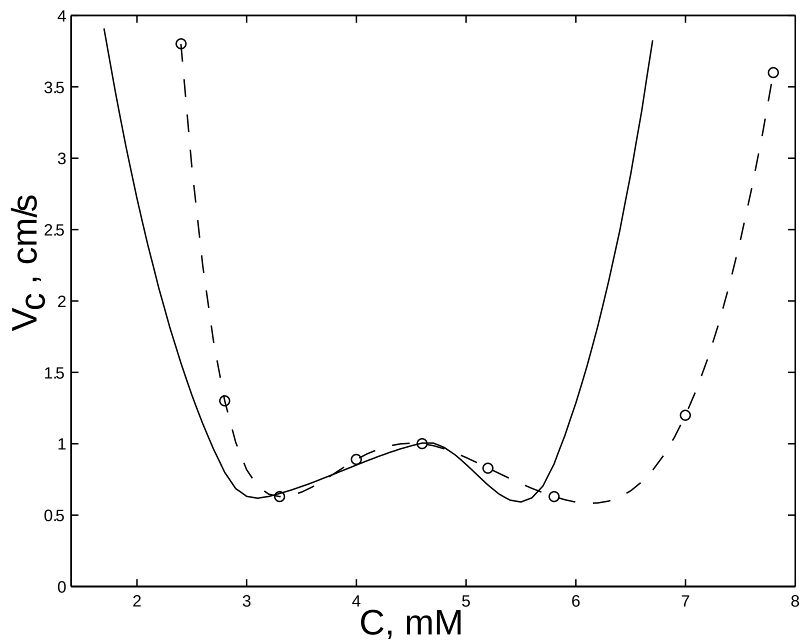
- Commonly used conjecture: $\gamma = Ca^{2/3}\tilde{\gamma}$ (trace amounts);
- Our conjecture: singular perturbation case with an inner scale $y = Ca^{1/3}\tilde{y}$ (order one surfactant effect)



# Conclusions on Part I

## Marginal stability & comparison with experiment




(solid line – theory; dashed line – experiment)

**The elementary interpretation**: *the instability is due to thickening of the wetting layer caused by significant Marangoni stresses, which originate in the accumulation of surfactants in the cap region*.

# Part II. Amazing drop

Discovered[a] in the course of pendant drop measurements with acid/alkaline reaction at the oil/water interface.

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[a] Fernandez & Homsy; Krechetnikov & Homsy, Phys. Fluids (2004); photos are courtesy of J. Fernandez.

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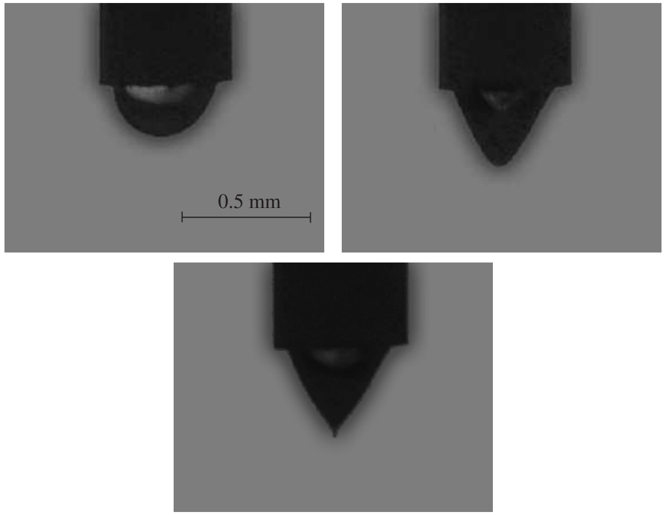


Nonlinear oscillations of a pendant drop shape

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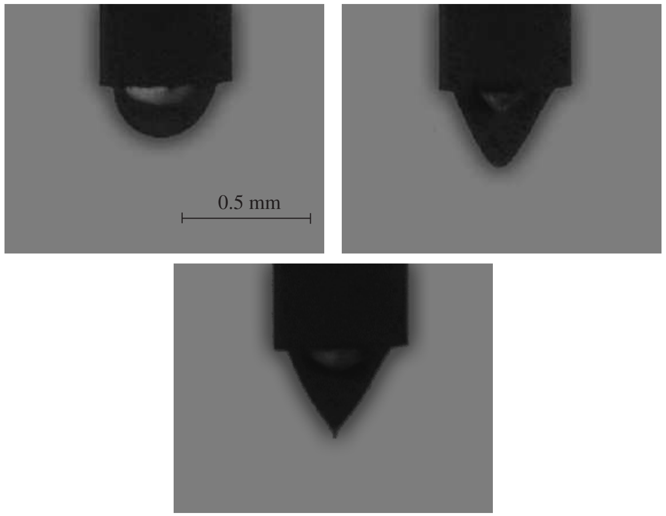


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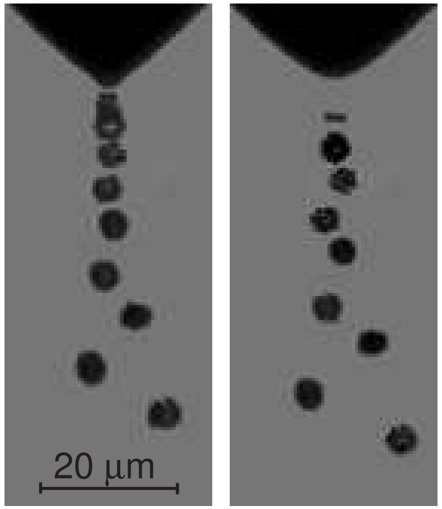


Tip-streaming and droplets splitting

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- **nonlinear oscillations** – periodic change of the drop shape from nearly hemi-spherical to conical;
- **tip-streaming** – formation of the conical drop shape with pointed ends and ejection of very small, $4\ \mu m$, droplets from the pointed ends;
- **droplet separation** – organized motion, when one ejected droplet moves to the right, while the subsequent one moves to the left.

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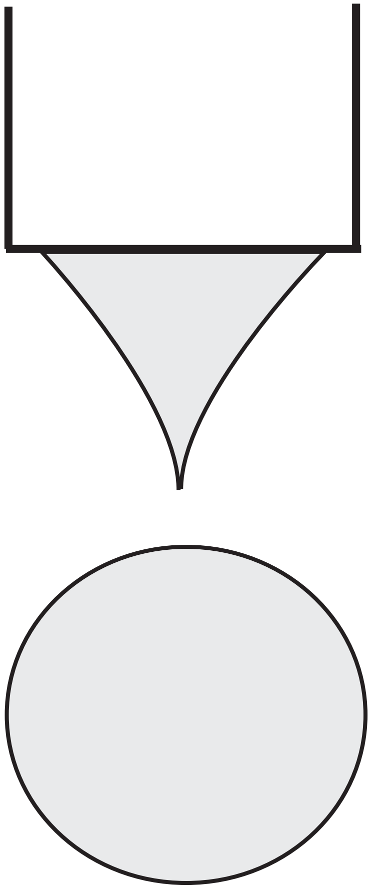

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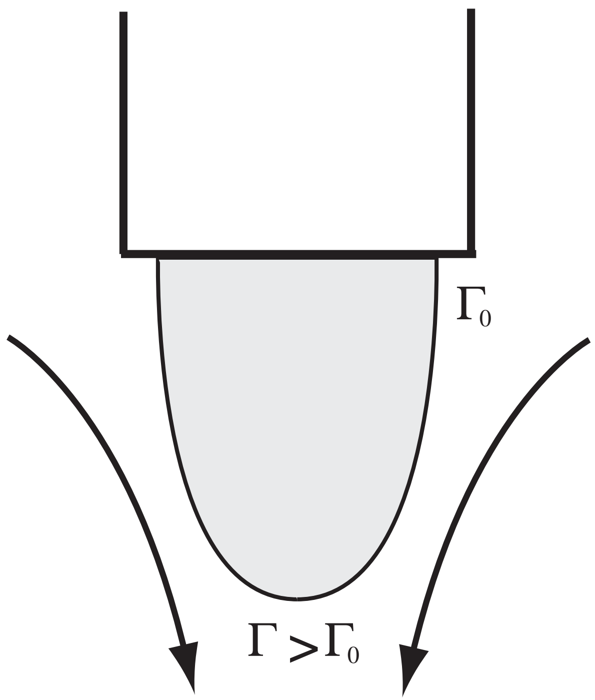


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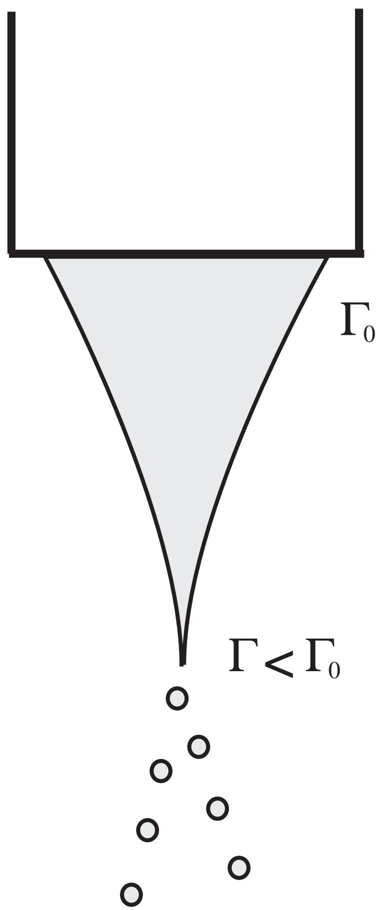


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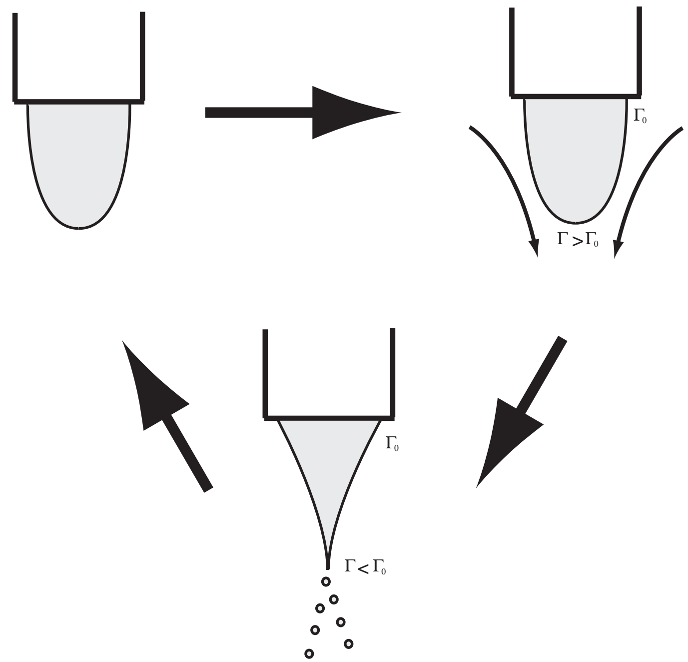


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**(iii)** the surfactant concentration gradient between the top and the tip of the drop so created drives Marangoni flow.

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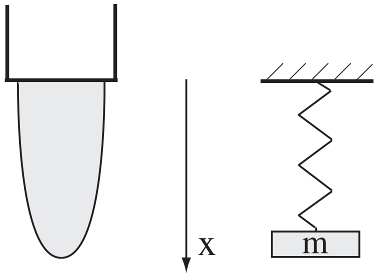


Before detachment

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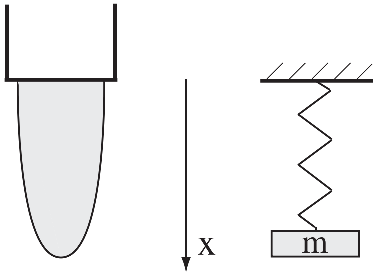


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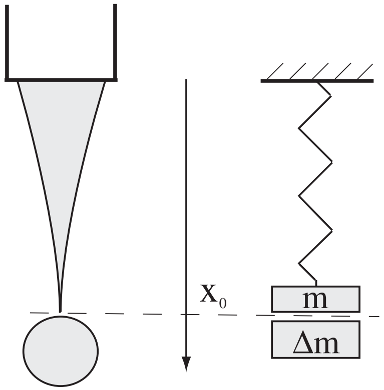


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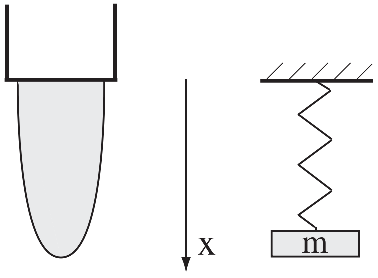


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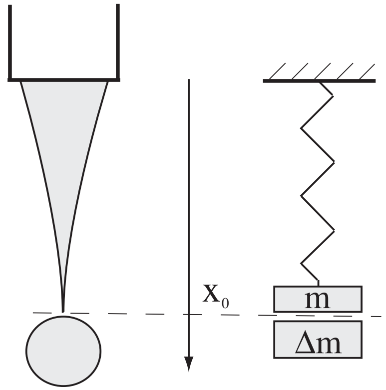


After detachment

Mass-Spring model

$$
\begin{aligned}
\frac{\mathrm{d}x}{\mathrm{d}t} &= v, \\
\frac{\mathrm{d}\,(mv)}{\mathrm{d}t} &= m - (x + bv)\,, \\
\frac{\mathrm{d}m}{\mathrm{d}t} &= r, \\
x = x_c : \ \Delta m &= \alpha m_c v_c, \\
\Delta x &= \beta \frac{\Delta m^{4/3}}{m_c}.
\end{aligned}
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Shaw *et al*. (1984,1985).

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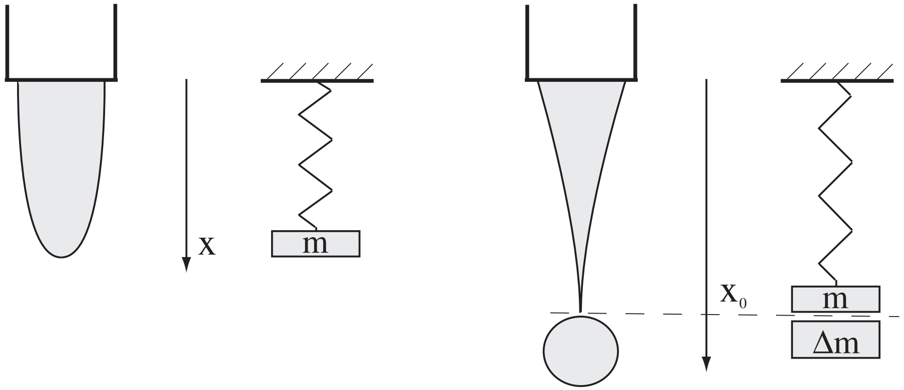
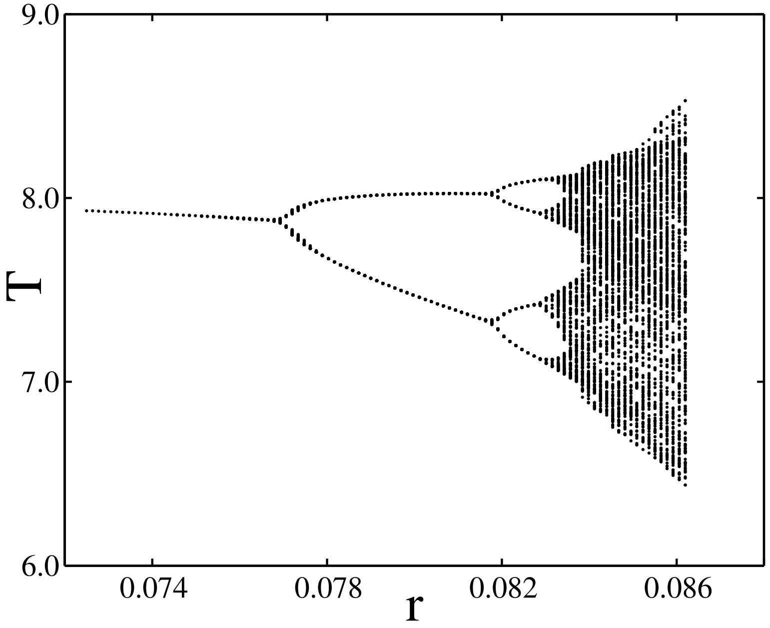



Before detachment | After detachment

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---

Shaw *et al*. (1984,1985).

# Relaxation oscillator model

The mathematical model:

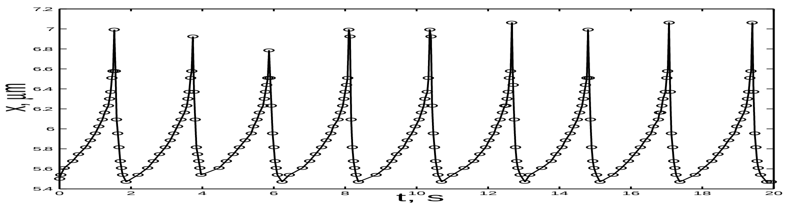
$$M\frac{d^2x}{dt^2} = \underbrace{Mg}_{gravity} - \underbrace{b\frac{dx}{dt}}_{friction} - \underbrace{k(\Gamma)\,x}_{surface\ tension},$$

$$\frac{d\Gamma}{dt} = R, \;\; \& \;\Gamma = \Gamma_c : \;\; \Gamma = \Gamma_c - \Delta\Gamma.$$

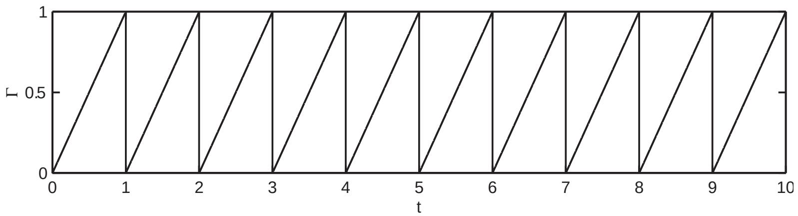
Control parameter: chemical reaction rate $R/R_0$ with

$$R_0 = 0.29 \cdot 10^{-5}\ \mathrm{mol\ m^{-2}\ s^{-1}}.$$

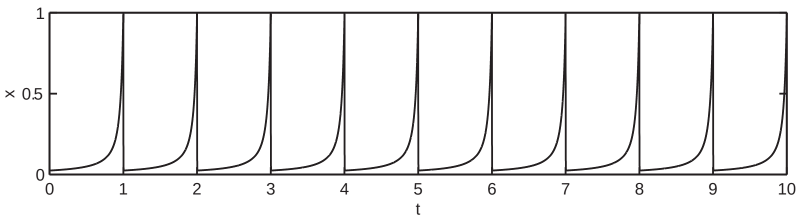
# Dynamics of the pendant drop



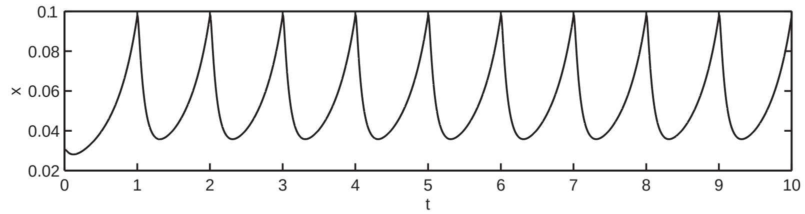

Experiments: tip dynamics.



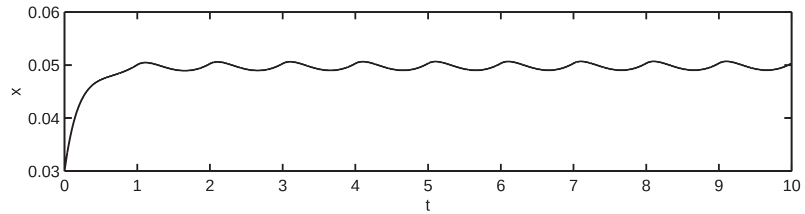

Dynamics of surfactant surface concentration.



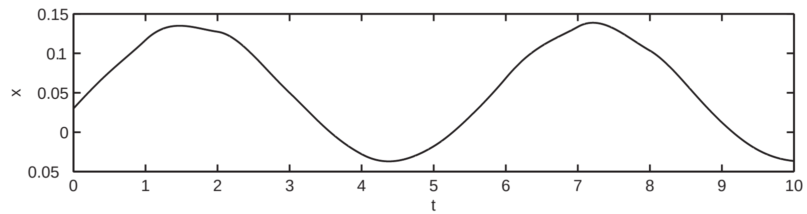

Slow reaction, $R_0/R = 1$: negligible dissipation.




Fast reaction, $R_0/R = 0.01$.




Fast reaction, $R_0/R = 0.0005$: steady tip-streaming.

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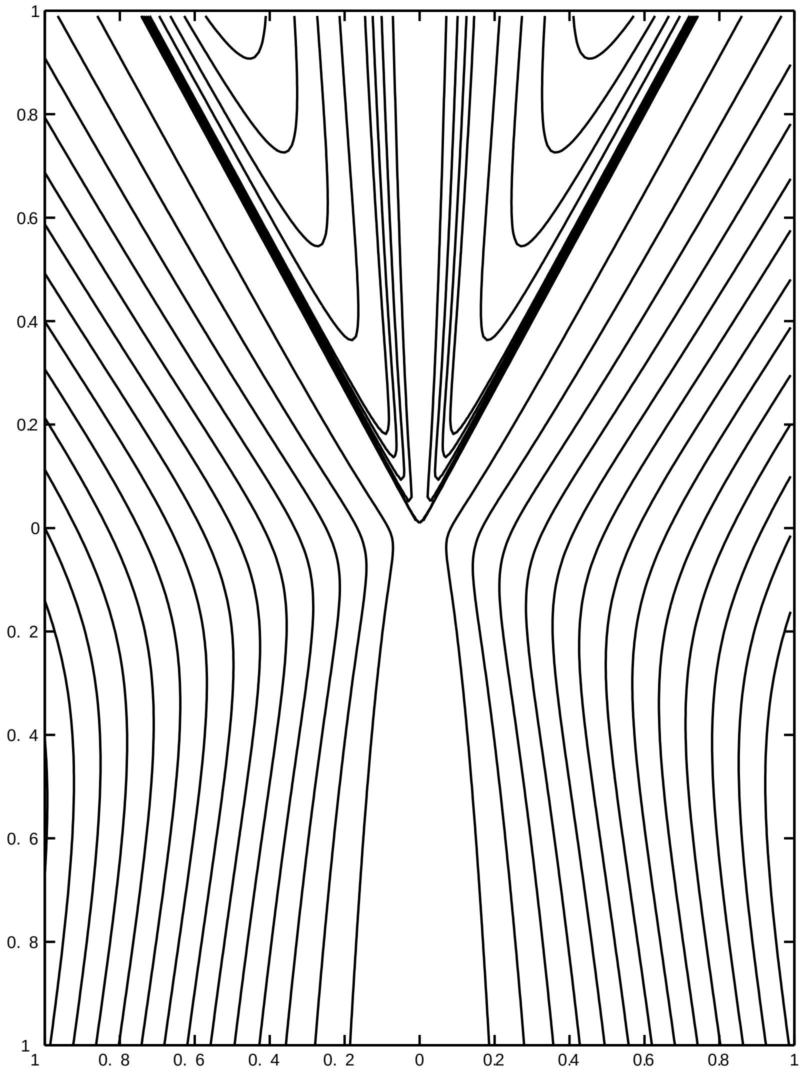
# Steady tip streaming self-similarity




For simplicity, we consider

$$We_1 \ll We_2 \ll 1, We = \rho\sigma_0 d/\mu^2,$$

self-similar solution is defined by

$$\Psi = r\varphi(x), \quad \sigma = \frac{\epsilon}{r}; \quad p = \frac{\pi(x)}{r^2},$$

where $\epsilon = \sigma_{min}$, $x = \cos\theta$, and $\Psi$ is a Stokes stream function in

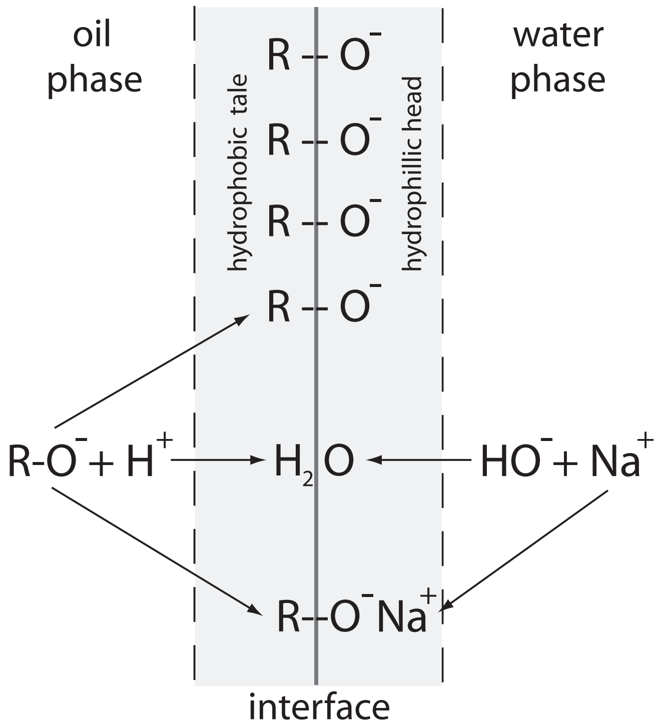
$$x' = r\sin\theta\cos\varphi,\ y' = \sin\theta\sin\varphi,$$
$$z' = r\cos\theta,$$

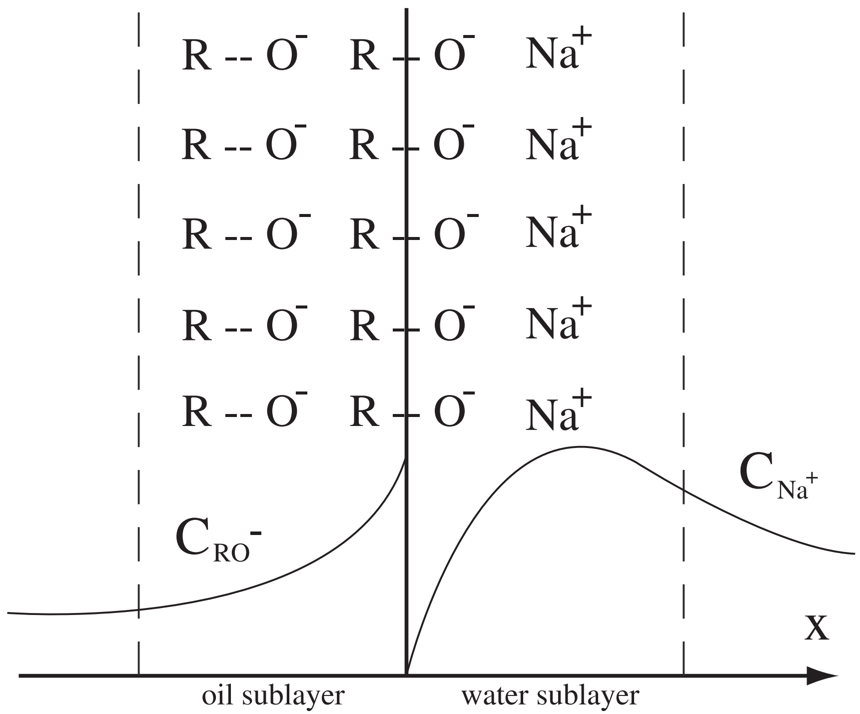
with $\theta \in [0, \pi],\ \varphi \in [0, 2\pi]$.

# Electrostatic interaction

The interfacial reaction is:

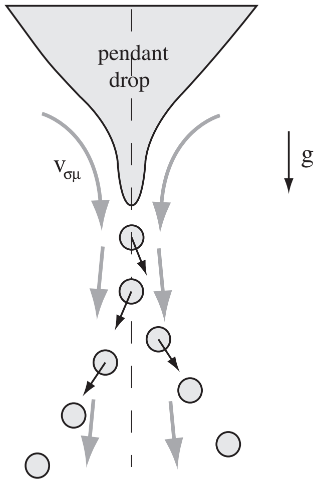
$$\underbrace{RO^- \;+\; H^+}_{linoleic\ acid} \;+\; \underbrace{Na^+ \;+\; HO^-}_{sodium\ hydroxide} \;\rightarrow\; H_2O \;+\; RO^-Na^+.$$



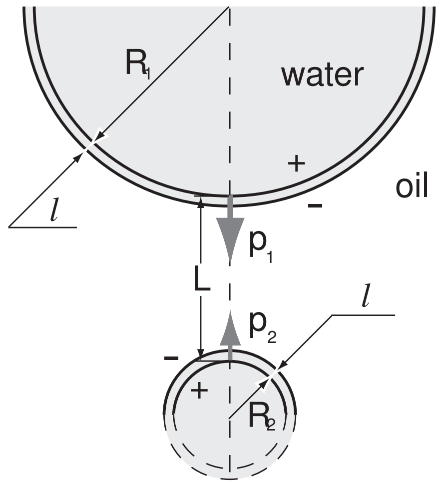




Double layer thickness: $\delta x \sim h^w \sim \left[\frac{\epsilon_0 \epsilon^w}{e^2} \frac{k_B T}{C^\infty_{Na^+}}\right]^{1/2} \sim 10^{-8} m.$

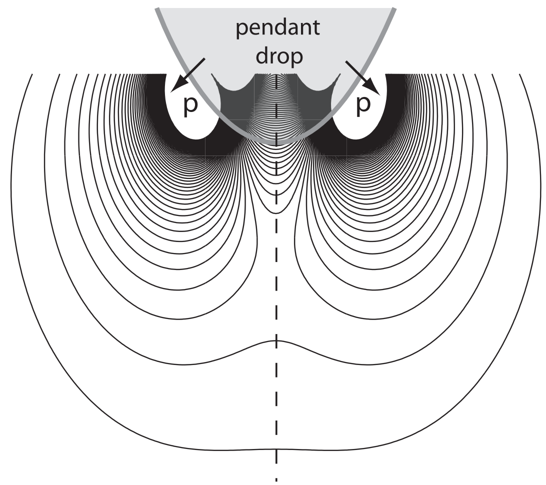
# Mechanism of droplets splitting




Schematics of the droplets splitting.




Dipole-dipole interaction of the drops.




Equipotentials of the electric field.

$$F_{p_1-p_2} = \frac{6}{4\pi\epsilon_0\epsilon^o}\frac{p_1p_2}{L^4}, \text{ where } p_i = 2\pi e R_i^2 \Gamma^{max} N_A h^w.$$

$$F_{p_1-p_2} \sim 0.5 \cdot 10^{-7}\ N,\ F_{p_2-p_2} \sim 1.0 \cdot 10^{-6}\ N;$$
$$F_{st} \sim 6\pi\mu^o R_2 v_{\sigma\mu} \sim 0.5 \cdot 10^{-6}\ N.$$

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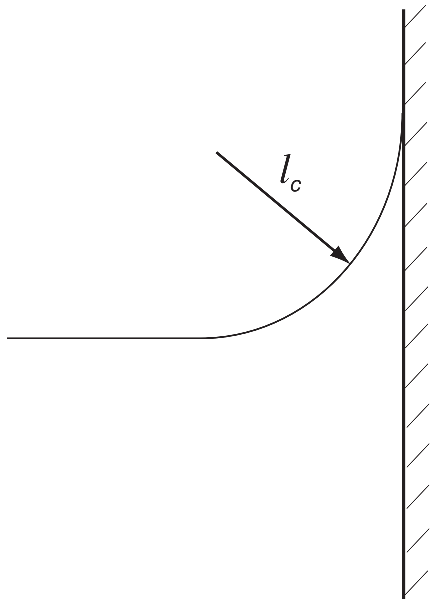
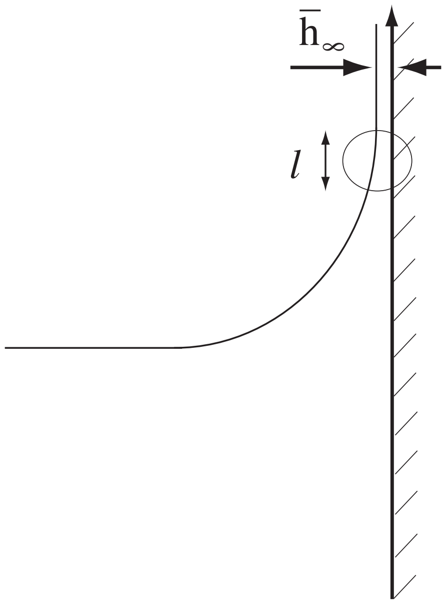
- Electrostatic interactions creates a specific **flow pattern** in which dipole-dipole interactions equilibrate with Stokes drag.

# Part III: Landau-Levich problem[a]




Static wetting




Dynamic wetting

$$\mu \frac{U}{\bar{h}_\infty^2} \sim \frac{\sigma / l_c}{l}, \qquad \frac{\bar{h}_\infty}{l^2} \sim l_c^{-1} \Longrightarrow \bar{h}_\infty \sim \; l_c \, Ca^{2/3} \text{ and } l \sim \; l_c \, Ca^{1/3}$$

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[a] Krechetnikov & Homsy, Phys. Fluids (2005) and JFM (2005).

# Landau-Levich problem: milestones

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*Clean* interface case:

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- Experimental prediction of $2/3$ law by Morey (1940)
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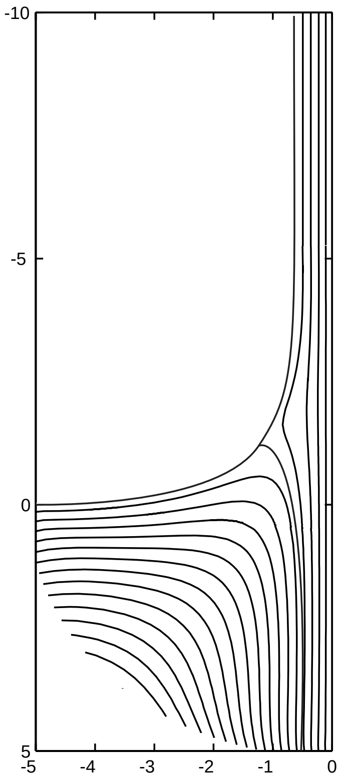
*Surfactant* interface case:

- Coating in circular tubes by Bretherton (1961)
- Coating flat substrates by Groenveld (1970)
- Fiber coating by Ramdane & Quéré (1997), Shen *et al.* (2002)
- **deviations**: film thickening

# Film thickening due to surfactants



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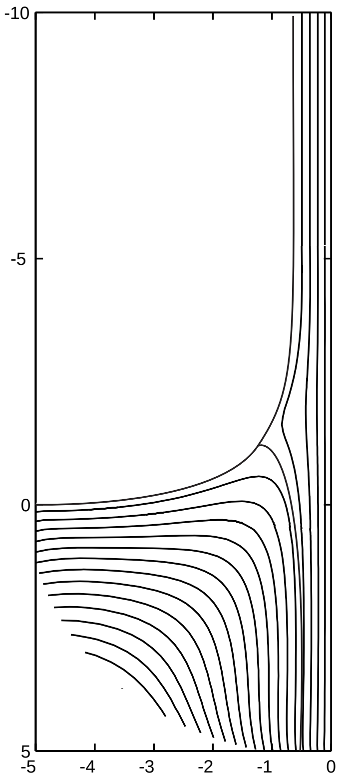


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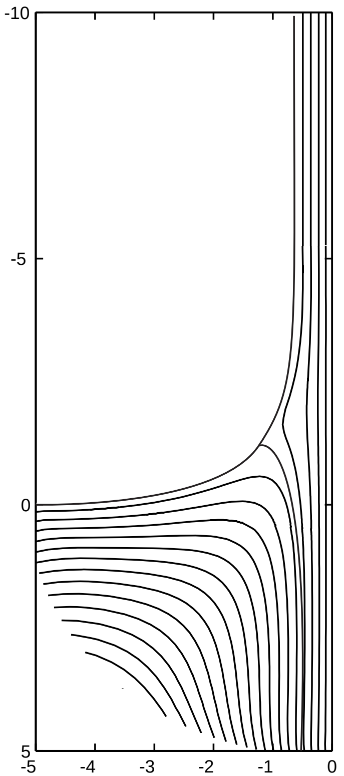


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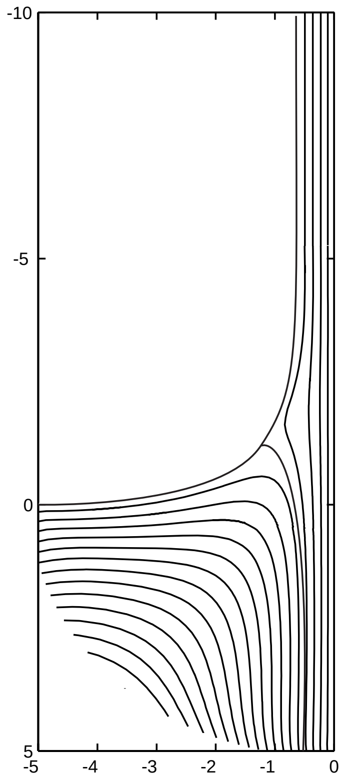


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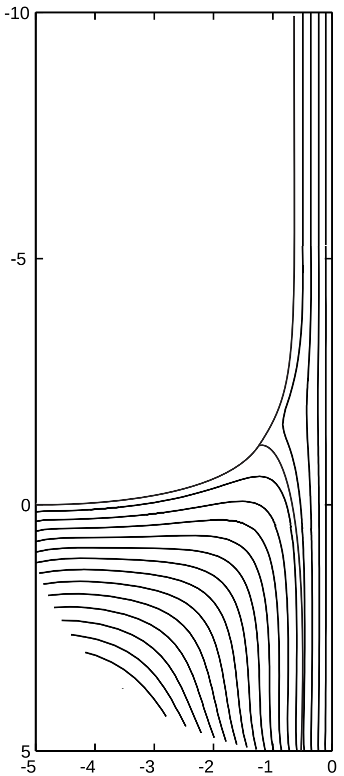


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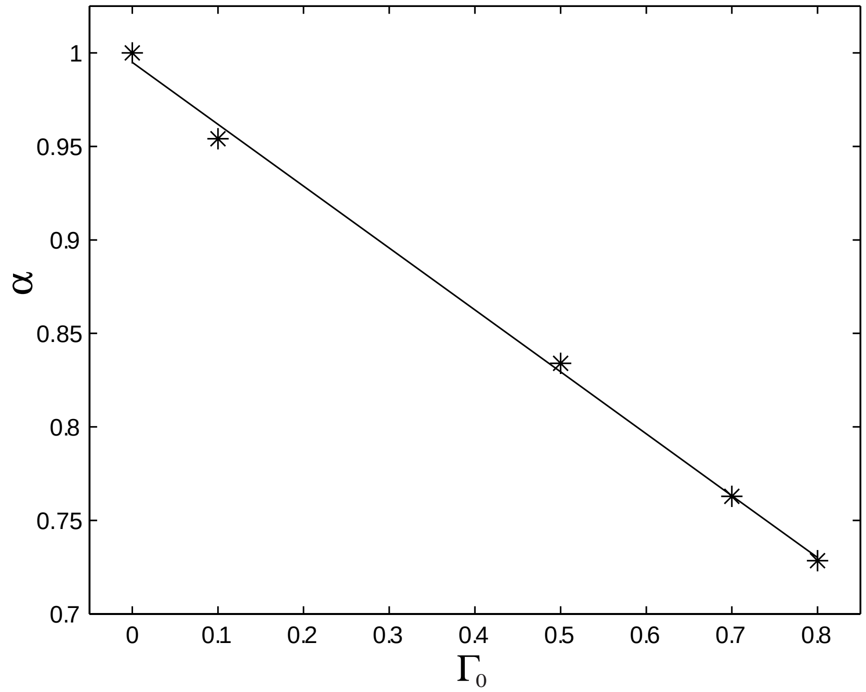
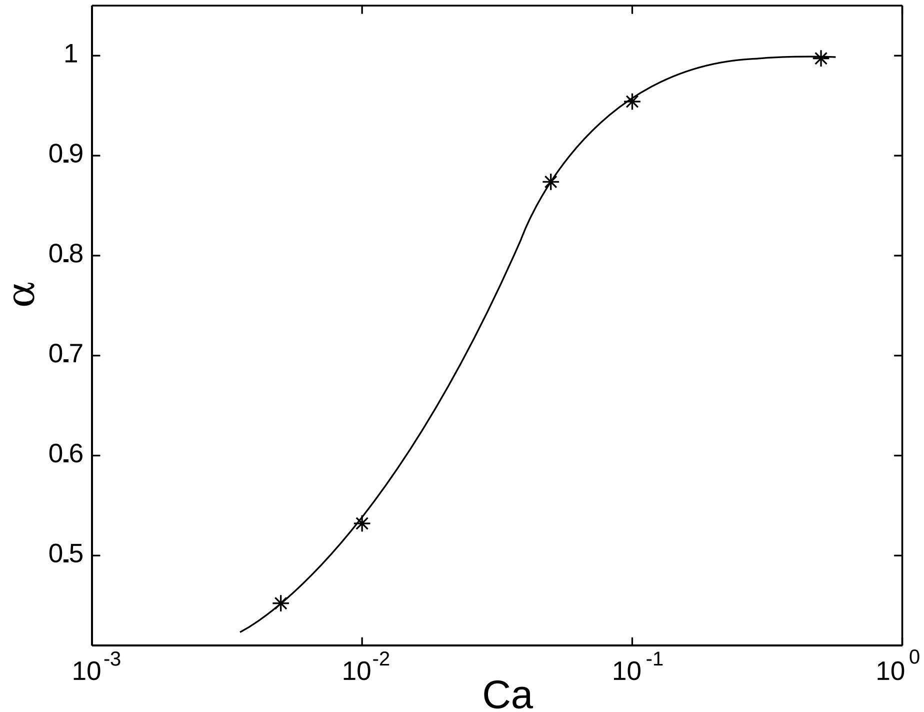
**Our goal**: to challenge the general belief and asymptotic theories.

# Theory: surfactant interface case

Thinning factor $\alpha = \overline{h}_\infty / \overline{h}_\infty^{\text{theory}}$

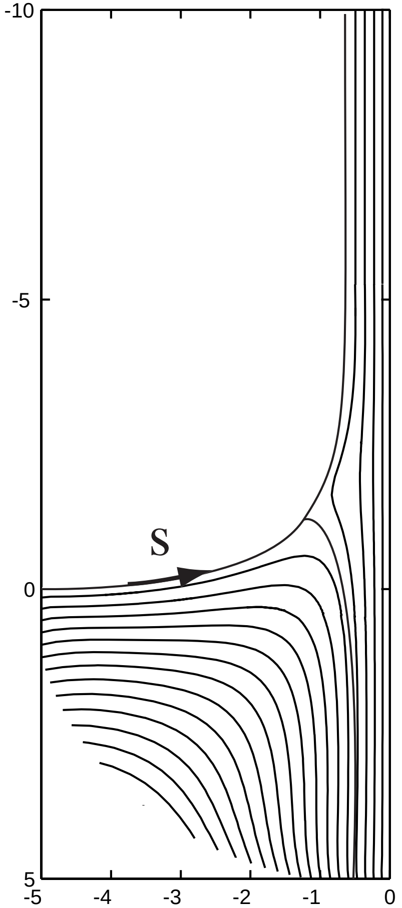


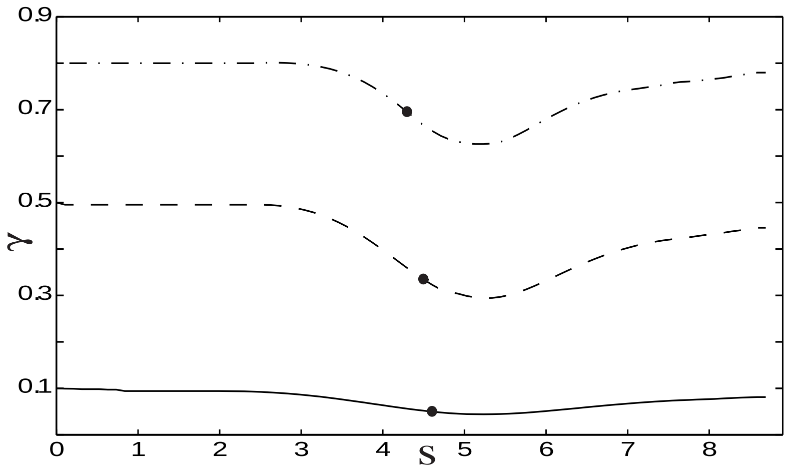




Dependence on $\Gamma_0$ for $Ca = 10^{-1}$.

Dependence on $Ca$ for $\Gamma_0 = 0.1$.

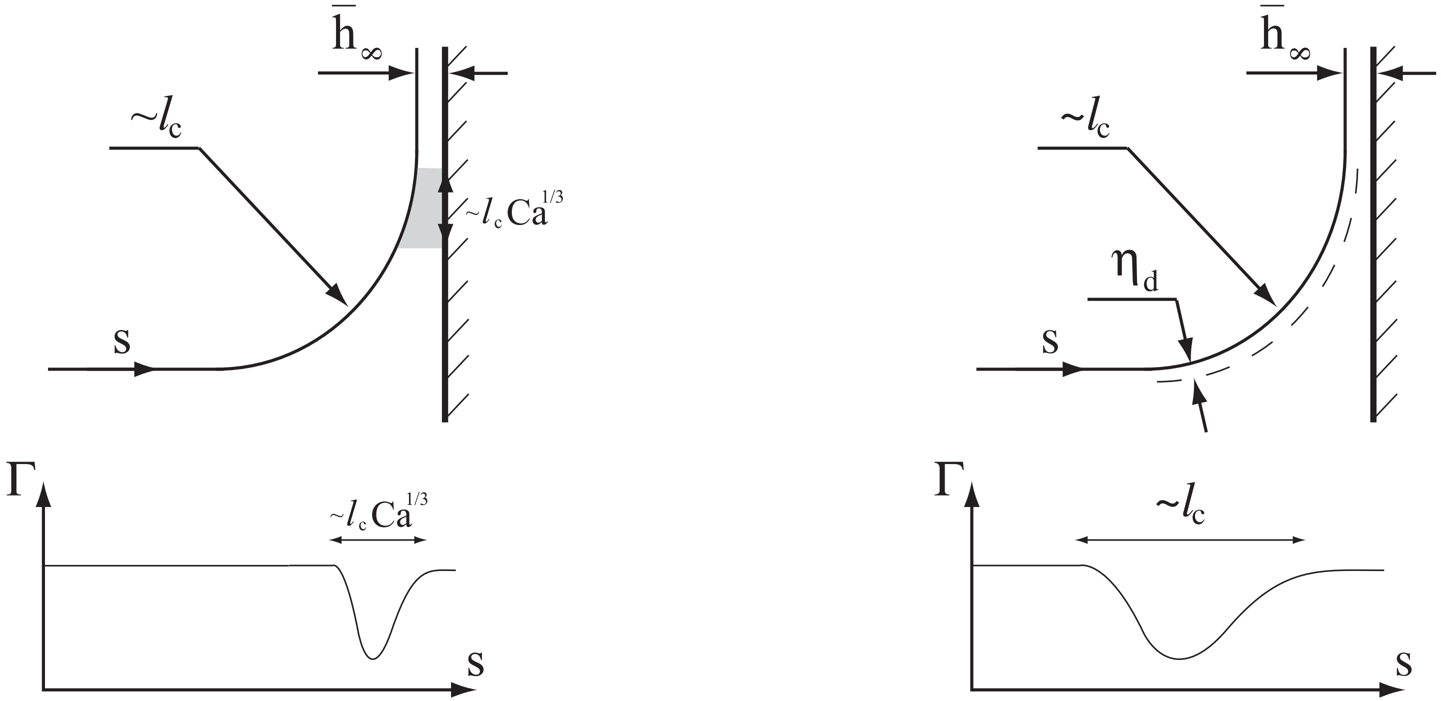
# Theory: surfactant interface case




Surfactant distribution at the interface for $Ca = 0.1$.

# What is wrong with current theories?




Standard asymptotic analysis. Fully dynamic meniscus.

- Dynamic meniscus: *time of adsorption* $t_a \sim \Gamma_m / k_a C \sim 0.2$ s is of the order of *interface stretching time* $t_v \sim l_c / U \sim 0.2$ s.
- Sorption-limited transport: sublayer is $\eta_\mathrm{d} \sim \Gamma / C \sim 1\ \mu\mathrm{m}$, thus *diffusion time* $t_\mathrm{diff} \sim \eta_d^2 / D \sim 10^{-3}\mathrm{s}$ is negligible compared to the *adsorption time* $t_a \sim 0.2$ s.

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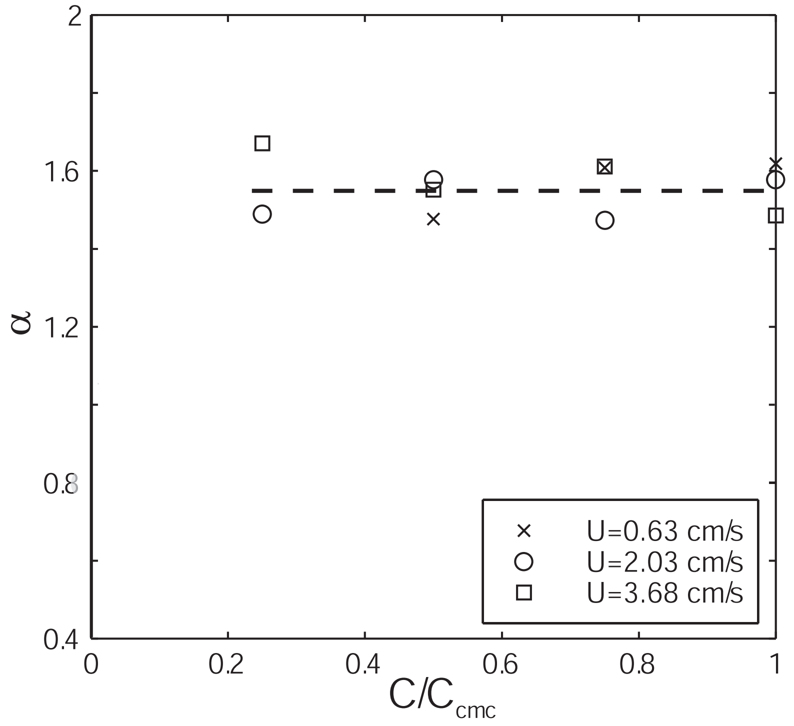
# Conclusions of our theoretical study:

- Pure hydrodynamic modelling of surfactant effect leads to film *thinning*, which contradicts the experimental facts.
- Thus, there are two options:
  - Film thickening **is** due to Marangoni effects, but there is a problem with fundamental equations, or
  - Film thickening **is not** due to Marangoni effects, and the pure hydrodynamic approach based on standard macroscopic equations is not satisfactory to explain the observations.

# Experimental study:




Film thickening factor $\alpha$.

# Is the thickening due to Maragoni?

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- As follows from the Langmuir-Hinshelwood kinetics,

$$\frac{d\Gamma}{dt} = k_a C \left(1 - \frac{\Gamma}{\Gamma_m}\right) - k_d \Gamma,$$

with $k_a = 0.64\ 10^{-5} m\ s^{-1}$ and $k_d = 5.87 s^{-1}$, Marangoni stresses become negligible if adsorption is faster than the interface stretching, *i.e.* the product $St\ \kappa > 1$, ($St = k_a/U$, $\kappa = l_c C/\Gamma_m$).

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- As the theory predicts, Marangoni stresses depend on $Ca$ (speed of withdrawal), and thus would distort the $2/3$ law.

# Indication of non-Marangoni origin

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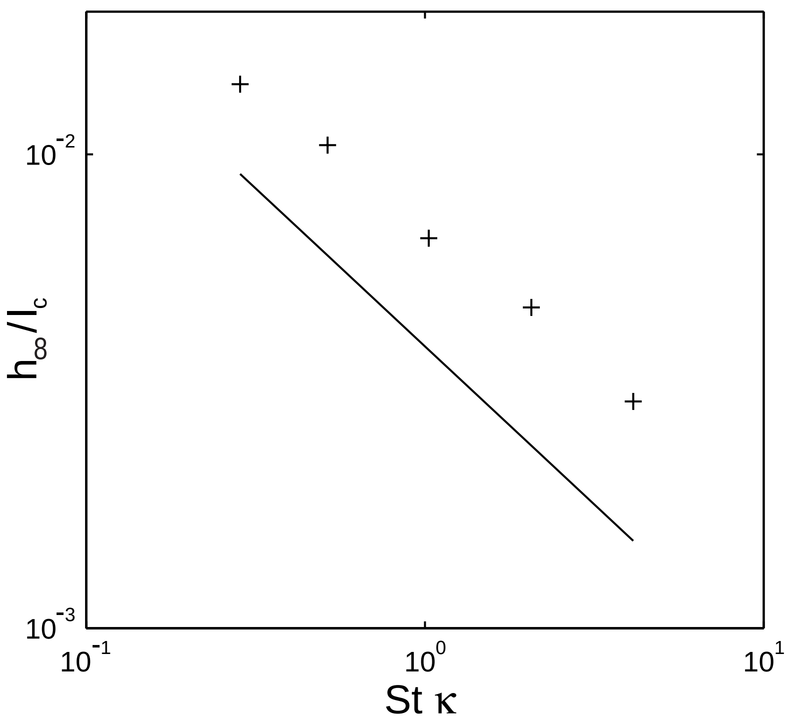


Film thickening in the case of fast adsorption.

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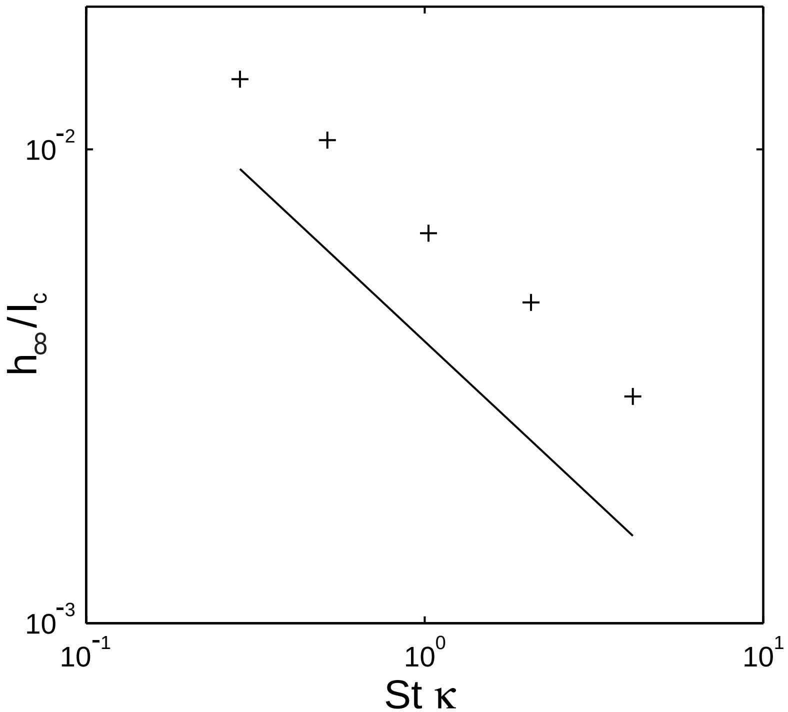


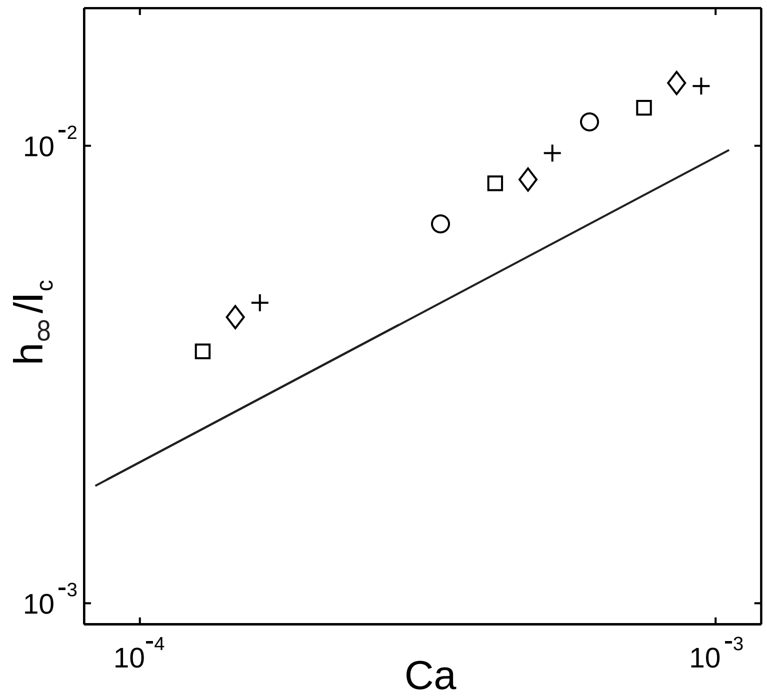


Film thickening in the case of fast adsorption.

LL law; $\circ$, $0.25$; $\square$, $0.50$; $\Diamond$, $0.75$; $+$, $1.00$ CMC.

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- Fully nonlinear theory based on a hydrodynamic modeling of surfactant effects yields *film thinning*.
- Experimental study, based on kinetic properties of surfactants, confirmed the non-Marangoni origin of the *film thickening*.
- The above controversy reveals the inconsistency of the existing asymptotic theories, and the lack of an appropriate theoretical explanation.

# References


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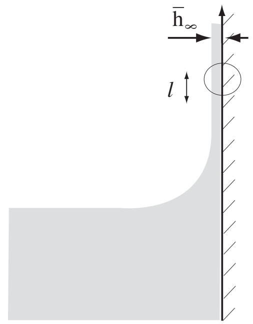
6. Krechetnikov R., Homsy G.M., *"Surfactant effects in the Landau-Levich problem,"* to appear in JFM (2006).

# The end


**Acknowledgements**: I would like to express my appreciation to *Prof. Bud Homsy* for introducing me to the great subject of interfacial dynamics, his valuable guidance and generous support.