TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

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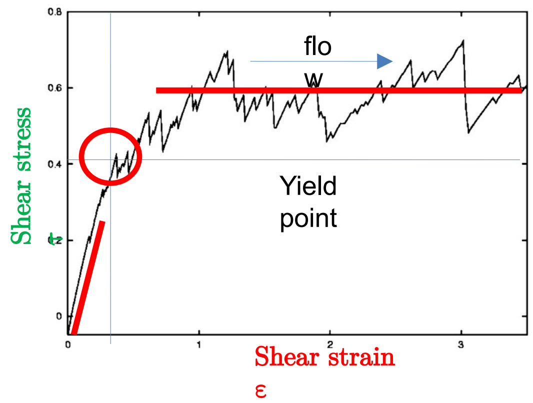
Lecture 10: Foam stability

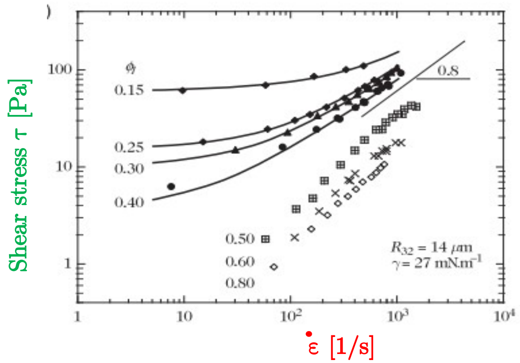
Structure

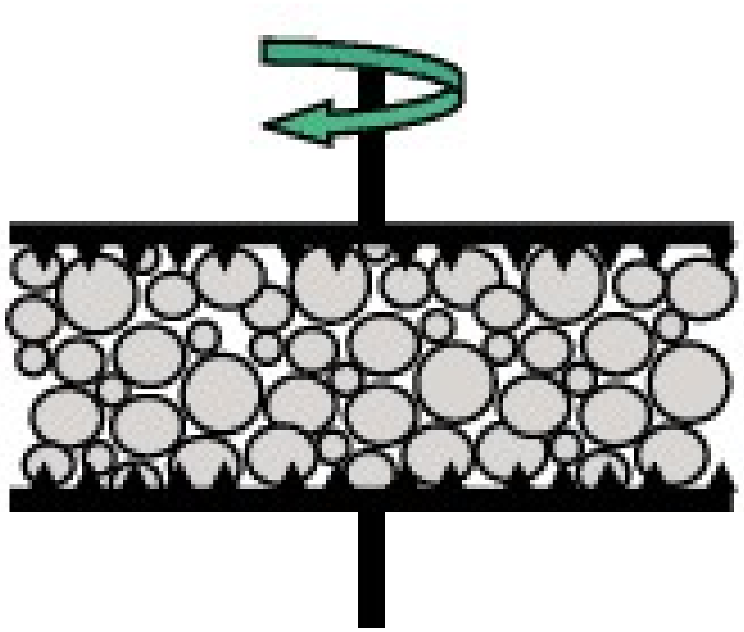
- Review lecture 9
- Film rupture
- Coarsening
- Stability testing
- Defoaming

Rheometer

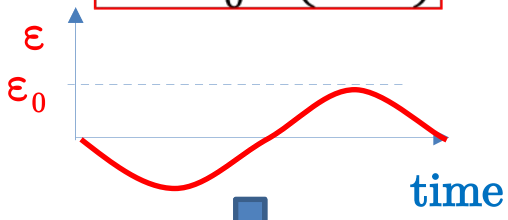
- Measure relation between strain (rate) and stress
- Well defined geometry
- → analytical solution of stress / strain distribution
- Avoid wall slip! → etching grooves, sandpaper



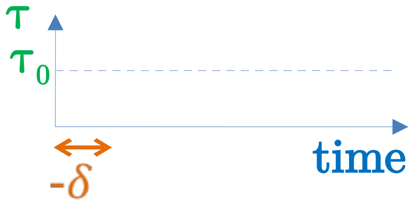


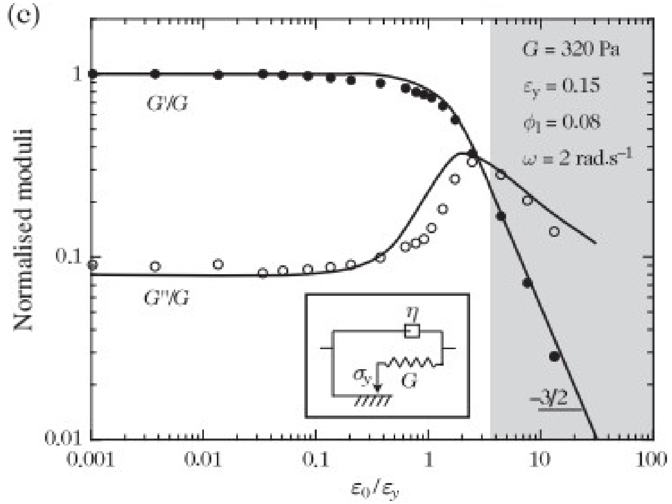


$$\varepsilon = \varepsilon_0 \, R(e^{i\omega t})$$



$$\tau = \tau_0 \, R(e^{i\omega t+\delta})$$

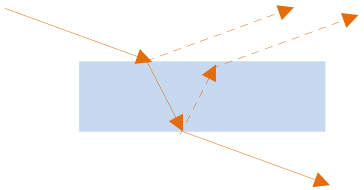


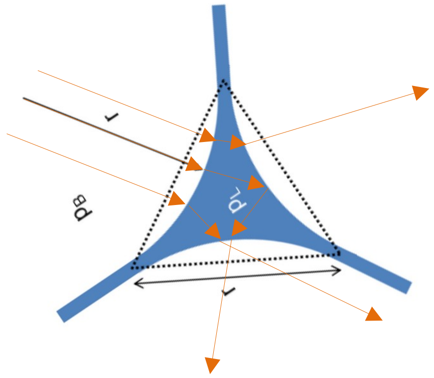


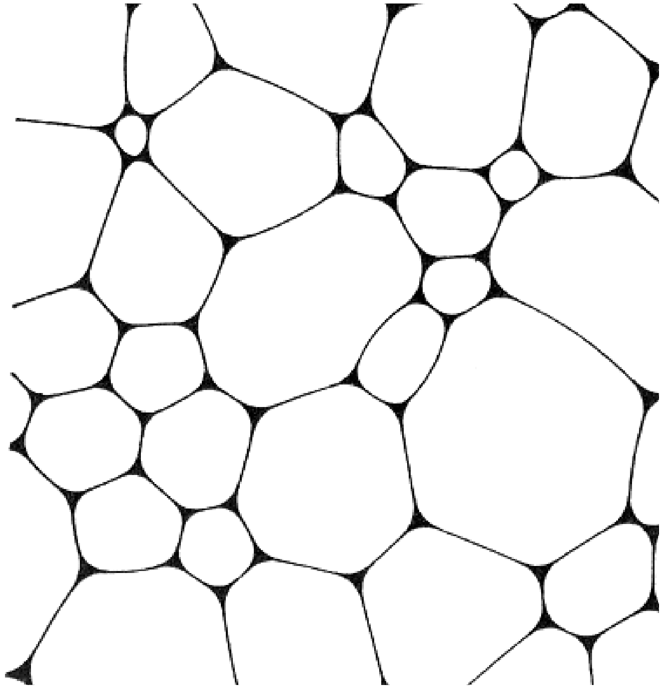
$$G^* = G' + iG''$$

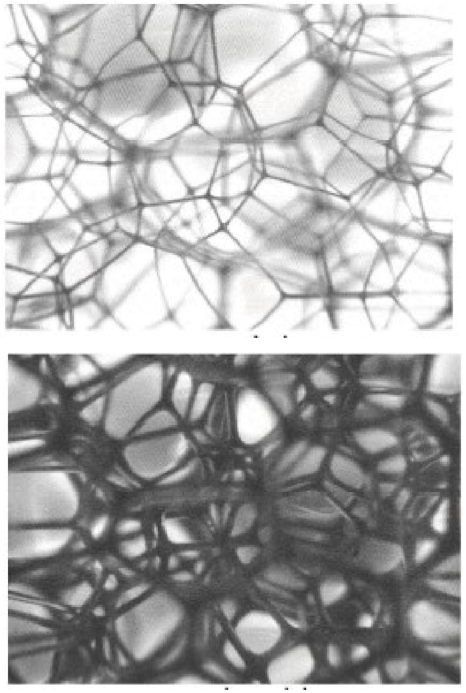
Light refraction

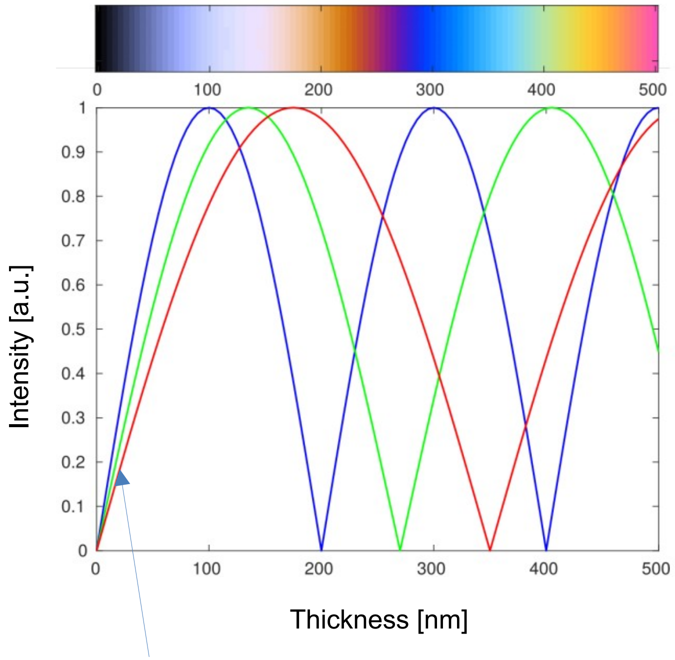
- Thick lamellas – partially reflected, CBF lamellas – no reflection
- Light is refracted/reflected by Plateau borders





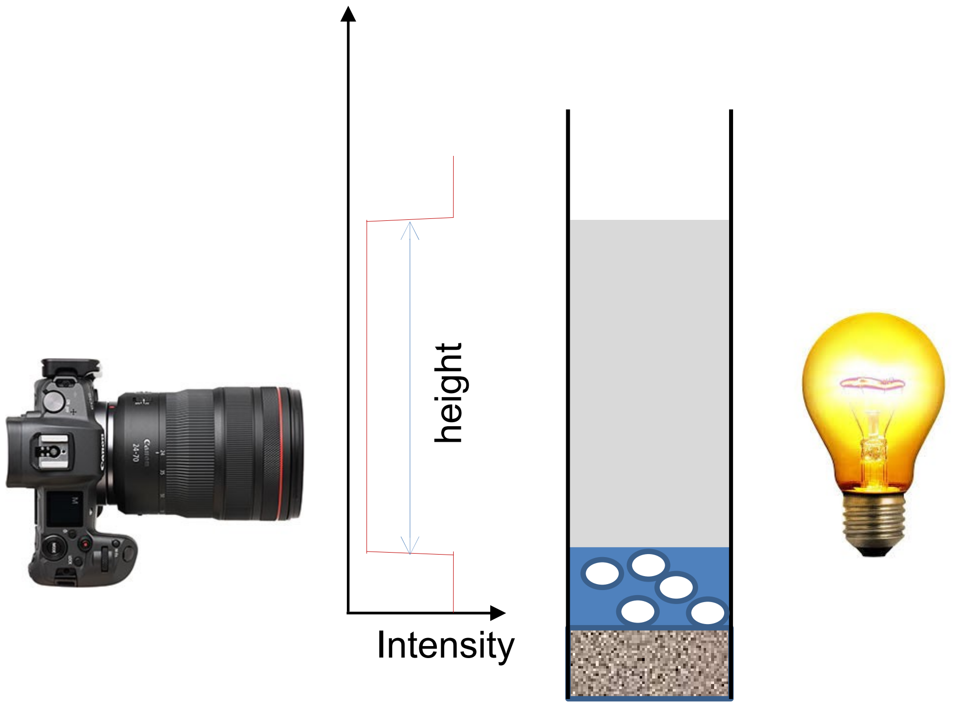


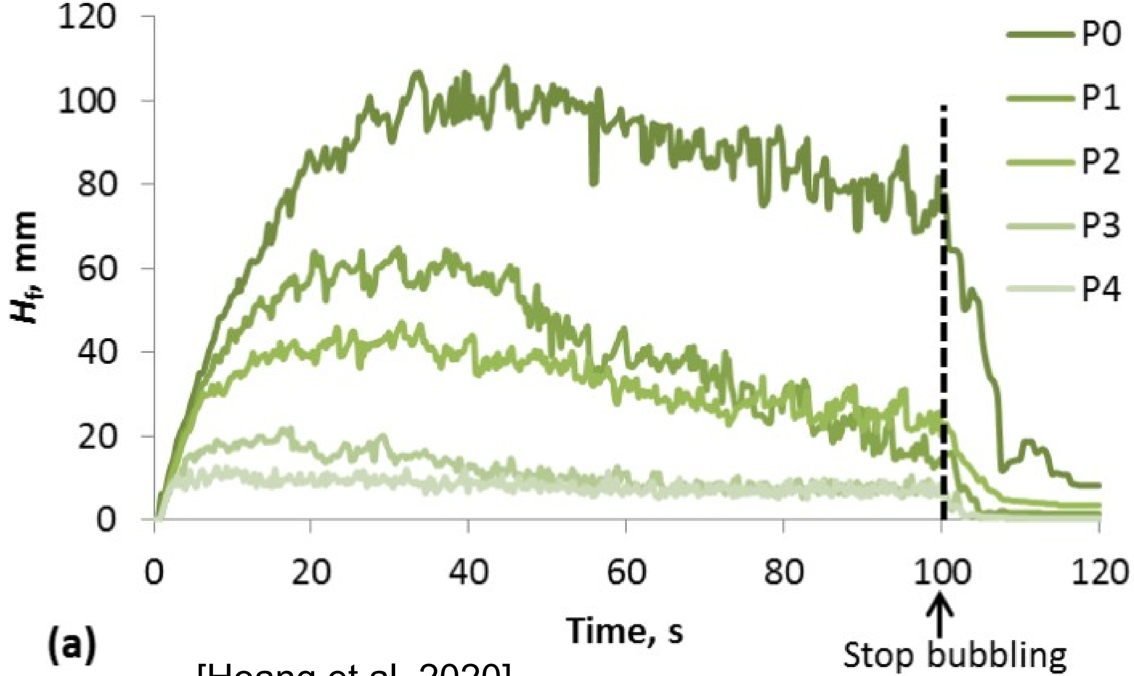


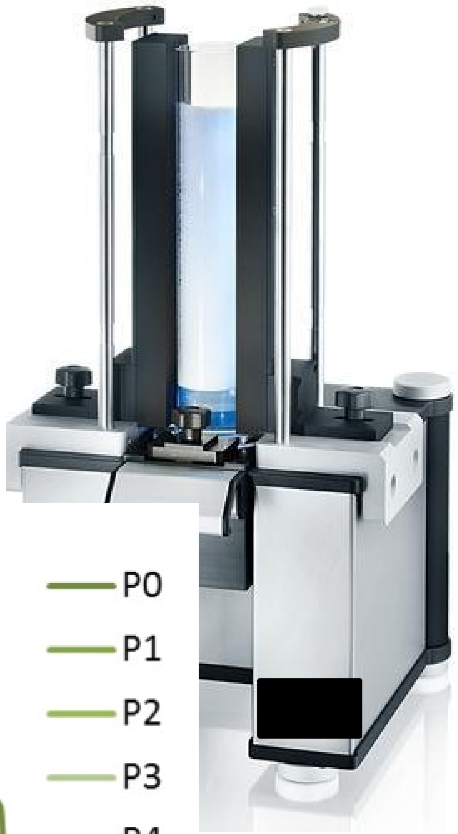


Foam height

- Automated measurement of foam height, using transmittency
- Commercialized in foam test devices

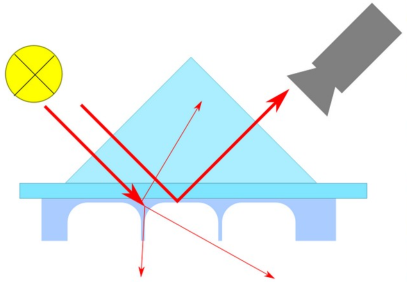


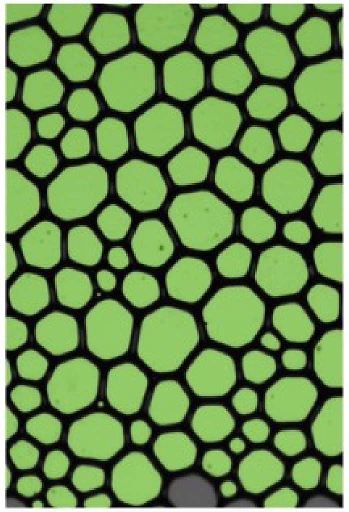


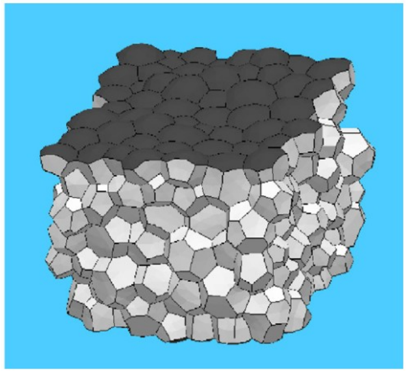


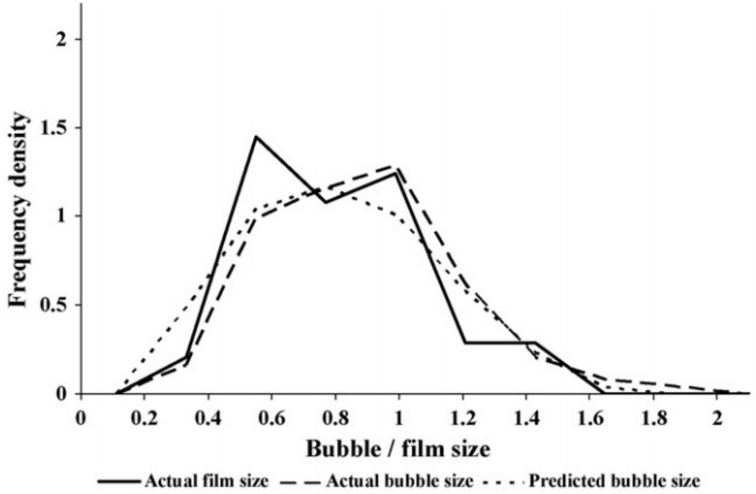
[Hoang et al. 2020]

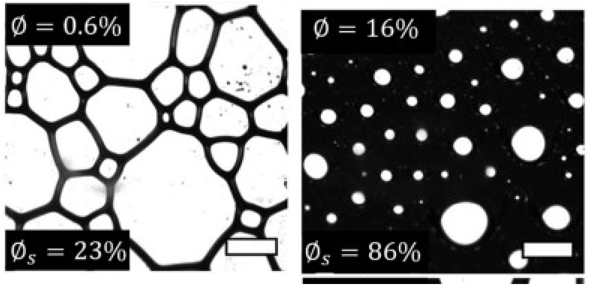
Optical measurement of foam surfaces

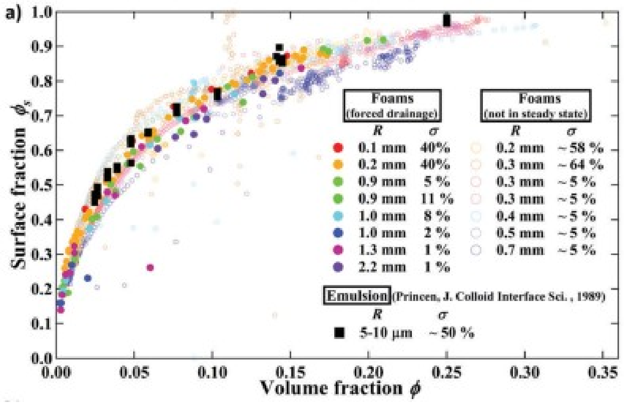


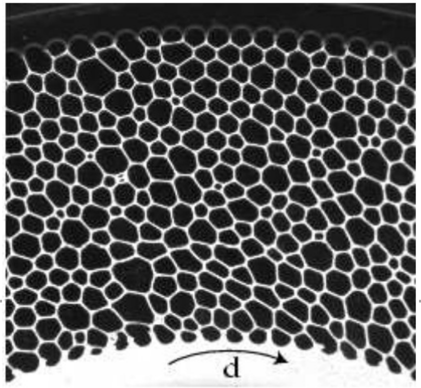


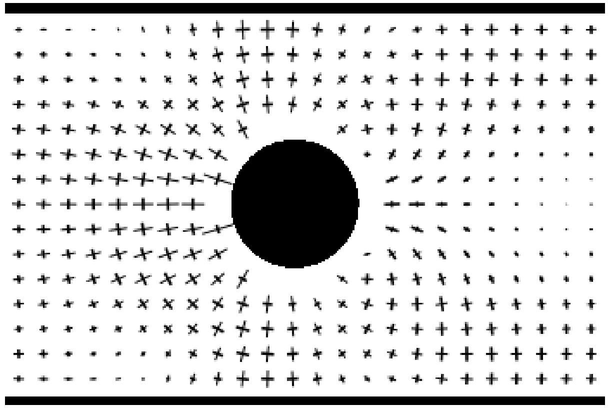






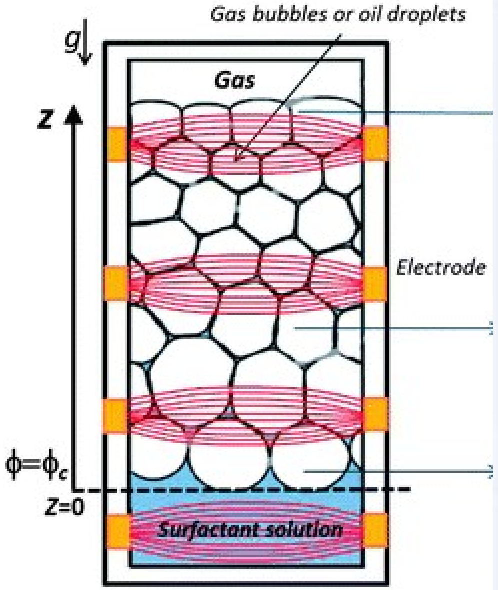




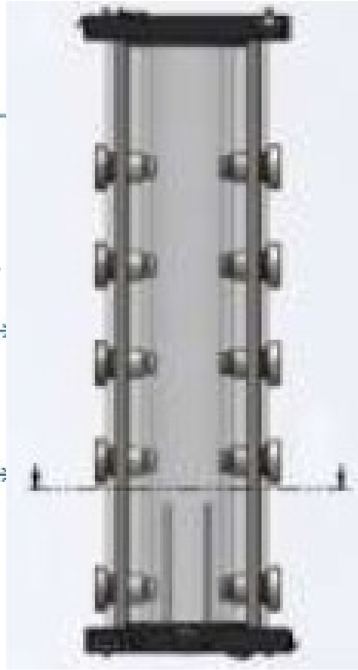


Liquid fraction ← → resistivity

- Gas has zero conductivity – current is transported by Plateau border network
- Conductivity is a good measure for liquid fraction

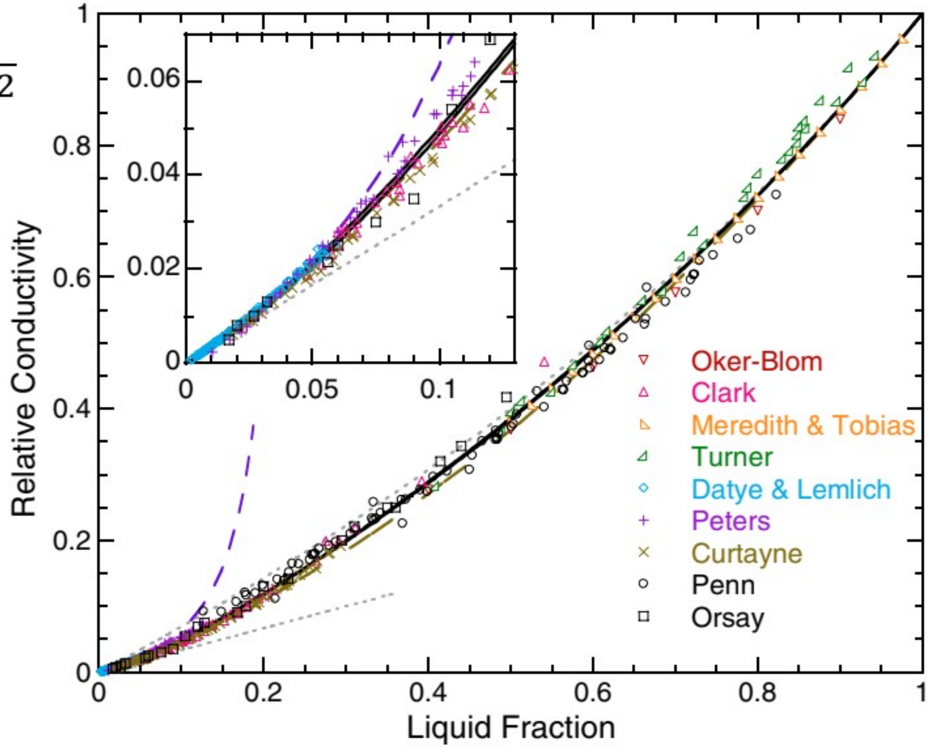


$$R \sim \frac{1}{\sigma}\frac{L}{A}$$



$$\frac{\sigma}{\sigma_{liquid}} = \varphi_l \frac{2\,(1+12\,\varphi_l)}{6+29\,\varphi_l-9\,\varphi_l{}^2}$$

$$\varphi_l = \sigma \frac{3\,(1+11\,\sigma)}{1+25\,\sigma+10\,\sigma^2}$$

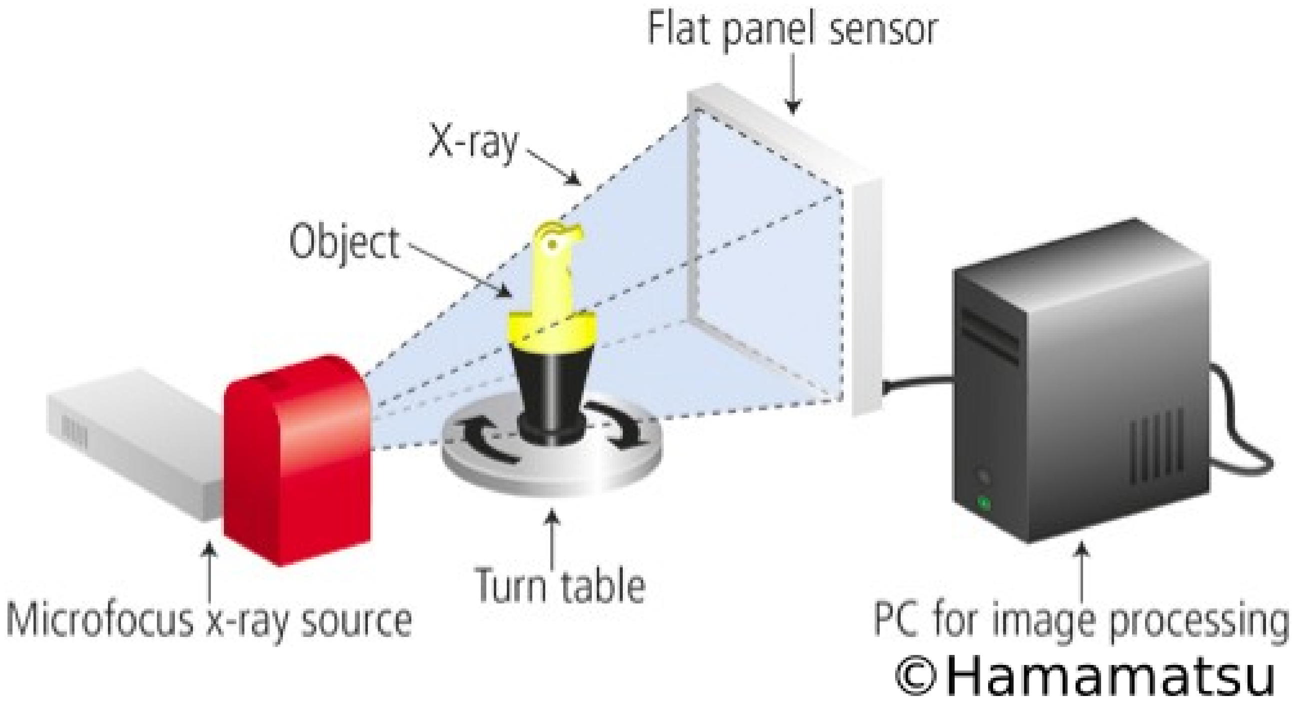


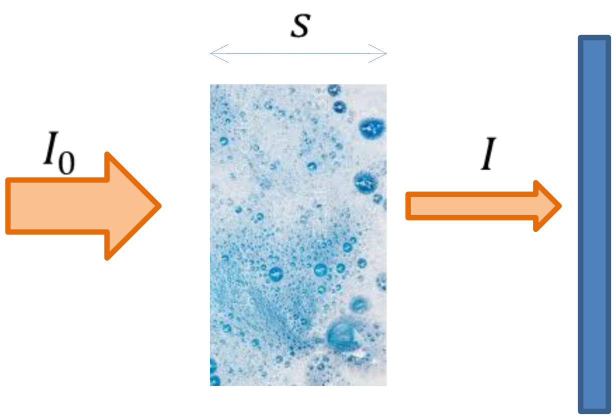
[Feitosa et al. 2005]

Radiography

- Radiation source and detector
- Radiation is attenuated by measurement object → Beer-Lambert law

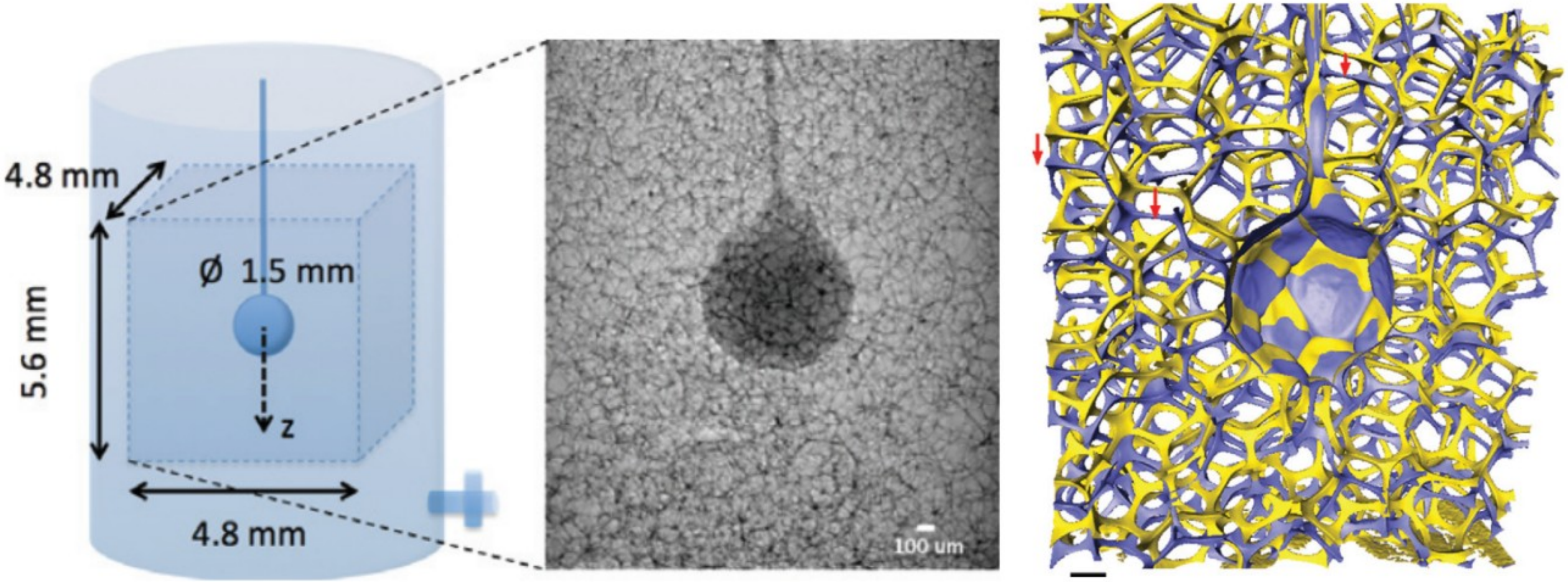
$$\frac{I}{I_0} = e^{-(\sigma s)}$$





X-ray tomography

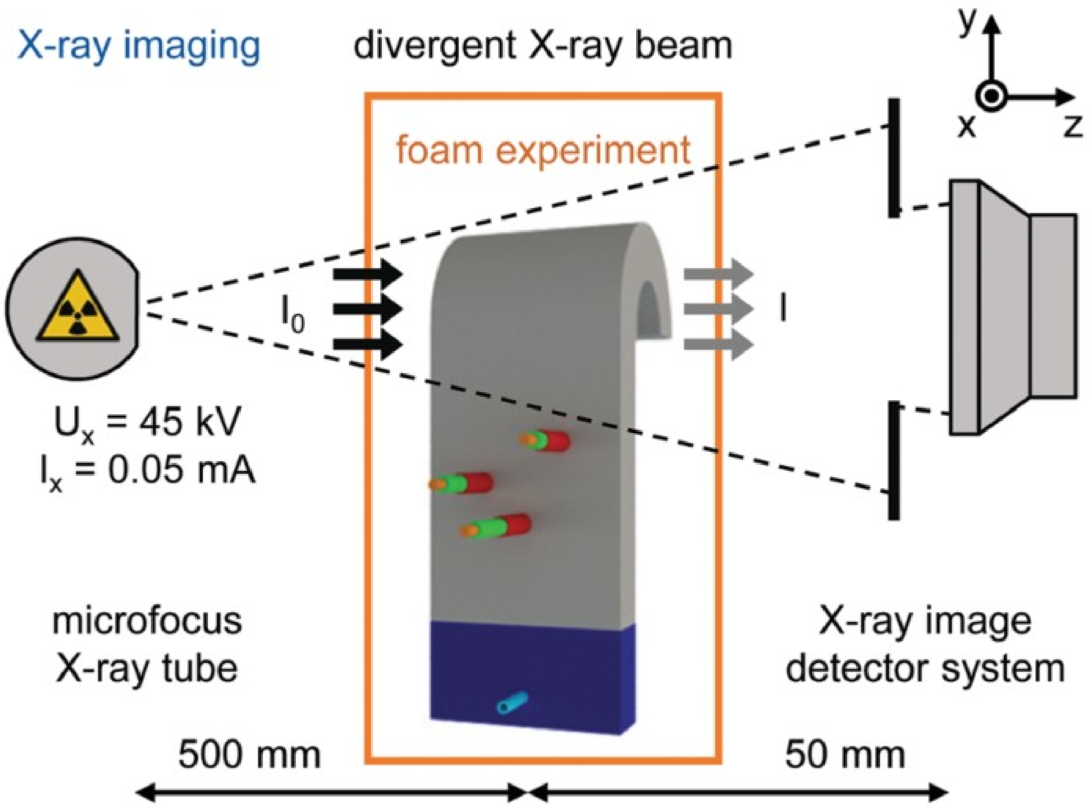
- High-energetic radiation from synchrotron source
- Very precise measurement requires long exposure
- → Small measurement volume, small velocities

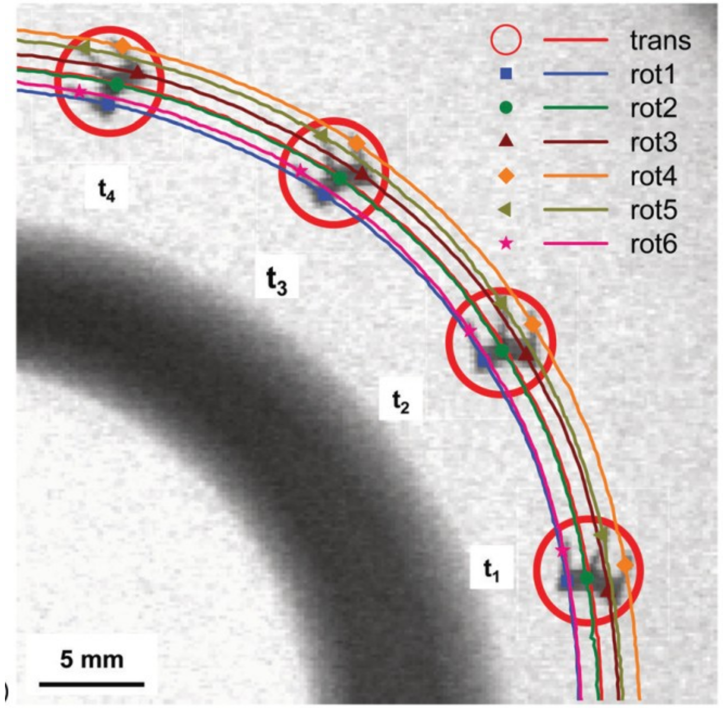


[Raufaste et al. EPL 2015]

Xray-Particle Tracking Velocimetry

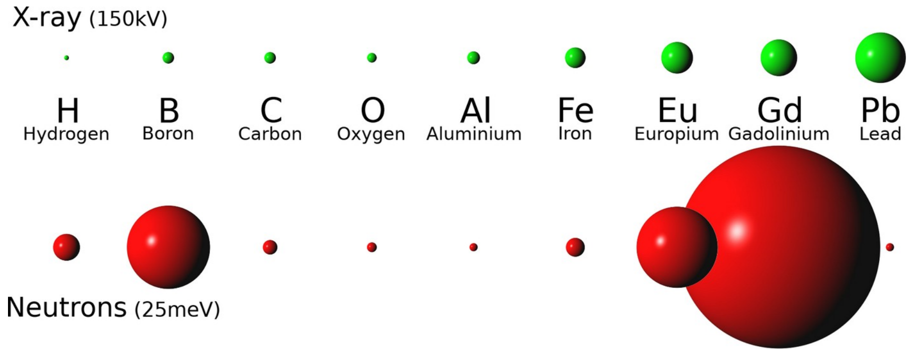
- 3D-printed particles with metal content, sticking in foam
- Tracking of particles yields velocity and vorticity of the foam flow





[Lappan et al. 2020]

Exercise: Attenuation



- Attenuation of different foam samples
- X-ray, 150 keV: “NIST Standard Reference Database 126” →
- (a) Shaving foam, 10 cm thickness, D_b=0.1mm, φ_l=10%

$$\frac{I}{I_0} = e^{-(\sigma s)} = e^{-(0.0575\,/cm\ \cdot\ 10\ cm\ \cdot\ 10\%)} = 94.4\%$$

$$\frac{\Delta I}{I_0} = 5.6\%$$

$$\frac{\Delta I}{I_0} = 97.6\%$$

$$\frac{\sigma}{\rho} = 0.0575\,\frac{cm^2}{g} \rightarrow \sigma = 0.0575\,\frac{1}{cm}$$

$$\sigma_{neutron} = 3.74\,\frac{1}{cm}$$

- (b) Plateau border (transversal oriented) of soap foam, D_b=5mm, φ_l=0.1%

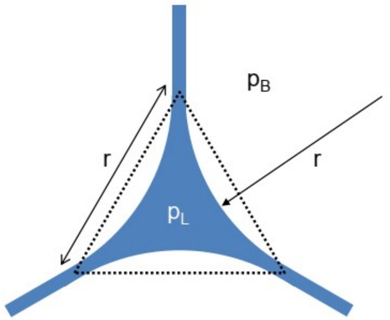
Decoration theorem: $\varphi_l \approx 0.72\,\frac{r^2}{{R_e}^2}$

$$r = R_e\sqrt{\frac{\varphi_l}{0.72}} \approx 0.093\ mm$$

$$\frac{I}{I_0} = e^{-(\sigma r)} = e^{-(0.0575\,/cm\ \cdot\ 0.0093\ cm\,)} = 99.946\%$$

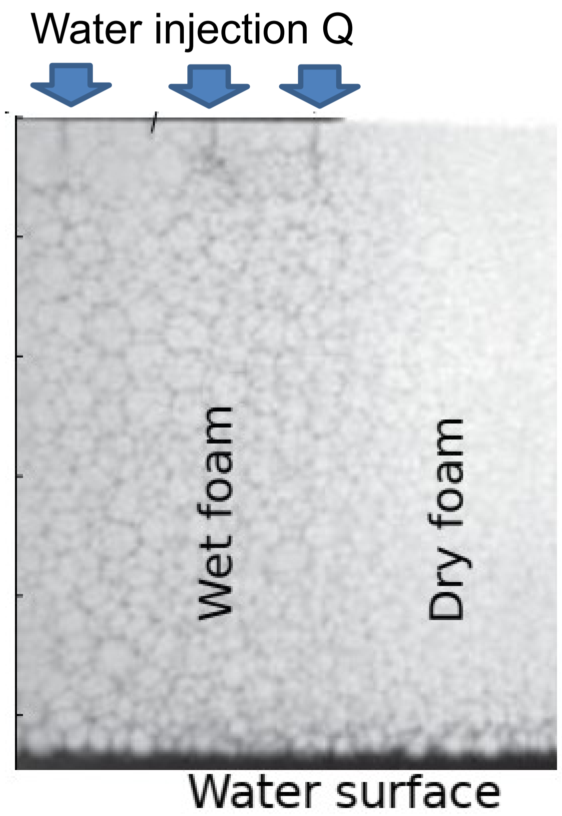
$$\frac{\Delta I}{I_0} = 0.054\%$$

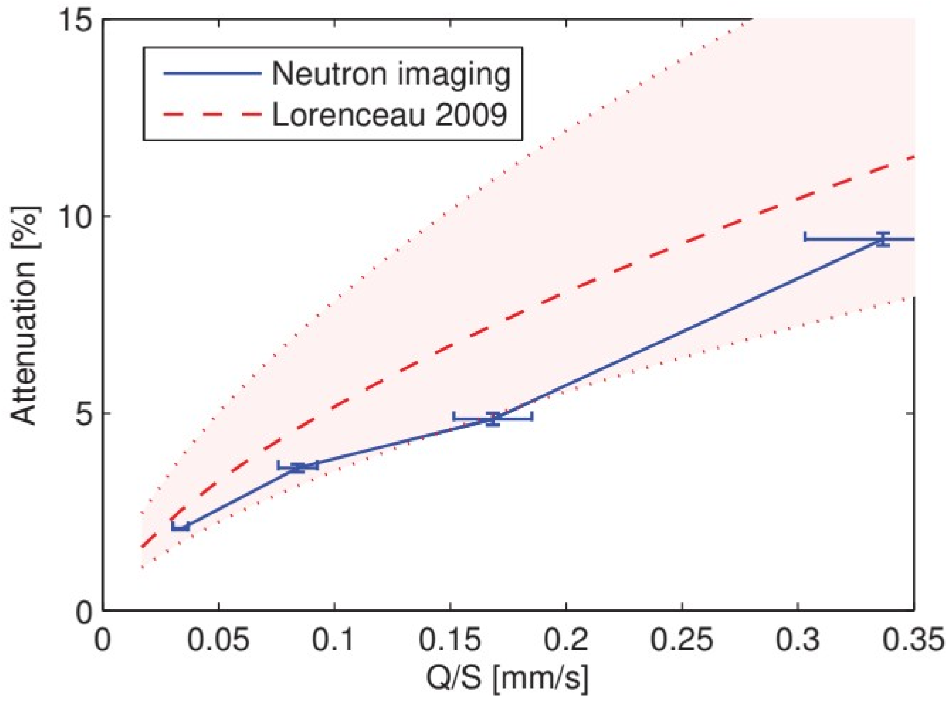
$$\frac{\Delta I}{I_0} = 3.5\%$$



Neutron radiography of liquid fraction

- Forced drainage setup in neutron radiography
- Plateau borders visible
- Liquid fraction can be quantified

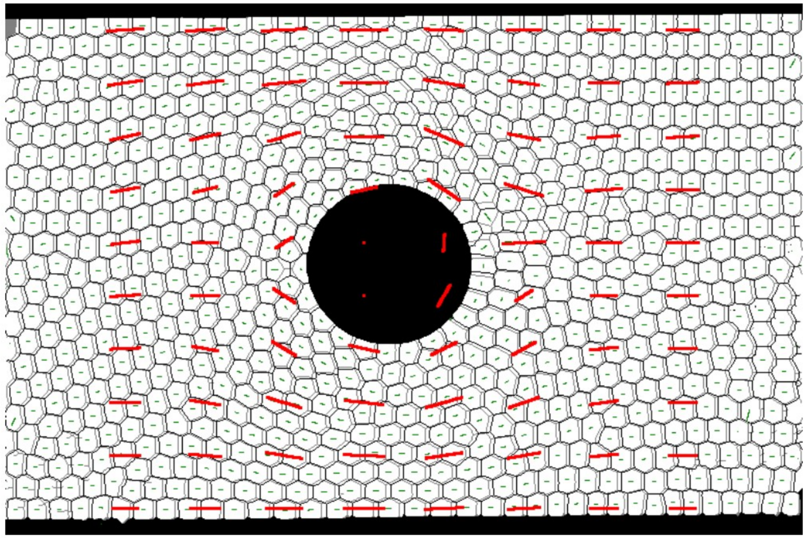




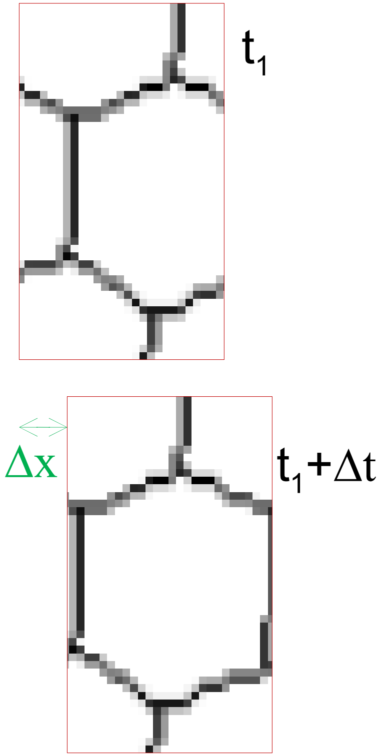
[Heitkam et al. 2018]

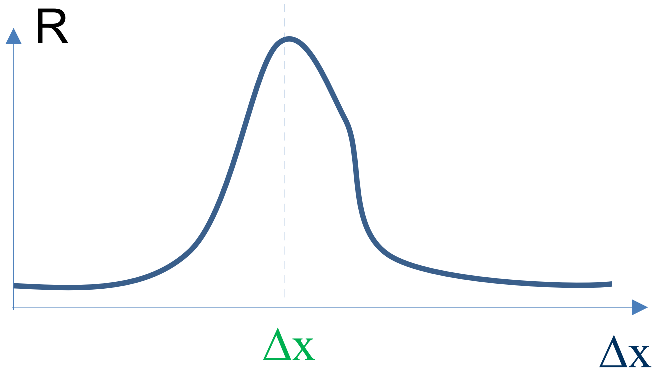
Optical velocity measurement

- Consecutive images with defined time shift Δt analysed
- A: Segmentation → shift of each bubble center position Δx_i → velocity $u_i = \Delta x_i / \Delta t$
- B: PIV-Algorithm → interrogation windows → correlation of consecutive images $\Delta x\ (x,y)$ velocity $u = \Delta x / \Delta t$



[B. Dollet]





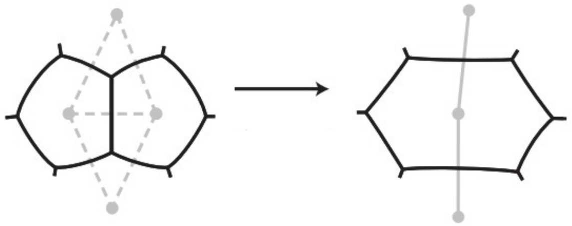
Structure

- Review lecture 9
- Film rupture
- Coarsening
- Stability testing
- Defoaming

Foam stability

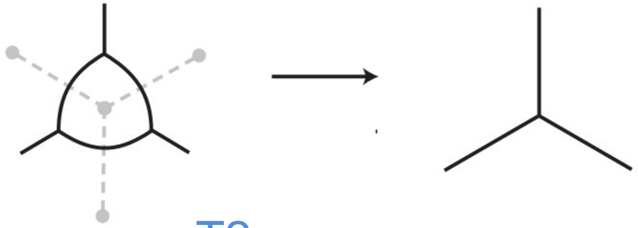
- Two modes of foam destruction:
- A: Coalescence / Film rupture

  → Increased bubble size / reduced foam volume



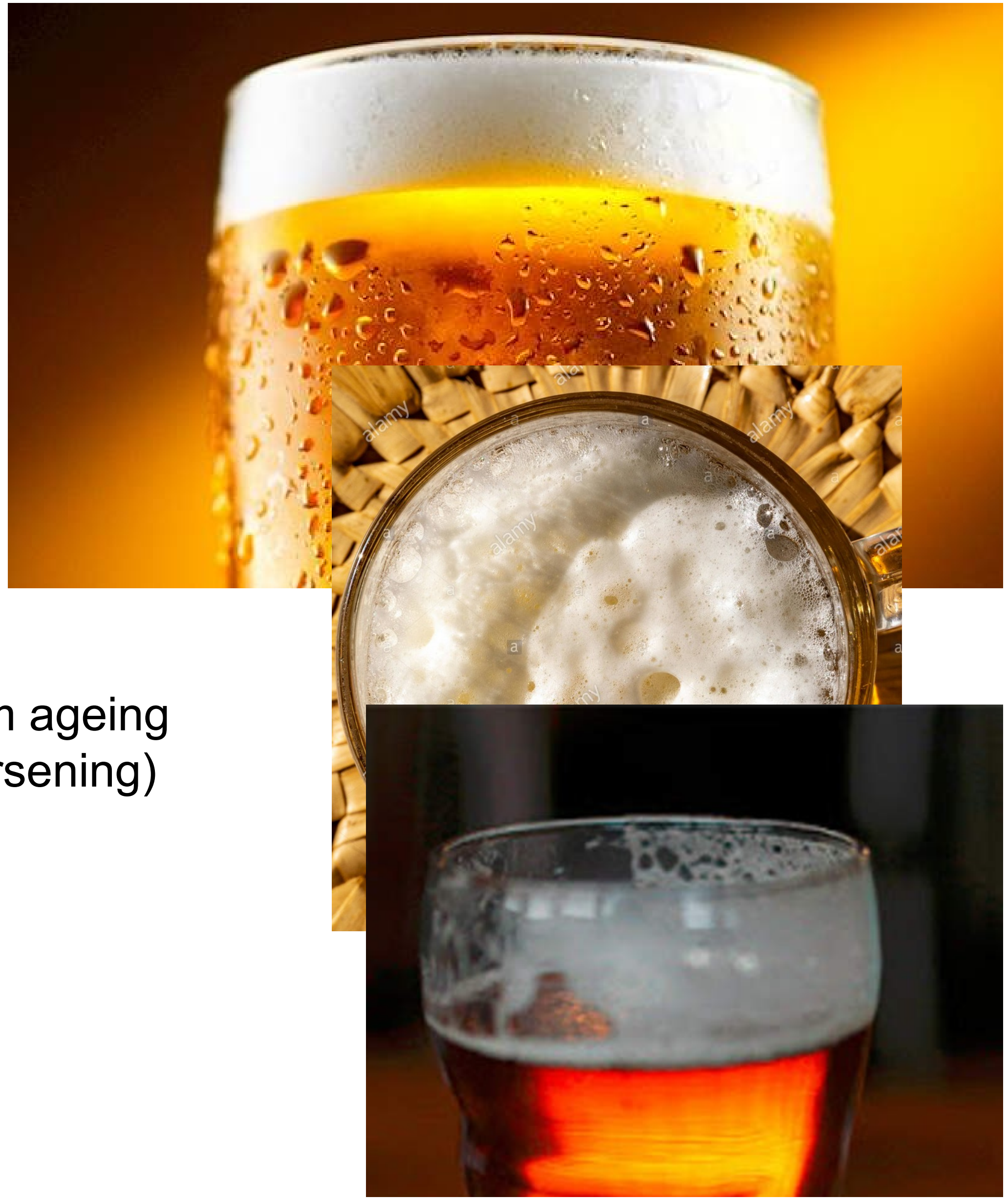
- B: Coarsening (Ostwald ripening)

  → increased bubble size



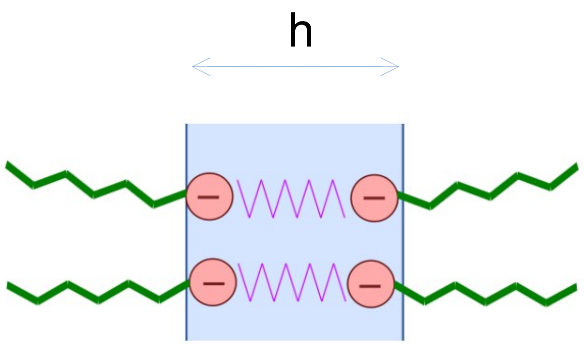
T2 process

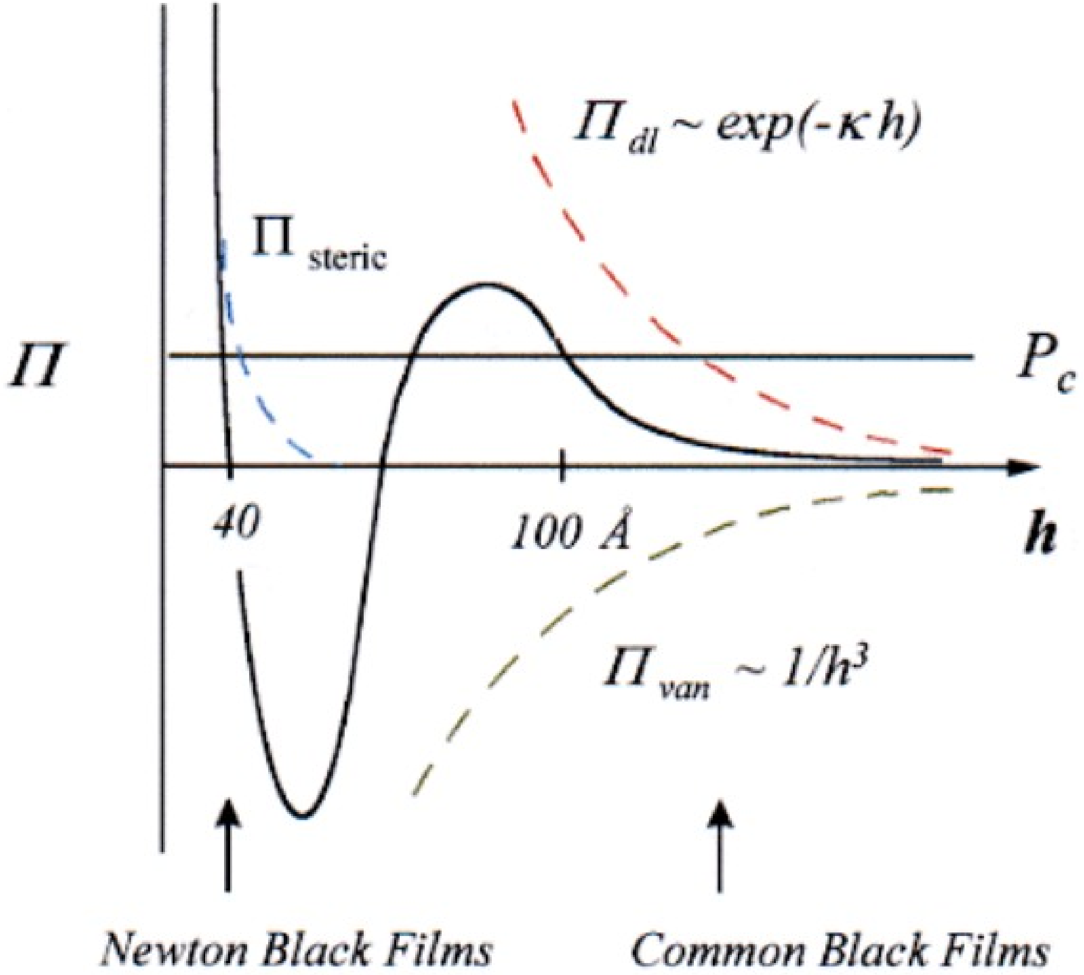
Foam ageing (coarsening)



L5: disjoining pressure

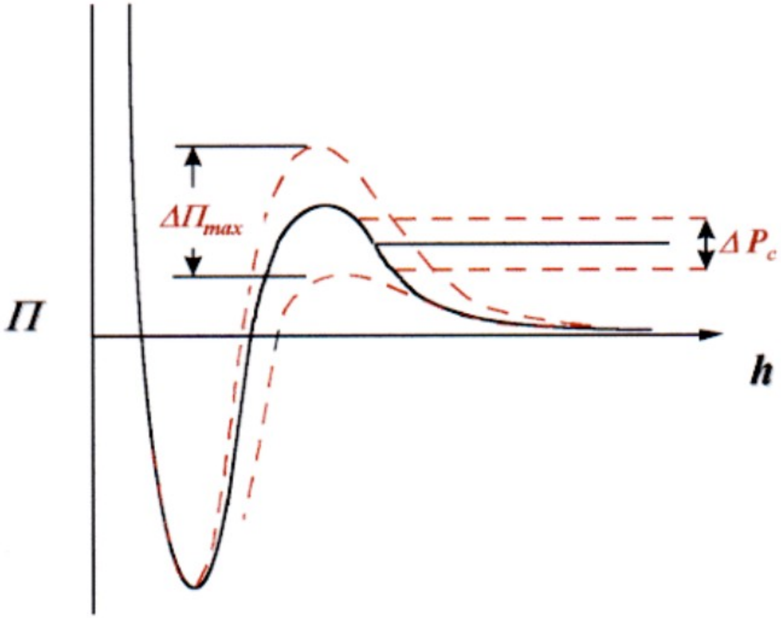
- Disjoining force is a function of film thicknes
- 3 contributions:
  - Electrostatic repulsion ~exp(-h)
  - Dipol (Van-der-Waals) ~h^{-3}
  - Steric (collision)
- Undisturbed superposition

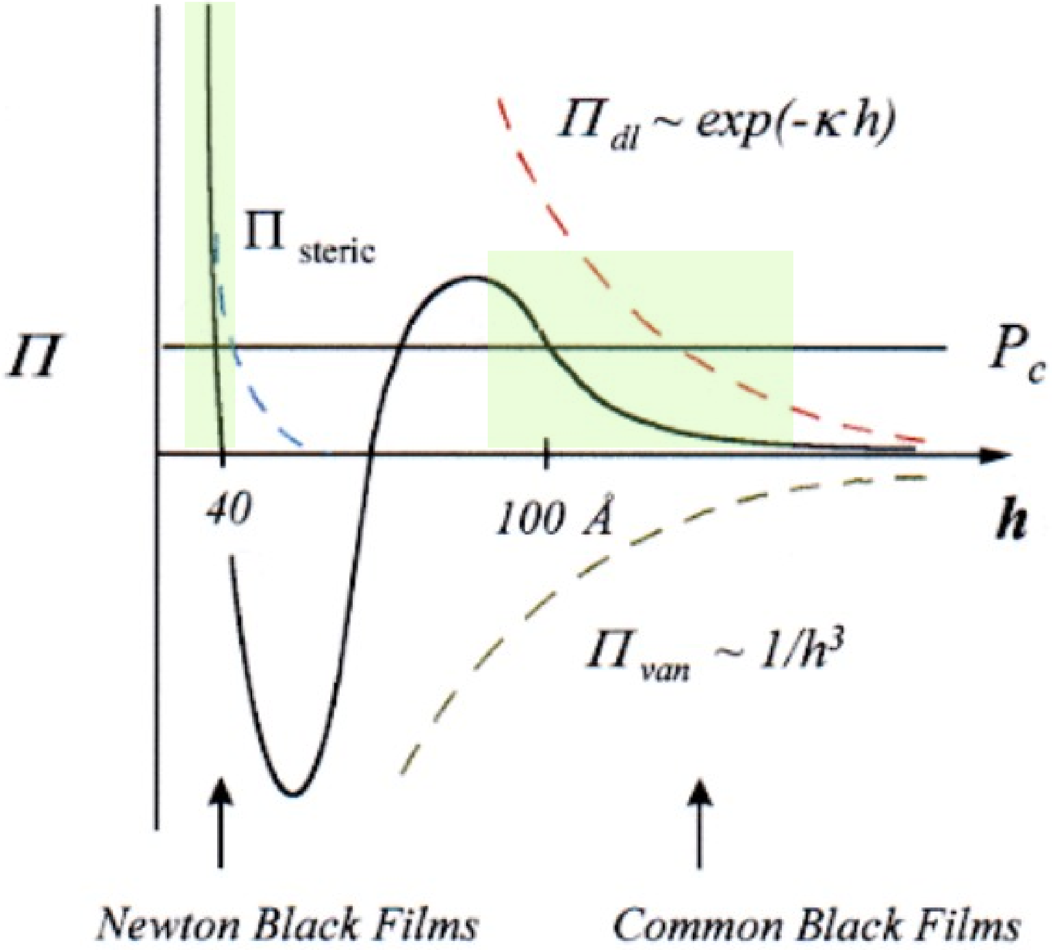




Film stability

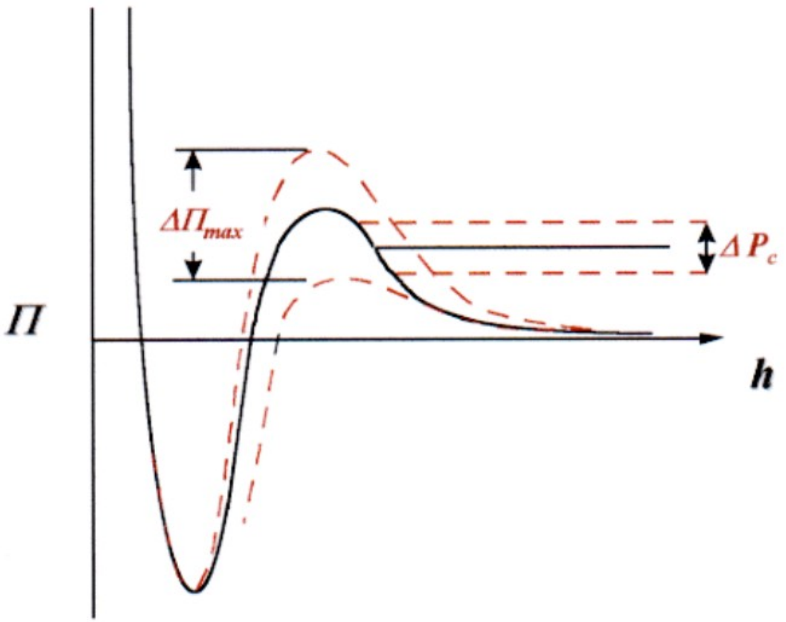
- 2 stable regions:
- Common Black Films (h ~ 50 nm)
- Newton Black Films (h ~ 4 nm)

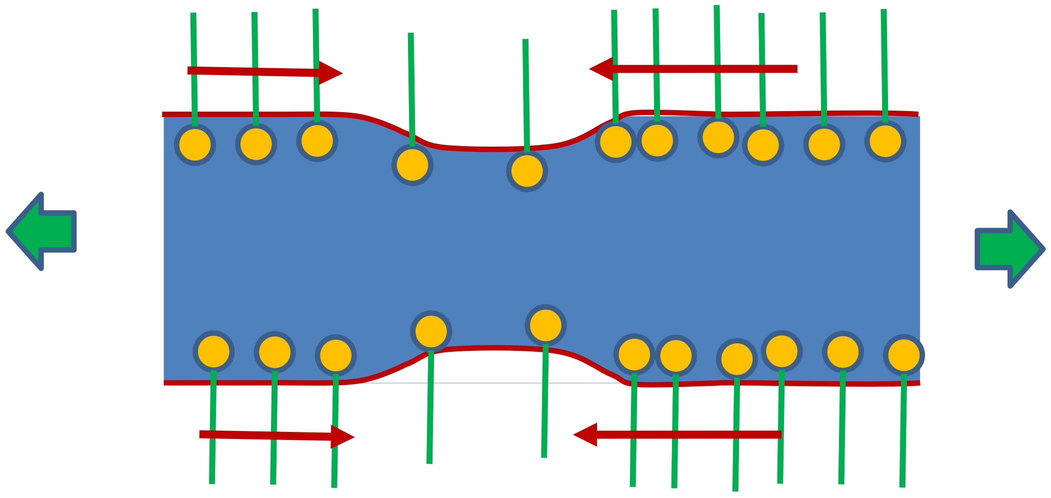




Film stability

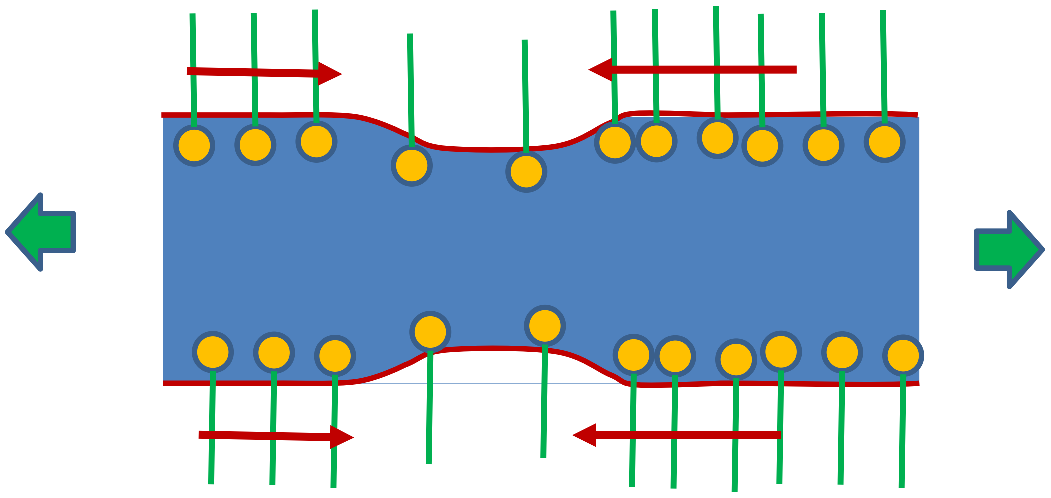
- Film stretching → locally lower surface coverage
- Marangoni effect cures weak spots

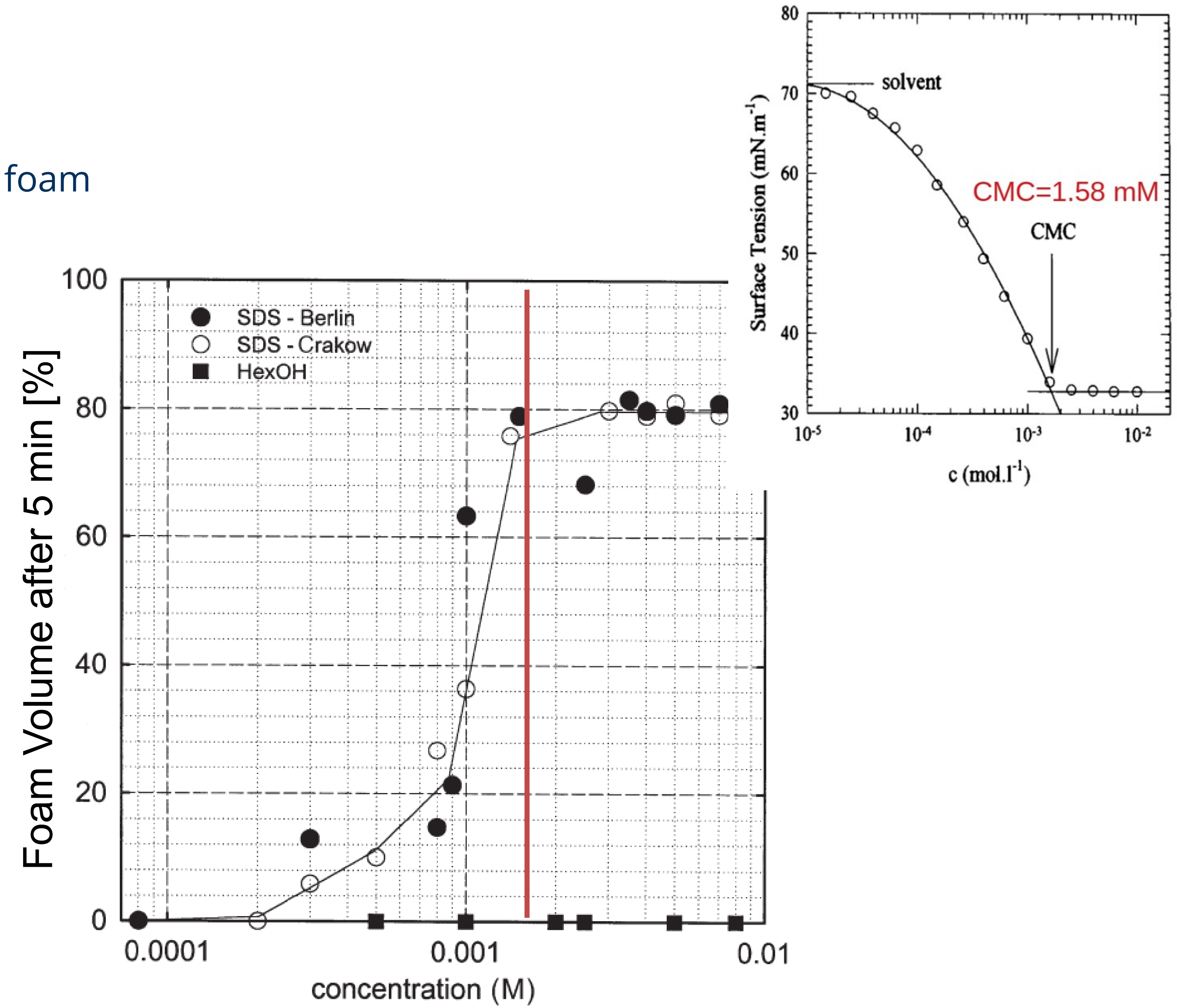




Film stability

- Sufficient surface coverage required for stable foam
- Required concentration typically near CMC

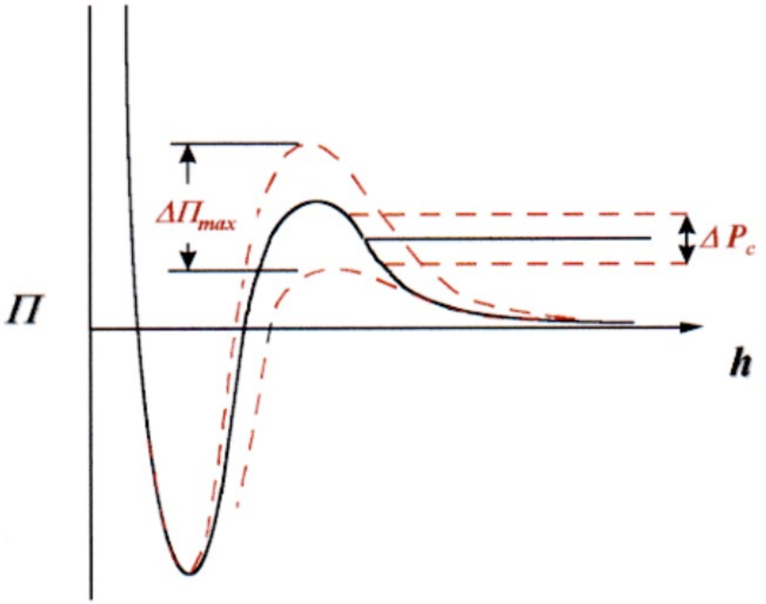


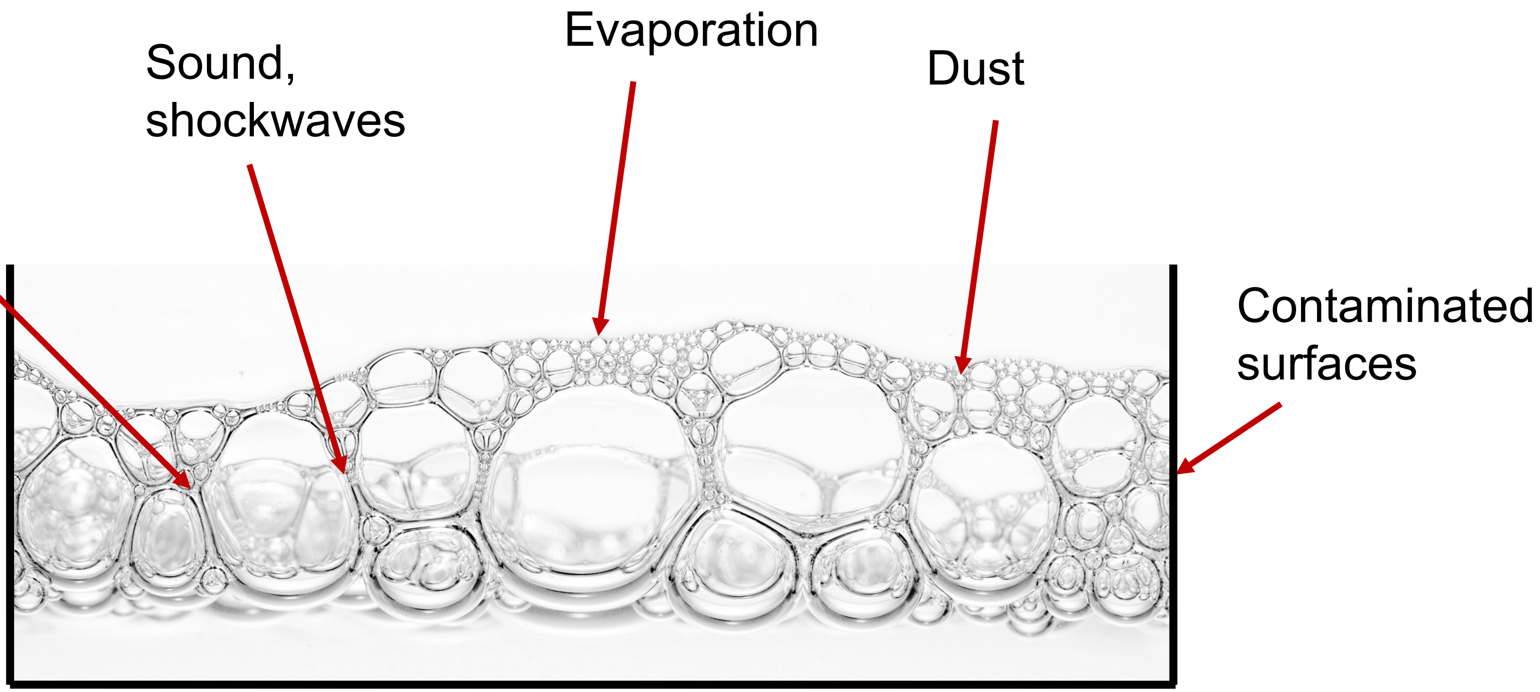


[Lunkenheimer & Malysa, 2003]

Film rupture

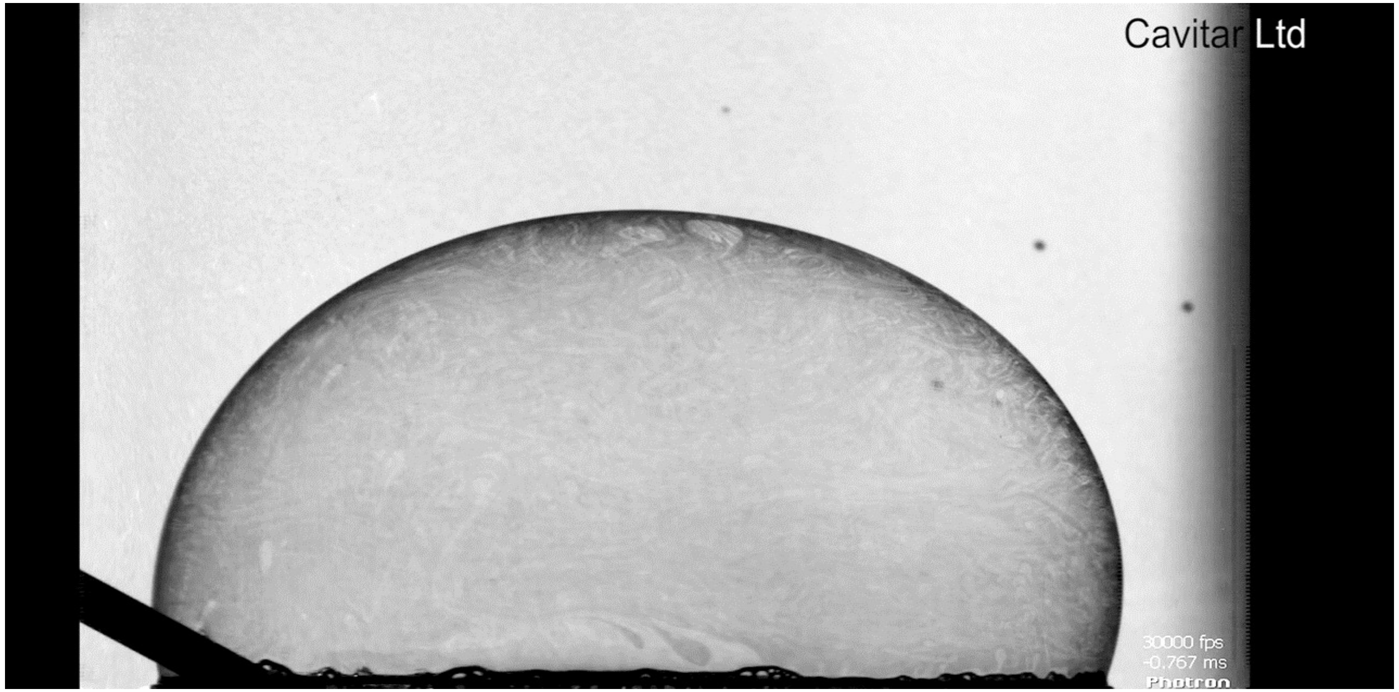
- Several possible mechanisms:





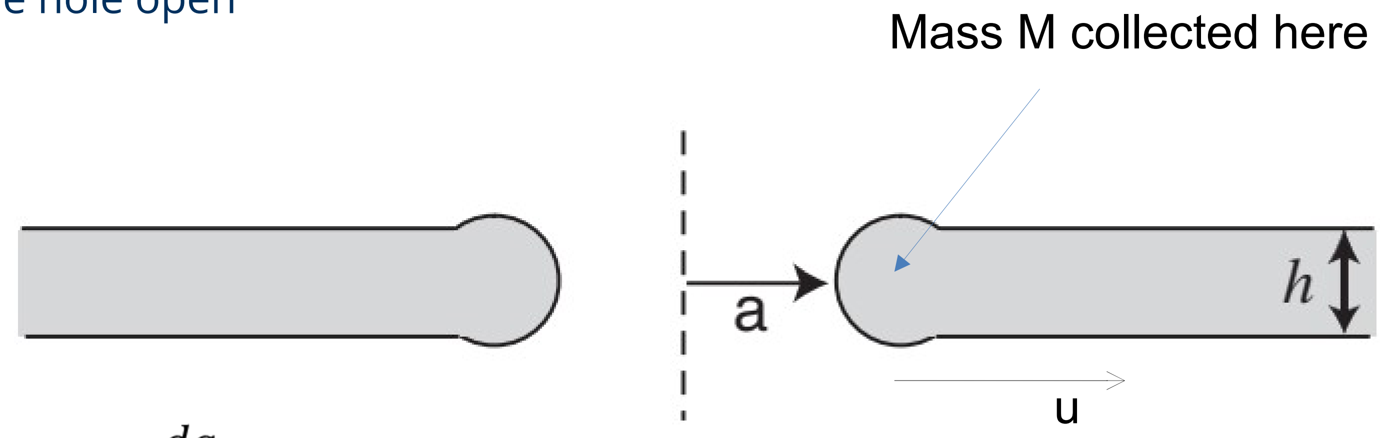
Film rupture velocity

- Fast motion of interface
- Thickening of edge
- Production of droplets



Film rupture velocity

- Surface tension pulls the hole open



$$\frac{d(M\,u)}{dt} = F = 2\,\gamma\;\;2\pi a\;\;, u = \frac{da}{dt}$$

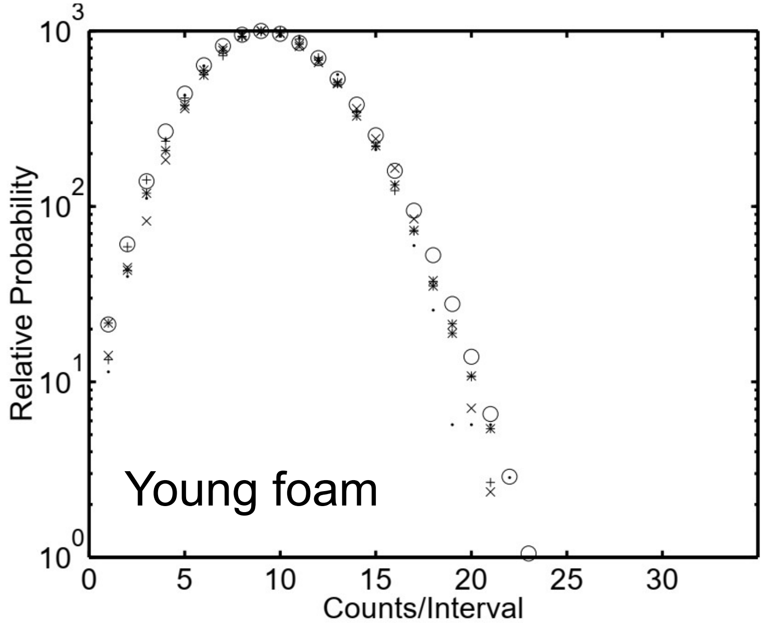
$$M = \rho_l\;\;\pi a^2 h$$

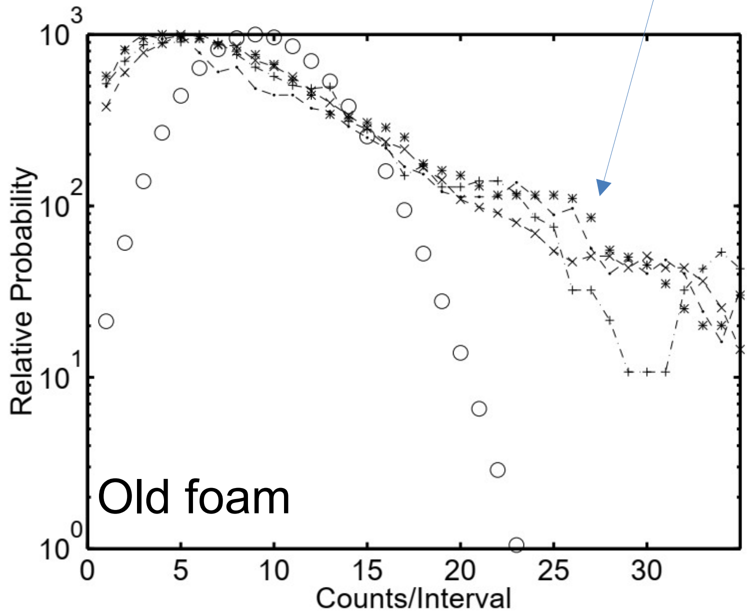
$$u = \sqrt{\frac{2\gamma}{\rho_l h}} \xrightarrow{h \approx 50\,nm} u \sim 40\,m/s \xrightarrow{R_e \approx 1\,mm} t \sim 25\,ms$$

Film rupture time scale

- Young, unstable foam: Poisson distribution for rupture rate
- Old, stable foam: rupture avalanches
- → no clear scaling law (liquid fraction, film thickness, disjoining pressure?)

Multiple ruptures in short time (Avalanches)

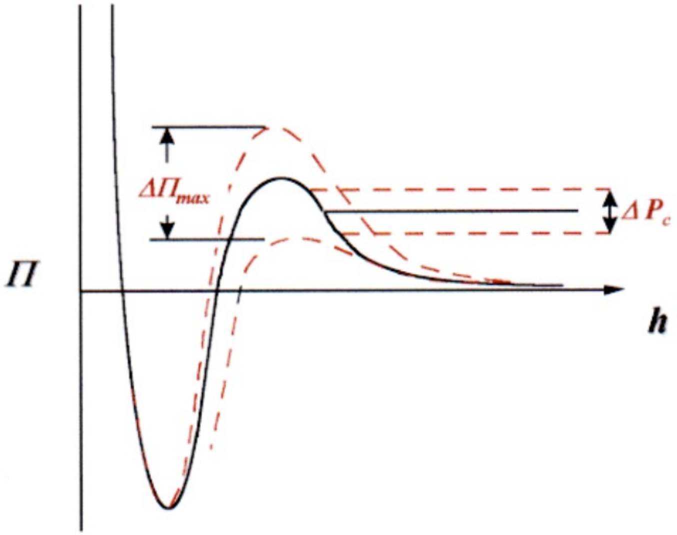


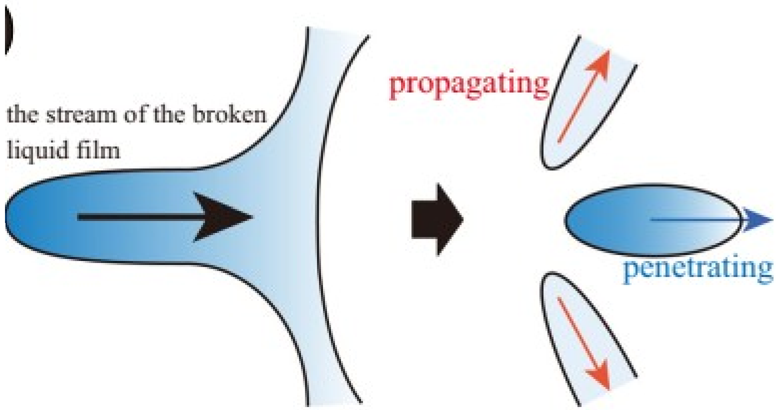


[Müller & di Meglio, 1999]

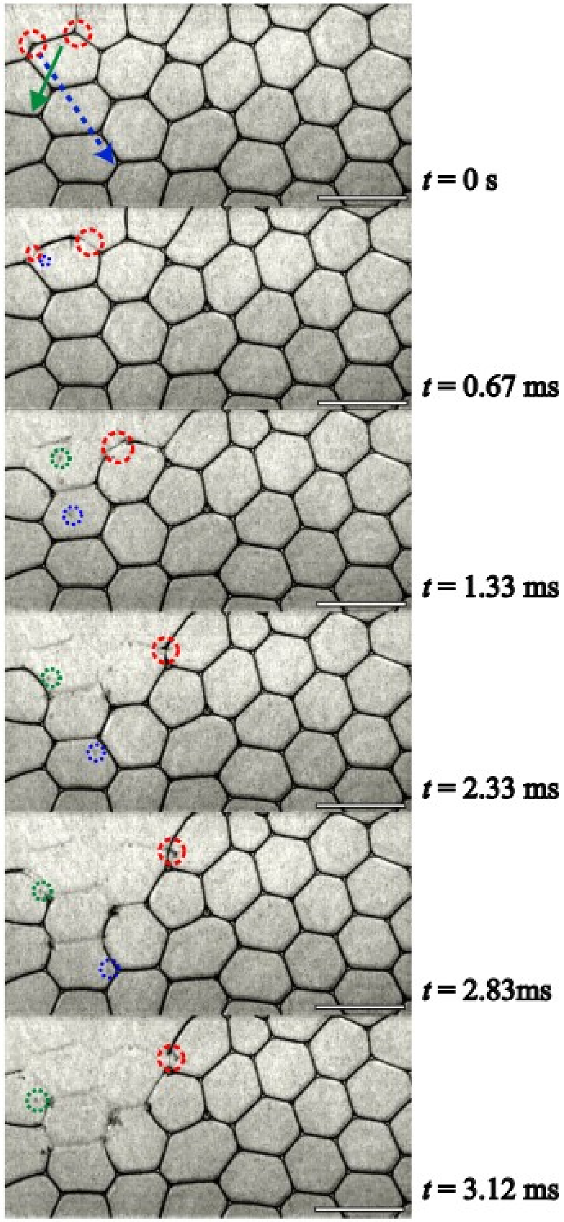
Rupture avalanche

- Film rupture might release droplets
- Impact of droplets causes next film rupture
- Alternatively: Relaxation causes film stretching





[Yanagisawa & Kurita, 2019]



Structure

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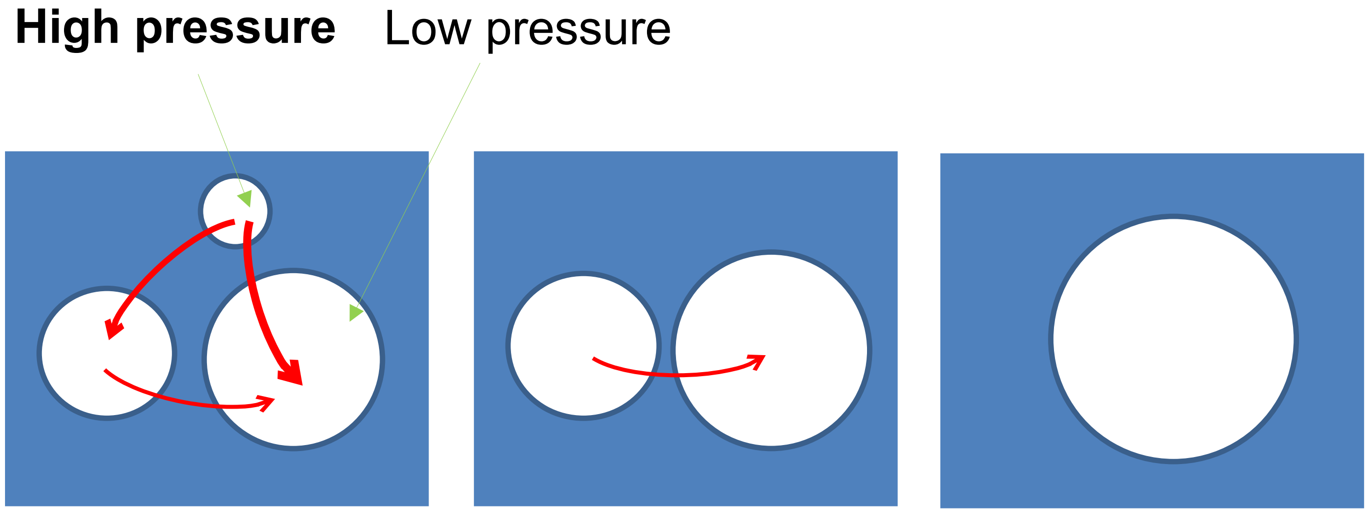
Ostwald ripening

- Ostwald ripening for bubbly liquid

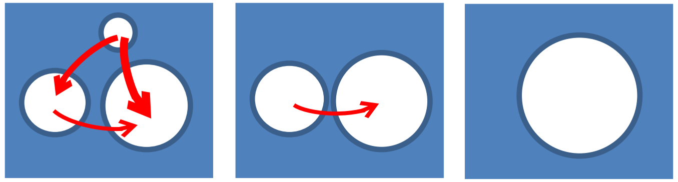
$$\Delta p = \frac{2\gamma}{R_1} - \frac{2\gamma}{R_2}$$



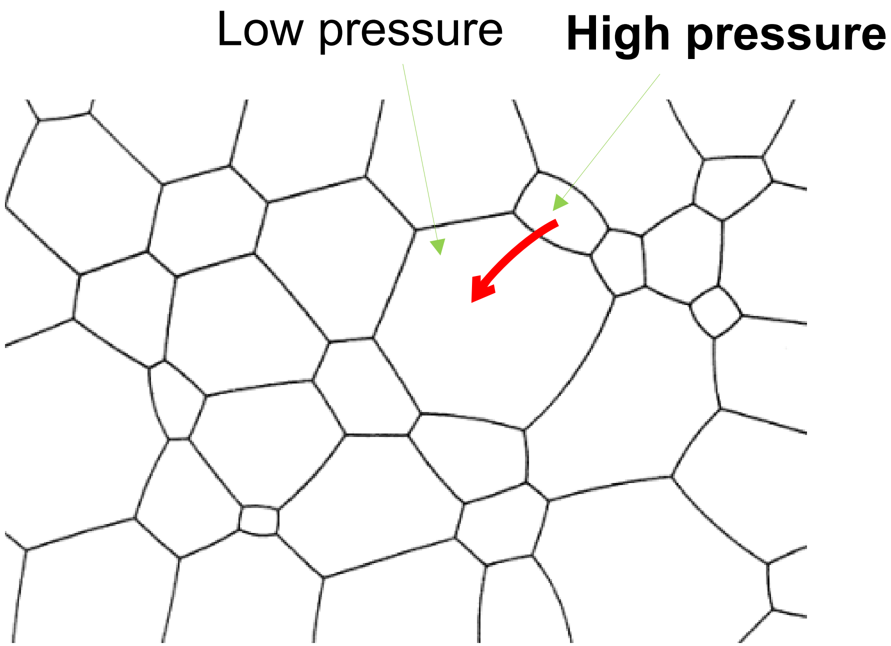
Ostwald ripening vs. von Neumann-Mullins coarsening

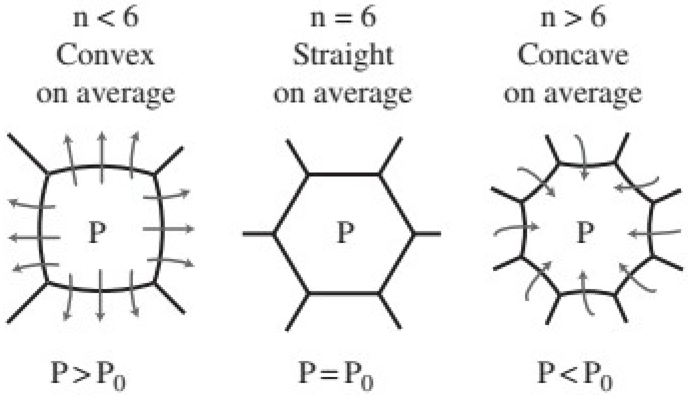
- Ostwald ripening for bubbly liquid
- Von Neumann-Mullins coarsening for dry foam

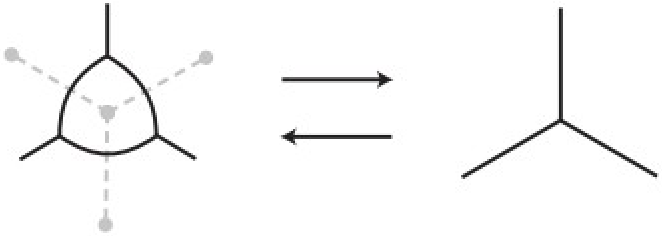
$$\Delta p = \frac{2\gamma}{R_1} - \frac{2\gamma}{R_2}$$



$$\Delta p = 2\gamma \, H_{i,j}$$

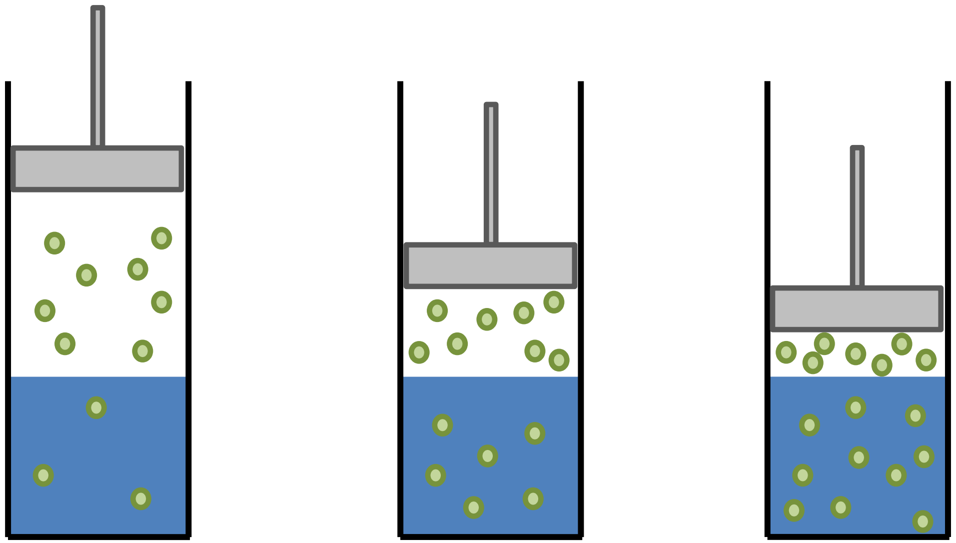






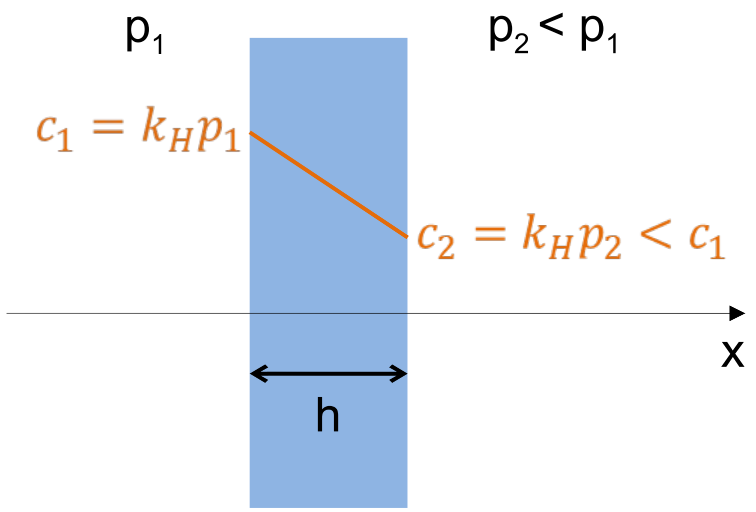
Gas solubility

- Solubility depends on (partial) pressure
- Partial pressure depends on composition of gas mixture $p_i = p\,\frac{n_i}{n}$ → neglected here
- Henry's law: $c = k_H\, p$
- Henry constant k_H depends on material and temperature



Gas diffusion

- Equilibrium over liquid lamella (steady state)
- Neglecting transport to/from the interface (pure gas)



$$c = k_H\, p$$

$$\frac{\Delta c}{h} = \frac{\partial c}{\partial x} = -k_H \frac{p_1 - p_2}{h}$$

Molecular flux through Area A (Fick's law):

$$\frac{\Delta n}{\Delta t} = -D_f\, A\, \frac{\partial c}{\partial x}$$

$$p_0\, V = n\, R\, T$$

$$\Delta V = \Delta n \frac{RT}{p_0}$$

Volumetric flux through Area A:

$$\frac{\Delta V}{\Delta t} = \frac{\Delta n}{\Delta t}\frac{RT}{p_0} = -D_f\, A\, \frac{\partial c}{\partial x}\frac{RT}{p_0}$$

Gradient over lamella:

$$\frac{\Delta V}{A\, \Delta t} = D_f\, k_H \frac{p_1 - p_2}{h}\frac{RT}{p_0}$$

$$\Delta p = 2\gamma\, H_{i,j}$$

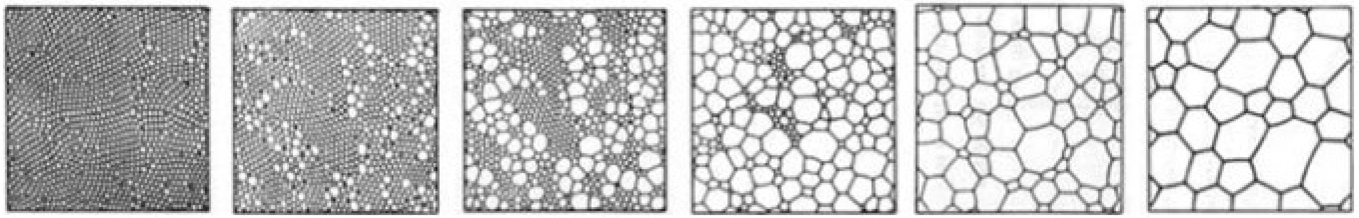
Effective diffusion coefficient D_{eff}

$$\frac{\Delta V}{A\, \Delta t} = D_f\, k_H \frac{p_1 - p_2}{h}\frac{RT}{p_0} = D_{eff} H_{1,2} \rightarrow \boxed{D_{eff} = D_f\, k_H \frac{2\gamma}{h}\frac{RT}{p_0}}$$

$$[D_{eff}] = m^2/s$$

Growth of bubble size

- Small bubbles → small number of neighbours → convex, high mean curvature $H_{i,j}$
- Small bubble vanish, larger bubbles grow

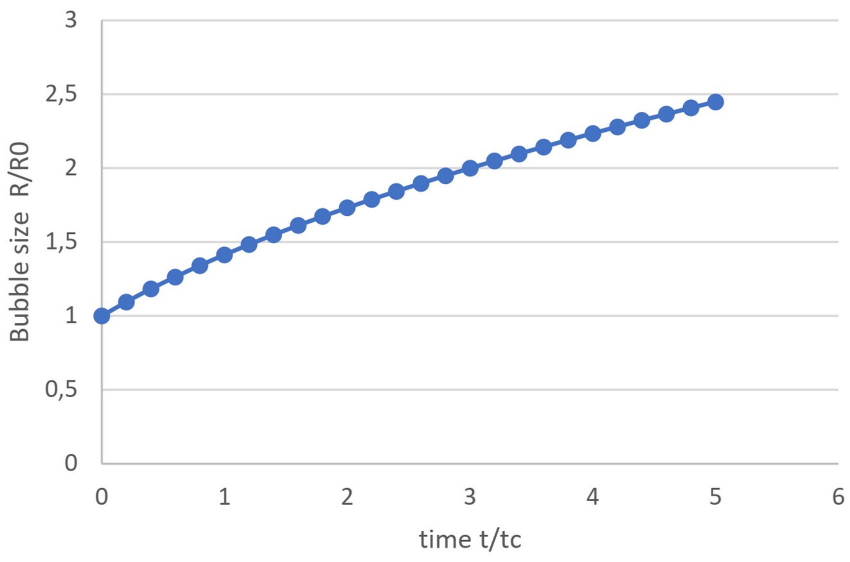


- Average bubble size evolution:

$$R = R_0 \sqrt{1 + \frac{t}{t_c}}$$

$$t_c \approx \frac{\langle V(t=0)\rangle^{2/3}}{b\, D_{eff}} \text{ , b} \approx 1$$

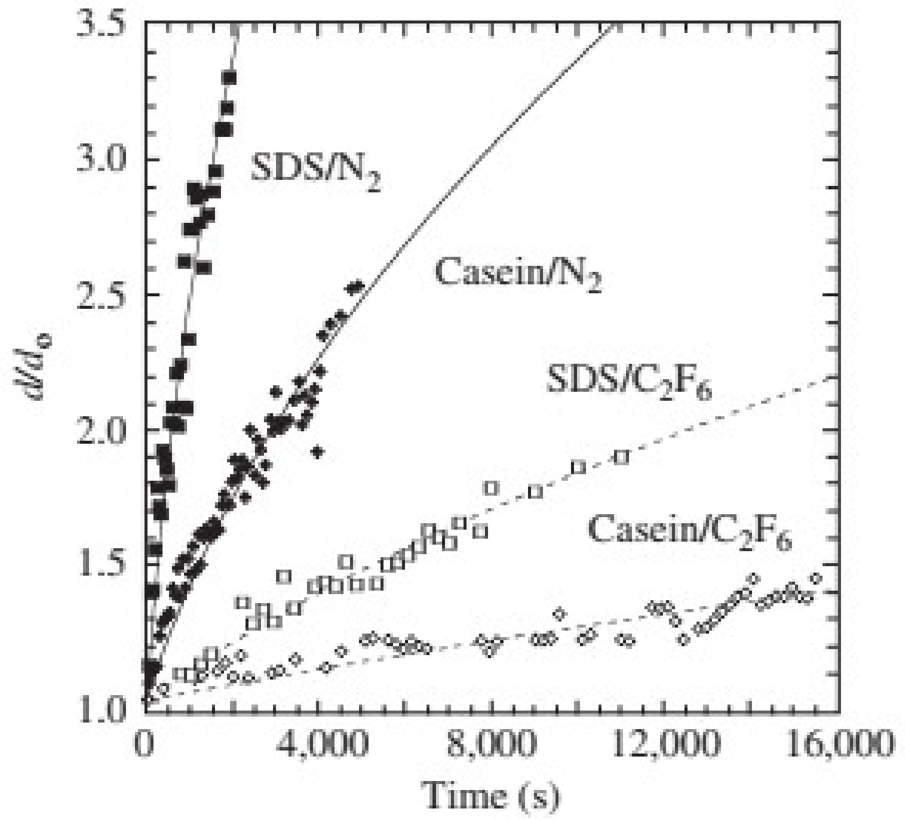
$$\frac{\Delta V}{A\, \Delta t} = D_{eff} H_{1,2}$$



Influence of type of gas

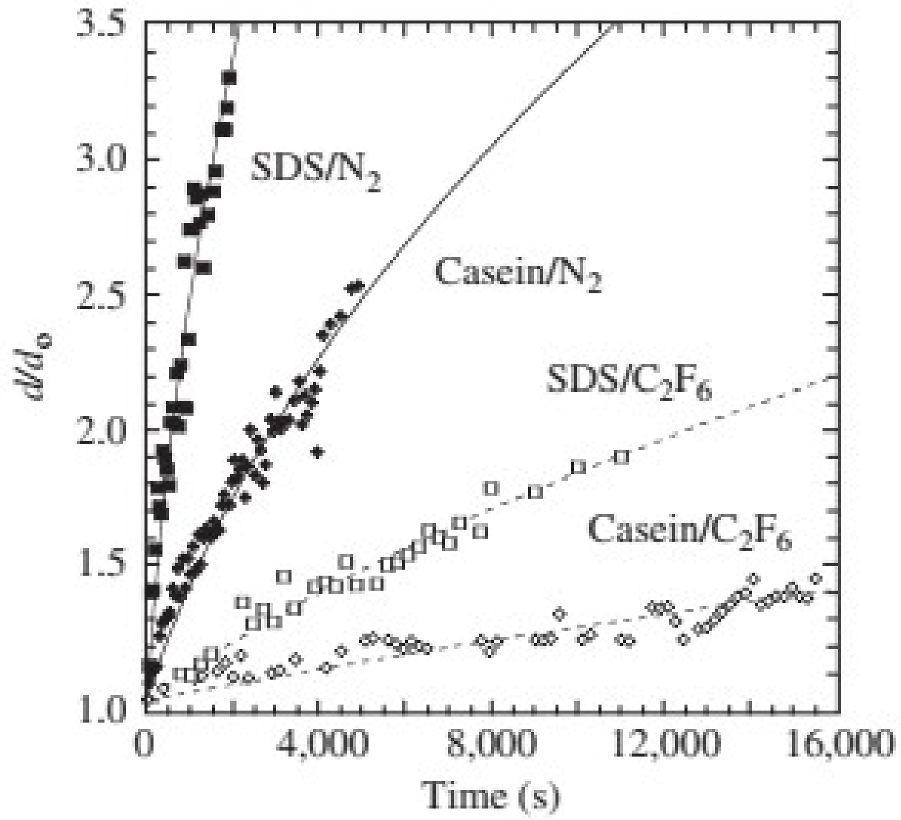
- Solubility k_H depends on gas
- Diffusion D_f depends on gas
- C2F6 → very stable foam
- N2, CO2 → fast coarsening

$$\frac{\Delta V}{A\,\Delta t} = D_{eff} H_{1,2} \rightarrow \quad D_{eff} = D_f\, k_H \frac{2\gamma}{h} \frac{RT}{p_0}$$



Influence of surfactant

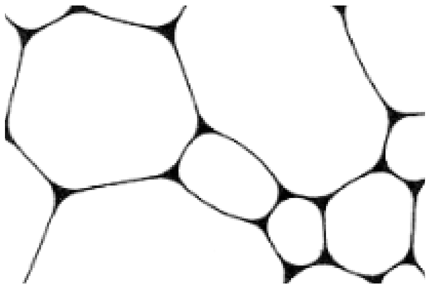
- Surface tension depends on surfactant
- Film thickness depends on surfactant
- Protein surfactant → large h → stable foam
- Ionic surfactant → small h → fast coarsening



$$\frac{\Delta V}{A\,\Delta t} = D_{eff} H_{1,2} \rightarrow \quad D_{eff} = D_f\, k_H \frac{2\gamma}{h} \frac{RT}{p_0}$$

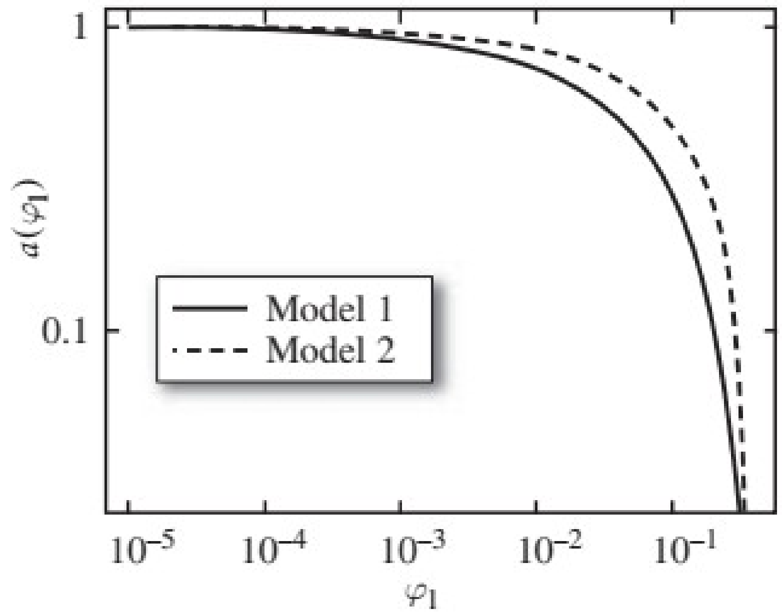
Influence of Liquid fraction

- Liquid accumulated in Plateau borders
- Thicker Plateau borders reduce effective lamella area



Model 1 $$a(\varphi_l) = 1 - \sqrt{\frac{\varphi_l}{\varphi_l^*}}$$

Model 2 $$a(\varphi_l) = \left(1 - \sqrt{\frac{\varphi_l}{\varphi_l^*}}\right)^2$$



$$\frac{\Delta V}{A\,\Delta t} = D_{eff} H_{1,2} \rightarrow \boxed{D_{eff} = D_f\, k_H \frac{2\gamma}{h} \frac{RT}{p_0}\, a(\varphi_l)}$$

Exercise: time scale for Coarsening

- Time for a foam to double its average bubble radius by coarsening?
- SDS foam, 50 nm film thickness,
- A) 0.1 mm bubble radius, CO_2, 10 % liquid fraction
- CO_2: $k_H = 3.4 \times 10^{-4} \frac{mol}{L\ bar}$ $D_f = 1.9 \times 10^{-9} \frac{m^2}{s}$
- B) 5 mm bubble radius, C_2F_6, 0.1 % liquid fraction
- C_2F_6: $k_H = 5.8 \times 10^{-5} \frac{mol}{L\ bar}$ $D_f \approx 1.2 \times 10^{-9} \frac{m^2}{s}$

$$R = R_0 \sqrt{1 + \frac{t}{t_c}}$$

$$t_c \approx \frac{\langle V(t=0)\rangle^{2/3}}{b\, D_{eff}}, \mathrm{b} \approx 1$$

$$D_{eff} = D_f\, k_H \frac{2\gamma}{h} \frac{RT}{p_0} a(\varphi_l)$$

$$a(\varphi_l) = 1 - \sqrt{\frac{\varphi_l}{\varphi_l^*}}$$

Gas constant: $R = 8.314 \frac{J}{mol\ K}$

Exercise: time scale for Coarsening

- Time for a foam to double its average bubble radius by coarsening?
- SDS foam, 50 nm film thickness,
- A) 0.1 mm bubble radius, CO_2, 10 % liquid fraction
- CO_2 :

$$k_H = 3.4 \, x \, 10^{-4} \frac{mol}{L \, bar} = 3.4 \, x \, 10^{-6} \frac{mol}{m^3 \, Pa}$$

$$D_f = 1.9 \, x \, 10^{-9} \frac{m^2}{s}$$

$$a(\varphi_l) = 1 - \sqrt{\frac{\varphi_l}{\varphi_l{}^*}} = 0.47$$

$$D_{eff} = D_f \, k_H \frac{2\gamma}{h} \frac{RT}{p_0} a(\varphi_l) = 9 \, x \, 10^{-11} \frac{m^2}{s}$$

$$t_c \approx \frac{\langle V(t=0) \rangle^{2/3}}{b \, D_{eff}} = 290 \, s$$

$$\frac{R}{R_0} = 2 = \sqrt{1 + \frac{t}{t_c}} \rightarrow t = 3 \, t_c = 870 \, s = 14 \, min$$

Exercise: time scale for Coarsening

- Time for a foam to double its average bubble radius by coarsening?
- SDS foam, 50 nm film thickness,
- B) 5 mm bubble radius, C_2F_6, 0.1 % liquid fraction
- C_2F_6 :

$$k_H = 5.8\,x\,10^{-5}\,\frac{mol}{L\,bar} = 5.8\,x\,10^{-7}\,\frac{mol}{m^3\,Pa} \qquad D_f \approx 1.2\,x\,10^{-9}\,\frac{m^2}{s}$$

$$a(\varphi_l) = 1 - \sqrt{\frac{\varphi_l}{\varphi_l{}^*}} = 0.95$$

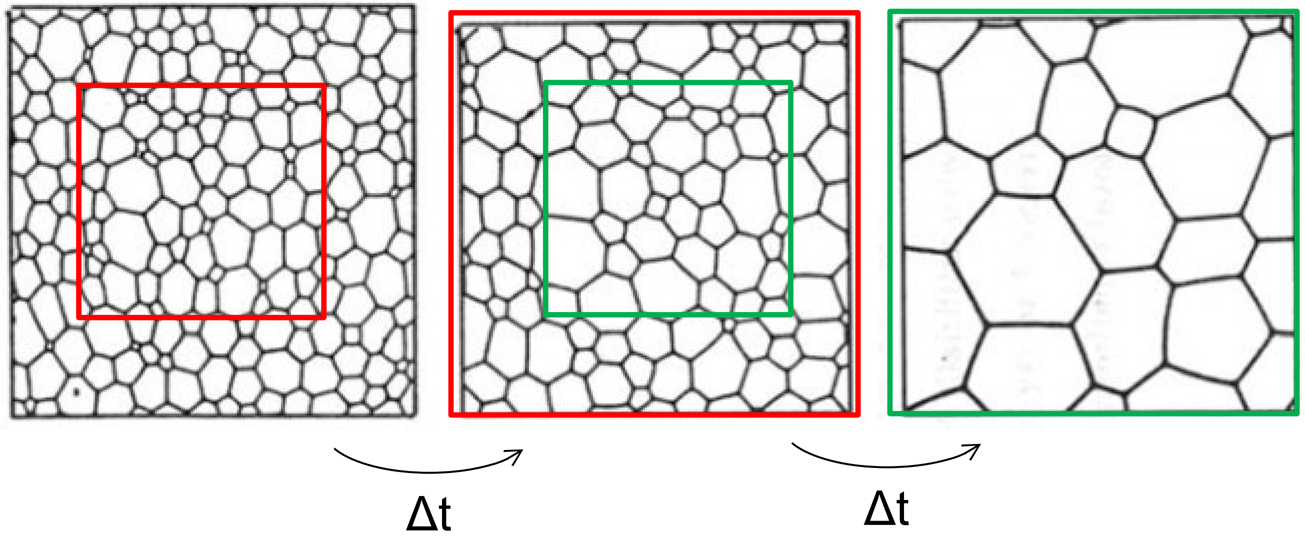
$$D_{eff} = D_f\,k_H\,\frac{2\gamma}{h}\frac{RT}{p_0}\,a(\varphi_l) = 1.9\,x\,10^{-11}\,\frac{m^2}{s}$$

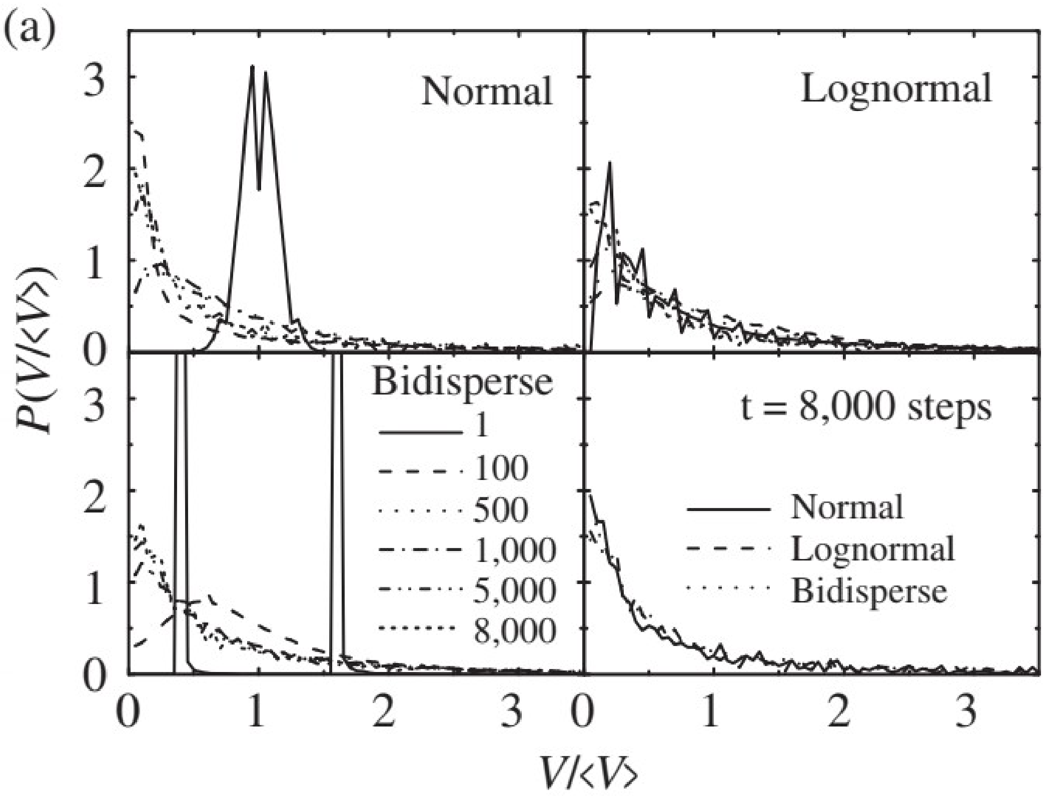
$$t_c \approx \frac{\langle V(t=0)\rangle^{2/3}}{b\,D_{eff}} = 3.4\,x\,10^6 s \qquad \frac{R}{R_0} = 2 = \sqrt{1+\frac{t}{t_c}} \rightarrow t = 3\,t_c = 10^7 s = 100\,days$$

Air: 12 days

Self-similar regime

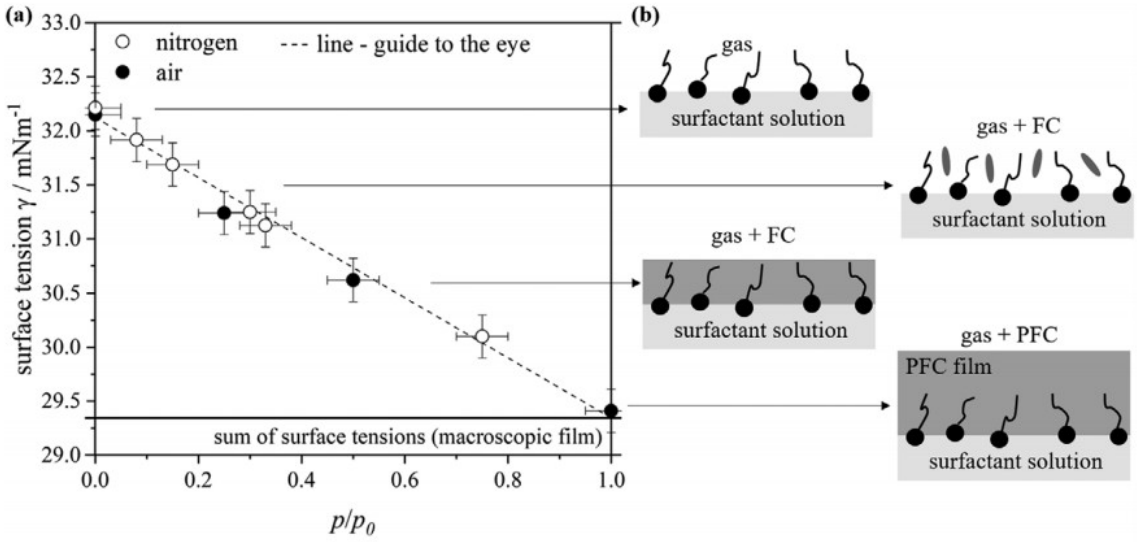
- Coarsening process leads to increasing average bubble size <V>
- Eventually reaching self-similar regime:
- → Identical topology, identical size distribution P(V/<V>)





Influence on coalescence?

- Traces of C6F14 sufficient
- C6F14 also reduces coalescence (film rupture)
- Film formation at interface???



RESEARCH ARTICLE

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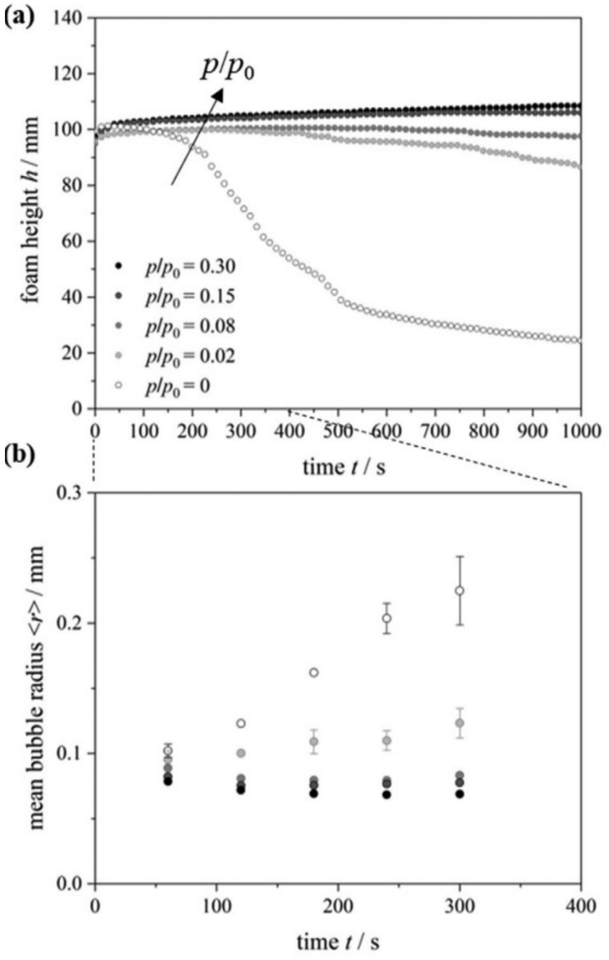
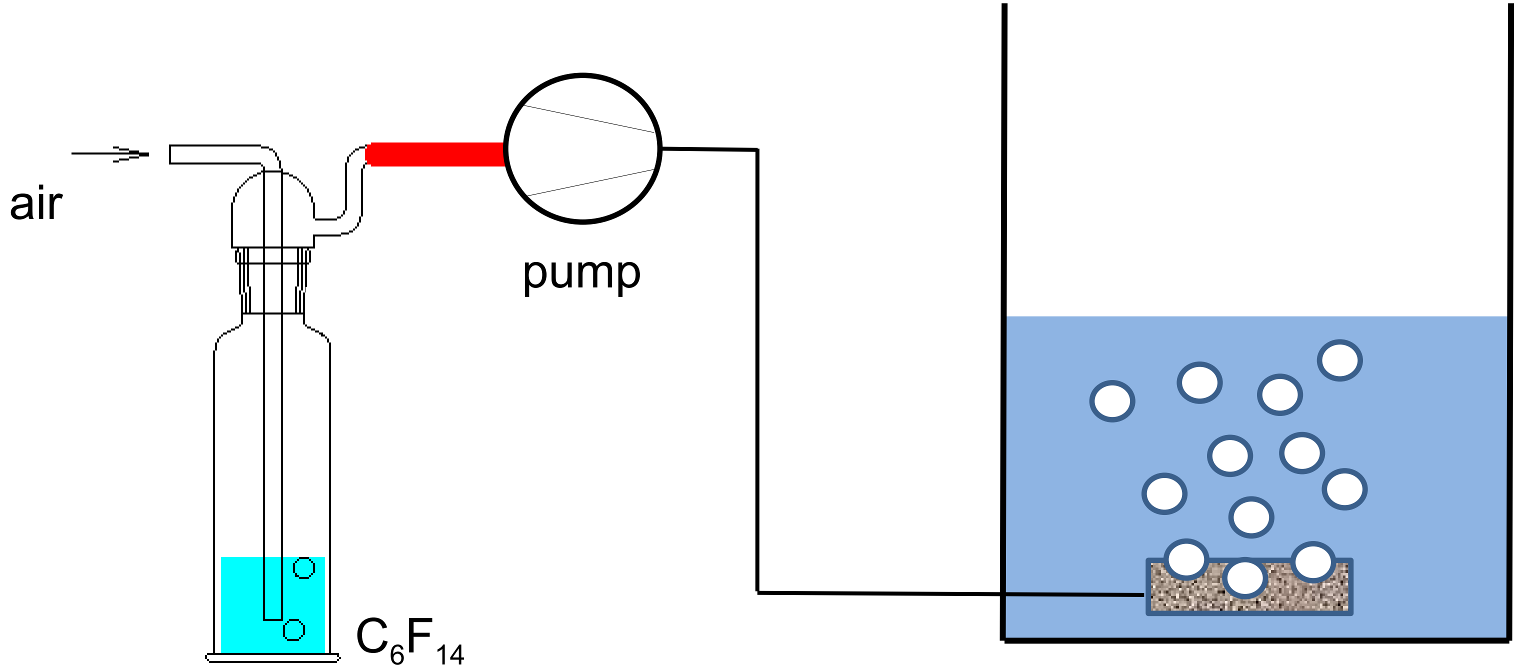
Fluorocarbon Vapors Slow Down Coalescence in Foams

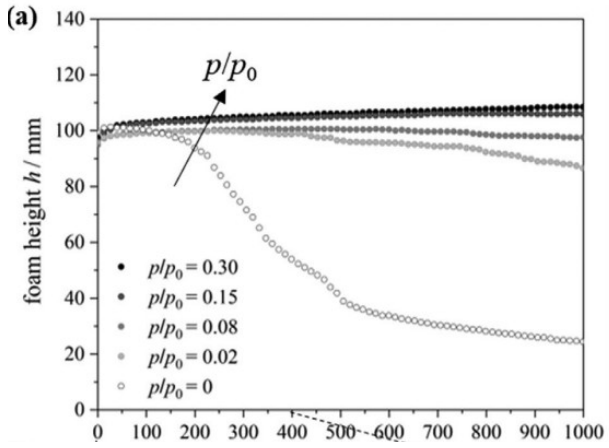
Katja Steck,* Martin Hamann, Sébastien Andrieux, Pierre Muller, Patrick Kékicheff, Cosima Stubenrauch, and Wiebke Drenckhan



Application of C6F14

- Traces of C6F14 sufficient
- Partial pressure at 25°C: 218 mmHg = 29kPa





Structure

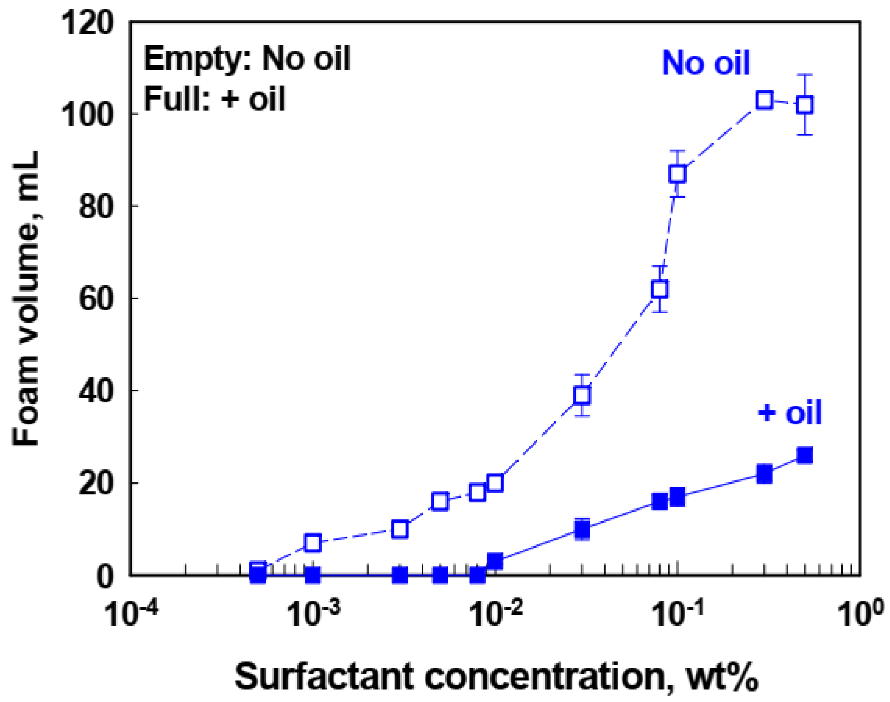
- Review lecture 9
- Film rupture
- Coarsening
- Stability testing
- Defoaming

Relevance of film stability

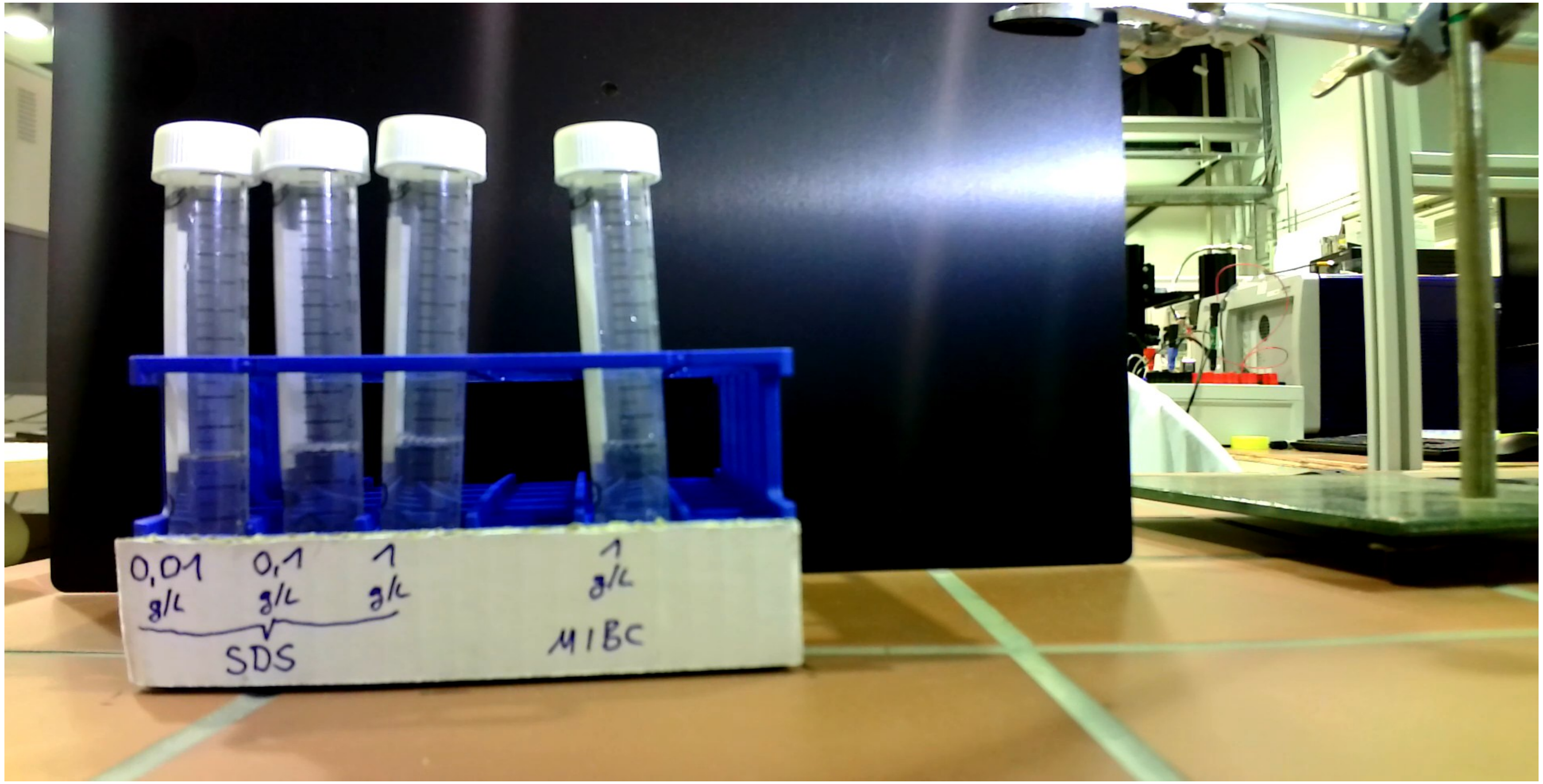
- Food texture
- Cleaning
- Industrial processes
- → requirement of stability test

Bartsch test

- Shaking with defined frequency, time
- Measurement of resulting foam volume

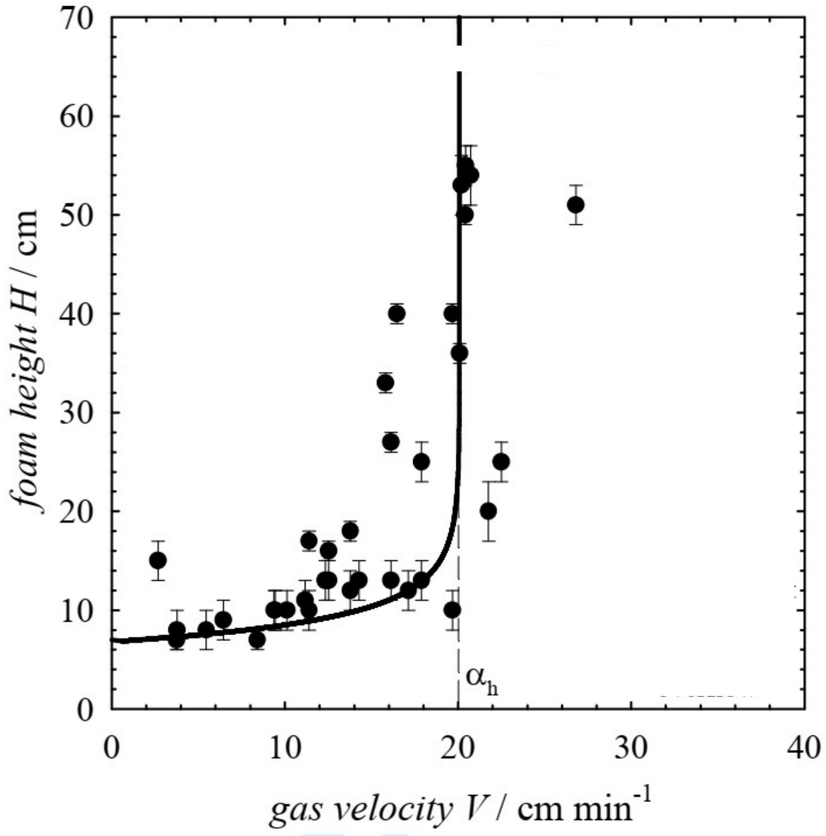


Foamability test



Bikerman standardized test

- Constant gas flow rate through a porous plate
- Measurement of (steady) resulting foam height



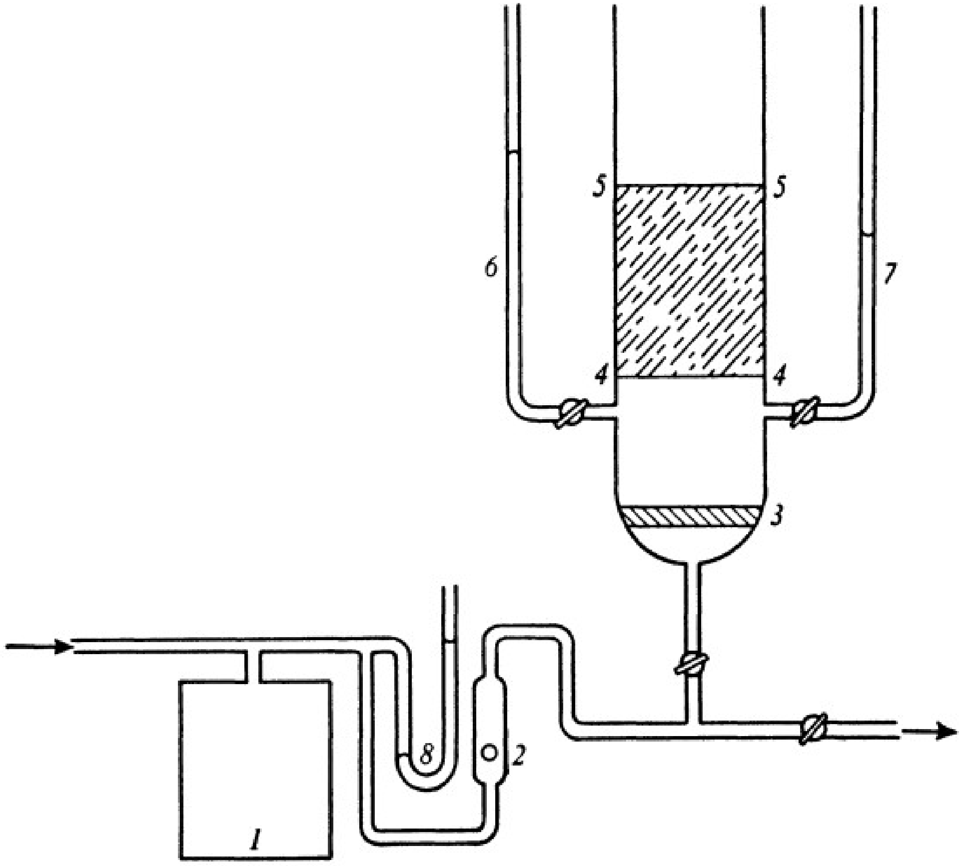
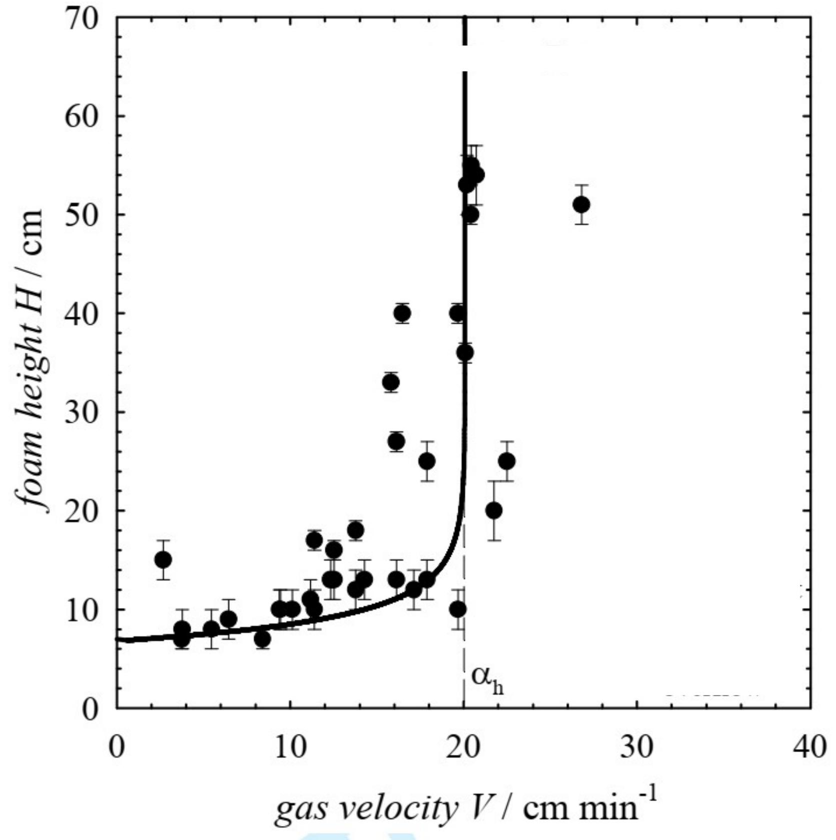


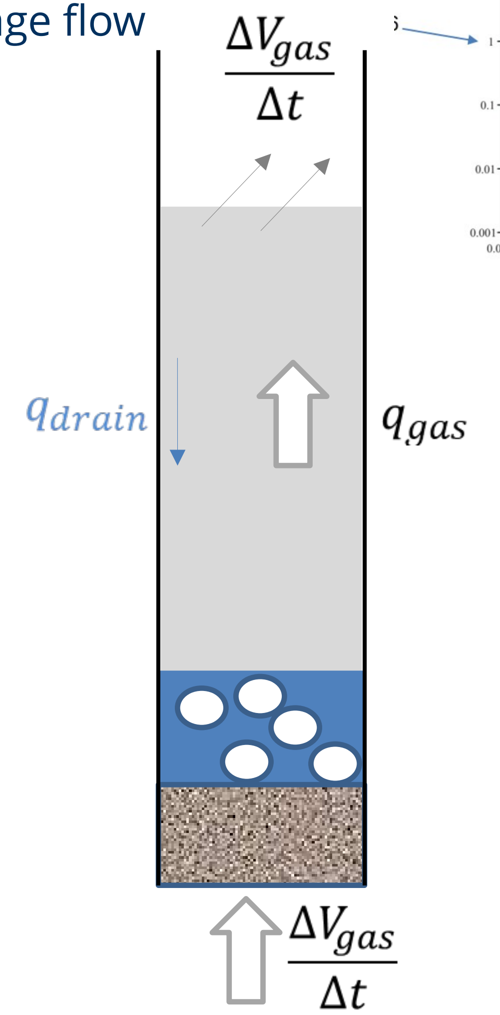
Fig. 3.6. Determination of the liquid volume in foam during bubbling. *1* is the nitrogen reservoir; *2* is the flow meter; *3* is the porous plate; *4*, *4* and *5*, *5* are the boundaries of the foam column; *6* is a buret; and *7* and *8* are manometers (after reference [49]).

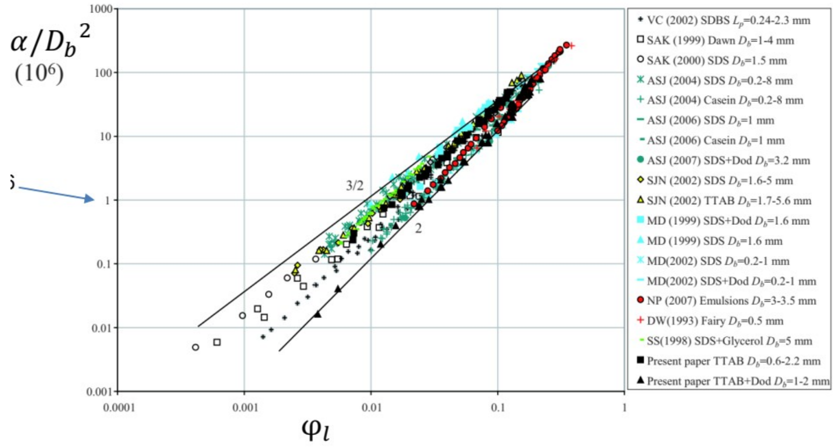
[Bikerman, Foams, 1973]

Bikerman standardized test

- Equilibrium between vertical convection and drainage flow
- Drainage equation yields critical gas velocity

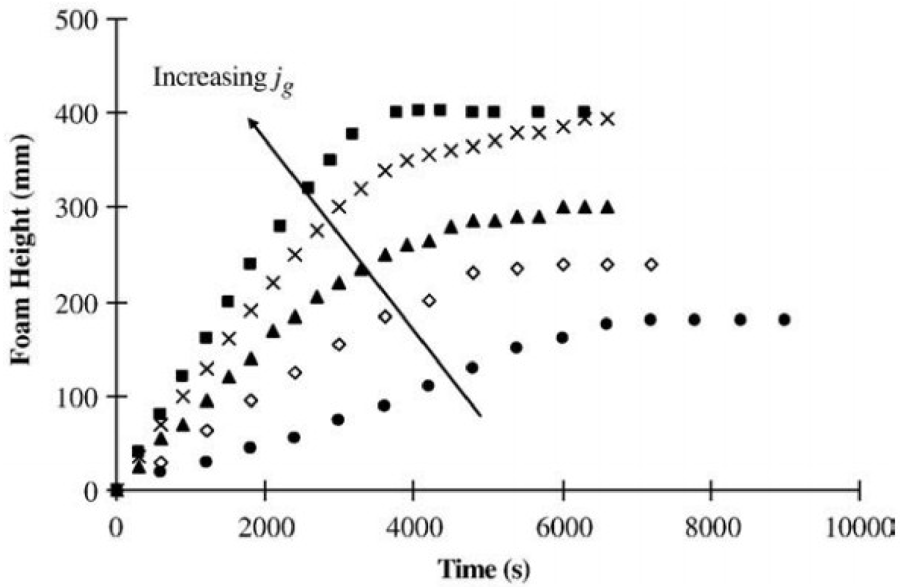


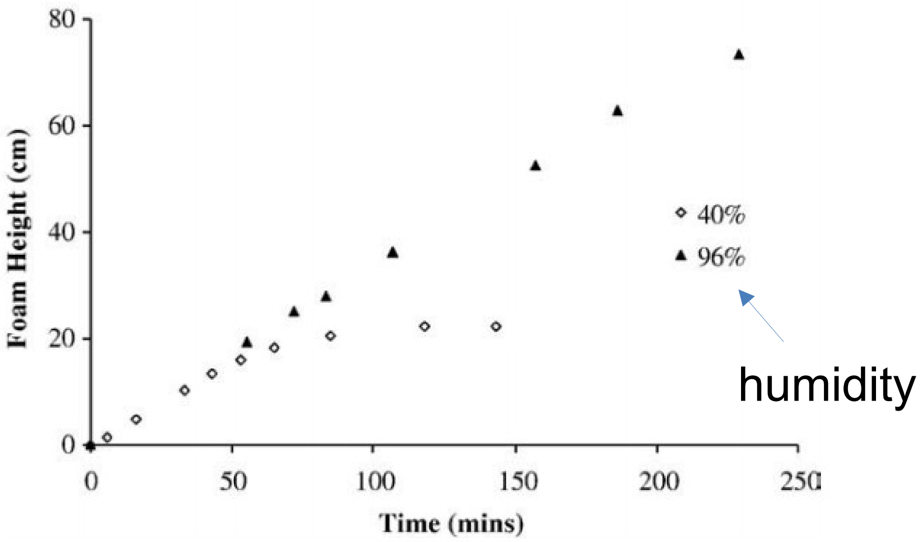


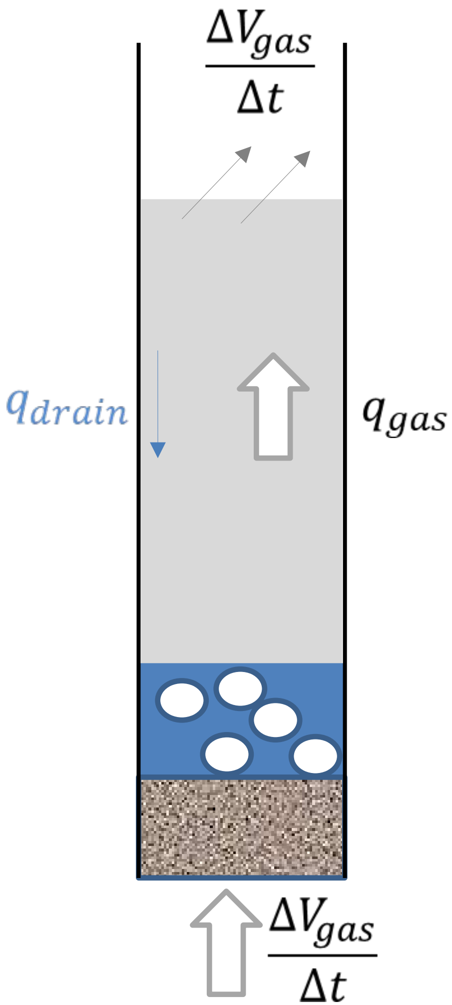


Foamability test

- Motivated by Bikerman test (same setup)
- Observe growth rate and final height
- Strongly influenced by humidity!



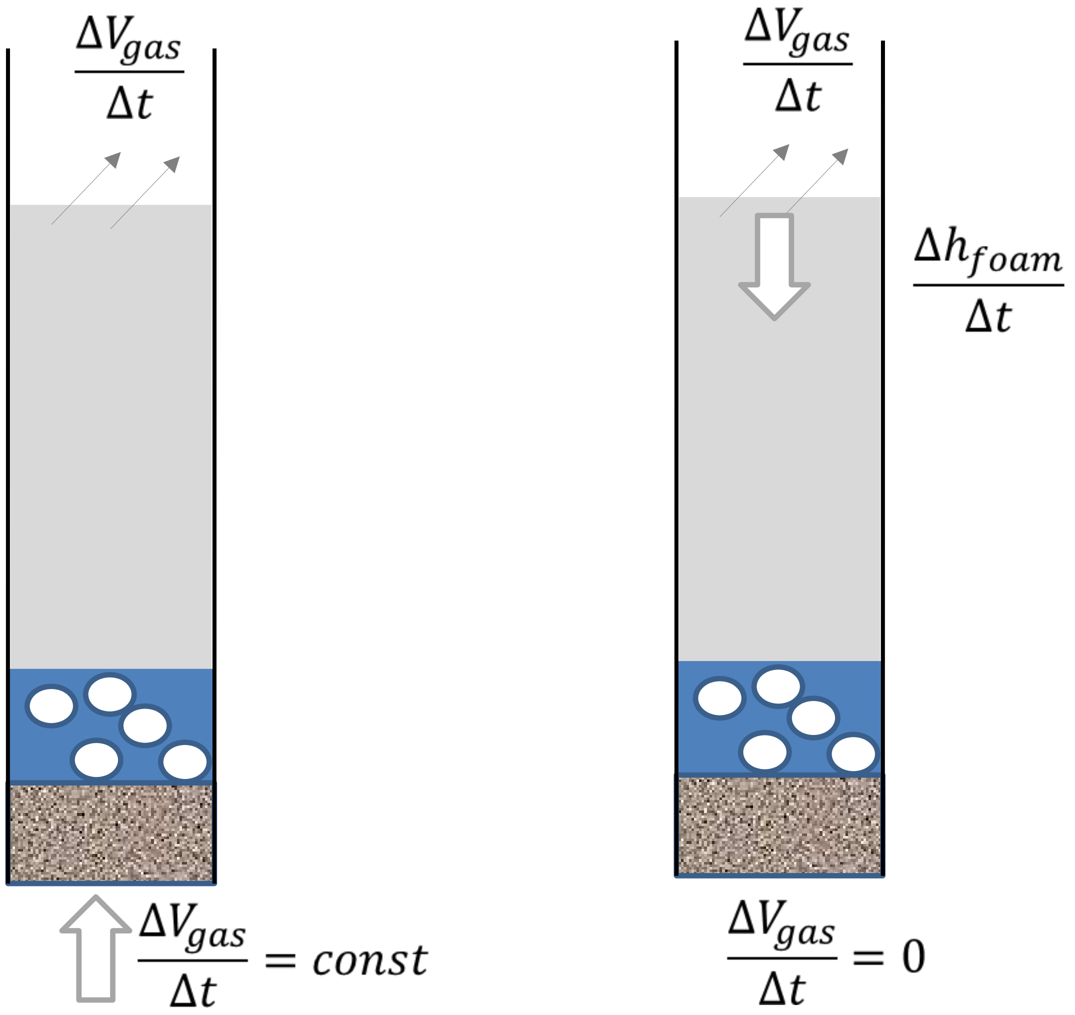




[Li et al, J. Mineral. Process, 2009]

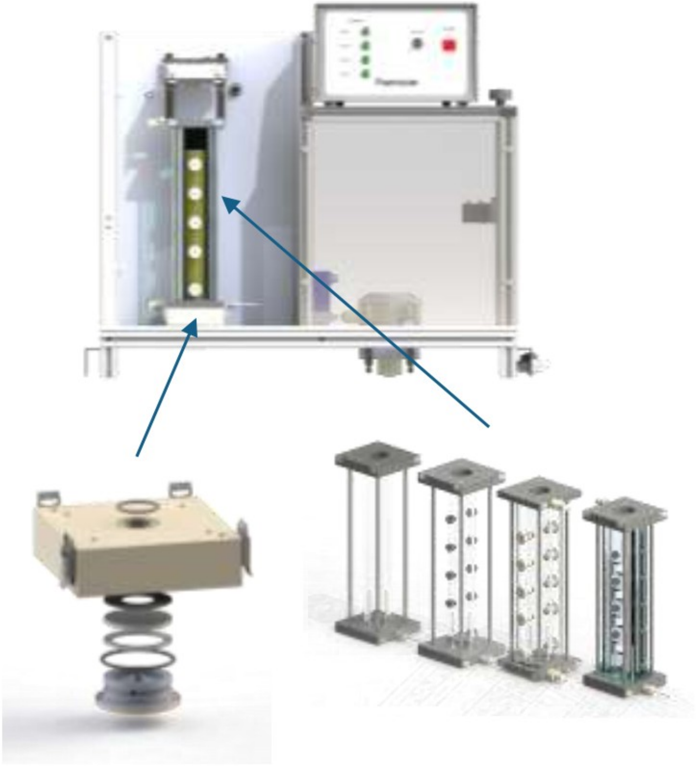
Foamability vs. Foam stability

- Constant gas flow: foamability
- Gas flow switched off – foam stability



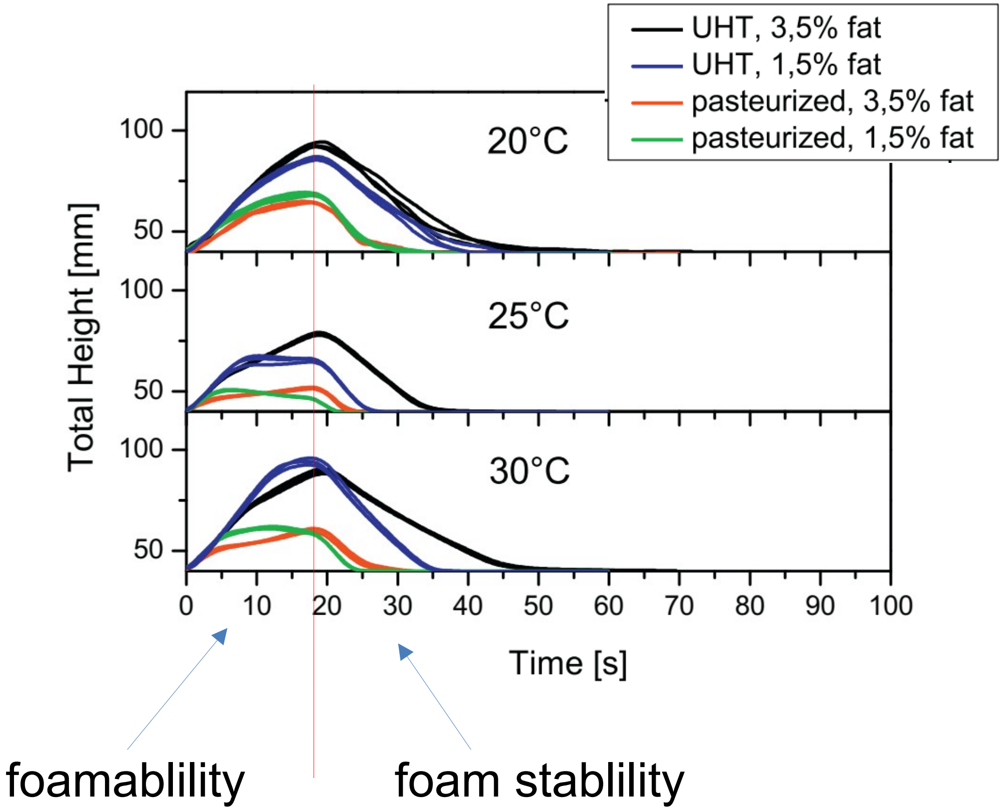
Commercial devices

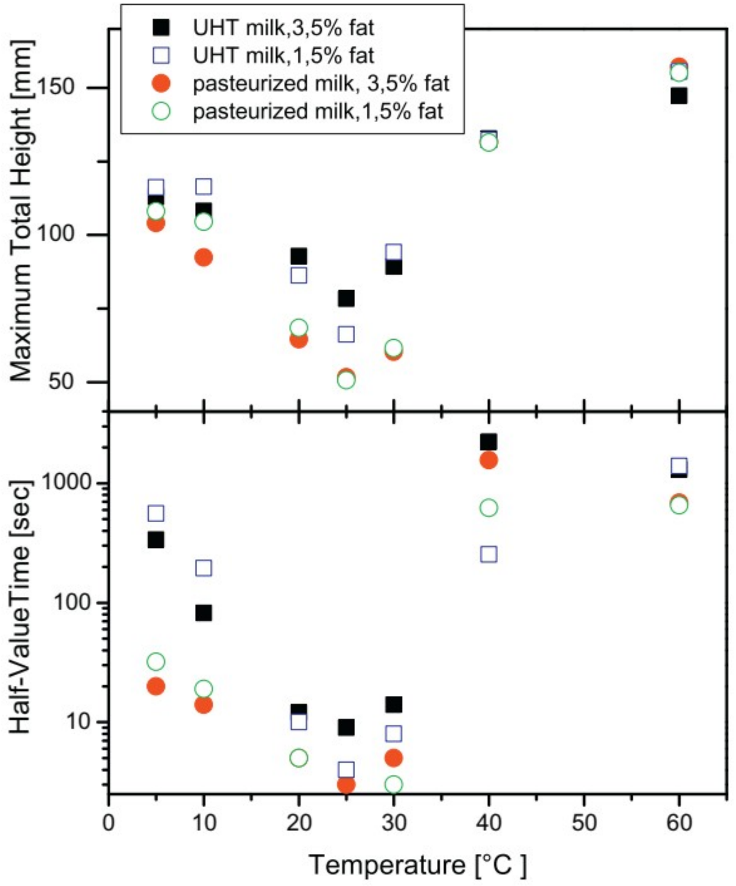
- Controlled gas flow rate, volume
- Foam height measurement
- Bubble size measurement
- Liquid fraction distribution
- Different manufacturer
- Automated, reproducible
- Measures foamability and foam stabilit



Examples of foamability / foam stability

- Foam height of milk foam
- Different pre-treatment, different temperatures
- Gas flow switched off after 18 sec

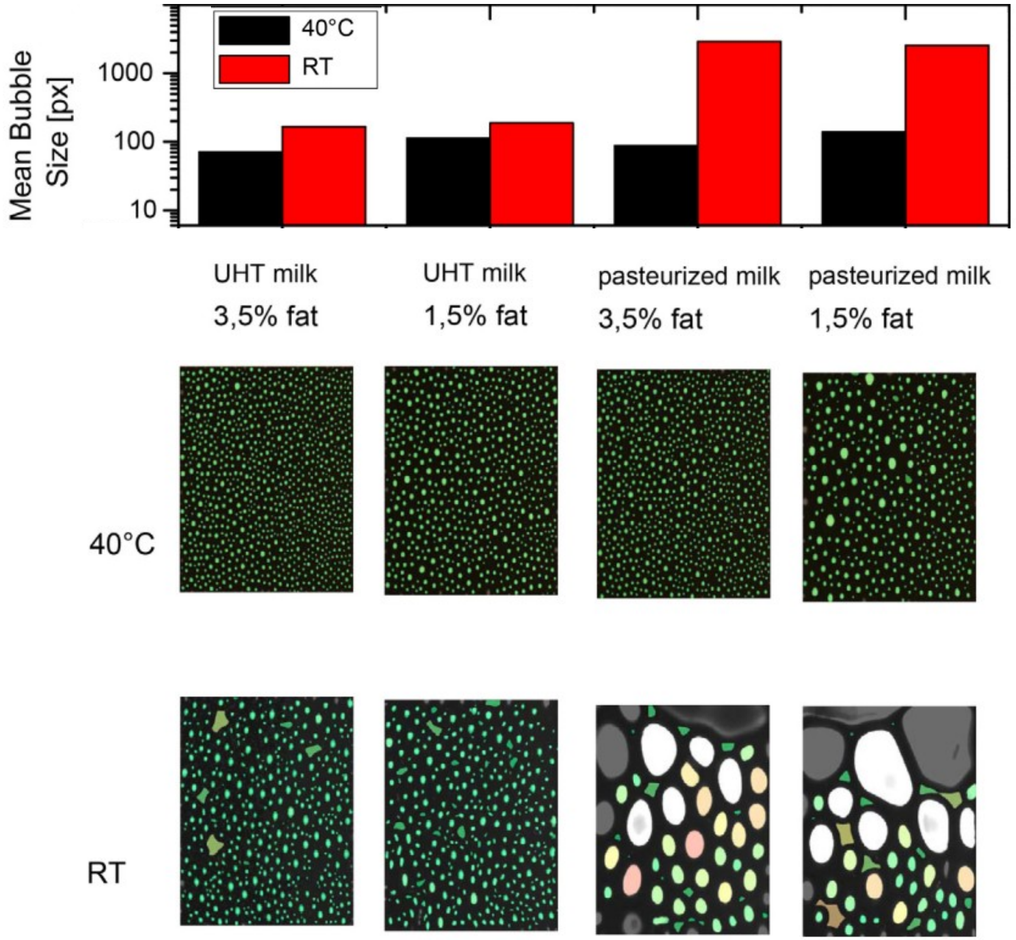


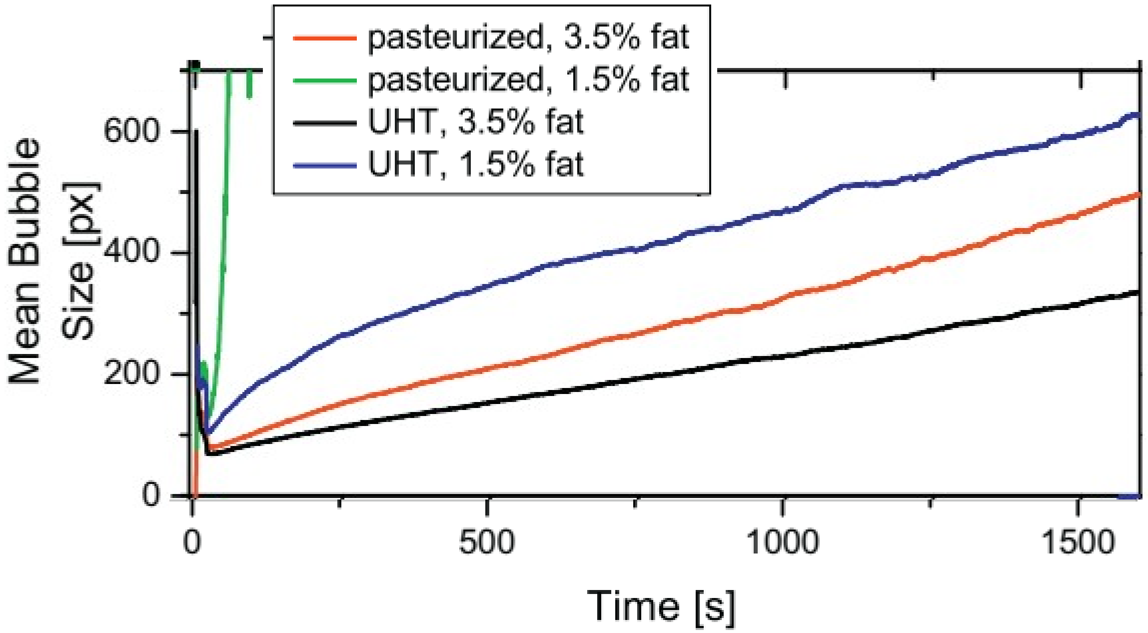


[Oetjen et al., 2014]

Examples of foam stability

- Bubble size measurement

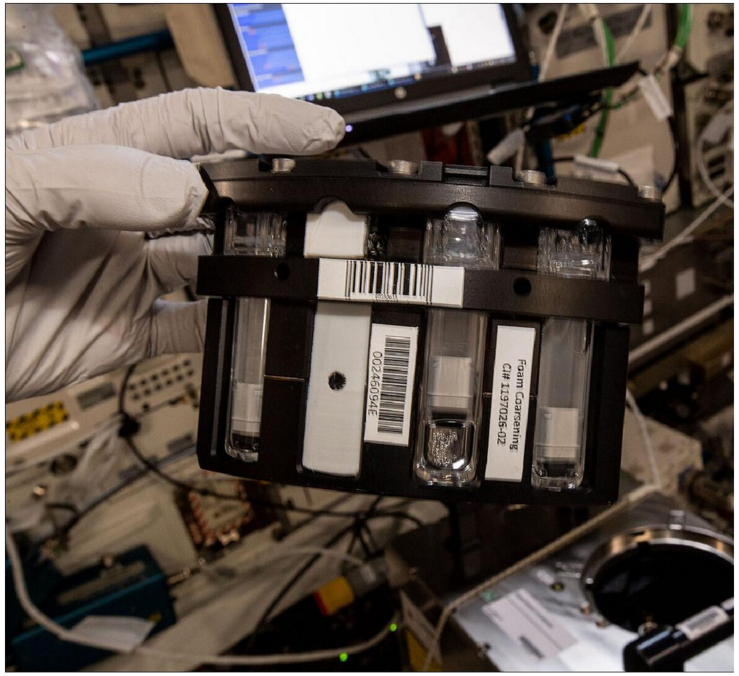


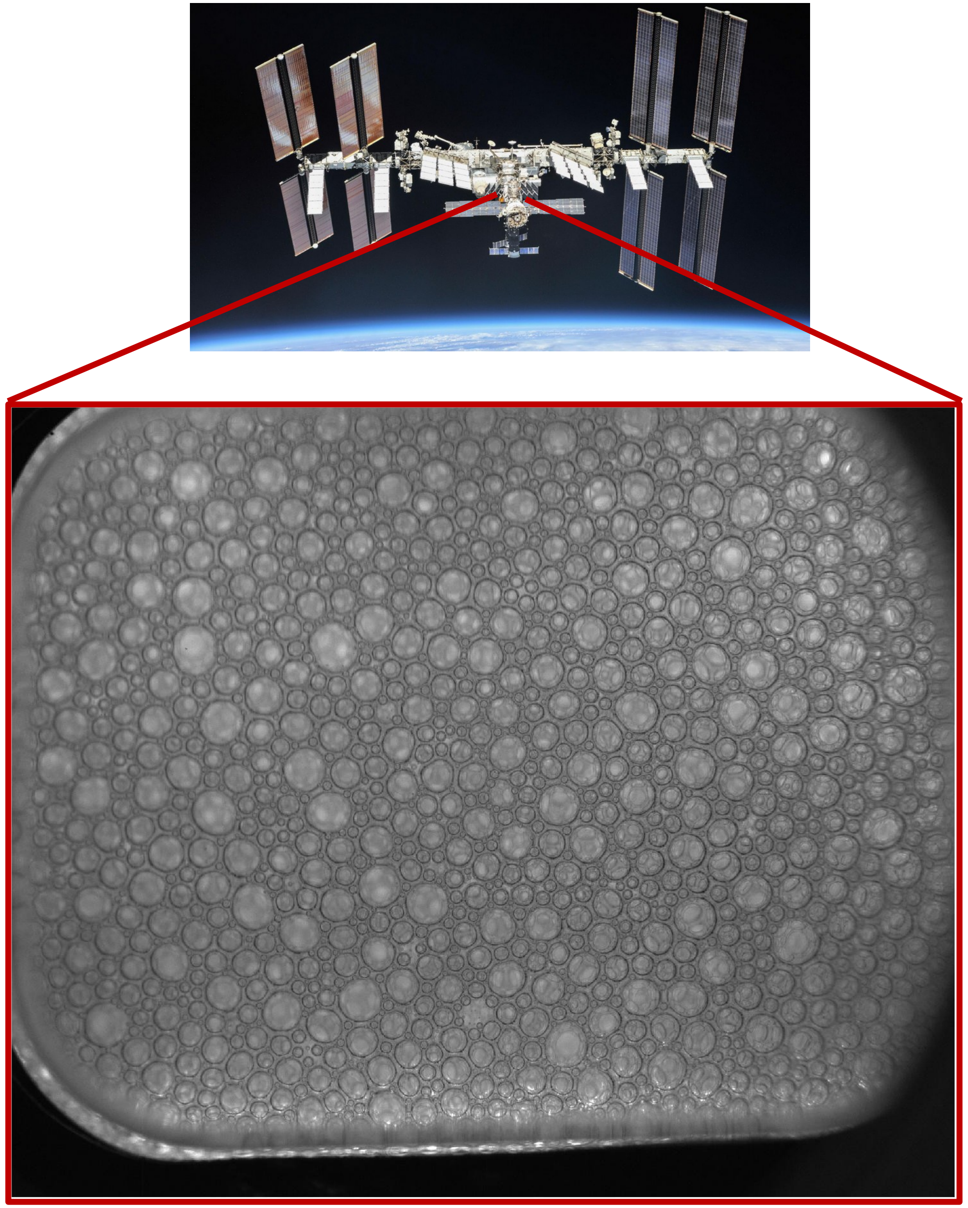


[Oetjen et al., 2014]

Foam stability under zero-g

- Long term experiment on the ISS
- Stable foam at high liquid fraction, zero drainage
- Precise measurement of coarsening



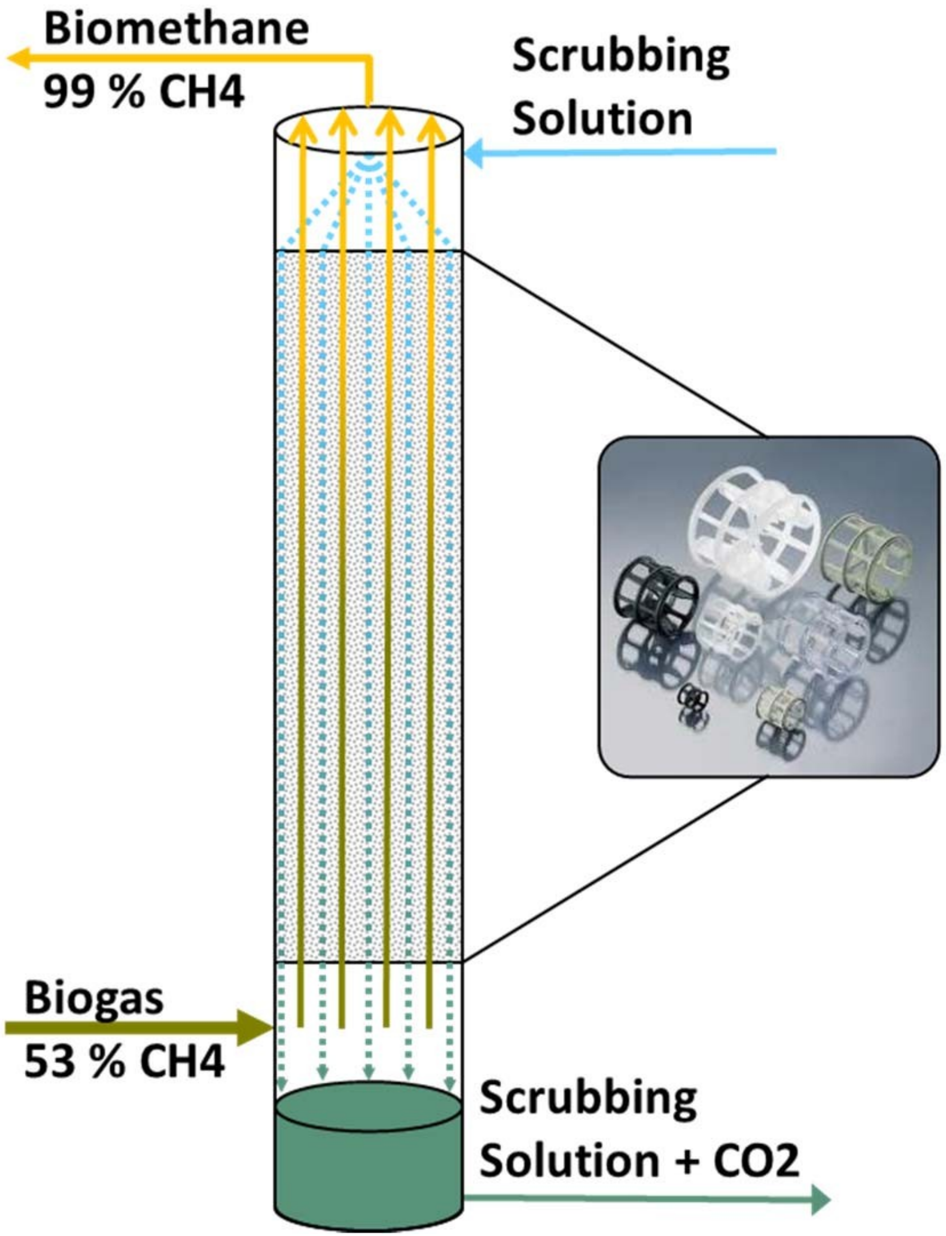


Structure

- Review lecture 10
- Film rupture
- Coarsening
- Stability testing
- Defoaming

Typical applications

- Removal of CO_2 from biogas
- Packed bed of wrinkled bodies → foam generation
- Foam blocks device, reduces efficiency
- Scrubbing solution contains defoaming agent
- → film rupture



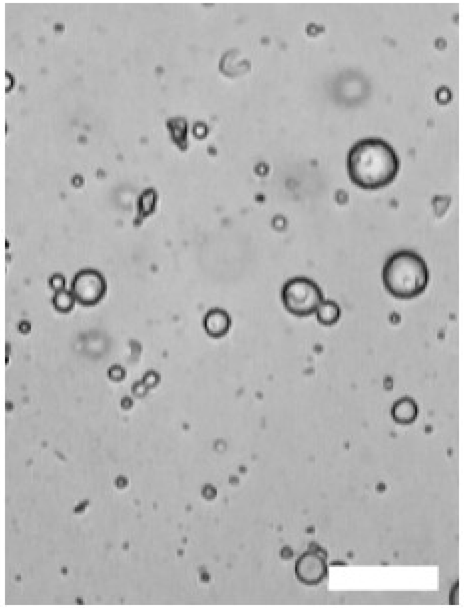
Types of Antifoams

- Additives to the solution that prevent foam formation and/or destroy foam
- Solid antifoams
  - silica, wax, polymer
- Liquid antifoams
  - triglycerides
  - silicon oils, mineral oils
- Solid+liquid antifoams
  - oil + particles

Silica particles

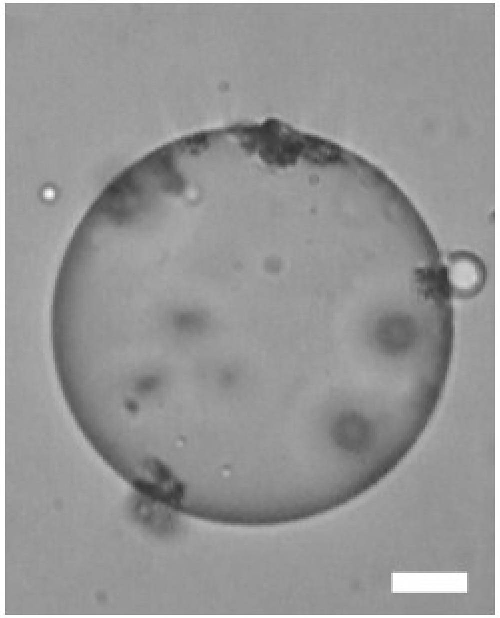
100 nm

Oil emulsion



30 μm

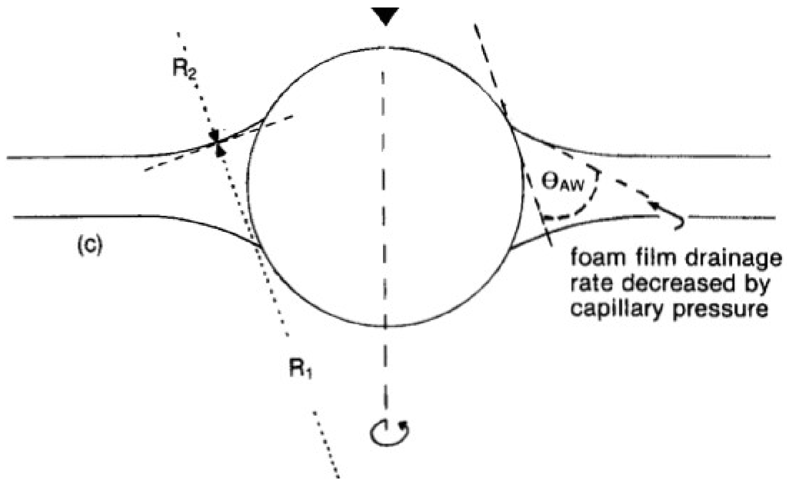
Oil+particles

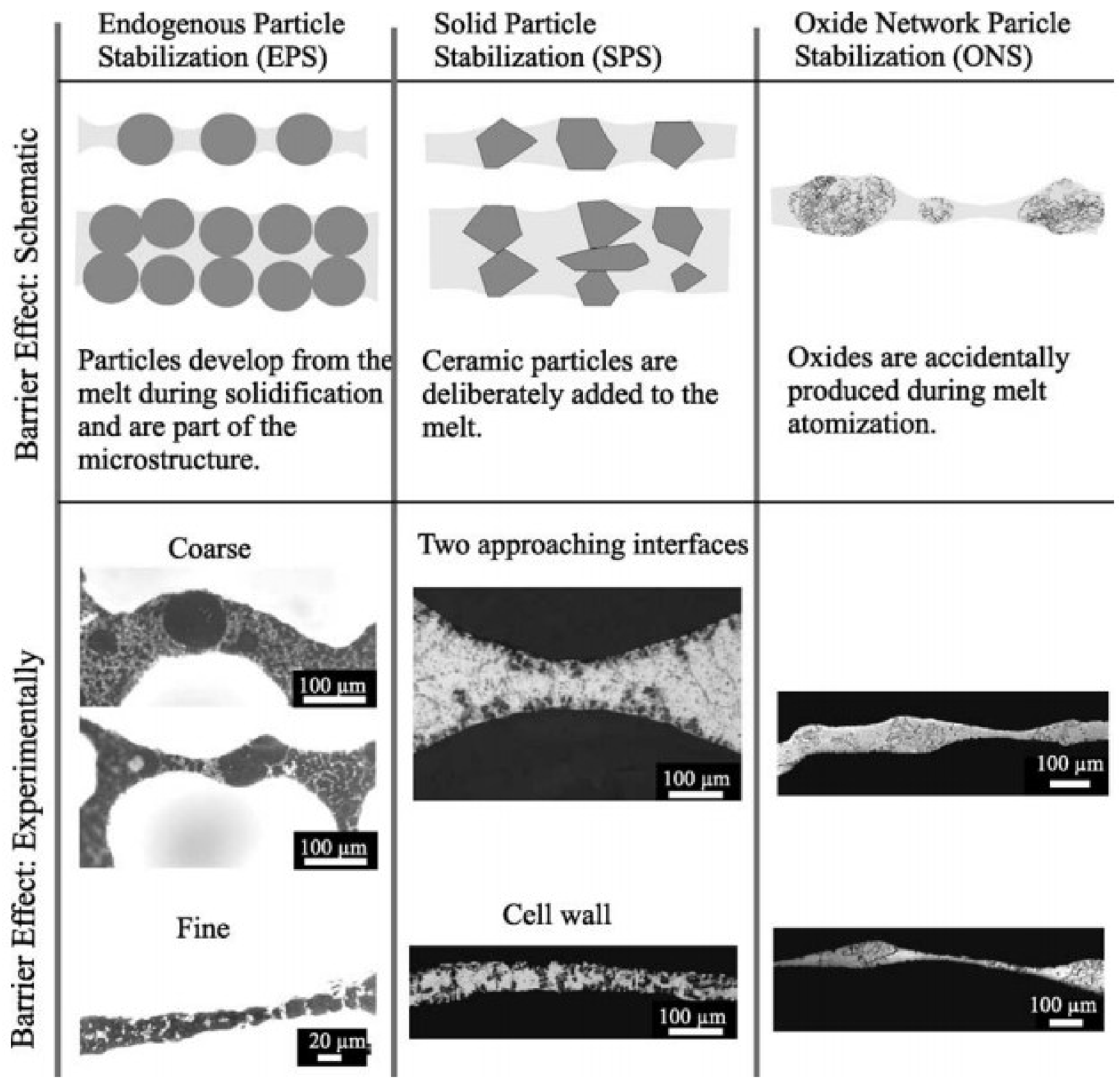


1 μm

Film stabilisation by particles

- Depending on contact angle
- Hydrophilic particles ($\theta < 90°$) reach to stable position

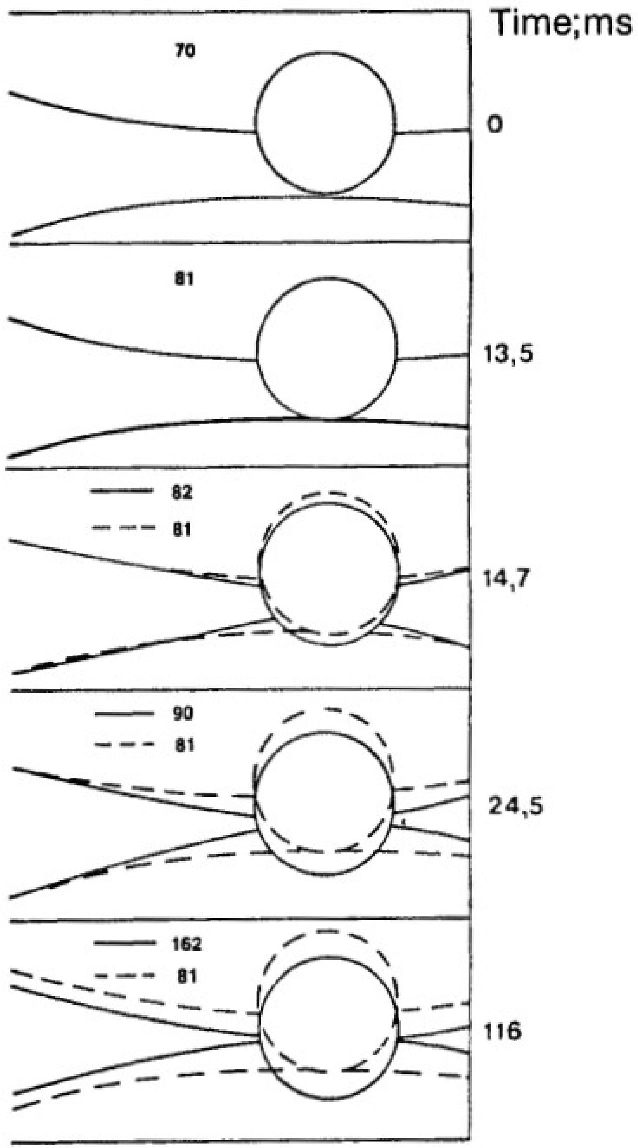




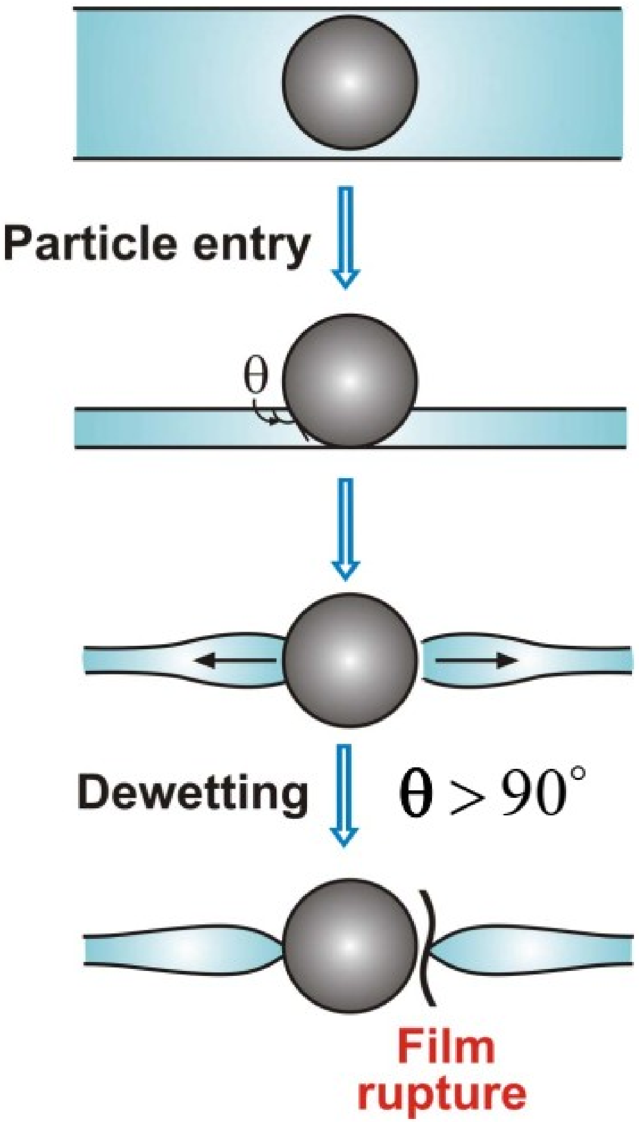
[Körner et al., 2005]

Film rupture by particles

- Depending on contact angle
- Hydrophobic particles ($\theta > 90°$)
- Cause de-wetting and film rupture

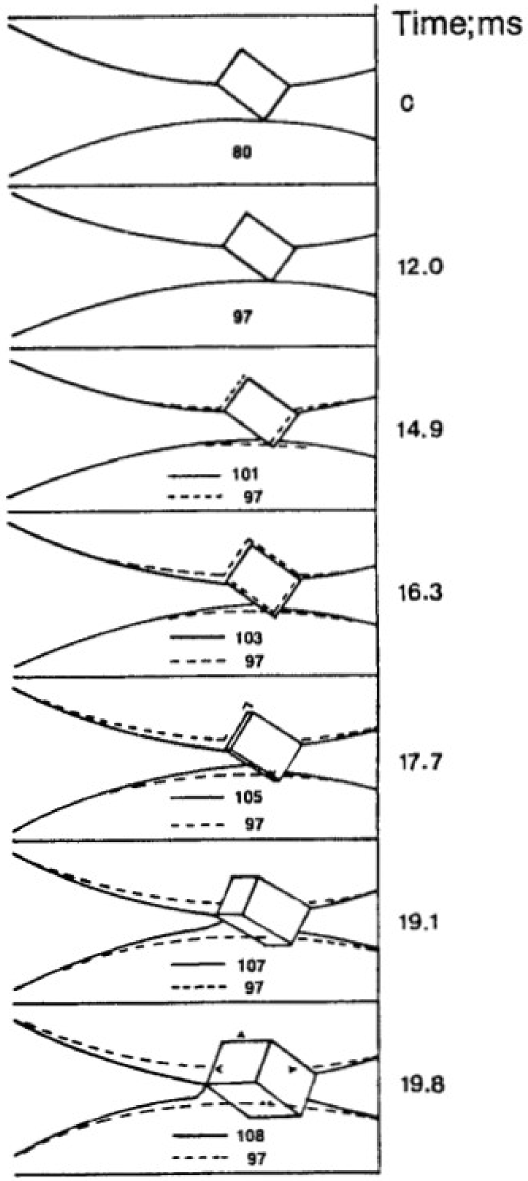


[Garret, Defoaming, 1992]

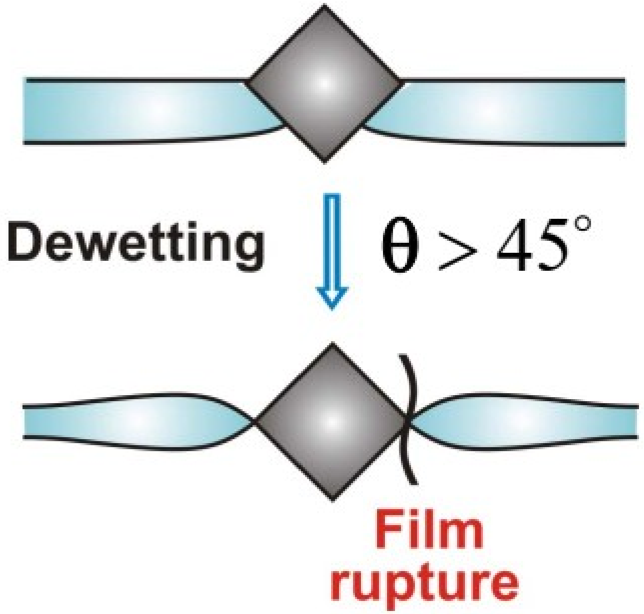


Film rupture by particles

- Shape of particles can support film rupture
- Sharp edges prevent stable situations
- Relevant e.g. for mineral particles

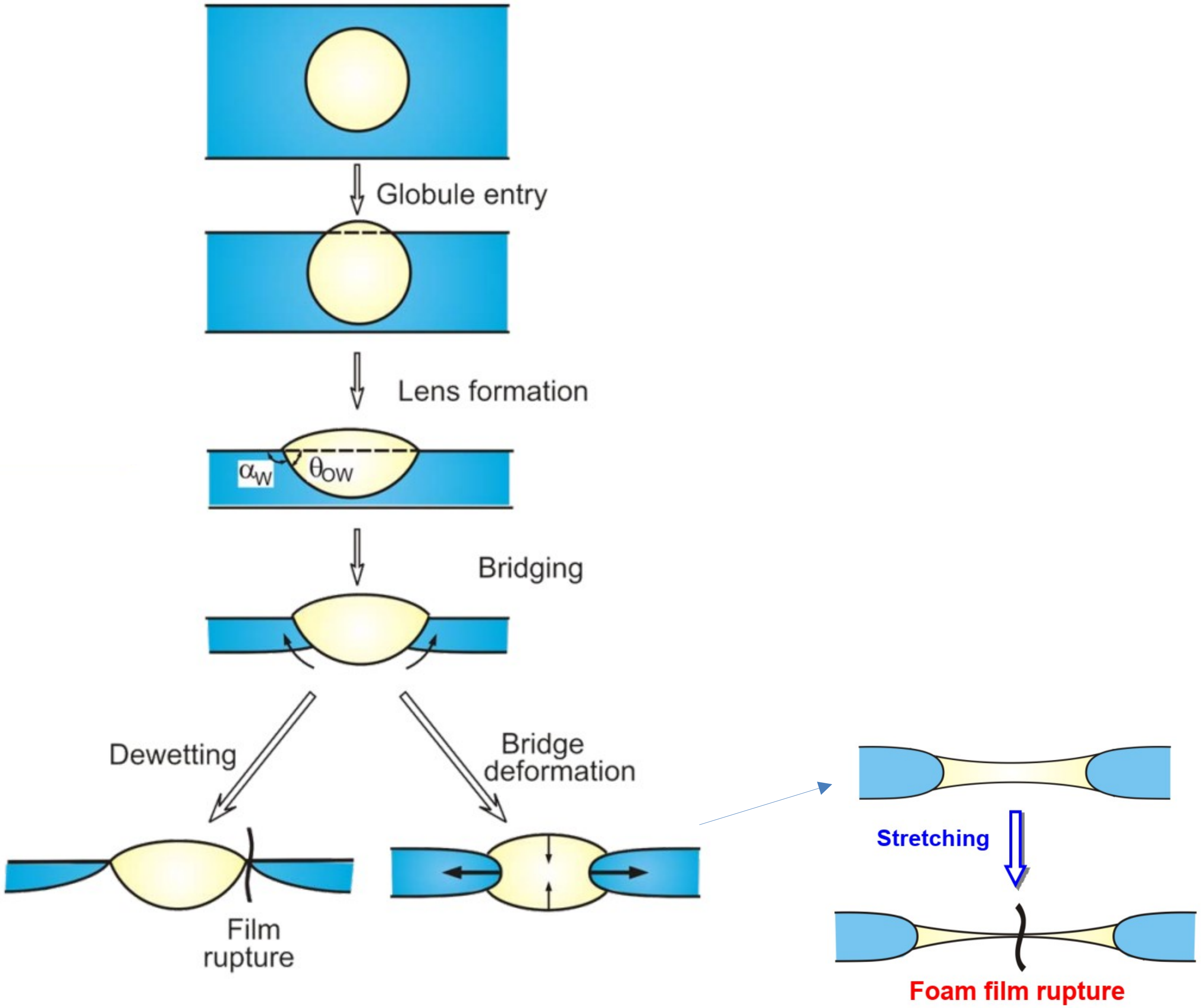


[Garret, Defoaming, 1992]



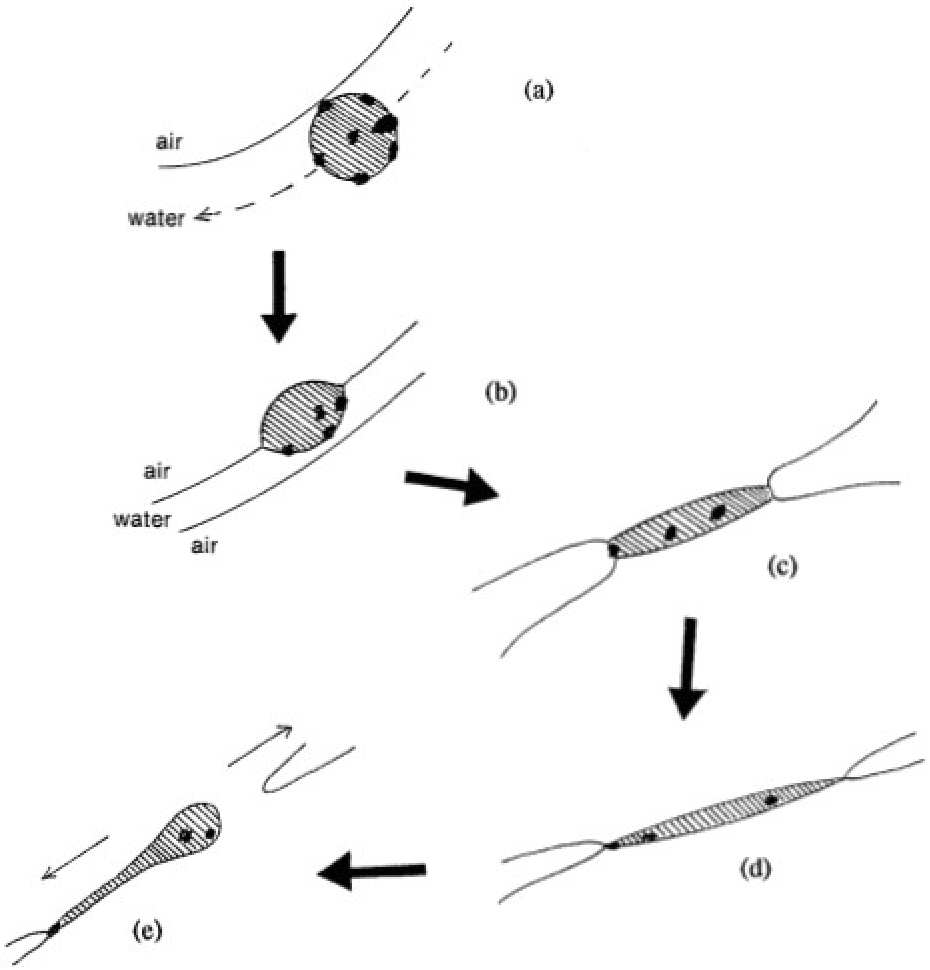
Film rupture by liquids

- Droplets adsorbs at water-air interfac
- Droplet bridges film
- Either dewetting or bridge-stretching
- Depending on contact angles
- Depending on drop rheology



Film rupture by compounds

- Particles support rupture of air-water-oil filr
- Oil ruptures film by de-wetting



[Garret, Defoaming, 1992]