SURFACE SCIENCE: Introductory Lecture 4

Surface Forces, Colloid Stability & Wetting

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For Particle and Material Interfaces

The Wark™

Content

Part 1: Thermodynamics

- Fundamental Equation
- Work
- Free Energy
- Equilibrium

Fundamental Equation

The value of the internal energy, U [J], entirely defines the state of the system.

1st Law $\boxed{dU = dQ - dW}$

2nd Law $\boxed{dQ = TdS}$

The mechanical work done by the system, W [J], is calculated as :

$$dW = fdx = \frac{f}{A} Adx = PdV$$

The fundamental equation combines the two basic principles. It is the general energy balance:

Fundamental Equation $\boxed{dU = TdS - PdV}$

Work

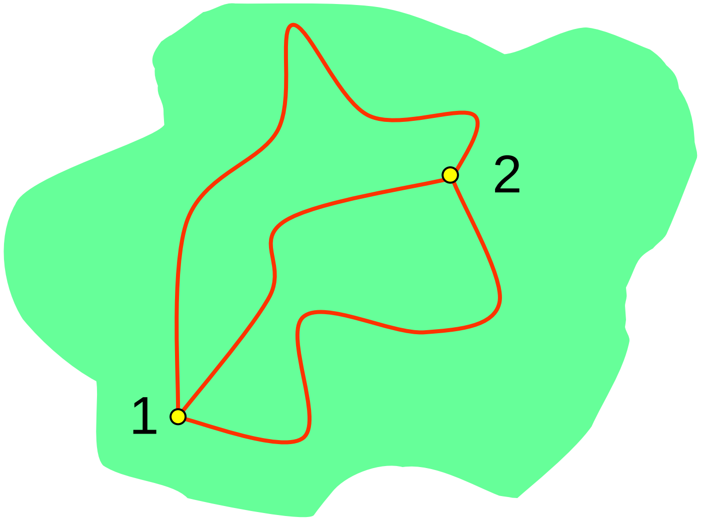
$$dU = \underbrace{TdS}_{\text{Heat}} - \underbrace{PdV}_{\text{Bulk Work}} + \underbrace{\gamma dA}_{\text{Surface Work}} + \underbrace{\mu dN}_{\text{Chemical Work}} - \underbrace{\varphi dq}_{\text{Electrical Work}} + \ldots$$

Generalized Forces (intensive parameters):

- T – temperature, K
- P – pressure, Pa
- γ – surface tension, J/m²
- μ – chemical potential, J/mol
- φ – electric potential, V

Generalized Coordinates (extensive parameters):

- S – entropy, J/K
- V – volume, m³
- A – surface area, m²
- N – number of moles, mol
- q – electric charge, C



The changes in internal energy are path-independent (not true for heat or work):

$$\oint dU = 0$$

Free Energy

<u>Helmholtz</u> Free Energy, *F*
<u>Gibbs</u> Free Energy, *G*

$$dU = TdS - PdV$$

→

$$F = U - TS$$
$$G = H - TS$$

→

$$dF = -SdT - PdV$$
$$dG = -SdT + VdP$$

The free energy change gives the maximum work obtainable from the system:

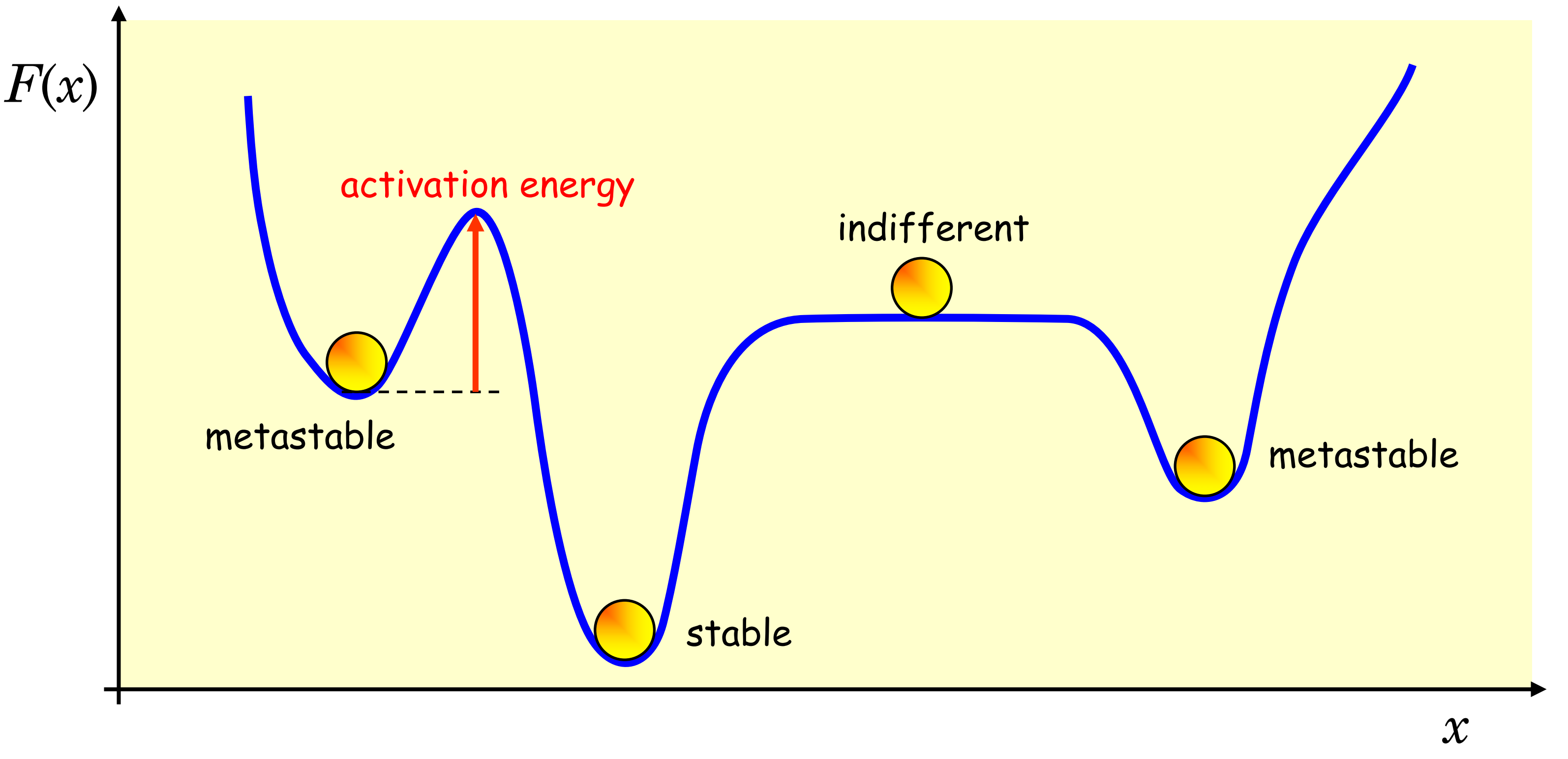
$$(dF)_T = -PdV = dW_{max}$$
$$(dG)_T = VdP = dW_{max}$$

Equilibrium Condition

$$(dF)_{T,V} = 0 \Leftrightarrow F \rightarrow \min$$
$$(dG)_{T,P} = 0 \Leftrightarrow G \rightarrow \min$$

At equilibrium the free energy is at minimum

Equilibrium

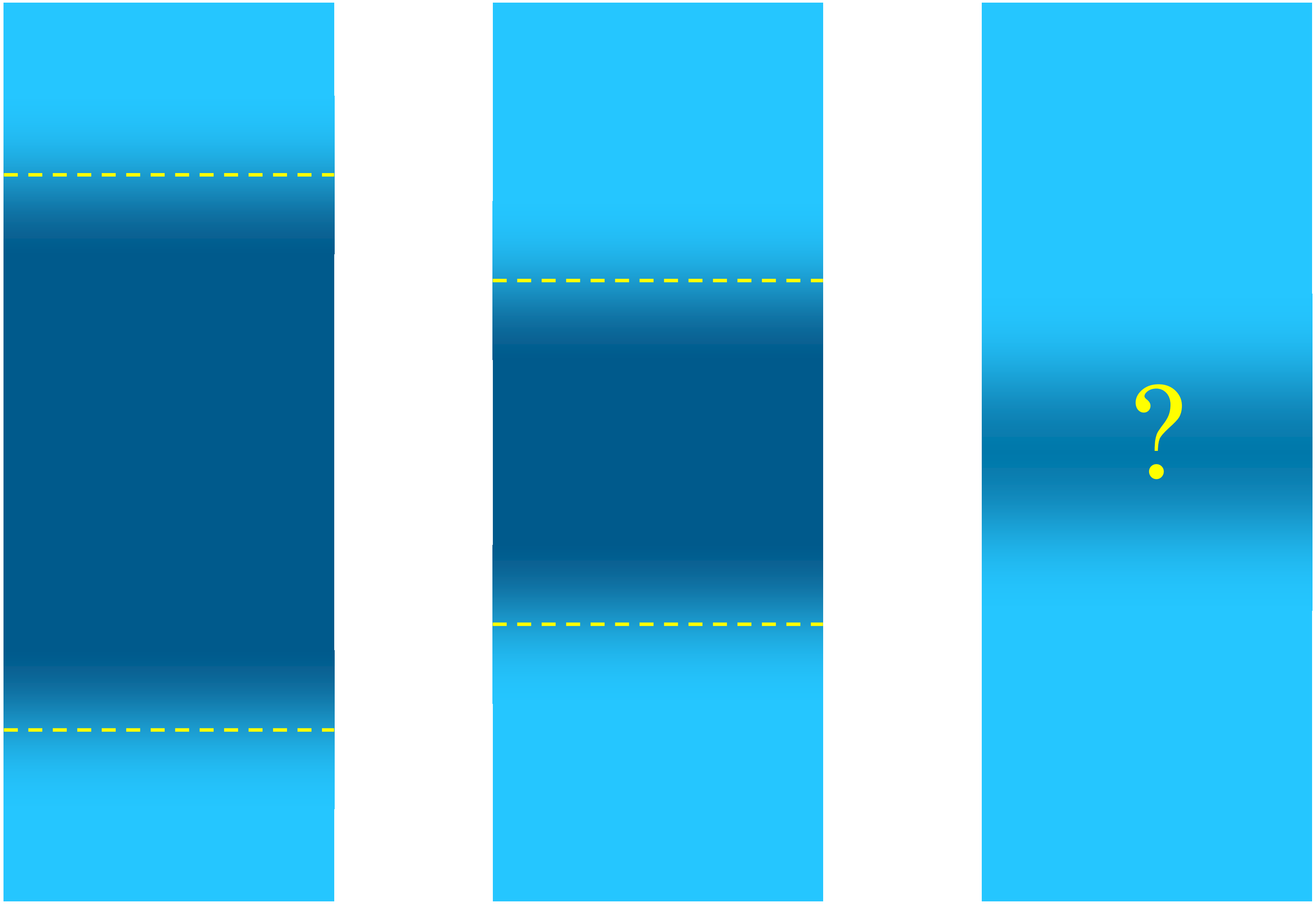


Stable equilibrium – <u>global</u> minimum of *F*
Metastable equilibrium – <u>local</u> minimum of *F*
Activation energy, ΔF, required for a transition between metastable states

Part 2: Surface Forces

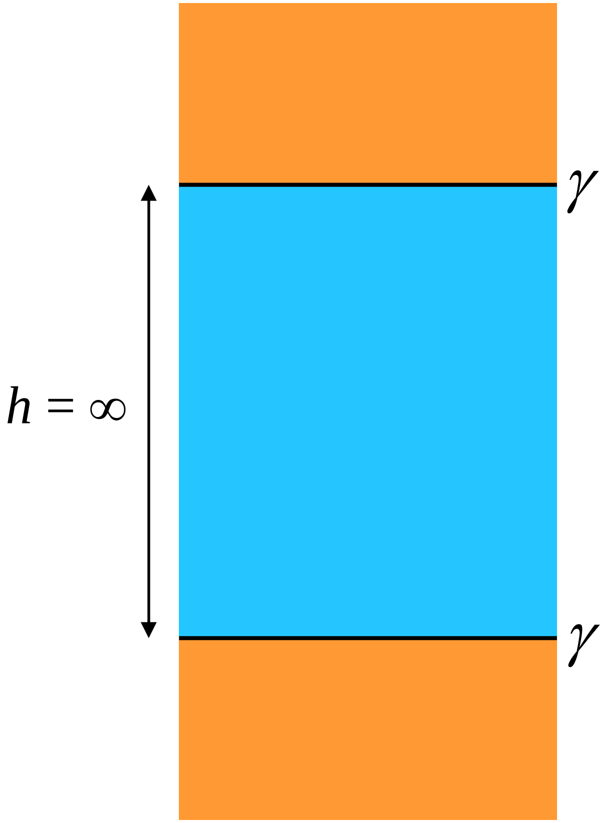
- Thin Liquid Films
- Disjoining Pressure
- Colloidal Stability
- Measurement

Two Interfaces



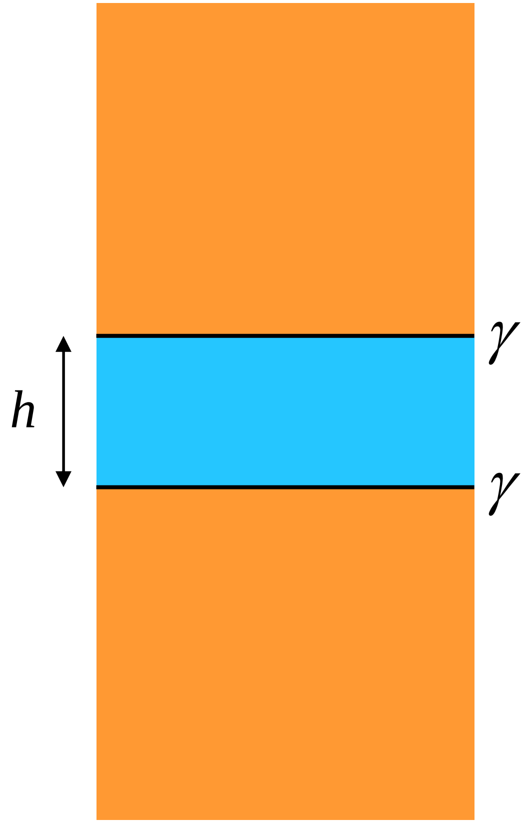
A Liquid Film – Tick or Thin?

independent interfaces = thick film



$$f = 2\gamma$$

Interacting interfaces = thin film



$$f = 2\gamma + f_{\mathrm{interaction}}$$

Disjoining Pressure (Surface Force)

The interaction between the two interfaces is given by the disjoining pressure, Π:

$$\Pi = P(h) - P(\infty)$$

The interaction between the two interfaces can be discussed in terms of disjoining pressure (force per unit area) or, alternatively, free energy (per unit area):

Pressure

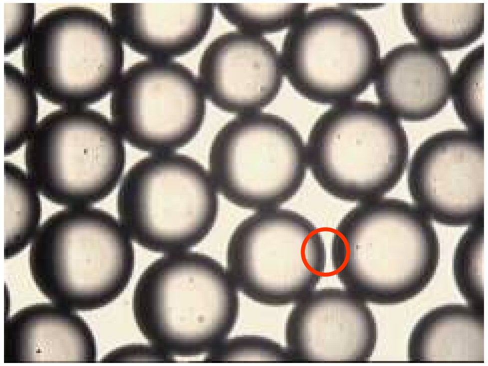
$$\Pi = -\left(\frac{\partial f}{\partial h}\right)_{T,V,\mu_i}$$

Energy

$$f = -\int_{\infty}^{h} \Pi \, dh$$

Film Stability vs. Colloid Stability

Emulsion

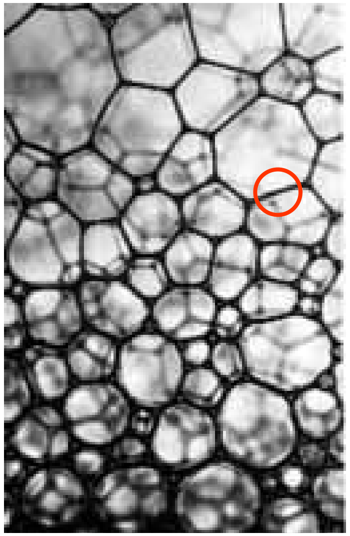


oil

water

oil

Foam

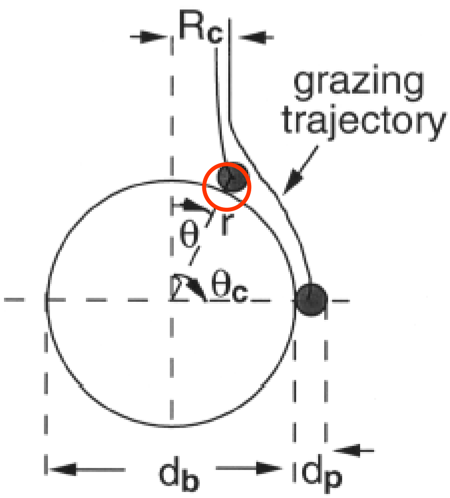


vapour

water

vapour

Flotation



vapour

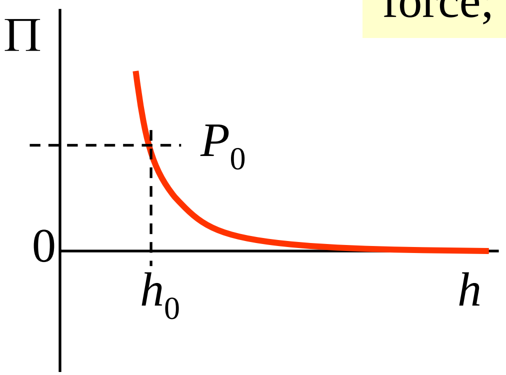
water

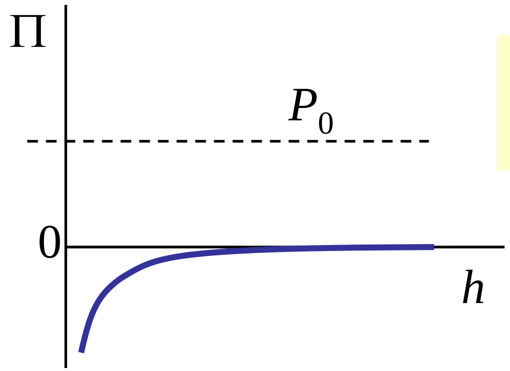
quartz

The stability of colloidal systems is intrinsically related to the stability of the films.

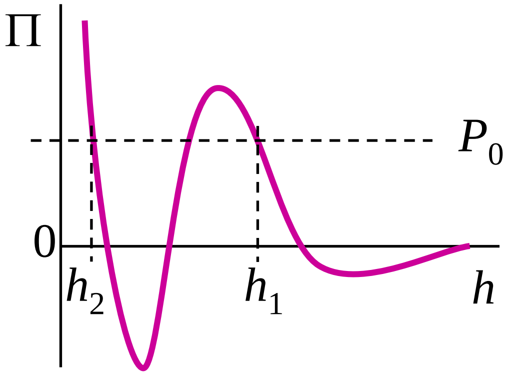
Film Stability & Disjoining Pressure

As the interfaces approach each other they experience a repulsive force; the film will be stable (thickness h_0 at pressure P_0).



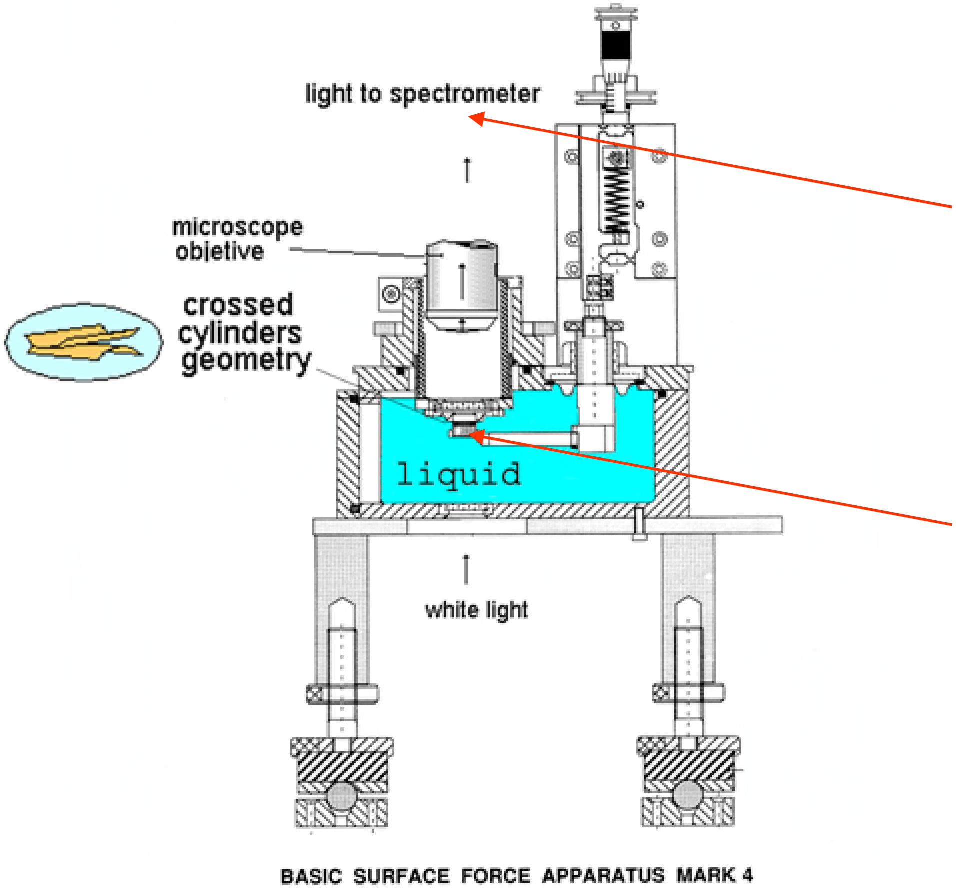


If there is attraction the film will be unstable.



Real systems are more complicated; e. g. films with thickness h_1 will be metastable and in time jump to the stable thickness h_2.

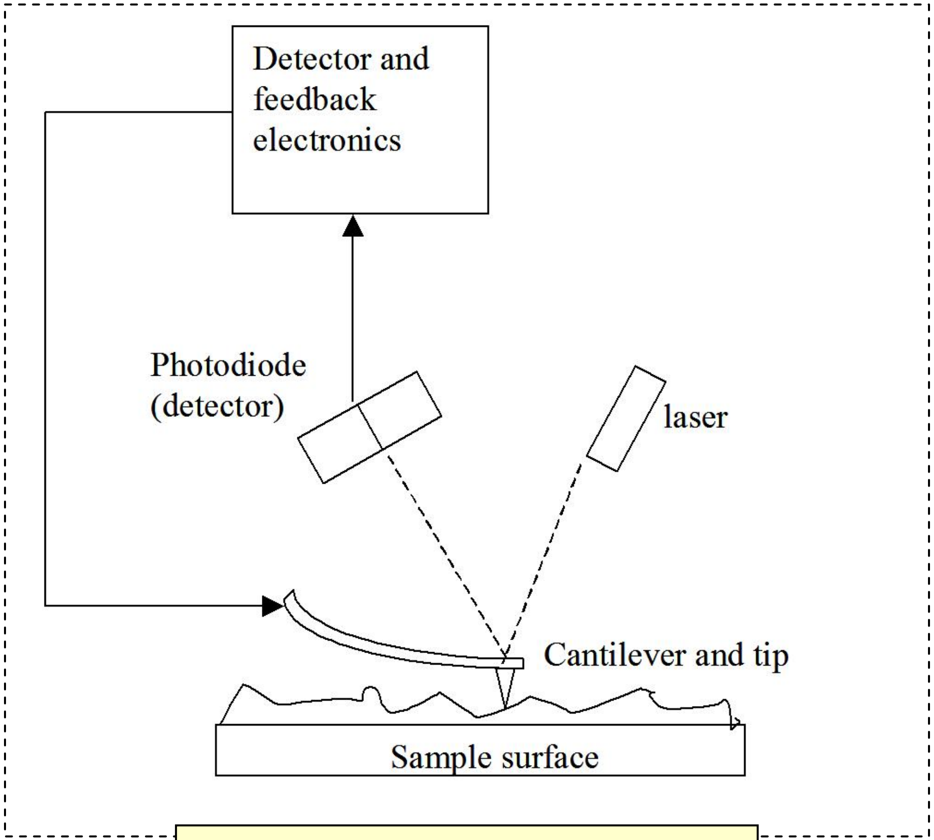
Surface Force Apparatus



Distance (Film Thickness) is determined by interferometry; resolution is about 0.1 nm.

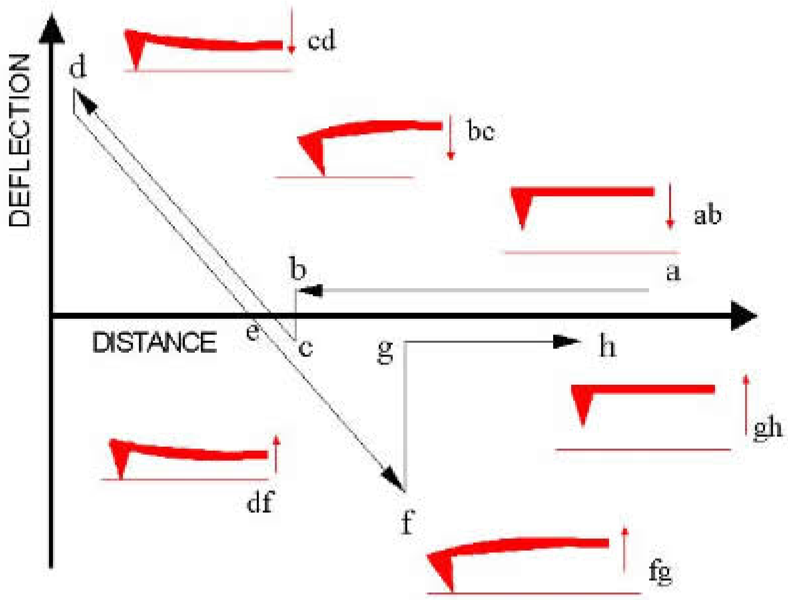
Force is obtained from the elastic deformation of a cantilever spring; sensitivity is about 10 nN.

Colloid Probe Microscopy

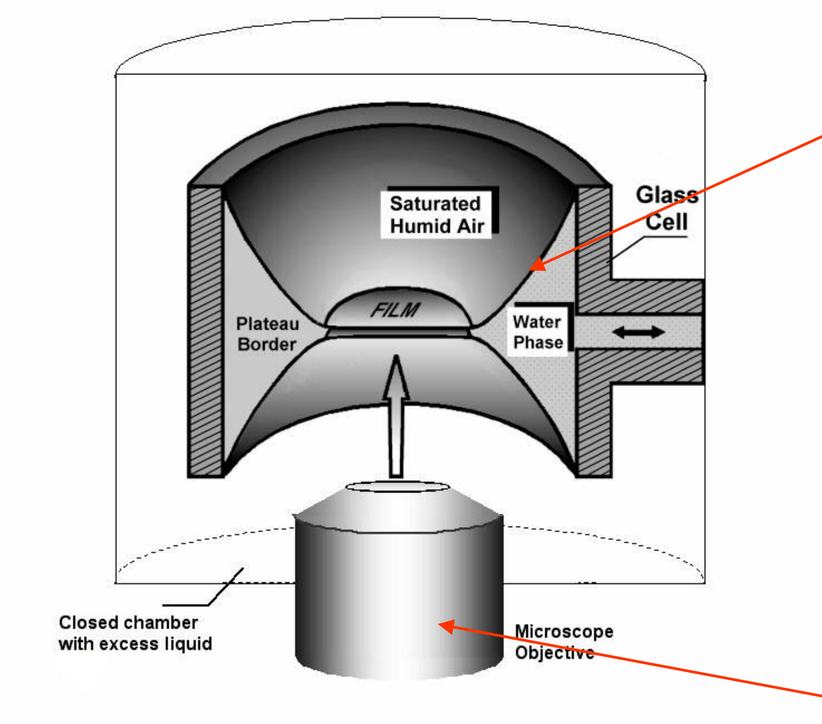


Atomic Force Microscope

The force between the tip and the surface (0.01 – 100 nN) leads to a deflection of the cantilever.



Thin Film Balance



The pressure in the film is set by the capillary pressure of the meniscus (e.g. 10-100 Pa; a version with a porous plate allows up to 100 kPa).

Film Thickness is determined by interferometry; resolution is about 0.1 nm.

Part 3: DLVO Theory

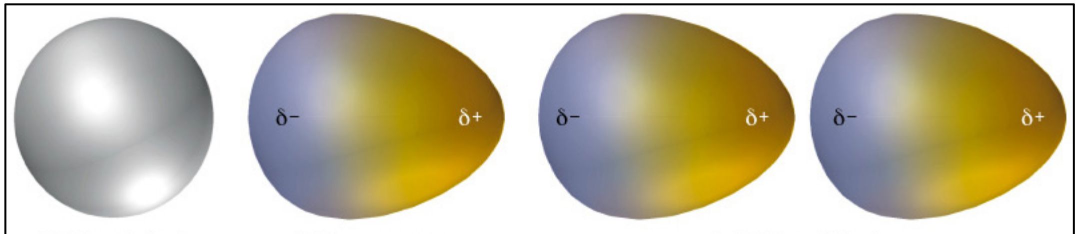
- Additivity
- van der Waals component
- electrostatic component

Disjoining Pressure Components

The disjoining pressure can be split into two components:

$$\Pi = \Pi_{VW} + \Pi_{EL}$$

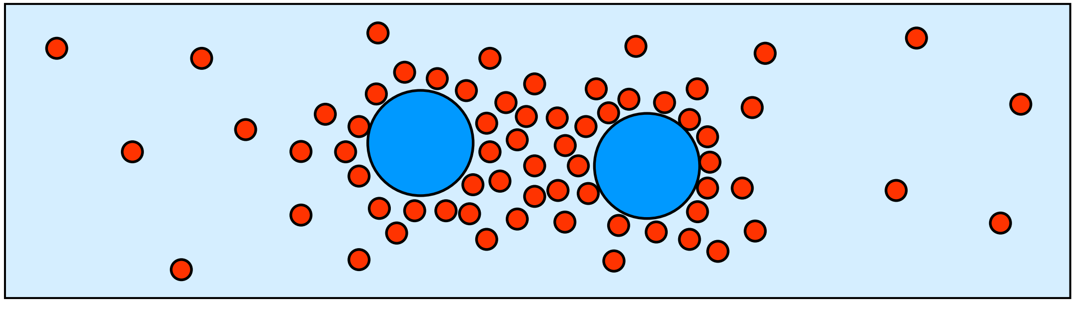
• van der Waals component (Π_{VW}): electromagnetic interactions between any two bodies



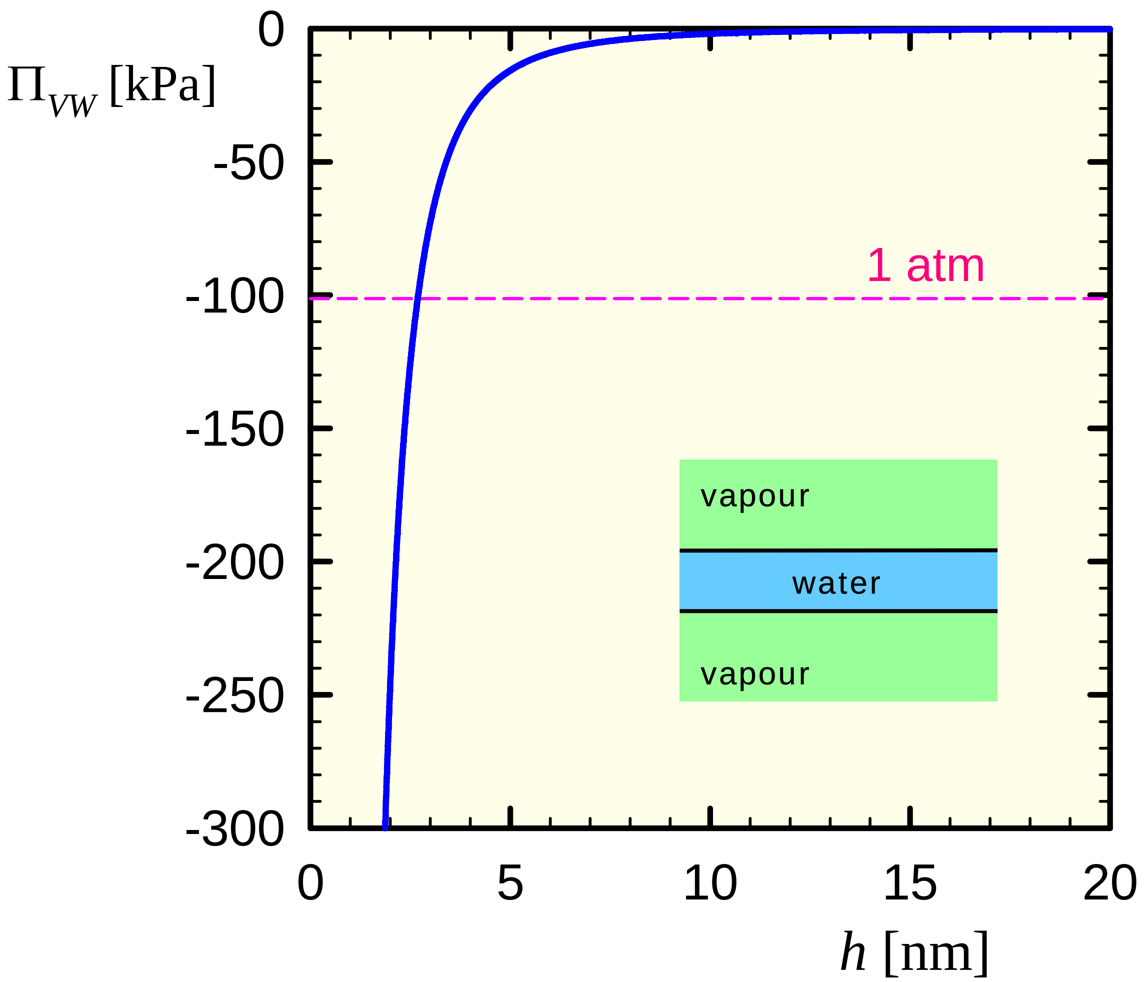
(a) Unpolarized molecule **(b)** Instantaneous dipole **(c)** Induced dipole

Hill & Petrucci (2002)

• Electrostatic component (Π_{EL}): repulsion between the diffuse double layers



van der Waals Attraction

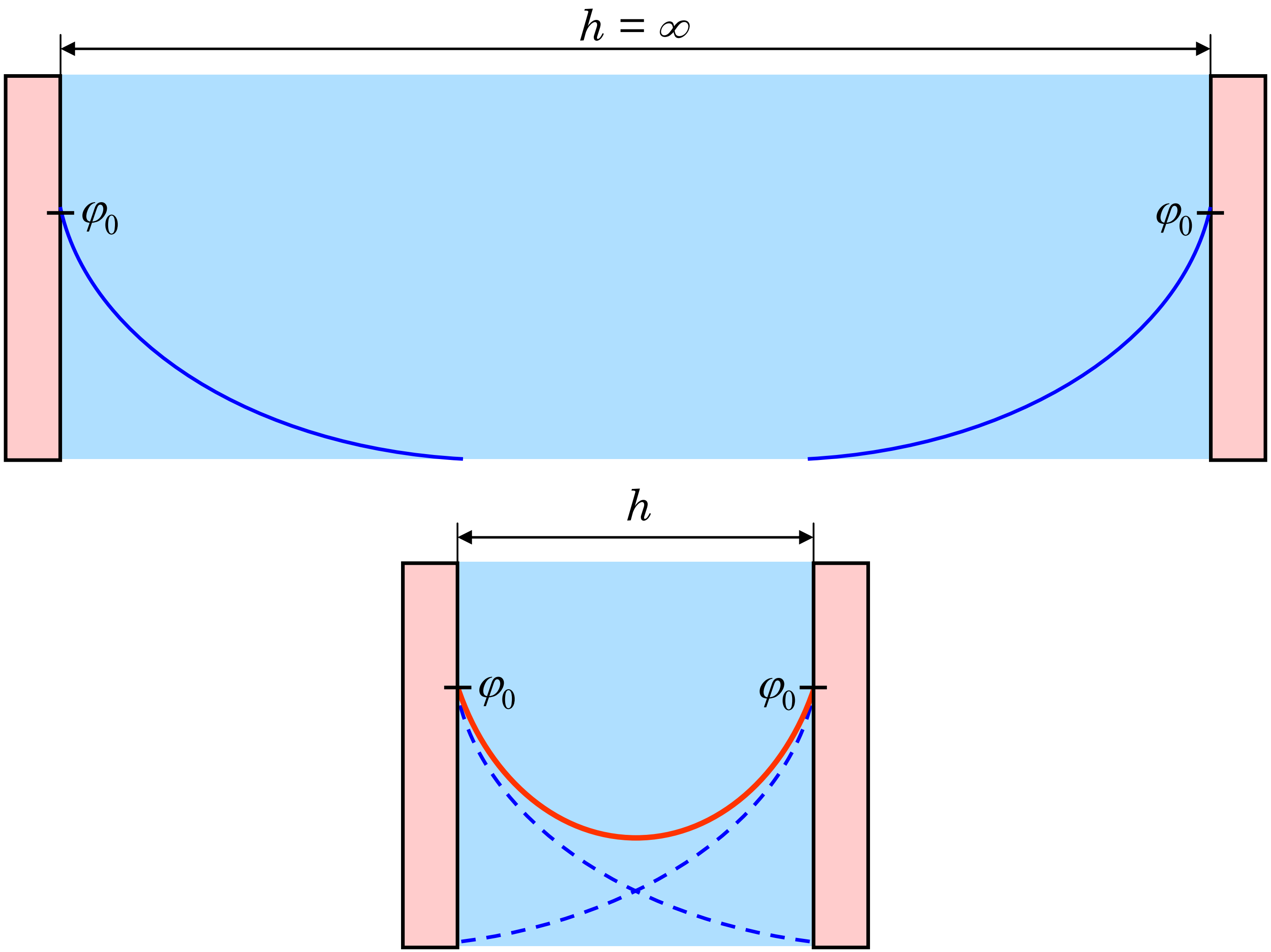


Hamaker Constant

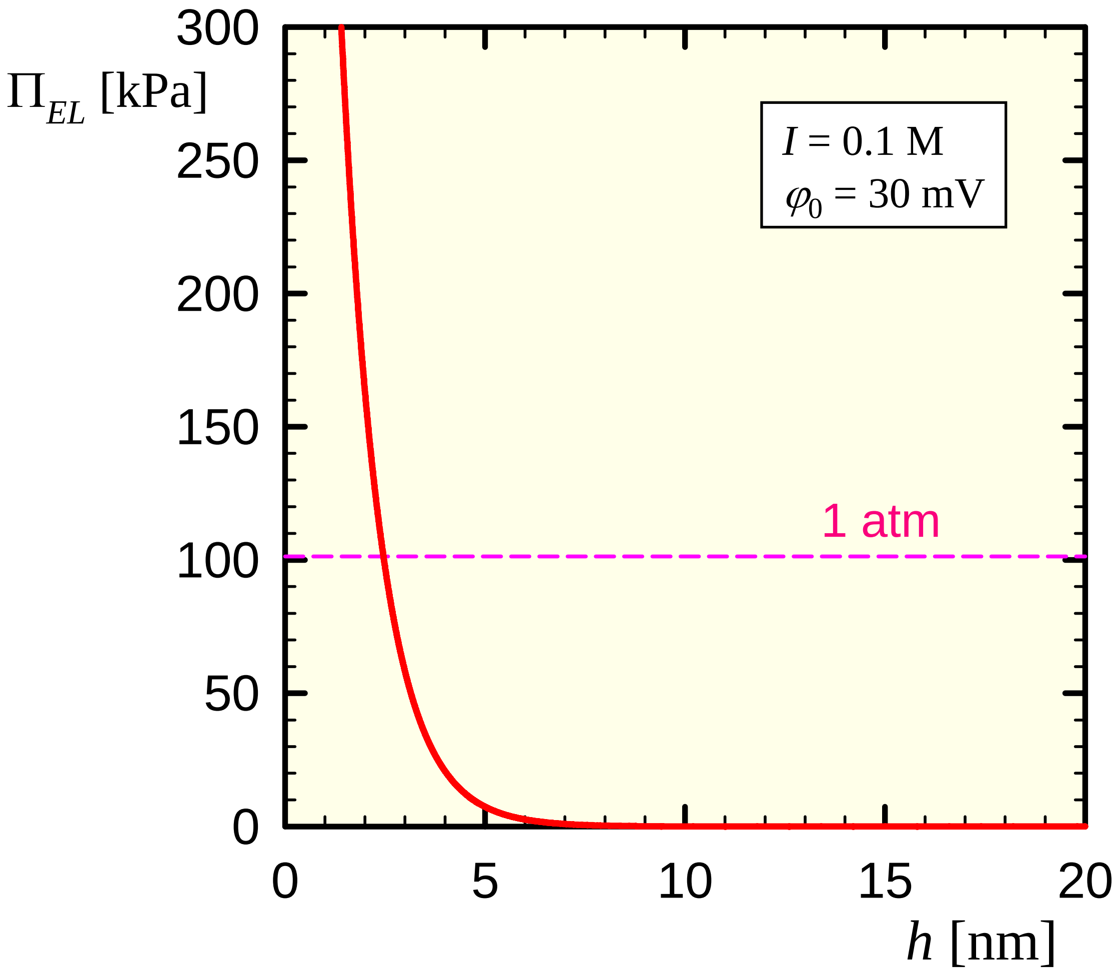
$$\Pi_{VW} = -\frac{A}{6\pi h^3}$$

$$A \sim 10^{-20}\ \mathrm{J}$$

Overlapping Double Layers



Electrostatic Repulsion



$$\Pi_{EL} = 64 n_0 k_B T y^2 e^{-\kappa h}$$

$$y = \tanh \frac{z e \varphi_0}{4 k_B T}$$

$$\kappa^{-1} = \frac{1}{ze} \left(\frac{\varepsilon \varepsilon_0 k_B T}{2 n_0} \right)^{1/2}$$

The DLVO Theory

The Derjaguin-Landau-Vervey-Overbeek (DLVO) theory explains the stability of colloids by combining van der Waals & electrostatic interactions only:

$$\Pi = \Pi_{VW} + \Pi_{EL}$$

For a symmetric system the van der Waals interaction is always attraction and the electrostatic interaction is always repulsion.

$$\Pi = -\frac{A}{6\pi h^3} + 64 n_0 k_B T \tanh^2 \frac{ze\varphi_0}{4k_B T} e^{-\kappa h}$$

$$F = -\frac{A}{12\pi h^2} + \frac{64 n_0 k_B T}{\kappa} \tanh^2 \frac{ze\varphi_0}{4k_B T} e^{-\kappa h}$$

Part 4: Non-DLVO Forces

- Steric Forces
- Structural Forces
- Hydrophobic Forces

Disjoining Pressure Components

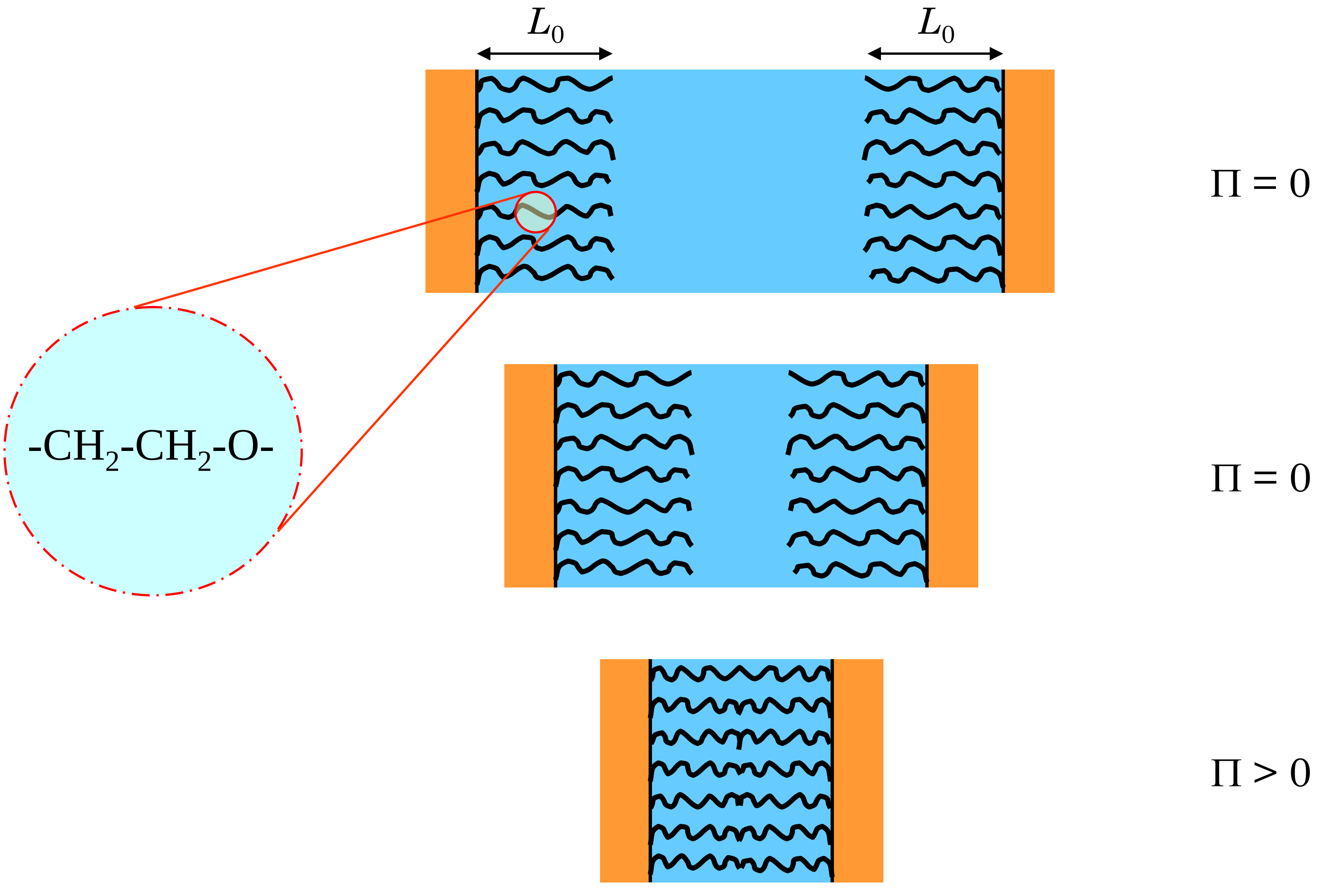
$$\Pi = \underbrace{\Pi_{VW} + \Pi_{EL}}_{\text{DLVO}} + \Pi_{ST} + \Pi_{H} + \ldots$$

- **Steric Repulsion** (Π_{ST}): excluded volume for tethered polymer chains (the grafted chains are "protecting" the surfaces from reaching each other);

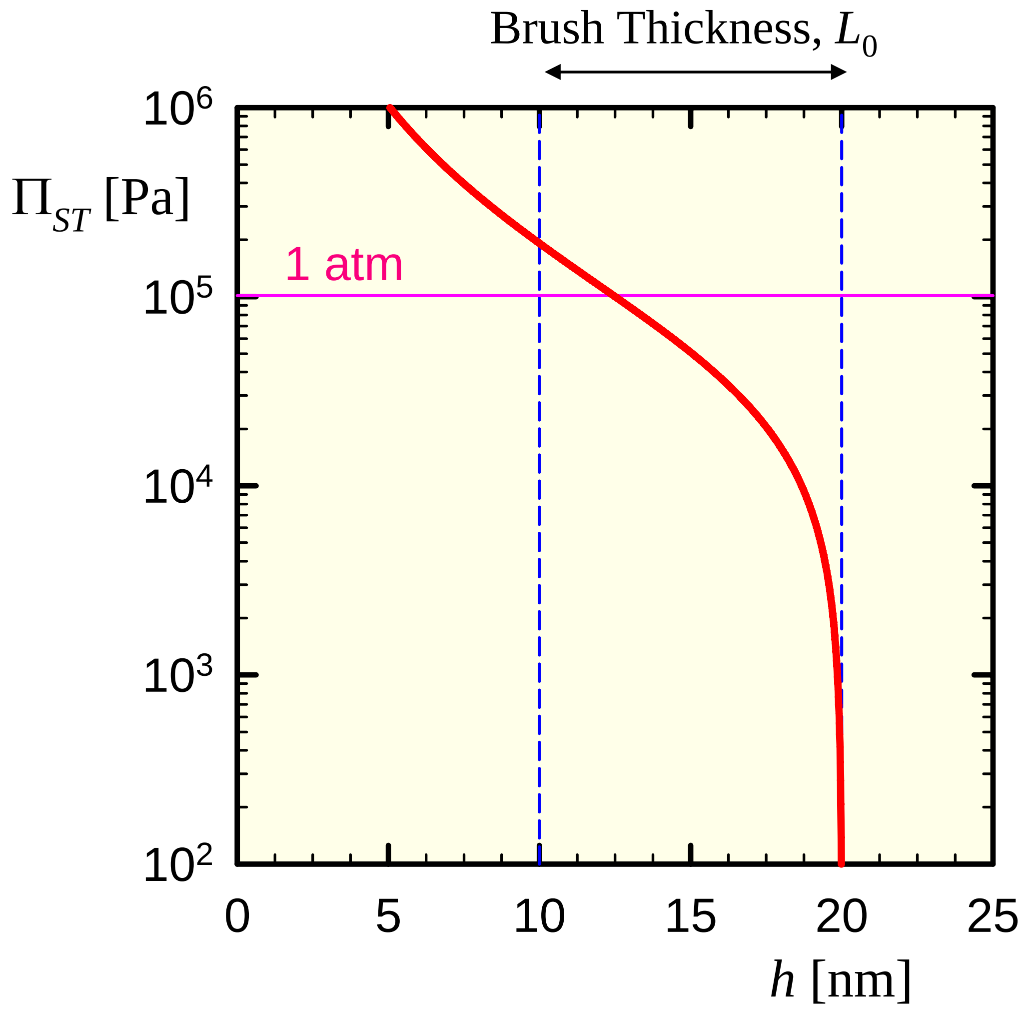
- **Hydration repulsion** (Π_{H}): repulsion between structured solvent layers near the interface (the solvent "loves" the solid surface);

- **Hydrophobic attraction** (Π_{HB}): attraction between hydrophobic surfaces (the solvent "dislikes" the solid surface).

Steric Repulsion



Brush-to-Brush Repulsion

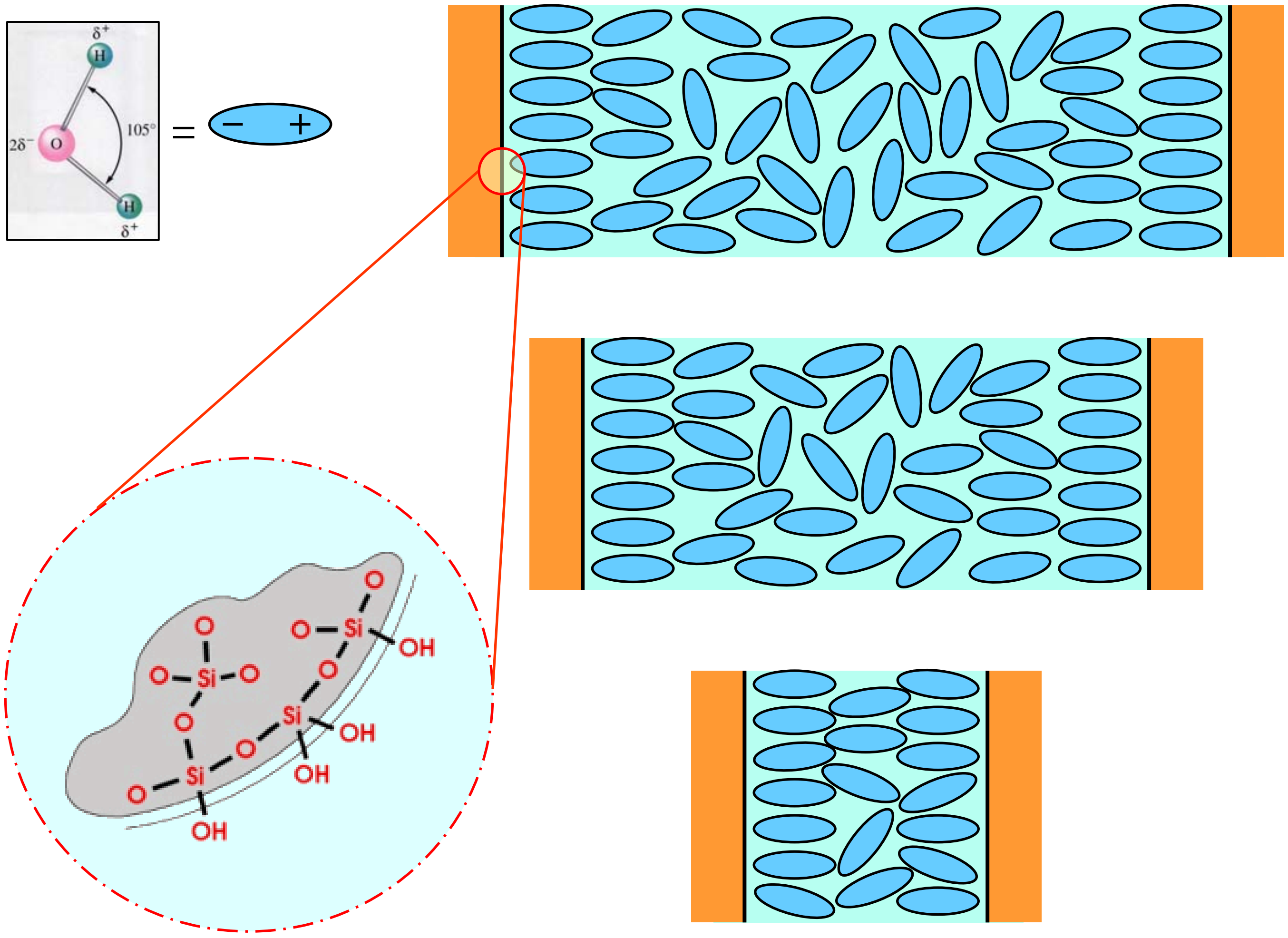


$$\Pi_{ST} = \frac{k_B T}{A^{3/2}}\left(H^{-9/4} - H^{3/4}\right)$$

$$H = \frac{h}{2L_0}$$

de Gennes (1987)

Hydration Repulsion

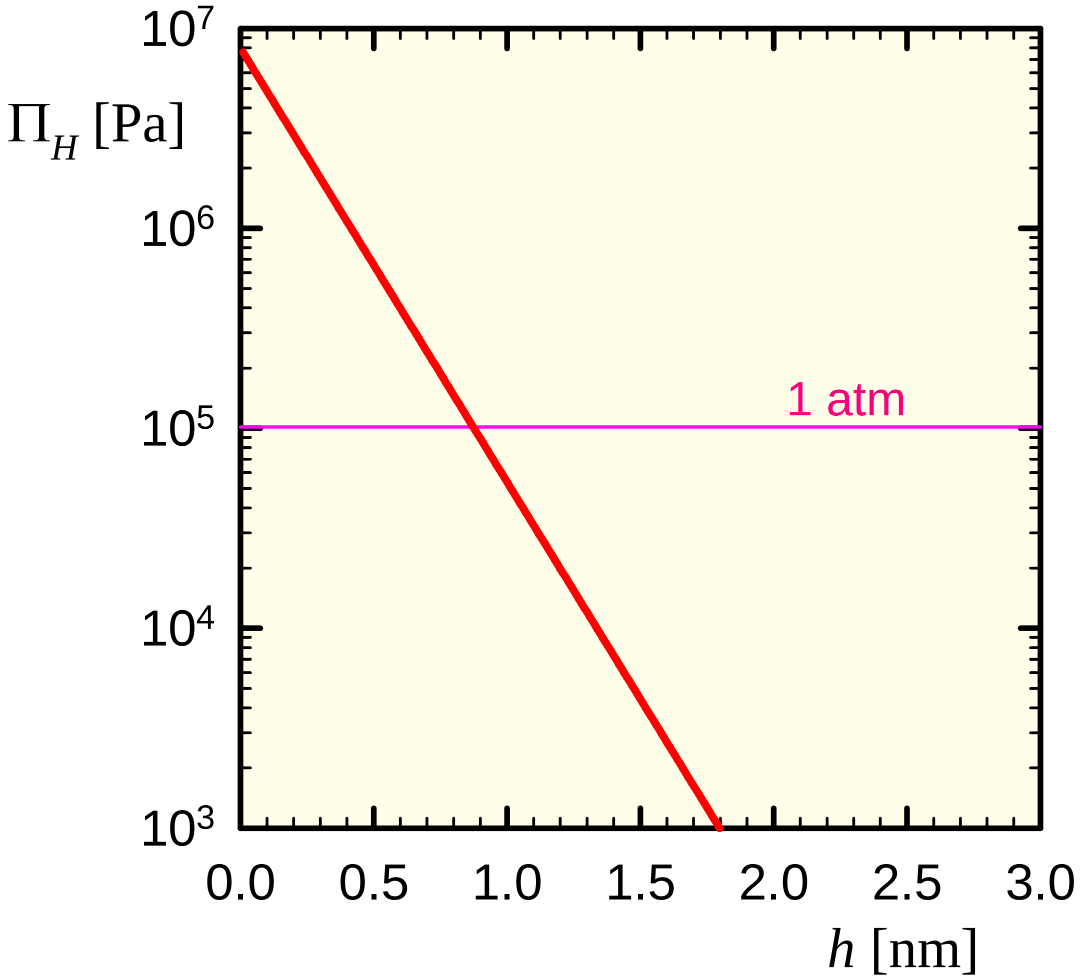


$\Pi = 0$

$\Pi = 0$

$\Pi > 0$

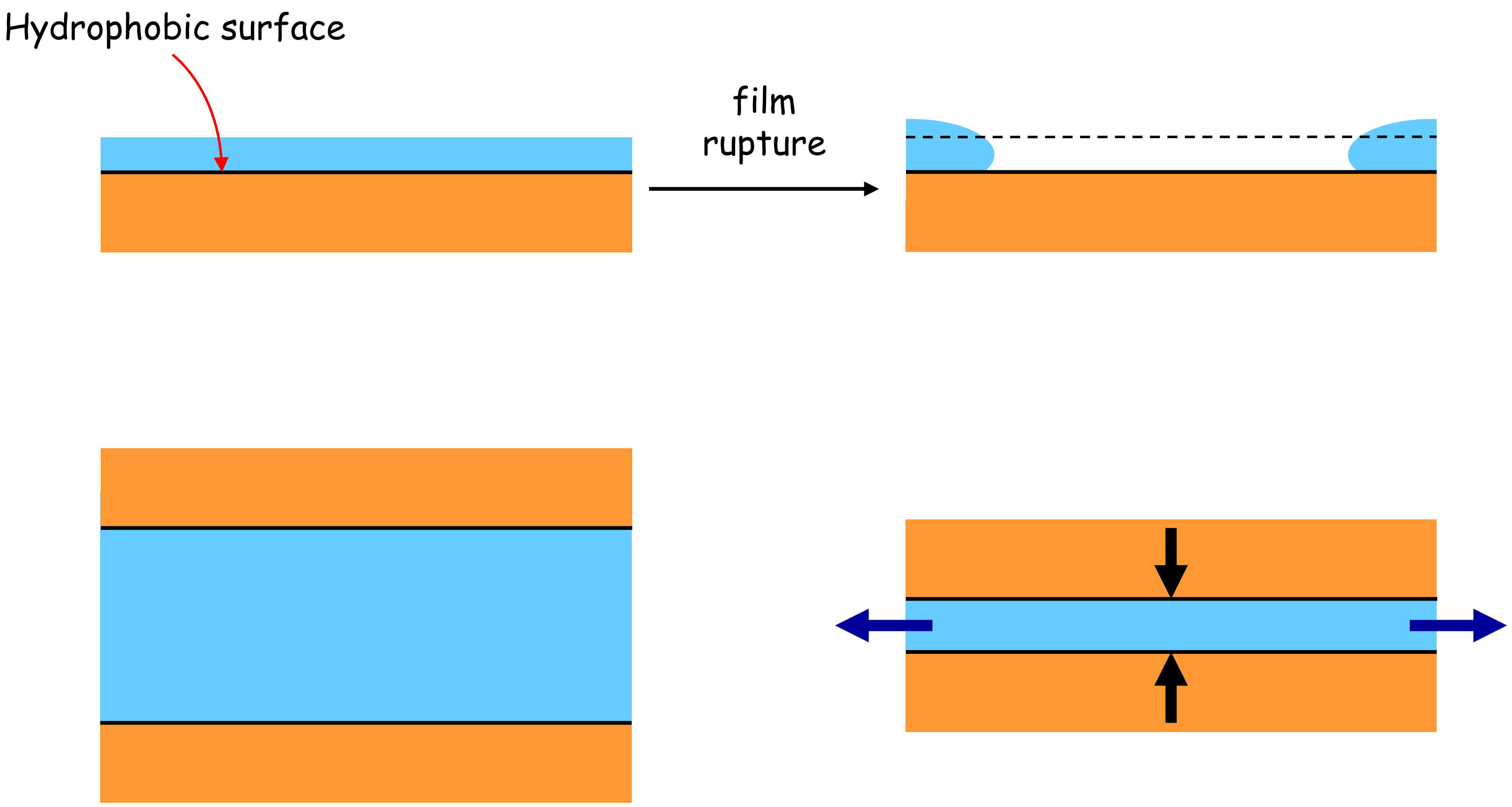
Hydration Force



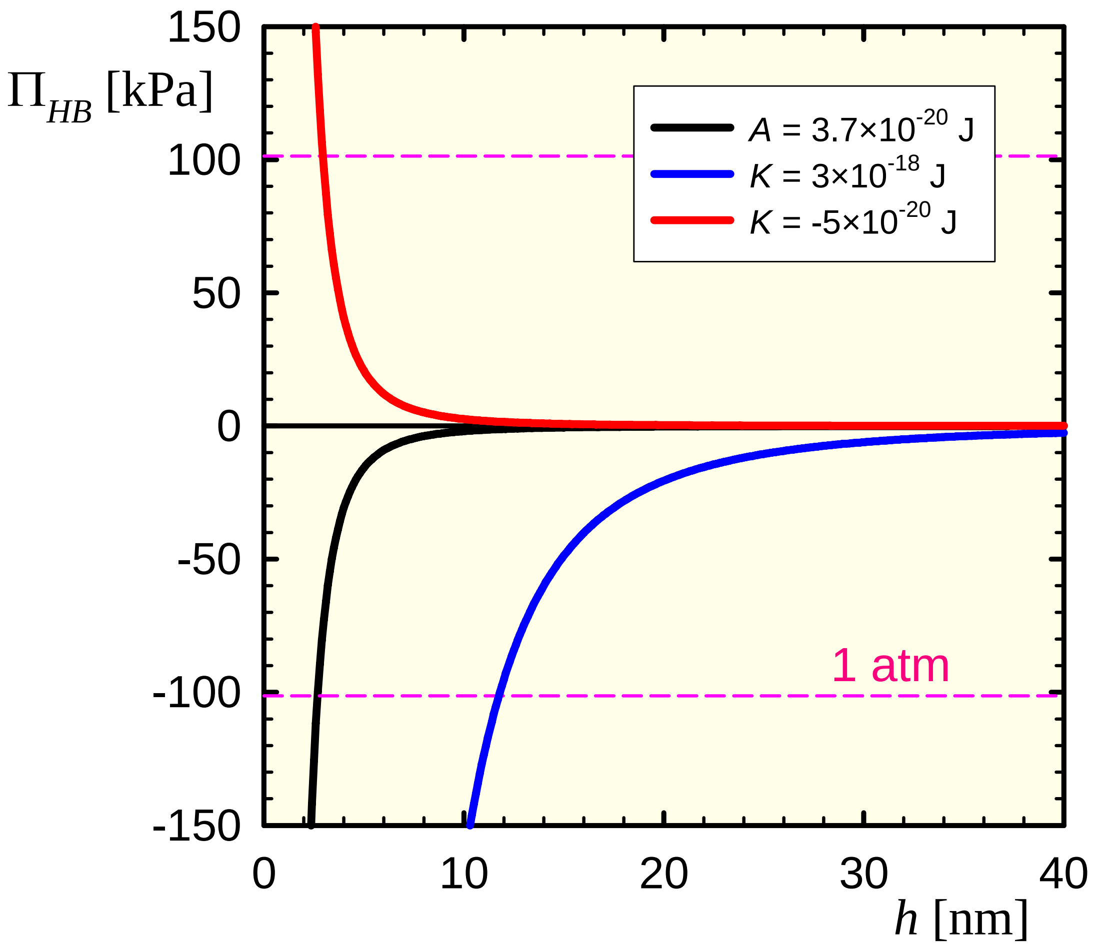
$$\Pi_H = A_H \exp\left(-\frac{h}{\lambda_H}\right)$$

$\lambda_H \sim$ 1-3 Å

Hydrophobic Attraction



Hydrophobic Force



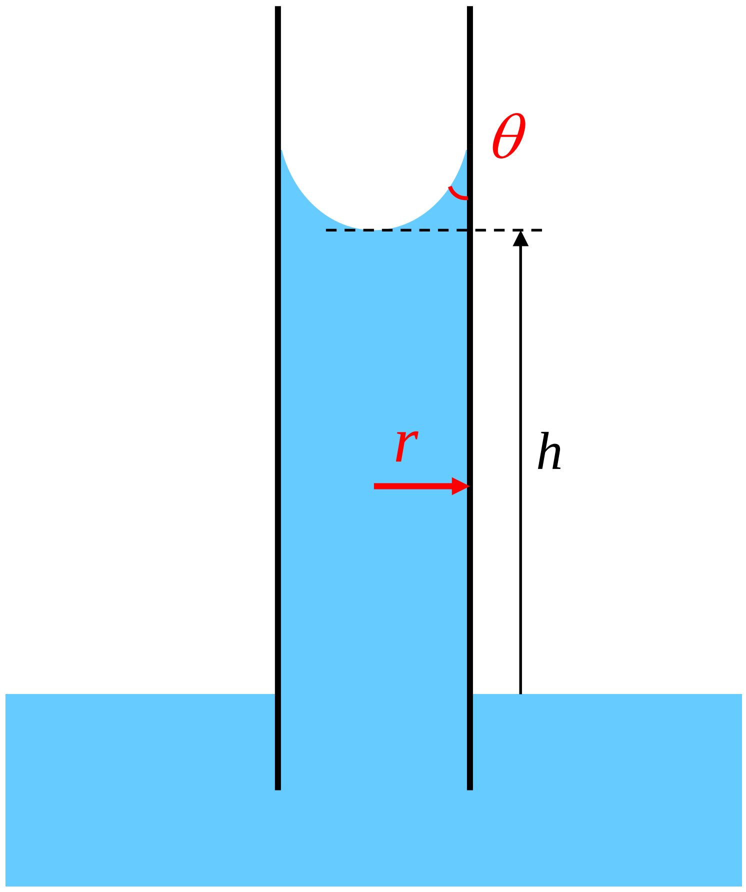
$$\Pi_{HB} = -\frac{K}{6\pi h^3}$$

$|K| \sim 10^{-18}$ J

Part 5: Wettability

- Capillarity
- Contact Angle
- Cohesion & Adhesion

Capillary Rise



Force balance:

$$P_{\text{capillary}} = P_{\text{hydrostatic}}$$

Surface Tension

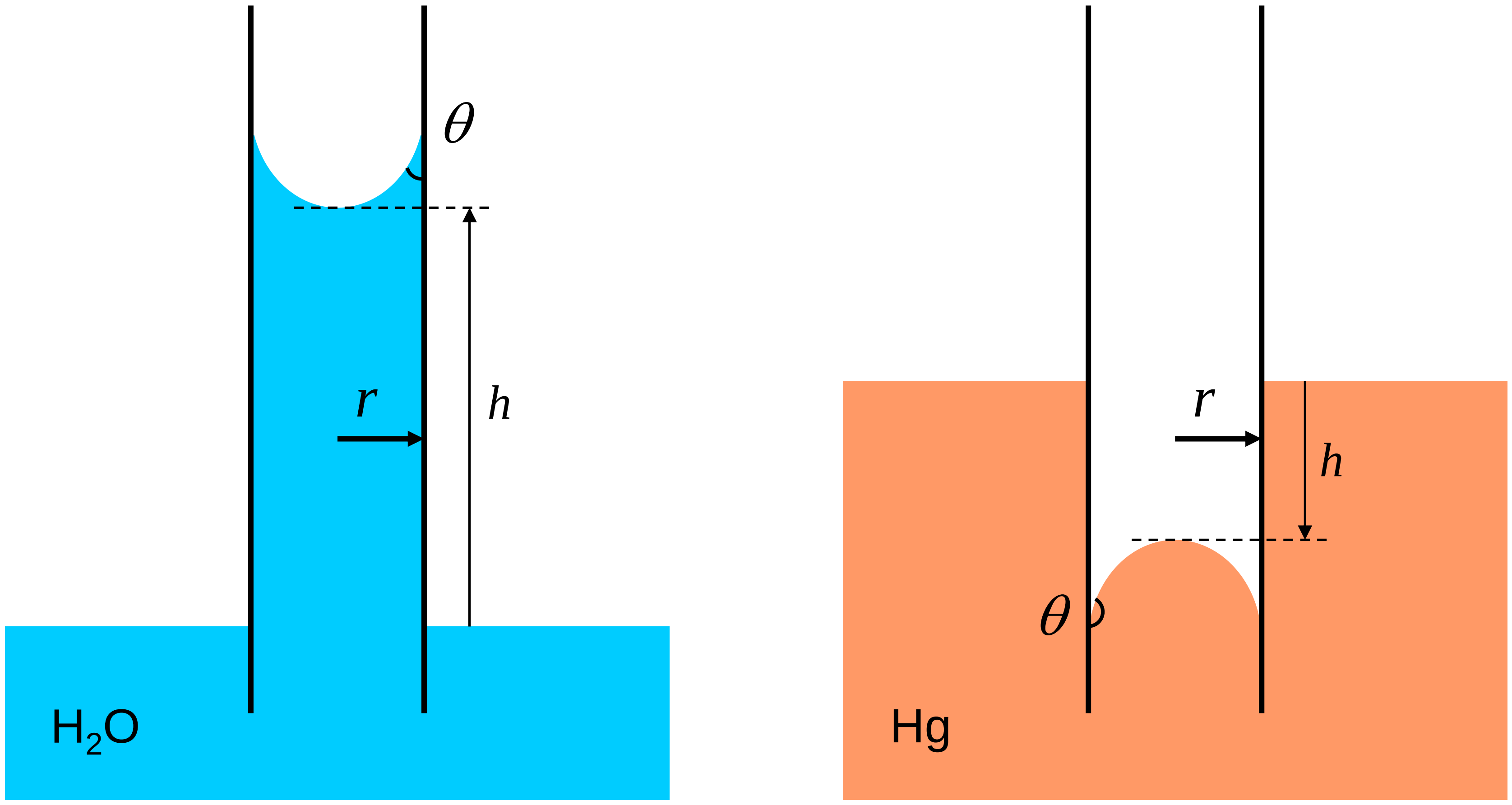
Gravity

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

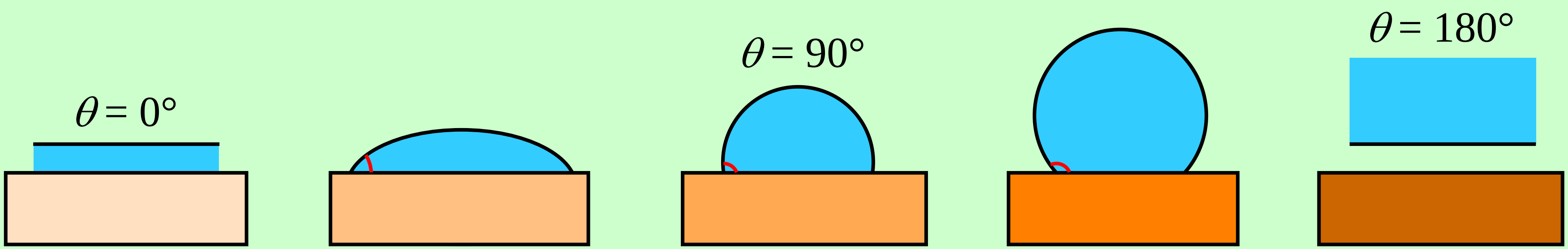
Contact Angle

Density

Capillary Rise & Capillary Depression



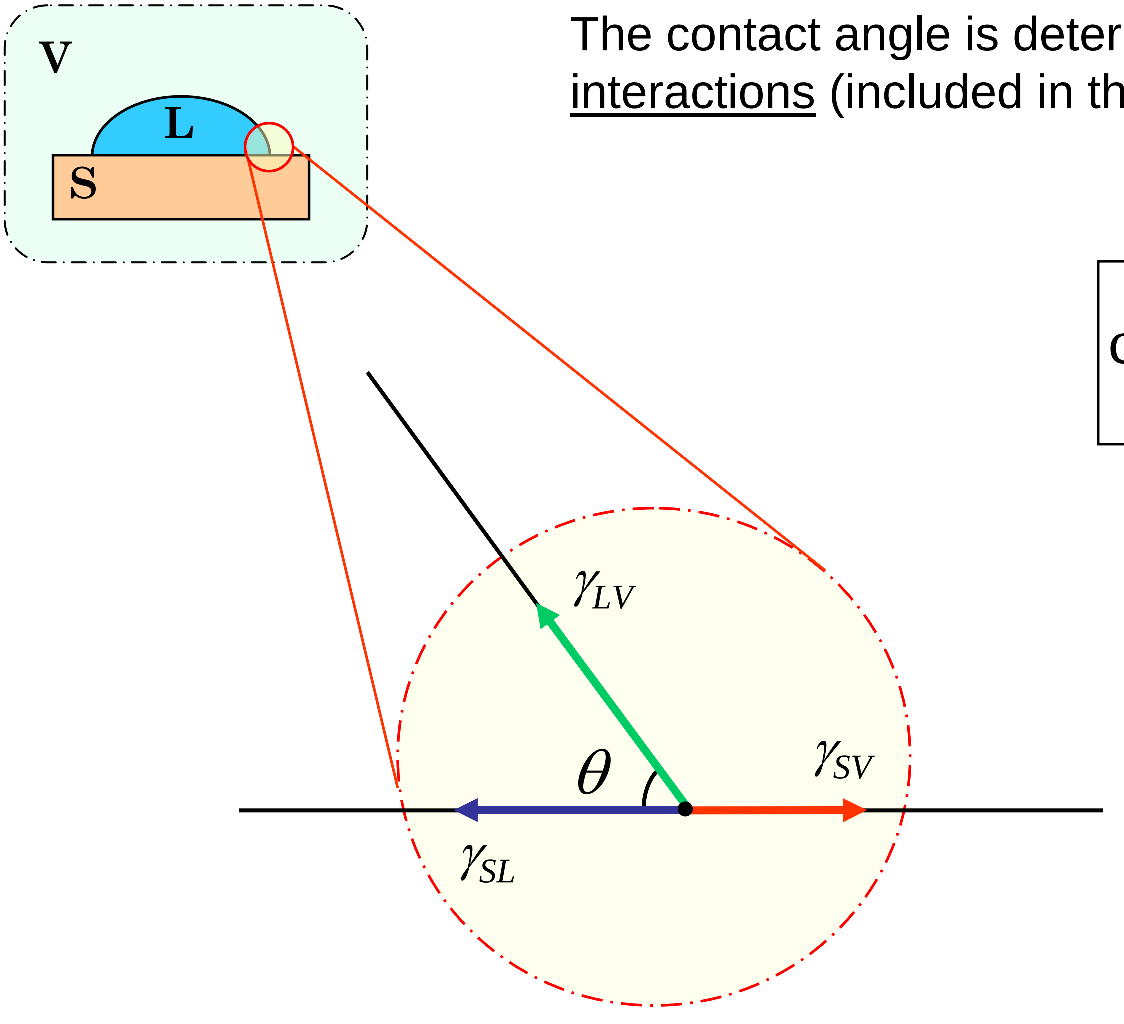
Contact Angle – A Measure of Wettability



Hydrophobicity →

Adhesion ←

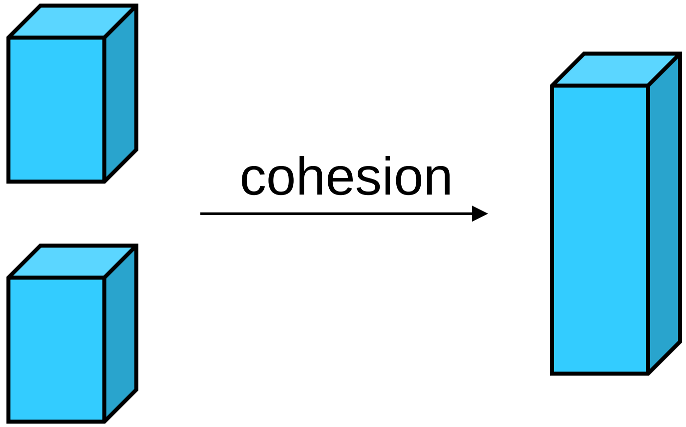
Young Equation



The contact angle is determined by intermolecular interactions (included in the gammas):

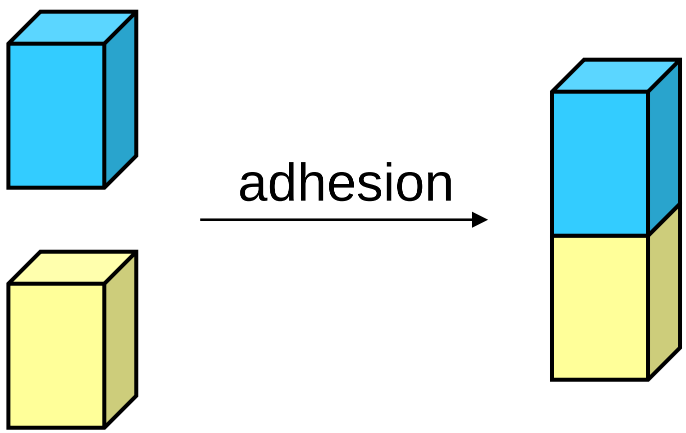
$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Cohesion & Adhesion



Work of Cohesion:

$$W_C = \gamma_{LV} + \gamma_{LV} - 0 = 2\gamma_{LV}$$



Work of Adhesion:

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$$

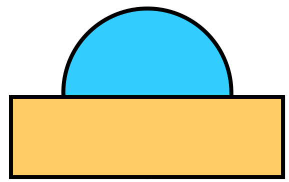
Wettability & Adhesion

$$W_A = \gamma\left(1 + \cos\theta\right)$$

$\theta_0 = 0 \Leftrightarrow W_A = 2\gamma$

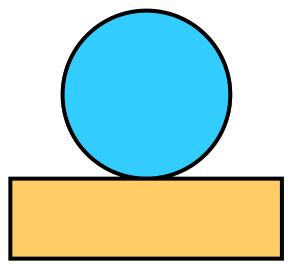
Maximum adhesion

$\theta_0 = 90^\circ \Leftrightarrow W_A = \gamma$



Intermediate adhesion

$\theta_0 = 180^\circ \Leftrightarrow W_A = 0$



Minimum adhesion

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