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On the classical Landau-Levich problem

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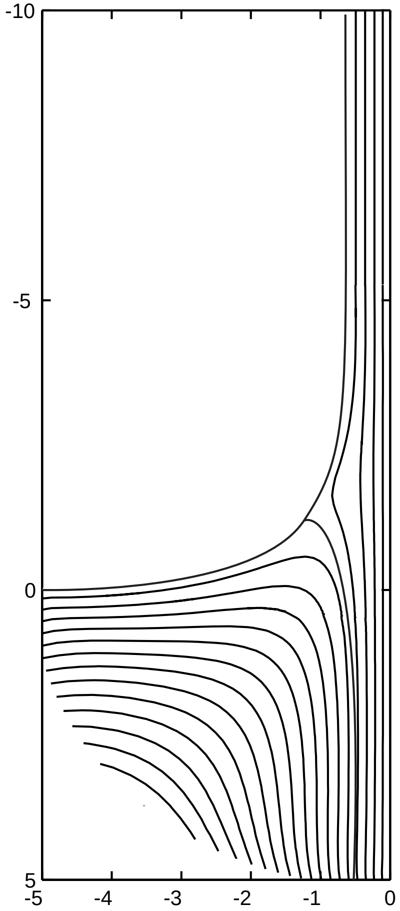
Outline:



- Problem statement and open questions
- Theoretical study and unexpected results
- Experimental study and expected results
- Conclusions

Landau-Levich problem: basic milestones

Clean interface case:

- Experimental prediction of 2/3 law by Morey (1940)
- Theoretical derivation of 2/3 law by Landau & Levich (1942)
- **deviations**: water paradox by Tallmadge & Stella (1968)

Surfactant (contaminated, polluted) 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

Conclusions

General belief:

- Thickening effect is of a purely hydrodynamic nature – the Marangoni stresses pump additional mass flux into the film, Quéré (1999).

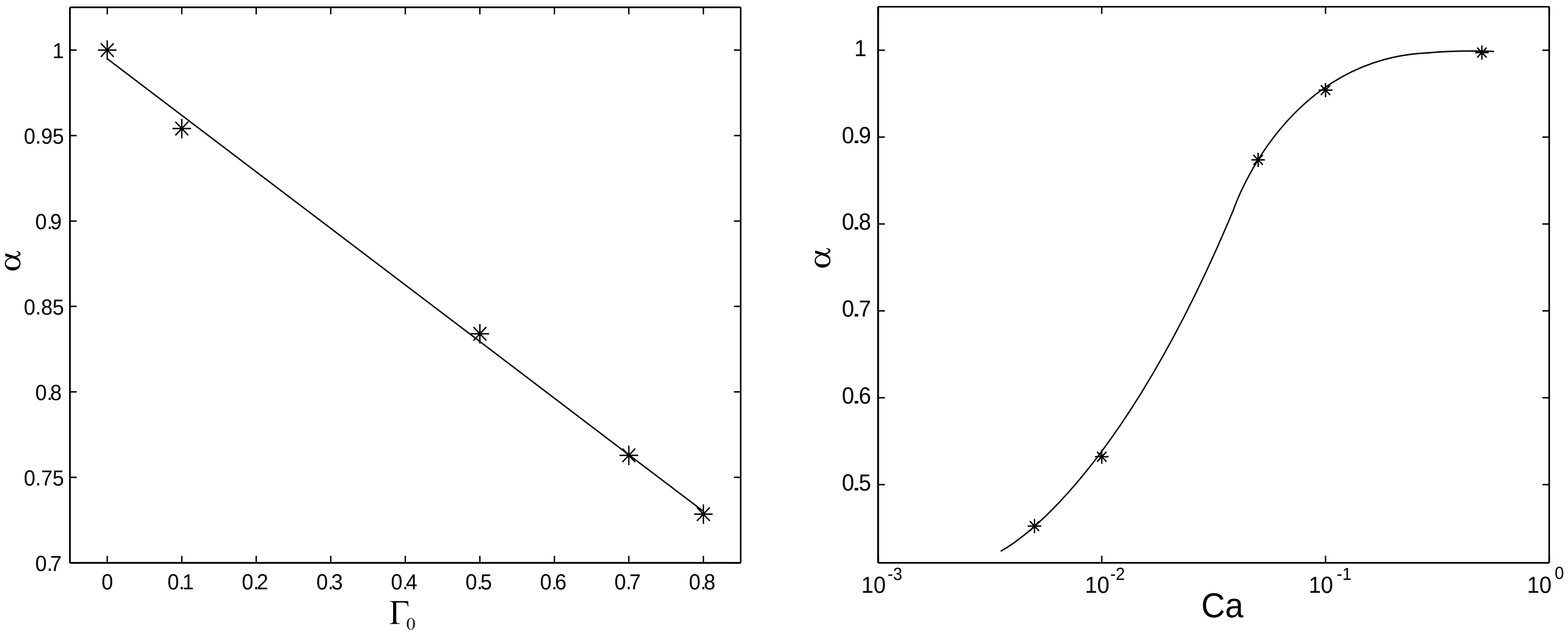
Observation:

- the common feature of all experiments is the occurrence of very thin films, $\overline{h}_\infty \leq 20\mu$, for which the thickening is observed.

Conclusion:

- there is no convincing theory and definitive set of experiments to confirm the viewpoint that the observed thickening is due to Marangoni stresses.

Theoretical study: surfactant interface case



(a) Dependence on Γ_0 for $Ca = 10^{-1}$. (b) Dependence on Ca for $\Gamma_0 = 0.1$.

Figure 1: Thinning factor $\alpha = \overline{h}_\infty / \overline{h}_\infty^{\text{theory}}$.

Theoretical study: surfactant interface case

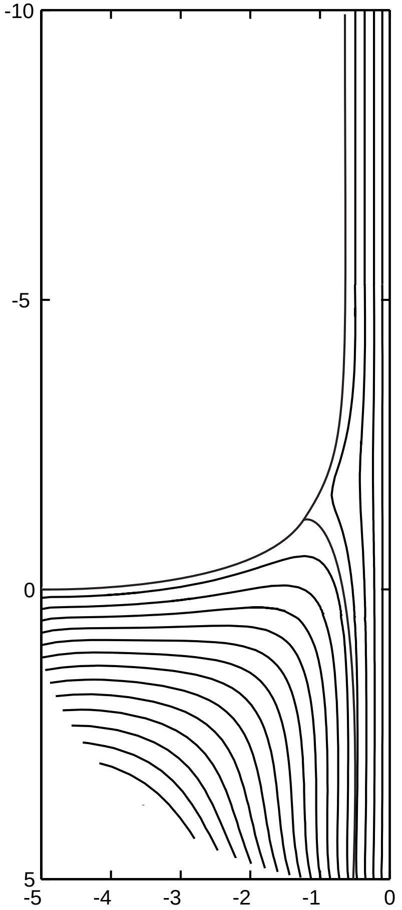


Figure 2: Flow pattern.

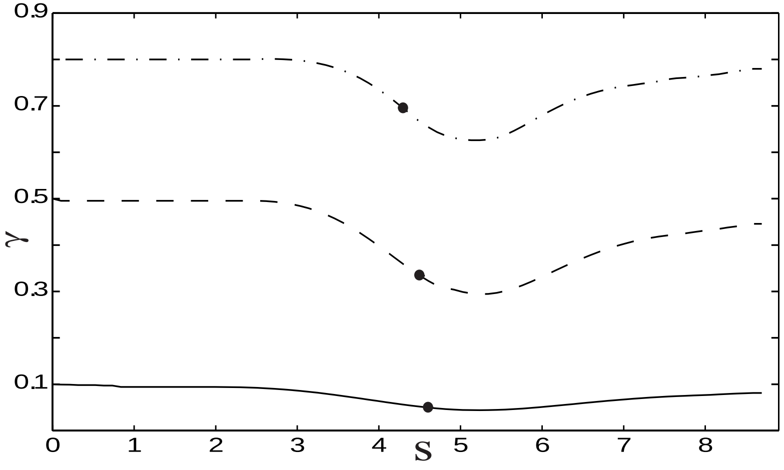


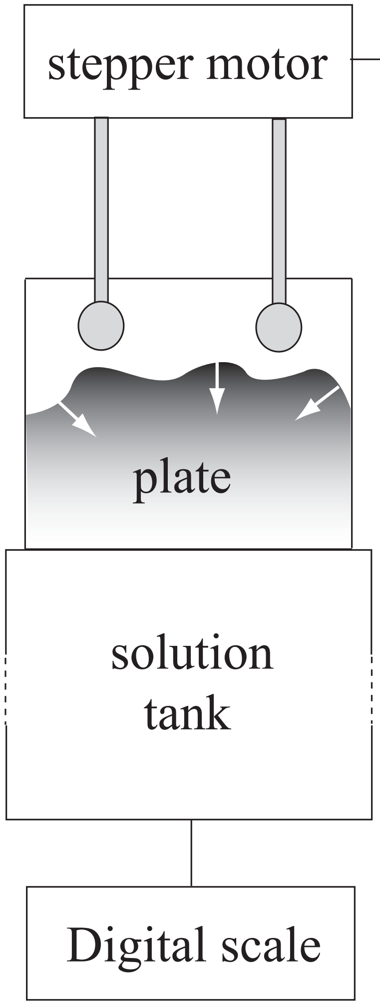
Figure 3: Surfactant distribution along the interface for $Ca = 0.1$

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(\gamma\psi_n\right) = \frac{1}{Pe_s}\frac{\mathrm{d}^2\gamma}{\mathrm{d}s^2} + j.$$

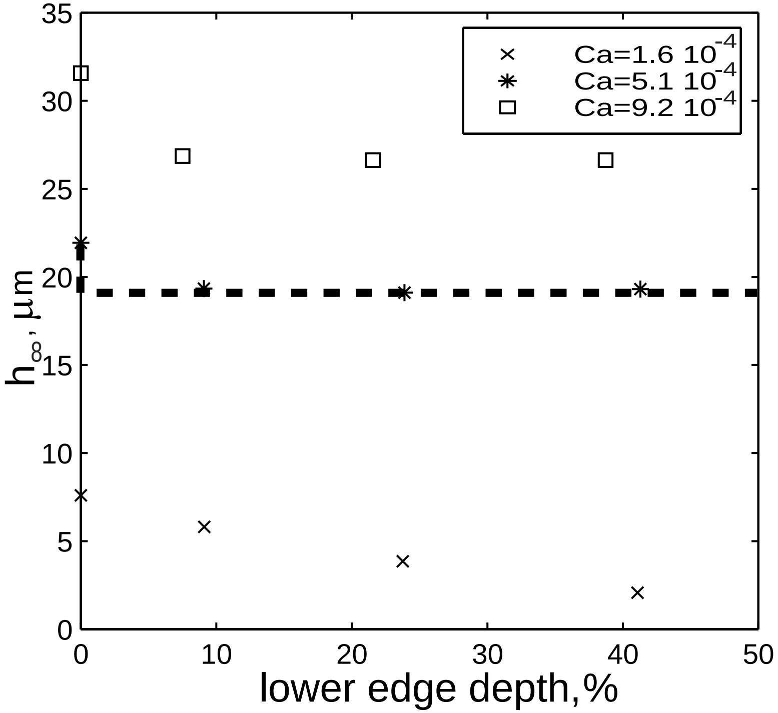
Conclusions:

1. Pure hydrodynamic modelling of surfactant effect leads to film *thinning*, which contradicts the experimental observations.
2. Thus, there are two options:
    - There is a problem with fundamental equations, or
    - The pure hydrodynamic approach is not satisfactory to explain the observations, and the model should be extended to include microscopic phenomena.

Experimental study: set-up and procedure

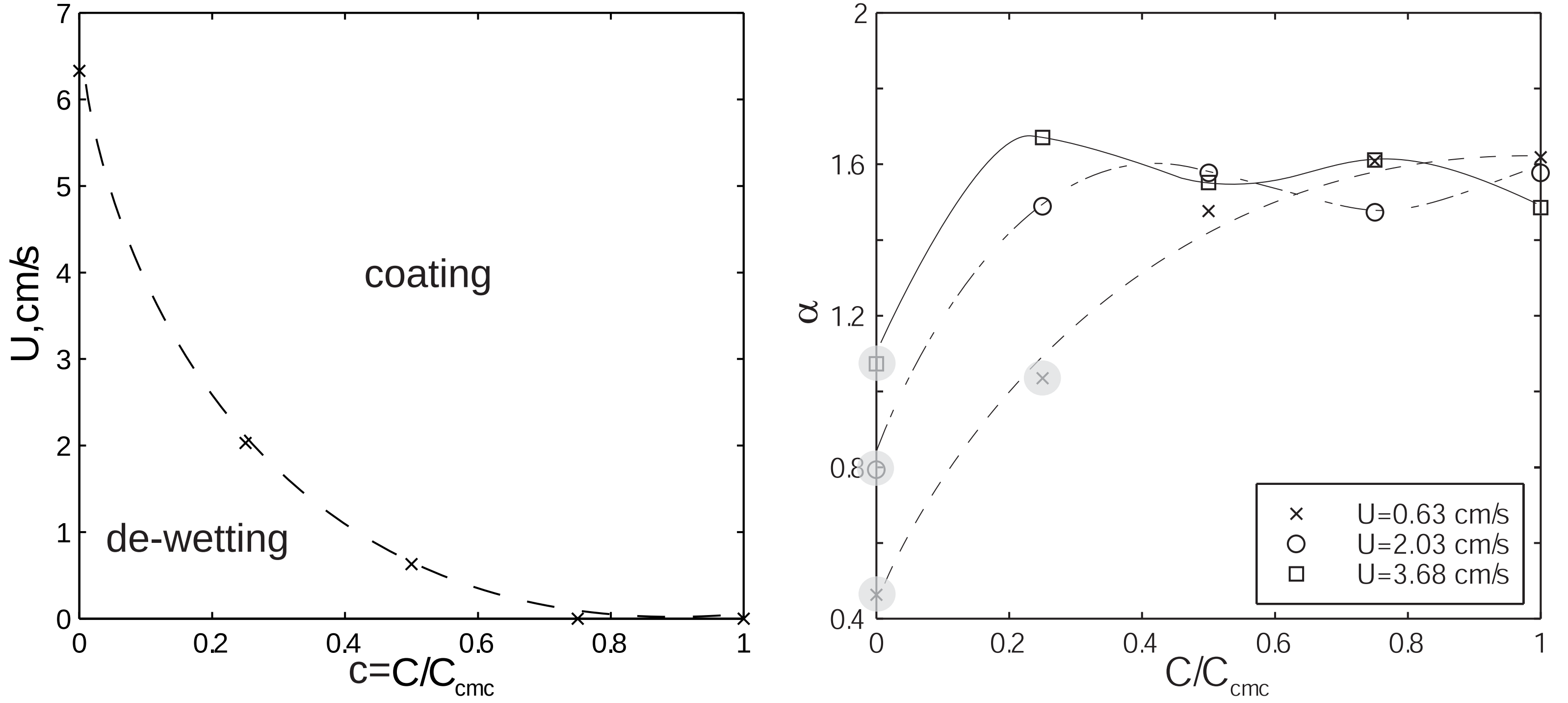


Lower edge effect:



$$h = \left(\frac{\delta m}{N} - \frac{\delta m'}{N'} \right) \frac{1}{2\,(l - l')\,w\rho}.$$

Experimental study: measurability and thickening



(a) Transition curve: dimensional.

(b) Thickening factor α.

Is the thickening due to Maragoni?

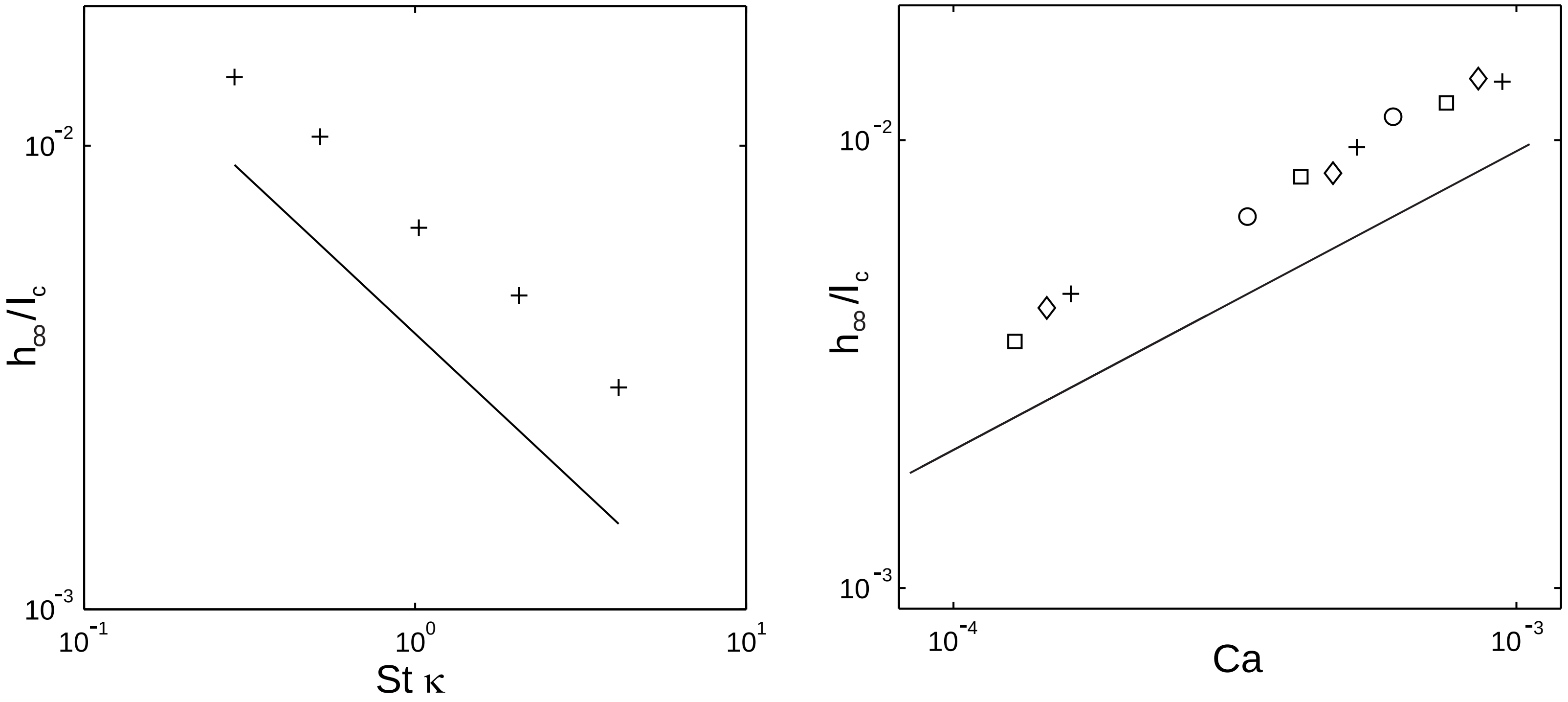
- As follows from Langmuir-Hinshelwood kinetic equation,

  $$\frac{d\Gamma}{dt} = k_a C(1-\theta) - k_d \Gamma, \quad \text{with } k_a = 0.64\ 10^{-5} m\ s^{-1},\ k_d = 5.87 s^{-1},$$

  Marangoni stresses become negligible if the product $St\ \kappa$ is above unity ($St = k_a/U$, $\kappa = d\ C/\Gamma_m$).

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

Proof



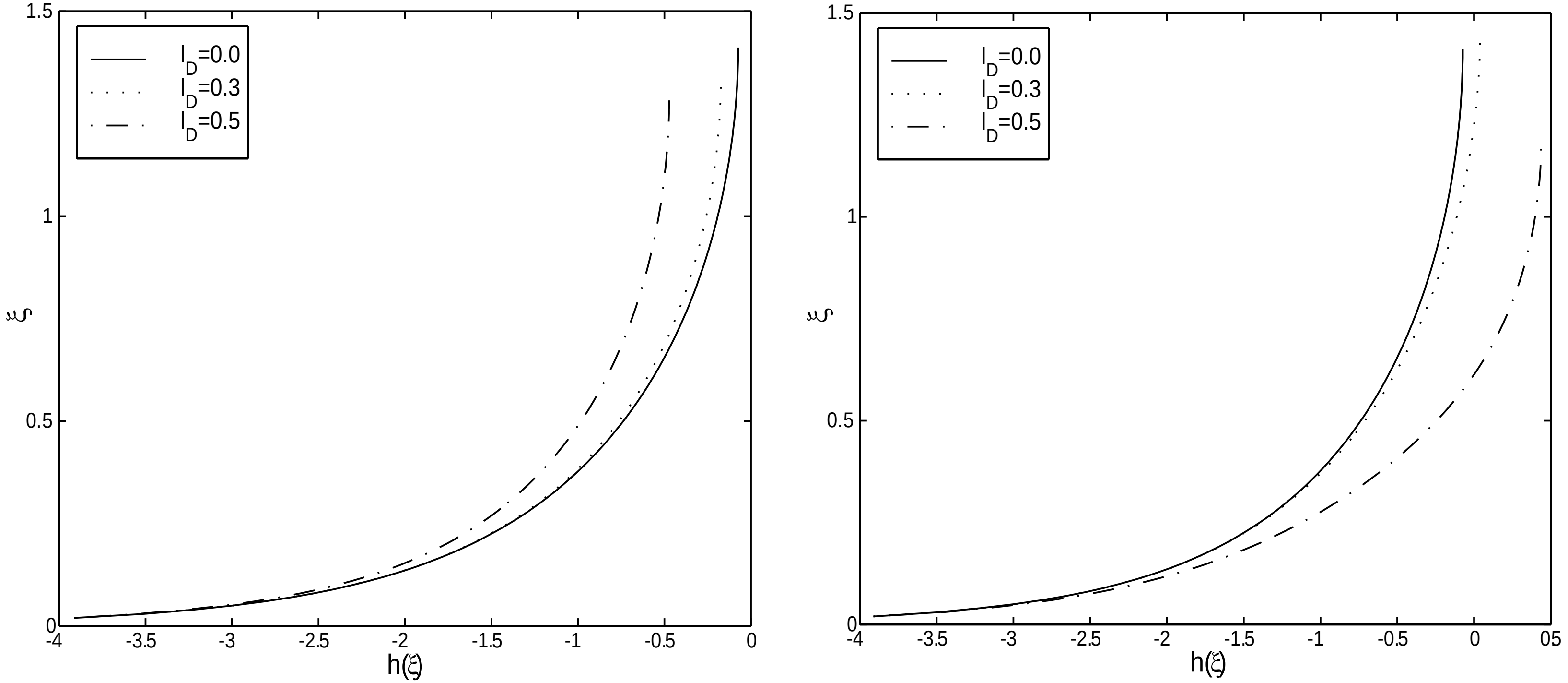
(c) Film thickening in the case of fast adsorption.

(d) Landau-Levich law; ○, 0.25; □, 0.50; ◇, 0.75; +, 1.00 CMC.

Possible effects

- adsorbed surfactant layer as an effective rough surface
- changes of rheological properties
- disjoining pressure – the interaction of the liquid (or solution) and substrate through London-van der Waals forces $\sim 0.03\mu$m, diffuse double layers $l_D \sim 0.3$ μm, and structural forces. *However, their strong effect on the film stability was found by Padday (1970) experimentally at very great thicknesses,* 10^{-2} *cm.*

Landau-Levich model with extra body force



(e) attractive interaction; $\lambda_0 = 1.0$.

(f) repulsive interaction; $\lambda_0 = 1.0$.

Basic result: non-Landau-Levich matching procedure.

Conclusions

- Fully nonlinear theory based on purely hydrodynamic modelling of surfactant effects yields *film thinning*.
- Elaborate experimental study, based on kinetic properties of surfactants, confirmed non-Marangoni origin of the *film thickening*.
- Thus we were led to consider the alternative explanations and the extra body force seems to be the only convincing option at this time.

Dip-coating of rough surfaces

Characterization

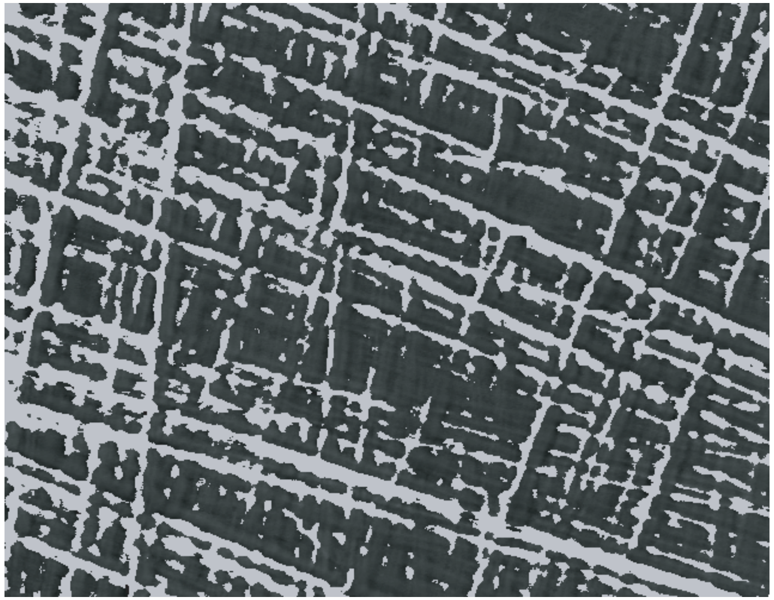


Figure 4: 230 μm × 300 μm.

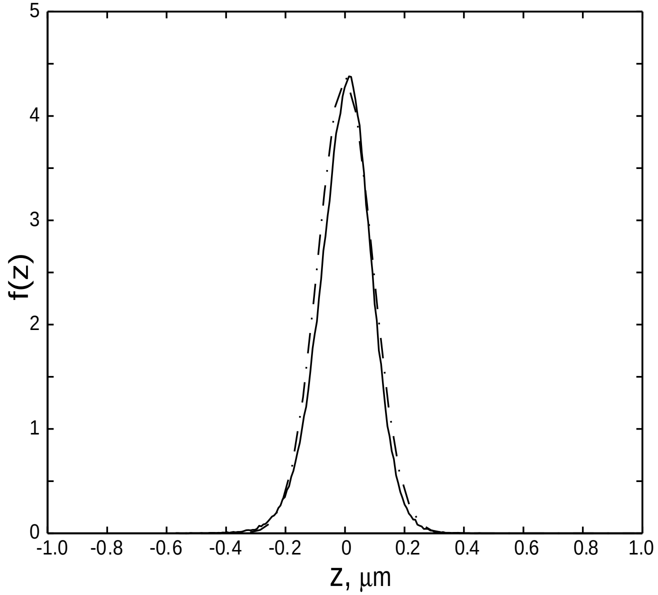
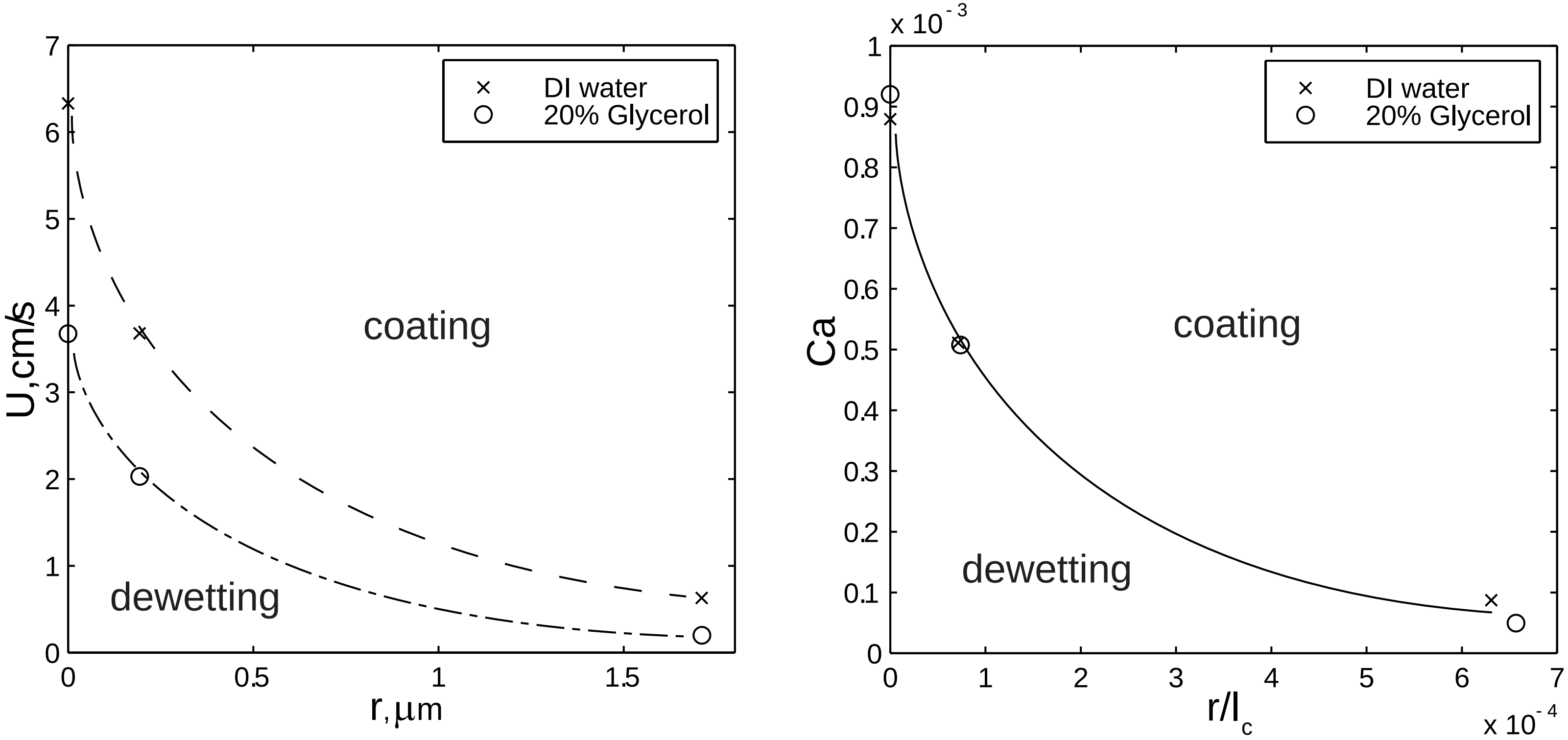


Figure 5: PDF of roughness z.

$$f(z) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(z-\overline{z})^2/2\sigma^2},\ \overline{z} = \frac{1}{n}\sum_{i=1}^{n} z_i \equiv \langle \mathbf{z} \rangle, \sigma^2 = \left\langle (\mathbf{z}-\overline{z})^2 \right\rangle.$$

On measurability of the Landau-Levich law



(a) dimensional space (b) scaled variables

Stabilization effect : $S_{\text{eff}} = (\alpha_s - 1)\sigma + \alpha_s S,\ S \equiv \sigma_{sg} - \sigma_{sl} - \sigma$

Dynamic effect of roughness: $Ca^{0.6}$ vs. $Ca^{2/3}$

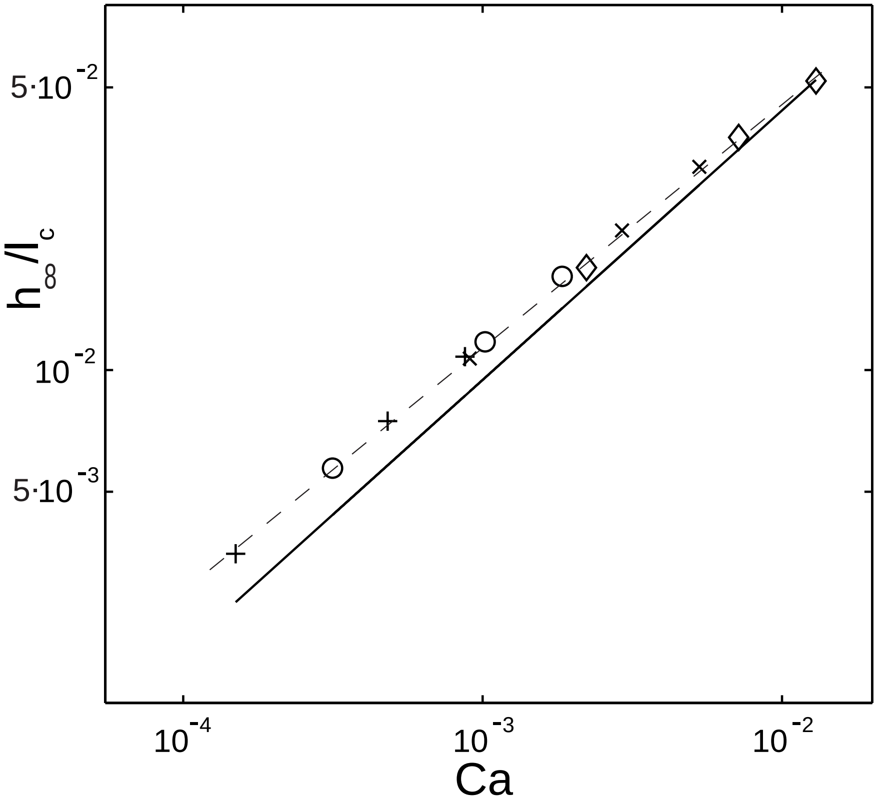


Figure 6: Thickness of film deposited on a roughened substrate.

A simple model: motivation

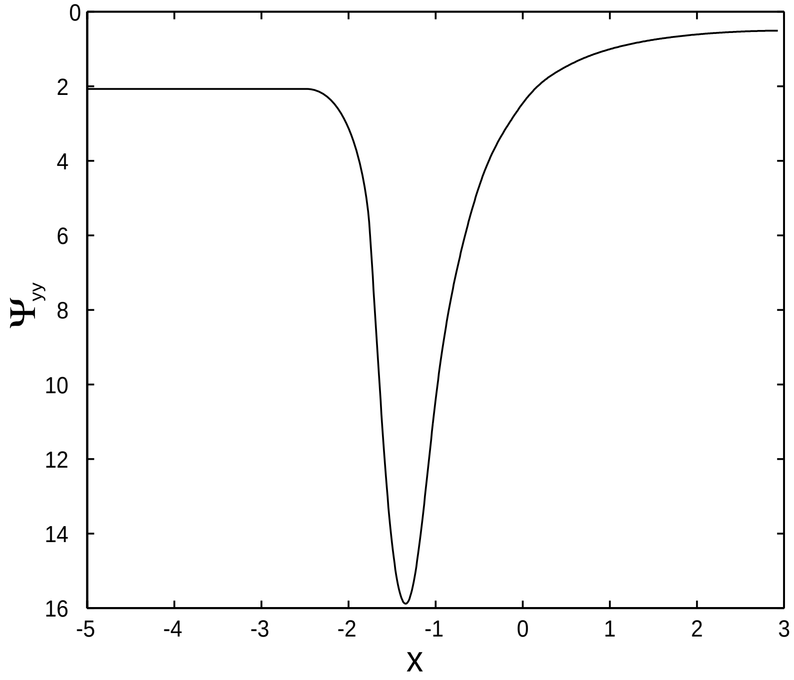
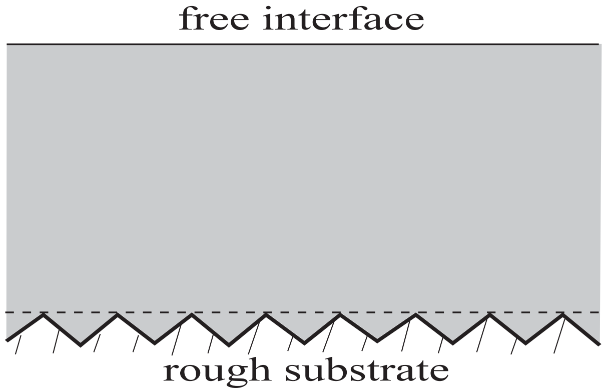
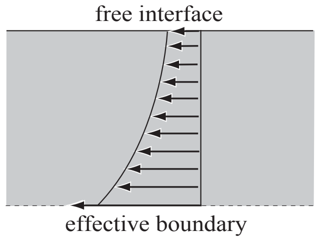


Figure 7: Shear distribution



(a) True situation.



(b) Eff. slip

(c) Grooves

$$y = 0: \ \psi_y = -1 + l\psi_{yy},$$

A simple model: results

With transformation $x \to \beta\widetilde{x},\ h \to h_\infty \widetilde{h}$;

$$\widetilde{h}_{\tilde{x}\tilde{x}\tilde{x}}\widetilde{h}^3 - \beta(\widetilde{h}^3 - 1) + 3\frac{Ca}{\beta^3}(\widetilde{h} - 1) + 3l\frac{1 - \widetilde{h}^2}{\beta} + 3l\frac{\widetilde{h}^2\widetilde{h}_{\tilde{x}\tilde{x}\tilde{x}}}{\beta^2} = 0.$$

- Therefore, if $l \ll Ca^{2/3}$ one gets $\beta \sim Ca^{1/3}$, *i.e.* the L.-L. law;
- If $l \gg Ca^{2/3}$ then $\beta \sim \sqrt{l}$ and a law independent of the capillary number as indicated at the beginning of this subsection.
- In the intermediate regime, $l \sim Ca^{2/3}$ all terms in the above general equation are important.

Conclusions: surfactant *vs.* roughness

Exceptional stability is observed for

1. a film substantially contaminated with surfactant, or
2. a film deposited on a rough glass substrate, even though rms is much smaller than the film thickness.

Film existence is dictated by the energies of **film interaction with**

- **the substrate** (affected by the nature of the liquid and substrate and can be amplified by roughening the liquid-solid interface, and/or by introducing surfactants);
- **gravity** (usually destabilizing since it drives the film drainage)
- **itself** (primarily a manifestation of surface tension forces which tend to minimize the interfacial area.)