

capillary ?

Gibbs ?

disjoining ?

PRESSURES IN A FOAM

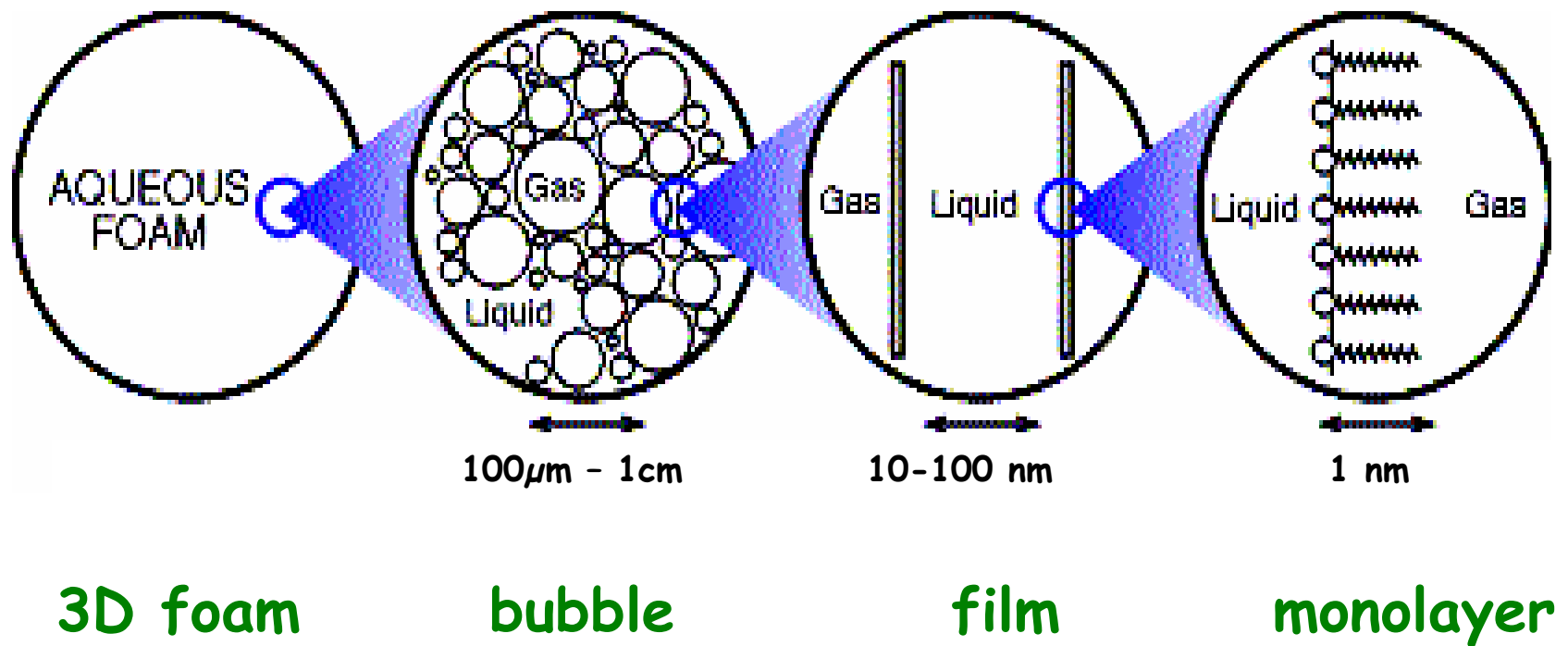
osmotic ?

Laplace ?

Langmuir ?

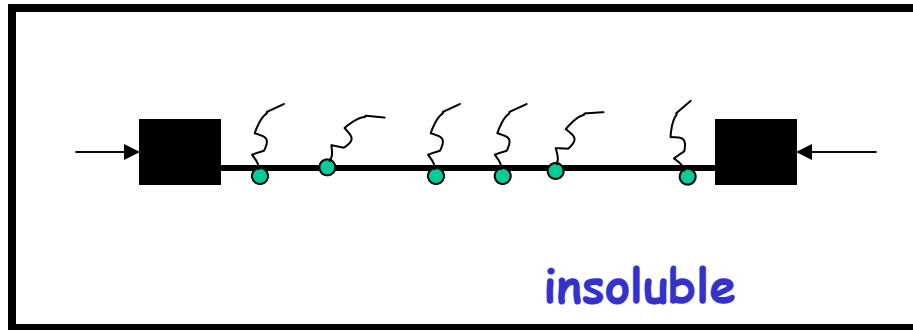
hydrostatic ?

different lengthscales...



... different pressures

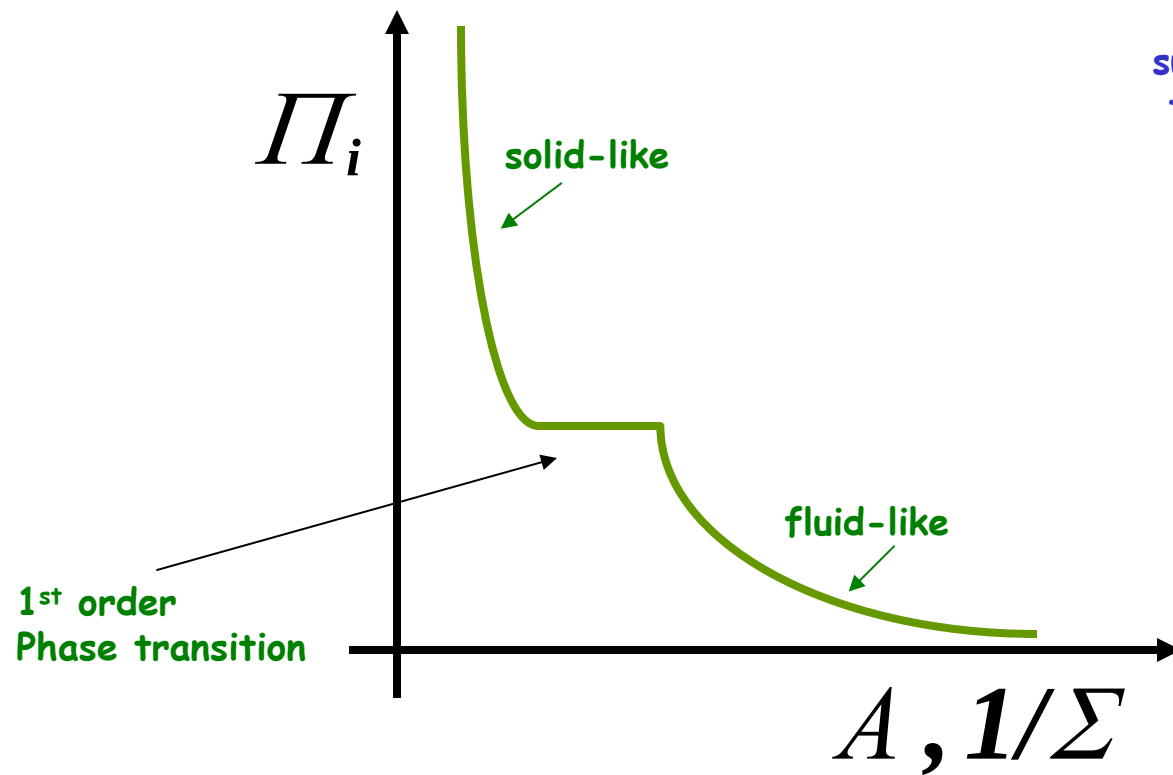
Liquid interfaces



« Langmuir » monolayer

$$\Pi_i = \gamma_0 - \gamma$$

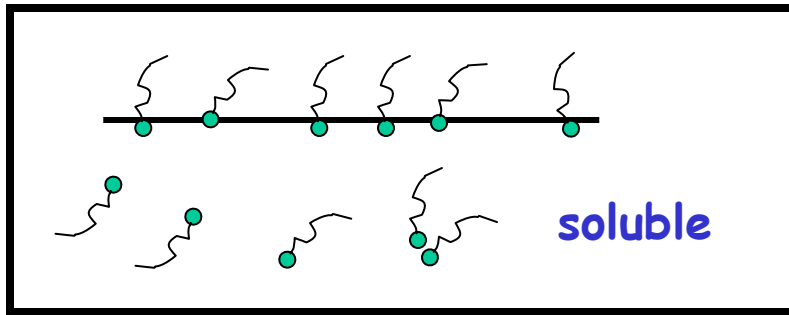
↑
surface tension of
the pure liquid



A = area per molecule

Σ = surface density

Liquid interface



Gibbs equation :

$$\Gamma = - \frac{1}{kT} \frac{\partial \gamma}{\partial \ln c}$$

A simple model (Langmuir) : equilibrium between adsorption and desorption

$$\Gamma / (\Gamma_{\infty} - \Gamma) = \frac{c}{a}$$

$$\Gamma = (a/c + 1)^{-1} \Gamma_{\infty}$$

With a = Szyszkowski concentration

With Γ_{∞} = saturation surface concentration

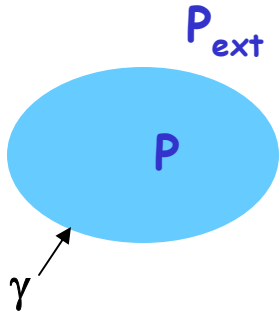
Finally, the « Langmuir » (interfacial) equation of state :

$$\Pi_i = - kT \Gamma_{\infty} \ln (1 - \Gamma / \Gamma_{\infty})$$

More refinements are possible

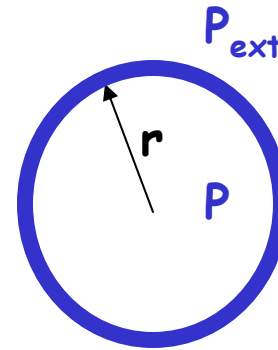
Though, it can be used dynamically

curved interfaces and Laplace pressure



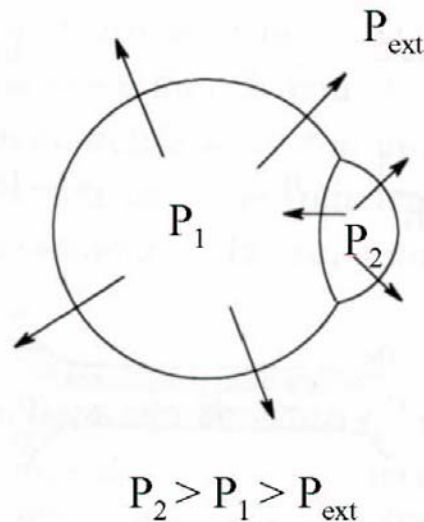
$$P - P_{ext} = \gamma (1/R_1 + 1/R_2)$$

For a single spherical bubble :



$$P - P_{ext} = 4\gamma / R$$

Two bubbles of different sizes, in contact :



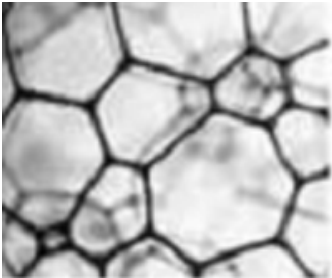
A useful lengthscale :

$$l_c = \sqrt{\frac{\gamma}{\rho g}}$$

$l < l_c$: capillarity dominates gravity

Liquid pressure in Plateau borders

DRY

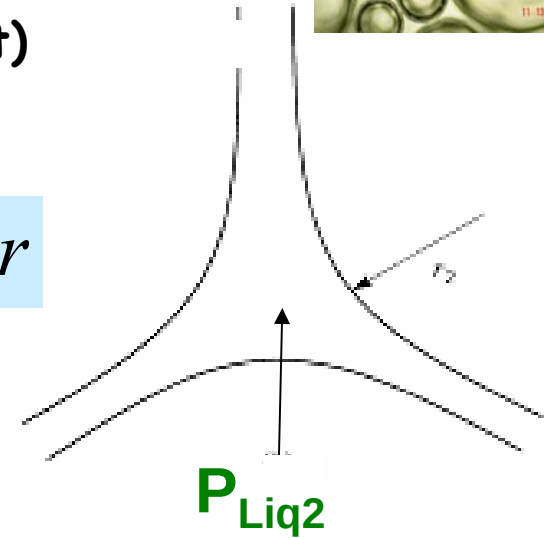
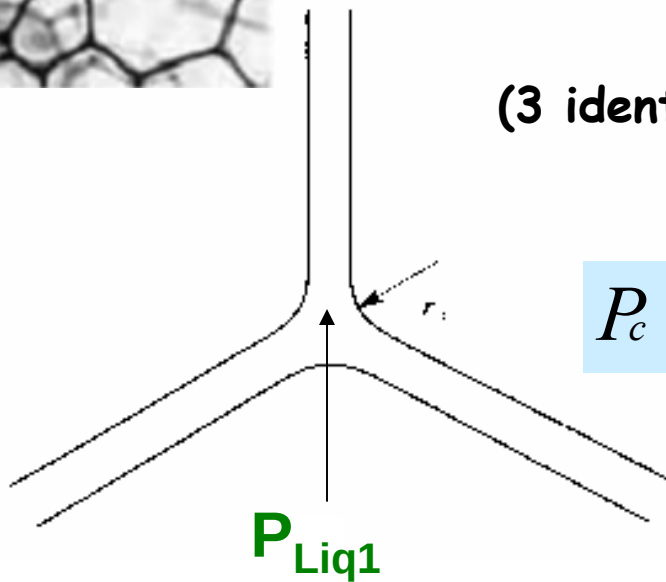
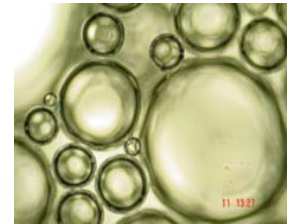


The Laplace pressure also describes the pressure inside the Plateau borders :

(3 identical bubbles at $P_g = \text{cst}$)

$$P_c = P_{\text{gas}} - P_{\text{liquide}} = \gamma / r$$

WET

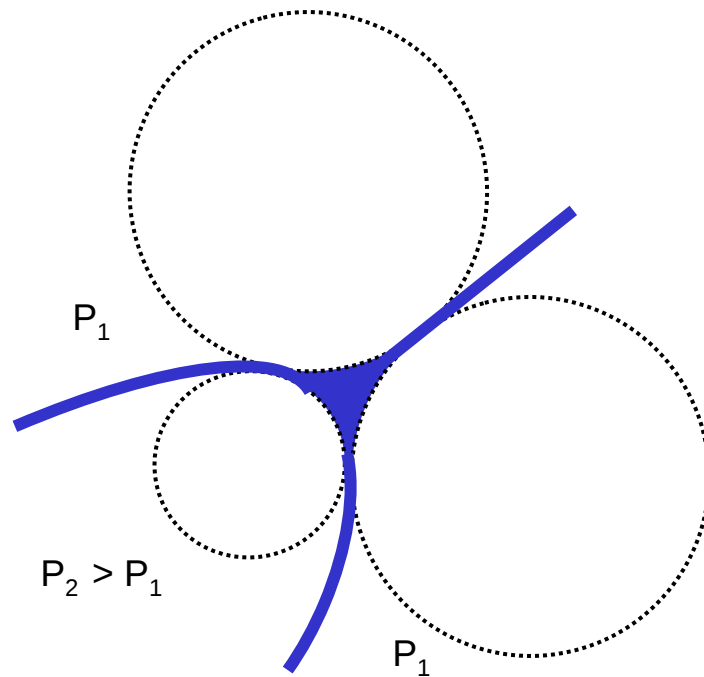


$$P_{\text{Liq2}} > P_{\text{Liq1}}$$



Gradients of liquid fraction = gradients of pressure = ...

Considering bubbles of different volumes...

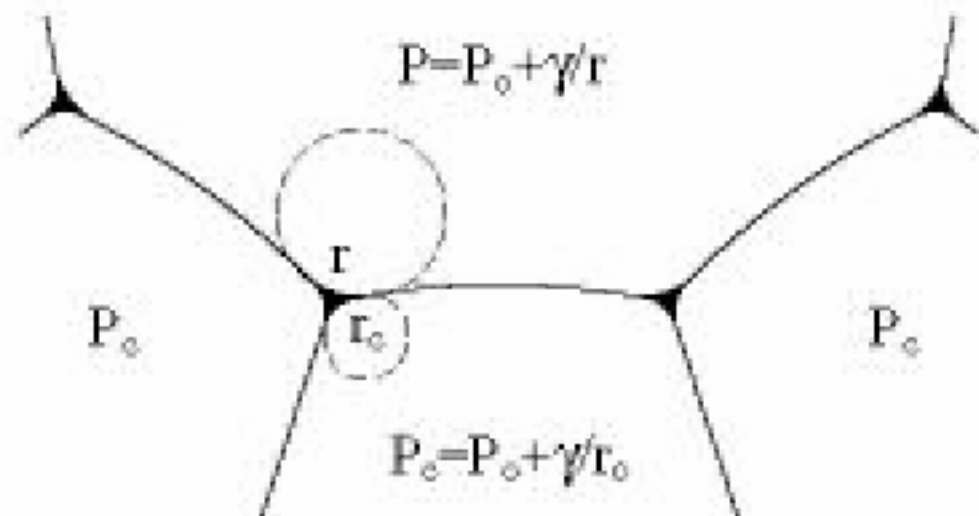


differences in thin film curvature

...as well as...

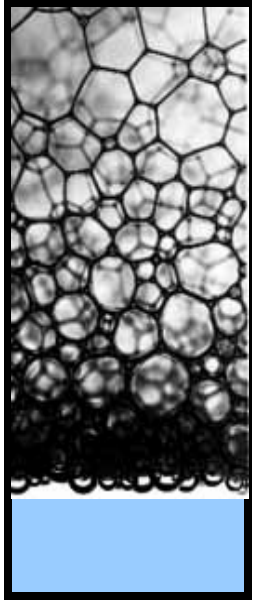
differences in Plateau borders radii

$$P_c = P_{gas} - P_{liquide} = \gamma/r$$



Equilibrium under gravity and hydrostatic pressure

$$P_c = P_{\text{gas}} - P_{\text{liquide}} = \gamma / r$$



Hydrostatic pressure : $P_{\text{liq}} = P_0 + \rho g z$

$$\longrightarrow r(z) = \frac{\gamma}{(P_g - P_0 - \rho g z)}$$

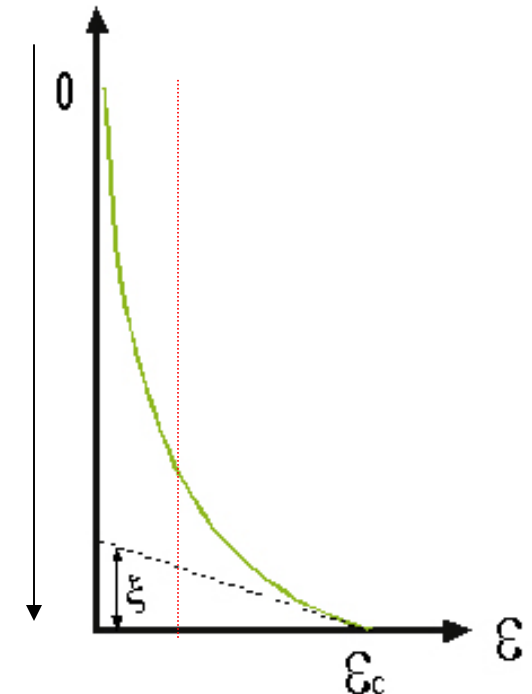
using $\varepsilon = c (r/D)^2$

$$\longrightarrow \varepsilon(z) = \frac{c\gamma^2}{D^2} \frac{1}{(P_g - P_0 - \rho g z)^2}$$

With the bottom boundary condition :

$$\varepsilon_c = 0.36$$

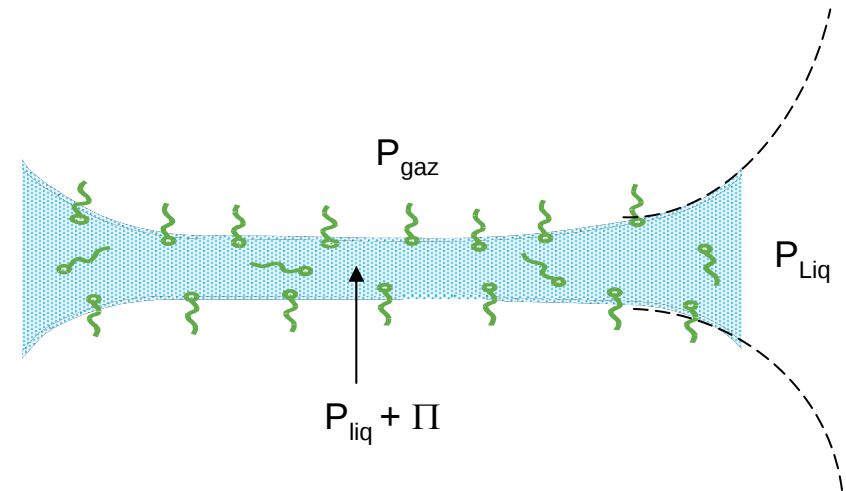
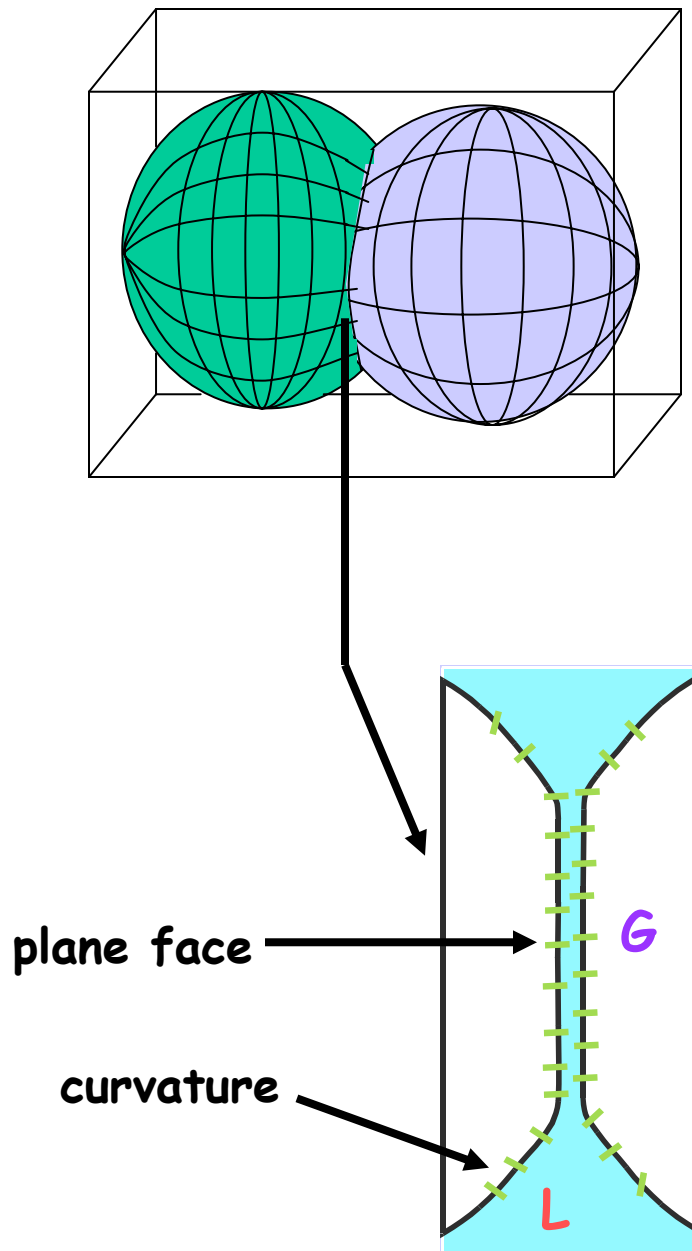
$$\longrightarrow P_g - P_0 = \rho g H + \sqrt{\frac{c}{\varepsilon_c}} \frac{\gamma}{D}$$



Height of the
« wet layer »:

$$\xi = \frac{\gamma}{\rho g R}$$

Something wrong in the thin films ?



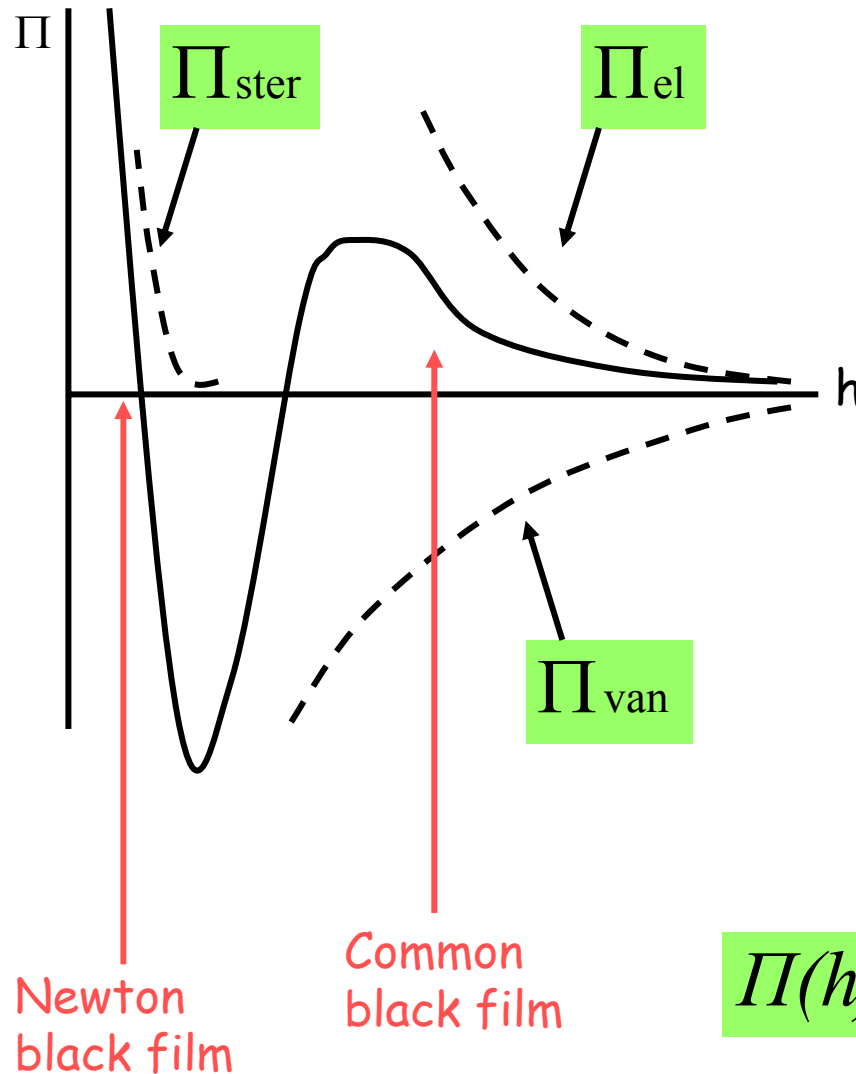
$$\Pi_d + P_{\text{liquide}} = P_{\text{gas}}$$



$$\Pi_d = P_{\text{gas}} - P_{\text{liquide}} = P_c$$

At equilibrium

which forces between surfaces?



✓ **electrostatic repulsion :**

$$\Pi_{el} = 64 kT \rho_{\infty} \gamma^2 \exp(-kh)$$

✓ **dipolar interaction
(Van Der Waals):**

$$\Pi_{van} = - \frac{A_h}{6 \pi h^3}$$

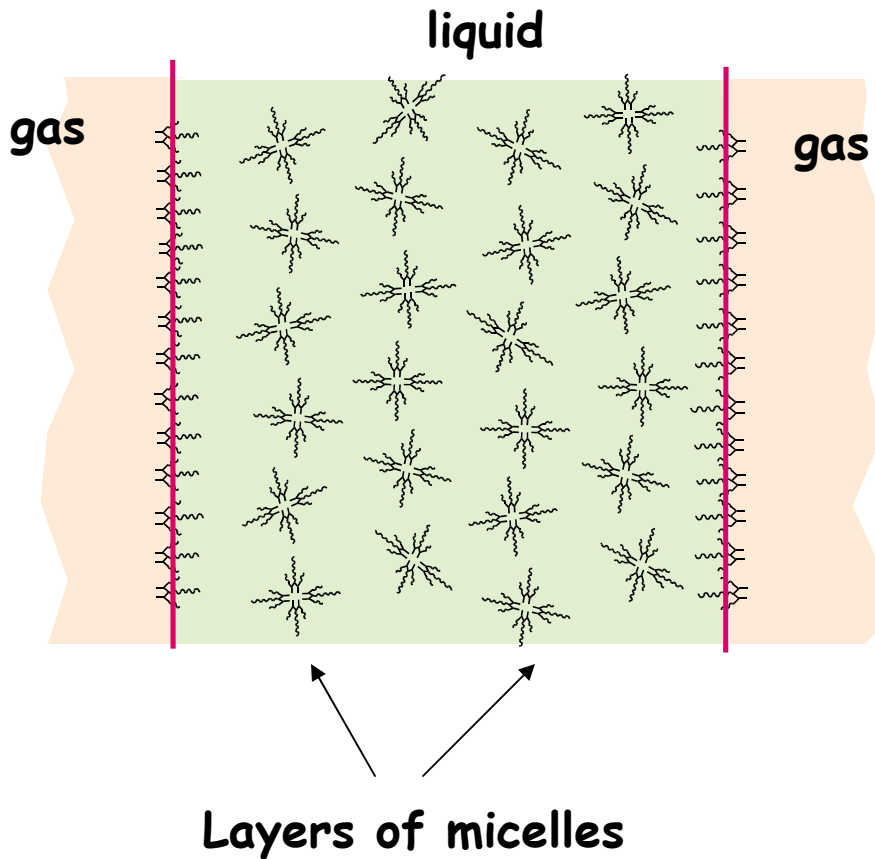
✓ **steric contribution :
confinement**

$$\Pi(h) = \Pi_{el} + \Pi_{van} + \Pi_{ster}$$

(DLVO model)

Typical h , and Π are...

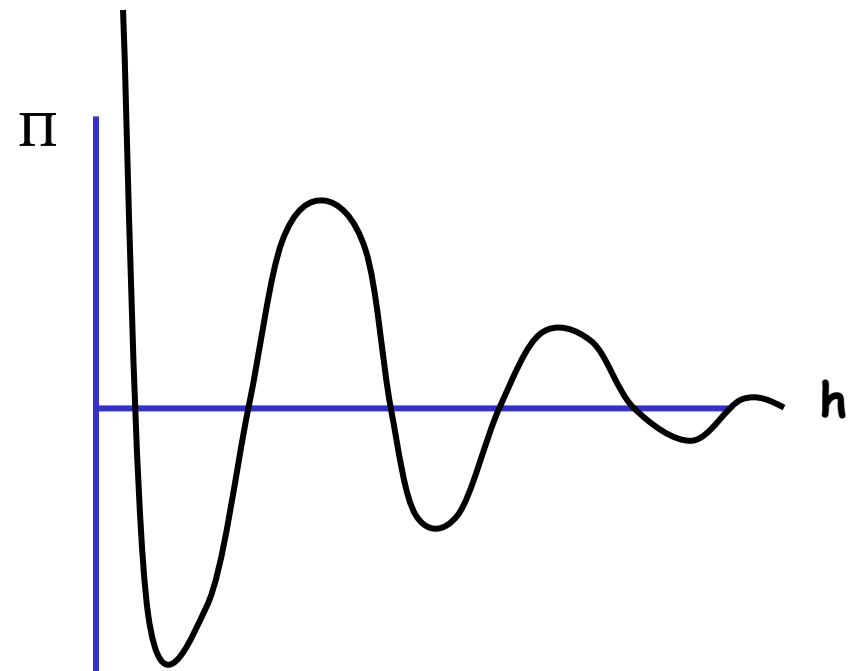
Another type of force : supramolecular forces



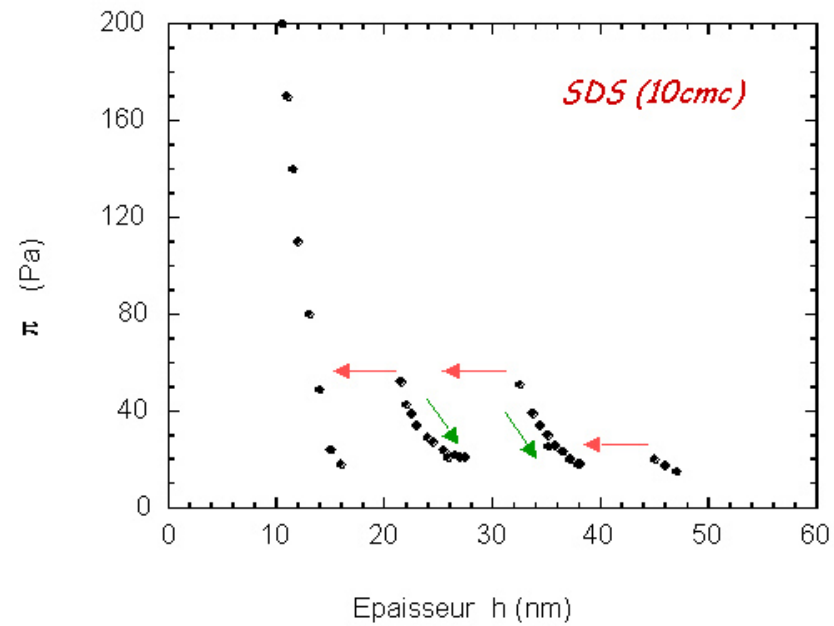
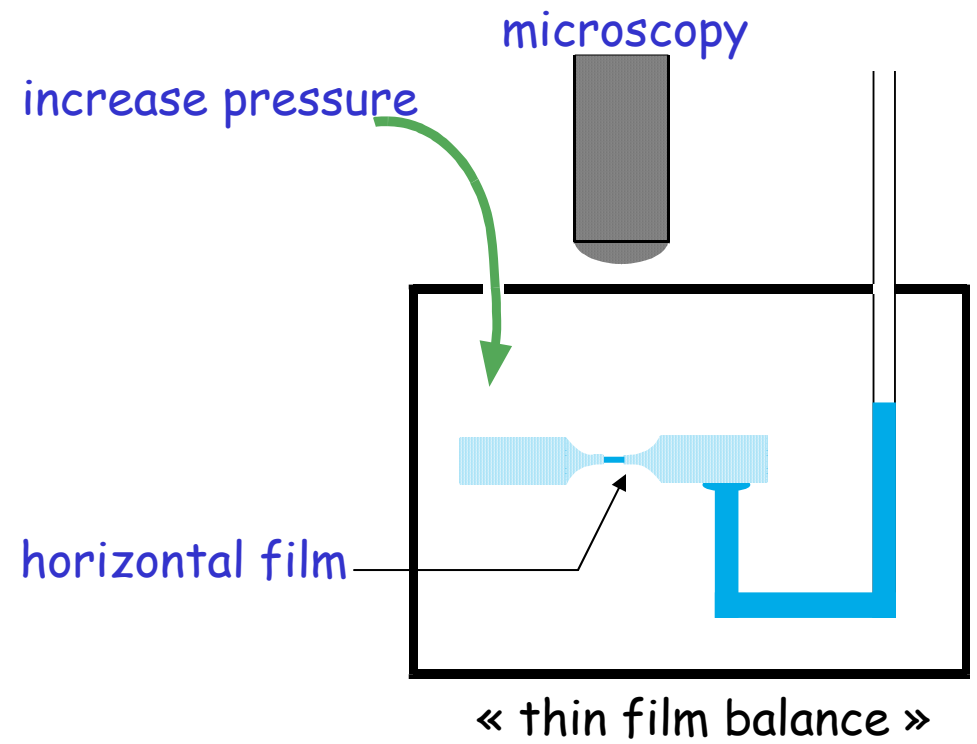
confinement effect in the film

Arrangements in layers

Oscillation in the disjoining pressure

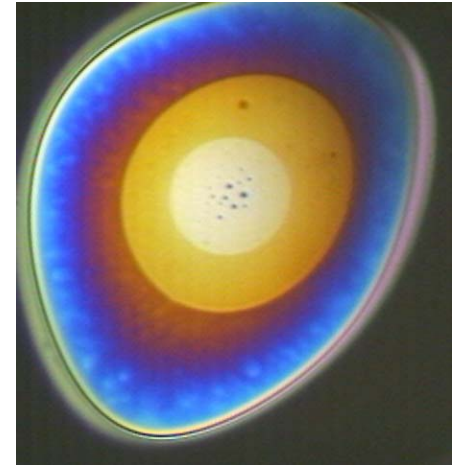
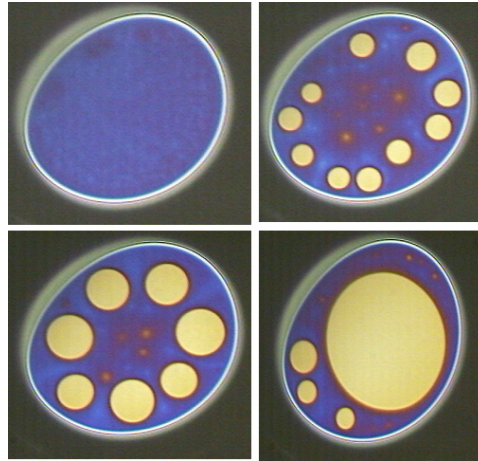


implies thickness steps,
and a thinning layer by layer



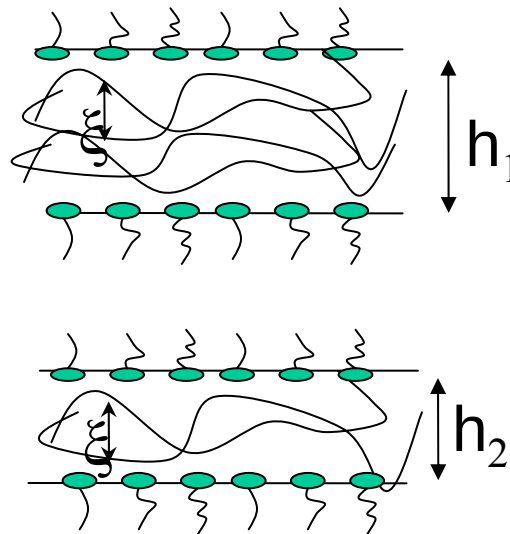
(data from
V. Bergeron)

Other types of film stratification,
at high thickness :



Stratification with surfactant-polyelectrolytes systems :

Confinement effects
in thin films



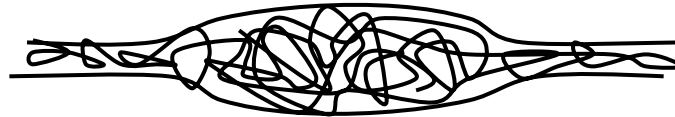
layer thickness
corresponds
to the bulk mesh size (!?)

$$\xi \sim h_1 - h_2$$

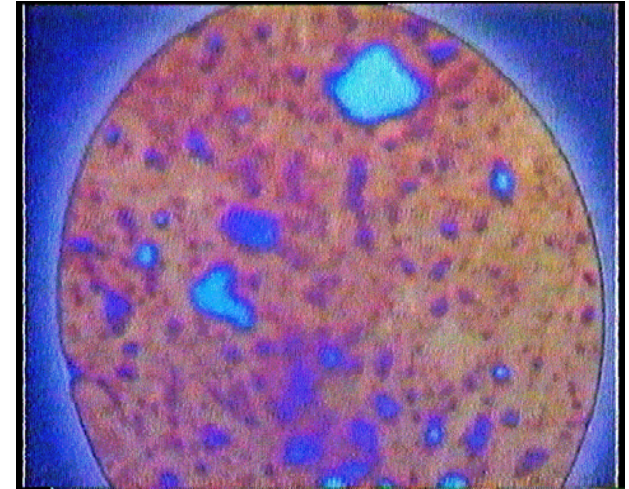
high concentration of polyelectrolytes and surfactant :

→ non-homogeneous and non-flat films

gelified structure : high local viscosity

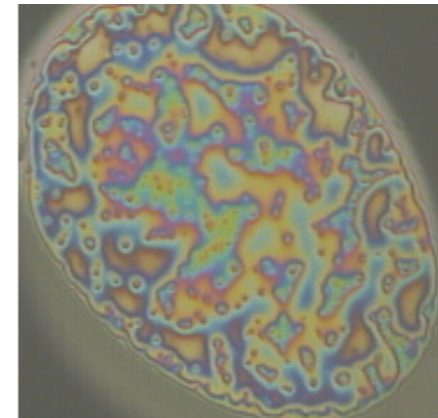
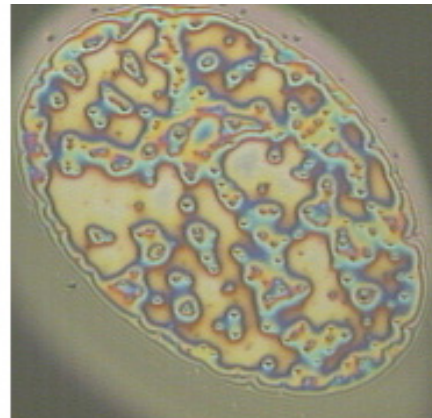
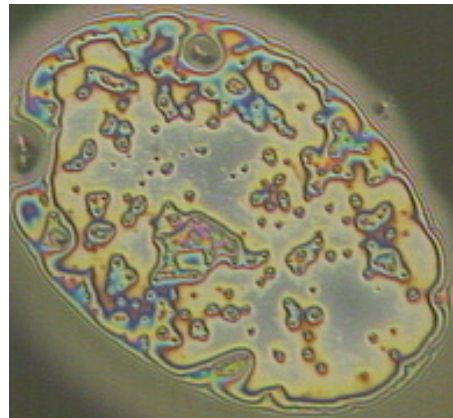


Origins of stability ?



Increasing the protein concentration →

casein
films



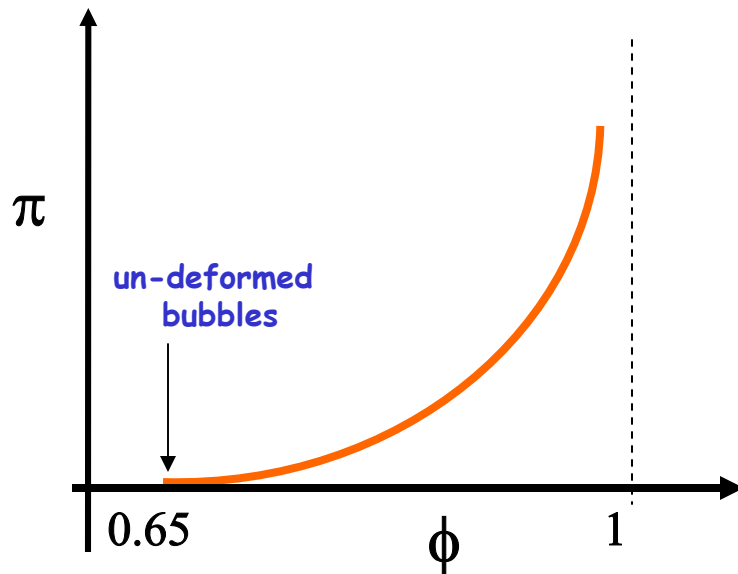
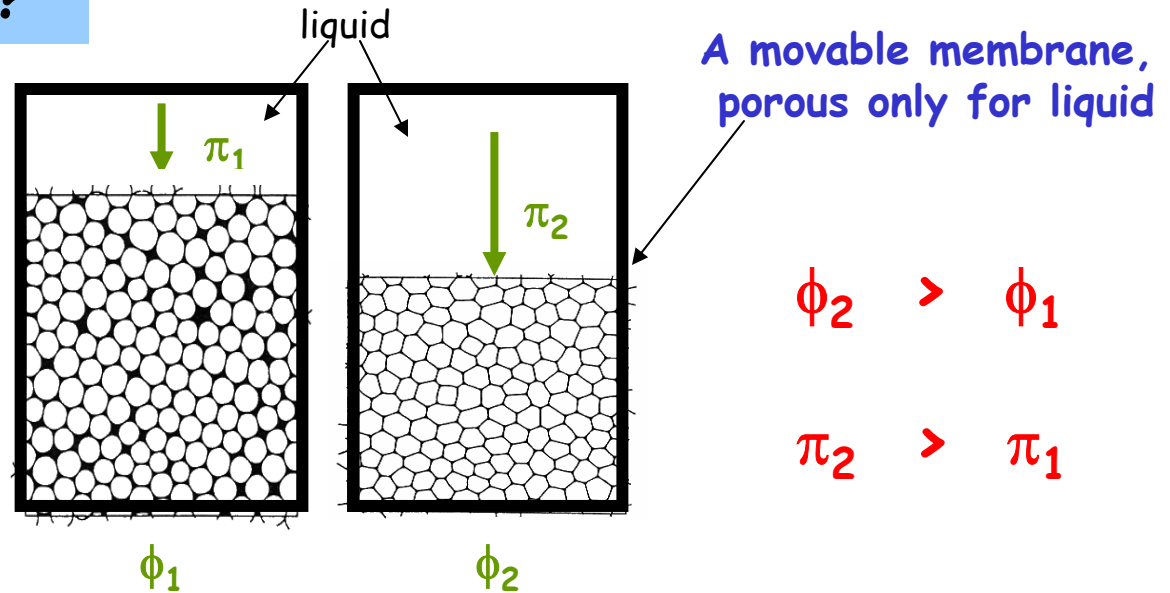
→
stability

osmotic pressure, π ?

Princen (1979)

$A(\phi) ? E(\phi) ?$

in analogy
with solutions...



$$\pi(\phi) = \frac{\gamma}{r} \phi^2 \frac{\partial}{\partial \phi} \left[\frac{A}{A_0} \right]$$