Dr.-Ing. Sascha Heitkam,

Institute of Process Engineering and Environmental Technology

Lecture 1: Interfaces

Structure

- Administrative Issues

- Surface Tension

- Young-Laplace law
- Exercise: Pressure inside a bubble

- Tensiometry

- Surfactants
- Exercise: Amounts of molecules

Organisational issues

- Lecture every week – recordings provided on request
- Lectures fully in ZOOM (not hybrid)
- Each lecture contains small exercises
- Slides provided in OPAL
- Password: bubble_bath2020
- If OPAL does not work → Slides provided for download on request (email!)

  → sascha.heitkam@tu-dresden.de

- Recordings for individual lectures provided on request

Schedule

- In OPAL
- Not fixed!!!
- Guest speakers

Date	Field	Lecture topic	Exercise	Technique
16.10.	Surfactants	Surfactants, sorption, surface tension, Young-Laplace law	Surface/Bulk concentration	Tensiometry
23.10.	Surfactants	Interface rheology, Marangoni effect, sorption of particles	Energy barrier for particles	Pending droplet tensiometer
30.10.	Bubbles	Bubble generation, size distribution	Measures of size distribution	Bubble viewer
06.11.	Bubbles	Bubble shapes, rising velocity, no-slip/free-slip, impurities	Time scale of phase separation	Viscosimetry
13.11.	Films	Film stability, film thinning	Time scale of film rupture	Optical film thickness measurement
20.11.				
27.11.	Foam	Foam structure, general geometric properties	Structural properties	Surface Evolver
04.12.	Foam	Foam drainage	Liquid content of steady foam	Electric resistance measurements
11.12.	Foam	Foam rheology, bubble rearrangement	Yielding of foam piles	Rheometers for foam
18.12.	Foam	Foam flow measurement	Liquid fraction bilance	Radiographic techniques
08.01.	Foam	Foam stability, coarsening, defoaming	Diffusion time scale	Foam stability analyzer
15.1.	Solid Foam	Solid foams, properties, plastic deformation	Buckling limit	Light weight applications
22.1.	Froth	Particle entrainment, Particle behavior, stability	Settling of particles	Froth flotation
29.1.		Wrap-up, exam preparation		
05.02.		Backup Slot		

Schedule

- 3 Lab courses
- Groups of 3..4 Persons
- Interest? → Send email sascha.heitkam@tu-dresden.de
- Approx. 120 min

- Pending droplet tensiometry (Milad Eftekhari)
- Foam stability measurement (Peggy Jähnigen)
- Froth Flotation (Artem Skrypnik)

Certificates

- Declare requirements with your examination office !

- Certificate of attendance: > 75% (chat is saved) → 2 LP / ECTS

  → Use your full name

- Certificate of attendance with small test → 2 LP / ECTS

  → Tiny oral exam (virtual meeting, english or german)

- Certificate with grade: → 3 LP / ECTS

  → Lab Course

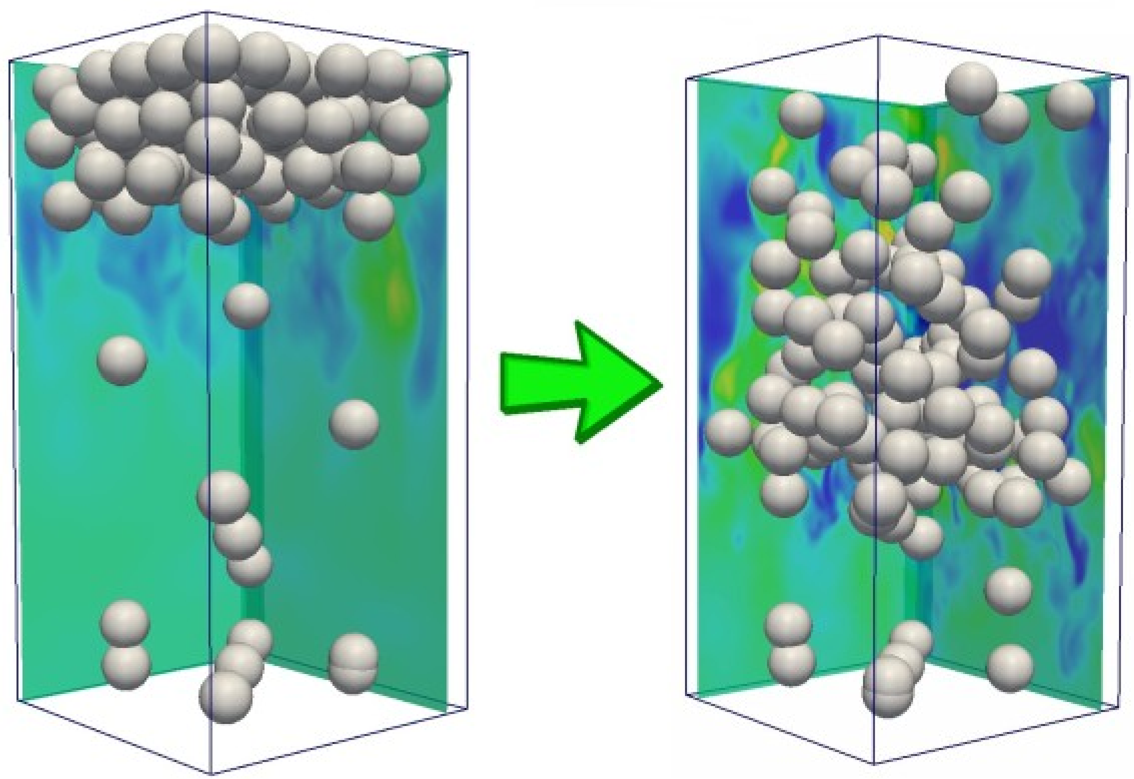
  → Oral exam (virtual meeting, english or german)

- PhD examination (Rigorosum)

- Others: please contact me. We will find a solution!

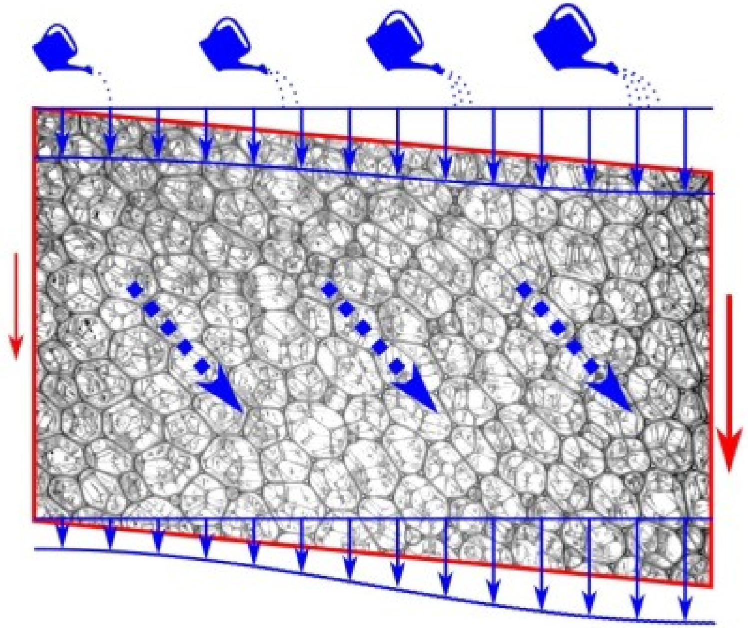
Introduction: Sascha Heitkam

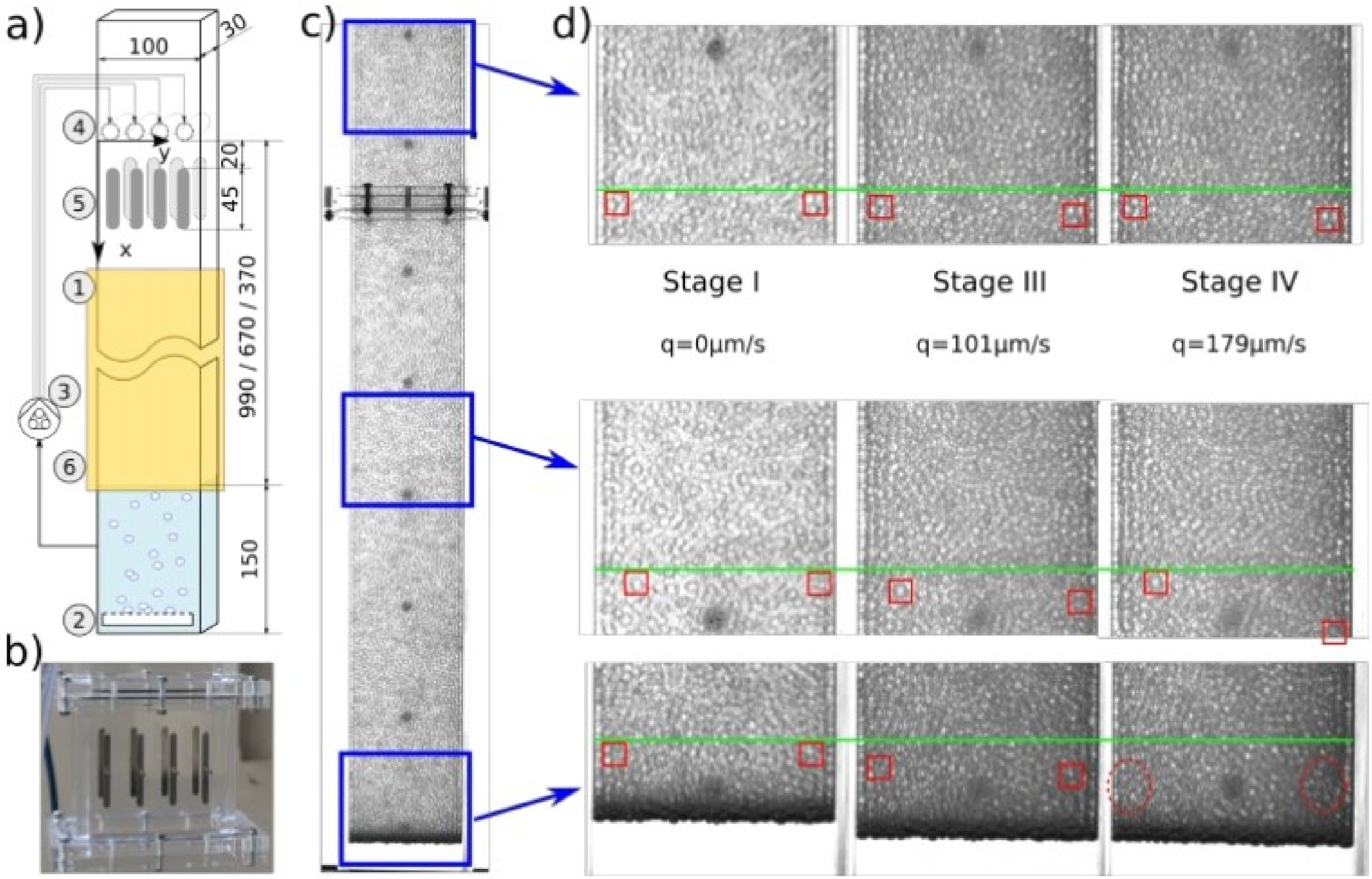
- Mechanical Engineering / Fluid Mechanics
- PhD in 2014: Numerical simulation of metal foam generation in electromagnetic fields
- Supervised by: Prof. Jochen Fröhlich, Dominique Langevin, Wiebke Drenckhan



Introduction: Sascha Heitkam

- 2016-2019 Post-Doc: Drainage and Convective Instability in foam





Introduction: Sascha Heitkam

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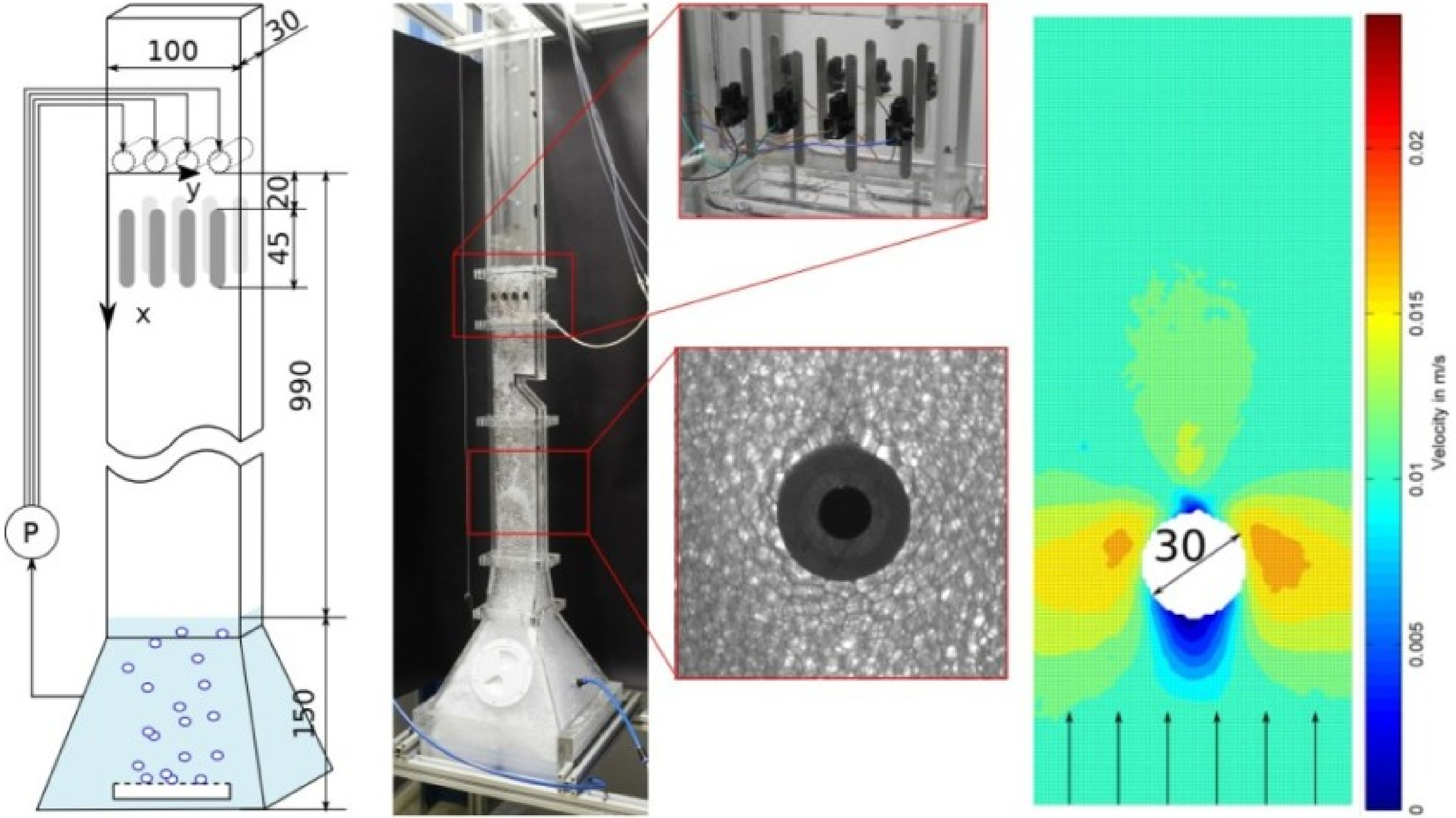
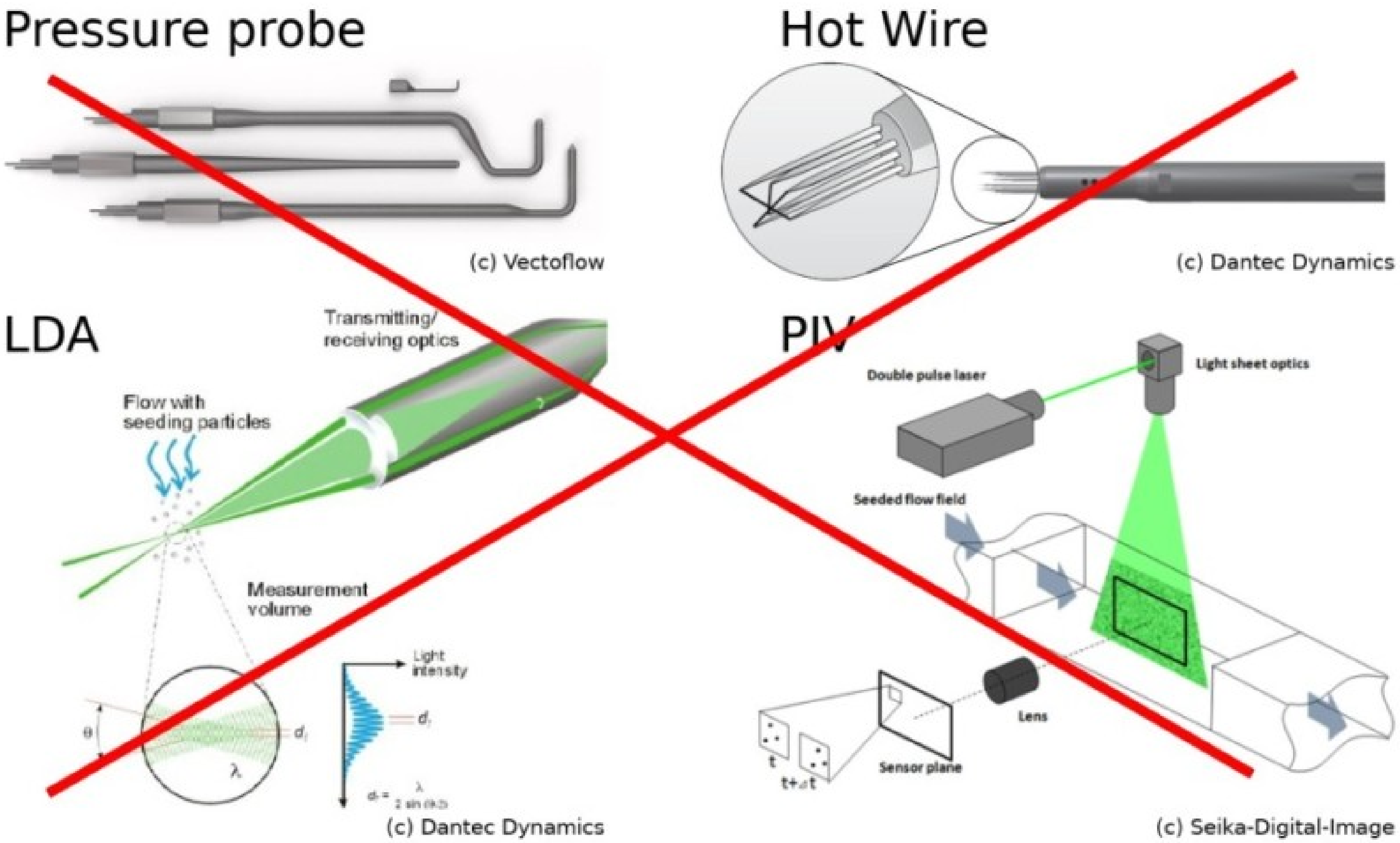


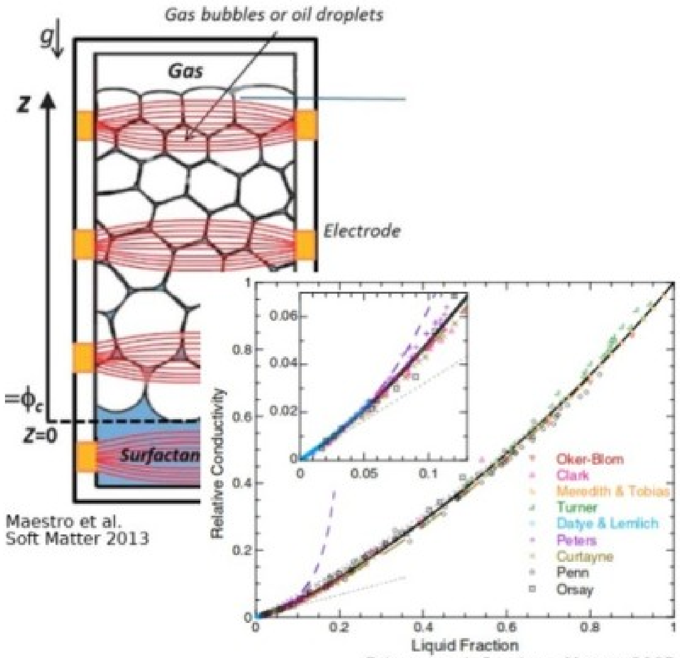
Introduction: Sascha Heitkam

- Since 2020 Emmy-Noether group: Towards Fluid Dynamics of Foam and Froth



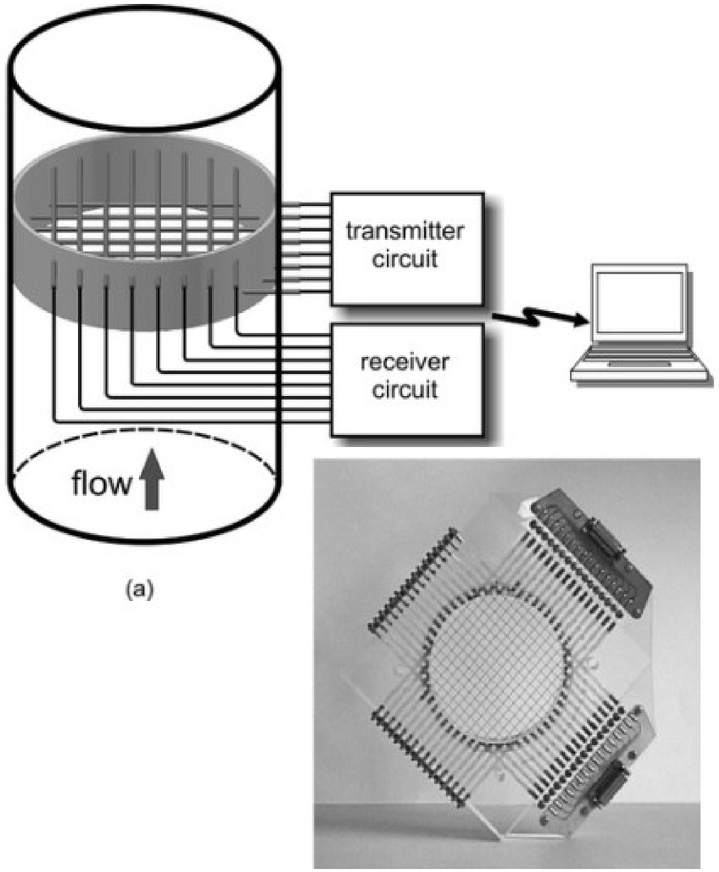
Introduction: Sascha Heitkam

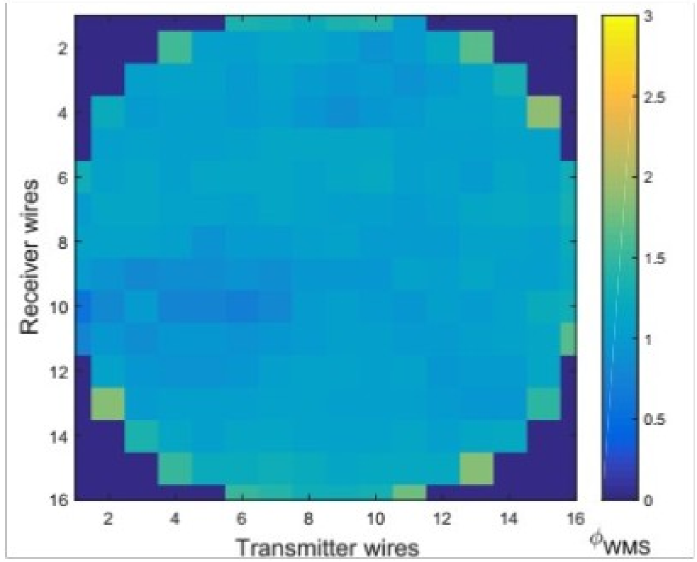
- Electric conductivity measurement of foam, also with Wire-Mesh sensor



Maestro et al.
Soft Matter 2013

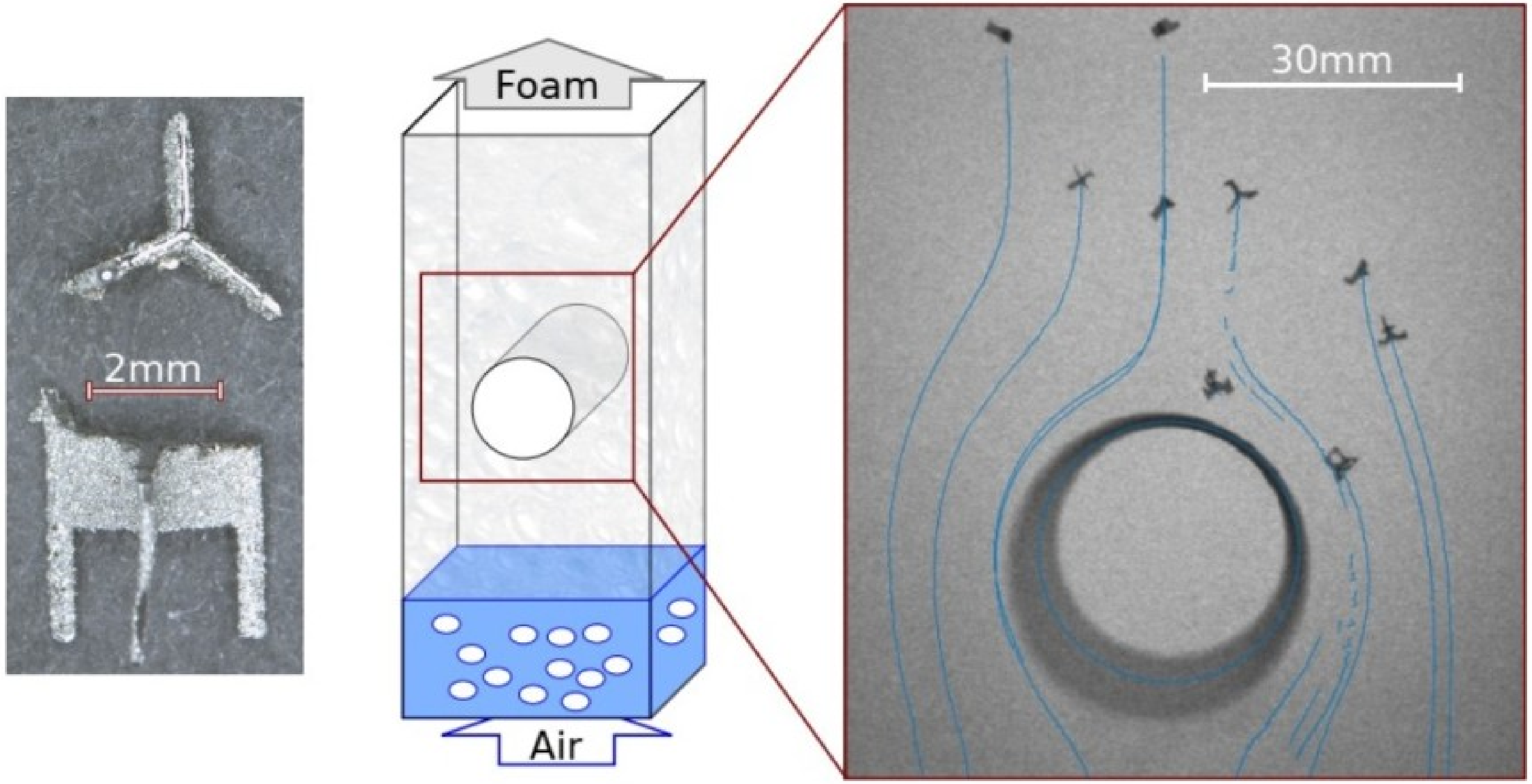
Feitosa et al. Condens. Matter, 2005





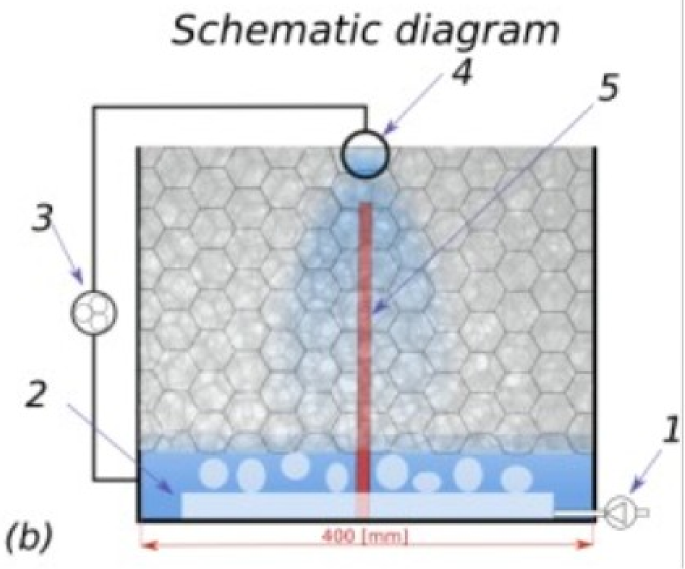
Introduction: Sascha Heitkam

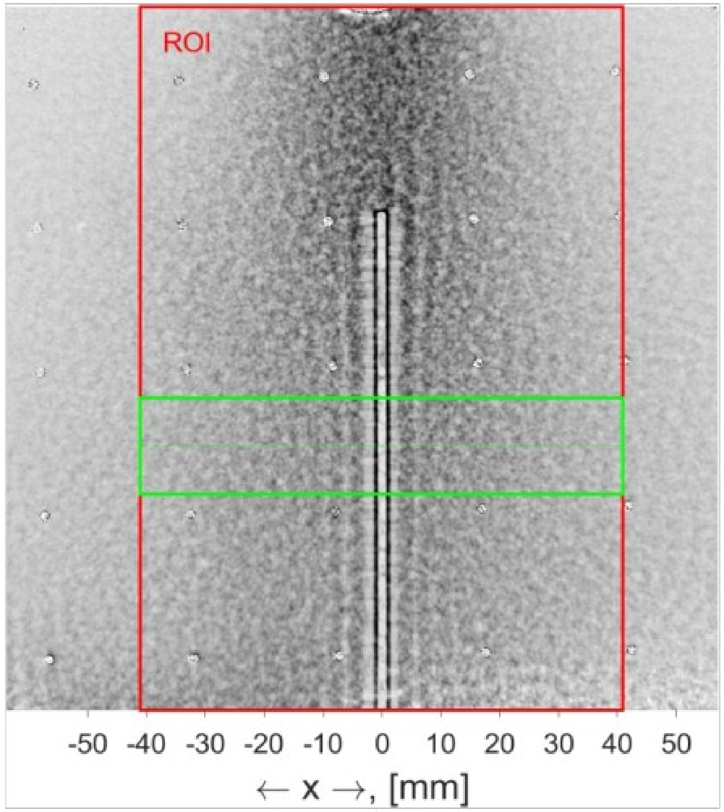
- Tracking of tracer particles using X-ray radiography

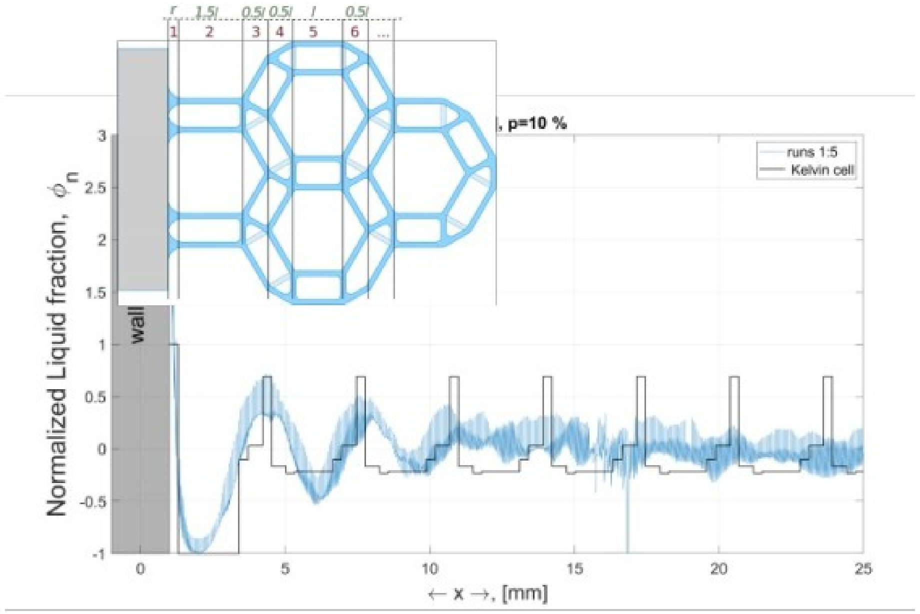


Introduction: Sascha Heitkam

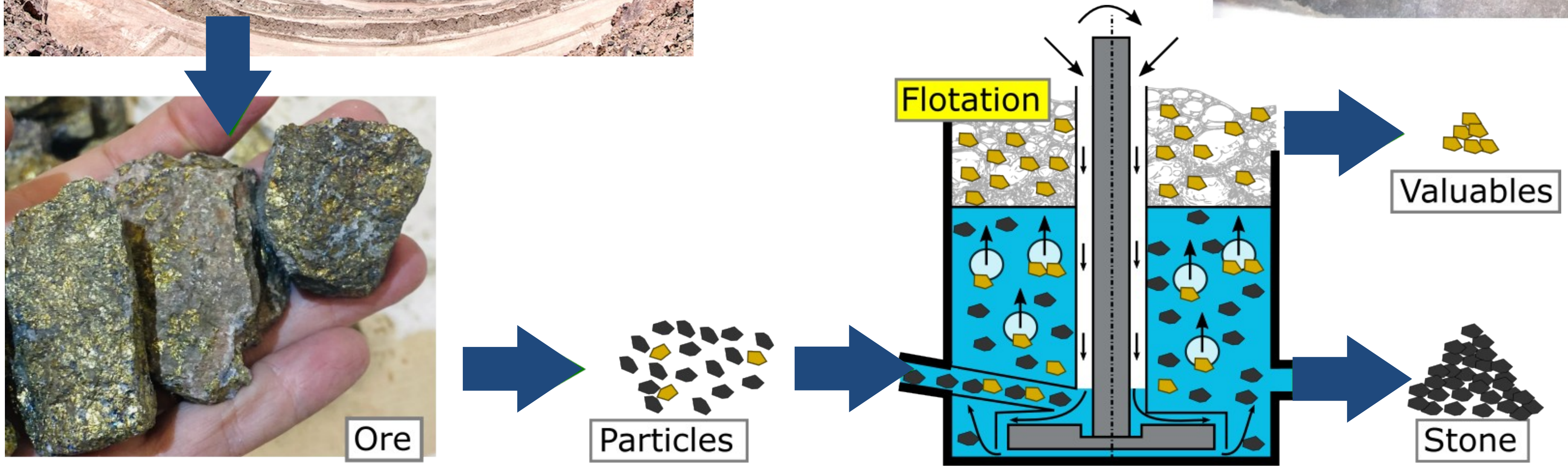
- Neutron Radiography of foam and froth







Introduction: Sascha Heitkam



Scope of the lecture

- Teach students / (a.k.a. future process engineers) in an important subject
- Transport and summarize relevant knowledge, i.e. for PhD students
- Inspire (future) researchers to tackle foam an froth

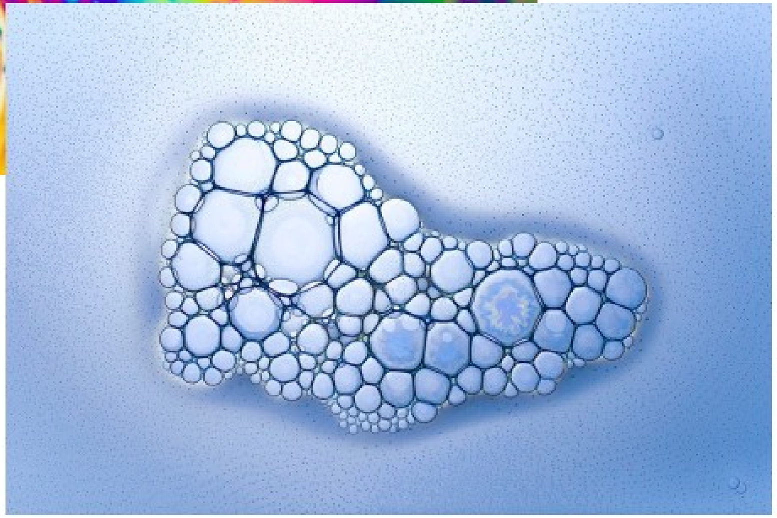
Requirements

- Basic understanding of fluid mechanics
- High School level Chemistry/Physics/Mathematics

Why would you care about foam???

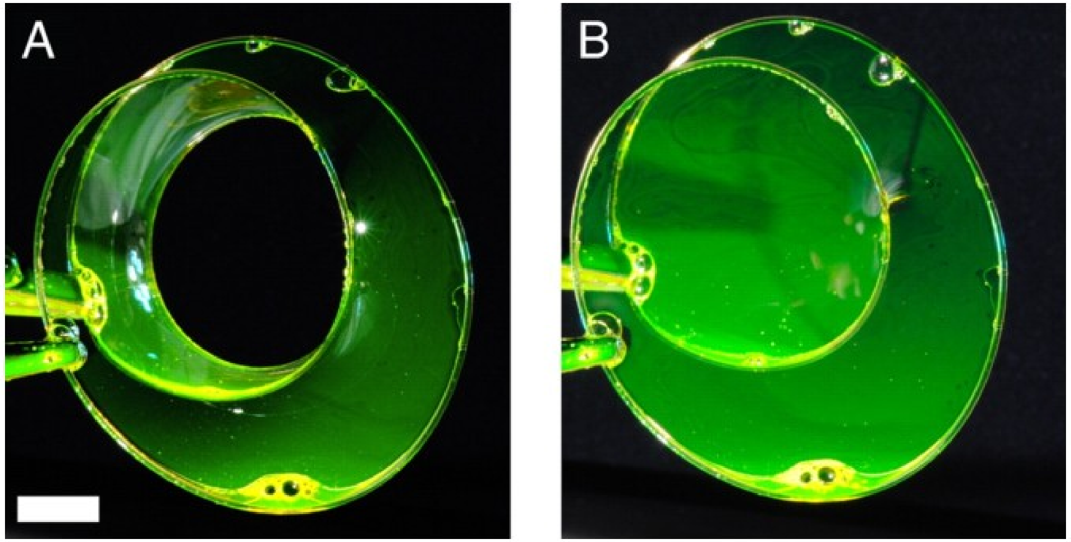
- Foams are beautiful

(C) Kym Cox

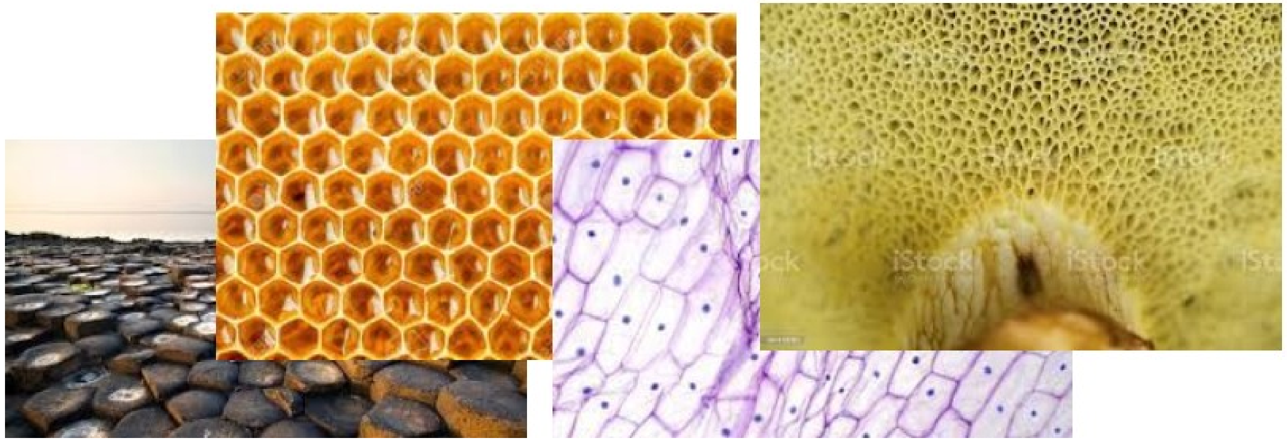


Why would you care about foam???

- Foams are interesting



[Goldstein et al. PNAS 2010]



Why would you care about foam???

- Foams are relevant

Structure

- Administrative Issues
- Surface Tension
- Young-Laplace law
- Exercise: Pressure inside a bubble
- Tensiometry
- Surfactants
- Exercise: Amounts of molecules

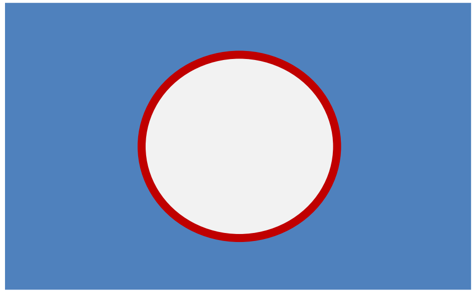
What is an interface/surface?

- Heterogeneous mixtures of immiscible substances

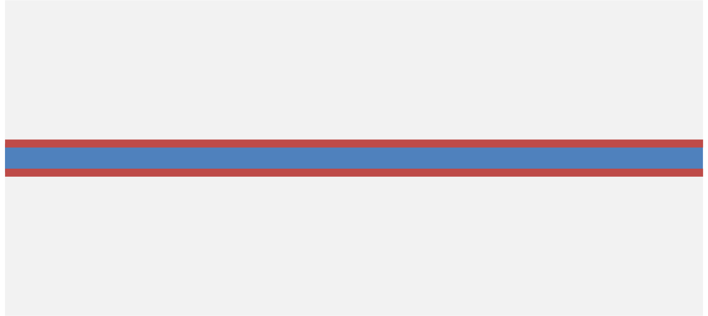
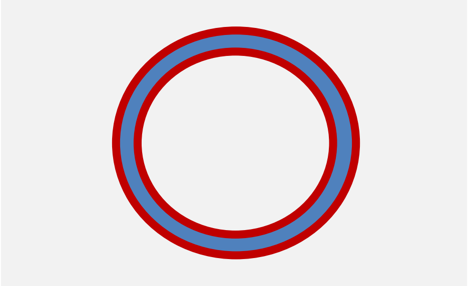
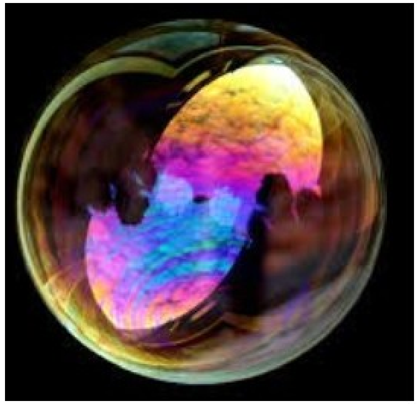
		Continuous material		
		gas	liquid	solid
Dispersed material	gas	---	bubbles/ foam	sponge/ solid foam
	liquid	aerosol/ spray	droplets/ emulsions	gel
	solid	smoke/ dust	suspension	(non-eutectic alloys)

What is an interface/surface?

- Interface

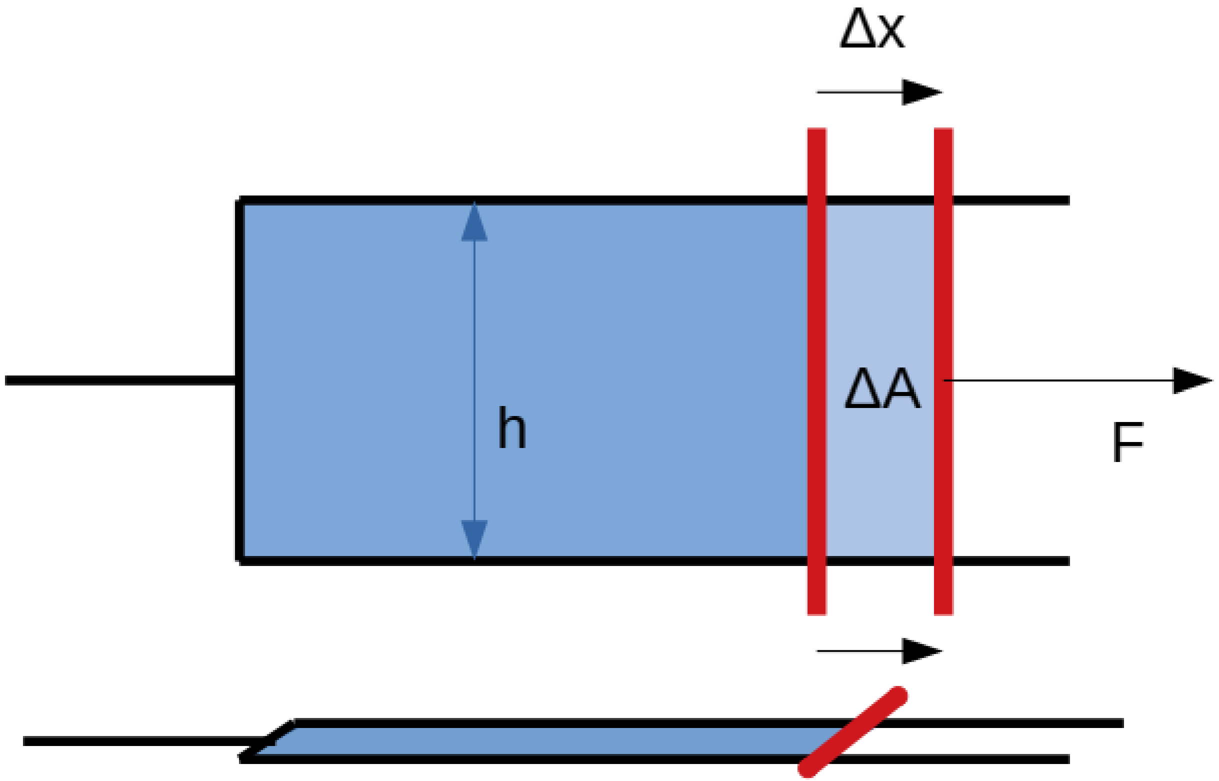




- Film / Lamella

Surface tension

- Generation of surface requires additional energy
- Counteracting force tries to minimize surface area



$$\frac{F}{h}=\frac{F\Delta x}{h\Delta x}=\frac{\Delta E}{\Delta A}=\gamma \qquad \gamma=\frac{Energy}{Surface\ Area}$$

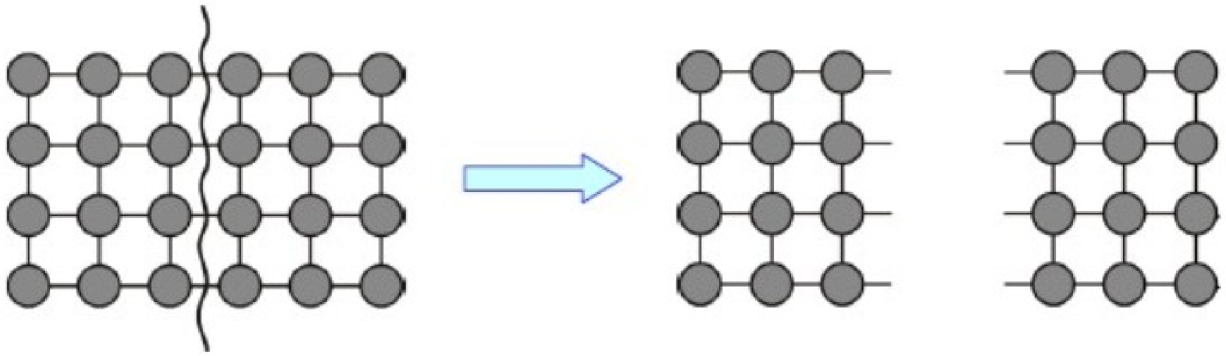
$$\frac{F}{2h}=\frac{F\Delta x}{2h\Delta x}=\frac{\Delta E}{2\Delta A}=\gamma$$

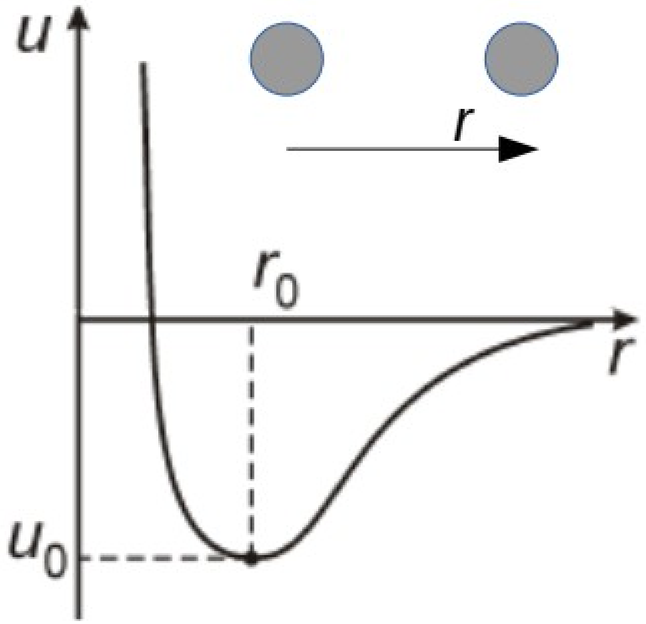
Backside!

Units: $$[\gamma]=\frac{Nm}{m^2}=\frac{N}{m}=1000\,\frac{dyne}{cm}$$

Cohesion forces

- Interaction force between molecules
- Energetic minimum for distance r_0



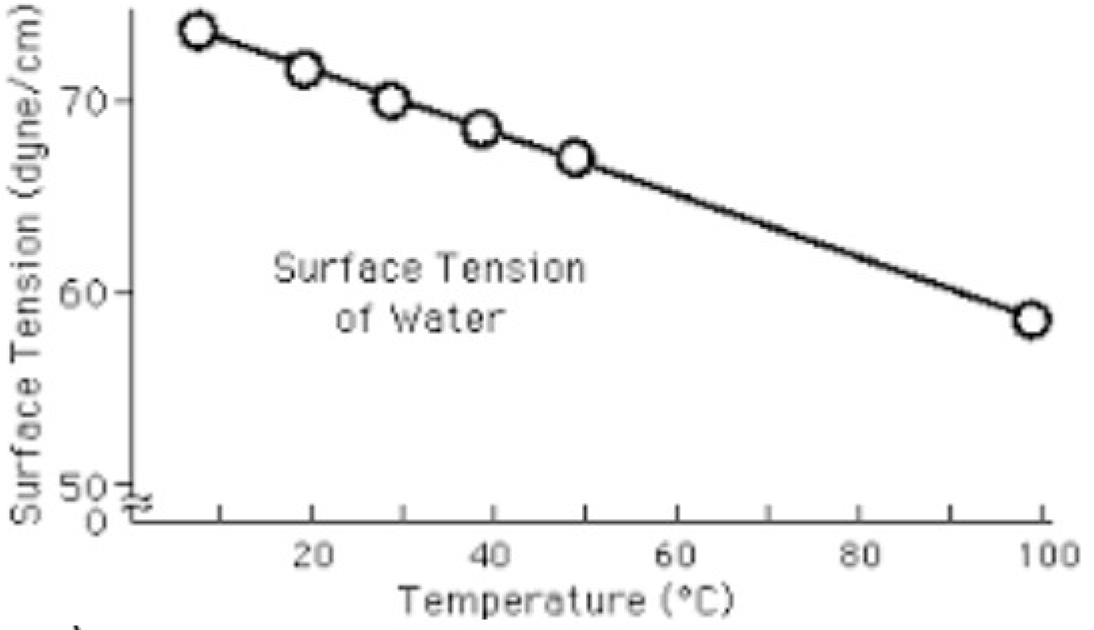


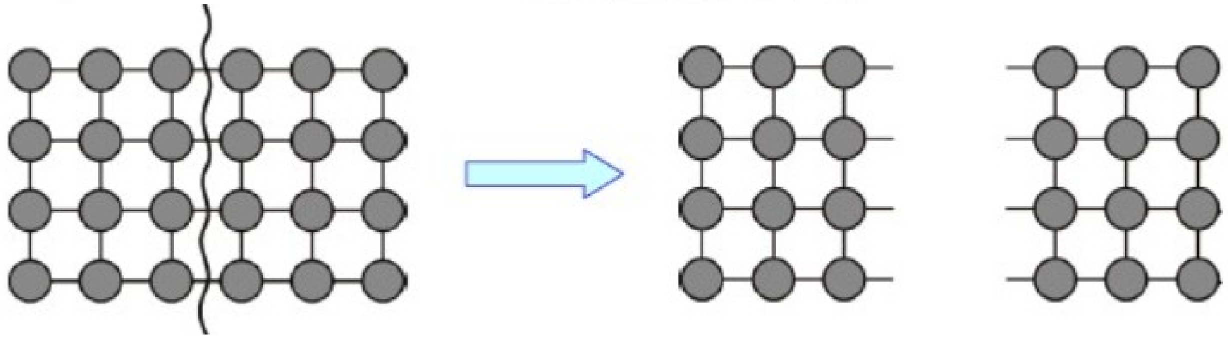
$$\frac{E}{\Delta A} \approx \frac{N u_0}{A} \approx \frac{u_0}{r_0^2} \approx \gamma$$

Typical surface tension

$$\frac{E}{\Delta A} \approx \frac{N u_0}{A} \approx \frac{u_0}{r_0^2} \approx \gamma$$

Material	Surf. Tens. [mN/m=dyne/cm]
Water 25°C	71.97
Soap water	30..40
Mercury 15°C	487
Ethanol 20°C	22.27
6M NaCl in H_20 20°C	82.55
Liquid N_2 -196°C	8.85





Structure

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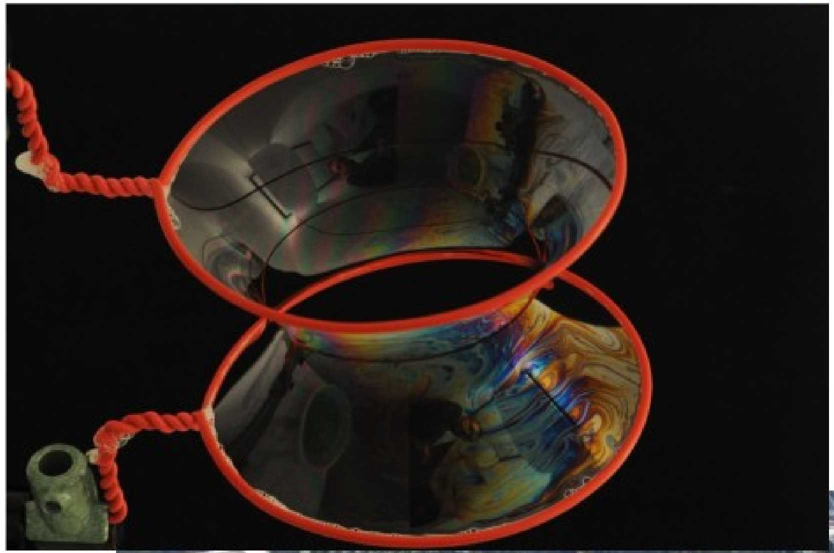
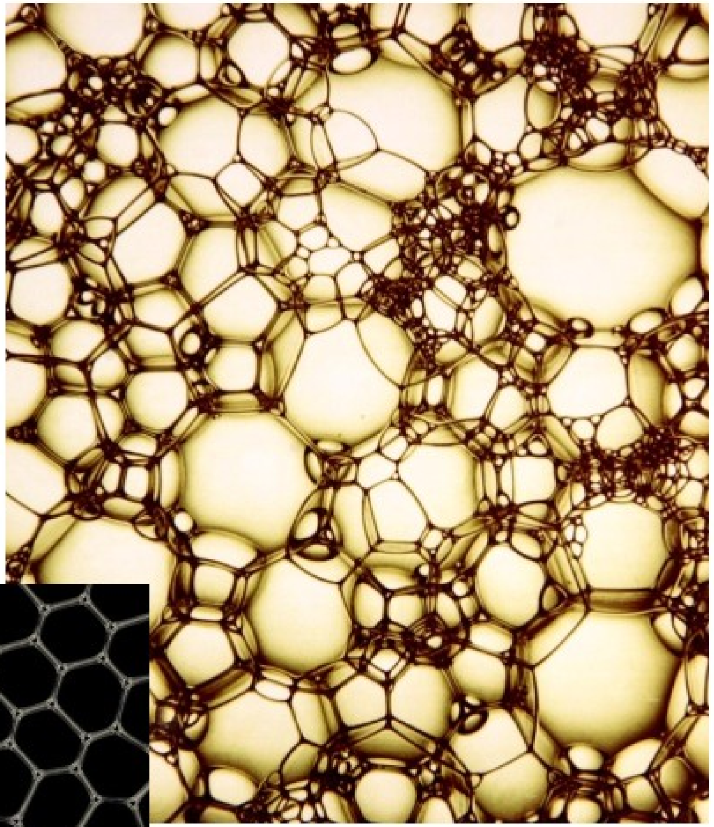
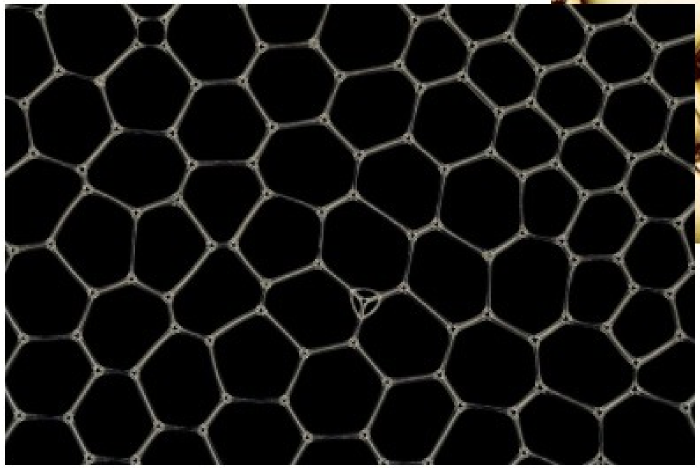
Young-Laplace law

- Shape represents a solution of Young-Laplace law



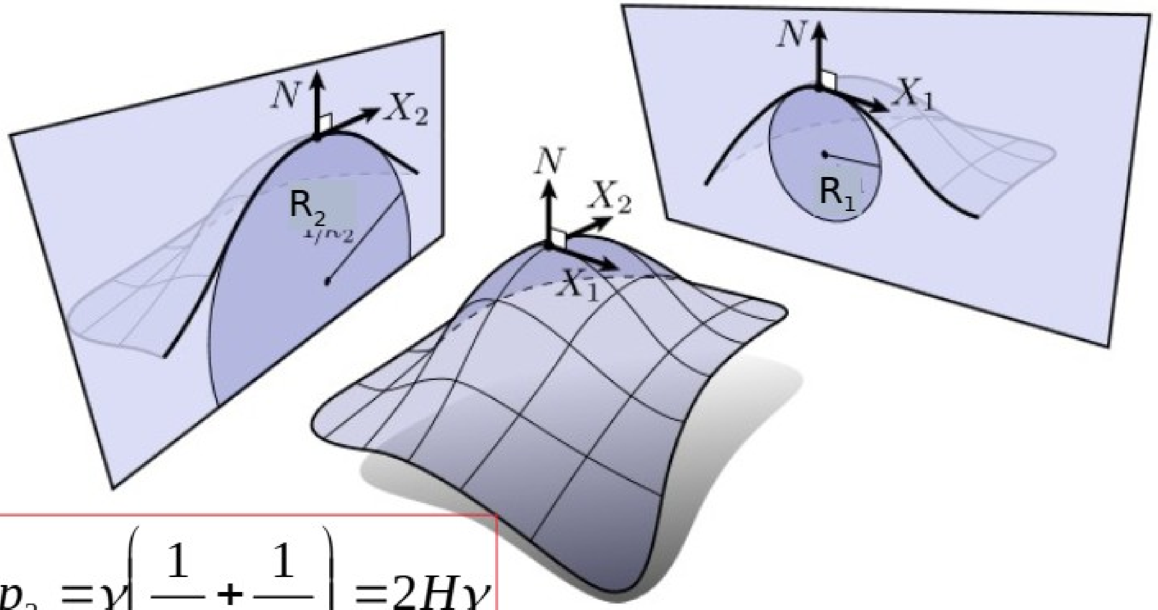




Young-Laplace law

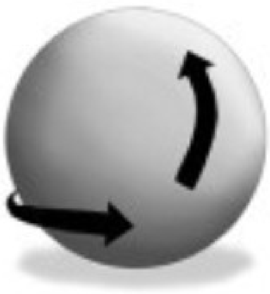
- Local „mean curvature“ H defines local pressure difference

$$H = \frac{1}{R} \rightarrow \Delta p = \frac{2\gamma}{R},$$

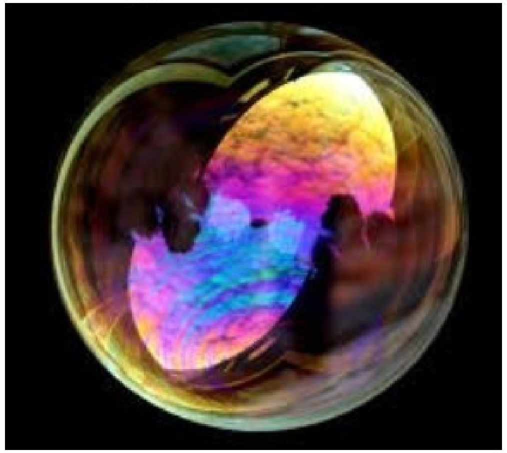


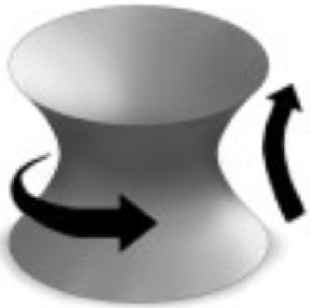
$$\boxed{\Delta p = p_1 - p_2 = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = 2H\gamma}$$

$$H = \frac{1}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

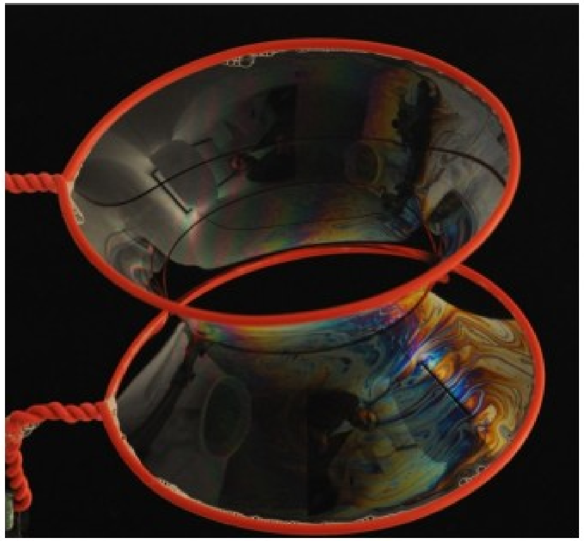


H>0





H=0



Pressure in a bubble

$$H=\frac{1}{R}\rightarrow\Delta p=\frac{2\gamma}{R}$$

- Local „mean curvature“ H defines local pressure difference

$$dE=\gamma dA$$

$$\rightarrow\frac{dE}{dR}=\frac{dE}{dA}\frac{dA}{dR}=\gamma 8\pi R$$

$$A=4\pi R^2\rightarrow\frac{dA}{dR}=8\pi R$$

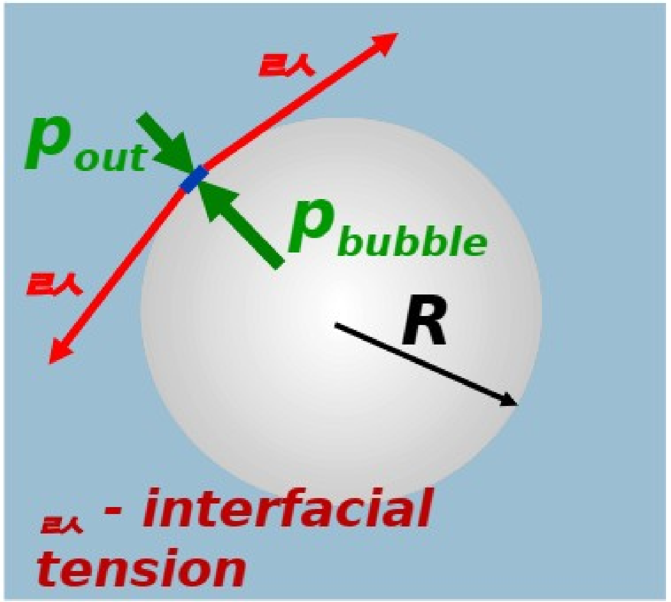
$$dE=-(p_{bubble}-p_{out})dV$$

$$\rightarrow\frac{dE}{dR}=-(p_{bubble}-p_{out})4\pi R^2$$

$$\frac{dE}{dR}=0=\gamma 8\pi R-(p_{bubble}-p_{out})4\pi R^2$$

$$\rightarrow\gamma 8\pi R=(p_{bubble}-p_{out})4\pi R^2$$

$$\frac{2\gamma}{R}=(p_{bubble}-p_{out})$$



Structure

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Exercise

- Inititial bubble radius: 1 cm

  Surface tension (soap water): 40 mN/m

→ What amount of work is required to inflate the bubble to 2 cm radius?

- Neglect compressibility of the air!

- Method 1: Change of surface area = change of surface energy

$$\frac{\Delta E}{\Delta A} = \gamma$$

- Method 2: Work W to inflate bubble

$$W = \int_{V(r_1)}^{V(r_2)} (p_{bubble} - p_{out})\, dV$$

$$A = 4\pi R^2$$

$$\frac{4\gamma}{r} = (p_{bubble} - p_{out})$$

Exercise

- Intitial bubble radius: 1 cm

  Surface tension (soap water): 40 mN/m

→ What amount of work is required to inflate the bubble to 2 cm radius?

- Neglect compressibility of the air!

- Method 1: Change of surface area = change of surface energy

$$\frac{\Delta E}{2\Delta A}=\gamma$$

$$W=2\gamma(A(r_2)-A(r_1))=2\gamma 4\pi(r_2^2-r_1^2)$$

$$W=0.3\,mJ$$

$$A=4\pi R^2$$

$$\frac{4\gamma}{r}=(p_{bubble}-p_{out})$$

Exercise

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$$A = 4\pi R^2$$

$$\frac{4\gamma}{r} = (p_{bubble} - p_{out})$$

$$W = \int_{r_1}^{r_2} \left(\frac{4\gamma}{r}\right) 4\pi r^2\, dr = 16\gamma\pi \frac{r^2}{2}\Bigg|_{r_1}^{r_2} = 8\gamma\pi(r_2^2 - r_1^2) = 0.3\, mJ$$

Structure

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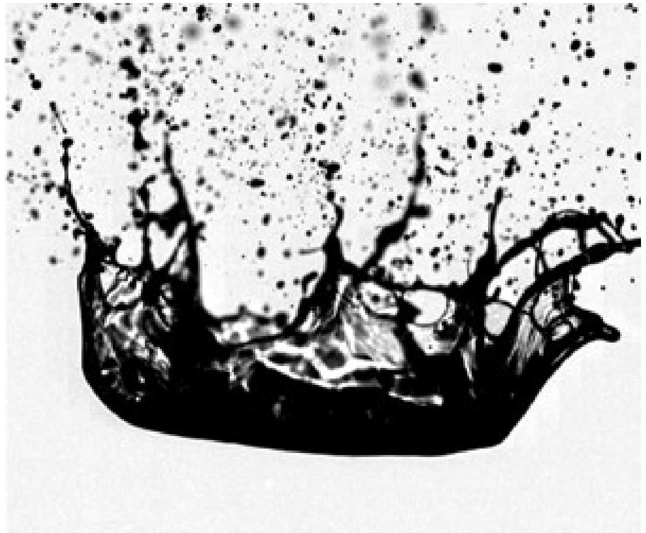
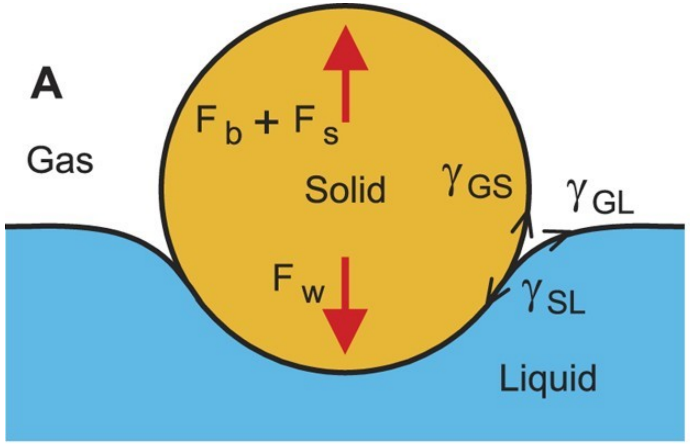
Tensiometry

- Measurement of surface tension
- Relevant for wetting/de-wetting behaviour → glue
- Relevant for droplet generation → spray, cleaning
- Relevant for particle dispersions → paint
- → Huge variety of measurement techniques, commercially available



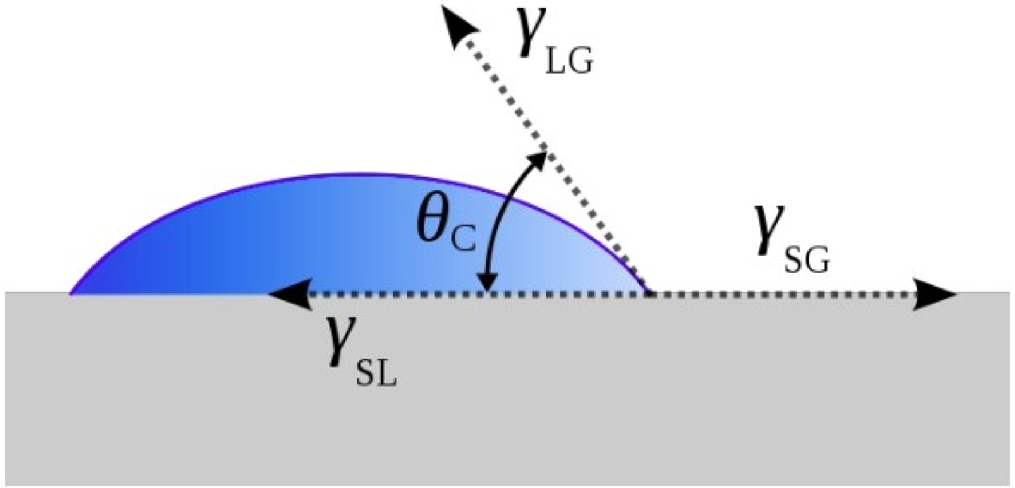


Contact angle measurement

- Contact line connects three interfaces
- Each interface „pulls“ on the contact line
- Equilibrium of forces yields contact angle

Mercury on polymer

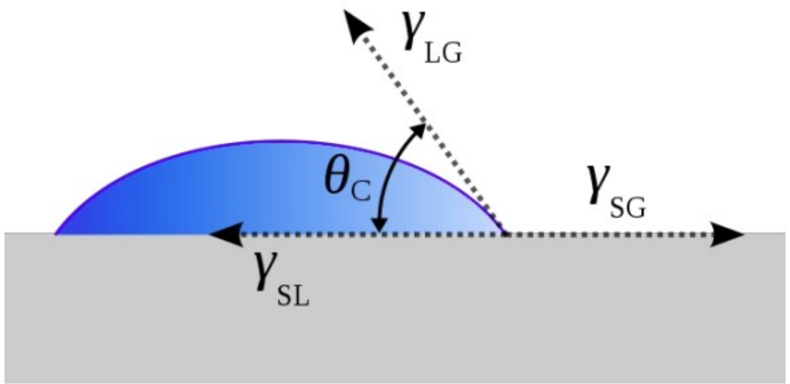
Water on glass



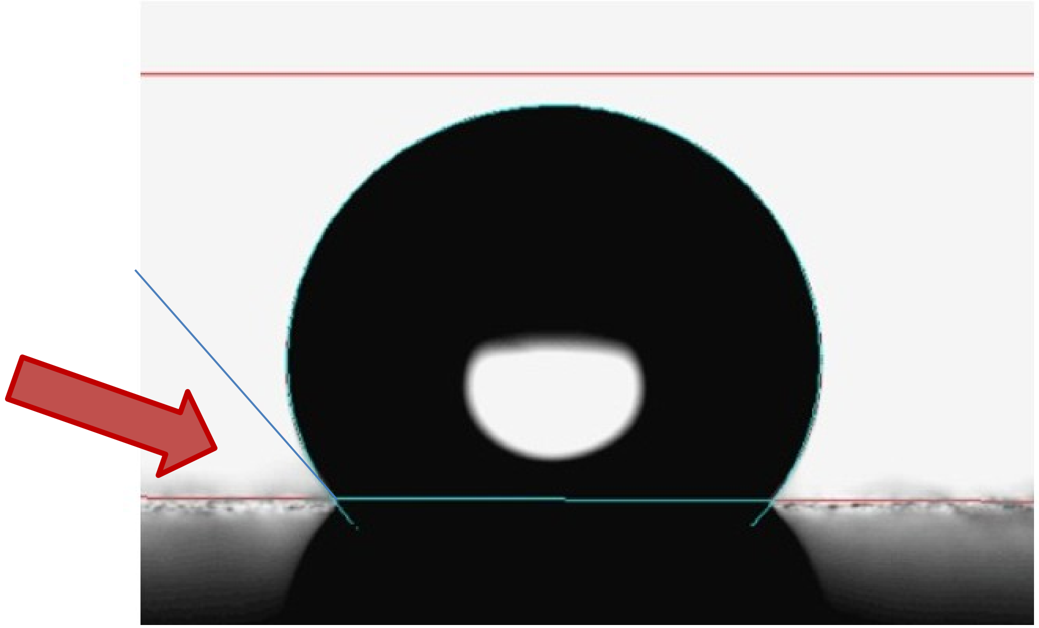
$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos(\theta)$$

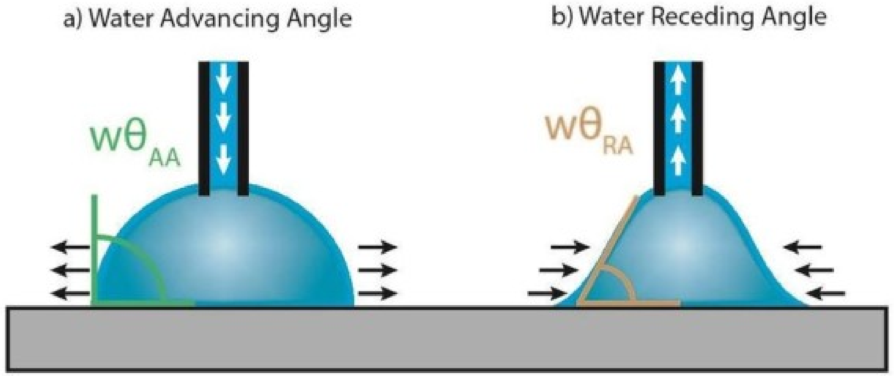
Contact angle measurement

- Sessile drop technique for hydrophobicity
- Does not yield surface tension directly



$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos(\theta)$$

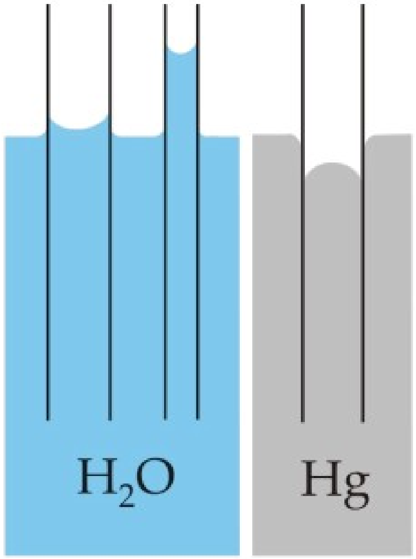


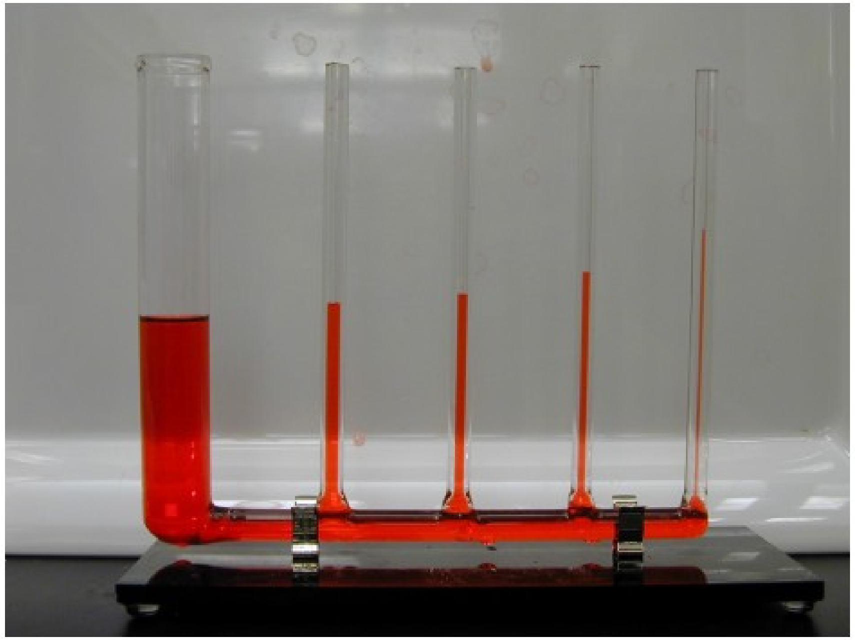


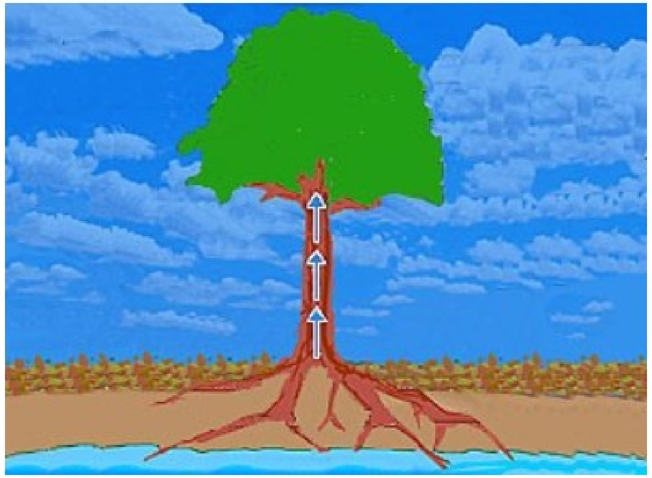
(C) Michelle Mattera

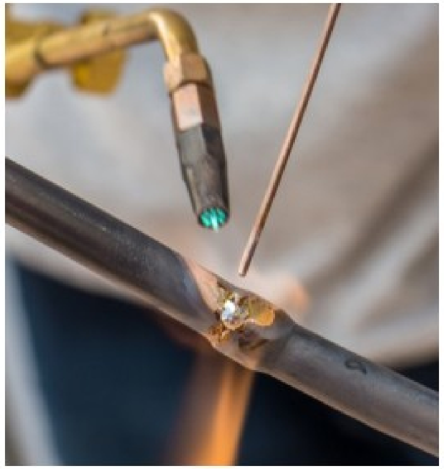
Capillary effect

- Surface tension (capillary force) pulls on liquid column
- Counteraction by gravity yields equilibrium







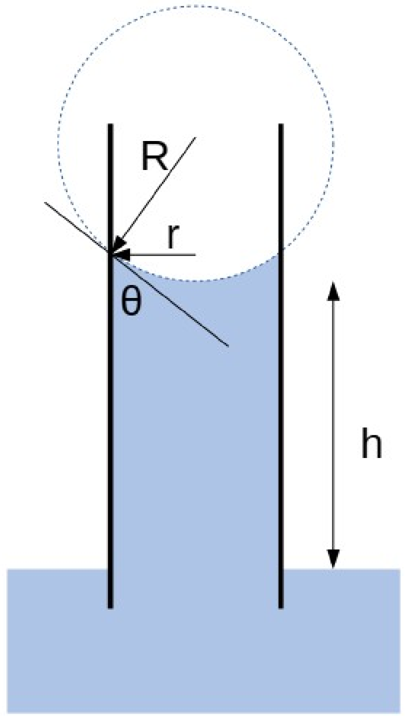


Capillary for surface tension measurement

$$\gamma = \frac{\Delta E}{\Delta A}$$

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$$

- Capillary with defined radius r (commercially available)
- Submerged vertically into pool of liquid
- Measurement of steady fill level h above pool level



Young-Laplace law

$$\Delta p = \rho g h = \frac{2\gamma}{R}$$

$$R\cos\theta = r$$

Force balance

$$F_{grav} = F_{cap}$$

$$\rho g h\, \pi r^2 = \gamma \cos\theta \;\; 2\pi r$$

Energetic minimum

$$W = \pi r^2 h\, \rho g \frac{h}{2} + 2\pi r h(\gamma_{SL} - \gamma_{SG})$$

$$\frac{d\,W}{d\,h} = 0 = \pi r^2 \rho g h + 2\pi r(\gamma_{SL} - \gamma_{SG})$$

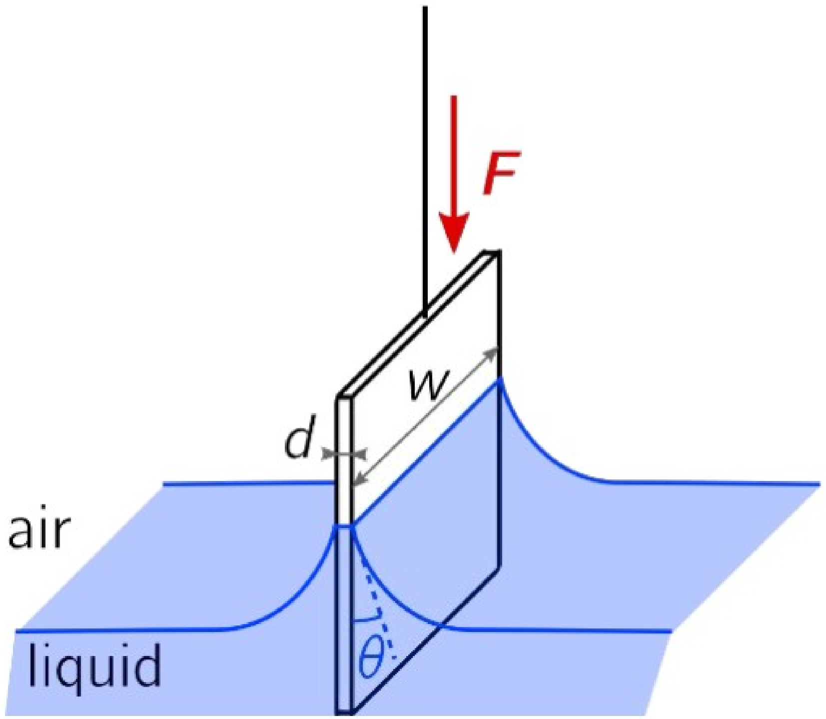
$$\pi r^2 \rho g h = -2\pi r(\gamma_{SL} - \gamma_{SG})$$

$$\rho g h = \frac{2\gamma\cos\theta}{r}$$

Wilhelmy plate

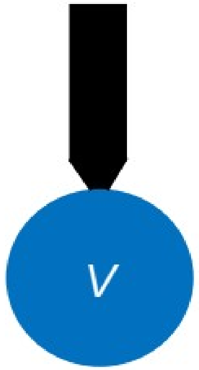
- Plate submerged and pulled out
- Static force measurement
- Plate with high surface energy (e.g. Pt)
- → contact angles assumed to be negligible
- Similar techniques for other objects (e.g. du Noüy ring)

$$F = \gamma \cos(\theta)\,(2w + 2d)$$



Measurement of surface tension

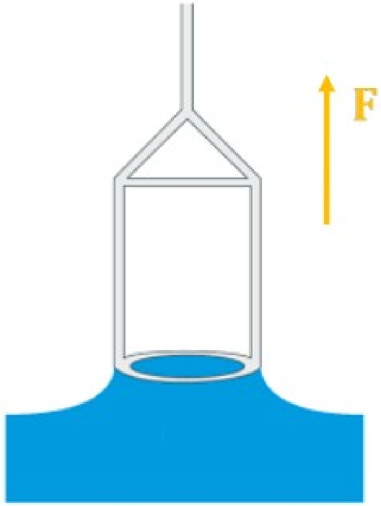
- Drop volume method



$$\gamma = \frac{\Delta\rho V g}{2\pi r}$$

γ	Surface tension
V	Drop volume
r	Needle inside diameter
g	Gravity acceleration
$\Delta\rho$	Density difference

- Du Noüy Ring method

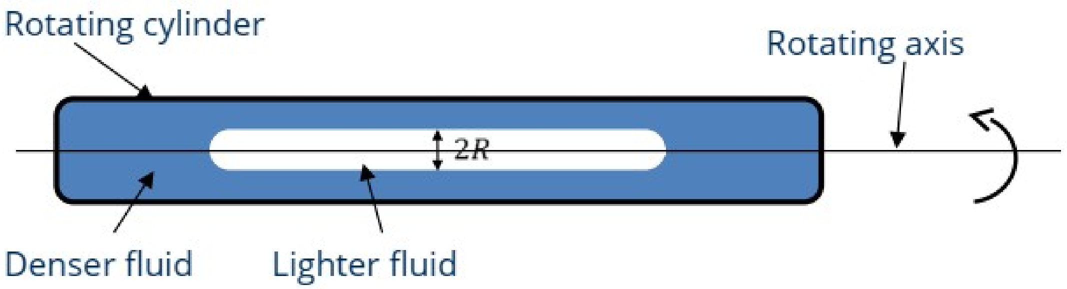


$$\gamma = \frac{\mathrm{F} - W_{ring}}{2\pi(r_i + r_o)}$$

γ	Surface tension
F	Applied Force
W_{ring}	Ring weight
r_i	Inside ring radius
r_o	Outside ring radius

Measurement of surface tension

- Spinning drop method
- → For low surface tensions

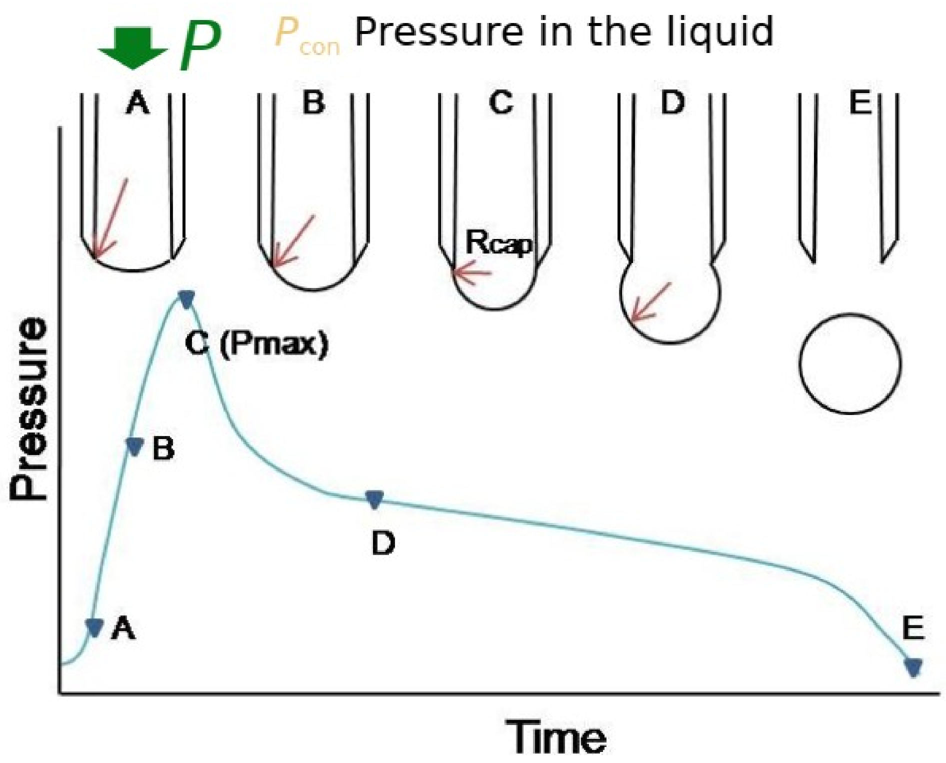


$$\gamma = \frac{\Delta\rho\omega^2 R^3}{4}$$

γ	Surface tension
ω	Angular velocity
R	Radius of lighter spinning fluid
$\Delta\rho$	Density difference

Max bubble pressure tensiometer

- Blowing bubble from needle/capillary with defined radius R_{cap}
- Continuously record pressure in the needle

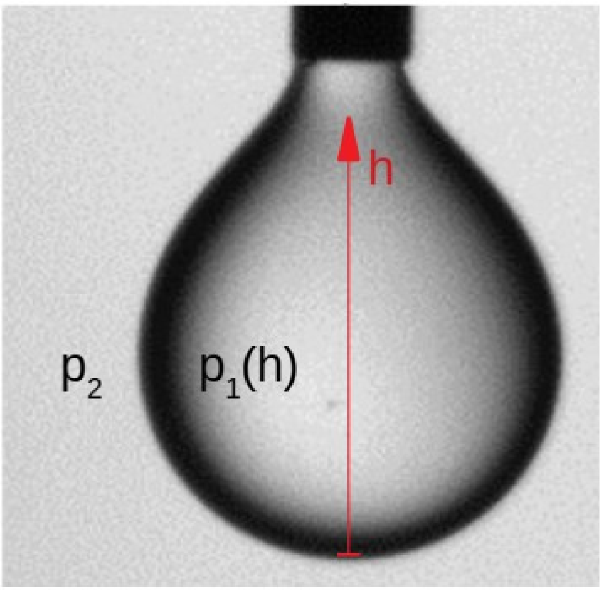


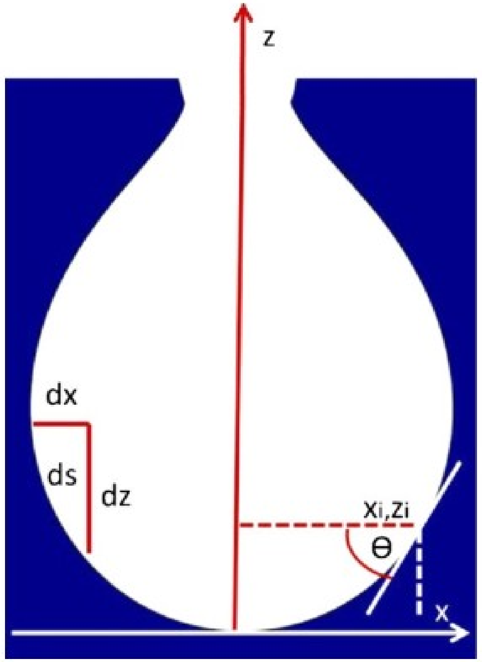
$$\Delta P = P - P_{con} = \frac{2\gamma}{R}$$

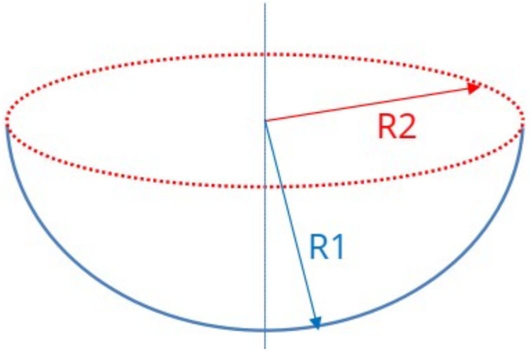
$$\Delta P_{max} = \frac{2\gamma}{R_{cap}}$$

Pendant drop tensiometer

- Static drop hangs on capillary
- Optical detection of the shape of the drop
- Young-Laplace law is fitted to shape
- No influence of third material!
- Low amounts of liquid required
- Measurement of time-dependent surface tension







$$\Delta p = p_1 - p_2 = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = 2H\gamma$$

$$\Delta p(h) = p_1(h=0) - \rho g h - p_2 = 2\gamma H(h)$$

Tensiometry

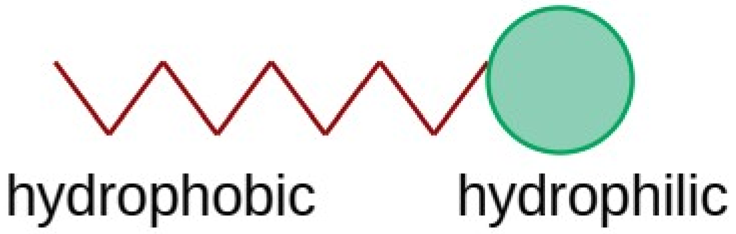
Method	Static	Dynamic
Capillary rise	✔	≈
Wilhelmy plate	✔	≈
du Noüy ring	✔	X
Drop weight	✔	X
Drop volume	✔	X
Pendant drop	✔	✔
Sessile drop	✔	✔
Oscillating jet	✔	✔
Spinning drop	✔	≈
Maximum bubble pressure	✔	≈
Maximum droplet pressure	✔	≈
Tilting plate	✔	≈

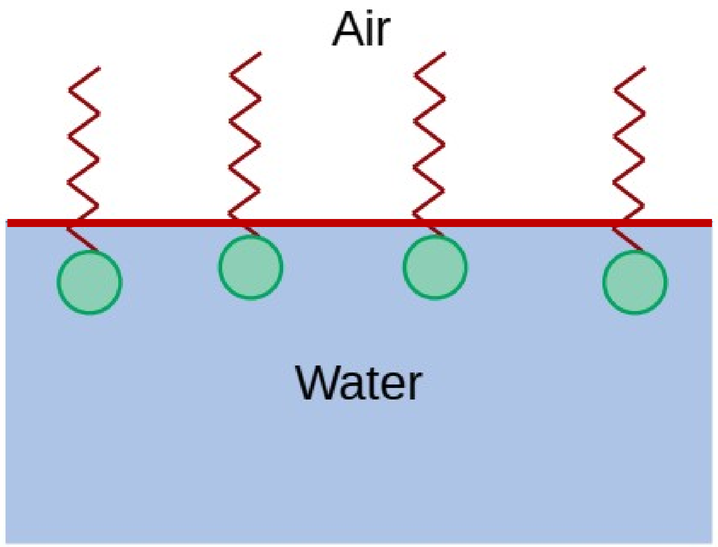
Structure

- Administrative Issues
- Surface Tension
- Young-Laplace law
- Exercise: Pressure inside a bubble
- Tensiometry
- Surfactants
- Exercise: Amounts of molecules

What are surfactants?

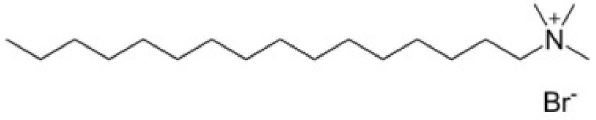
- Surfactants = SURFace ACTive AgeNTS
- Adsorb at interfaces, decreasing surface tension

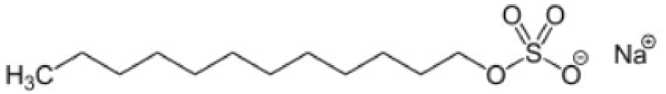


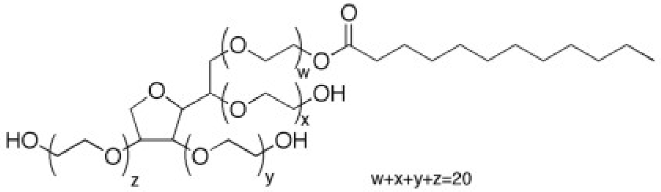


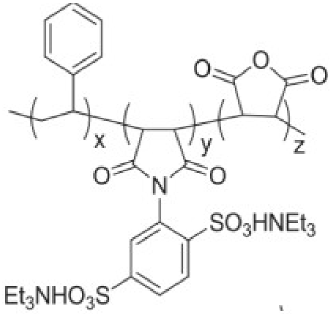
Types of surfactants

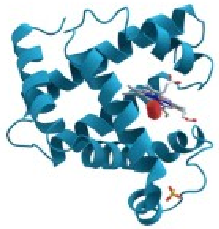
- Small molecules (mass up to 1000 g/mol)
  - – Ionic surfactants
    - ● Cationic surfactants CTAB, TTAB
    - ● Anionic surfactants SDS
  - – Non-ionic surfcatants Tween
- Large Molecules
  - – Polymers
  - – Proteins (Enzymes)
- Particles

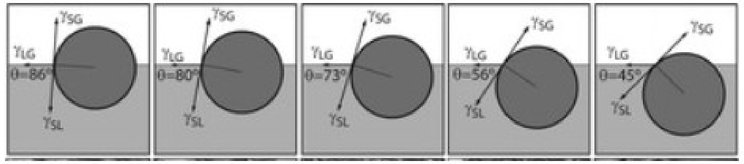






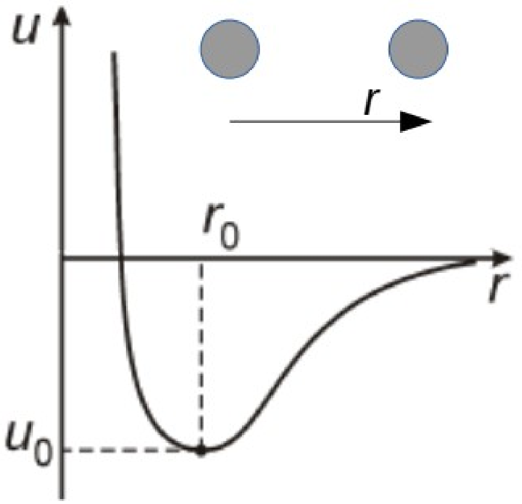


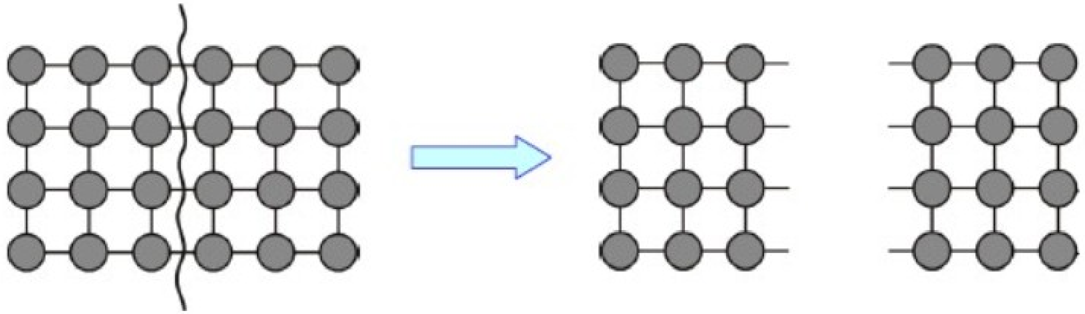




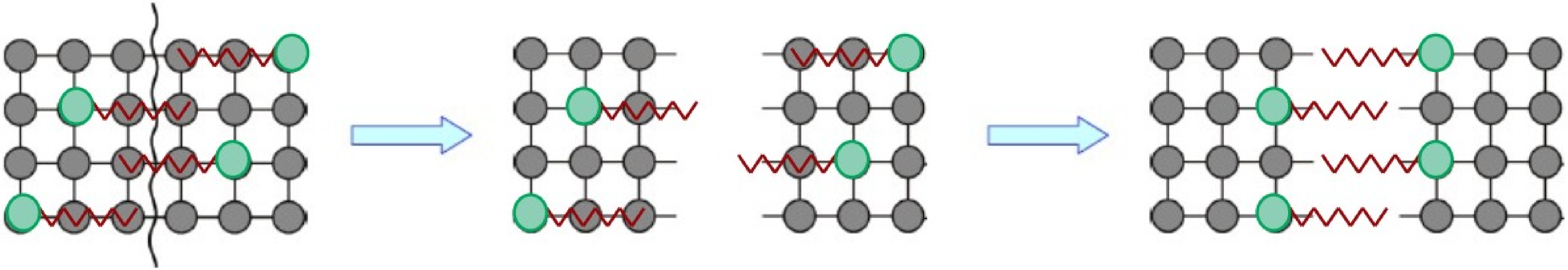
Reduction of surface tension

- Surfactant molecules replace water molecules at the interface
- Amount of additional surface energy is reduced



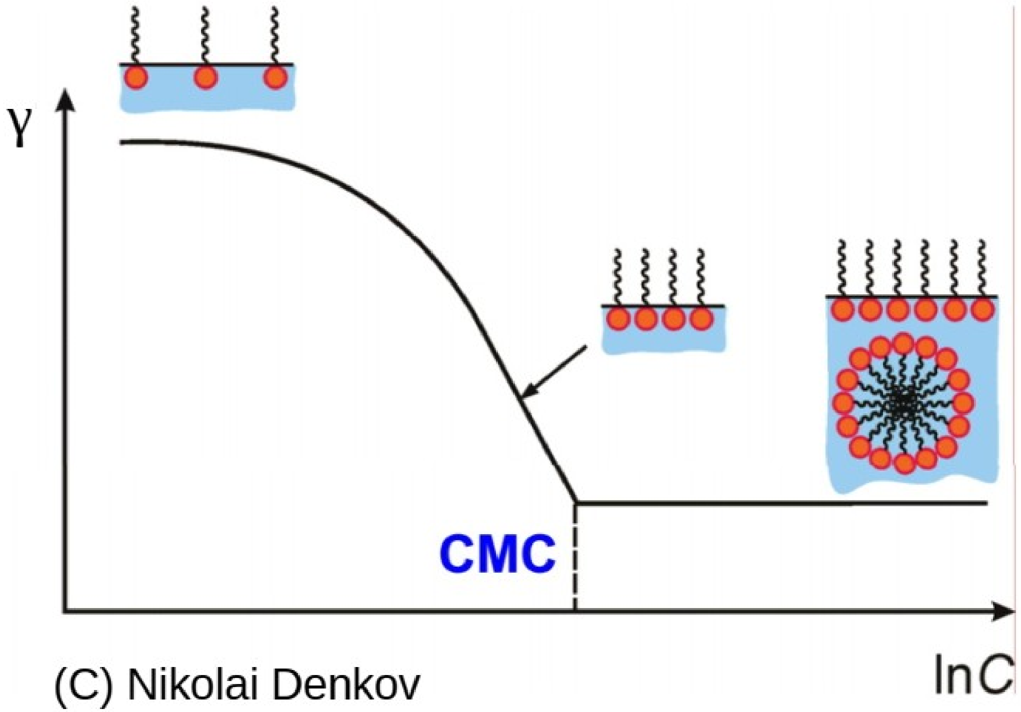


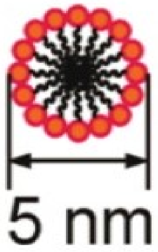
$$\frac{E}{\Delta A} \approx \frac{N u_0}{A} \approx \frac{u_0}{r_0^2} \approx \gamma$$

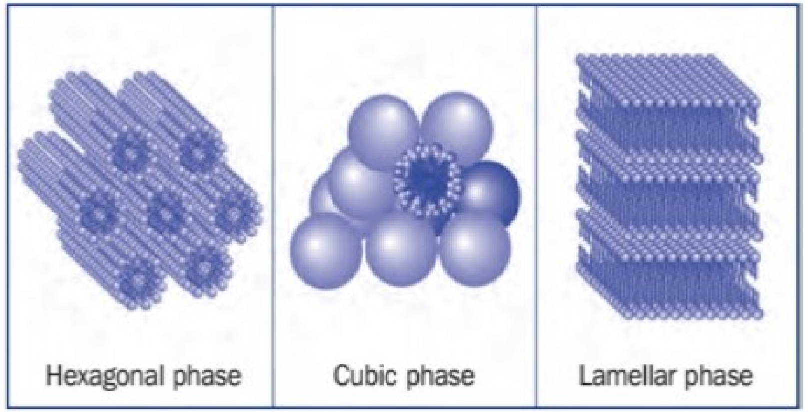


Critical Micelle Concentration - CMC

- Equilibrium between surface concentration and bulk concentration
- Below CMC surface tension is reduced with increasing bulk concentration
- Above CMC interface is fully covered and excess surfactants form micelles

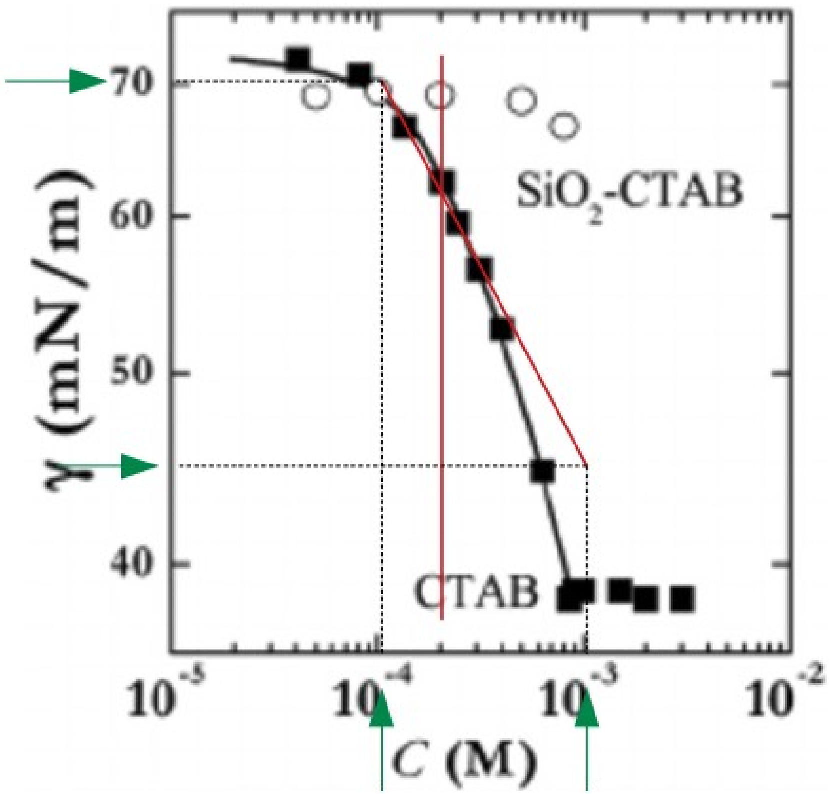






Gibbs adsorption isotherm

- Relation between Surface coverage Γ (in mol/m²), bulk concentration c (in mol/m³) and surface tension γ
- Depends on type (i.e. chemical potential) of surfactant x
- For ionic sufactants in solution with electrolytes (salt): x=1



$$\Gamma_S = \frac{-1}{R\,T\,x}\frac{d\,\gamma}{d\,\ln c}$$

$$\Gamma_S = \frac{-1}{8.314\,J\,mol^{-1}\,K^{-1}\,298\,K}\frac{-0.025\,N/m}{2.303}$$

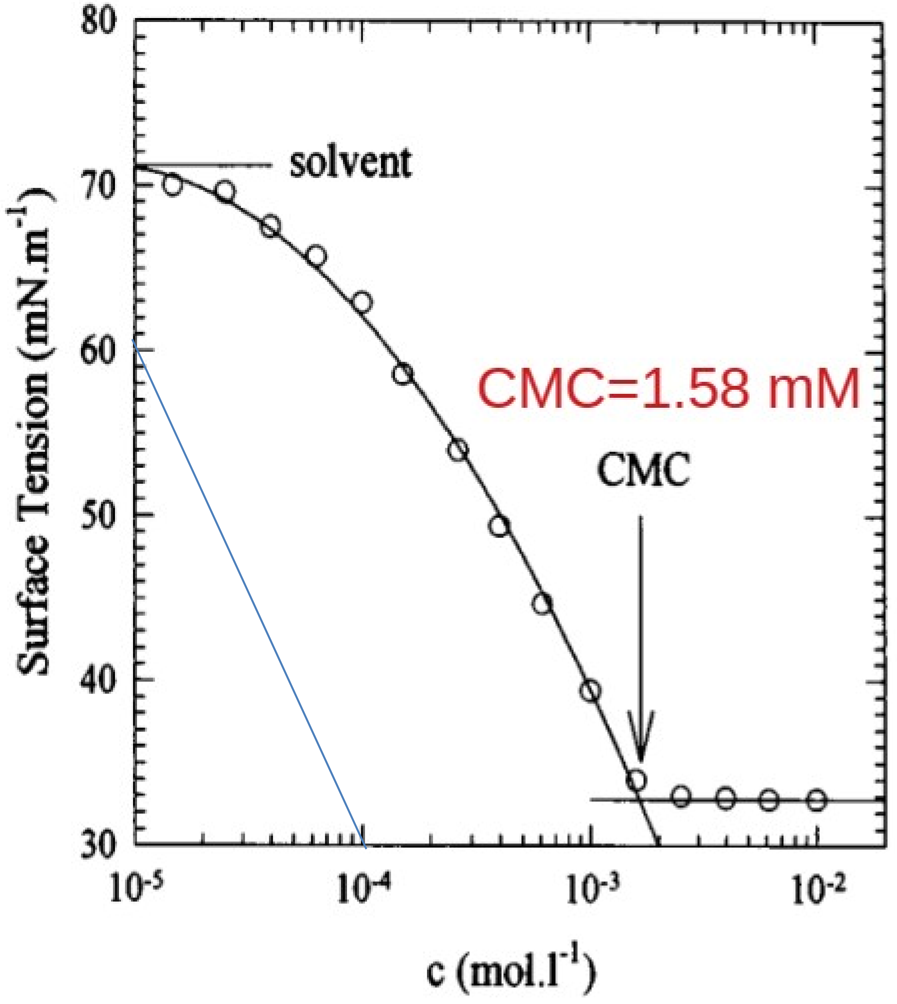
$$\Gamma_S \approx 4.4\,x\,10^{-6}\,mol/m^2$$

- → approx. 3 nm distance between surfactant molecules

Exercise

$$\Gamma_S = \frac{-1}{RTx}\frac{d\gamma}{d\ln c}$$

- What is the surface coverage Γ_{CMC} of an interface in SDS solution at CMC?
- How many bubbles (5 mm diameter) can be produced from 1 liter SDS solution at CMC, if all bubbles are covered by Γ_{CMC}?
- What is the total bubble volume?



Exercise

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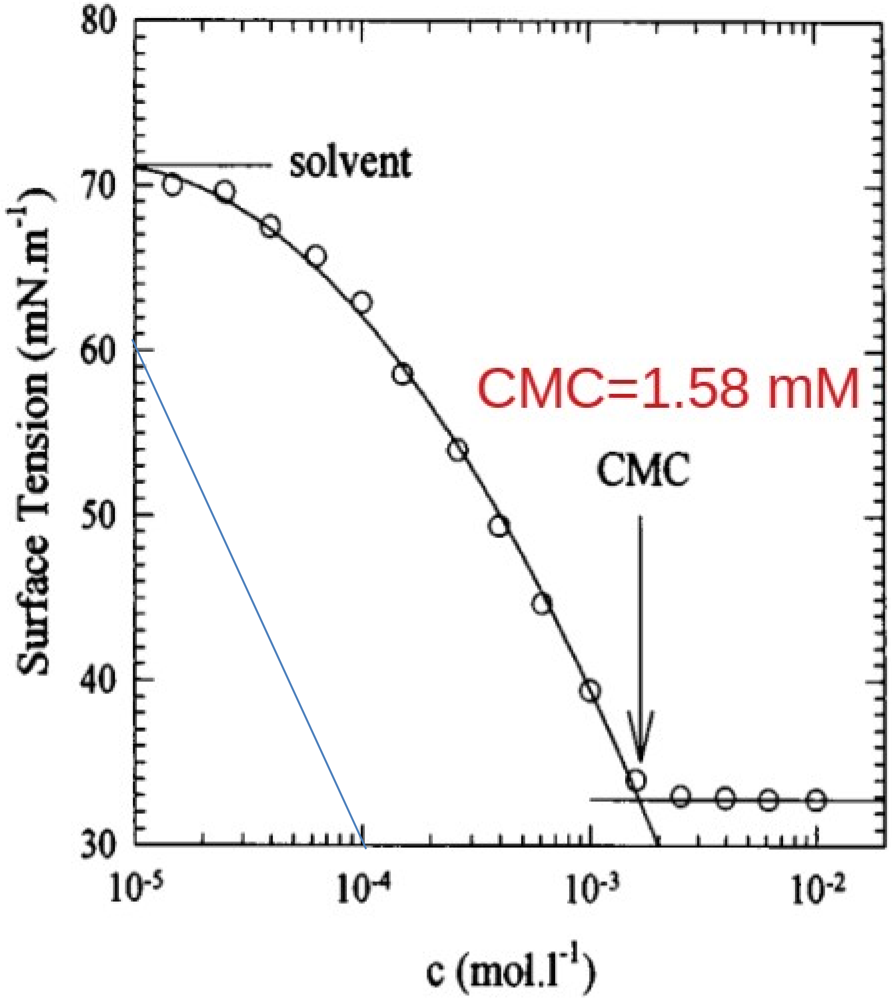
$$\Gamma_S = \frac{-1}{8.314\,J\,mol^{-1}\,K^{-1}\,298\,K} \frac{0.030\,N/m}{-2.303} \approx 5.3\,x\,10^{-6}\,mol/m^2$$

$$N_{1L} = 1.58\,x\,10^{-3}\,mol \rightarrow 0.45\,g$$

$$A_{bubble} = 4\pi r^2 = 78\,x\,10^{-6}\,m^2$$

$$n_{bubble} = \frac{N_{1L}}{\Gamma_S A_{bubble}} \approx 3.8\,x\,10^6$$

$$V_{bubble} = n_{bubble} * 4/3\ \pi r^3 = 0.25\,m^3$$

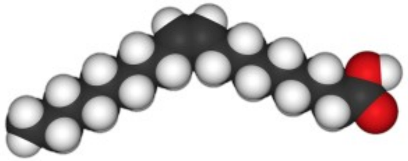


Size of a molecule

- Benjamin Franklin measured in 1774 the size of the lake area, covered by 1 teaspoon of oil (=2000 m^2)
- Assuming single-molecular layer, thickness yields the size/space of a molecule → ~1 nm
- Comparison to Γ_{CMC}?

$$\Gamma_S = \frac{-1}{8.314\,J\,mol^{-1}\,K^{-1}\,298\,K}\,\frac{0.030\,N/m}{-2.303} \approx 5.3\,x\,10^{-6}\,mol/m^2$$

$$d \approx 3\,nm$$



Oleic acid

Sodium dodecyl sulfate