Dr.-Ing. Sascha Heitkam,

Insitute for Process Engineering and Environmental Technology

Lecture 5: Films

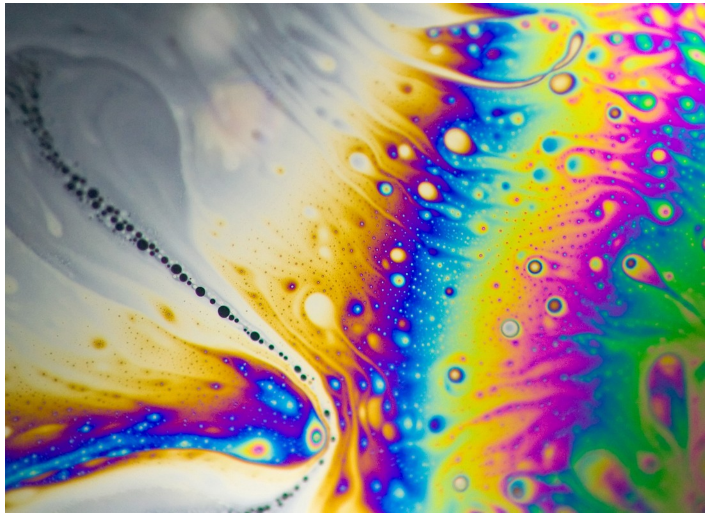
Structure

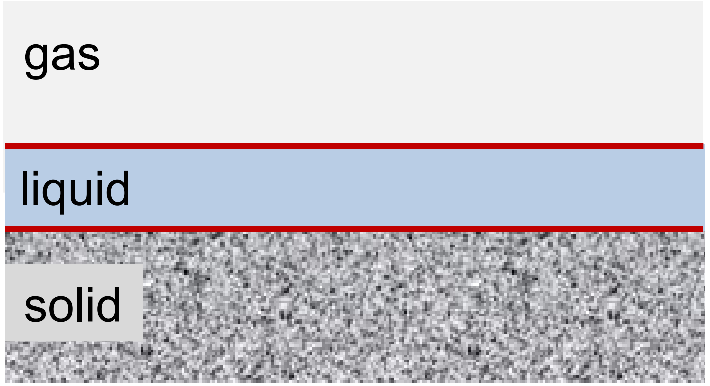
- Film drainage
- Film stability
- Film measurement techniques

What is a film/lamella

- Thin layer of liquid, bounded by air or solid
- Two interfaces!
- Relevant for bubble/droplet coalescence, break-up
- Relevant for foam/froth stability

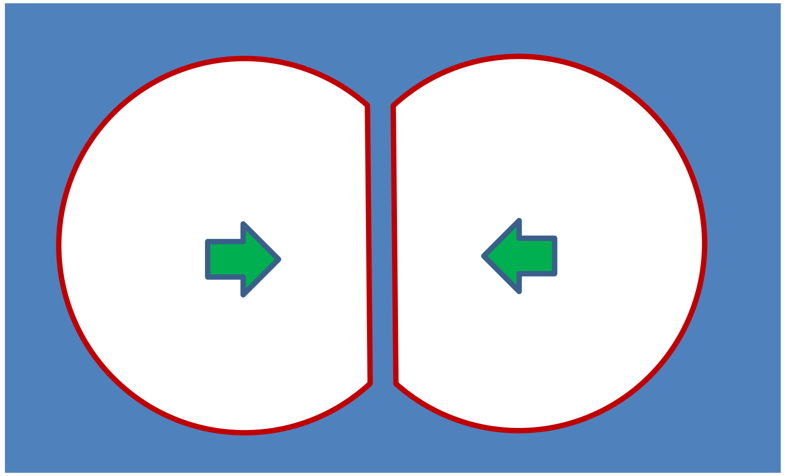
- Relevant for lubrication, wetting, cleaning

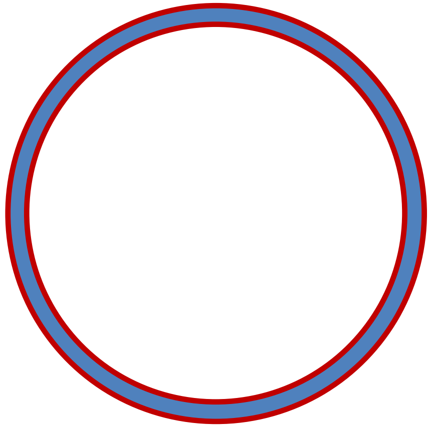


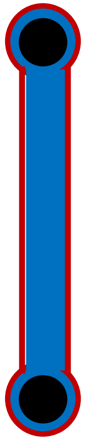


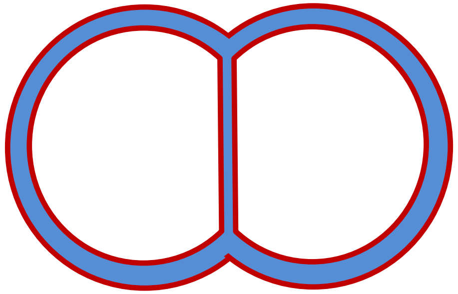
Film Topology

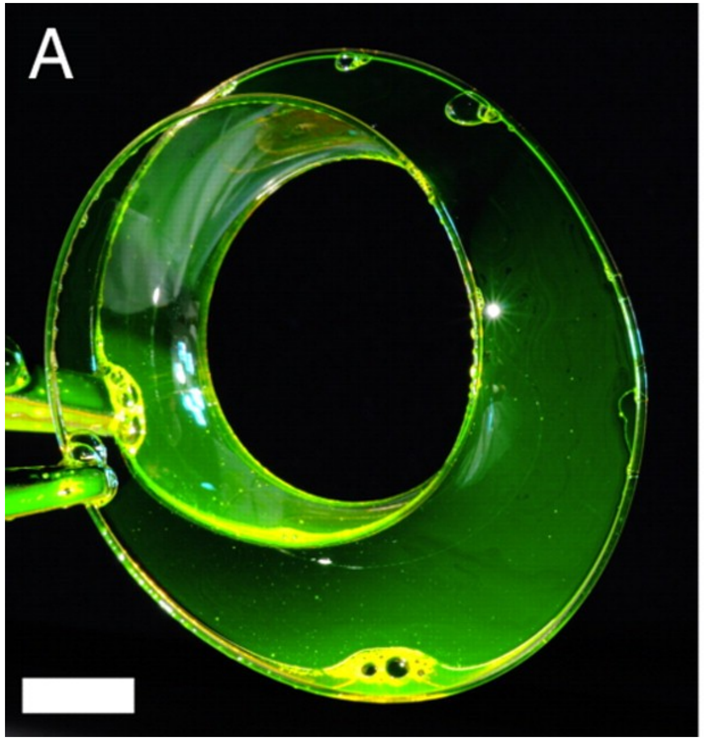
- Films can be a „closed surface“ or a „surface with boundary“
- Möbius strips are possible [Goldstein et al., PNAS, 2010]





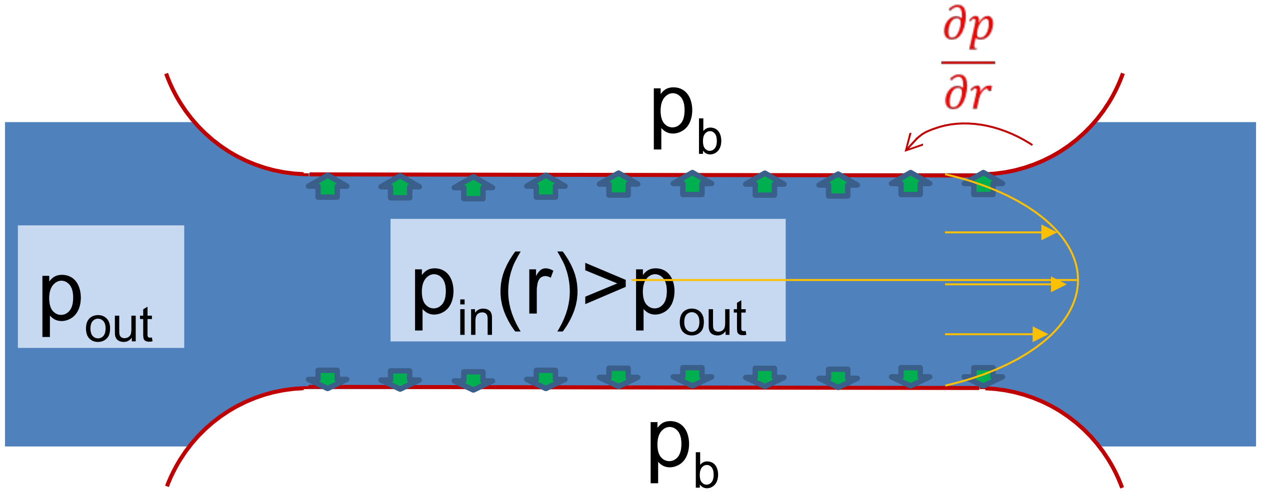


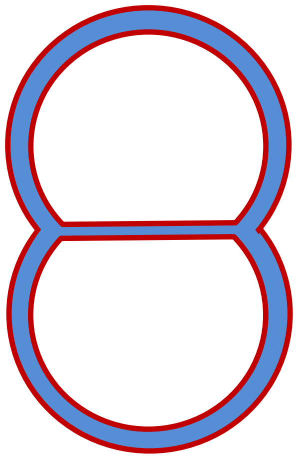




Film thinning

- Pressure inside the film is larger than outside
- → Pressure gradient drives drainage flow





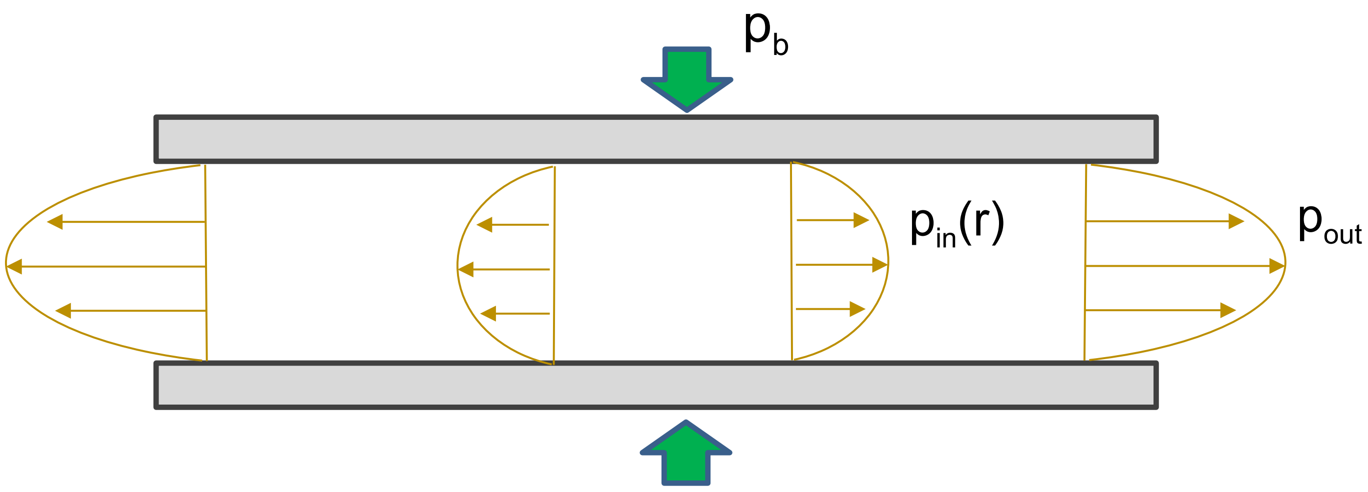
$$p_{in} > p_{out}$$

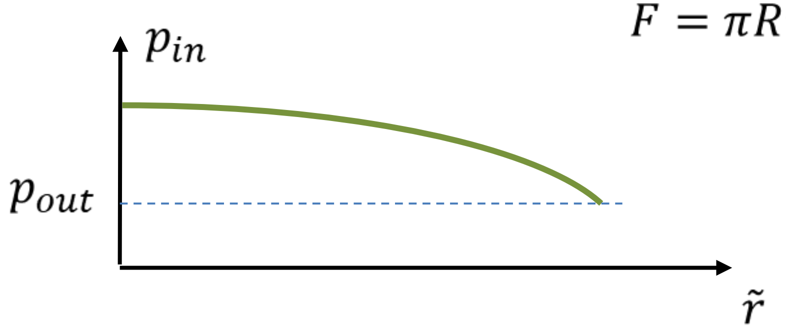
$$p_{in}(\tilde{r}) = p_{out} + \int_R^{\tilde{r}} \frac{\partial p}{\partial r} dr$$

Pressure loss due to viscous flow

Film thinning

- Reynolds equation from lubrication theory
- Assumptions: developed flow (Hagen-Poiseuille), no-slip boundary, constant thickness





$$\dot{V}(r) = \frac{\partial h}{\partial t} \pi r^2$$

Hagen-Poiseuille: $$\dot{V} = \frac{h^3 b}{12 \eta l} \Delta p$$

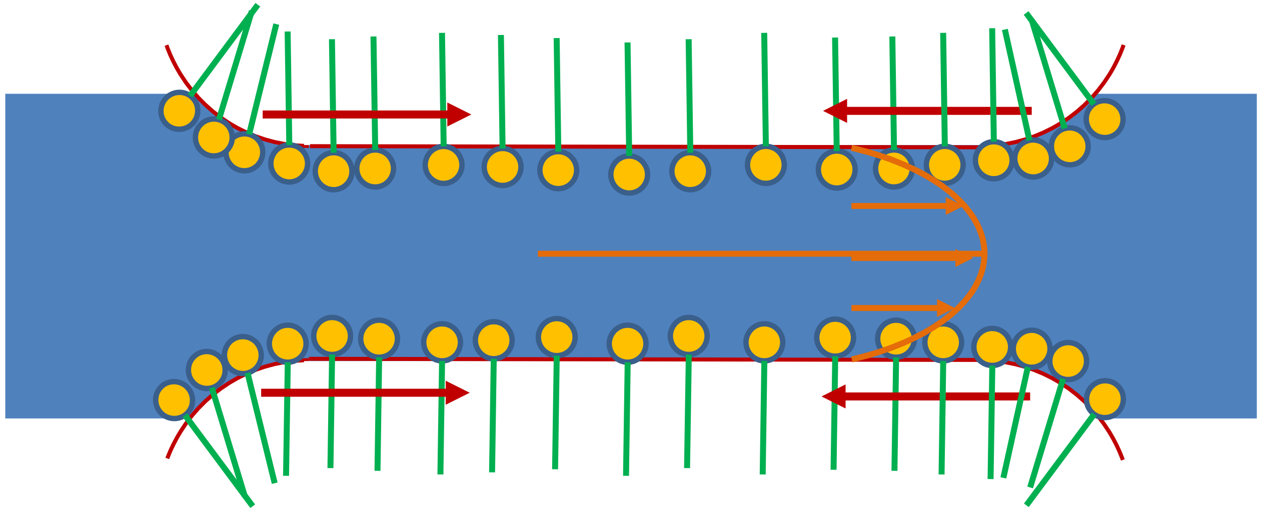
$$\dot{V} = \frac{h^3 \pi r}{12 \eta} \frac{dp}{dr}$$

$$F = \pi R^2 (p_b - p_{out}) = \int_0^R (p_{in}(r) - p_{out})\, 2\pi r\, dr$$

$$-\frac{\partial h}{\partial t} = \frac{2h^3 (p_b - p_{out})}{3 \eta R^2}$$

No-slip boundary condition?

- Free-slip would yield very high drainage flow
- Surfactants are driven outwards by drainage flow
- → Marangoni stress → redistributes surfactants
- → Marangoni stress counteracts drainage flow

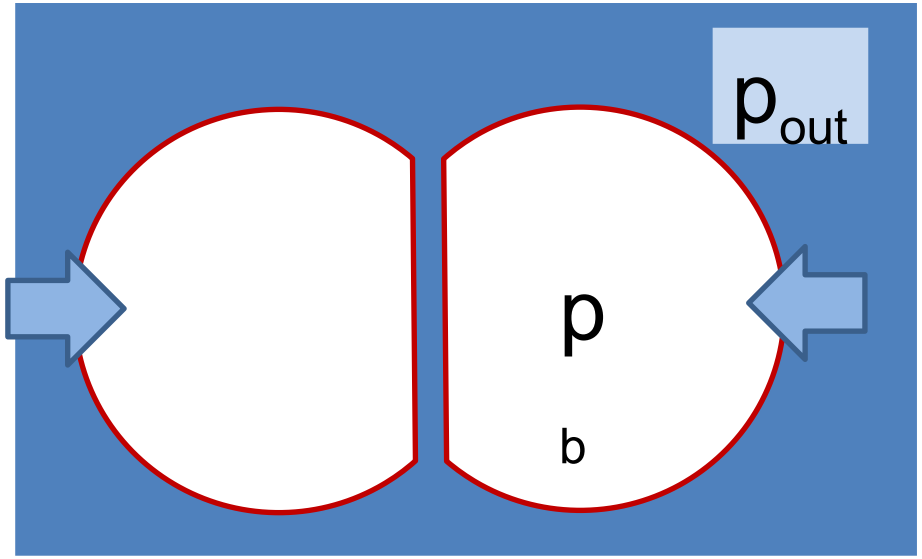


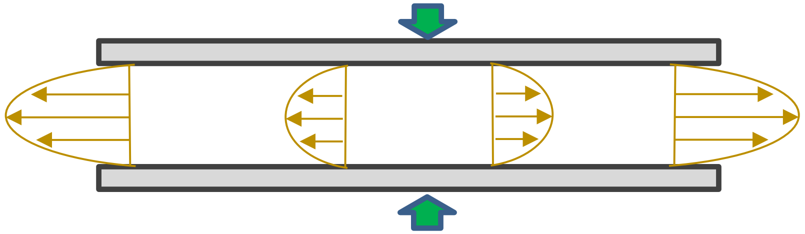
Exercise: film thinning

- How long does it take for a lamella to drain to Common Black Film thickness (50 nm)?
- Circular lamella, 5mm diameter, initial lamella thickness of 1mm
- Bubble radius of 5 mm, surface tension: 40 mN/m

$$-\frac{\partial h}{\partial t} = \frac{2h^3(p_b - p_{out})}{3\eta R^2}$$

$$-\frac{1}{h^3}dh = \frac{2(p_b - p_{out})}{3\eta R^2}dt$$





Exercise: film thinning

- How long does it take for a lamella to drain to Common Black Film thickness (50 nm)?
- Circular lamella, 5mm diameter, initial lamella thickness of 1mm
- Bubble radius of 5 mm, surface tension: 40 mN/m

$$(p_b - p_{out}) = \frac{2\gamma}{r_b} = 16\ Pa$$

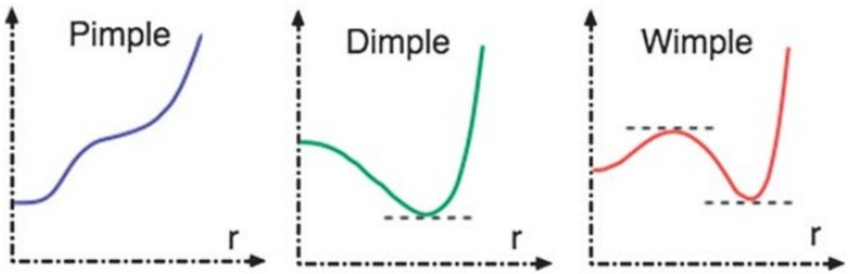
$$-\frac{\partial h}{\partial t} = \frac{2h^3(p_b - p_{out})}{3\eta R^2}$$

$$-\frac{1}{h^3}dh = \frac{32\ Pa}{3\eta R^2}dt$$

$$\int_{h0}^{hCBF} -\frac{1}{h^3}dh = \int_0^T \frac{32\ Pa}{3\eta R^2}dt$$

$$T = \frac{3\eta R^2}{32\ Pa}\frac{1}{2}\left(\frac{1}{h_{CBF}{}^2} - \frac{1}{h_0{}^2}\right) = 1.1 \cdot 10^5 s\ \approx 1.3 day$$

- Typically much faster because:
- Inhomogeneous thickness
- Semi-slip boundary conditions

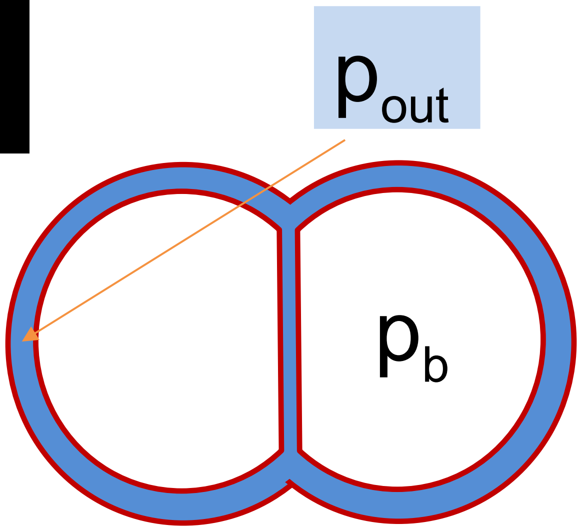


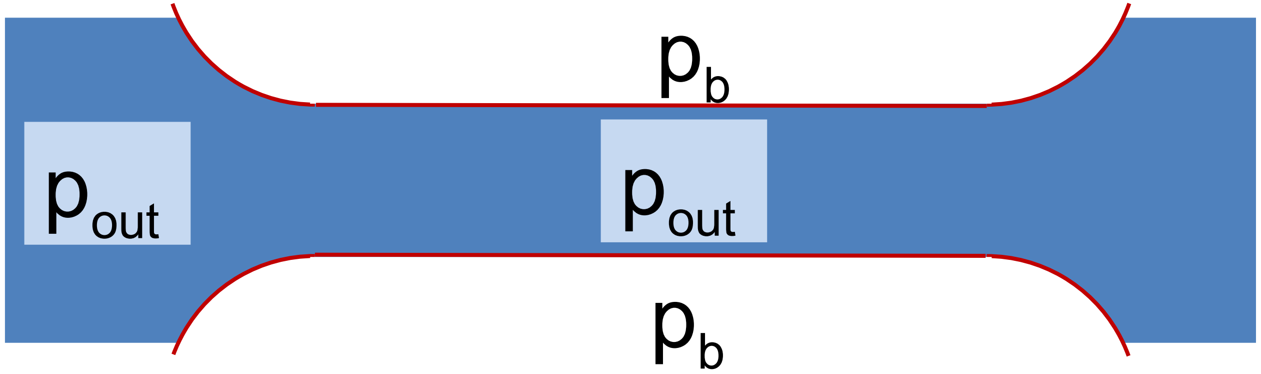
Structure

- Film drainage
- Film stability
- Film measurement techniques

What about Young-Laplace?

- Curved interface → bubble pressure p_b > liquid pressure p_{out}
- Interface at film is not curved
- What is the pressure inside the film?



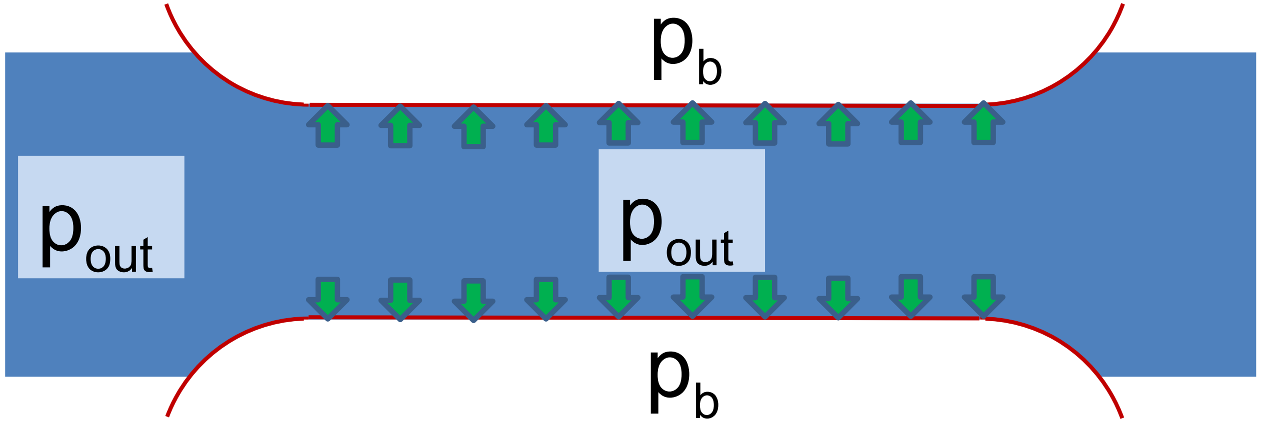


Bubble: $$p_b = p_{out} + 2\gamma H = p_{out} + \frac{2\gamma}{R}$$

Film: $$H = 0 \rightarrow p_b = p_{out}?$$

Disjoining pressure

- Repelling force between opposing interfaces
- Keeps the interfaces at distance
- Very low range → thin films

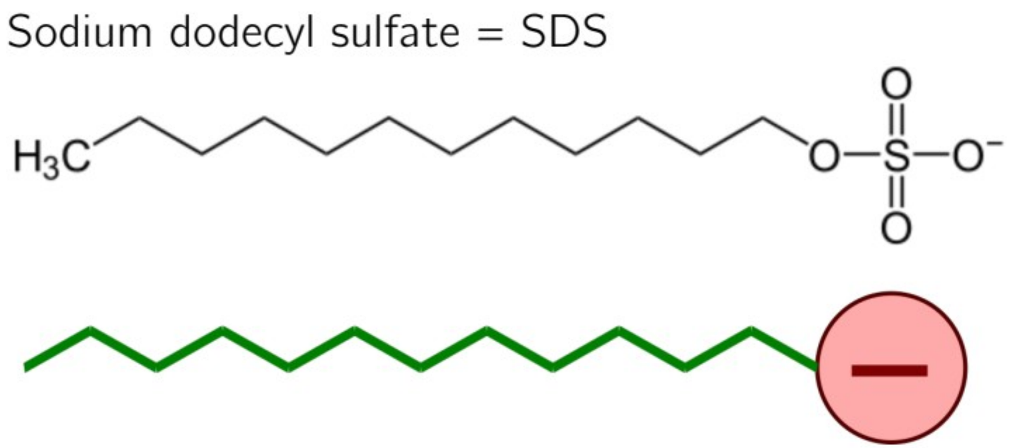


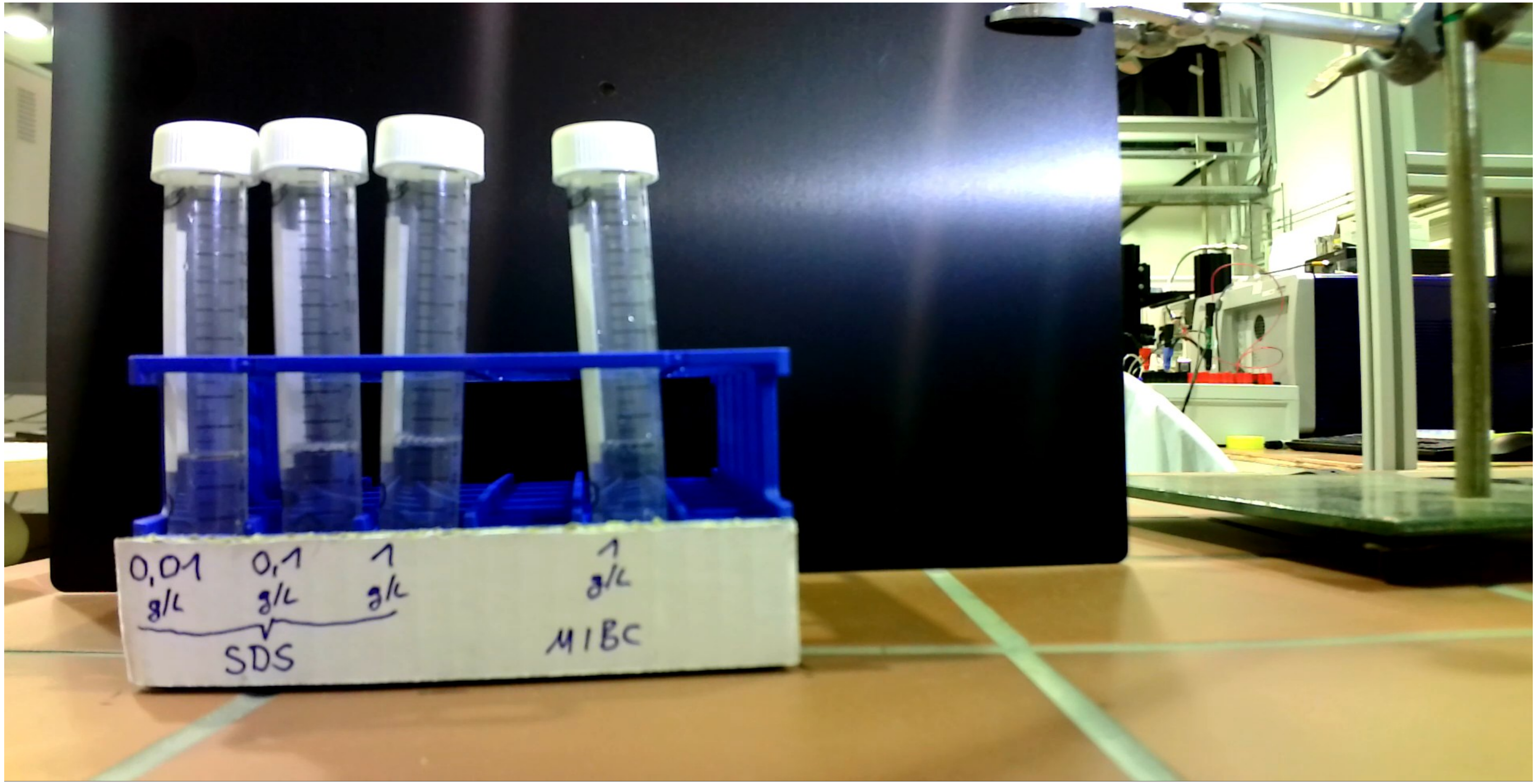
Bubble: $p_b = p_{out} + 2\gamma H = p_{out} + \frac{2\gamma}{R}$

Film: $H = 0 \ \rightarrow p_b = p_{out} + \Pi$

Cause of disjoining pressure

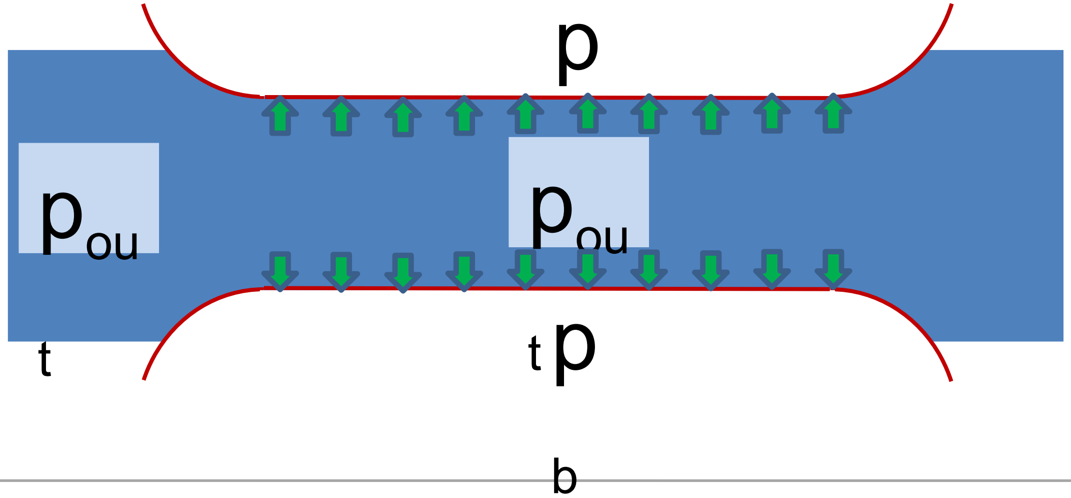
- Surfactants do stabilize the film / foam

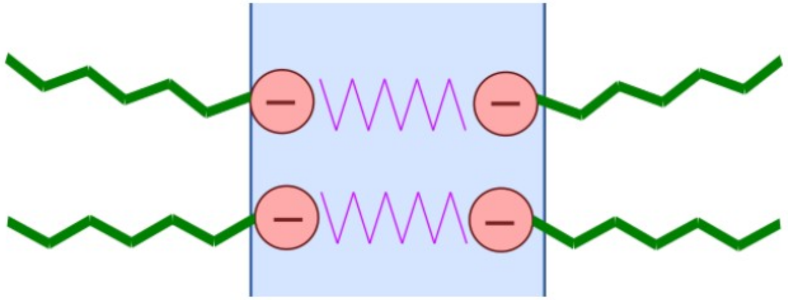


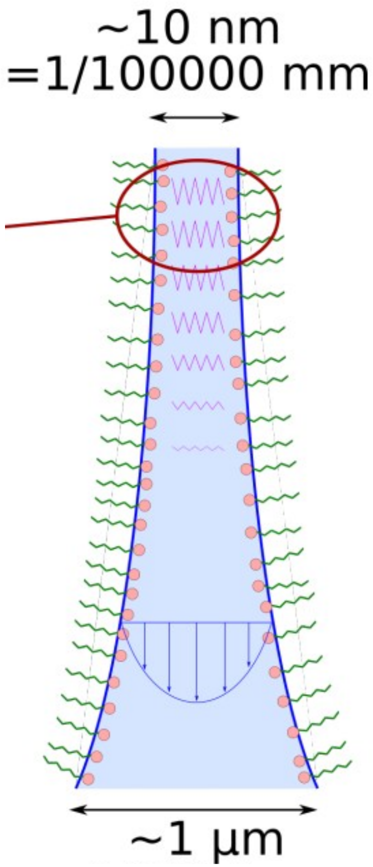

0,01 g/L
0,1 g/L
1 g/L
SDS
1 g/L
MIBC

Disjoining pressure from surfactants

- Interaction between adsorbed surfactants on opposing interfaces
- Dependent on film thickness, surfactant type, and concentration







Disjoining pressure

- Nice and detailed review article:

J. Phys.: Condens. Matter **11** (1999) R215–R238. Printed in the UK PII: S0953-8984(99)83711-4

REVIEW ARTICLE

Forces and structure in thin liquid soap films

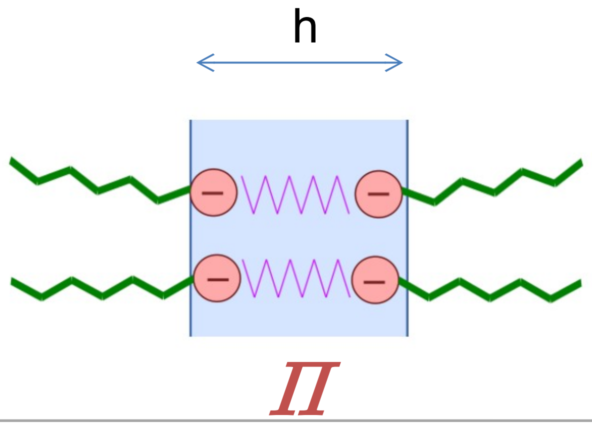
Vance Bergeron
Rhône Poulenc Industrialisation, 85, Avenue Des Freres Perret, BP 62, Saint-Fons Cédex, France

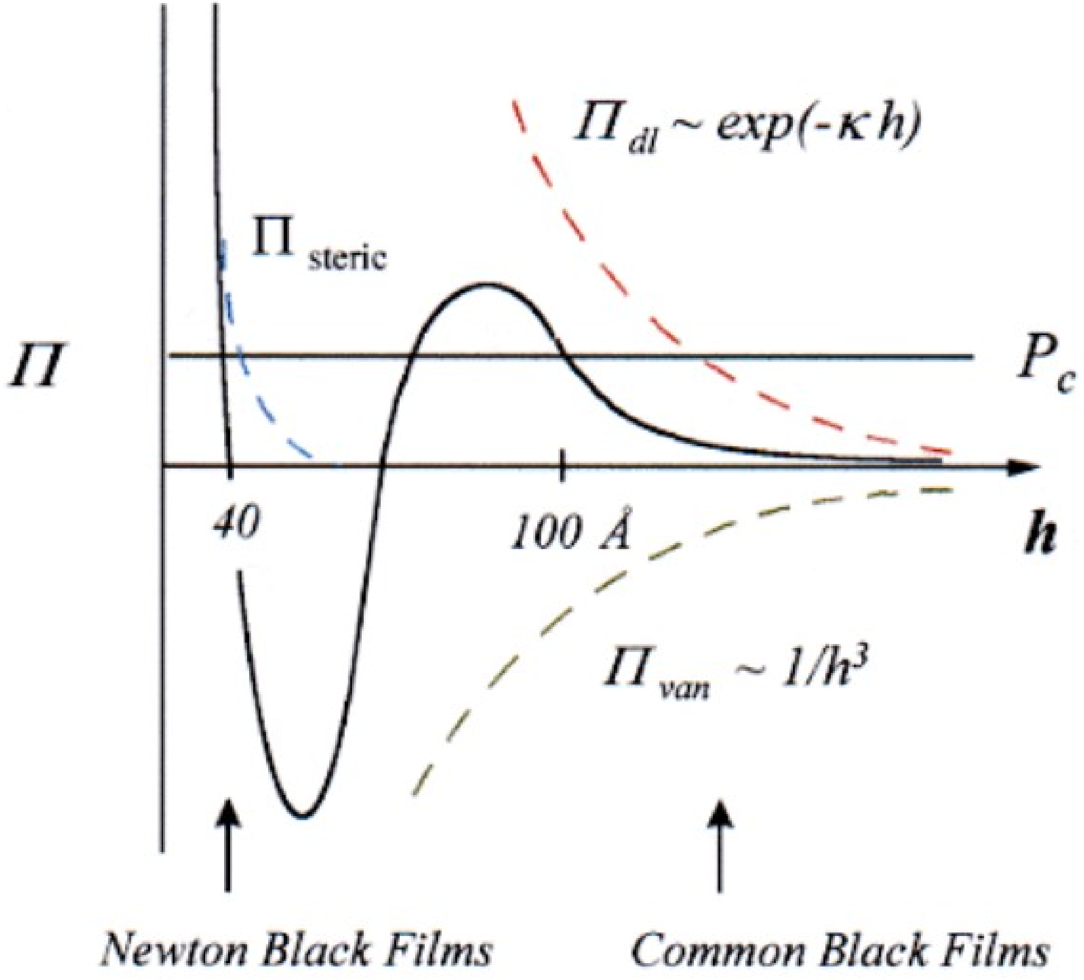
Received 11 January 1999

Abstract. This review is a topical survey of the forces and structures in thin liquid soap films.

Contributions to disjoining pressure

- Derjaguin–Landau–Verwey–Overbeek (DLVO
- Disjoining force is a function of film thicknes
- 3 contributions:
  - Electrostatic repulsion ~exp(-h)
  - Dipol (Van-der-Waals) ~h^{-3}
  - Steric (collision)
- Undisturbed superposition



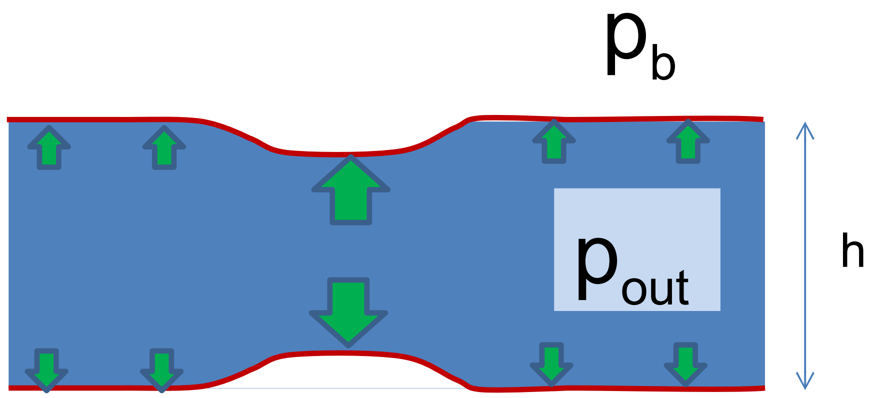


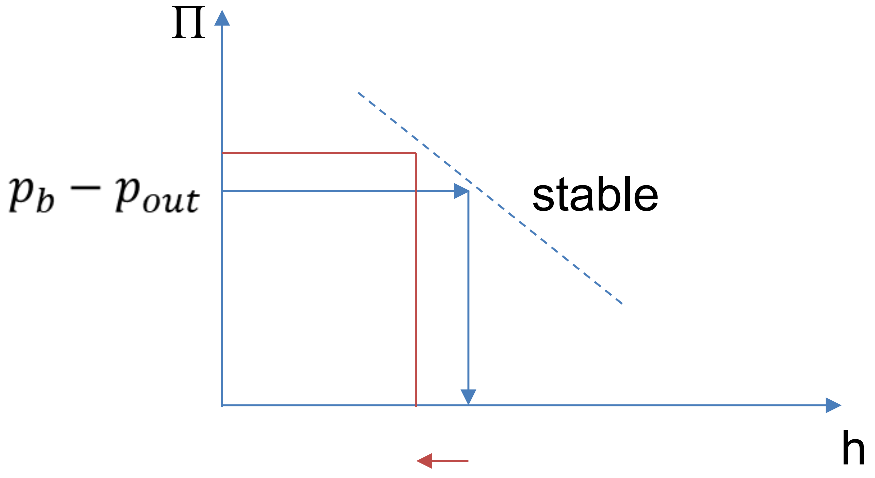
Film stability

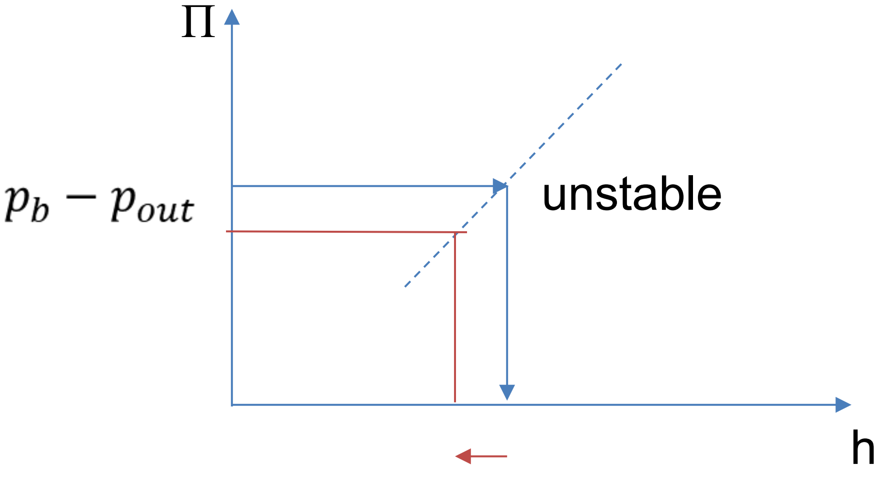
- Stable film: higher disjoining pressure for smaller thickness

$$p_b = p_{out} + 2\gamma H$$

$$2\gamma H = p_b - p_{out} = \Pi\,(h)$$

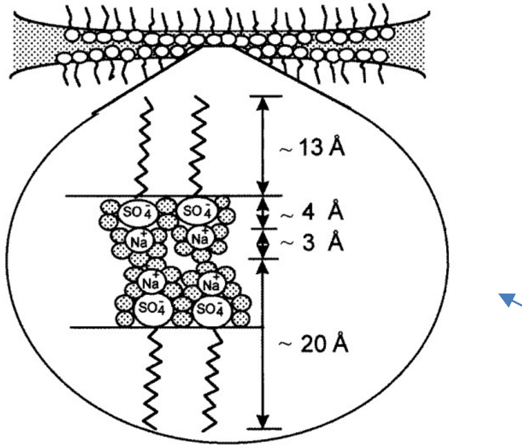


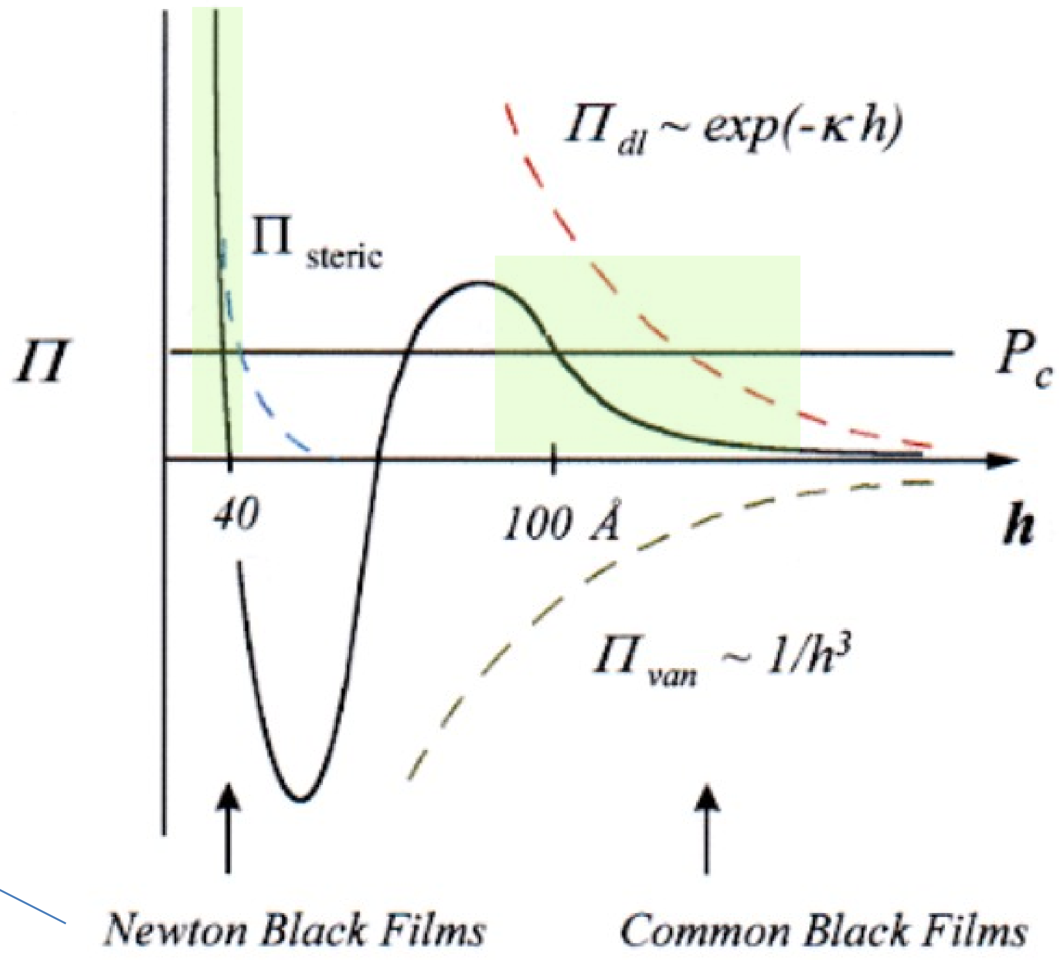




Contributions to disjoining pressure

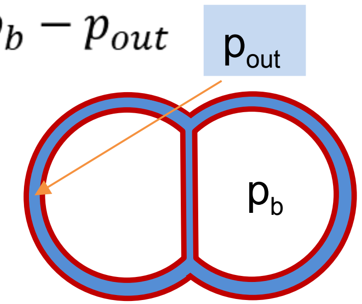
- 2 stable regions:
- Common Black Films (h ~ 50 nm)
- Newton Black Films (h ~ 5 nm)



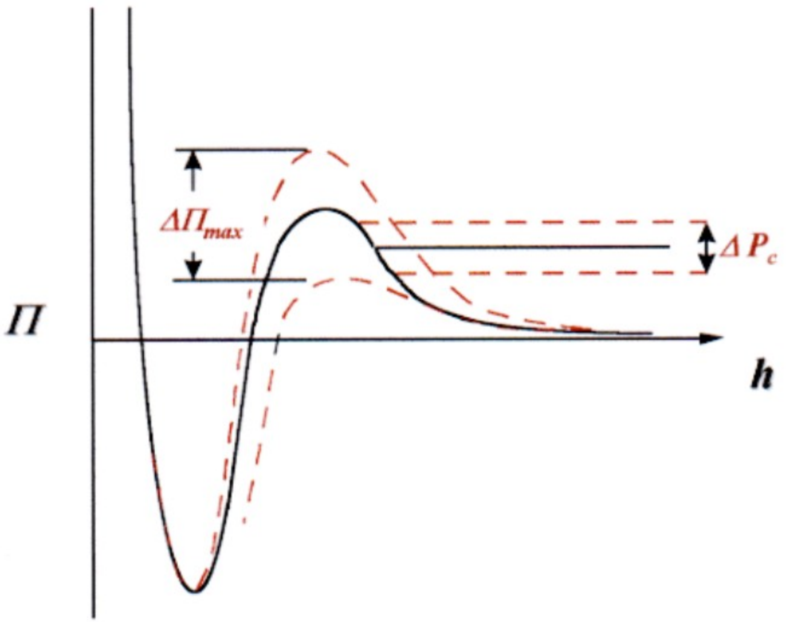


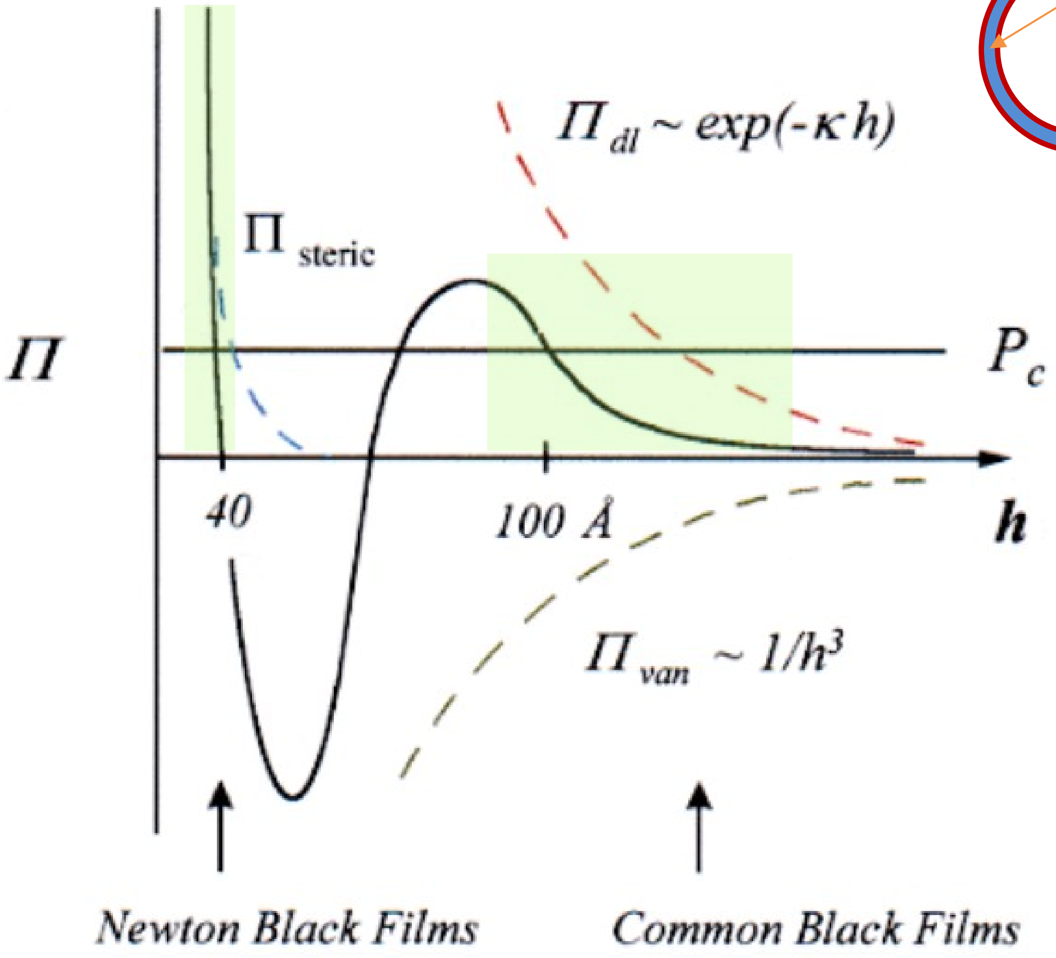
Film stability

$$\Pi = p_b - p_{out}$$



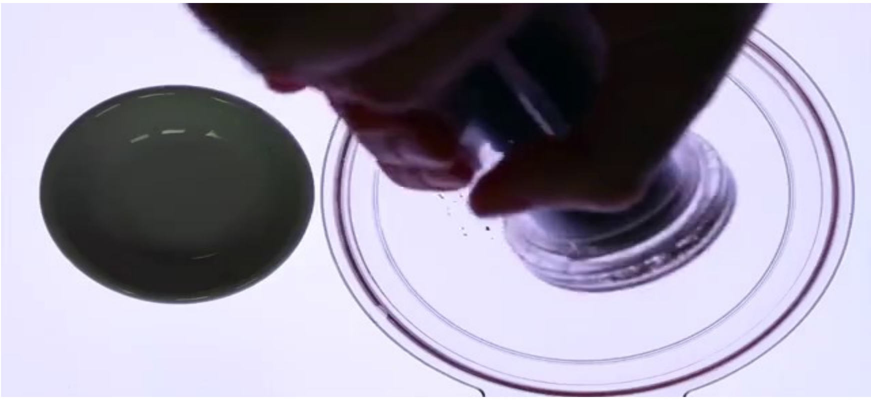
- 2 stable regions:
- Common Black Films (h ~ 50 nm)
- Newton Black Films (h ~ 4 nm)

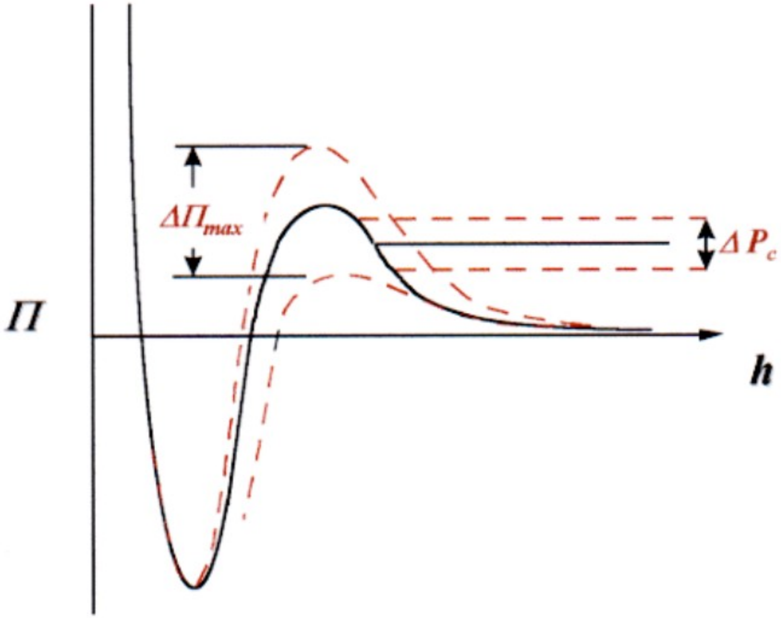


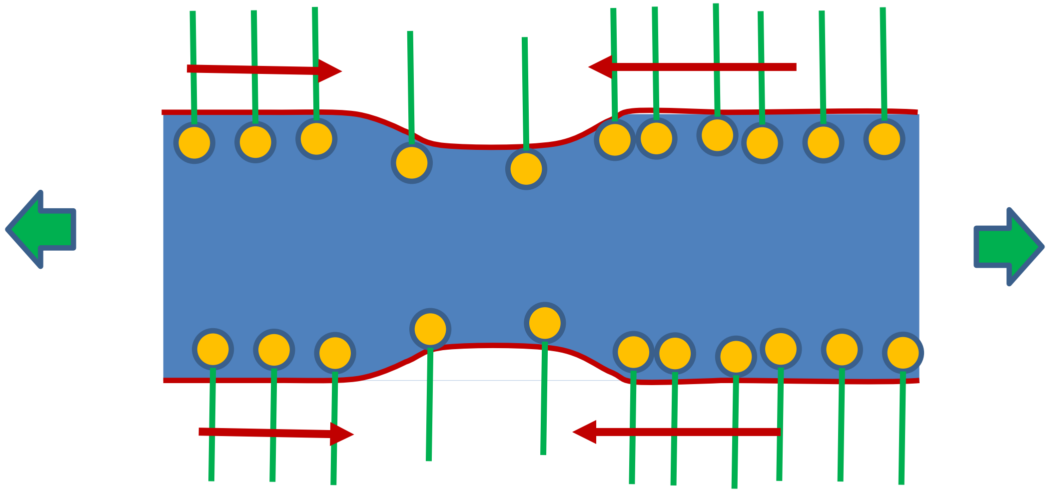


Film stability

- Film stretching → locally lower surface coverage
- Marangoni effect cures weak spots

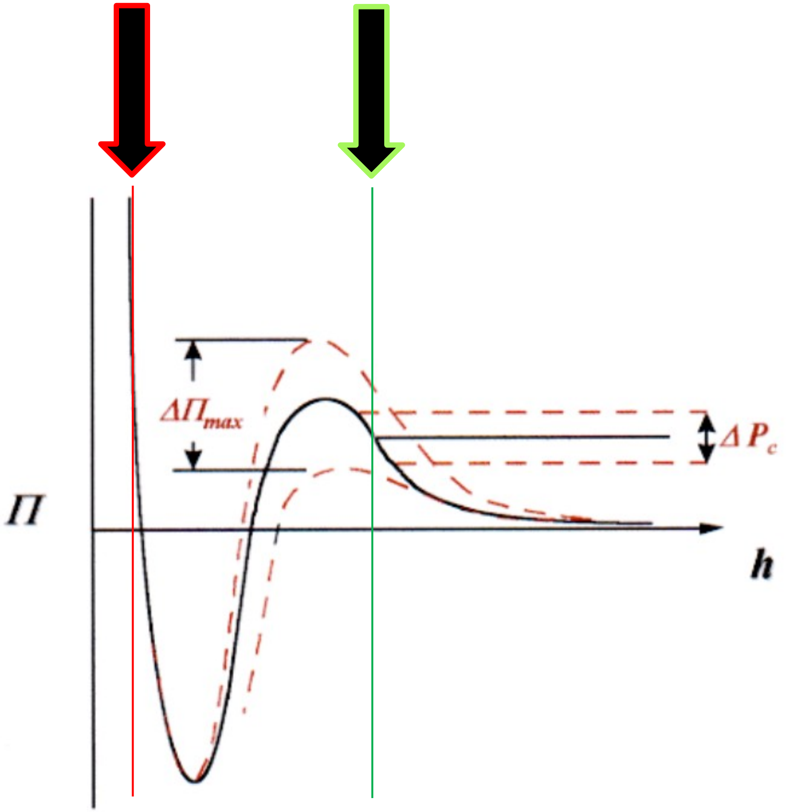


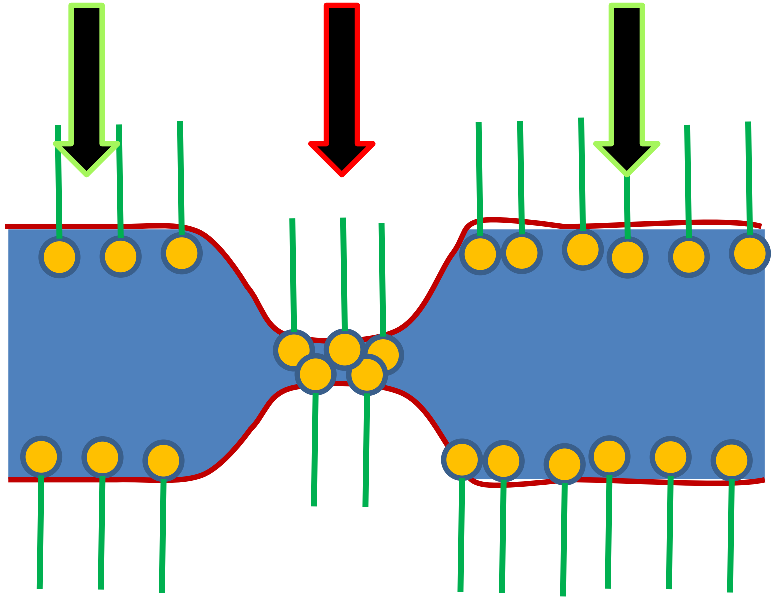




Film stability

- When barrier is overcome, Newton Black Film is formed (or rupture)
- Formation of Newton Black Film is hardly reversible





Surfactant recipy

- „Bulgarian sauce" → very stable films, tunable surface elasticity

Langmuir **2008,** *24,* 9956–9961

Surfactant Mixtures for Control of Bubble Surface Mobility in Foam Studies

K. Golemanov,[†] N. D. Denkov,*[,†] S. Tcholakova,[†] M. Vethamuthu,[‡] and A. Lips[‡]

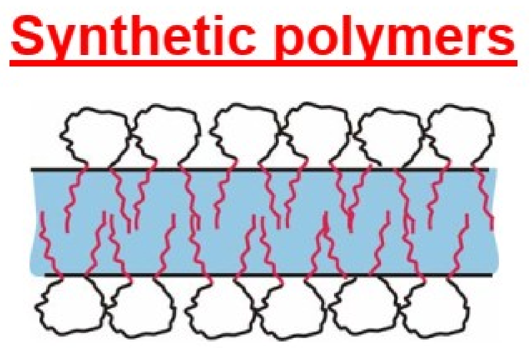
Laboratory of Chemical Physics & Engineering, Faculty of Chemistry, Sofia University, Bulgaria, and Unilever Global Research Center, Trumbull, Connecticut 06611

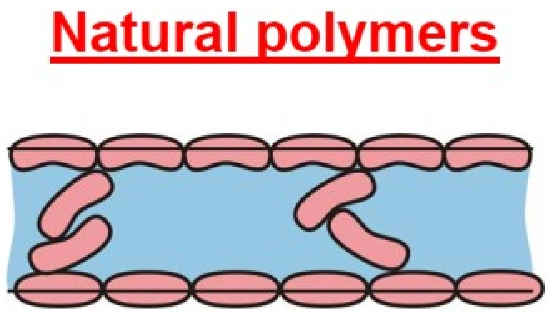
Received May 19, 2008. Revised Manuscript Received July 28, 2008

A new class of surfactant mixtures is described, which is particularly suitable for studies related to foam dynamics, such as studies of foam rheology, liquid drainage from foams and foam films, and bubble coarsening and rearrangement.

Polymeric surfactants

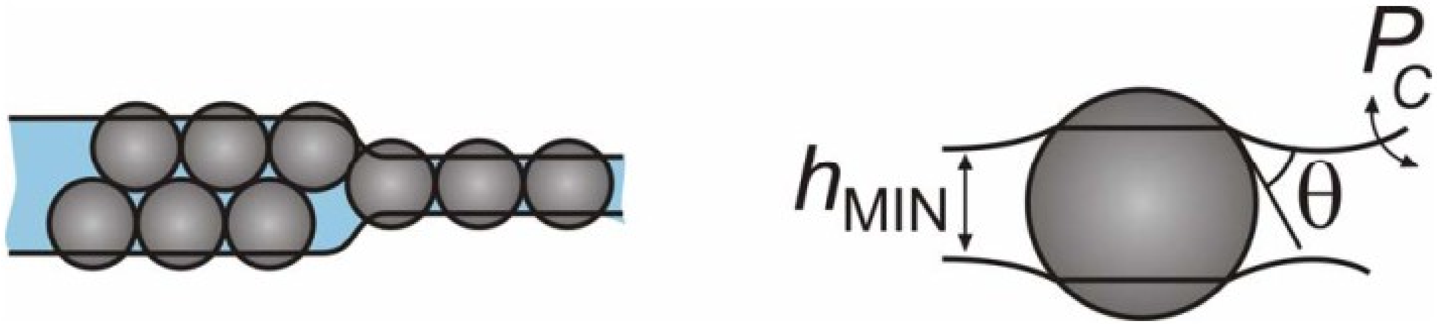
- Combination of steric and electrostatic forces
- Very stable films





Particle-stabilized films

- Relatively thick films (~particle diameter)
- Slow diffusion, slow adsorption → difficult to produce
- No Marangoni effect → films can rupture under shear
- E.g. Metal foam

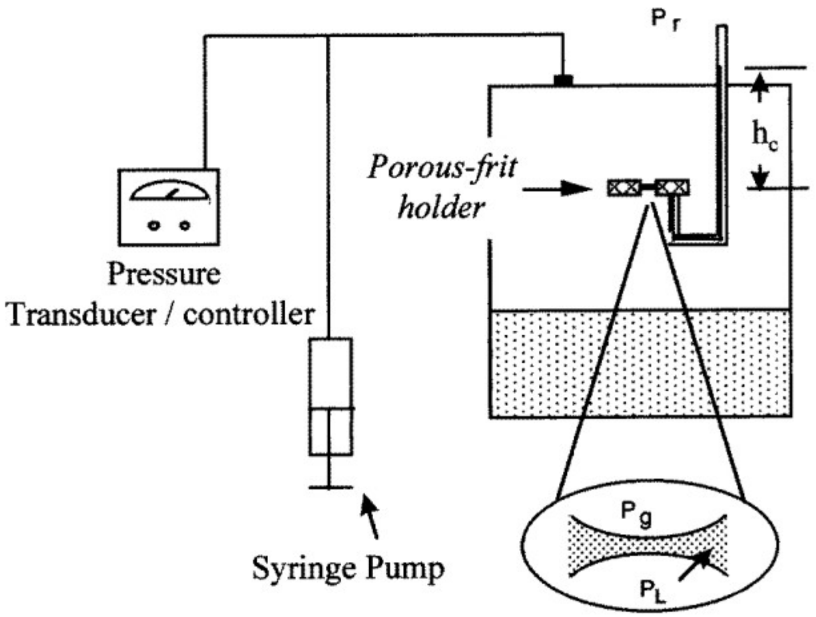


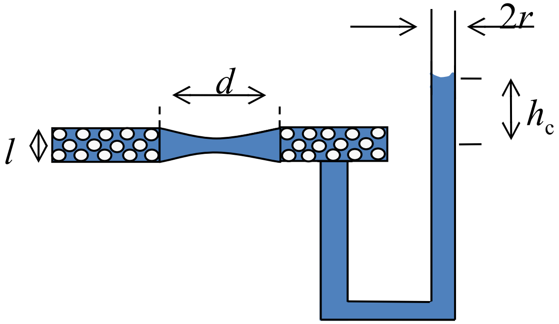
Structure

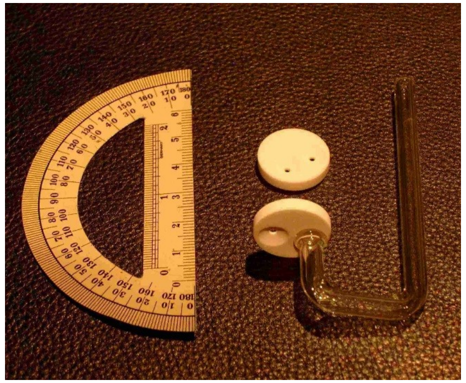
- Film stability
- Film drainage
- Film measurement techniques

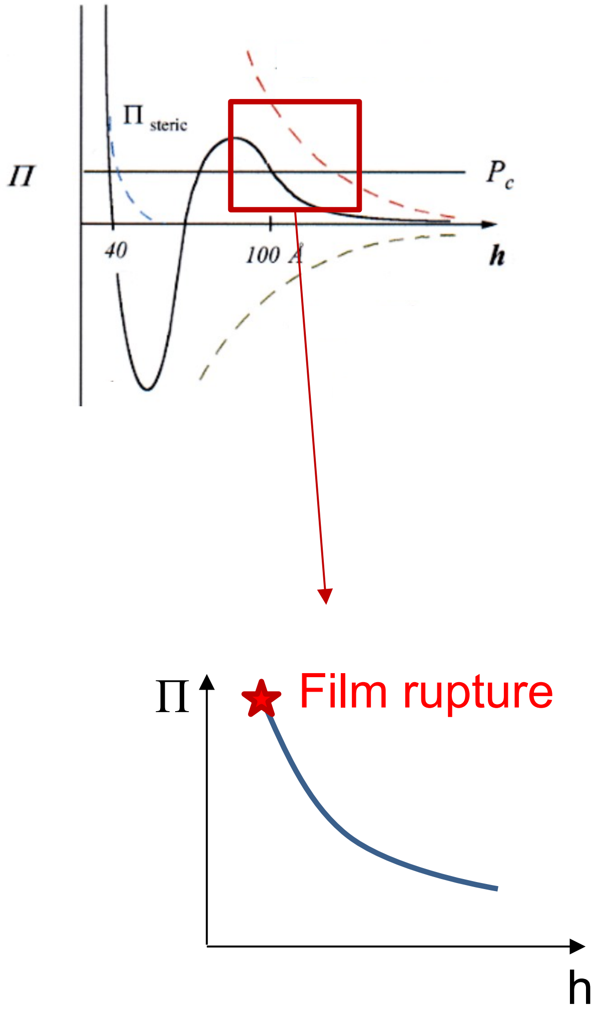
Disjoining pressure measurement

- „Thin film balance“ → Disjoining pressure vs film thickness
- Pump to control pressure in chamber
- Water reservoire to avoid evaporation









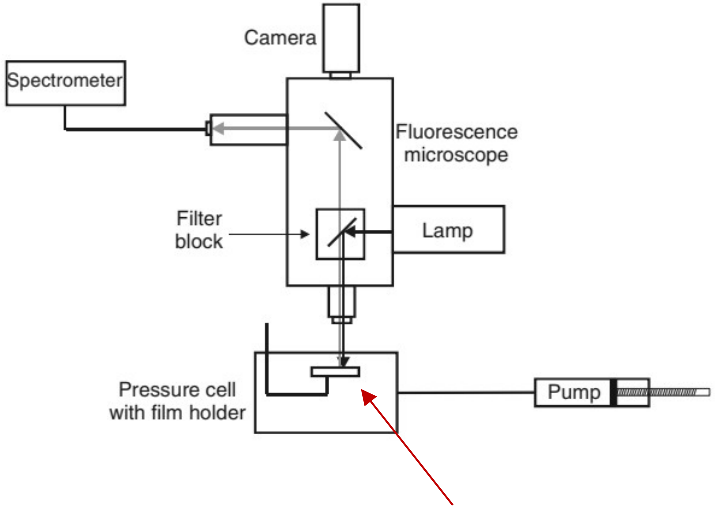
Disjoining pressure measurement

- Pressure measurement by digital pressure transducer (DPT)
- Film thickness measurement by intensity I of reflected light:

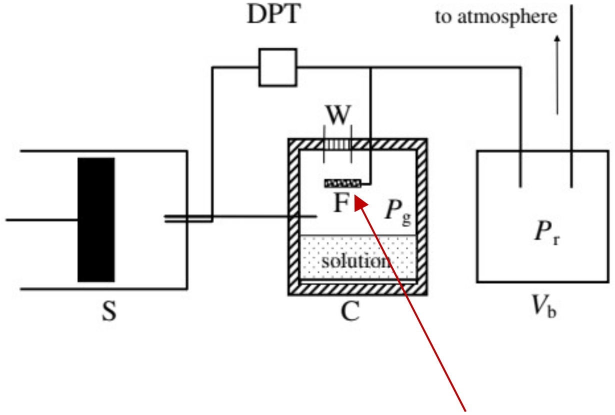
$$h_{eq} = \frac{\lambda}{2\pi n_s} \arcsin\left(\frac{\Delta}{1 + (4R(1-\Delta)/(1-R)^2)}\right)$$

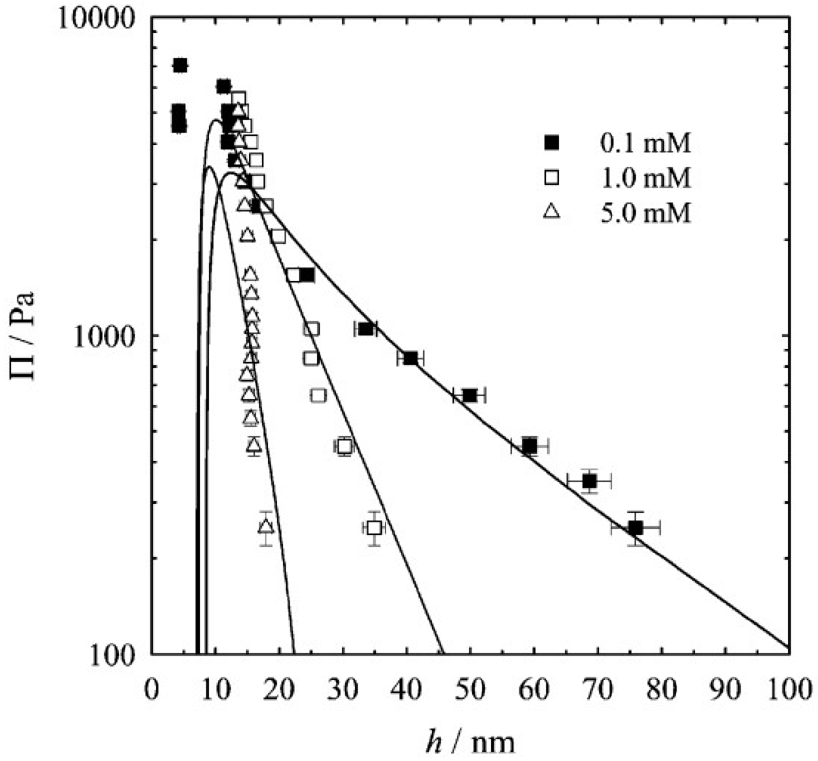
$$\Delta = (I - I_{min})/(I_{max} - I_{min}),\ R = (n_s - 1)^2/(n_s + 1)^2,$$

Film thickness measurement



Pressure measurement

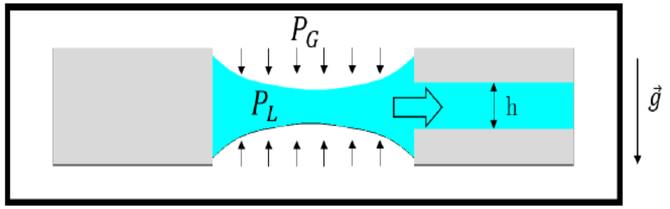




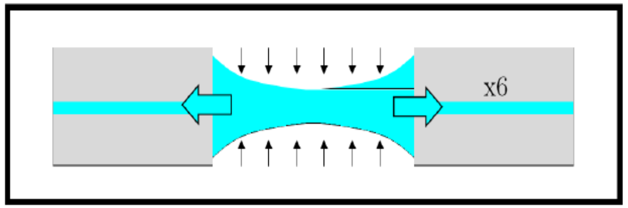
[Stubenrauch, C., Schlarmann, J., Strey, R., *PCCP*, **2002**, *4*, 4504]

Disjoining pressure measurement

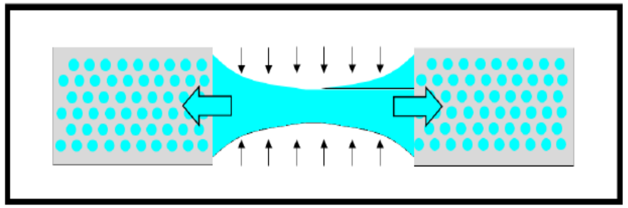
- Different realisations possible
- Also microfluidic chips



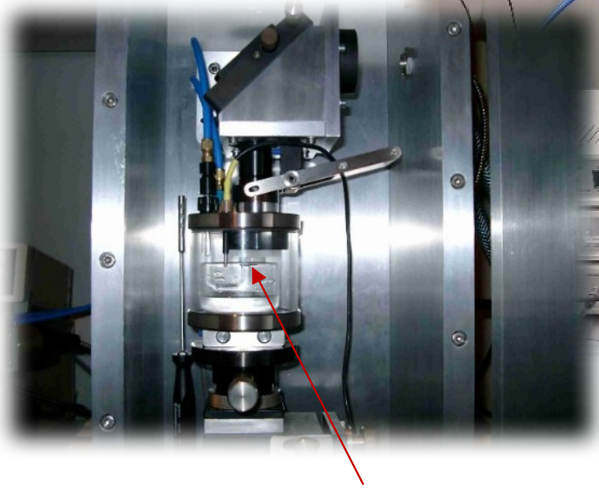
(a) Cellule de Scheludko

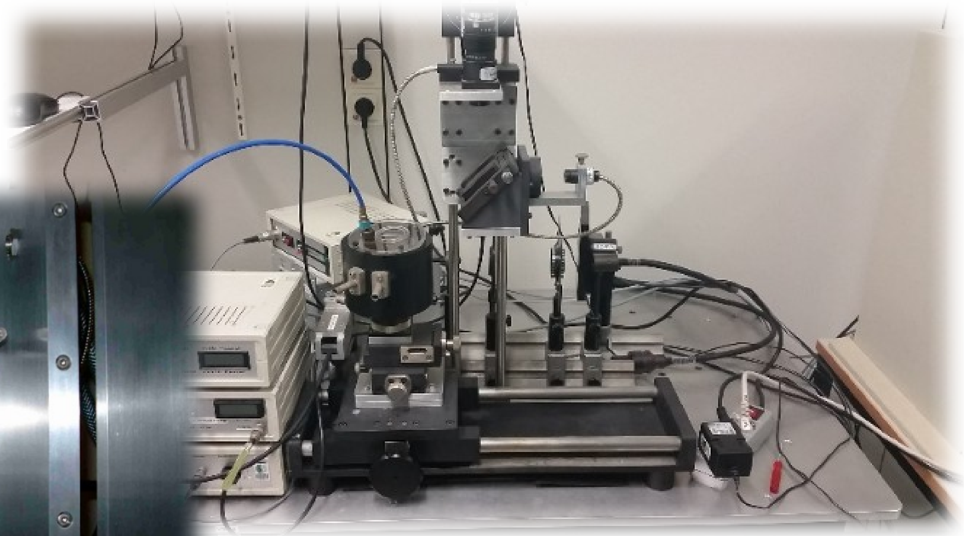


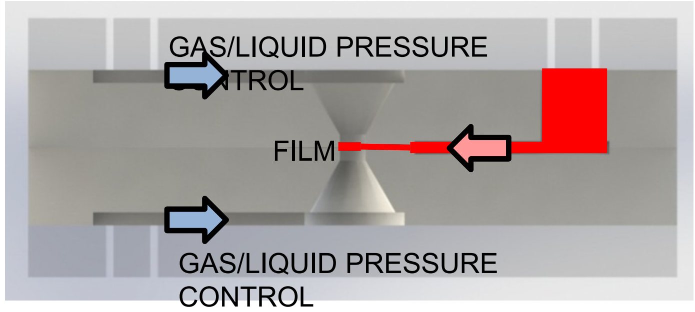
(b) TFB « Microfluidique »

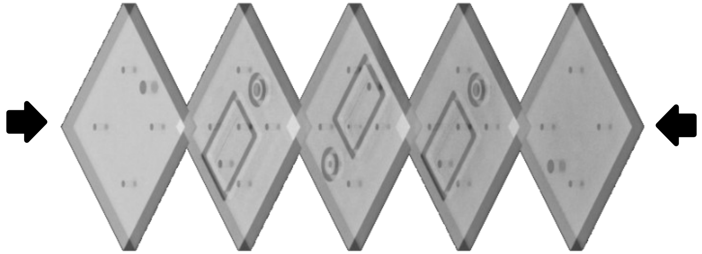


(c) Disque poreux



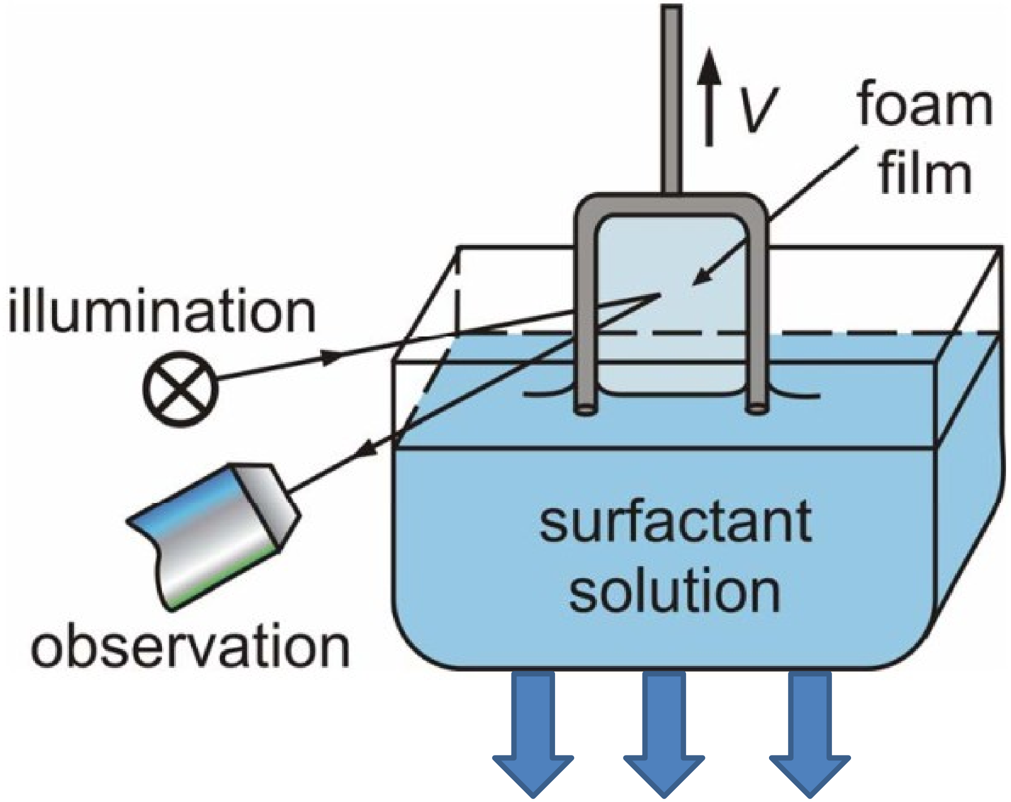






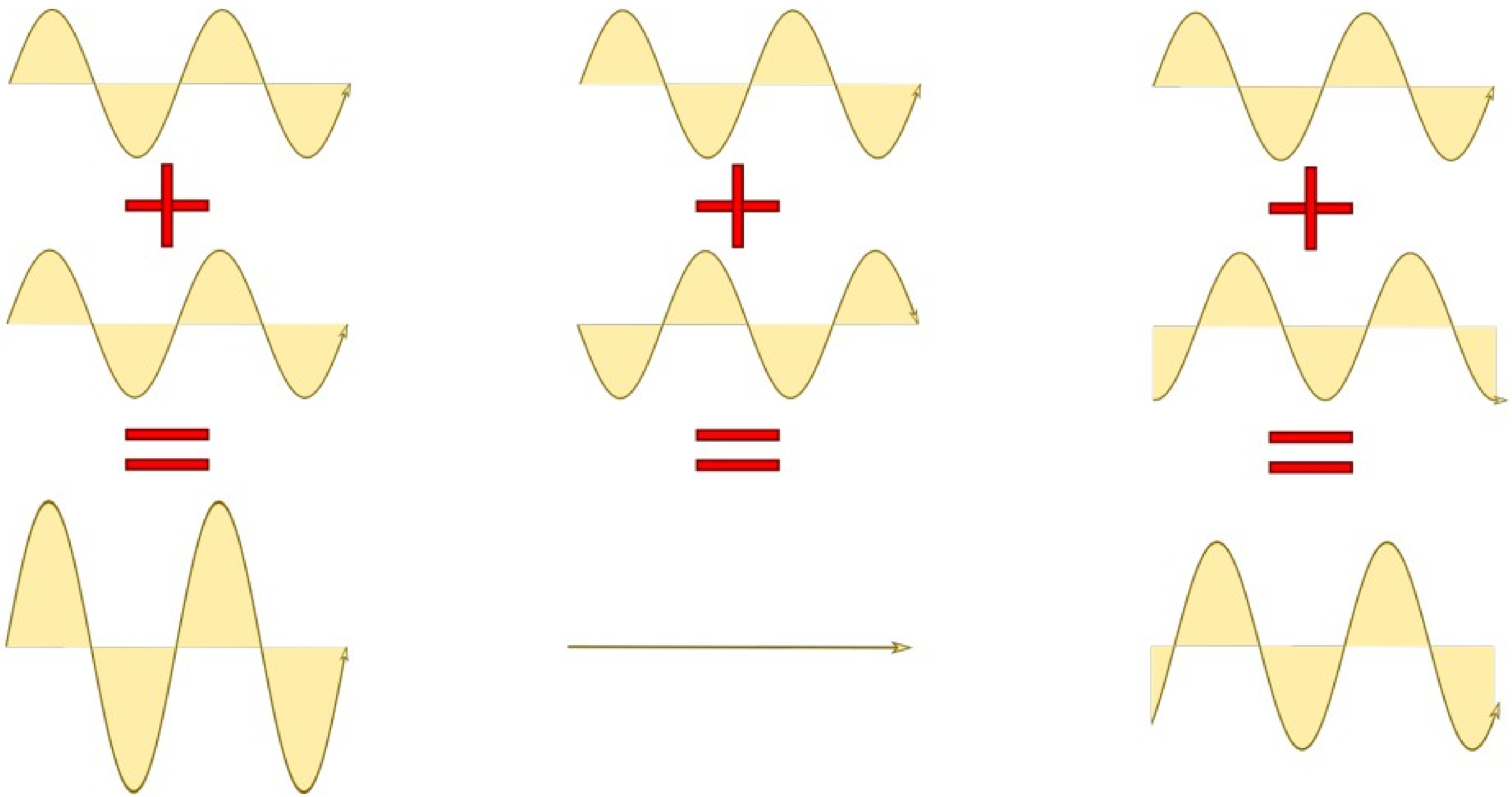
Film thickness measurement

- Measurement of film drainage, thickness profile, NBF
- Measurement of film rupture



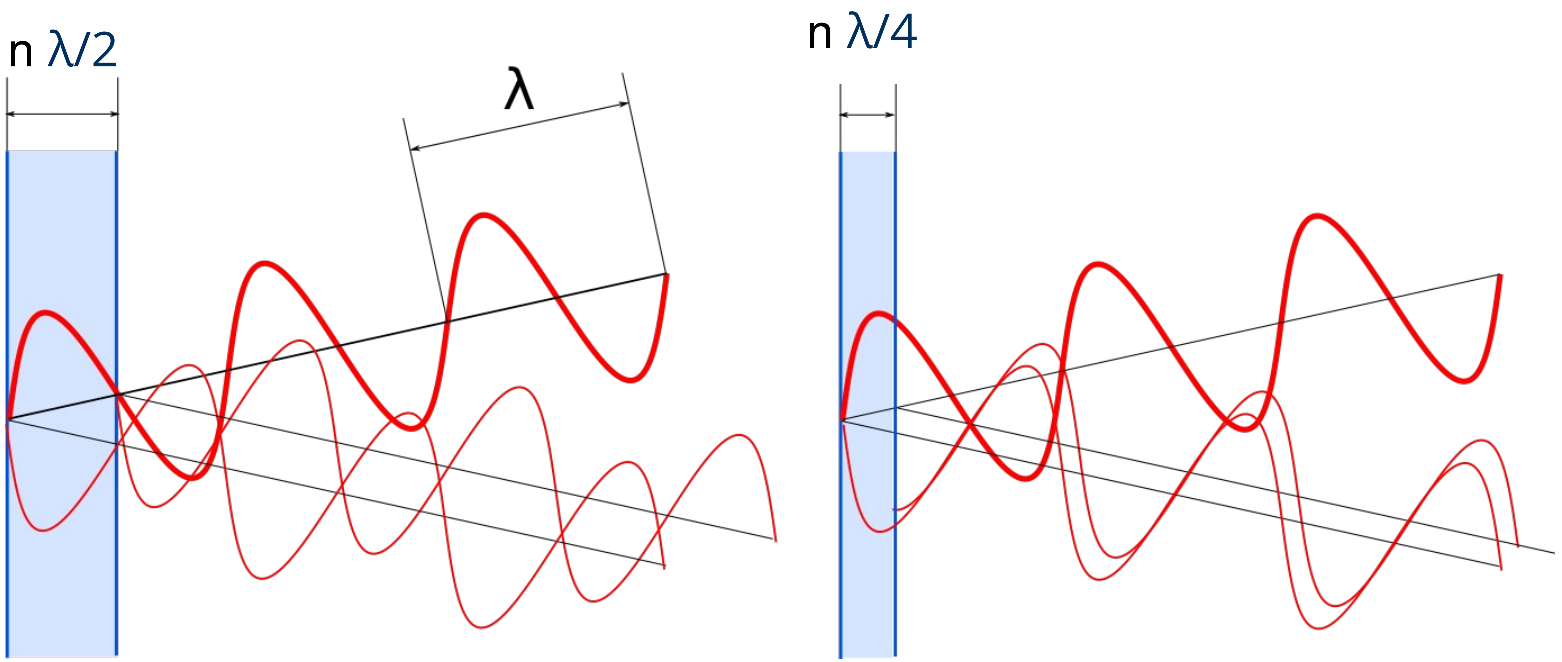
Otical interference

- Depending on phase shift, superpositioned light can cancel or reinforce each other
- Interaction only between waves of identical frequency (otherwise beats – not visible)



Reflection at thin films

- Reflection at both interfaces of the film
- At the front side: reflection on medium with higher refraction index → phase change by $\Delta\varphi_f = \pi$
- At the back side: phase shift by additional distance 2h → $\Delta\varphi_b = 2\pi * 2h / (n*\lambda)$



$\Delta\varphi_f = \pi$

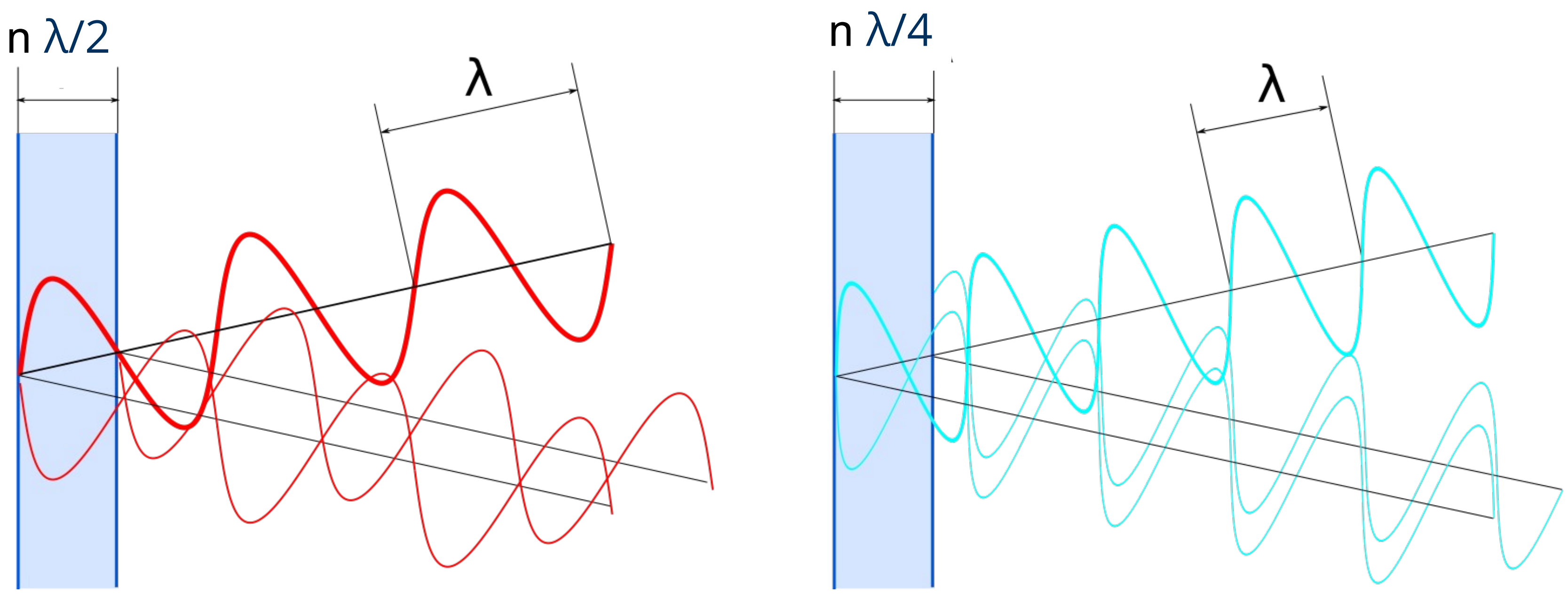
$\Delta\varphi_b = 2\pi$

$\Delta\varphi_f = \pi$

$\Delta\varphi_b = \pi$

Reflection at thin films

- The same film thickness gives different reflection for different colors (wavelengths)
- Some colors are canceled, some are reinforced



$\Delta\varphi_f = \pi$

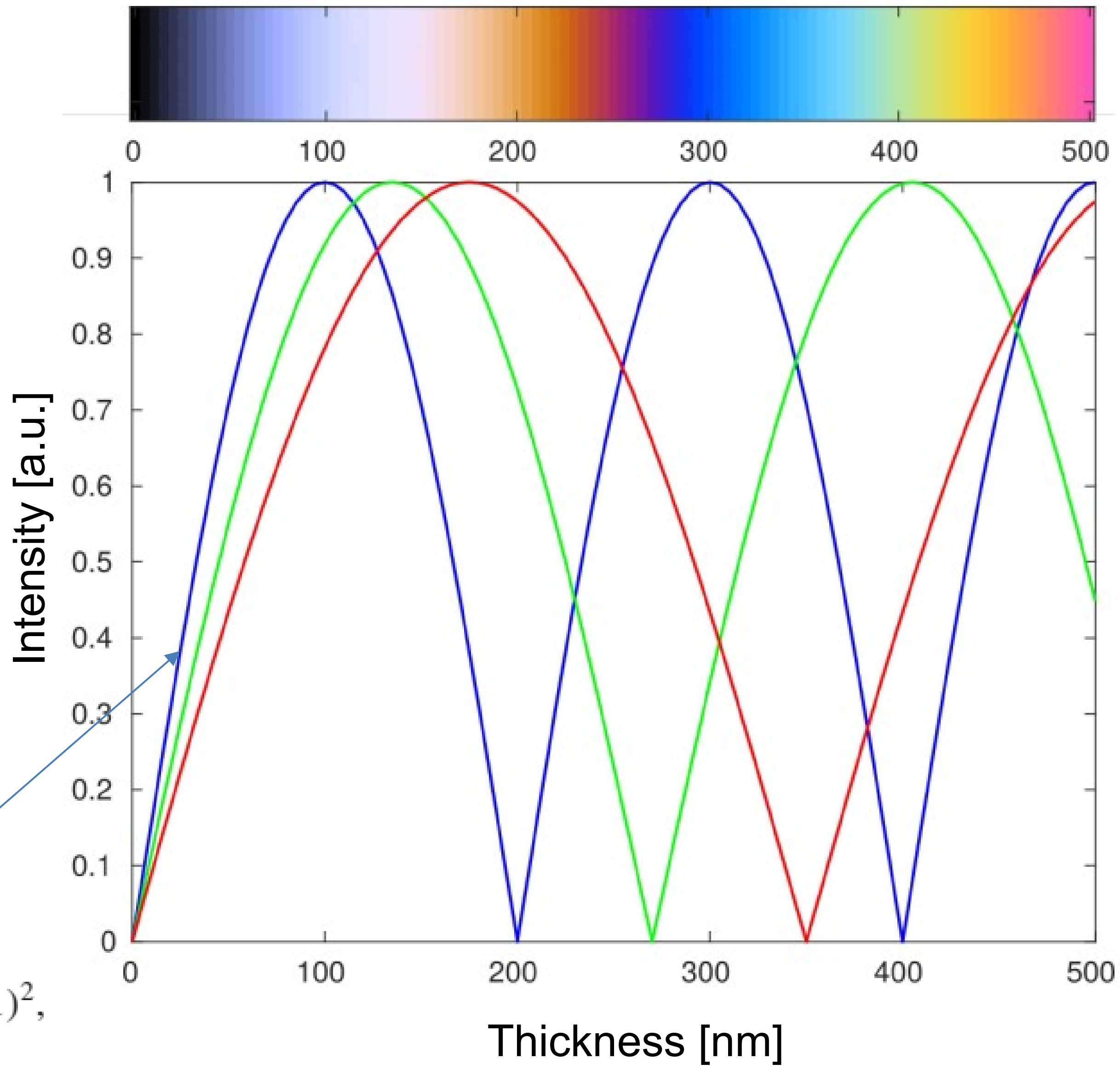
$\Delta\varphi_b = 2\pi$

$\Delta\varphi_f = \pi$

$\Delta\varphi_b = \pi$

Reflection at thin films

- Superposition of reinforced frequencies
- Combination of red, green and blue yields color impression

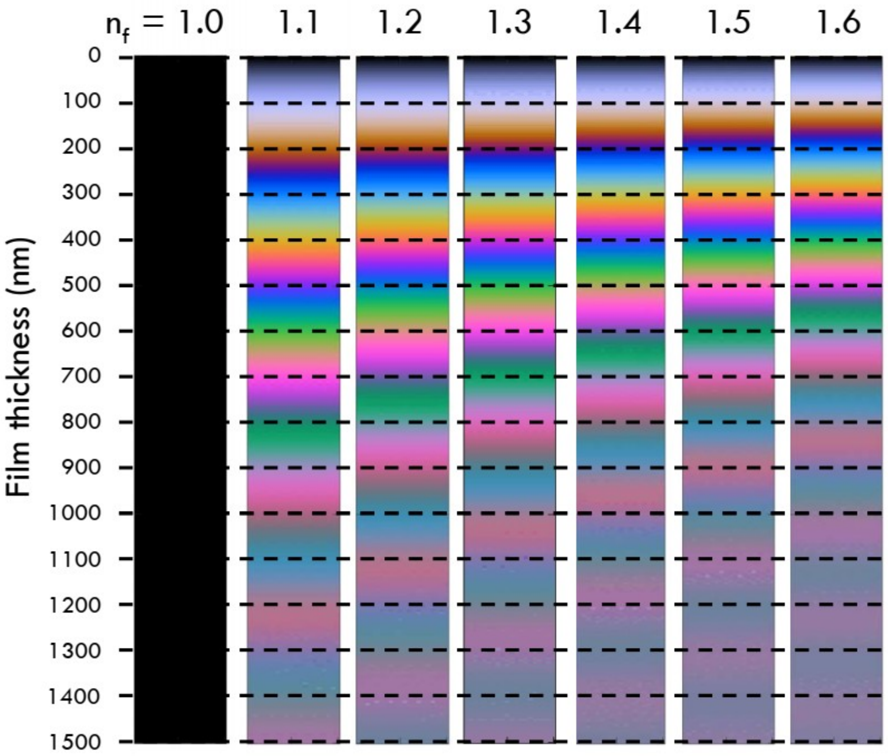


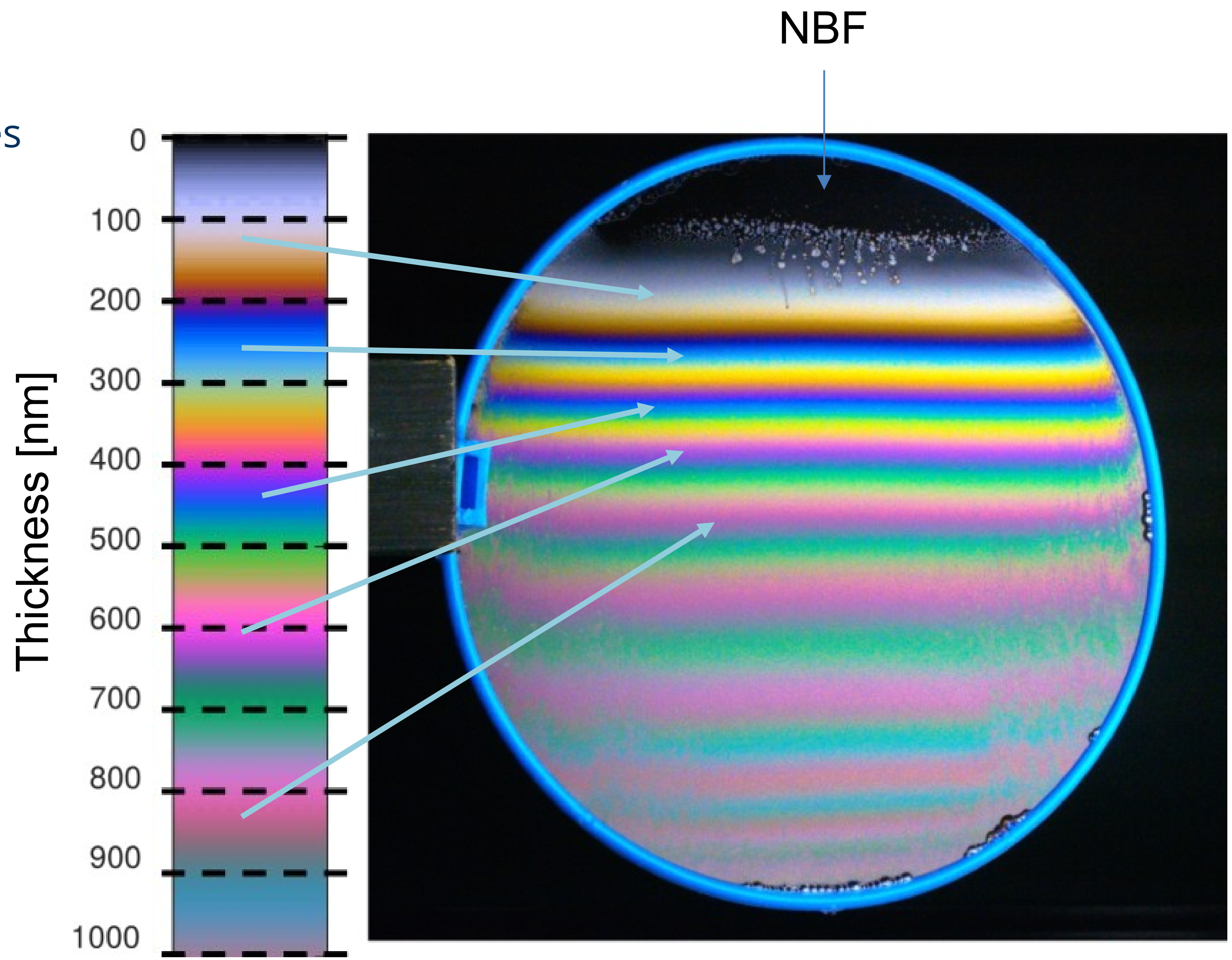
$$h_{eq} = \frac{\lambda}{2\pi n_s} \arcsin\left(\frac{\Delta}{1 + (4R(1-\Delta)/(1-R)^2)}\right)$$

$$\Delta = (I - I_{min})/(I_{max} - I_{min}),\ R = (n_s - 1)^2/(n_s + 1)^2,$$

Reflection at thin films

- Thickness can be measured by counting lines
- More easy with monochromatic light
- Newton Black Film at top



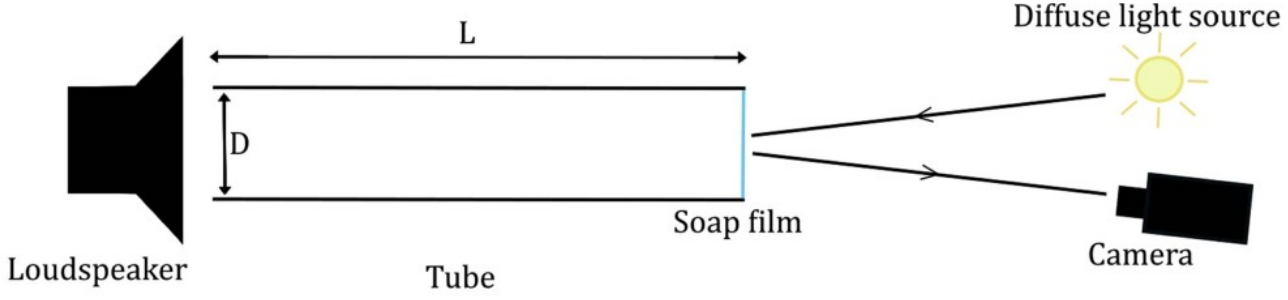


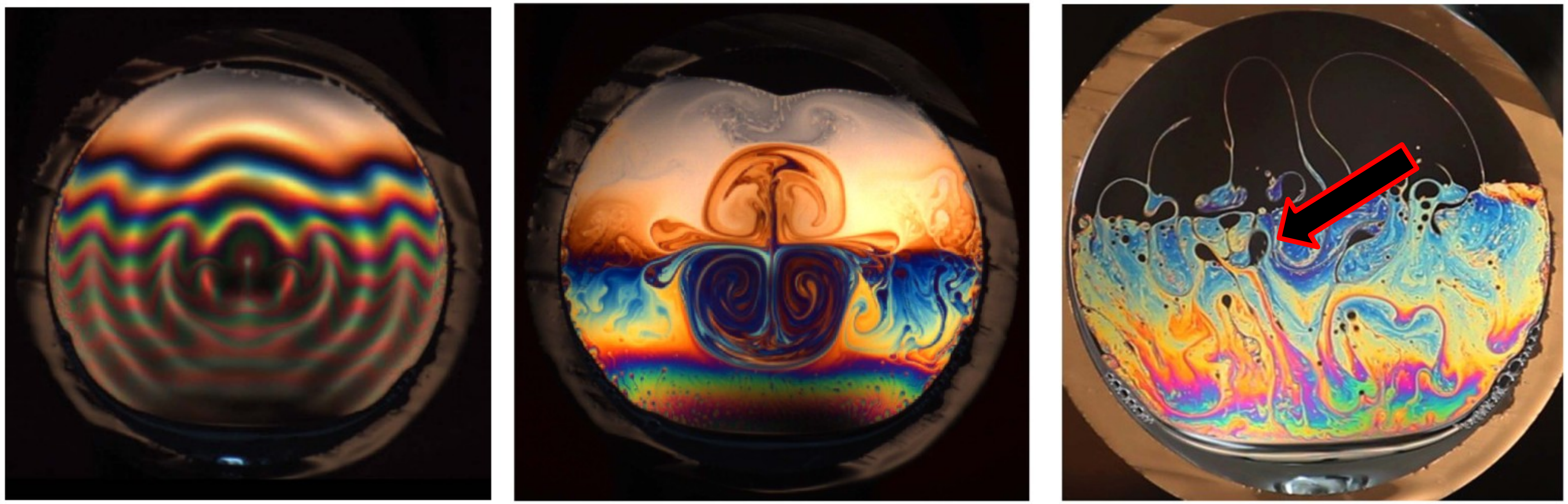
Soap film opera

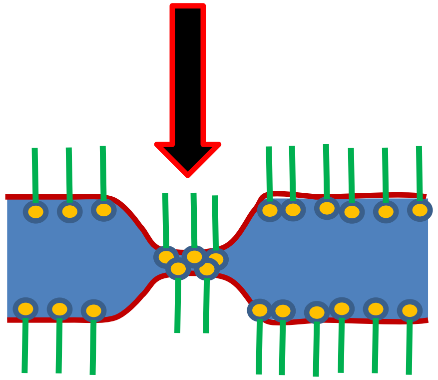
IOP Publishing European Journal of Physics
Eur. J. Phys. 38 (2017) 045804 (18pp) https://doi.org/10.1088/1361-6404/aa7147

Sound and vision: visualization of music with a soap film

C Gaulon[1], C Derec[1], T Combriat[2], P Marmottant[2] and F Elias[1,3]







Soap film opera

- https://www.youtube.com/watch?v=wMFrfWZpVMM
- © Florence Elias