TECHNISCHE UNIVERSITÄT DRESDEN

DRESDEN concept

Dr.-Ing. Sascha Heitkam,

Insitute for Process Engineering and Environmental Technology

Lecture 6: Foam Structure

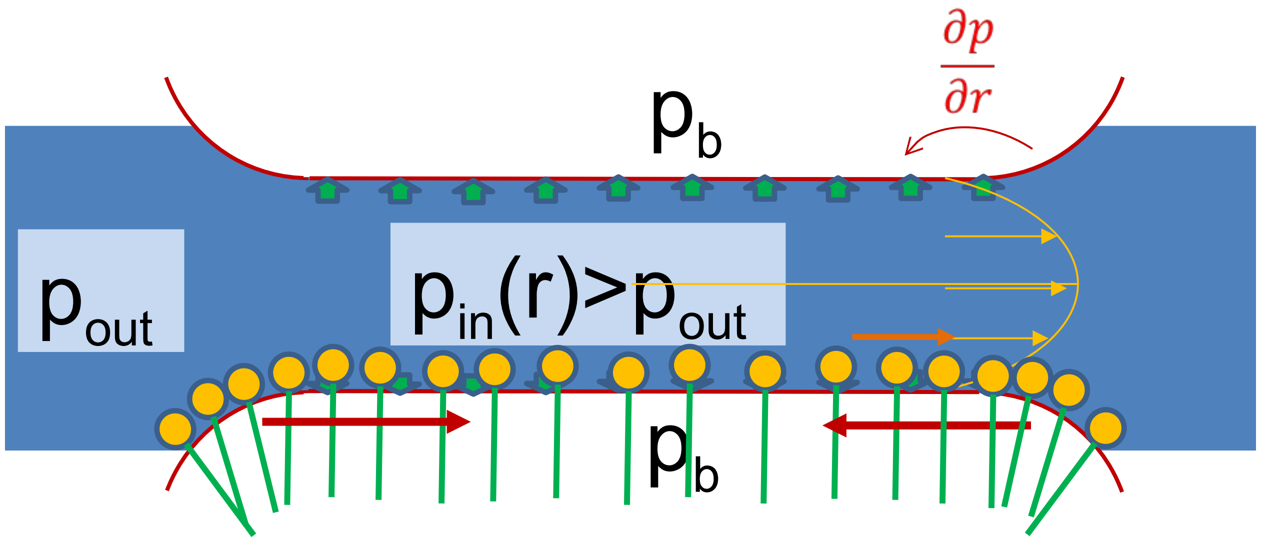
Structure

- Review lecture 6
- Dry foam topology
- Plateau's laws
- Neighbour statistics
- Wet foam
- Bubble crystals

Film thinning

- No equilibrium with disjoining pressure
- Pressure inside the film is larger than outside
- → Pressure gradient drives drainage flow

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



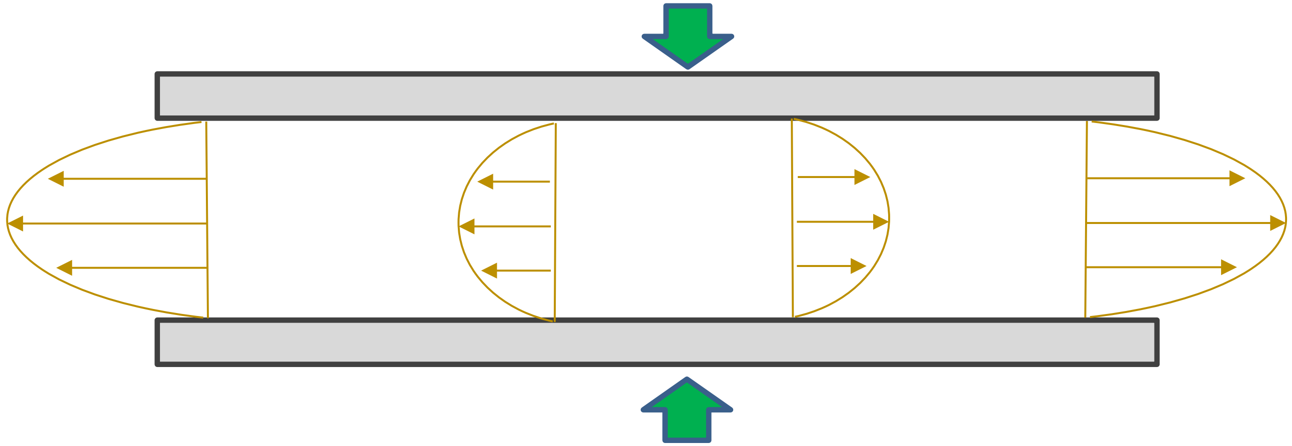
$$p_{in}(\tilde{r}) = p_{out} + \int_R^{\tilde{r}} \frac{\partial p}{\partial r} dr$$

Pressure loss due to viscous flow

Film thinning

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

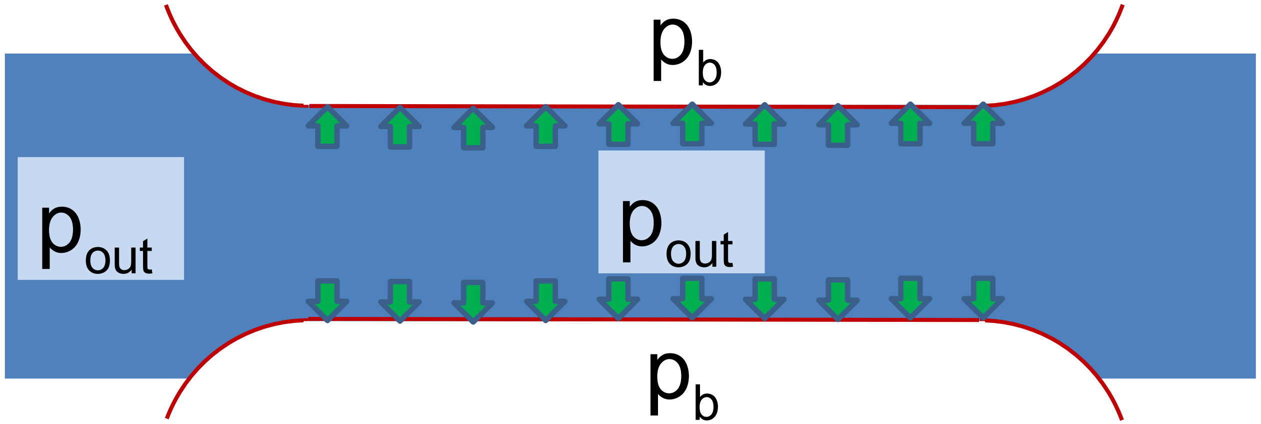
$$-\frac{\partial h}{\partial t} = \frac{2h^3(p_b - p_{out} - \Pi)}{3\eta R^2}$$

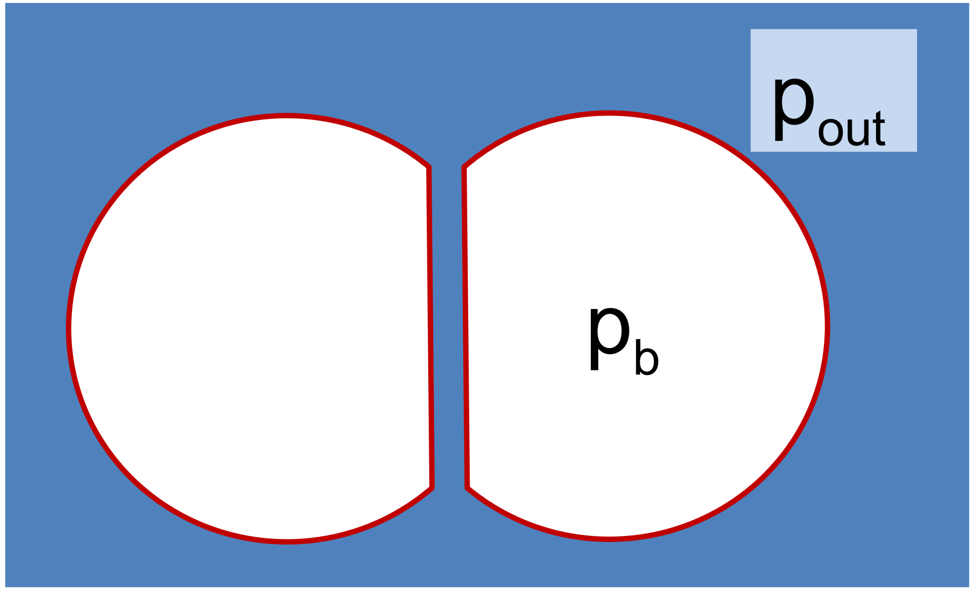


$$T = \frac{3\eta R^2}{32\ Pa}\frac{1}{2}\left(\frac{1}{{h_{CBF}}^2} - \frac{1}{{h_0}^2}\right) = 1.1 \cdot 10^5 s \approx 1.3 day$$

What about Young-Laplace?

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



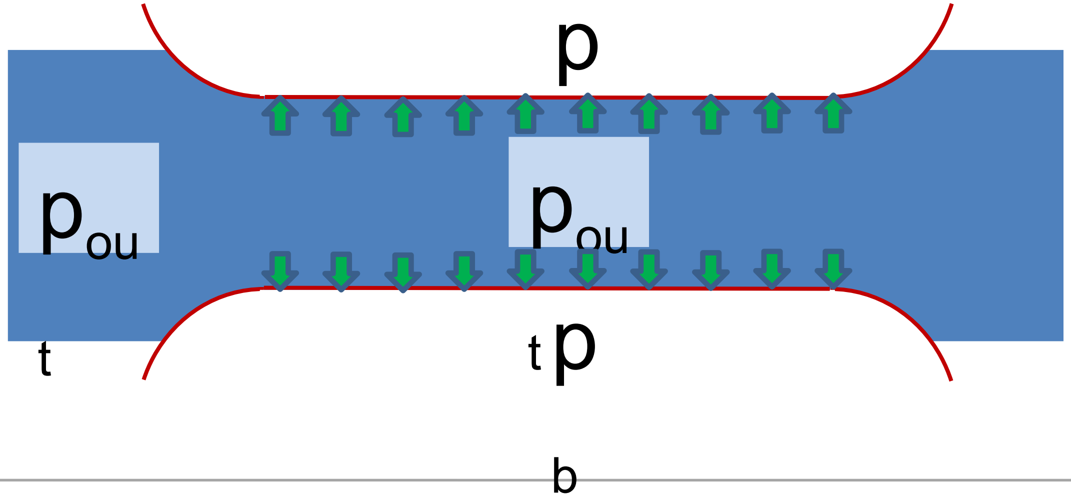


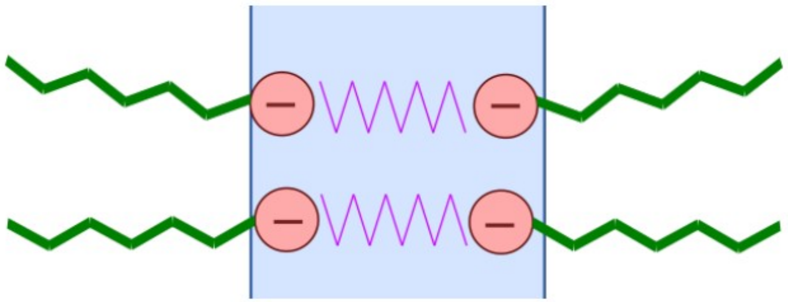
Bubble: $$p_b = p_{out} + 2\gamma H = p_{out} + \frac{2\gamma}{R}$$

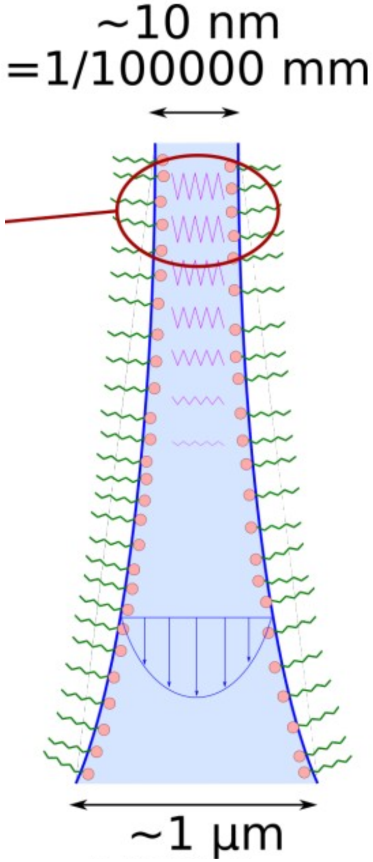
Film: $$H = 0 \;\rightarrow p_b = p_{out} + \Pi$$

Disjoining pressure from surfactants

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

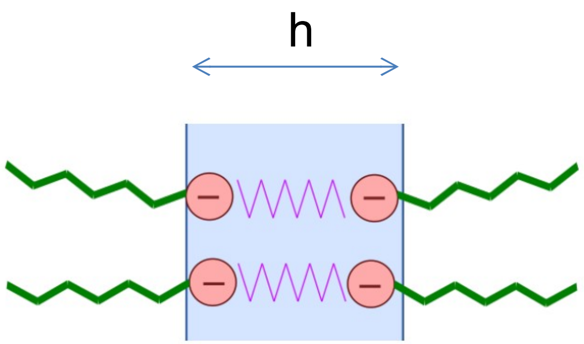


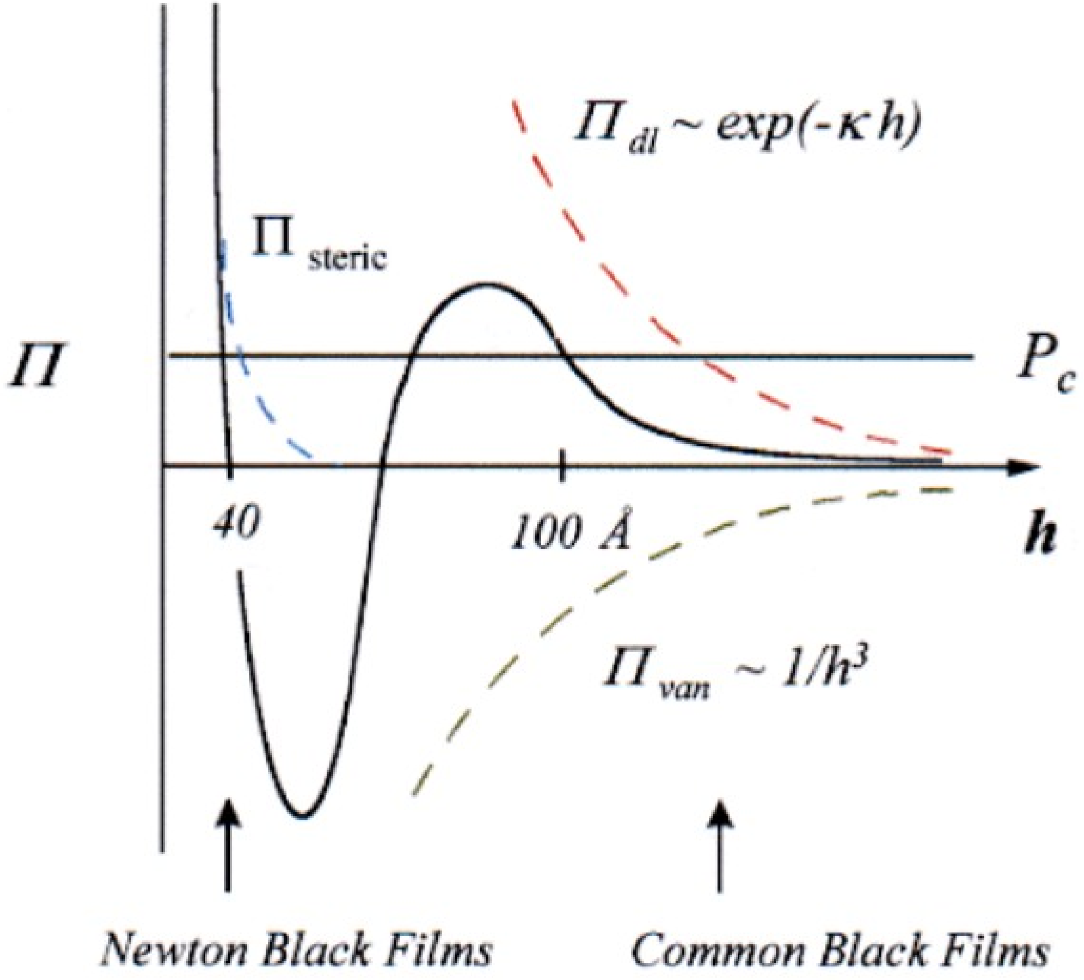




Contributions to disjoining pressure

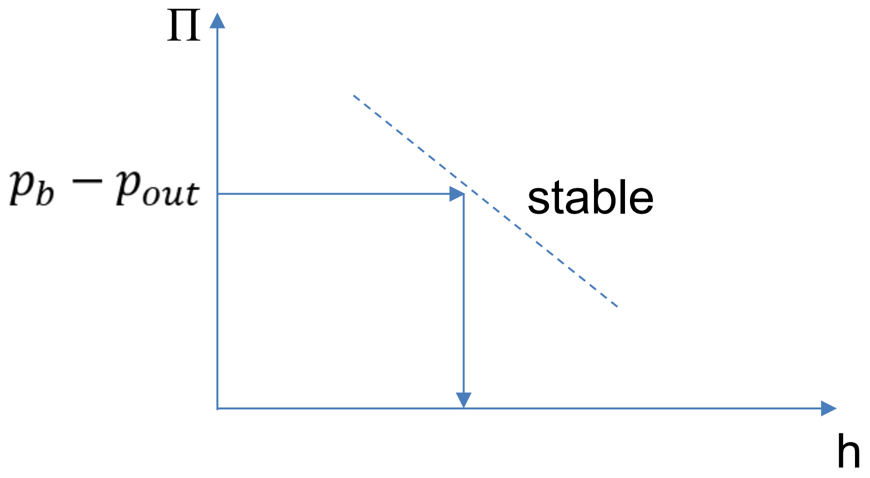
- Disjoining force is a function of film thicknes
- 3 contributions:
  - Electrostatic repulsion ~exp(-h)
  - Dipol (Van-der-Waals) ~h^{-3}
  - Steric (collision)
- Undisturbed superposition

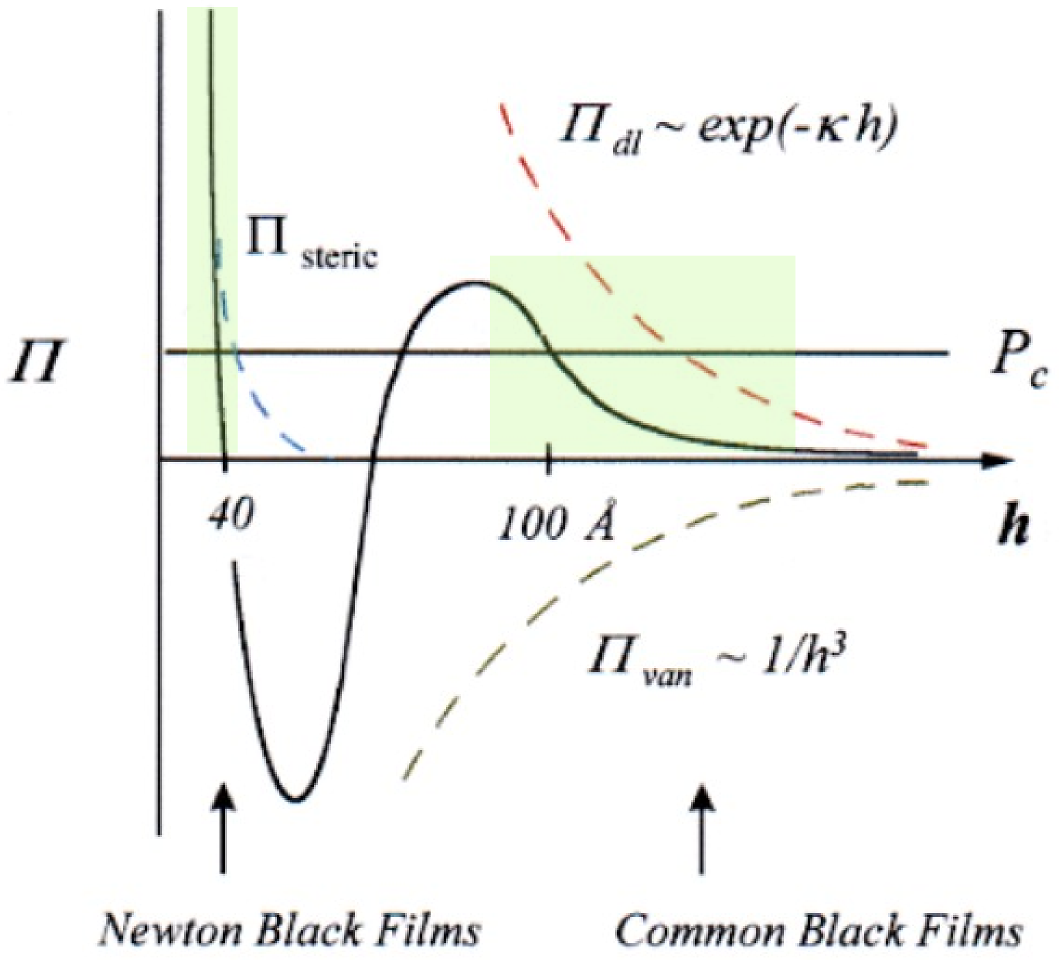




Contributions to disjoining pressure

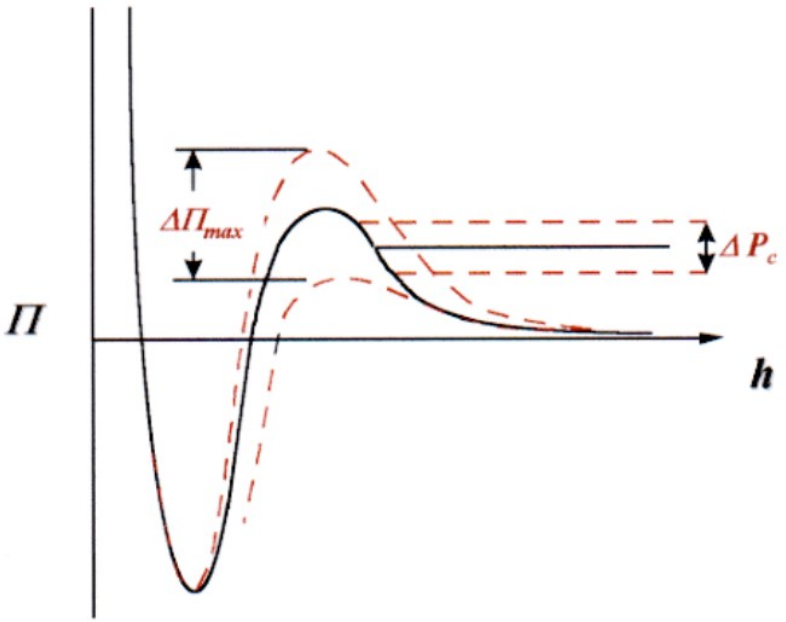
- 2 stable regions:
- Common Black Films (h ~ 50 nm)
- Newton Black Films (h ~ 4 nm)

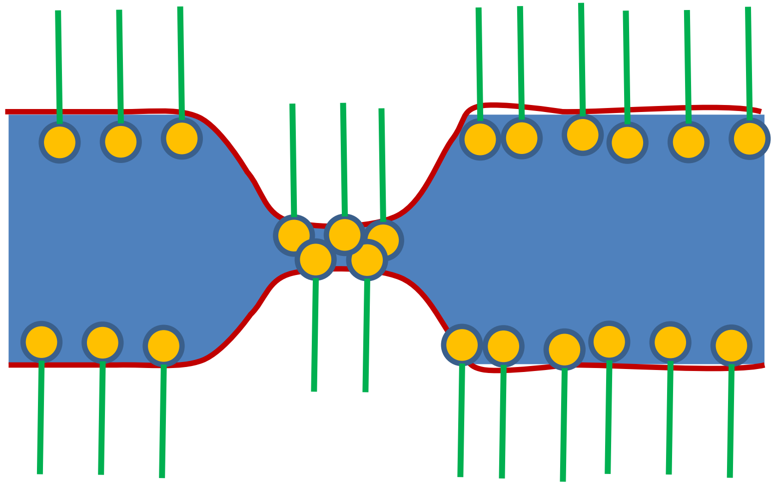




Film stability

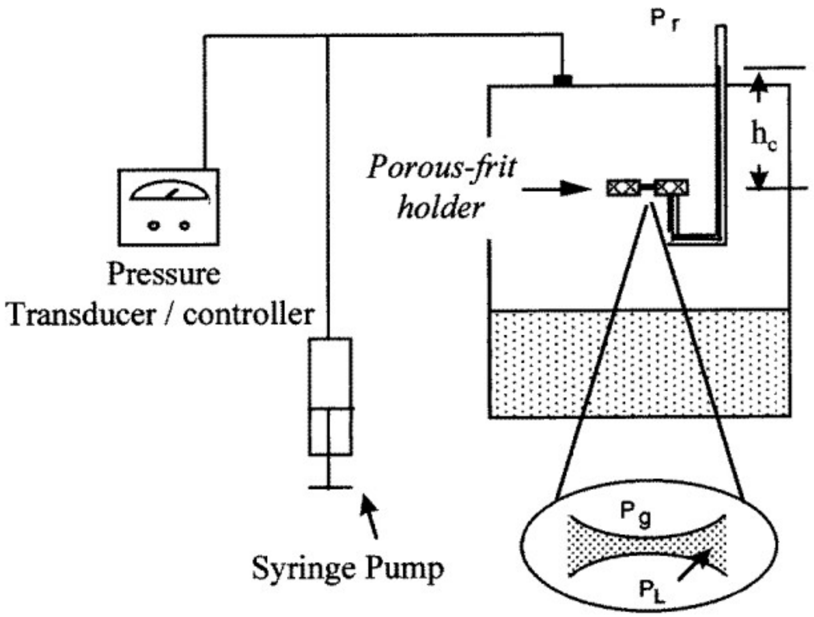
- When barrier is overcome, Newton Black Film is formed (or rupture)
- Formation of Newton Black Film is hardly reversible

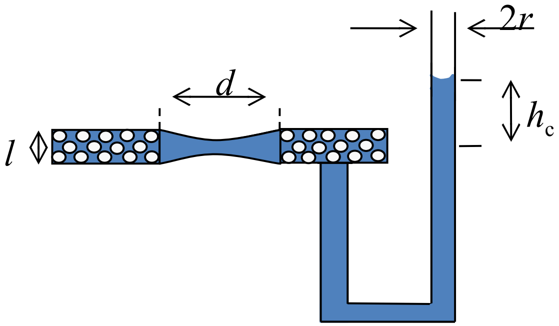


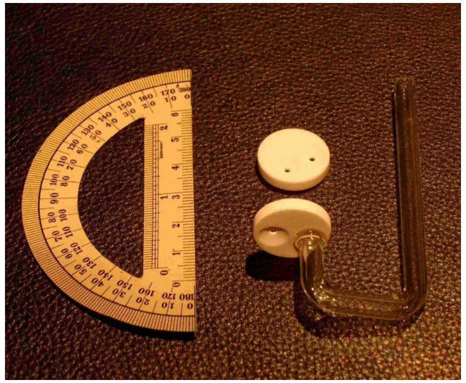


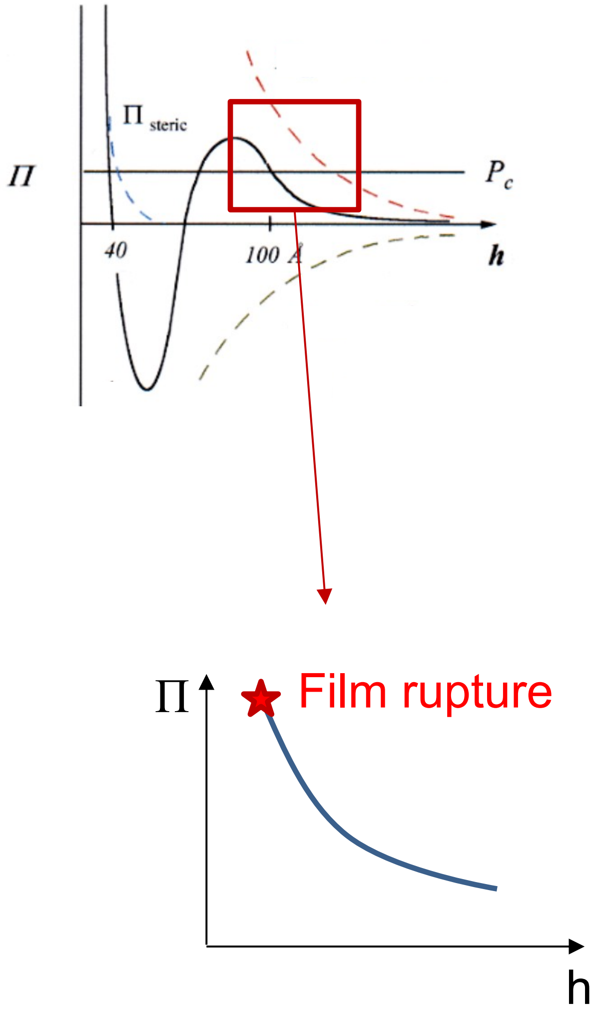
Disjoining pressure measurement

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



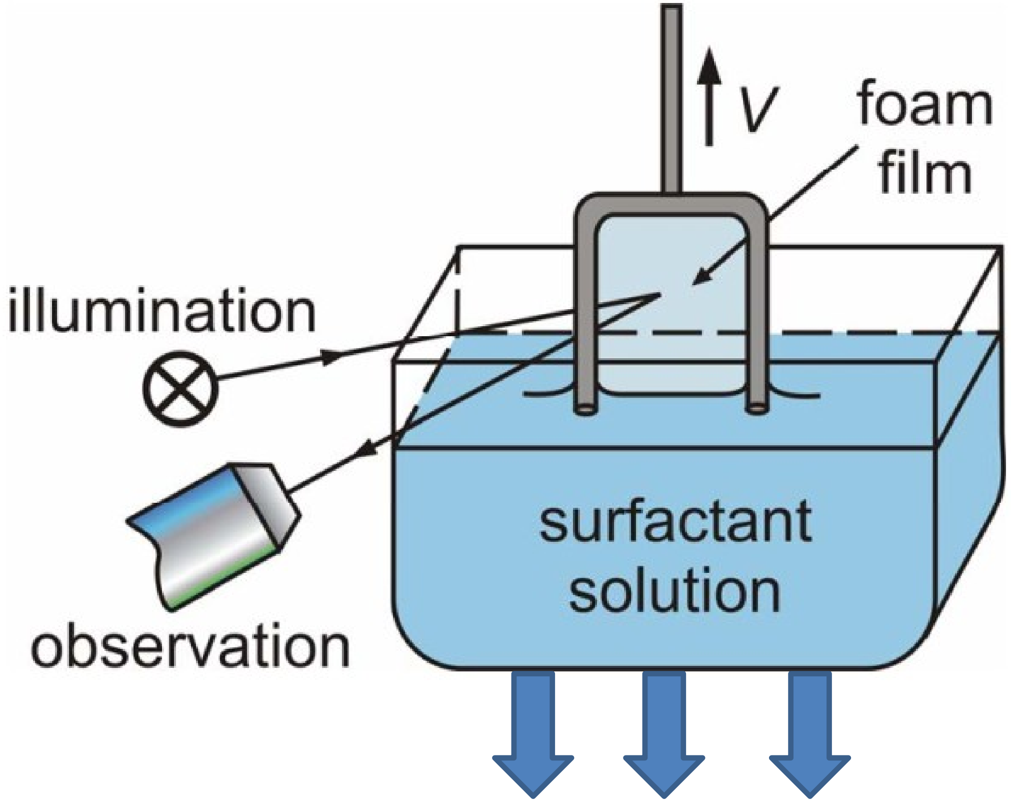






Film thickness measurement

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

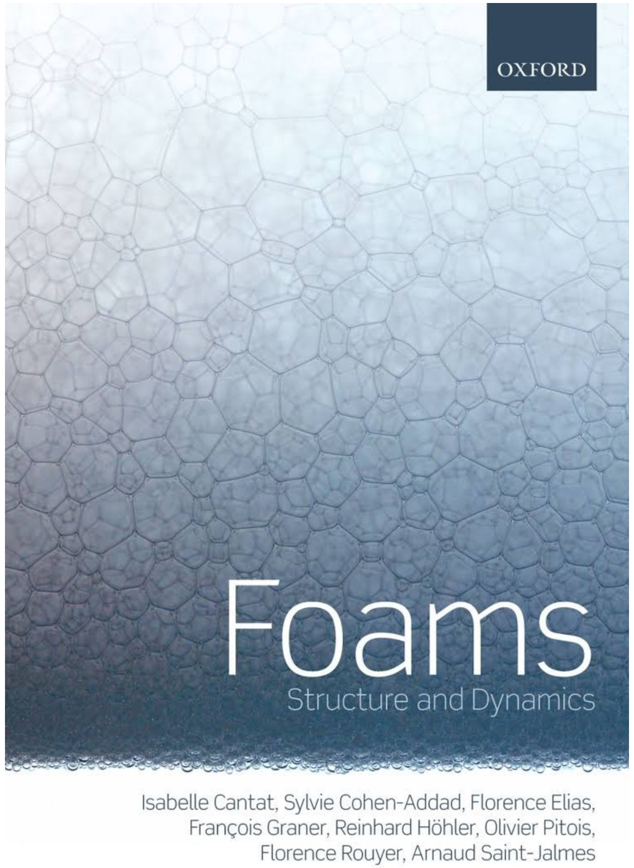


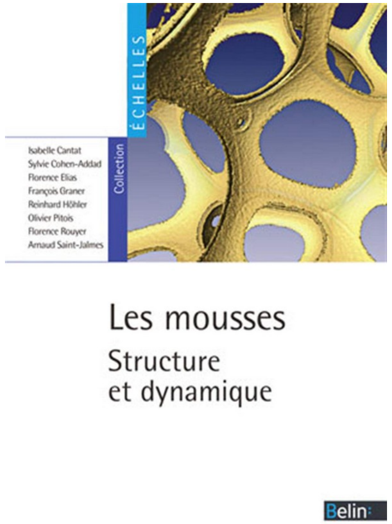
Structure

- Review lecture 6
- Dry foam topology
- Plateau's laws
- Neighbour statistics
- Wet foam
- Bubble crystals

Literature

- [Cantat et al. *Oxford University Press*, 2010]
- Very nice review, covering most physics-related topics
- Basis for most of the lecture (yet to come)
- Short on chemical aspects
- Short on experimental techniques





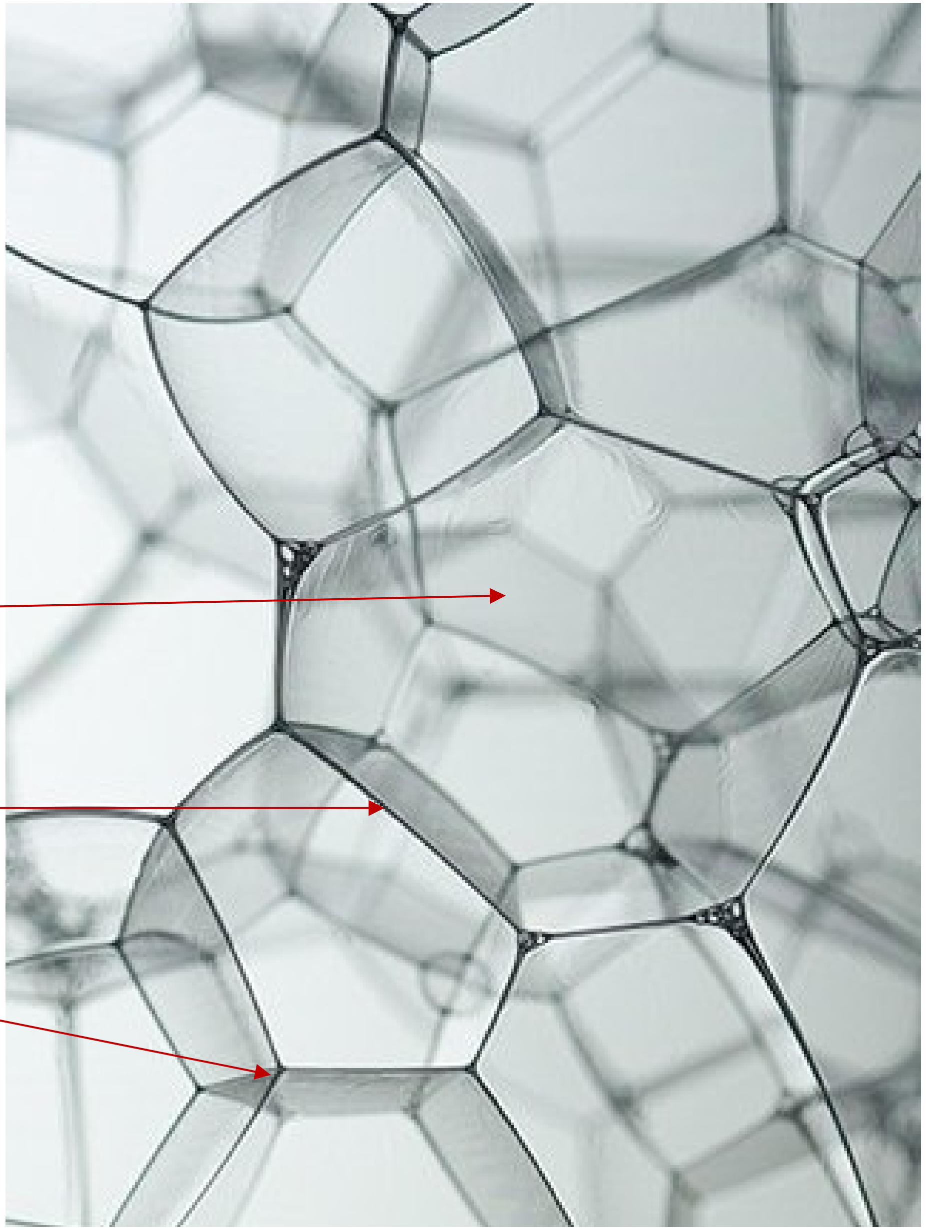
Structural elements

- Lamella/Film separates two bubbles
- Three Lamellas intersect in a **P**lateau border
- Four Plateau borders intersect in a vertex/node

Lamella

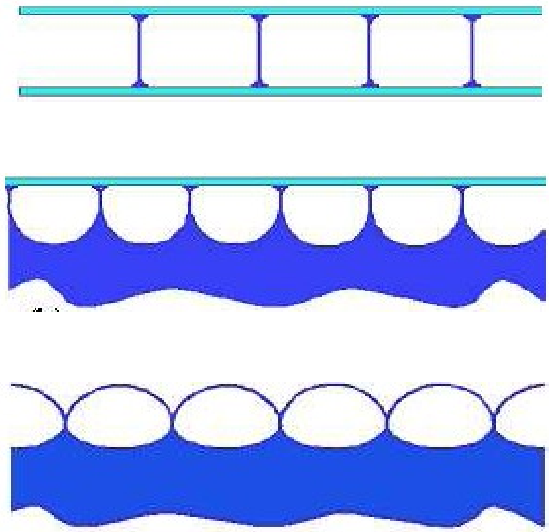
Plateau border

Vertex

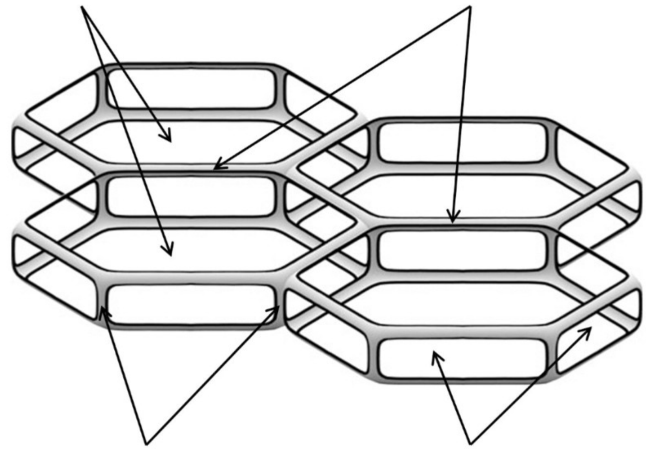


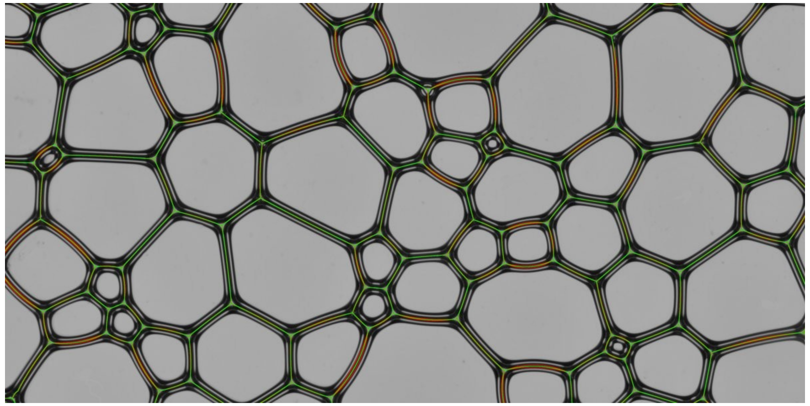
2D-foam

- Foam confined in 2D geometry
- Easy and exact optical measurement



S. Cox, E. Janiaud, Phil. Mag. Lett, 2008





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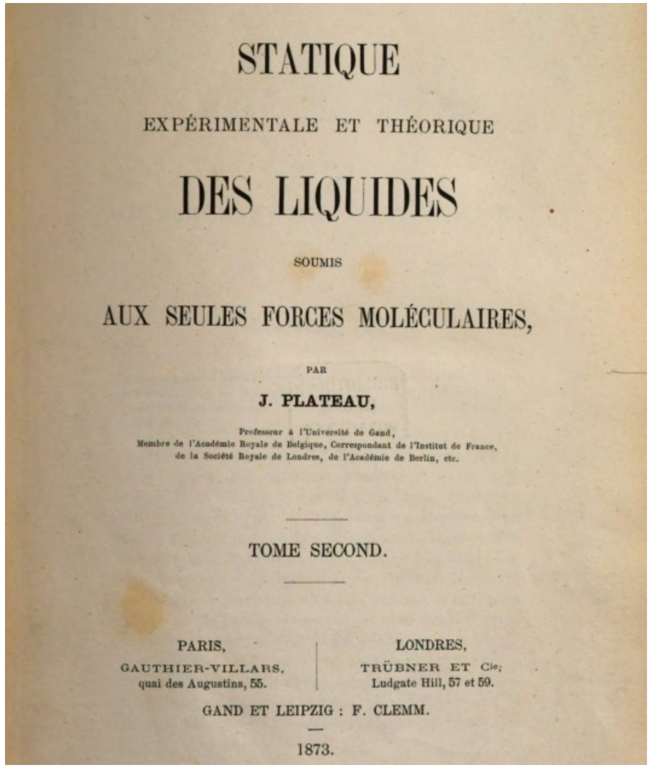
Joseph Antoine Ferdinand Plateau (1801-1883)

- Research regarding colour vision, “moving images” and soap films
- Lost eyesight in 1844, maybe after “observing the sun for 25 sec”
- Research regarding soap films published 1873, assisted by his son



STATIQUE

EXPÉRIMENTALE ET THÉORIQUE

DES LIQUIDES

SOUMIS

AUX SEULES FORCES MOLÉCULAIRES,

PAR

J. PLATEAU,

Professeur à l'Université de Gand,
Membre de l'Académie Royale de Belgique, Correspondant de l'Institut de France,
de la Société Royale de Londres, de l'Académie de Berlin, etc.

TOME SECOND.

PARIS,
GAUTHIER-VILLARS,
quai des Augustins, 55.

LONDRES,
TRÜBNER ET Cie;
Ludgate Hill, 57 et 59.

GAND ET LEIPZIG : F. CLEMM.

1873.

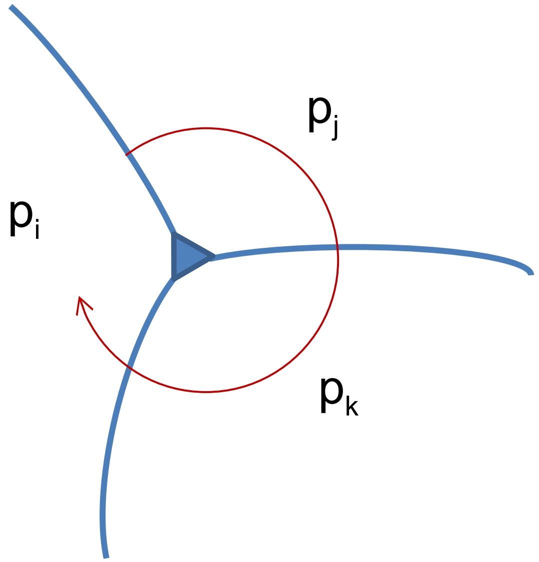
Plateau's Laws

- Assumptions: negligible liquid fraction, mechanical equilibrium, constant surface tension, incompressible foam
- 1st law: Constant mean curvature of each film

$$p_i - p_j = 2\gamma H_{ij} = const$$

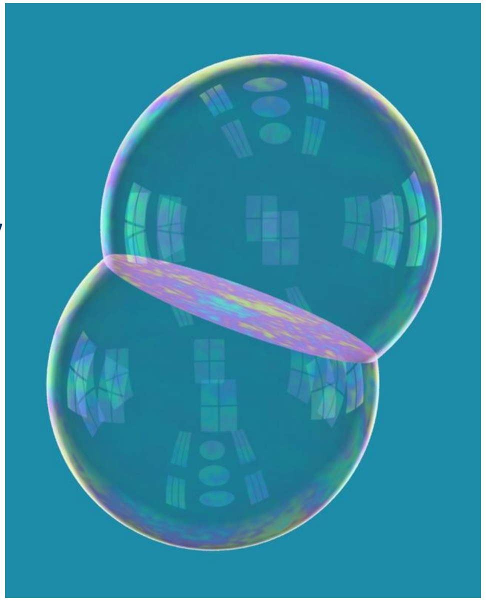
$$(p_i - p_j) + (p_j - p_k) + (p_k - p_i) = 0$$

$$H_{ij} + H_{jk} + H_{ki} = 0$$

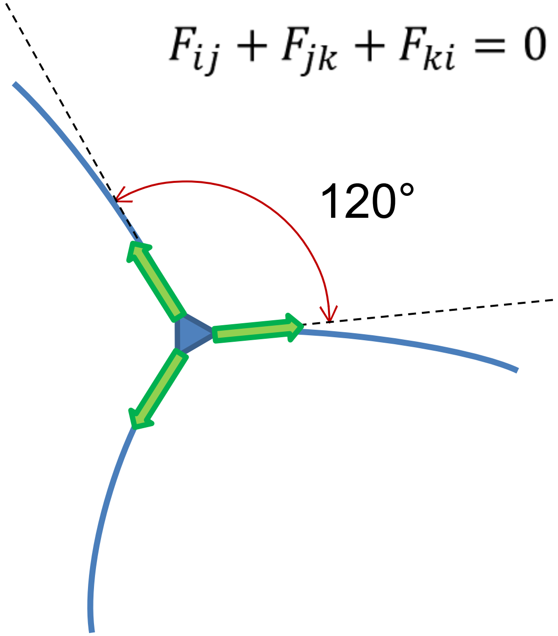


Plateau‘s Laws

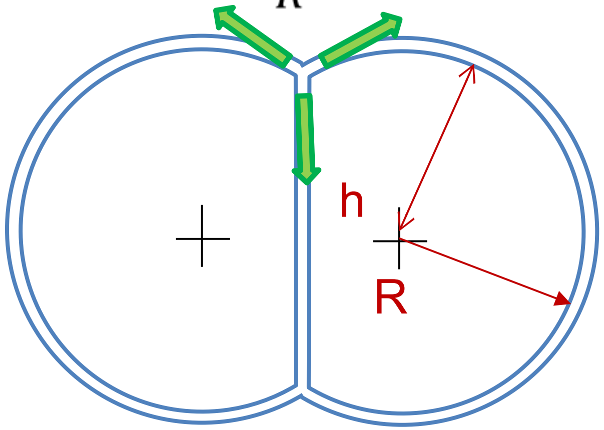
- Assumptions: negligible liquid fraction, mechanical equilibrium, constant surface tension, incompressible foam
- 2nd law: Three films meet in a Plateau border under 120° → force balance



$$F_{ij} + F_{jk} + F_{ki} = 0$$

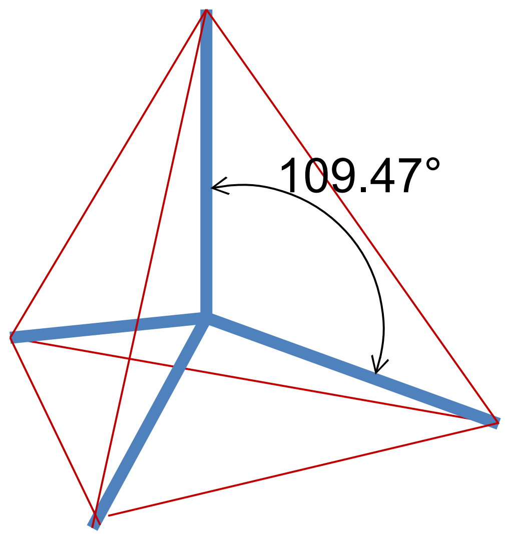


$$\frac{h}{R} = \cos(60°)$$



Plateau‘s Laws

- Assumptions: negligible liquid fraction, mechanical equilibrium, constant surface tension, incompressible foam
- 3rd law: Four Plateau borders meet in a vertex with tetrahedral symmetry



Structural elements

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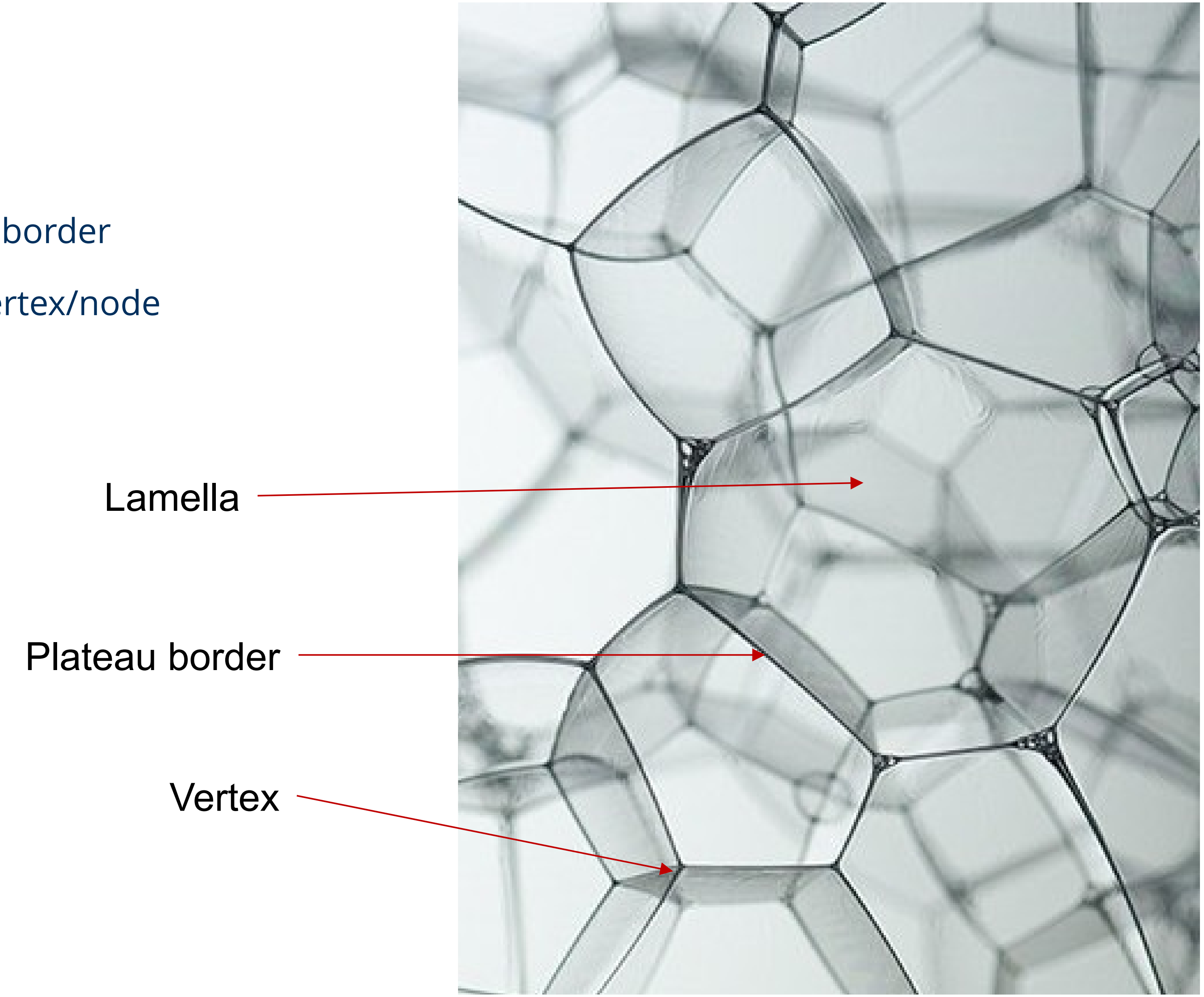
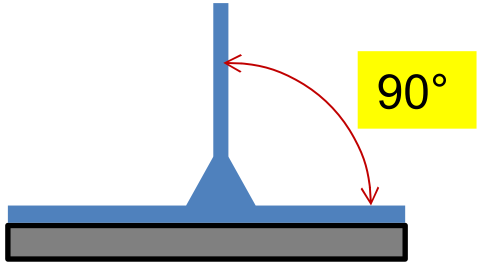
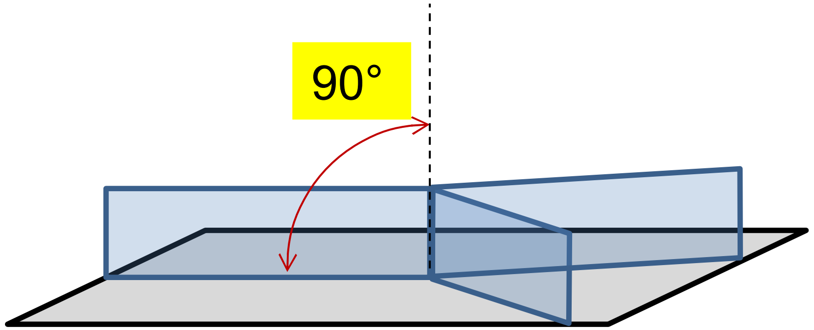
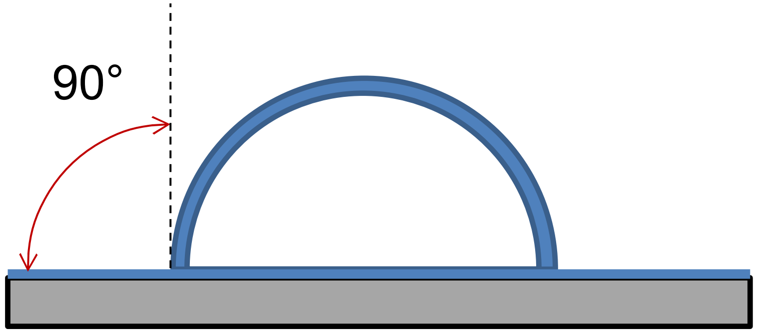


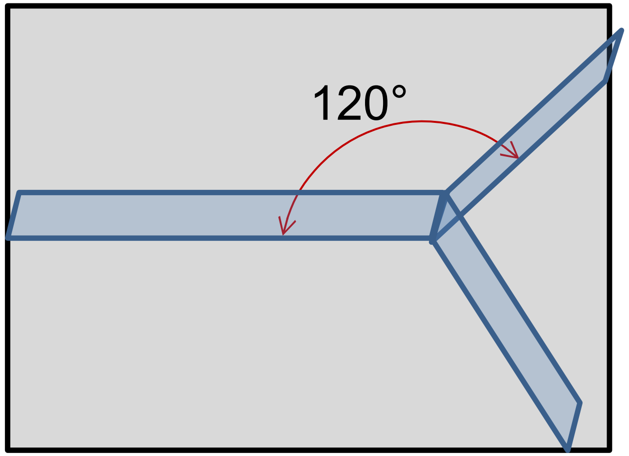
Plateau‘s Laws in 2D

- Different conditions close to the wall:
- Plateau borders and Lamellas are perpendicular to the wall



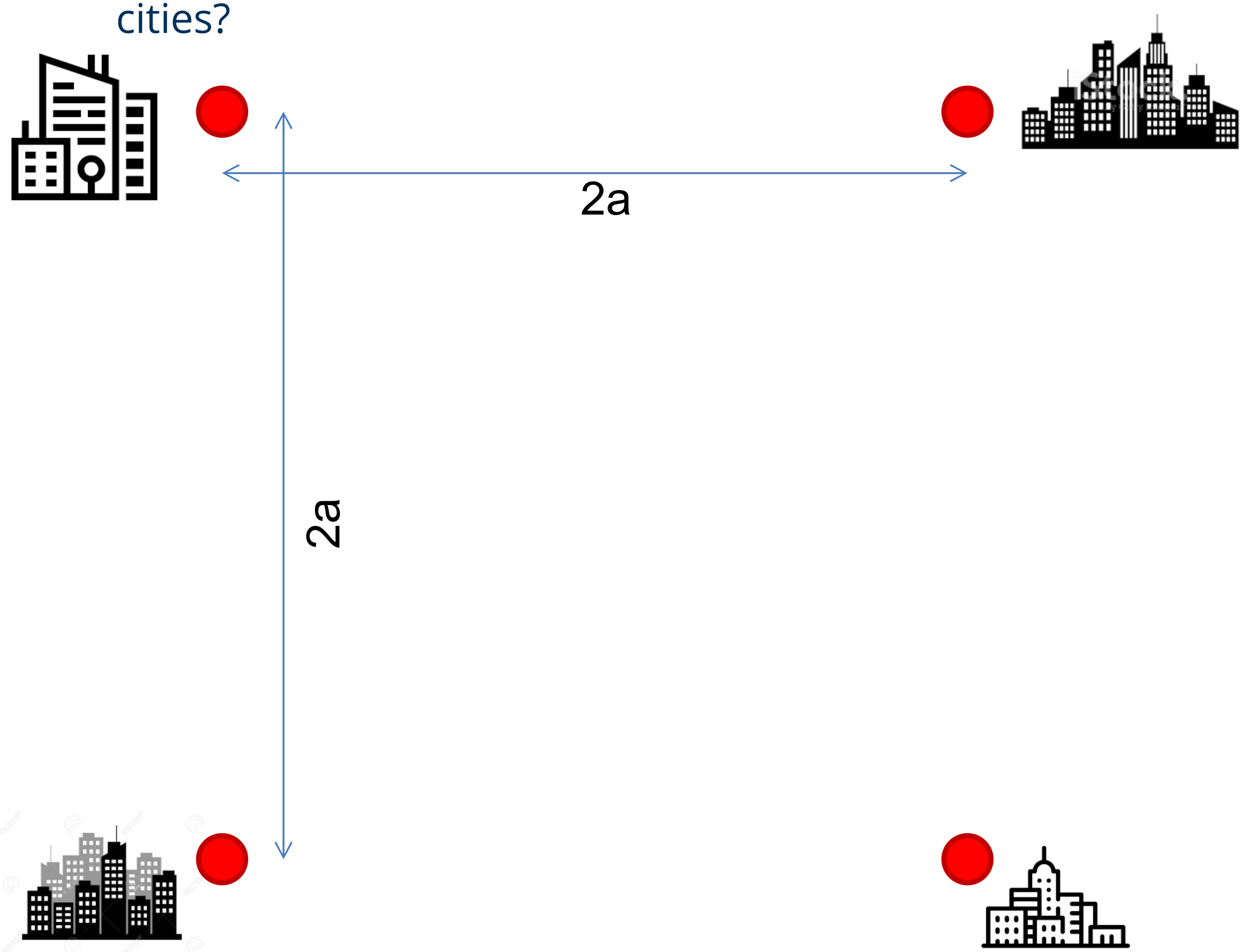




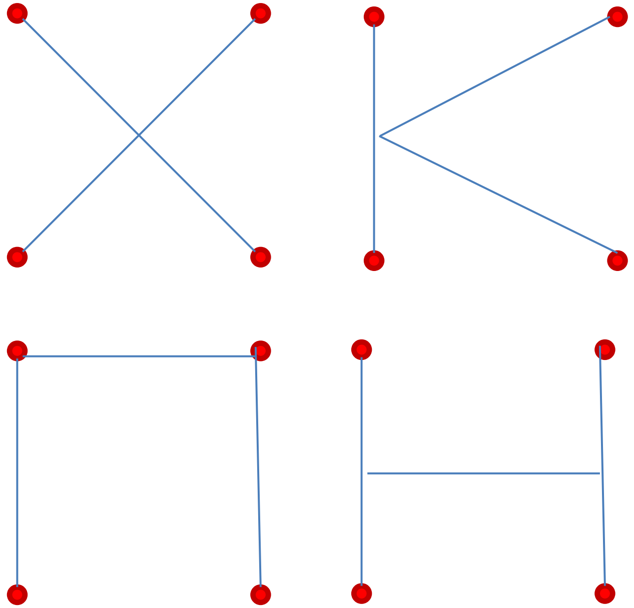


Exercise: Optimization problem

- What is the minimum length of a street network to connect these 4 cities?

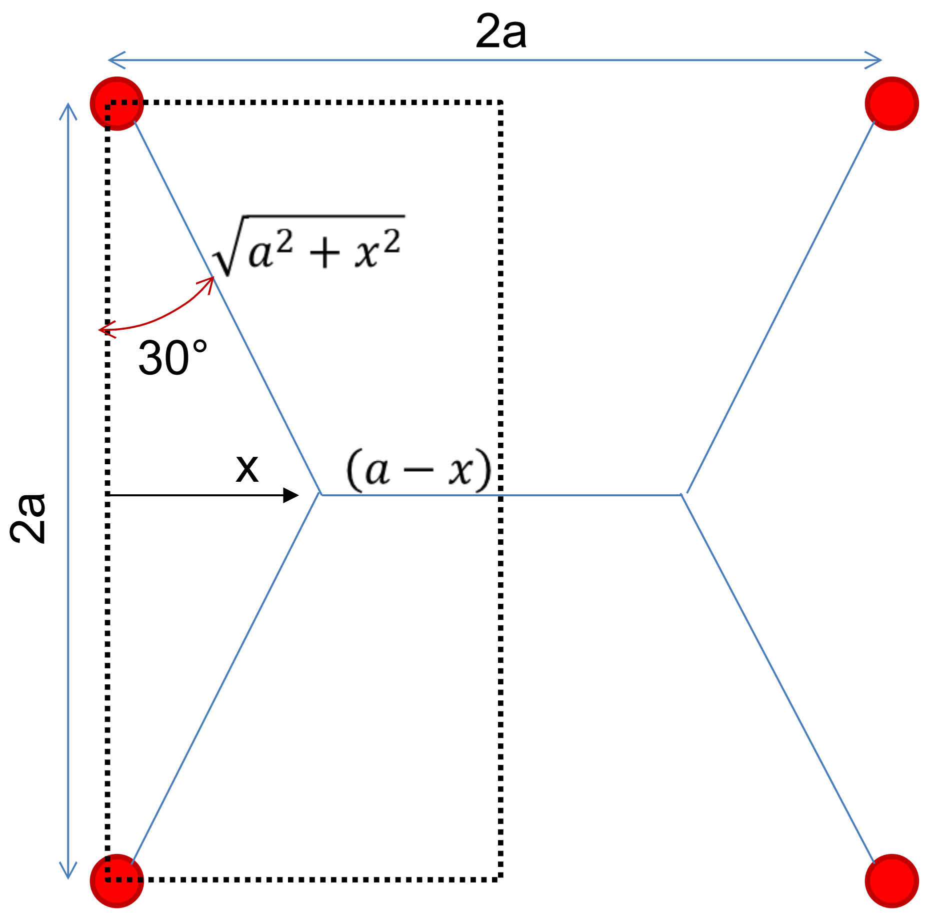


Examples:



Exercise: Optimization problem

- Optimization of vertex position?



$$L = (a-x) + 2\sqrt{a^2+x^2}$$

$$\frac{d\,L}{d\,x} = -1 + \frac{2x}{\sqrt{a^2+x^2}} = 0\,!$$

$$2x = \sqrt{a^2+x^2}$$

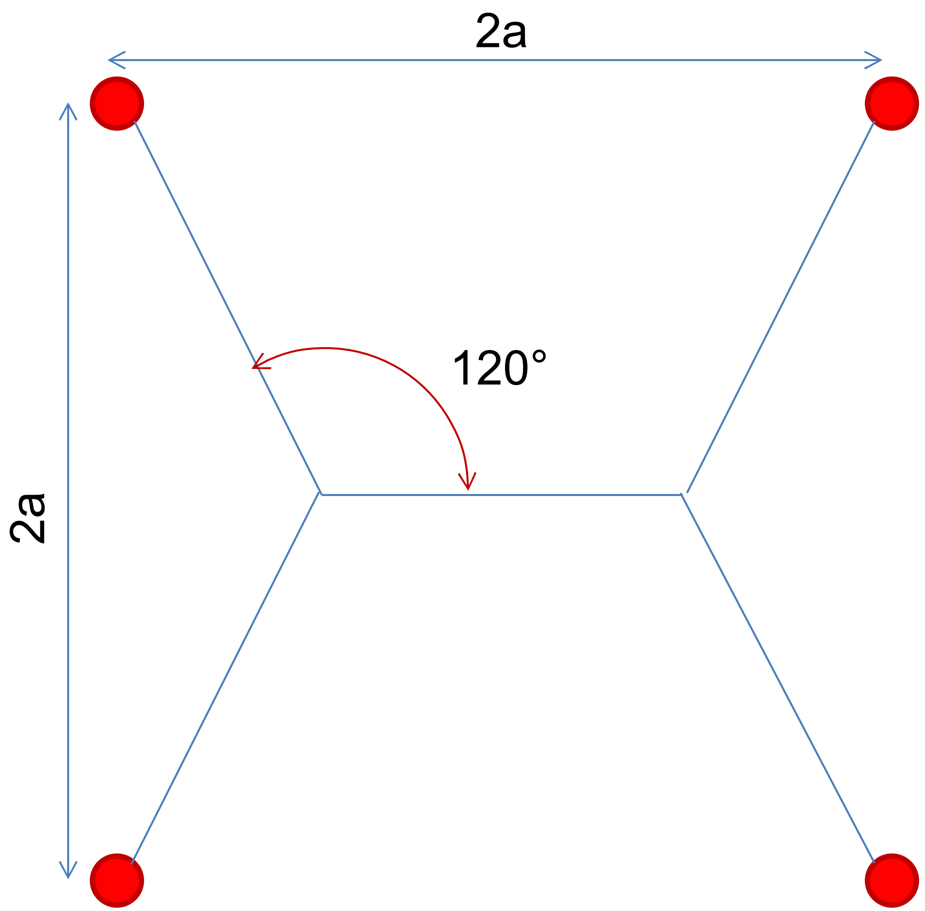
$$3x^2 = a^2$$

$$\frac{x}{a} = \frac{1}{\sqrt{3}} = \tan(30°)$$

$$L = 2a\left(1-\frac{1}{\sqrt{3}}\right) + 4\sqrt{a^2+\left(\frac{a}{\sqrt{3}}\right)^2}$$

Exercise: Optimization problem

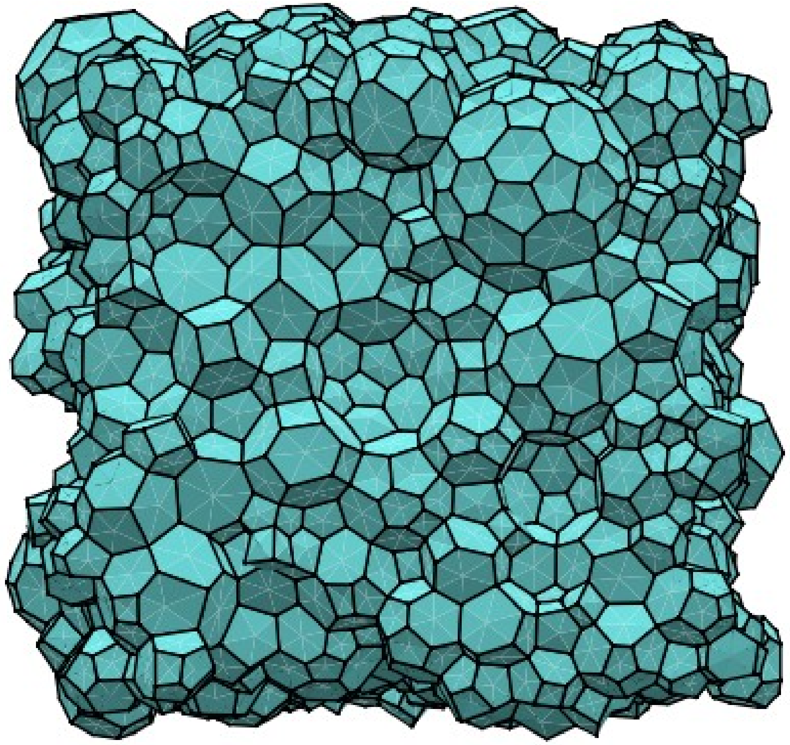
- Plateau’s Law



$$L = 2a\left(1 - \frac{1}{\sqrt{3}}\right) + 4\sqrt{a^2 + \left(\frac{a}{\sqrt{3}}\right)^2}$$

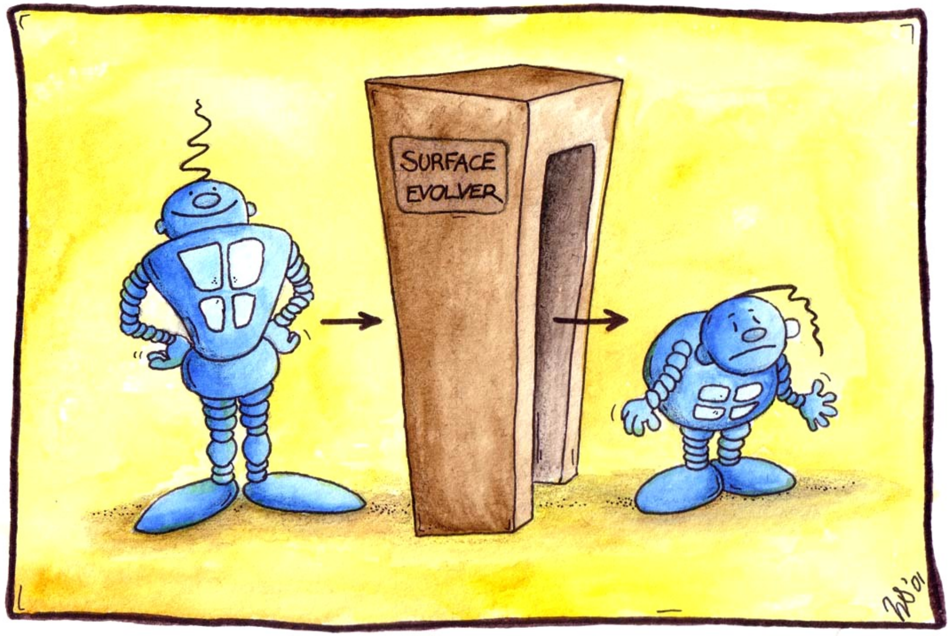
Surface Evolver

- Free, open source
- Developed and generously provided by Ken Brakke
- Available for Windows, Linux and Mac
- Download and introduction: http://facstaff.susqu.edu/brakke/
- [Brakke, Kenneth A. "The surface evolver." *Experimental mathematics* 1.2 (1992): 141-165.]   > 2000 citations!
- Experienced users: Andrew Kraynik, Stephen Neethling, Simon Cox



Surface Evolver

- Restriction on volume conservation of defined bodies
- Redistribution of vertices to minimize surface area
- Simulation of bubbles, dry and wet foam



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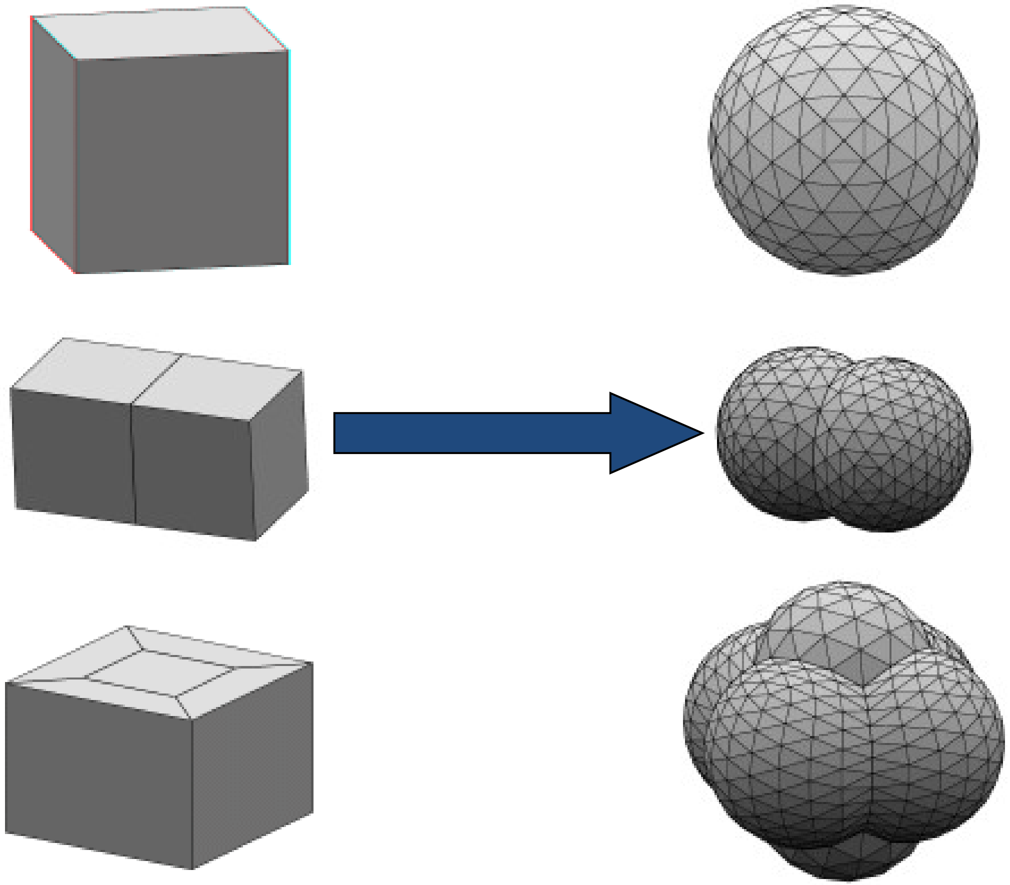
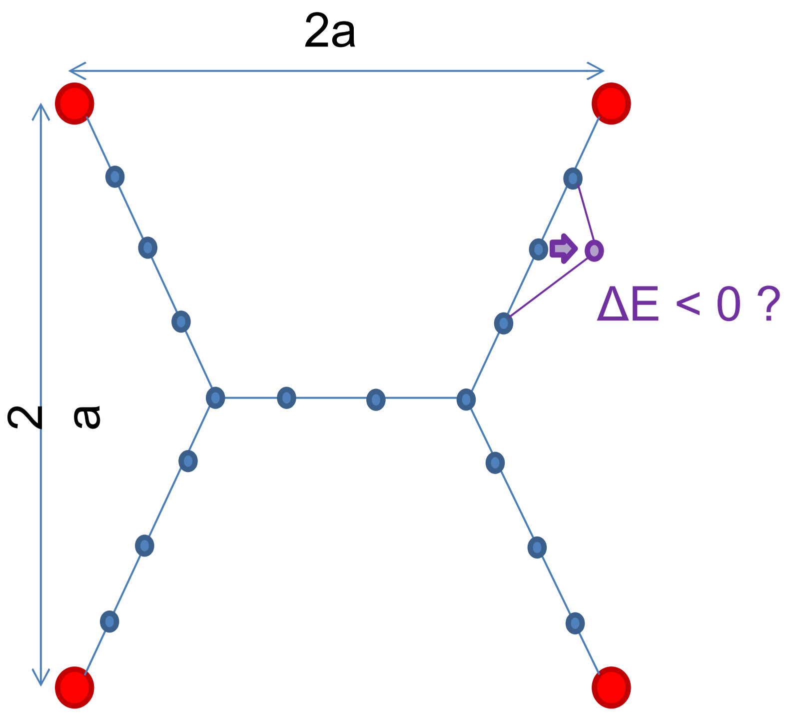
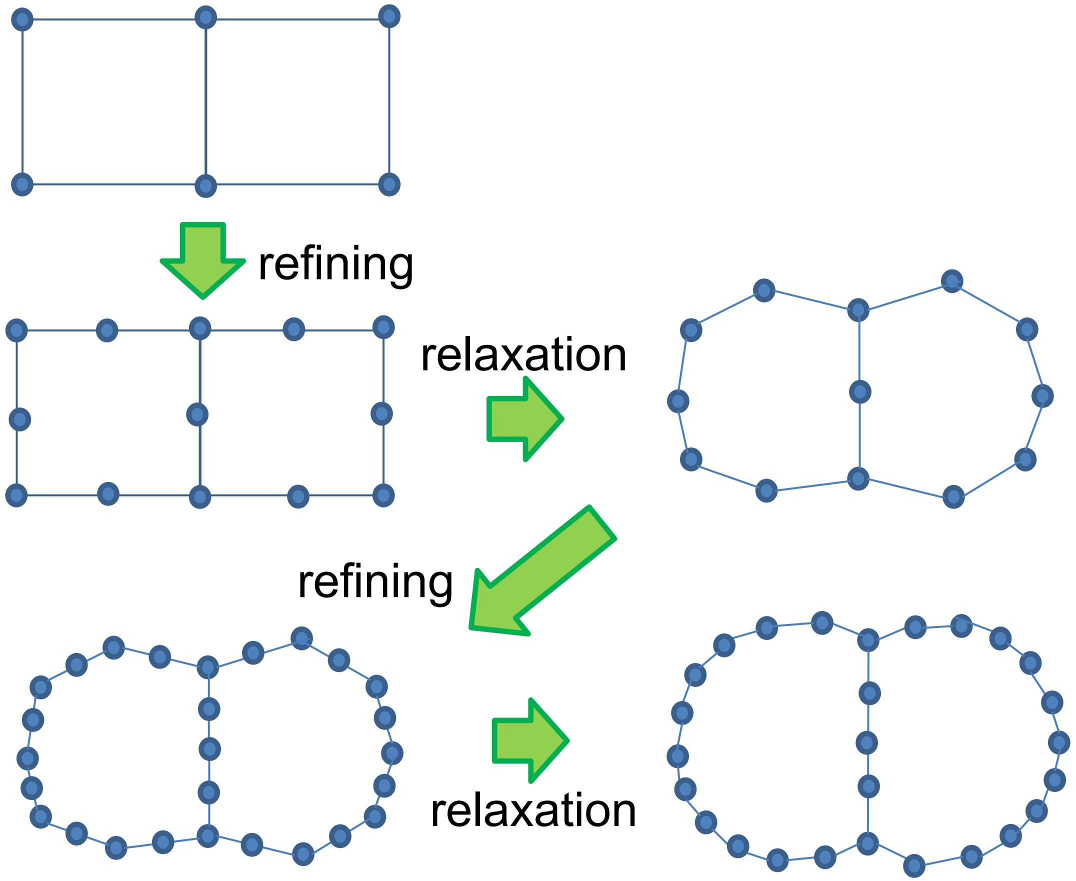


Surface optimization

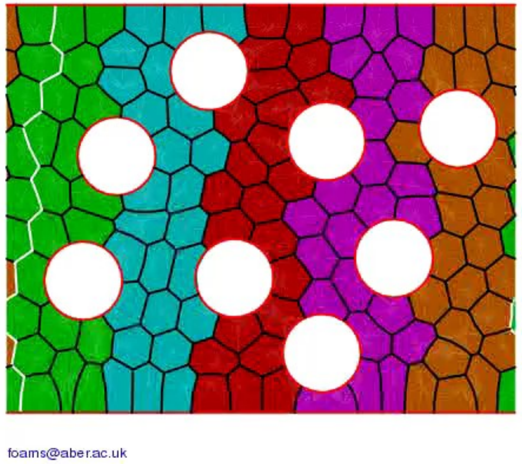
- Define Topology, generate Mesh on surface
- → move Mesh towards local energy minimum

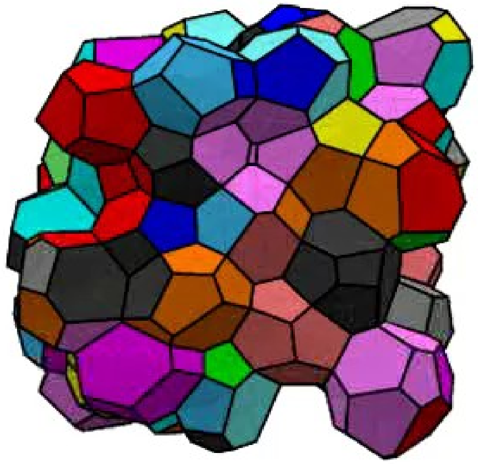




Surface Evolver

- Multiple works by Simon Cox et al.
- https://users.aber.ac.uk/sxc/foam_movies.html
- Take a look!





foams@aber.ac.uk

Structure

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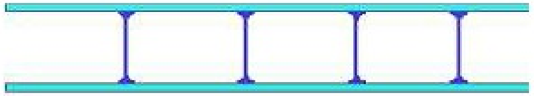
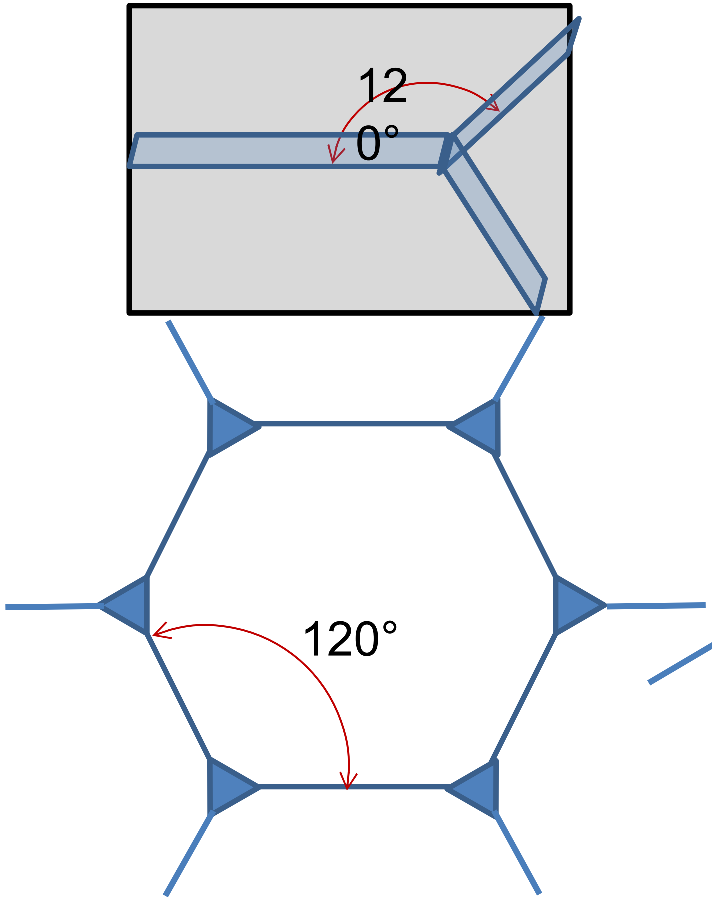
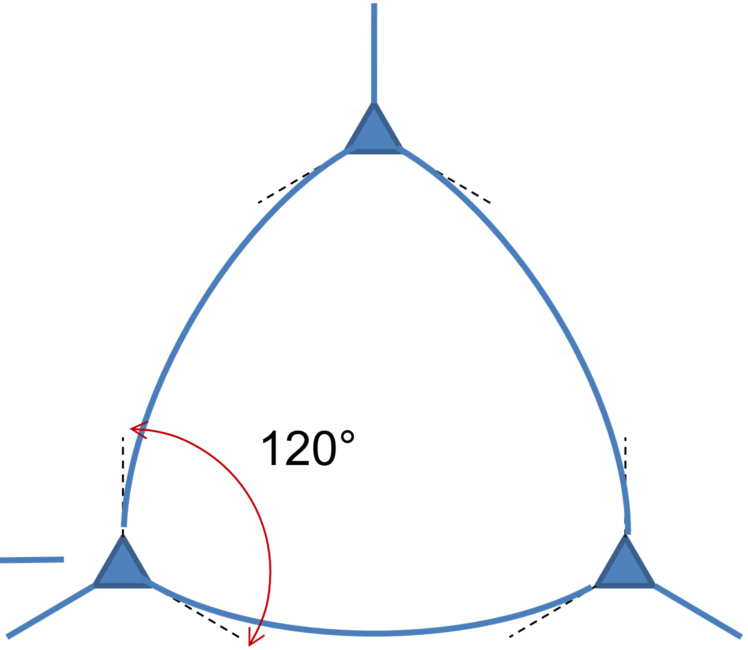
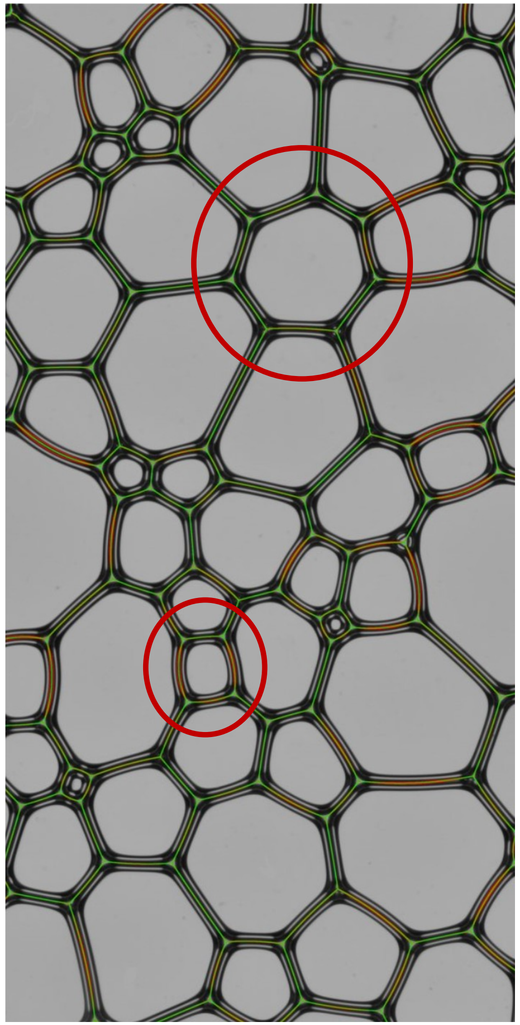
Shape of films and Plateau borders



- Plateau's Laws only valid at the meeting points
- Plateau borders can be bended to fulfil Plateau's Law

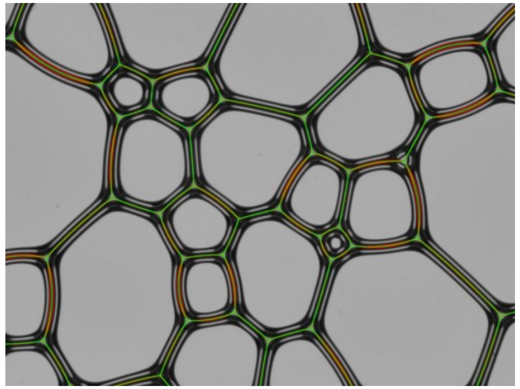






Shape of Plateau borders (2D)

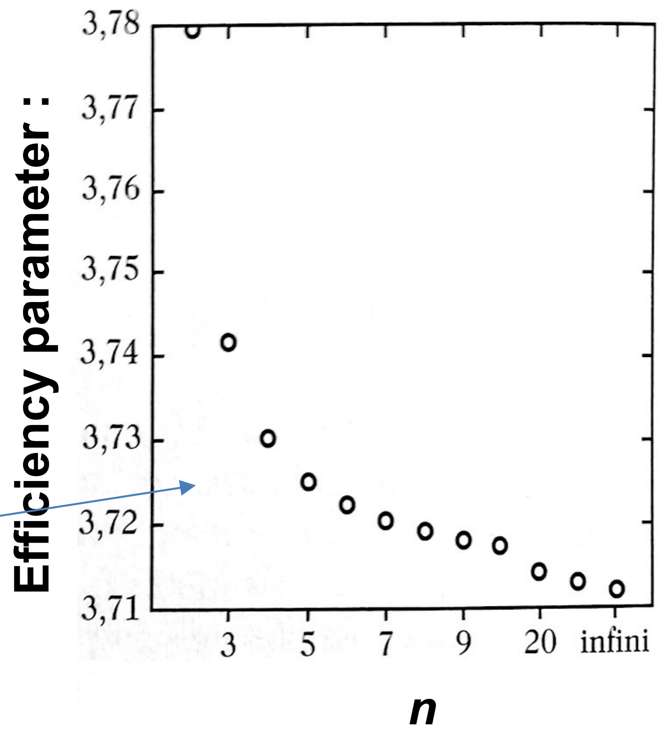
Efficiency parameter :



- Energy efficiency of bubble shape: Efficiency parameter
- Efficiency parameter: Ratio of Line length and equivalent radius

$$e(n) = \frac{\sum L}{A^{1/2}}$$

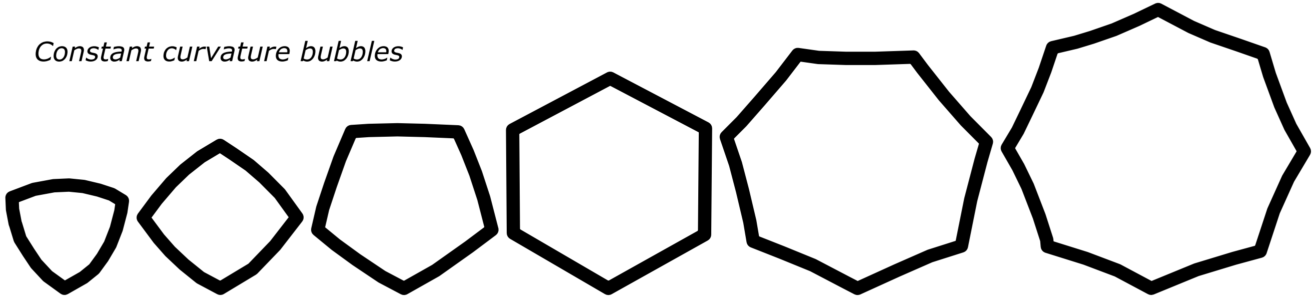
- For circle: $e(n) = \frac{2\,\pi\,r}{\sqrt{\pi r^2}} = 2\sqrt{\pi} = 3.545$
- For triangle: e = 4.56, for octagon: 3.64



[Graner et al., Phys. Rev. E, 2000]

curved outwards | straight edges | curved inwards

Constant curvature bubbles



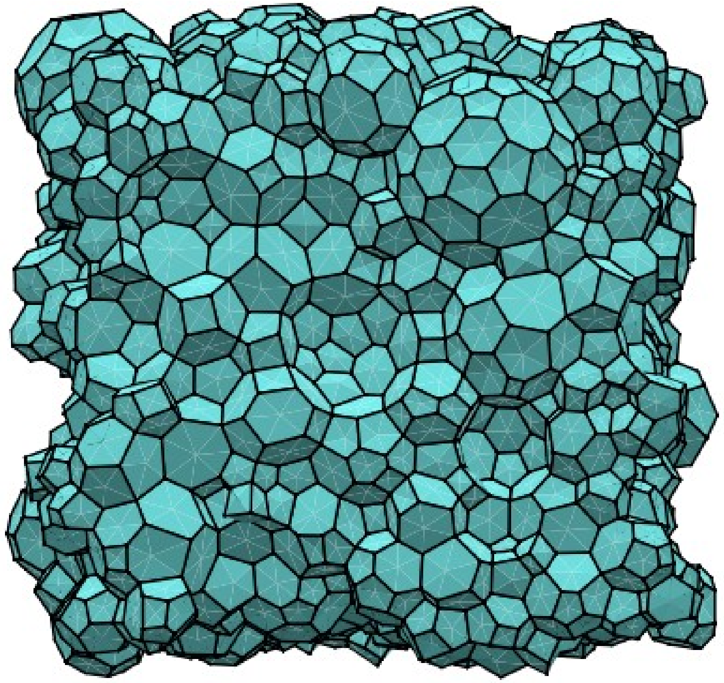
n

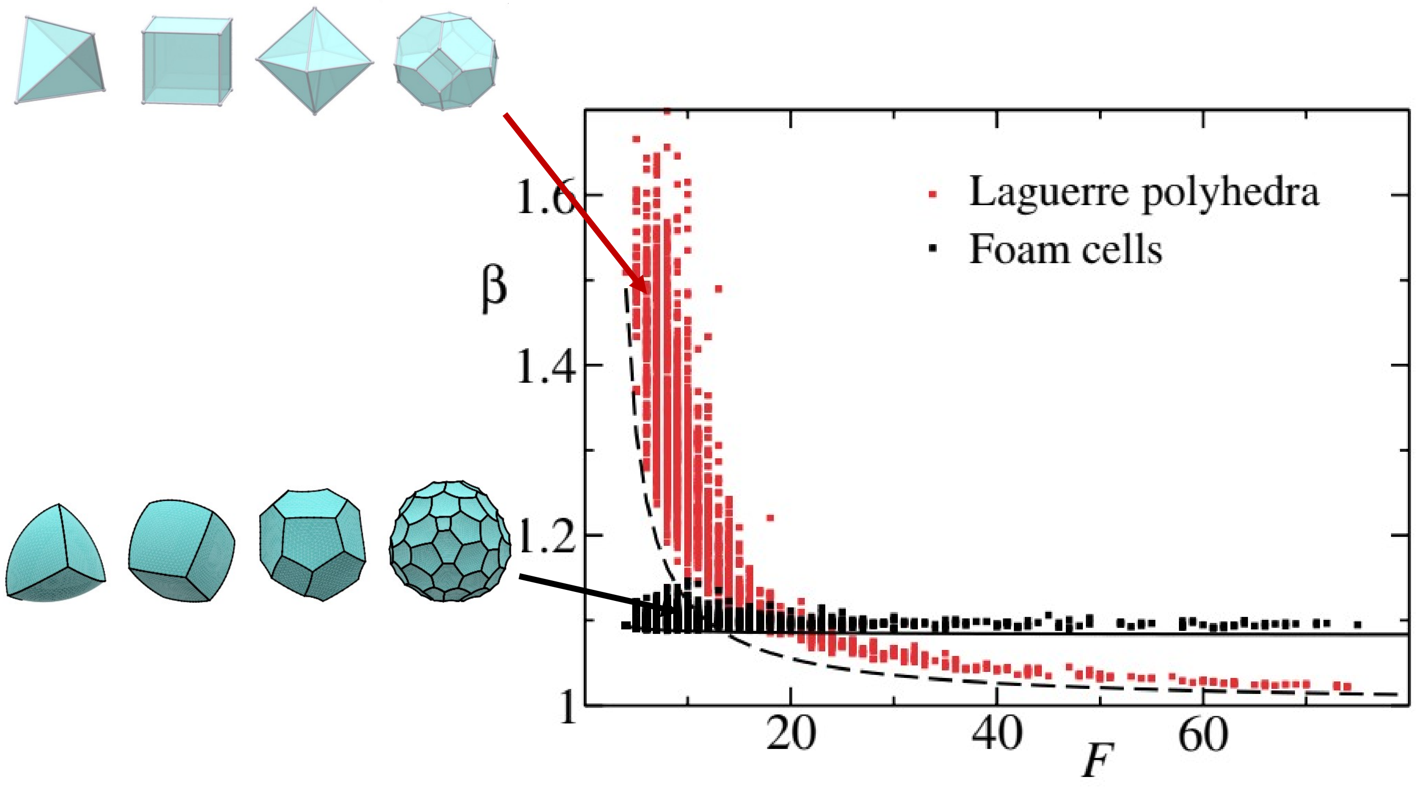
Shape of films (3D)

- Energy efficiency of bubble shape:
- Efficiency parameter β : Ratio of Surface area and equivalent sphere area

$$\beta = \frac{S}{(36\pi V^2)^{1/3}}$$

- For sphere: β = 1.0





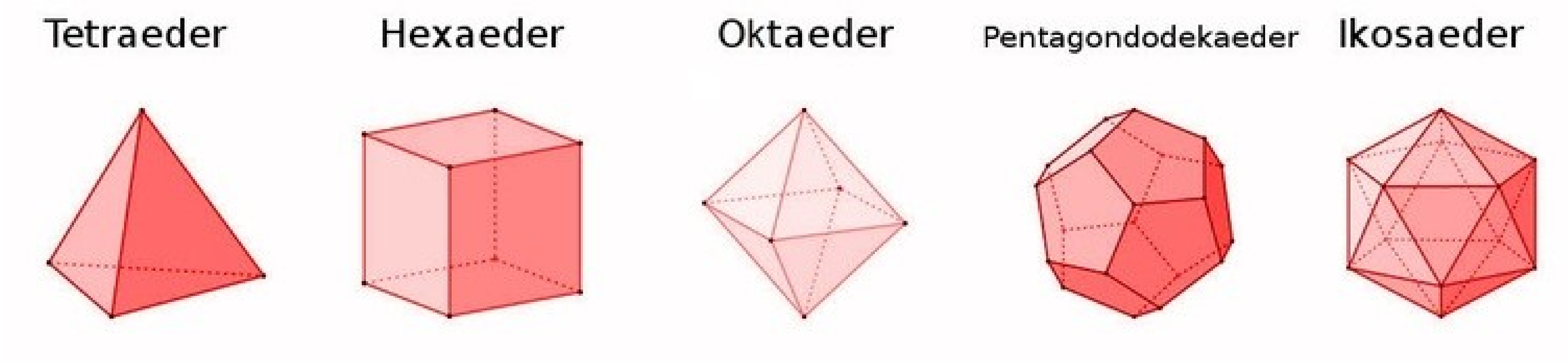
[Kraynik et al., PRL 93, 2004]

Number of neighbors

Euler‘s formula

- General conclusion from topological relations

$$-N_{body} + N_{vertices} - N_{edges} + N_{faces} = 1$$



$$-1 + 4 - 6 + 4 = 1$$

$$-1 + 8 - 12 + 6 = 1$$

$$-1 + 6 - 12 + 8 = 1$$

Euler's formula

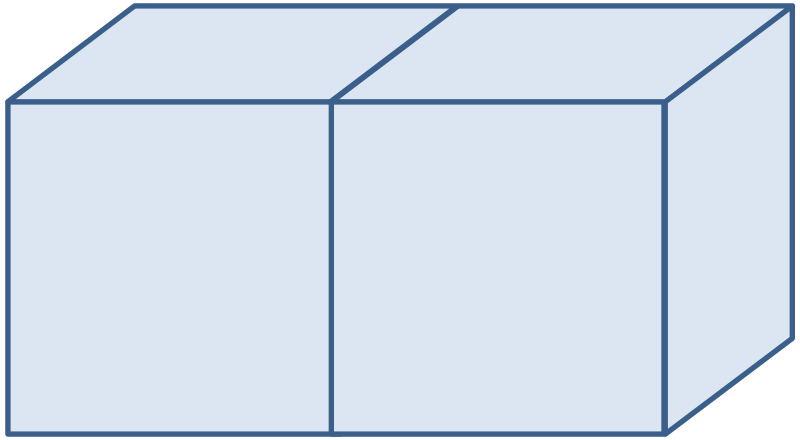
- Also for combination of bodies

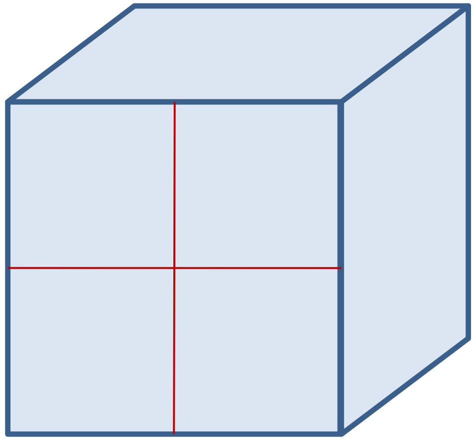
$$-N_{body} + N_{vertices} - N_{edges} + N_{faces} = 1$$

$$-2 \quad + \quad 12 \quad - \quad 20 \quad + 11 \quad = 1$$

$$-1 + 8 - 12 + 6 = 1$$

$$-1 + 8 + 1 - 12 - 4 + 6\ (+4 - 1) = 1$$

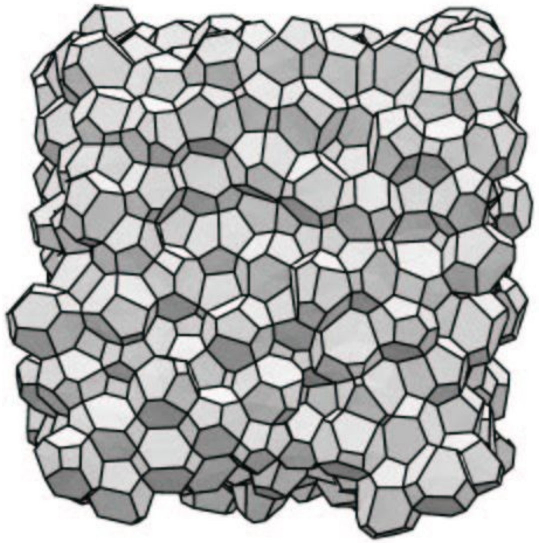




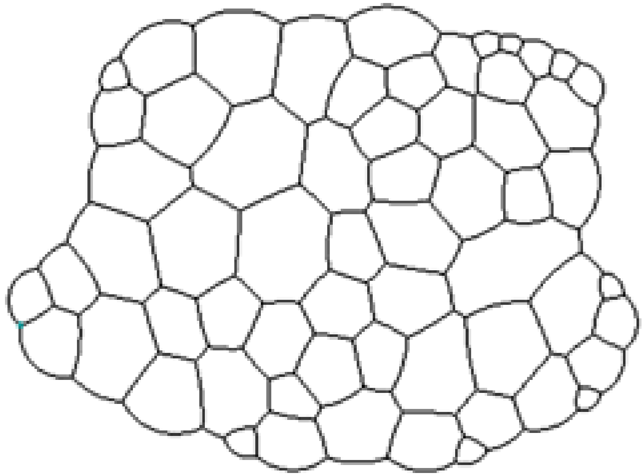
Euler‘s formula for foam

- Applies to any space filling tiling, i.e. foam
- Applies also in 2D (faces=bubbles)
- χ_{euler} is a small integer
- χ_{euler} might vary, due to boundary conditions

$$-N_{bubbles} + N_{vertices} - N_{edges} + N_{faces} = \chi_{euler}$$

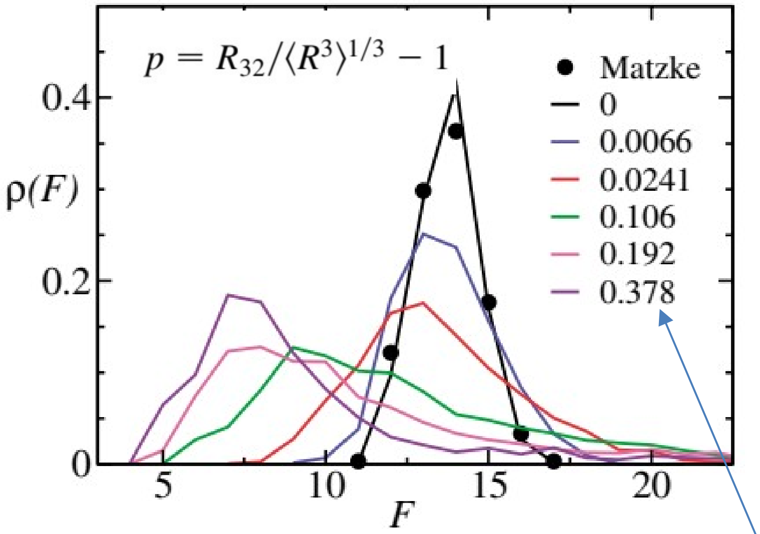


$$N_{bubbles} - N_{edges} + N_{vertices} = \chi_{euler}$$

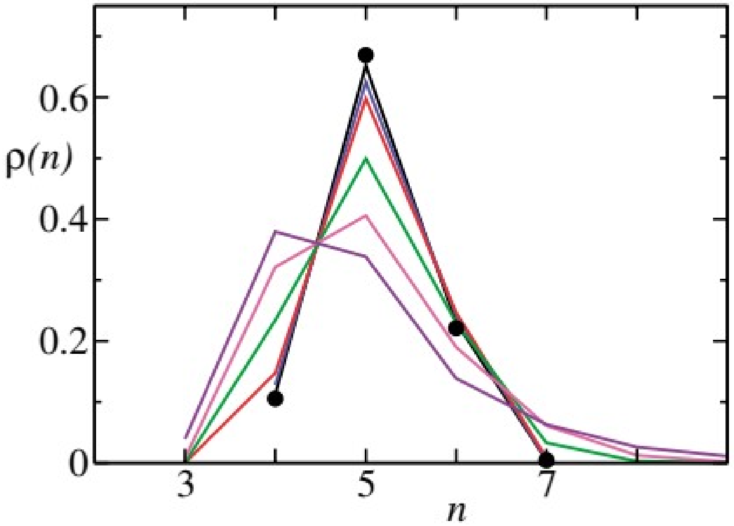


Numbers of Neighbors

- Measurement by Matzke (1945) with microscope (binocular stereoscope)
- Confirmation with Surface Evolver simulation
- Approx 14 neighbors, approx. 5 edges per face

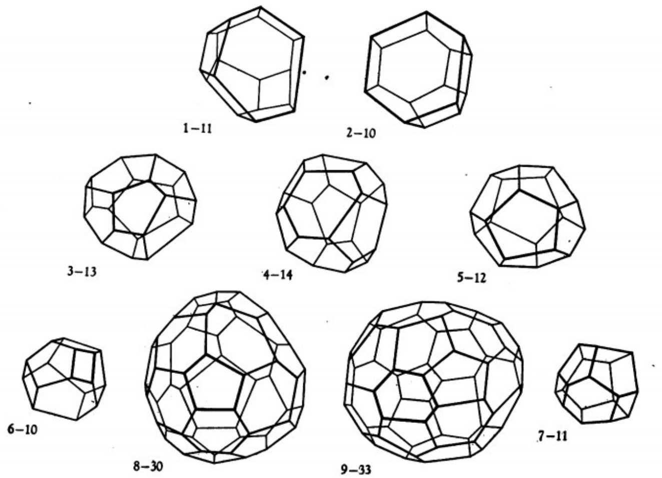


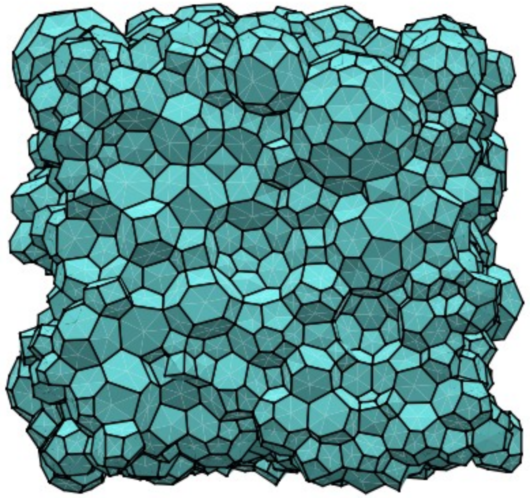
Number of neighbors, faces



Number of edges per face

polydispersity

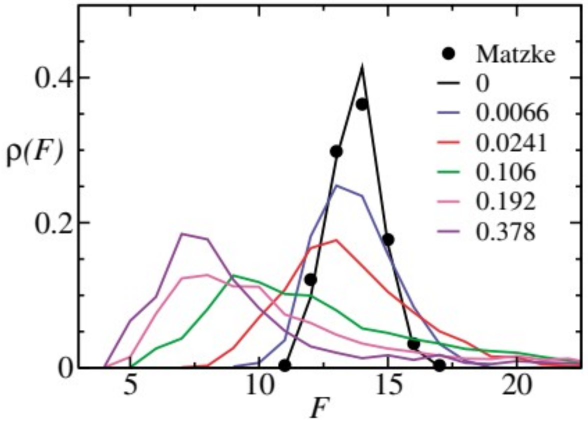




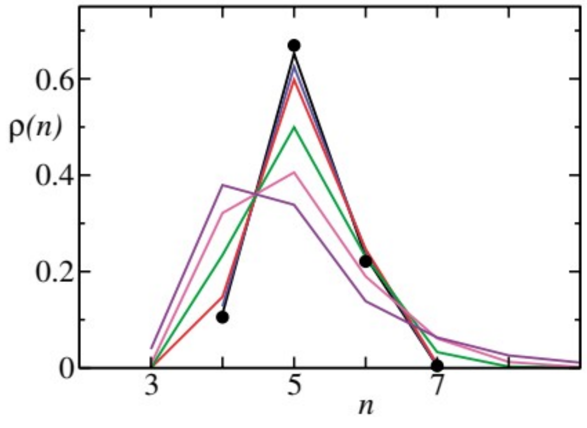
[Kraynik et al., PRL 93, 2004]

Eulers formula?

- Approx 14 neighbors, approx. 5 edges per face



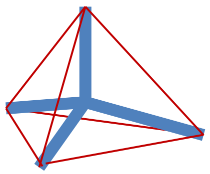
Number of neighbors, faces

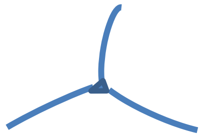


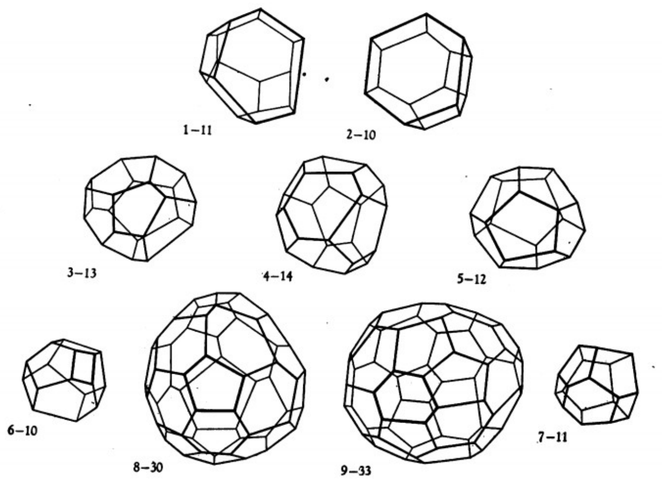
Number of edges per face

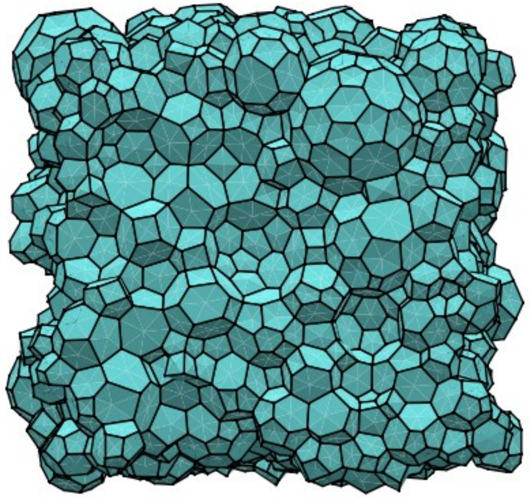
$$-N_{bubbles} + N_{vertices} - N_{edges} + N_{faces} = \chi_{euler}$$

$$-1 + \frac{5 \times 14}{4} - \frac{5 \times 14}{3} + \frac{14}{2} = 0.16 \approx 0$$





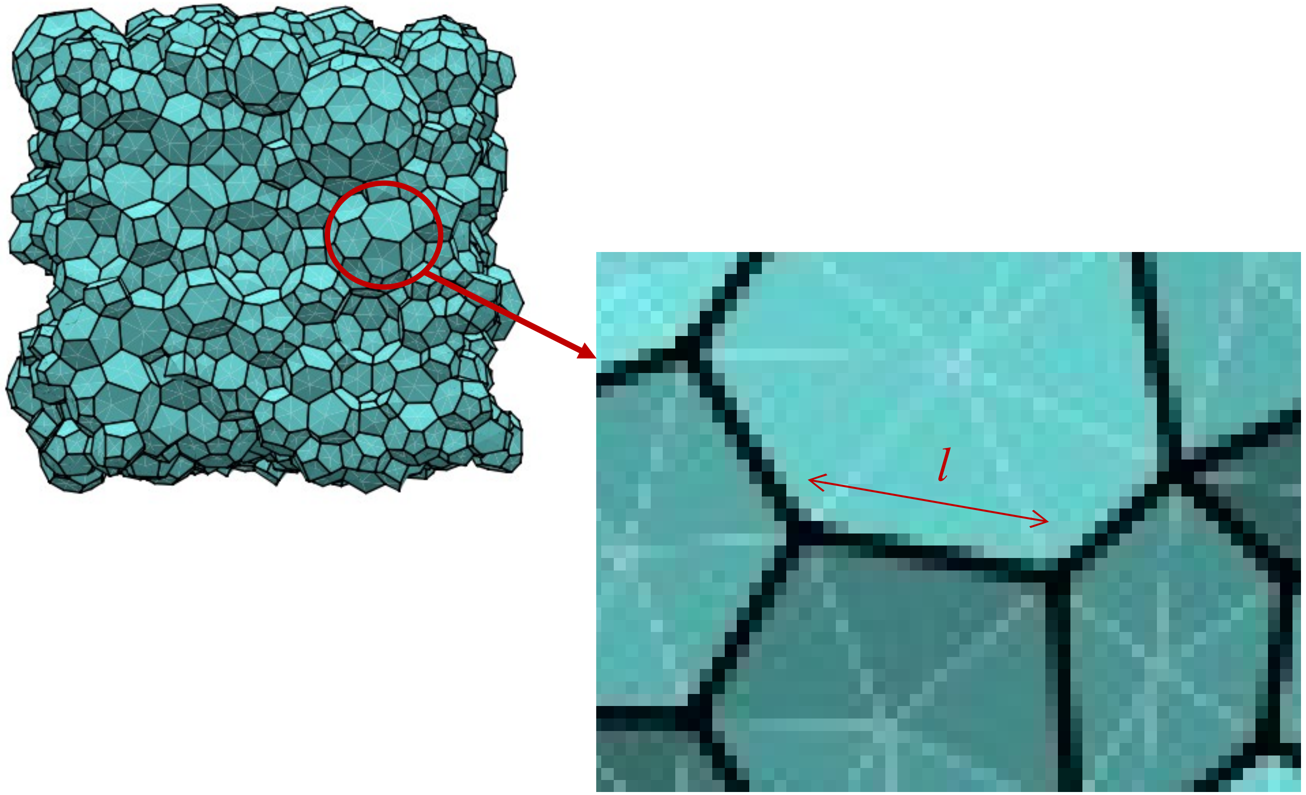


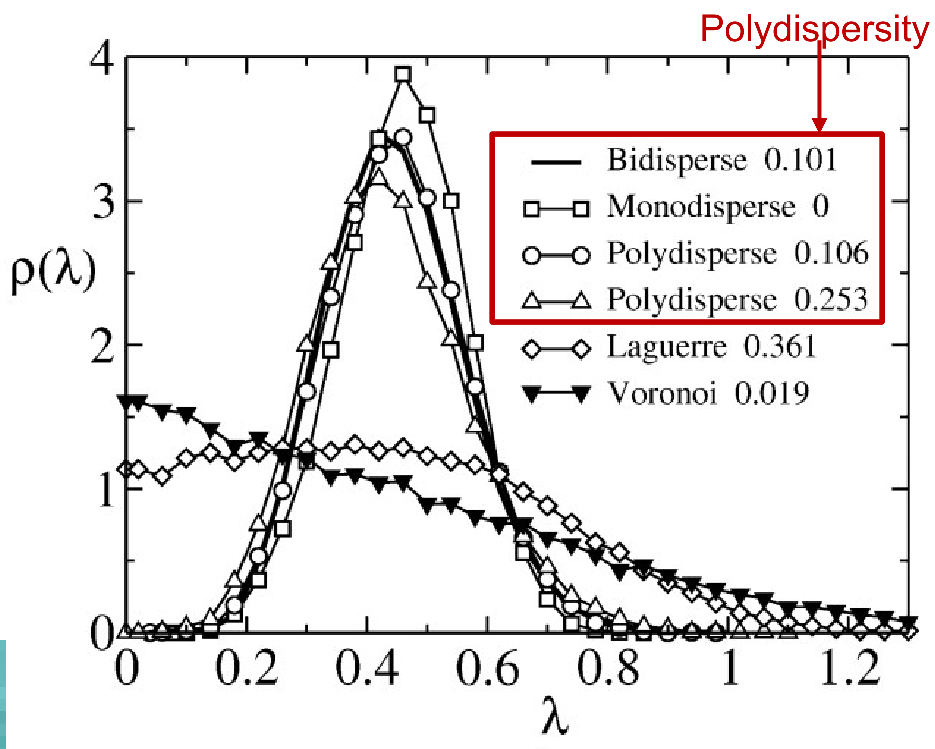


[Kraynik et al., PRL 93, 2004]

Length of Plateau borders

- Derived from Surface Evolver simulations
- Length compared to radius of equivalent sphere





$$\lambda = \frac{l}{\langle V \rangle^{1/3}}$$

$$\lambda \approx 0.5 \rightarrow l \approx 0.5 \langle V \rangle^{1/3} \approx 0.8 R_e$$

[A. Kraynik, Adv. Eng. Mat. 2006]

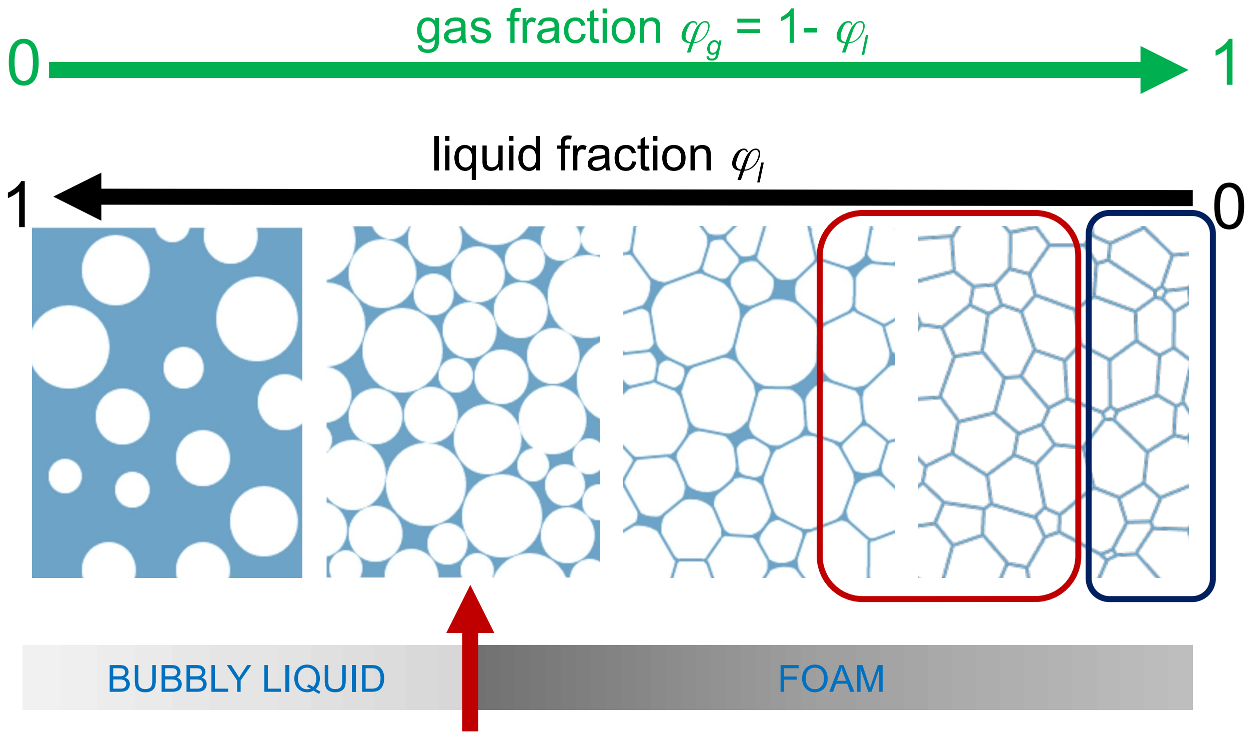
Structure

- Review lecture 6
- Dry foam topology
- Plateau's laws
- Neighbour statistics
- Wet foam
- Bubble crystals

Jamming limit

- Liquid fraction: Ratio of liquid volume and foam volume
- Jamming point at ≈36% liquid fraction
- Below that point: foam

$$\varphi_l = \frac{V_{liq}}{V_{foam}} = \frac{V_{liq}}{V_{gas} + V_{liq}}$$

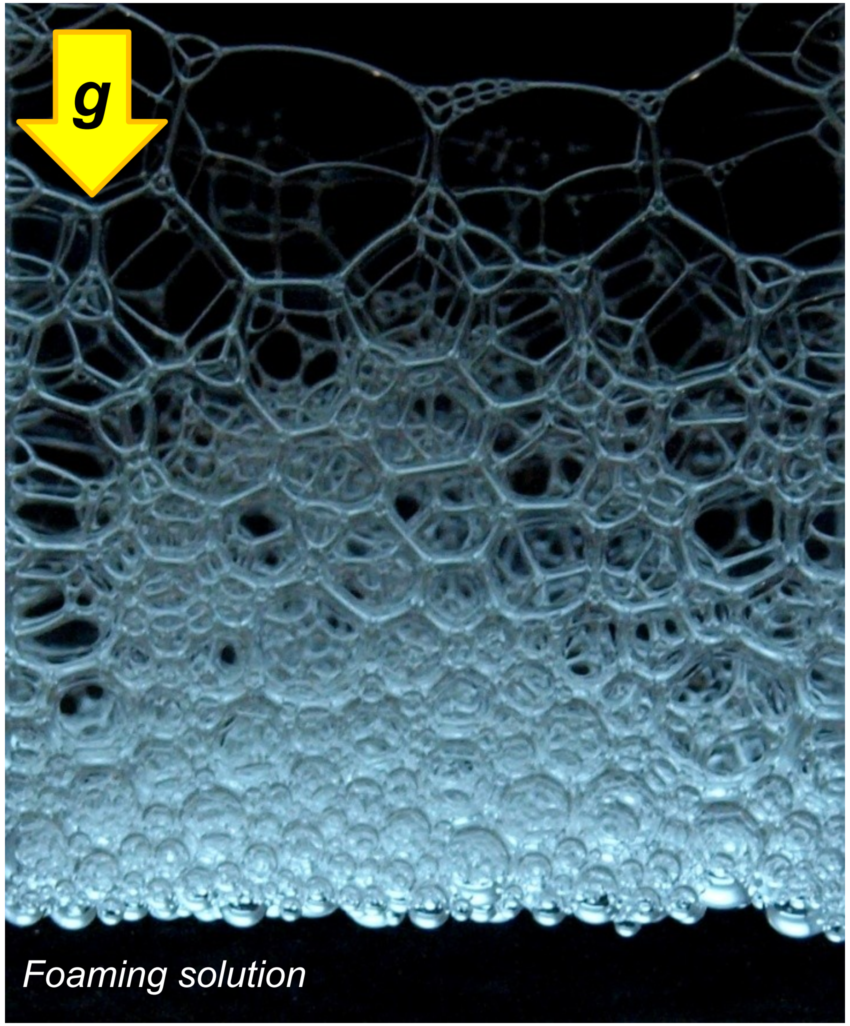


Critical liquid fraction $\varphi_c \approx 0.36$

Jamming point – Bubbles are in contact with each other

Jamming limit

- Coexistence of wet and dry foam
- Drainage influences liquid fraction



DRY LIMIT

DRY FOAM

$\varphi \approx$ 1% … 5%

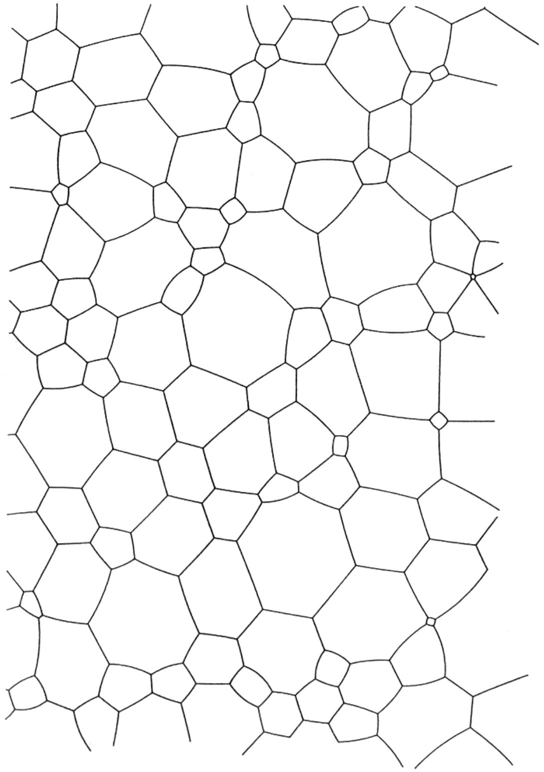
WET FOAM

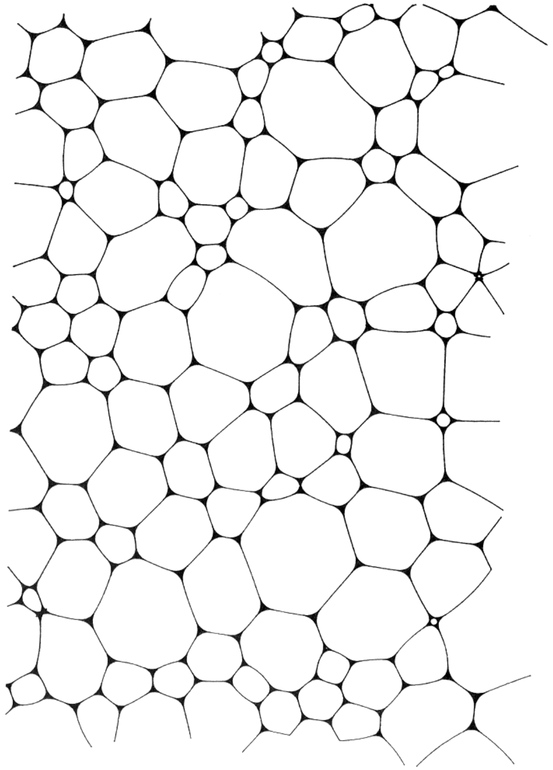
WET LIMIT

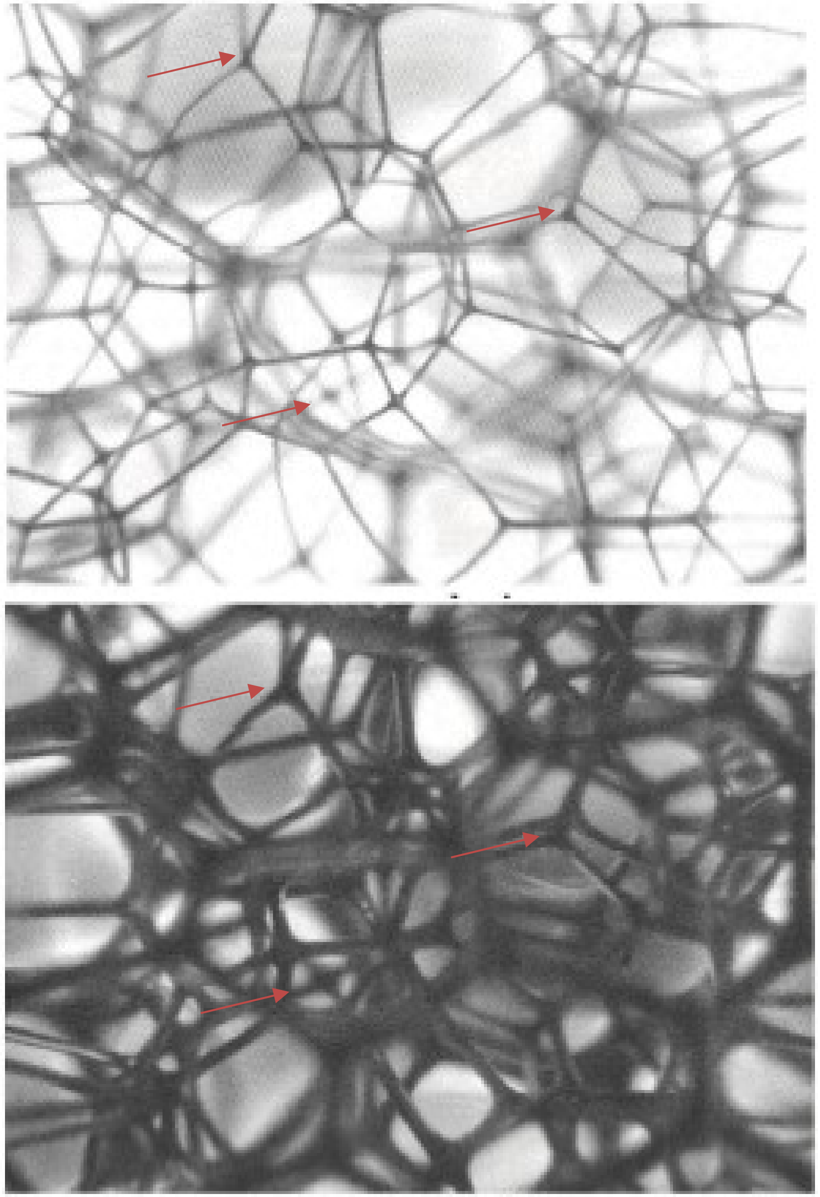
$\varphi \approx 0.36$

Liquid distribution

- Decoration theorem: Liquid is accumulated in Plateau borders
- Foam structure is identical to dry foam

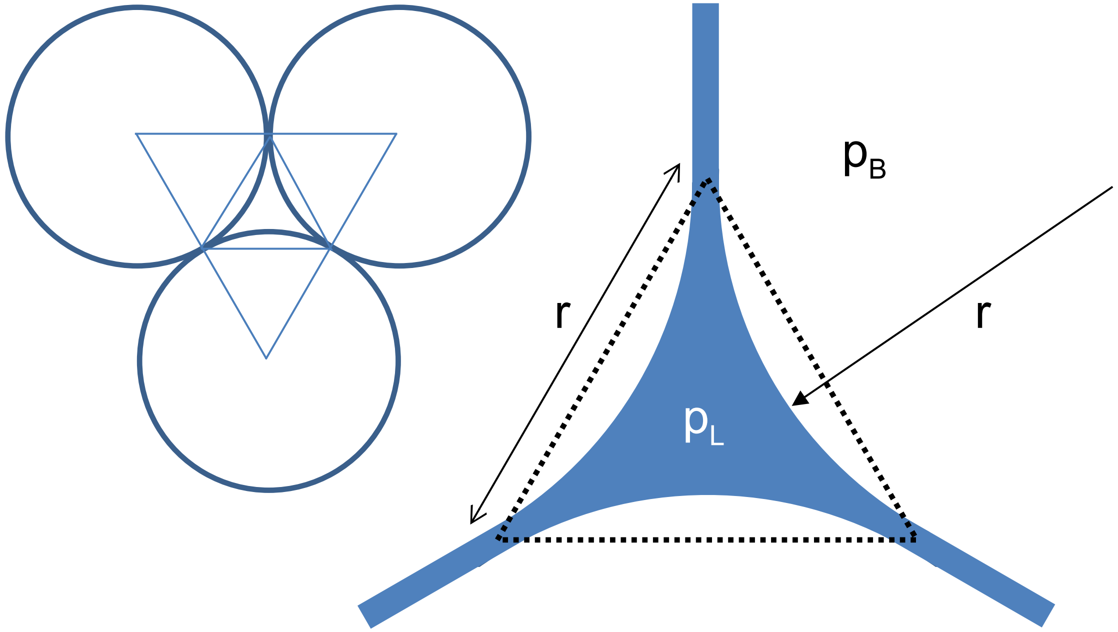






Plateau border geometry

- Size of Plateau border ≈ r
- Radius of curvature ≈ r



Capillary pressure:

$$\Delta p = p_c = p_B - p_L \approx \frac{\gamma}{r}$$

Plateau border area:

$$A_{Pb} = \left(\sqrt{3} - \frac{\pi}{2}\right) r^2$$

Plateau border volume:

$$V_{Pb} = A_{Pb} l$$

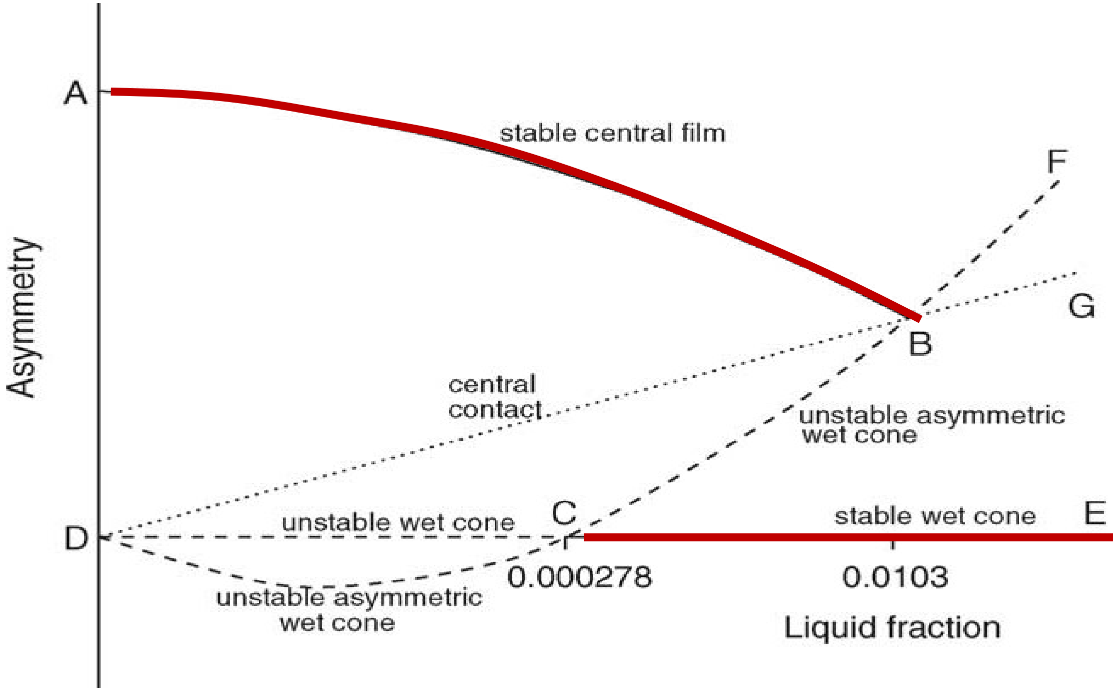
$$\varphi = \frac{n_{Pb}\, l_{Pb} A_{Pb}}{V_B} = \frac{\frac{14 \times 5}{3}\; 0.8\, R_e \left(\sqrt{3} - \frac{\pi}{2}\right) r^2}{\frac{4}{3}\pi {R_e}^3} \approx 0.72\, \frac{r^2}{{R_e}^2}$$

Pre-factor depends on foam structure, often 0.33 used, which is the analytical result for Kelvin-cell (see below)

- Bath tub foam, $R_e \approx 3$ mm, $\varphi \approx 0.5\%$ → r ≈ 0,3 mm

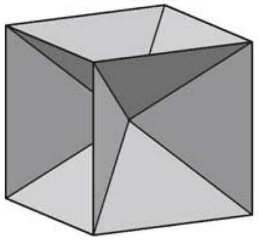
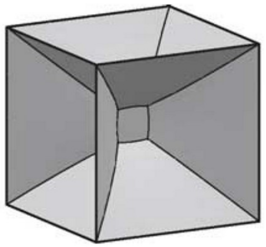
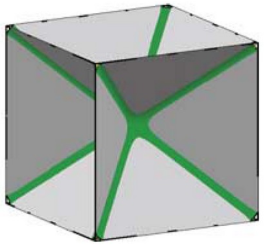
Plateau‘s law for wet foam

- Plateau’s laws can fail when foam is very wet



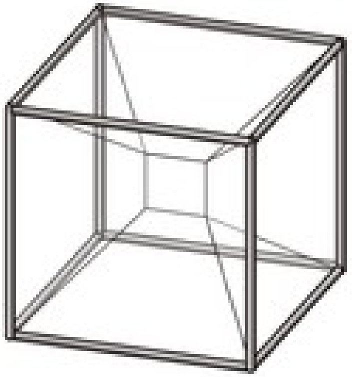
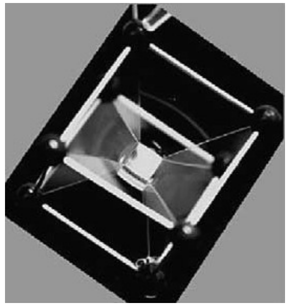
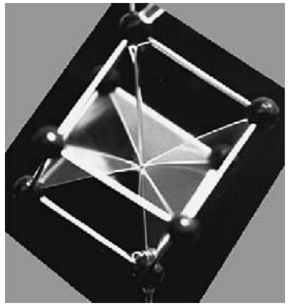
Not to scale

unstable | stable | stable

$V_L < 0.000278$ | $V_L > 0.0103$

[Brakke, Coll. Surf. A, 2004]

[S. Hutzler, PhD Thesis]

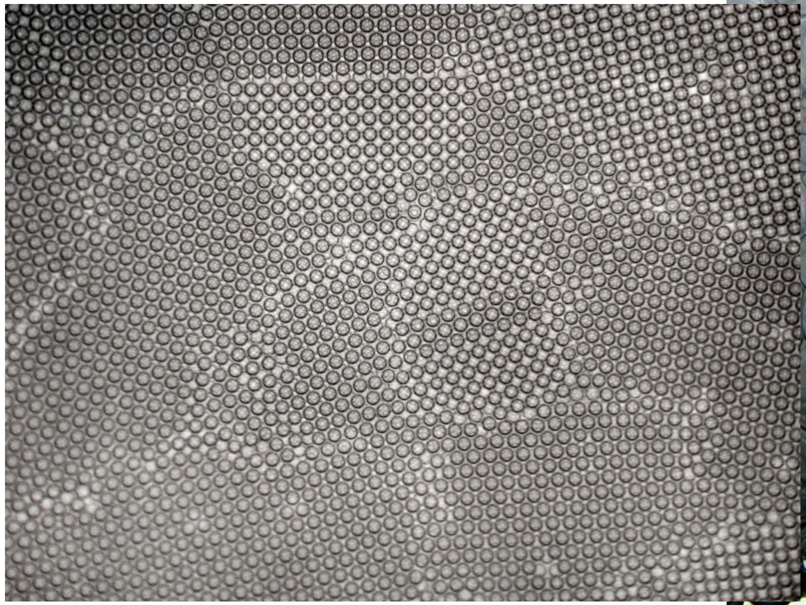
Structure

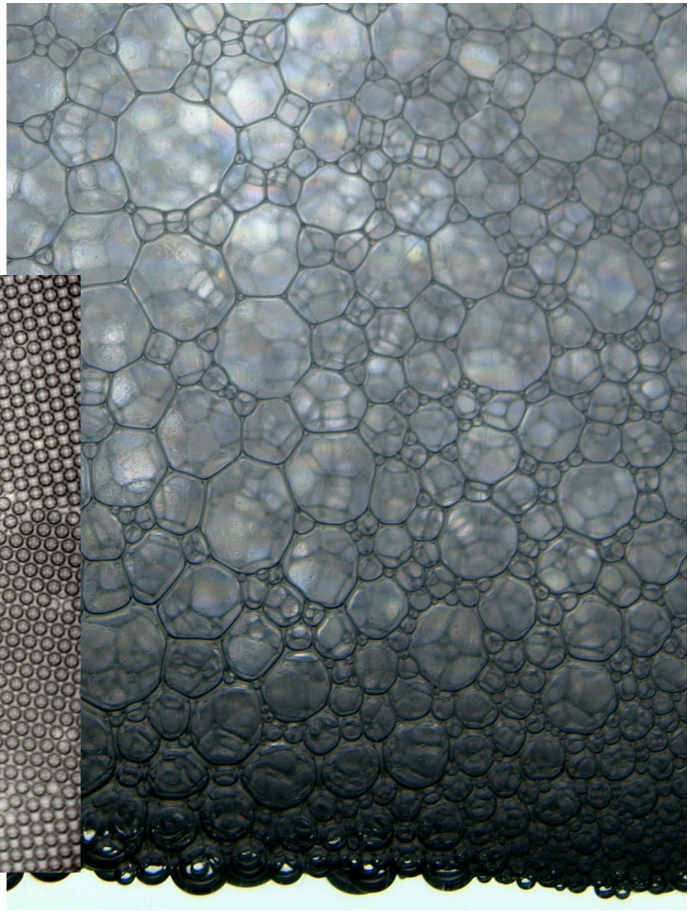
- Review lecture 6
- Dry foam topology
- Plateau’s laws
- Neighbour statistics
- Wet foam
- Bubble crystals

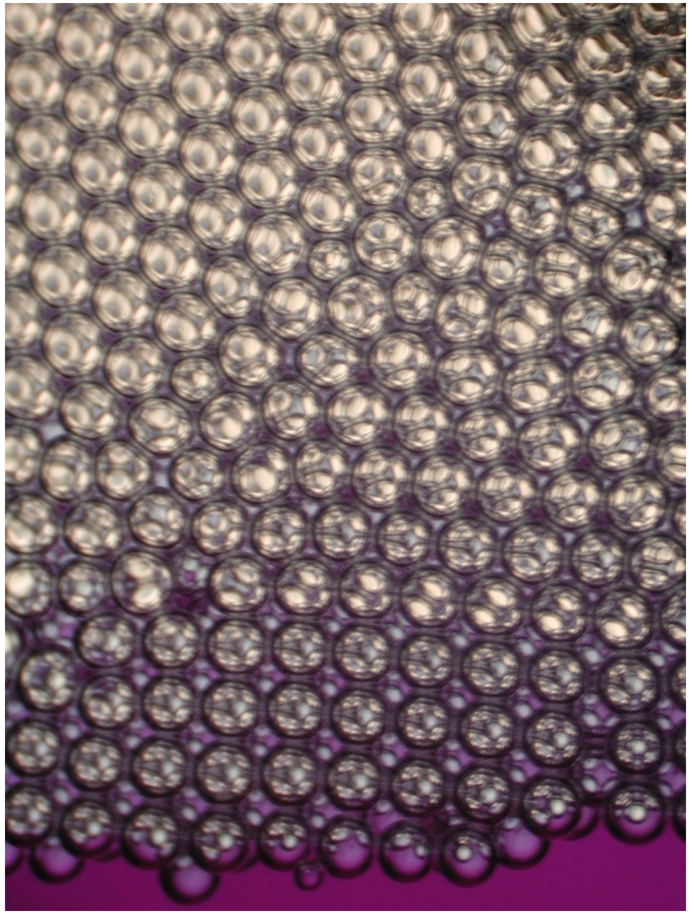
Monodispersed foam

- Polydispersity < 5%

$$PD = \frac{\sigma_R}{\langle R \rangle}$$

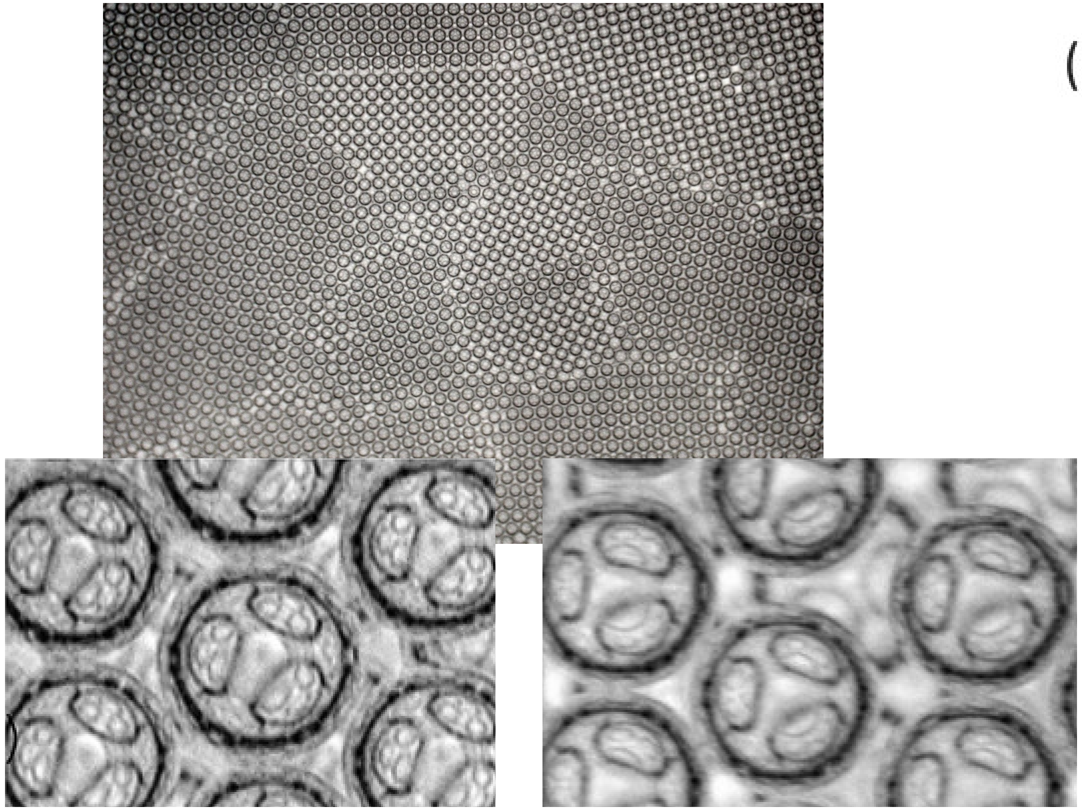






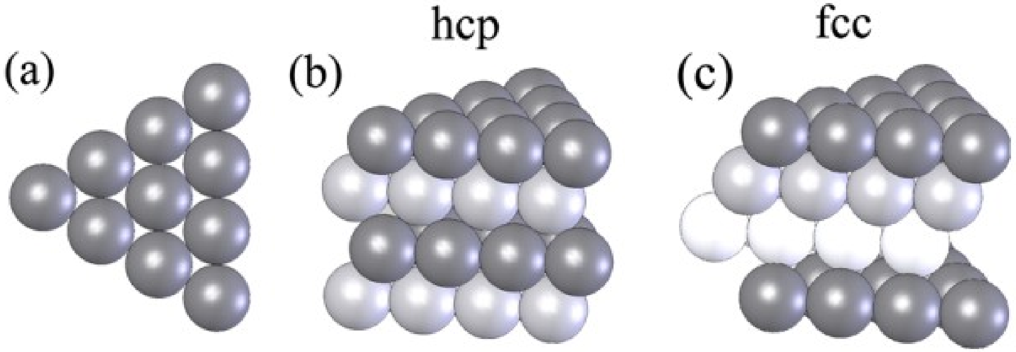
FCC vs HCP

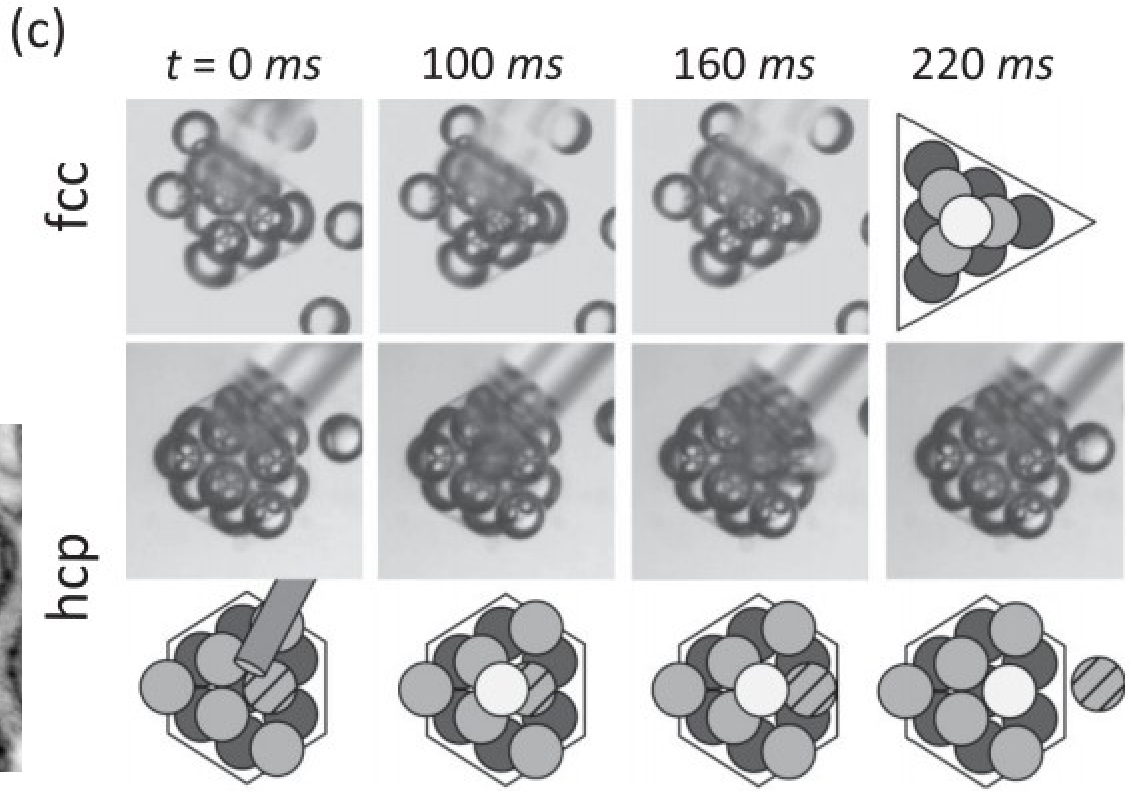
- Identical in packing density / energy
- Preference for fcc due to stability



fcc

hcp

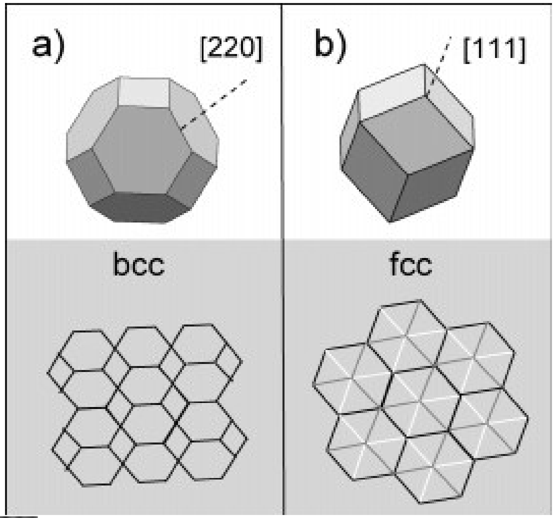




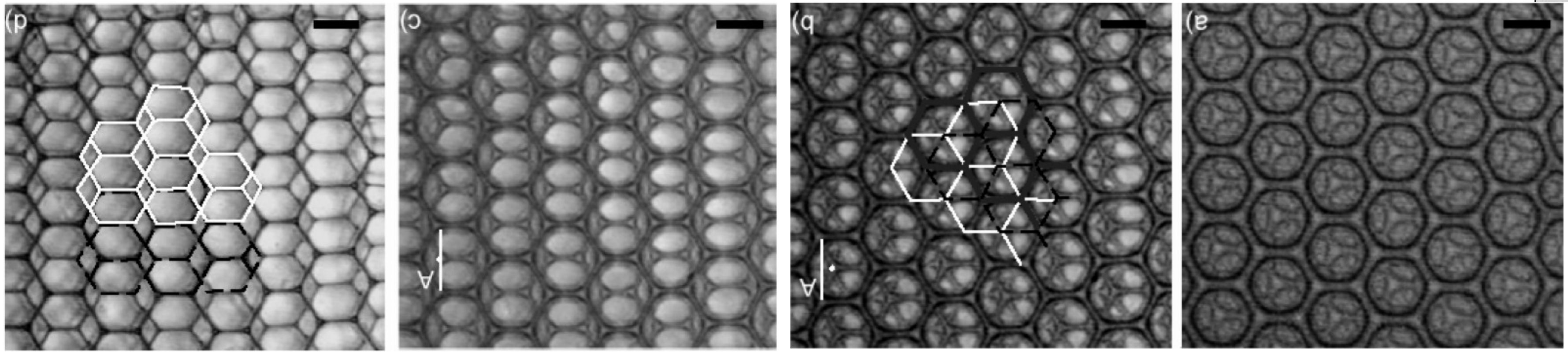
[Heitkam et al., PRL, 2012]

Crystalline structures

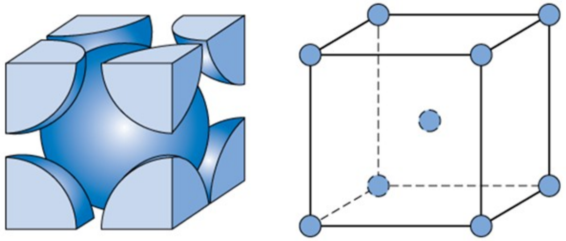
- Monodisperse foams show crystalline structures
- Structure resembles minimum-energy state
- Structure/Energy depends on liquid fraction



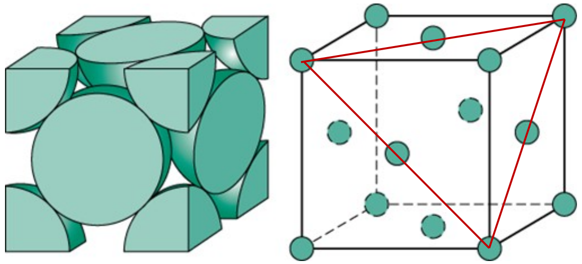
$\uparrow \varphi_l$



Kelvin



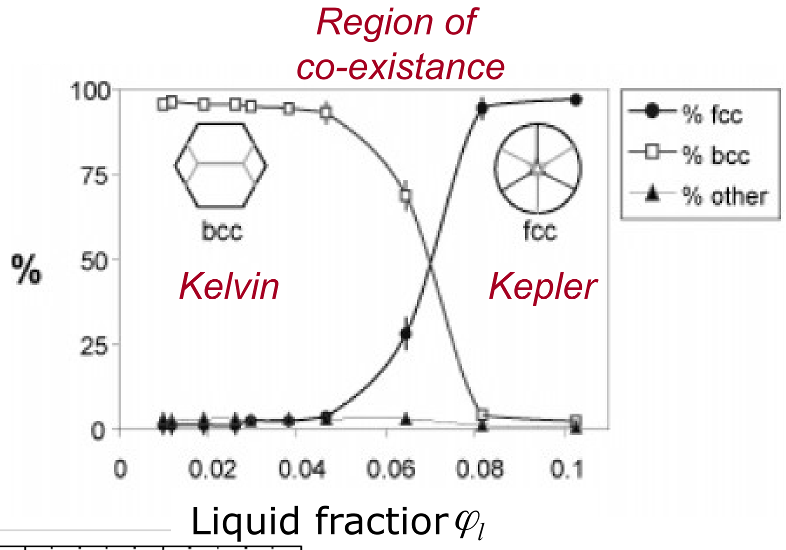
Keppler



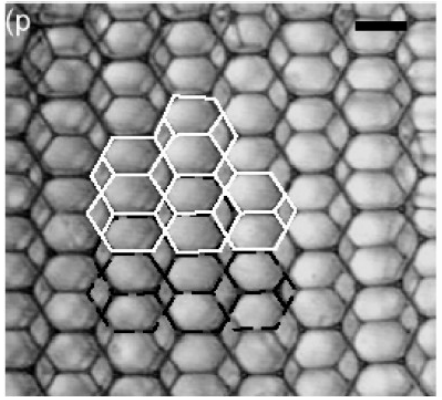
[Hohler et al., Langmuir, 2007]

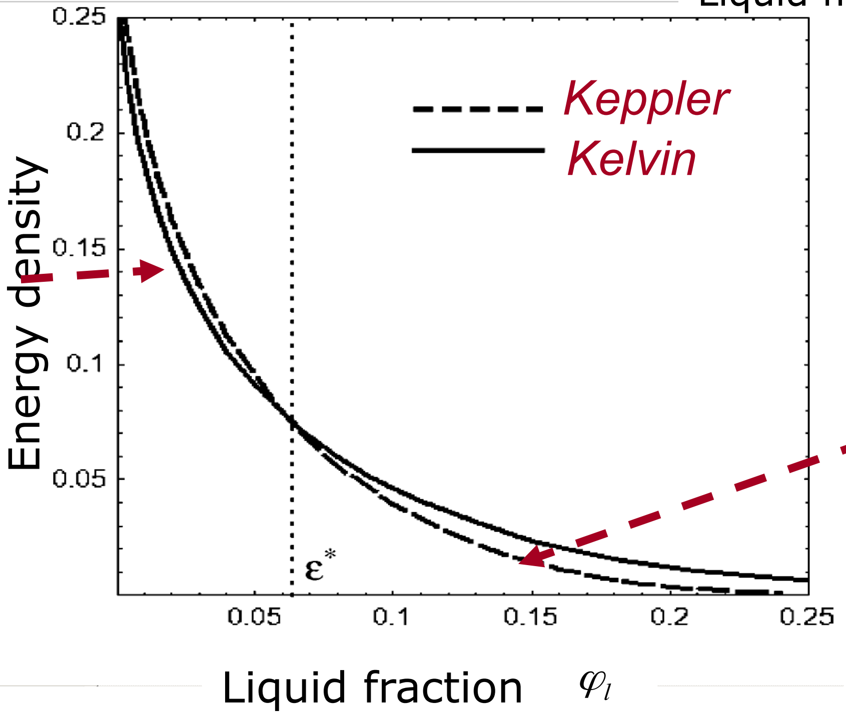
Kelvin vs. Keppler

- Energy minimization yields different structure

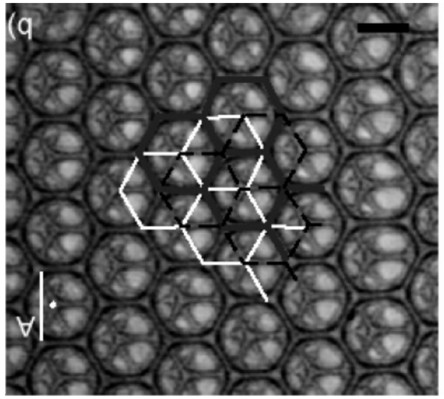


Kelvin





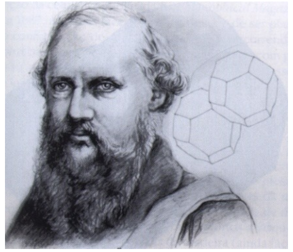
Keppler



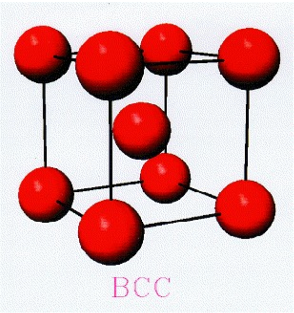
[Hohler et al., Langmuir, 2007]

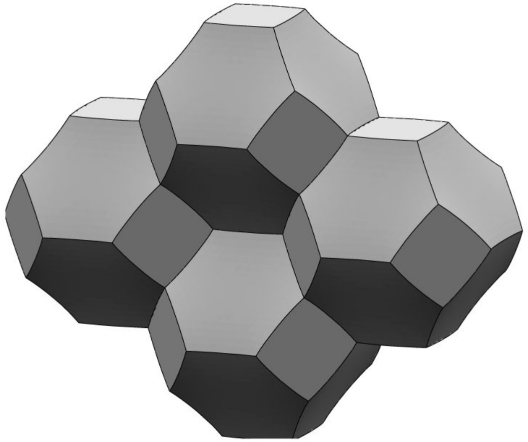
Weaire-Phelan structure

- Even lower Energy per Volume ratio
- Combination of two Bubble shapes



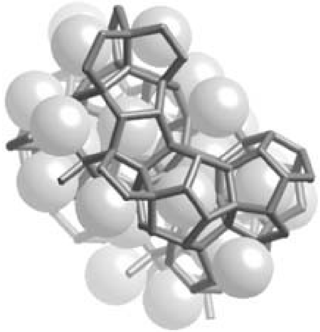
1887



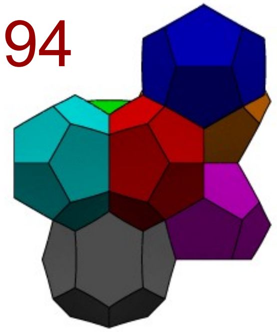


Kelvin structure

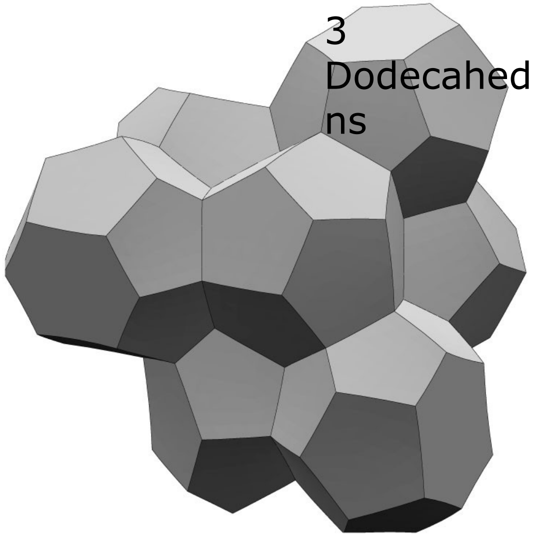
- 0.3 %



1994



1 Tetrakaidecahedron
3 Dodecahedrons



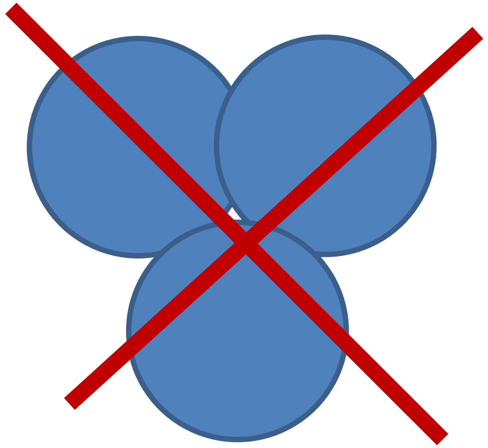
Weaire-Phelan structure

Perfect packing?

- Even lower Energy per Volume ratio
- Combination of two Bubble shapes

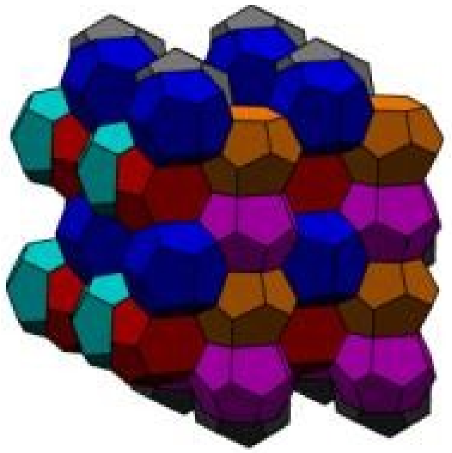
Spheres

$$\hat{E} = SV^{-\frac{2}{3}} = 4.836$$



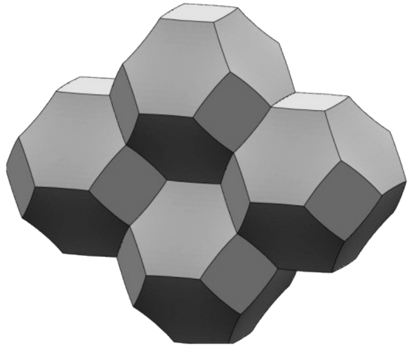
Weaire-Phelan

$$\hat{E} = SV^{-\frac{2}{3}} = 5.288$$



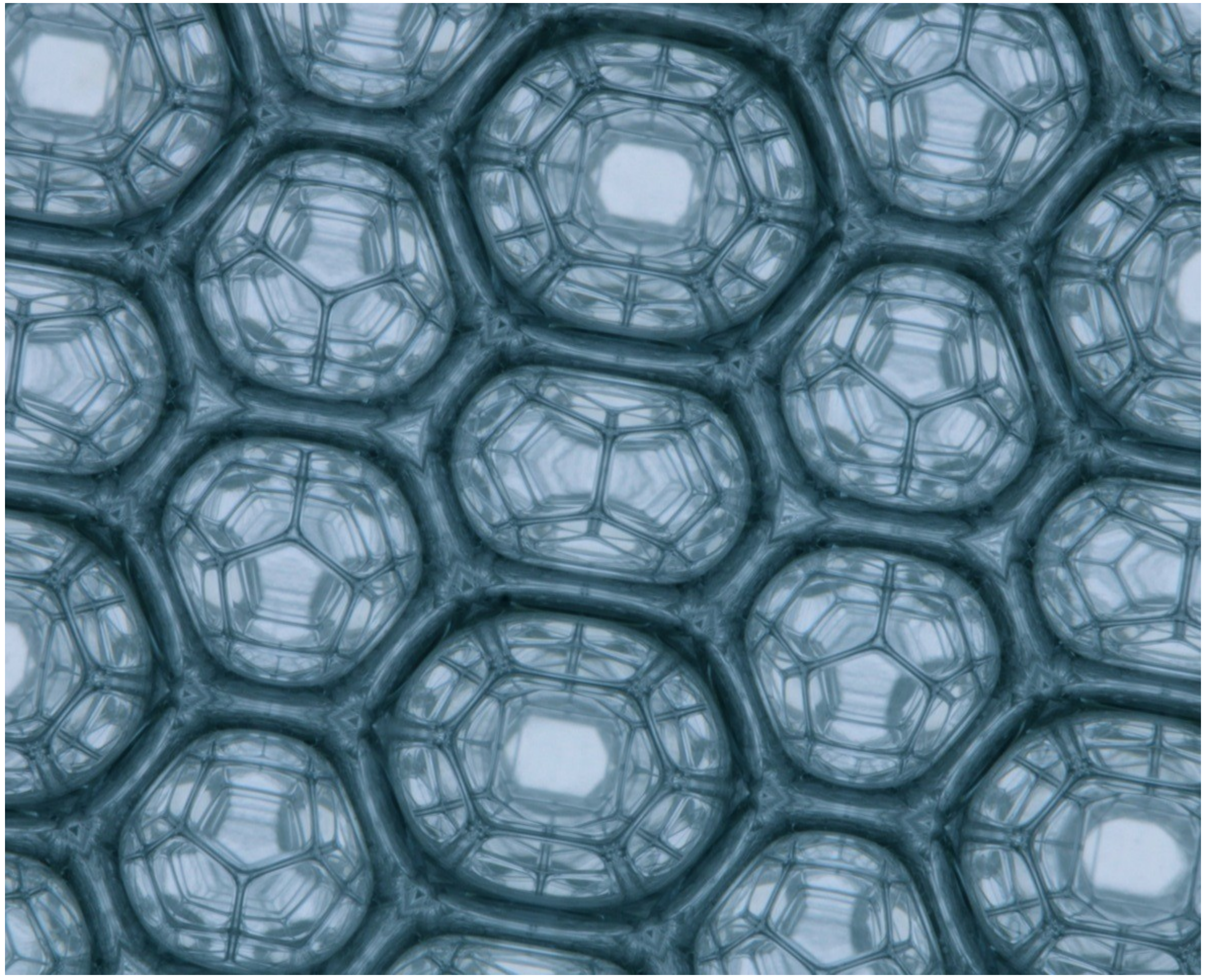
Kelvin

$$\hat{E} = SV^{-\frac{2}{3}} = 5.306$$

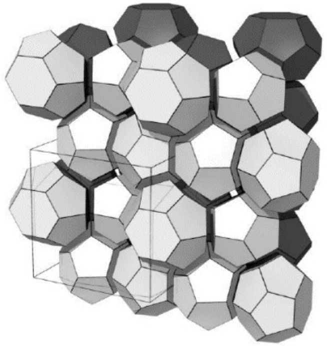


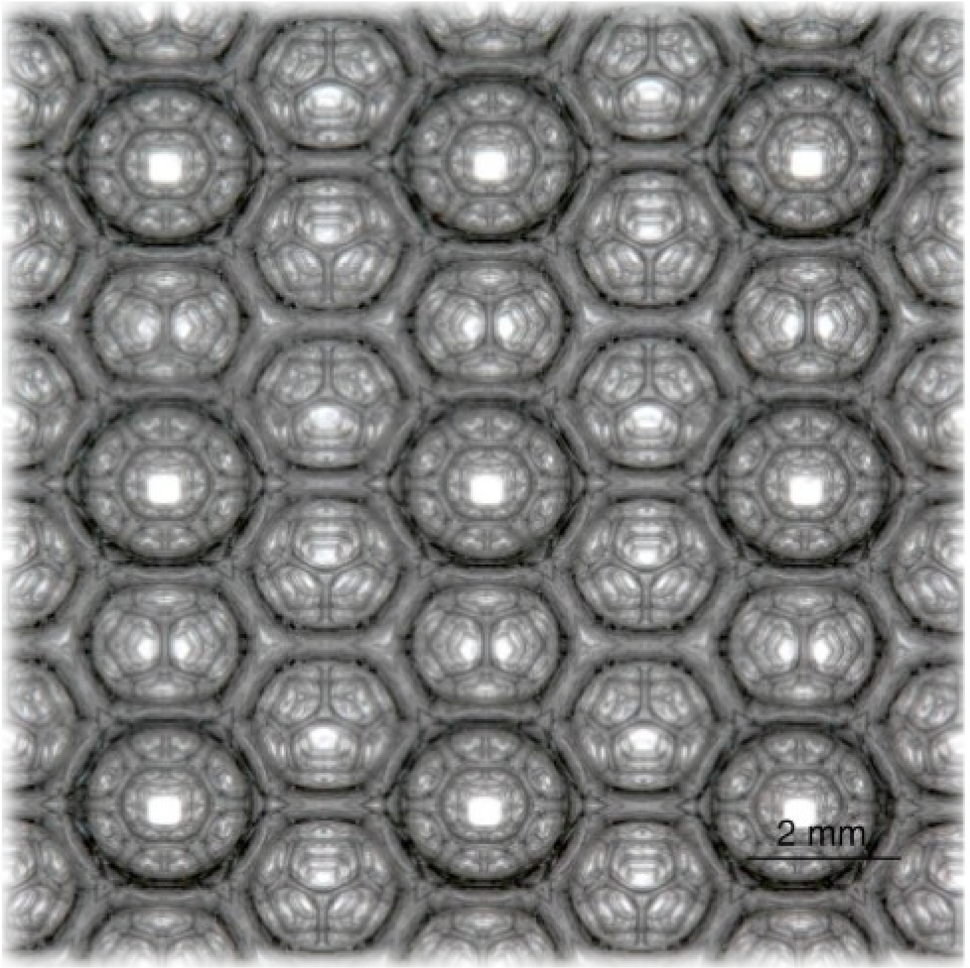
Energy per Volume

Weaire-Phelan structure

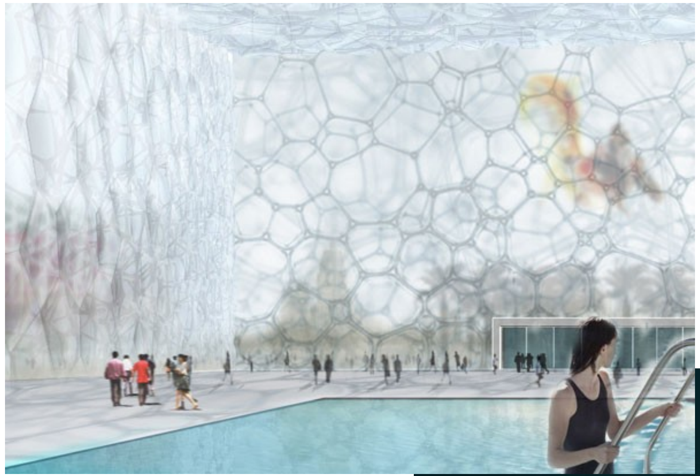


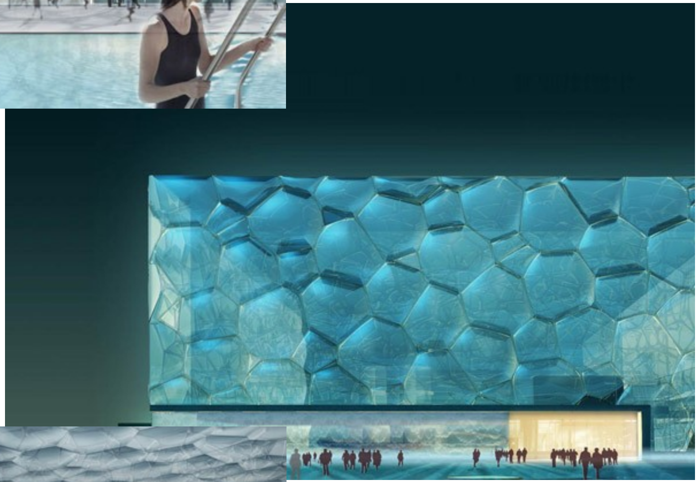
Experimental realisation?

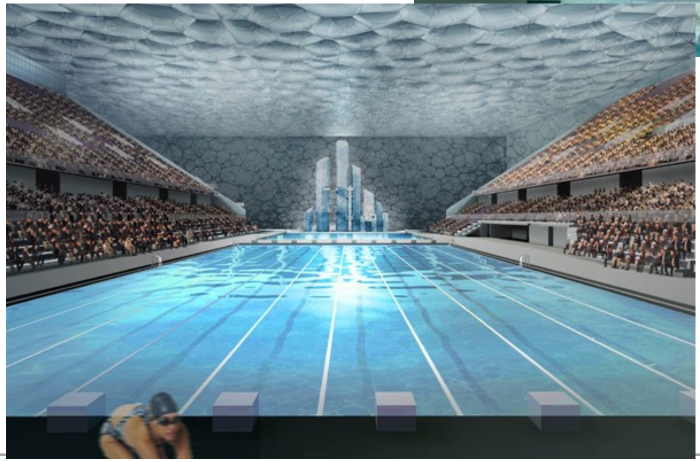




[Ruggero et al., Phil.Mag.Lett. 2011]







THE WATER CUBE

Olympic games Beijing 2008