

Interfacial Tension, Capillarity and Surface Forces

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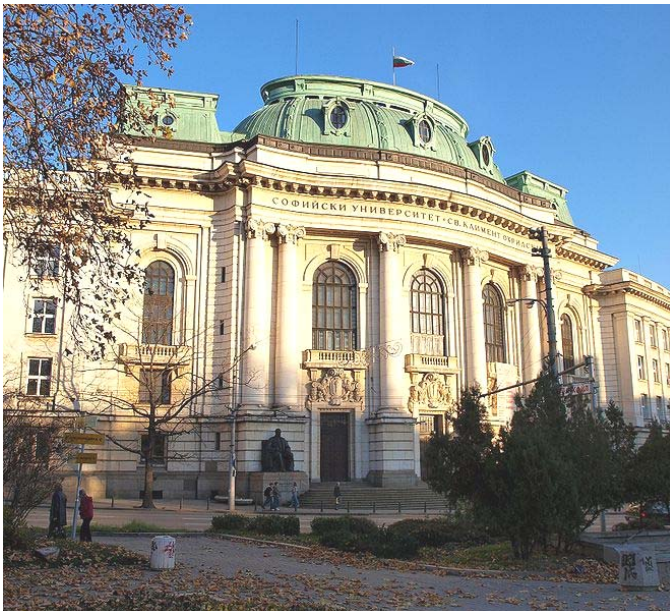
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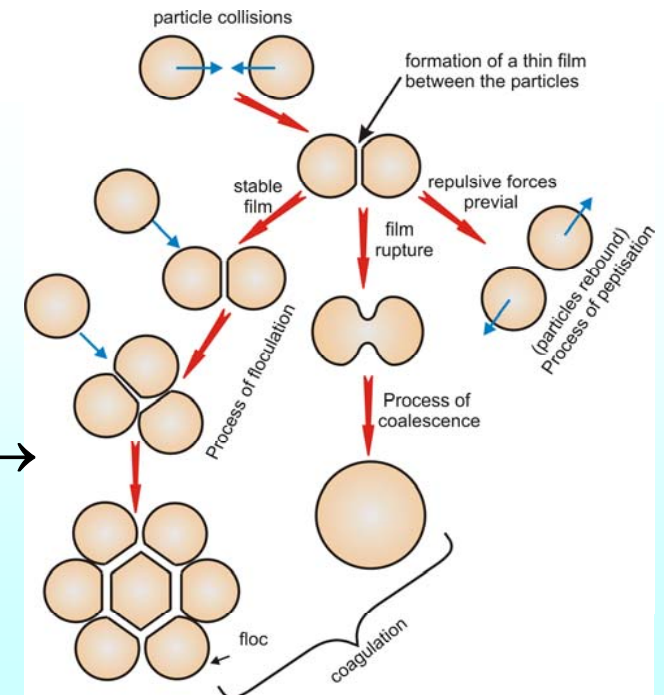
“Physics of droplets: Basic and advanced topics”

Borovets, Bulgaria, 12–13 July, 2010



← Sofia University

Scenarios for
drop – drop
interactions
in view of
the acting
surface forces →



Molecular Origin of Surface Tension



energy = $u_{AA} < 0$

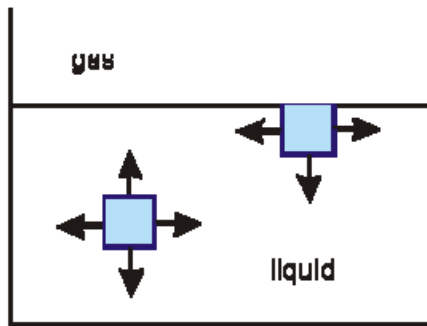


energy = 0

The molecules **attract** each other by **van der Waals forces**:
Interaction energy: u_{AA}

The molecules **at the surface** have **one neighbor less**.

Because of the formation of surface, **the energy of the system increases** with:



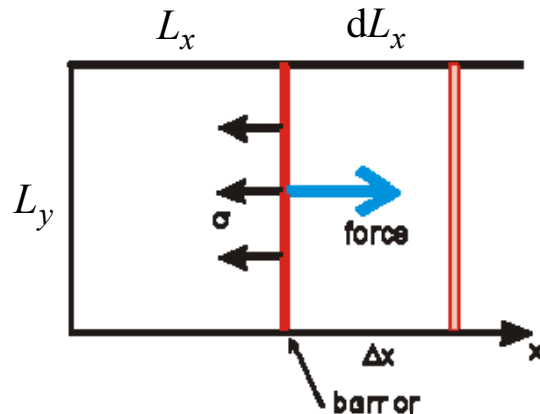
$$W = |u_{AA}| \Gamma L_x L_y$$

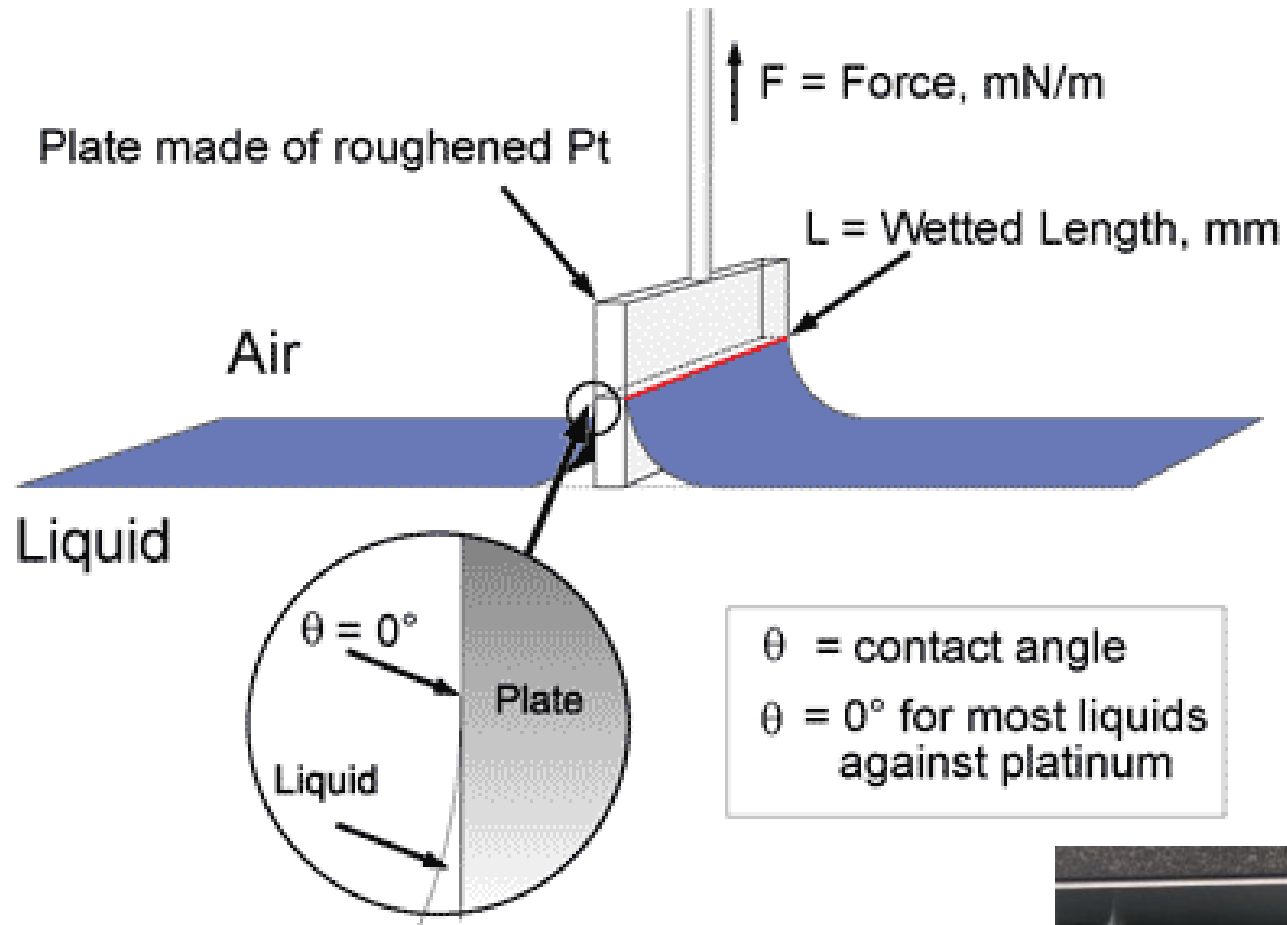
Γ = number of molecules per unit area

The force per unit length is:

$$\sigma \equiv \frac{1}{L_y} \frac{dW}{dL_x} = |u_{AA}| \Gamma$$

**surface tension =
surface excess energy per unit area**

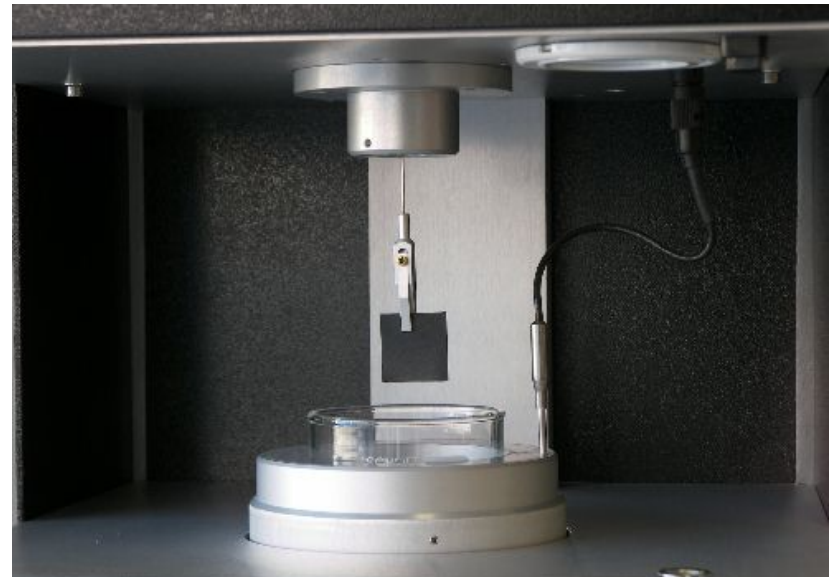




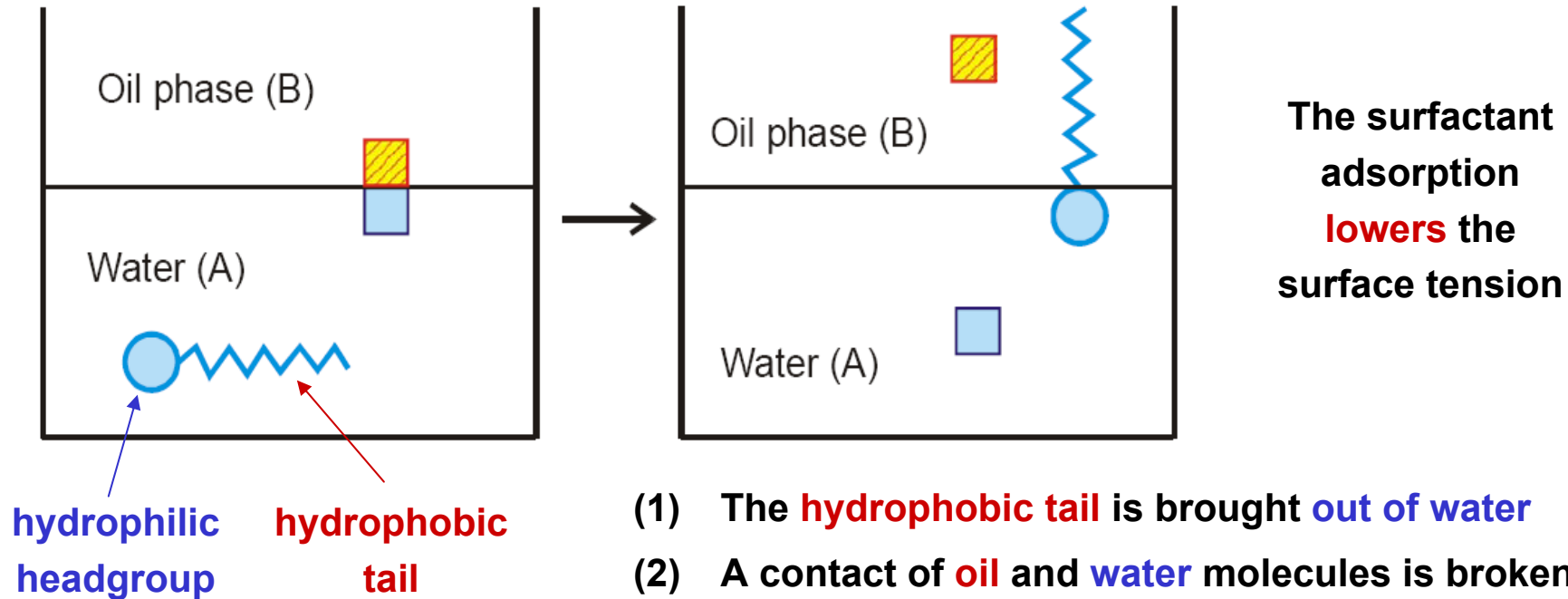
$$\sigma = \frac{F \cos \theta}{2L}$$

Wilhelmy plate method for surface tension measurements

Ludwig Wilhelmy (1812 – 1864)



Adsorption of Surfactants



Work of adsorption:

$$W_{\text{ads}} = w_0 + nw_{\text{CH}_2}$$

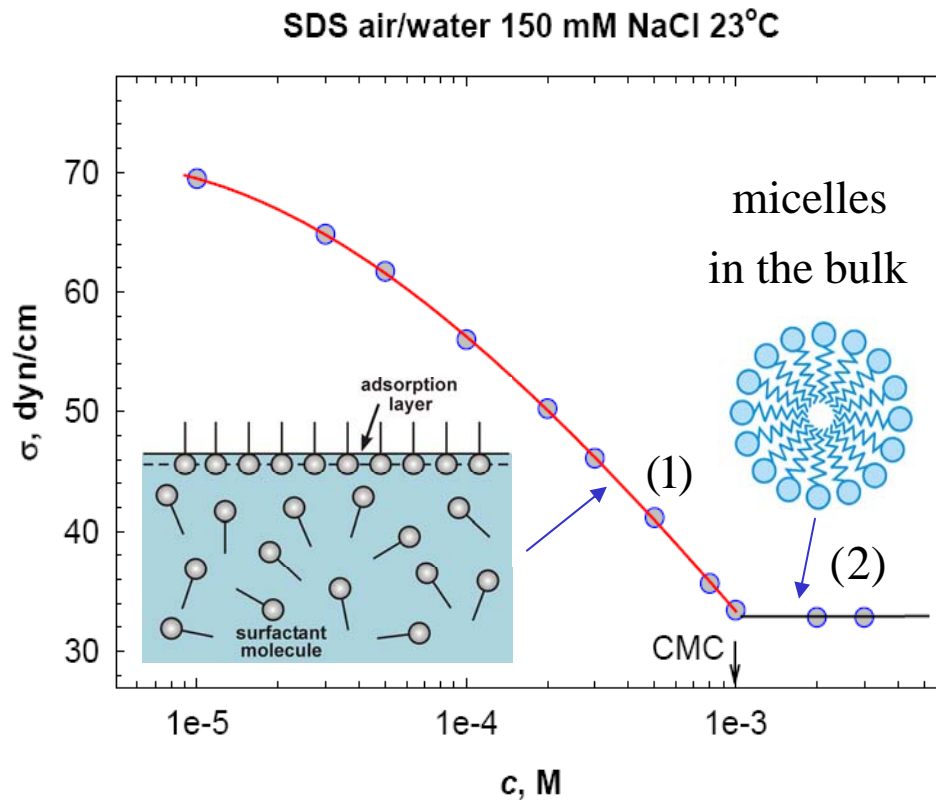
n – number of CH_2 groups in a paraffin tail

$$w_{\text{CH}_2} \approx 1kT$$

Traube rule

T – absolute temperature; k – Boltzmann constant

Adsorption Isotherm and Gibbs Adsorption Equation



$$d\sigma = -\sum_i \Gamma_i d(\ln c_i)$$

Γ_i – adsorption of component "i"

c_i – its bulk concentration

The Gibbs eq. describes the **lowering** of surface tension due to surfactant adsorption.

Chemical potential:

$$\mu_i = \mu_i^0 + kT \ln c_i$$

In Region (1) **dense adsorption layer** is formed, $\Gamma = \text{const.}$ and $\sigma(\ln c)$ is linear;

In Region (2) **micelles are formed** in the bulk, $\mu_i = \text{const.}$ and $\sigma = \text{const.}$

CMC = critical micelle concentration

Models with **Localized** Adsorption

Frumkin Model:

Adsorption isotherm $c = c(\Gamma) \Leftrightarrow \Gamma = \Gamma(c)$

$$Kc = \frac{\Gamma}{\Gamma_{\infty} - \Gamma} \exp\left(-\frac{2\beta\Gamma}{kT}\right)$$

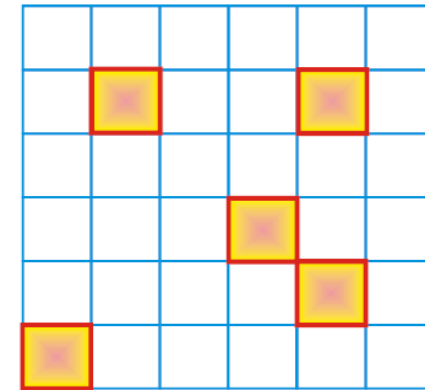
K – adsorption constant; Γ_{∞} – maximal adsorption;

β – accounts for the interaction between adsorbed molecules;

σ_0 – surface tension of pure solvent

Surface equation of state: $\sigma = \sigma(\Gamma)$

$$\sigma = \sigma_0 + \Gamma_{\infty} kT \ln\left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) + \beta \Gamma^2$$



The surface is modeled as a lattice with full and empty adsorption sites.

Model appropriate for adsorption on a solid surface

Langmuir Model: **Special case** of the **Frumkin model** with $\beta = 0$

no interactions between the adsorbed molecules.

Models with Non-Localized Adsorption

Van der Waals Model:

Adsorption isotherm $c = c(\Gamma) \Leftrightarrow \Gamma = \Gamma(c)$

$$Kc = \frac{\Gamma}{\Gamma_{\infty} - \Gamma} \exp\left(\frac{\Gamma}{\Gamma_{\infty} - \Gamma} - \frac{2\beta\Gamma}{kT}\right)$$

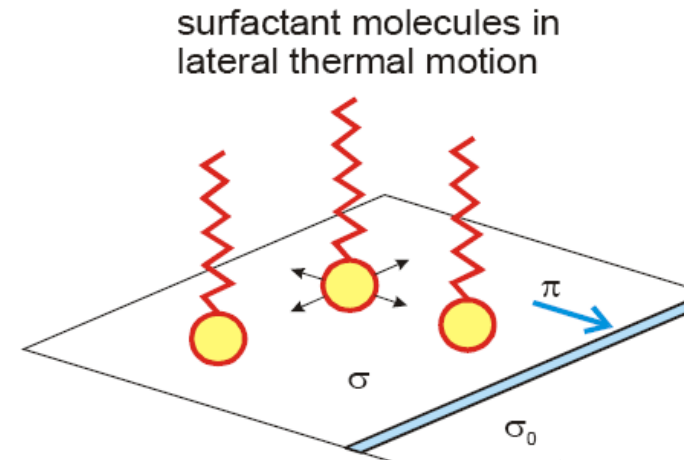
K – adsorption constant; Γ_{∞} – maximal adsorption;

β – accounts for the interaction between adsorbed molecules;

σ_0 – surface tension of pure solvent

Surface equation of state: $\sigma = \sigma(\Gamma)$

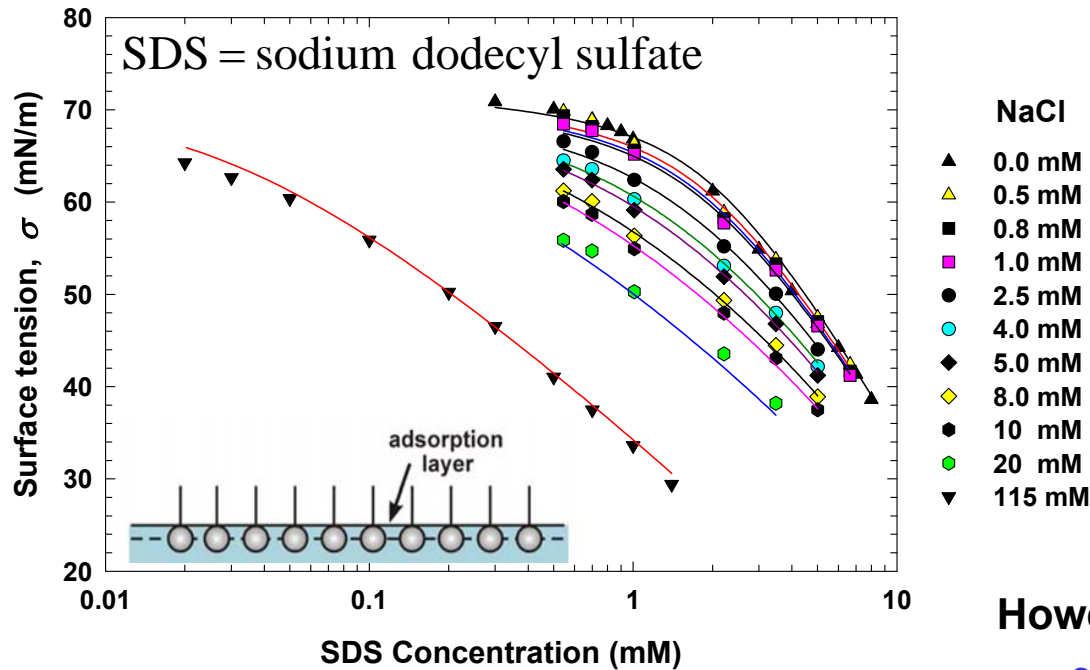
$$\sigma = \sigma_0 - \frac{\Gamma_{\infty}\Gamma kT}{\Gamma_{\infty} - \Gamma} + \beta\Gamma^2$$



The surface is modeled as a lattice with full and empty adsorption sites.

Model appropriate for adsorption on a liquid surface

Volmer Model: **Special case** of the **van der Waals** model with $\beta = 0$
no interactions between the adsorbed molecules.



Comparison of the van der Waals and Frumkin Models

Both models fit well data for $\sigma(c)$ for a liquid surface (indistinguishable curves).

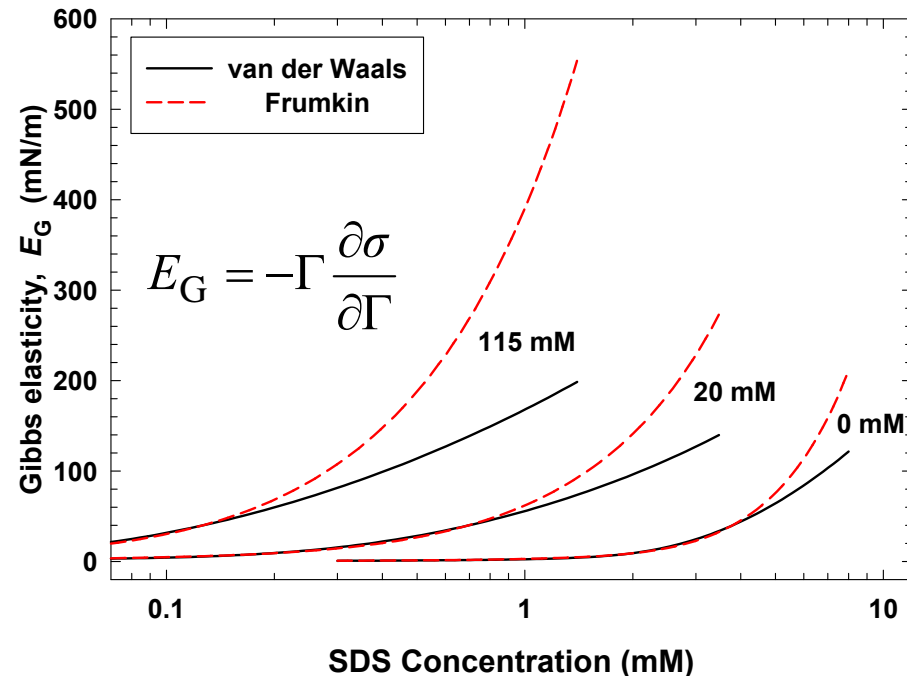
However, “van der Waals” gives the real excluded area per SDS molecule, whereas “Frumkin” yields a greater area:

$$\frac{1}{\Gamma_{\infty}} = 0.30 \text{ nm}^2$$

(van der Waals)

$$\frac{1}{\Gamma_{\infty}} = 0.40 \text{ nm}^2$$

(Frumkin)



The van der Waals model gives realistic values of surface elasticity, whereas the Frumkin models yields greater values.

Basic References

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2. P.A. Kralchevsky, K. Nagayama, *Particles at Fluid Interfaces and Membranes*, Elsevier, Amsterdam, 2001; Chapter 1
<http://www.lcpe.uni-sofia.bg/files/publications/2001/2001-22-Book1.pdf>
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<http://www.lcpe.uni-sofia.bg/files/publications/2008/2008-09-PK-KD-ND-Handbook-Birdi-3rd-Edition.pdf>

Additional References

4. K.D. Danov, P.A. Kralchevsky, et al. Interpretation of Surface-Tension Isotherms of n-Alkanoic (Fatty) Acids by Means of the van der Waals Model, *J. Colloid Interface Sci.* 300(2) (2006) 809-813.
<http://www.lcpe.uni-sofia.bg/files/publications/2006/2006-15-KD-PK-KA-AL-Fatty-Acids.pdf>
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6. P.A. Kralchevsky, K.D. Danov, V.L. Kolev, et al. Effect of Nonionic Admixtures on the Adsorption of Ionic Surfactants at Fluid Interfaces. Part 1. SDS and Dodecanol, *Langmuir* 19 (2003) 5004-5018.
<http://www.lcpe.uni-sofia.bg/files/publications/2003/2003-03-PK.pdf>
7. P.A. Kralchevsky, K.D. Danov, et al. Thermodynamics of Ionic Surfactant Adsorption with Account for the Counterion Binding: Effect of Salts of Various Valency, *Langmuir* 15 (1999) 2351-2365.
<http://www.lcpe.uni-sofia.bg/files/publications/1999/1999-02-PK.pdf>

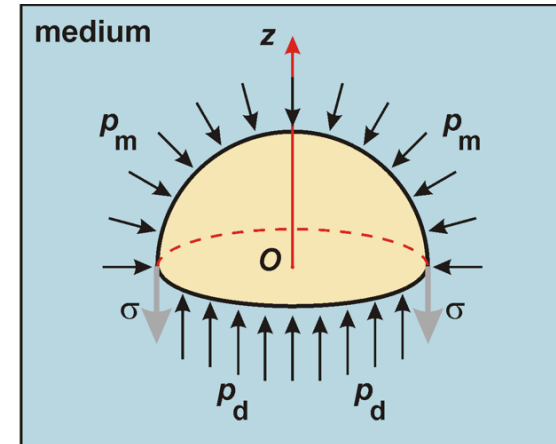
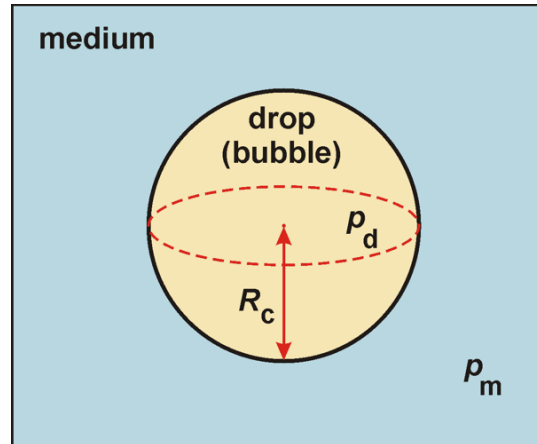
Capillarity – Laplace Equation

Force-balance derivation:

$$\frac{2\sigma}{R_c} = p_d - p_m \equiv P_c$$

(Laplace equation)

P_c – capillary pressure



$$(\pi R_c^2) p_d = (\pi R_c^2) p_m + (2\pi R_c) \sigma$$

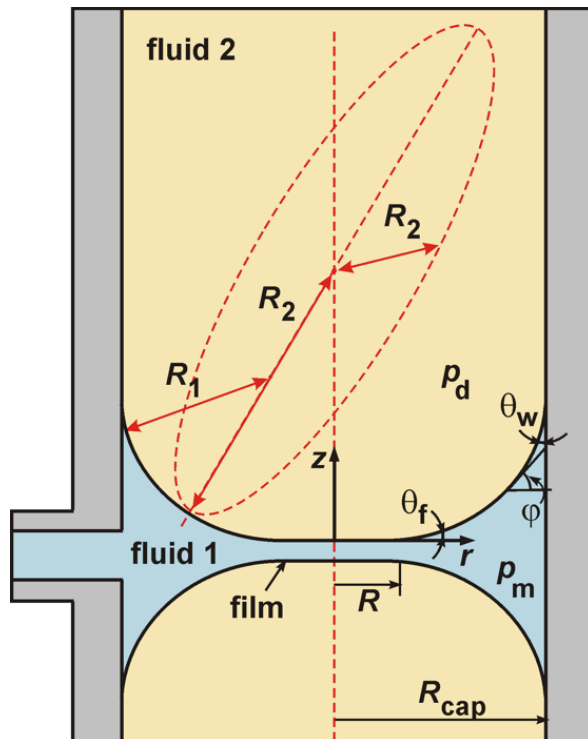
For general curved interfaces - two curvature radii:

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \sigma = P_c$$

$$\begin{aligned} z &= z(\varphi) \\ r &= r(\varphi) \end{aligned}$$

$$\left[\frac{d(\sin \varphi)}{dr} + \frac{\sin \varphi}{r} \right] \sigma = P_c \quad \left(\tan \varphi = \frac{dz}{dr} \right)$$

φ – running meniscus slope angle



Drop Shape Analysis (DSA) for Surface Tension Measurements

$$\frac{\sigma}{r} \frac{d}{dr} \left[\frac{r z'}{(1+z'^2)^{1/2}} \right] = P_c = \frac{2\sigma}{R_b} - \Delta\rho g z$$
$$z = z(r); \quad z' = \frac{dz}{dr}$$

pendant drop

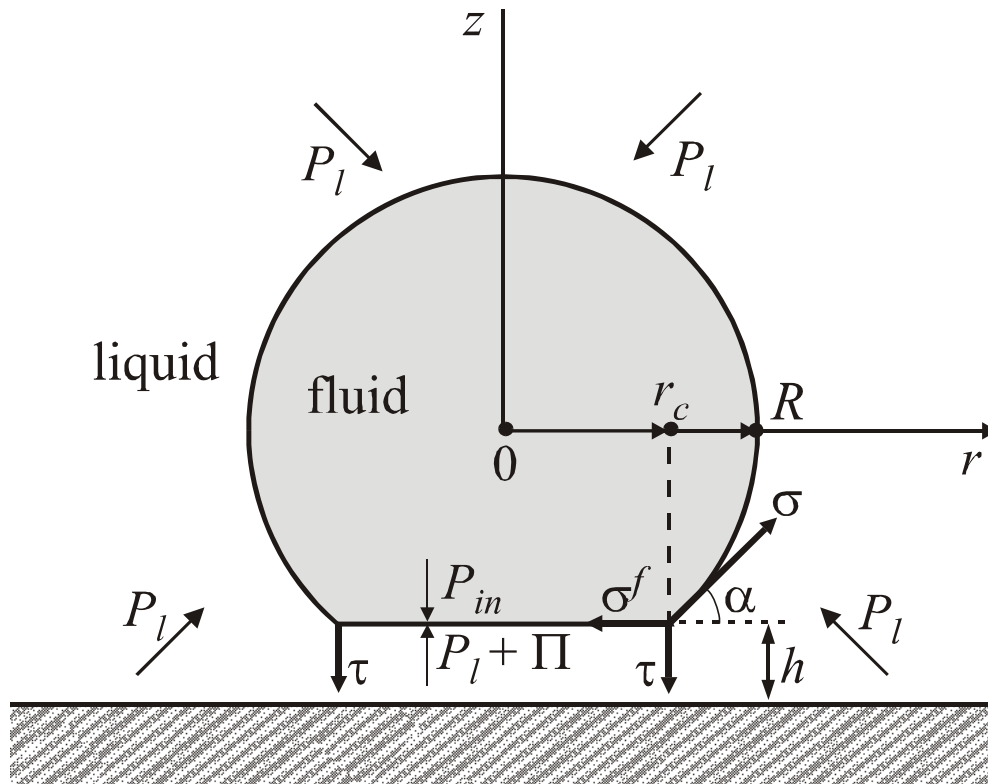


Picture by
apparatus
Kruss
DSA100

Laplace equation; R_b – curvature radius at the bottom of the drop
 P_c – capillary pressure

- 1) The drop profile is automatically digitized;
- 2) Then, the data for the profile are fitted numerically by the Laplace equation using σ and R_b as adjustable parameters.
- 3) The surface tension σ is obtained from the best fit; effect of surfactants on σ .
- 4) The method works with both drops and bubbles; both pendant and sessile profiles.
- 5) The method is accurate when the gravitational deformation (the deviation from spherical shape) is not too small.

Surface Force & Disjoining Pressure



Surface force = Force of interaction between two bodies (two phases) when the distance h between their surfaces is relatively small.

Typically, $h < 100$ nm.

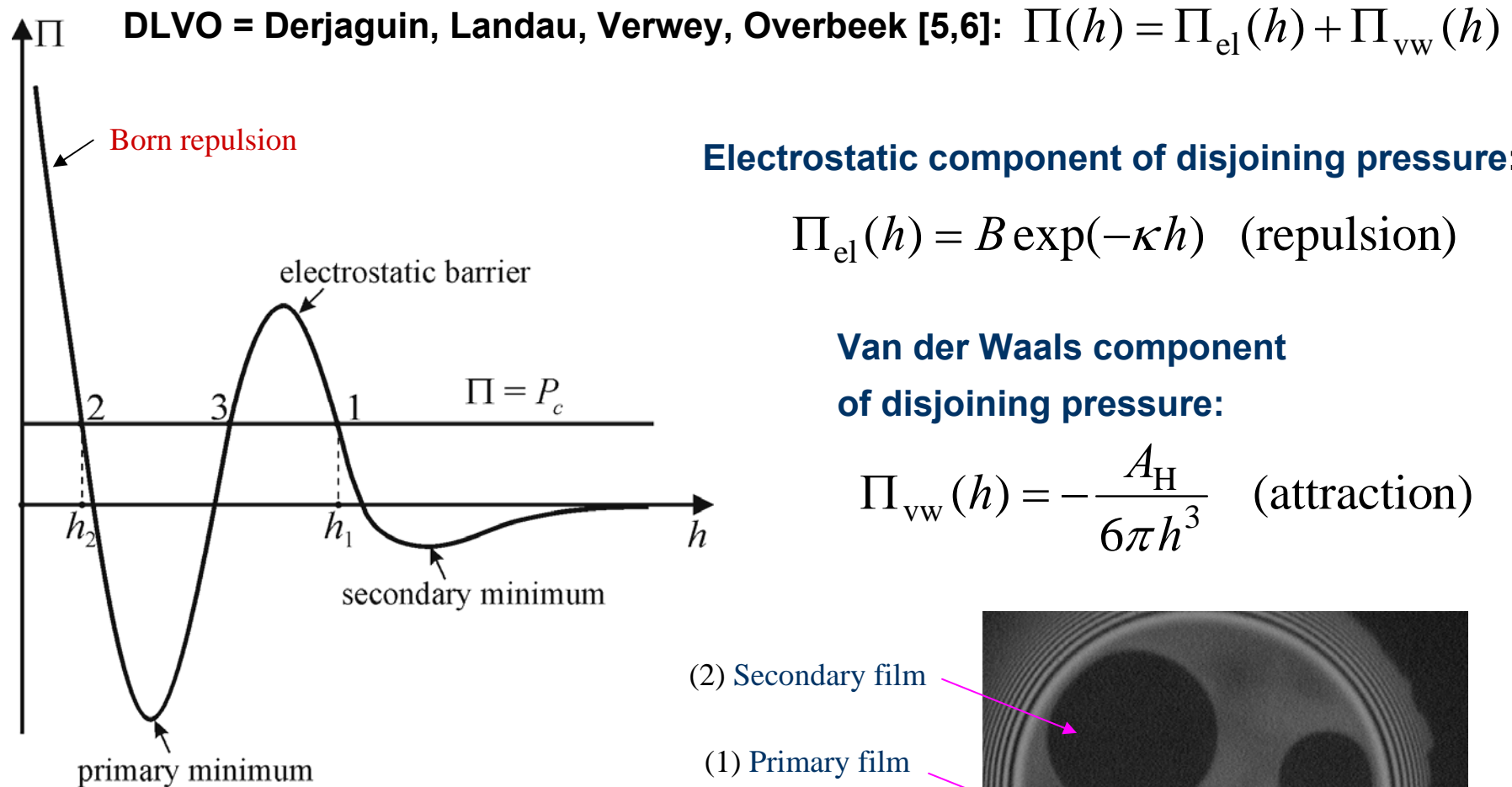
Disjoining pressure, $\Pi(h)$ = Surface force per unit area of a plane-parallel film [1-3].

Capillary (Laplace) pressure: $P_c = P_{in} - P_l = 2\sigma/R$ (σ – surface tension)

Force balance per unit area of the film surface: $P_l + \Pi = P_{in}$

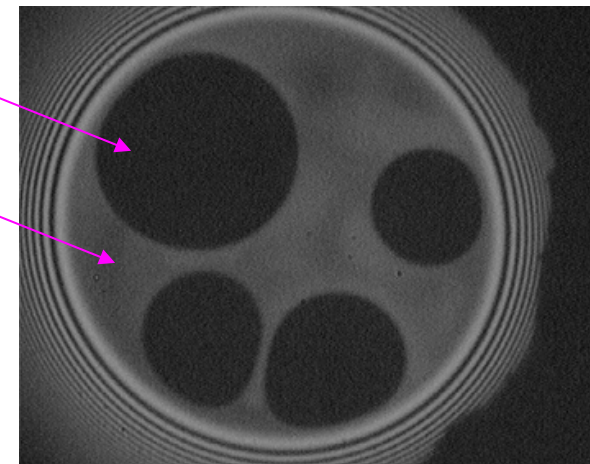
Hence: $\Pi = P_{in} - P_l = P_c$ (disjoining pressure = capillary pressure) [4].

DLVO Theory: Equilibrium states of a free liquid film

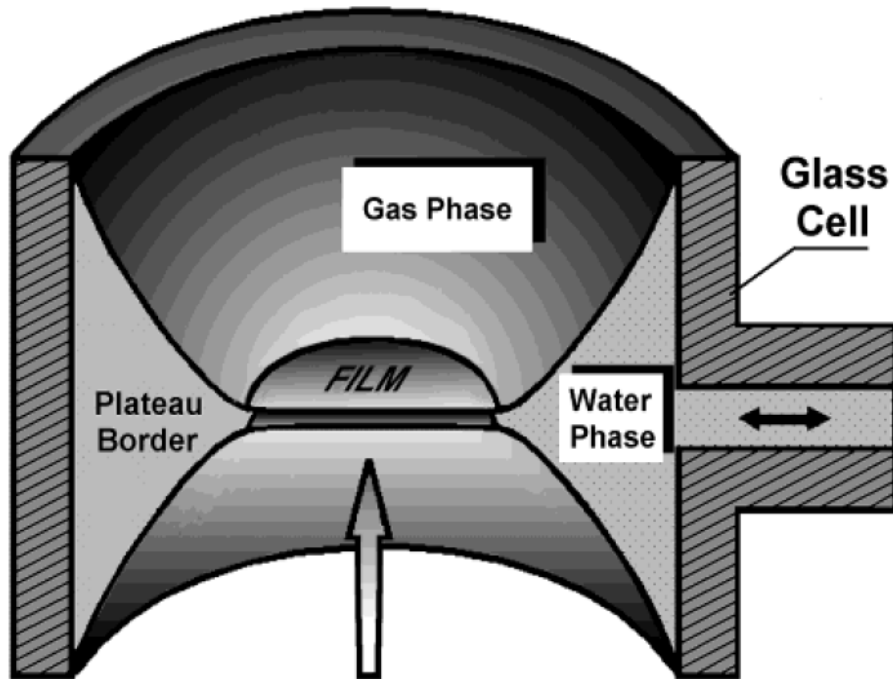


h – film thickness; A_H – Hamaker constant;

κ – Debye screening parameter



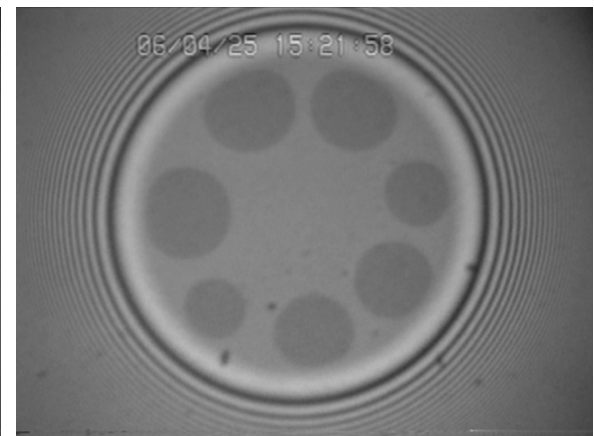
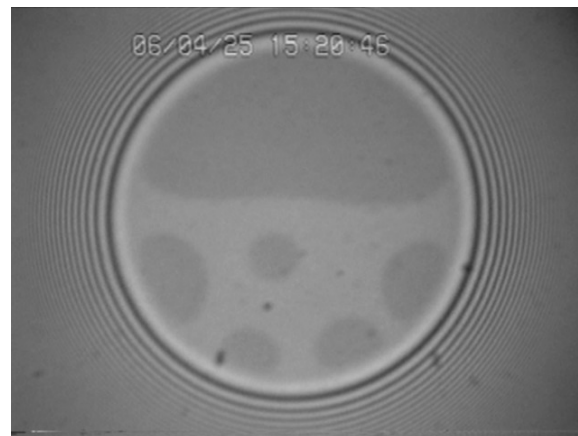
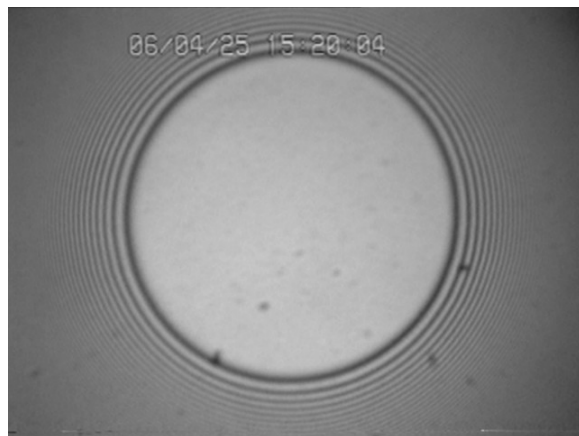
Scheludko-Exerowa capillary cell for thin-liquid-film (TLF) studies [7,8]



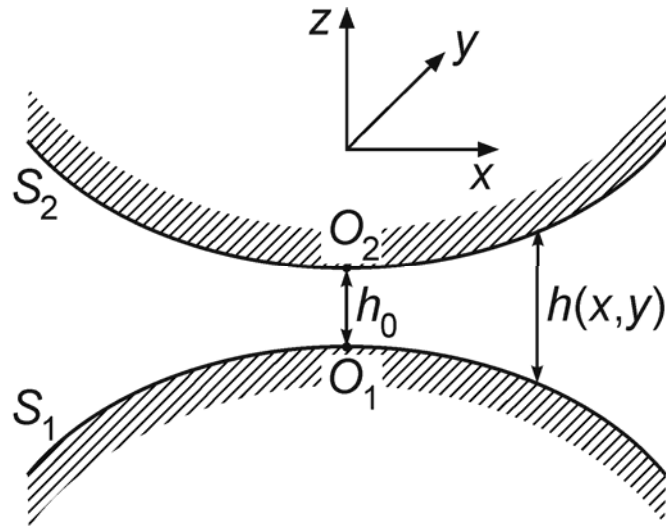
Measurements of:

- (1) Film thickness vs. time;
- (2) Contact angles of TLF;
- (3) Lifetime of the films.

Illustration: Stepwise thickness transitions in films from **0.1 M** solutions of the **nonionic Brij 35**:



Derjaguin's Approximation (1934):



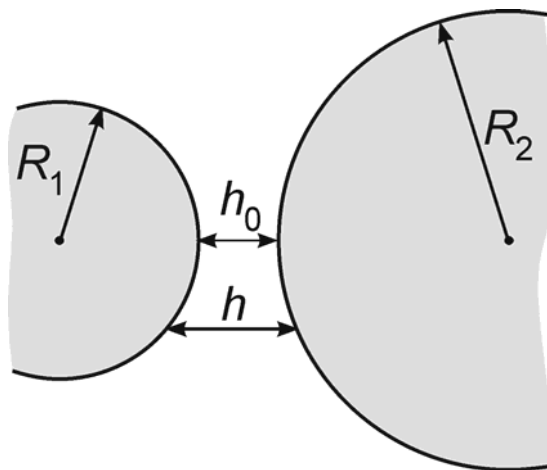
The energy of interaction, U , between two bodies across a **film of uneven thickness**, $h(x,y)$, is [9]:

$$U = \iint f(h(x, y)) dx dy$$

where $f(h)$ is the interaction free energy per unit area of a **plane-parallel** film:

$$f(h) = \int_h^{\infty} \Pi(\tilde{h}) d\tilde{h}$$

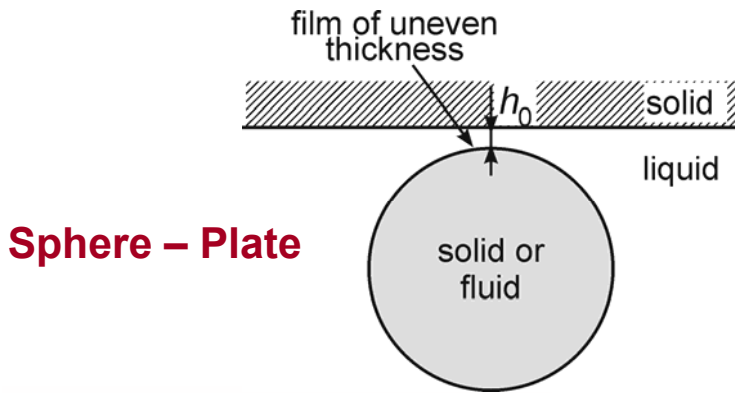
This approximation is valid if the range of action of the surface force is much smaller than the surface curvature radius.



For two spheres of radii R_1 and R_2 , this yields:

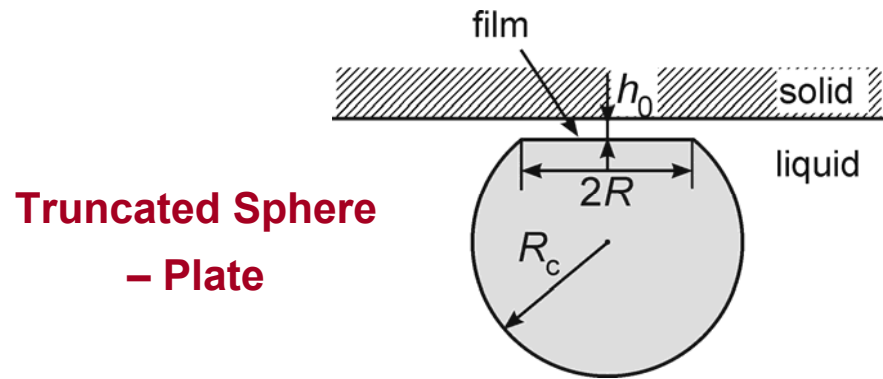
$$U(h_0) = \frac{2\pi R_1 R_2}{R_1 + R_2} \int_{h_0}^{\infty} f(h) dh$$

Derjaguin's approximation for other geometries [1-3,10]:



Sphere – Plate

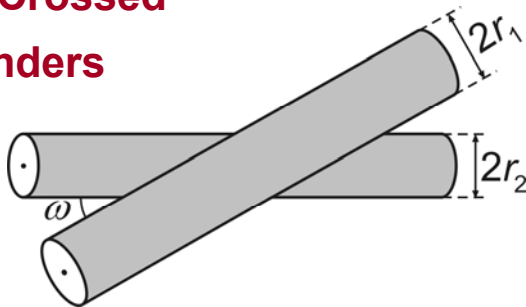
$$U(h_0) = 2\pi R_c \int_{h_0}^{\infty} f(h) dh$$



Truncated Sphere – Plate

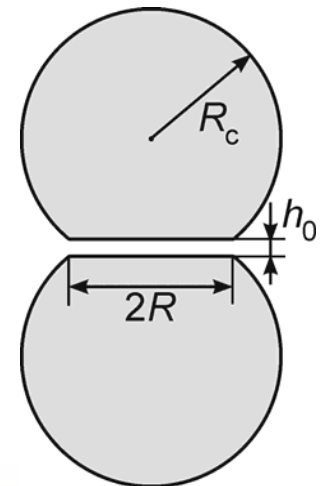
$$U(h_0) = 2\pi R_c \int_{h_0}^{\infty} f(h) dh + \pi R^2 f(h_0)$$

Two Crossed Cylinders



$$U(h_0) = \frac{2\pi \sqrt{r_1 r_2}}{\sin \omega} \int_{h_0}^{\infty} f(h) dh$$

Two Truncated Spheres



$$U(h_0) = \pi R_c \int_{h_0}^{\infty} f(h) dh + \pi R^2 f(h_0)$$

Molecular Theory of Surface Forces

DLVO Forces:

(1) Van der Waals force

(2) Electrostatic (double layer) force

Non-DLVO Forces:

(1) Hydration repulsion

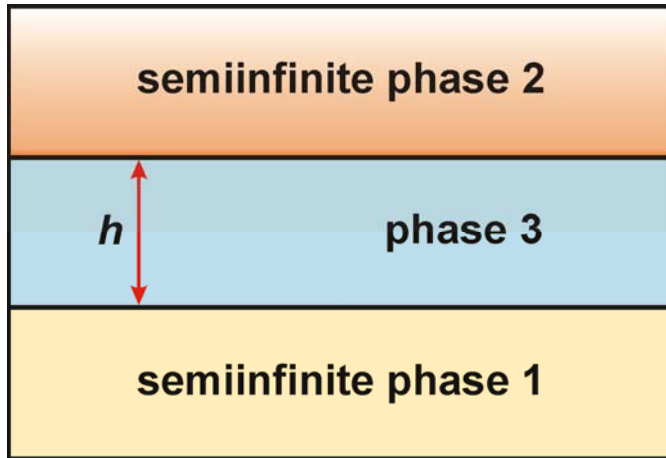
(2) Steric interaction due to adsorbed polymer chains

(3) Oscillatory structural force and Depletion attraction

Van der Waals surface forces:

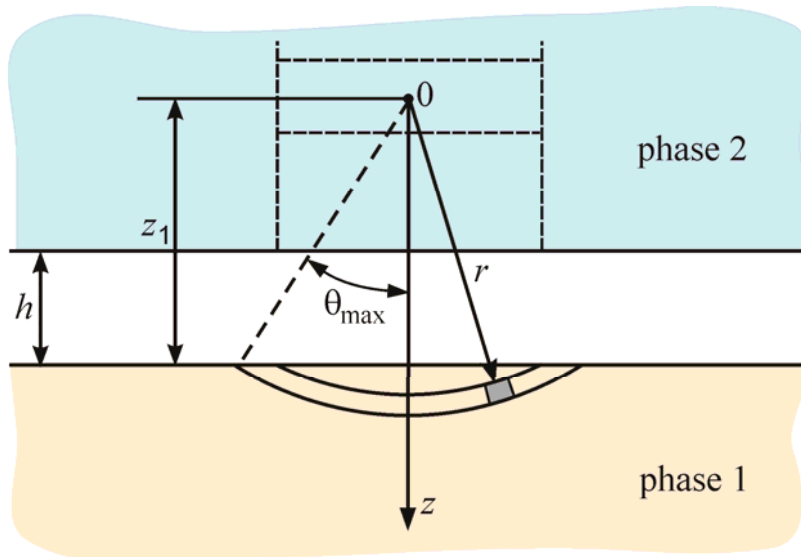
$$\Pi_{vw}(h) = -\frac{A_H}{6\pi h^3}$$

A_H – Hamaker constant



vdW between two molecules:

$$u_{ij}(r) = -\frac{\alpha_{ij}}{r^6}$$



Hamaker's approach [11]

The interaction energy is **pair-wise additive**:
Summation over all couples of molecules.

Result [11, 12]:

$$A_H = A_{12} - A_{23} - A_{31} + A_{33}$$

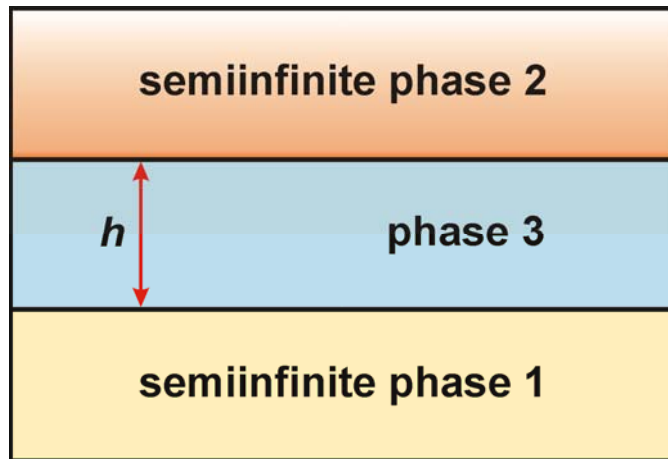
$$A_{ij} = \pi^2 \rho_i \rho_j \alpha_{ij}; \quad A_{ij} \approx (A_{ii} A_{jj})^{1/2}$$

Symmetric film: phase 2 = phase 1

$$A_H = A_{11} - 2A_{13} + A_{33} \approx (A_{11}^{1/2} - A_{33}^{1/2})^2 > 0$$

For symmetric films: always attraction!

Lifshitz approach to the calculation of Hamaker constant



E. M. Lifshitz (1915 – 1985) [13] took into account the **collective effects** in condensed phases (solids, liquids). (The total energy is **not** pair-wise additive over all pairs of molecules.)

Lifshitz used the **quantum field theory** to derive accurate expressions in terms of [1, 14]:

(i) **Dielectric constants** of the phases: ϵ_1 , ϵ_2 and ϵ_3 ;

(ii) **Refractive indexes** of the phases: n_1 , n_2 and n_3 :

$$A_H \equiv A_{132} \approx \frac{3}{4}kT \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3h_p \nu_e (n_1^2 - n_3^2)(n_2^2 - n_3^2)}{16\sqrt{2}(n_1^2 + n_3^2)^{3/4}(n_2^2 + n_3^2)^{3/4}}$$

Zero-frequency term: $A_{132}^{(v=0)}$

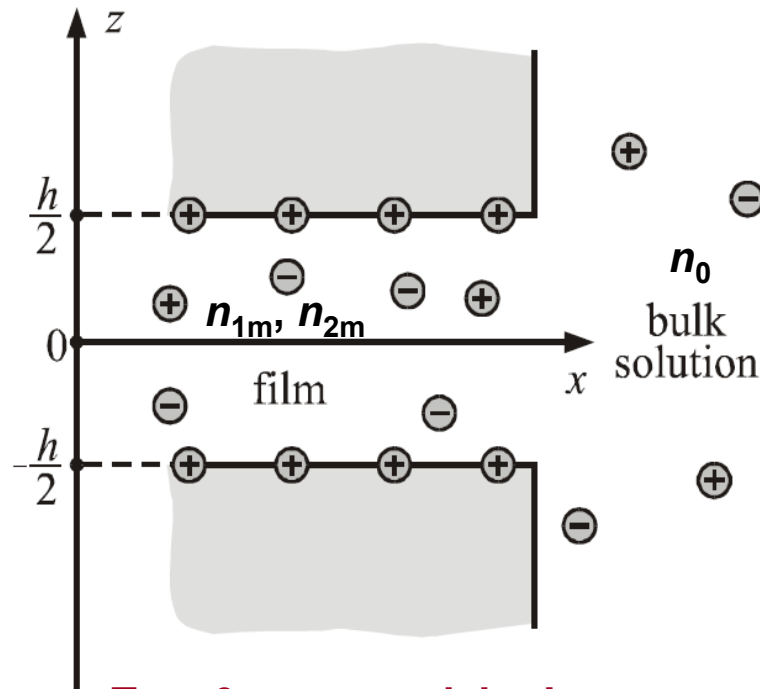
orientation & induction
interactions;
 kT – thermal energy.

Dispersion interaction term: $A_{132}^{(v>0)}$

$\nu_e = 3.0 \times 10^{15}$ Hz – main electronic
absorption frequency;

$h_p = 6.6 \times 10^{-34}$ J.s – Planck's const.

Electrostatic (Double Layer) Surface Force



$\Pi_{el} > 0 \Rightarrow$ **repulsion!**

Π_{el} = **excess osmotic pressure of the ions in the midplane** of a symmetric film (Langmuir, 1938) [15]:

$$\Pi_{el} = kT(n_{1m} + n_{2m} - 2n_0)$$

n_{1m}, n_{2m} – concentrations of **(1) counterions** and **(2) coions** in the midplane.

n_0 – concentration of the ions in the bulk solution; ψ_m **potential in the midplane**.

For solution of a symmetric electrolyte: $Z_1 = -Z_2 = Z$; Z is the valence of the **coions**.

Boltzmann equation; Φ_m – **dimensionless potential in the midplane** ($\Phi_m \ll 1$).

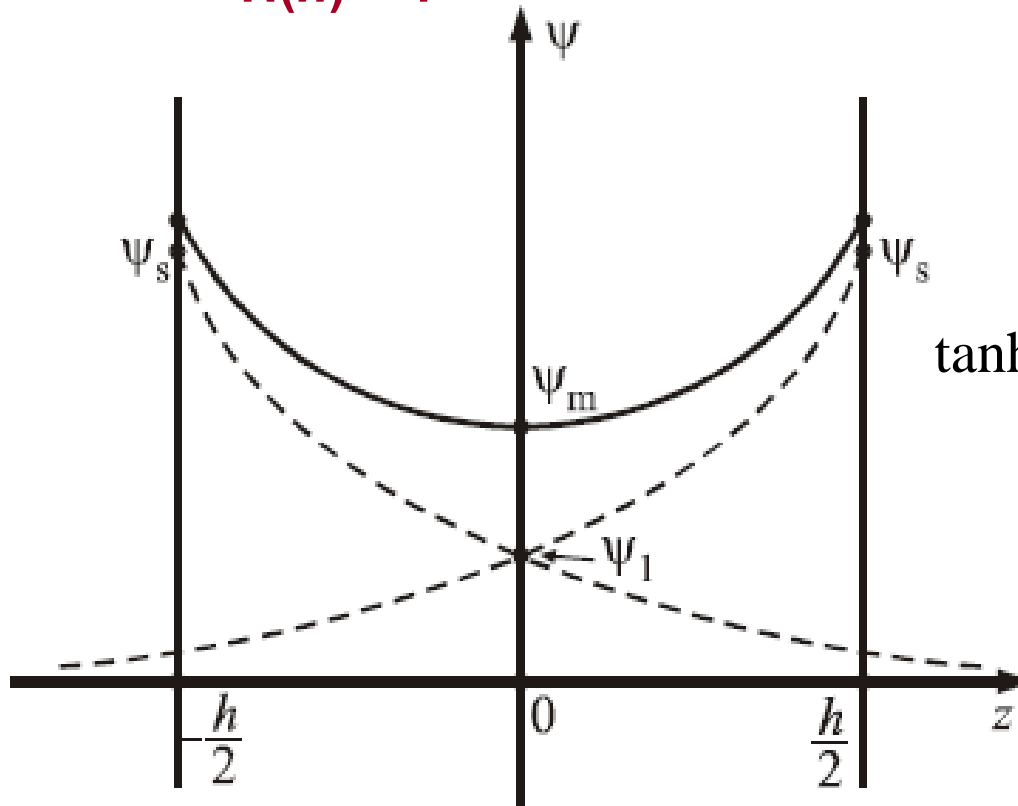
$$n_{1m} = n_0 \exp(\Phi_m); \quad n_{2m} = n_0 \exp(-\Phi_m); \quad \Phi_m = \frac{Ze\psi_m}{kT}$$

$$\Pi_{el} = 2n_0kT \left[\cosh(\Phi_m) - 1 \right] \approx n_0kT\Phi_m^2 > 0$$

$$\cosh(\Phi_m) = 1 + \frac{\Phi_m^2}{2} + O(\Phi_m^4)$$

$$\Pi(h) = ?$$

Verwey – Overbeek Formula (1948)



Near **single** interface, the electric potential of the double layer is [6]:

$$\tanh\left(\frac{Ze\psi_1}{4kT}\right) = \tanh\left(\frac{Ze\psi_s}{4kT}\right) \exp(-\kappa z_w)$$

Superposition approximation

in the midplane: $\psi_m = 2\psi_1$ [6]:

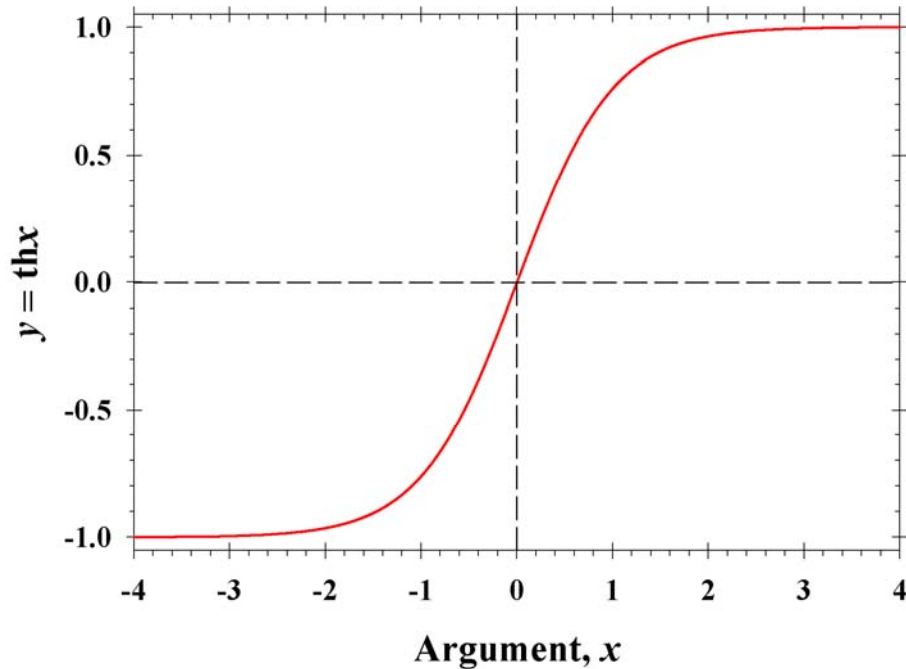
In the midplane $\frac{Ze\psi_1}{4kT} \ll 1$

$$\Phi_m = 2\psi_1 \frac{Ze}{kT} = 8 \tanh\left(\frac{Ze\psi_s}{4kT}\right) \exp\left(-\kappa \frac{h}{2}\right)$$

$$\tanh(x) = x + O(x^3)$$

$$\Pi_{el}(h) \approx n_0 kT \Phi_m^2 \approx 64 n_0 kT \gamma^2 \exp(-\kappa h)$$

$$\gamma \equiv \tanh\left(\frac{Ze\psi_s}{4kT}\right)$$



$\tanh(x) \approx 1$ for $x \geq 1.5$

$$\frac{4kT}{e} \approx 100 \text{ mV}$$

$$\Rightarrow \gamma \equiv \tanh\left(\frac{Ze\psi_s}{4kT}\right) \approx 1$$

for $Z\psi_s \geq 150 \text{ mV}$

$$\Pi_{\text{el}}(h) \approx 64n_0kT \exp(-\kappa h)$$

Debye screening length, κ^{-1} : $\kappa^2 = \frac{2e^2 I}{\epsilon\epsilon_0 kT}$; $I = \frac{1}{2} \sum_i Z_i^2 c_i$ (ionic strength)

$$\kappa^{-1} = \frac{0.304}{\sqrt{[\text{NaCl}]}} \text{ nm}$$

$$\kappa^{-1} = \frac{0.176}{\sqrt{[\text{CaCl}_2]}} \text{ nm}$$

$$\kappa^{-1} = \frac{0.152}{\sqrt{[\text{MgSO}_4]}} \text{ nm}$$

Z_i and c_i - valence and concentration of the i -th ion

I for 1:1 el. (M)	10^{-7} pure water	10^{-5}	10^{-3}	10^{-1}
κ^{-1} (nm)	960	96	9.6	0.96

Derjaguin – Landau – Verwey – Overbeek (DLVO) Theory [5,6]

Disjoining pressure:

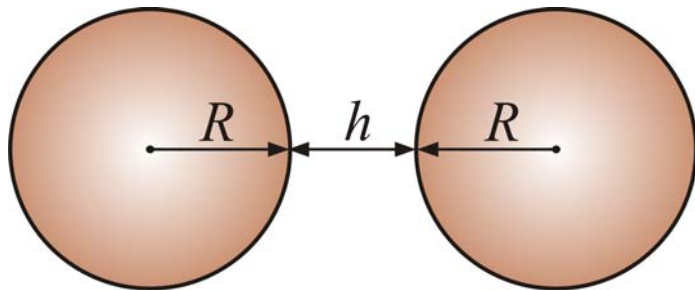
$$\Pi = \Pi_{\text{el}} + \Pi_{\text{vw}} = B e^{-\kappa h} - \frac{A_{\text{H}}}{6\pi h^3}$$

Free energy per unit area
of a plane-parallel film:

$$f(h) = \int_h^{\infty} \Pi(\tilde{h}) d\tilde{h} = \frac{B}{\kappa} e^{-\kappa h} - \frac{A_{\text{H}}}{12\pi h^2}$$

Energy of interaction between
two identical spherical particles
(Derjaguin approximation):

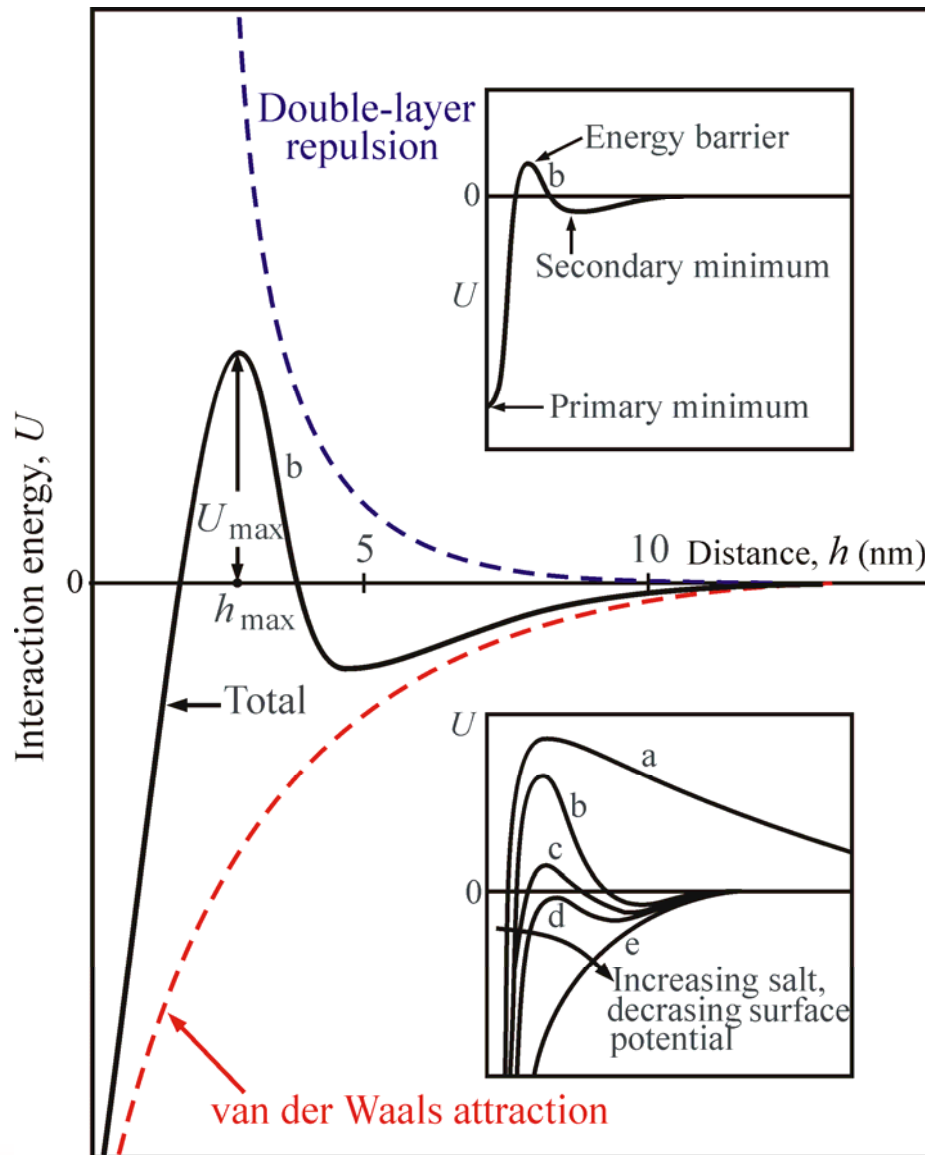
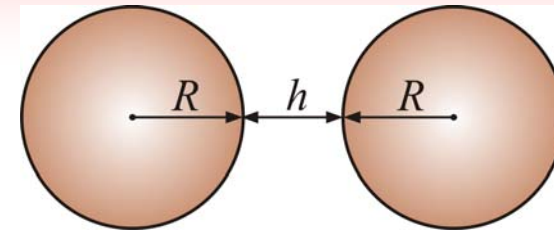
$$U(h) \approx \pi R \int_h^{\infty} f(\tilde{h}) d\tilde{h} = \pi R \left(\frac{B}{\kappa^2} e^{-\kappa h} - \frac{A_{\text{H}}}{12\pi h} \right)$$



$$B = 64n_0kT\gamma^2, \quad \gamma \equiv \tanh\left(\frac{Ze\psi_s}{4kT}\right)$$

(e – electronic charge; $e = 2.71828\dots$)

DLVO Theory: The electrostatic barrier



$$U(h) \approx \pi R \left(\frac{B}{\kappa^2} e^{-\kappa h} - \frac{A_H}{12\pi h} \right)$$

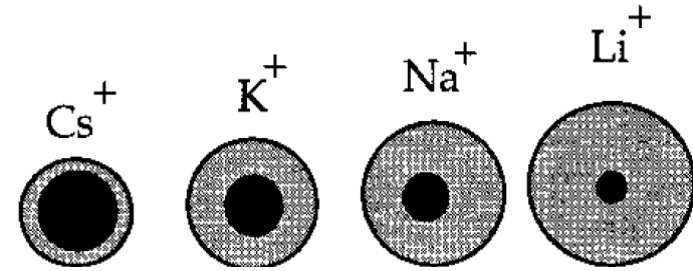
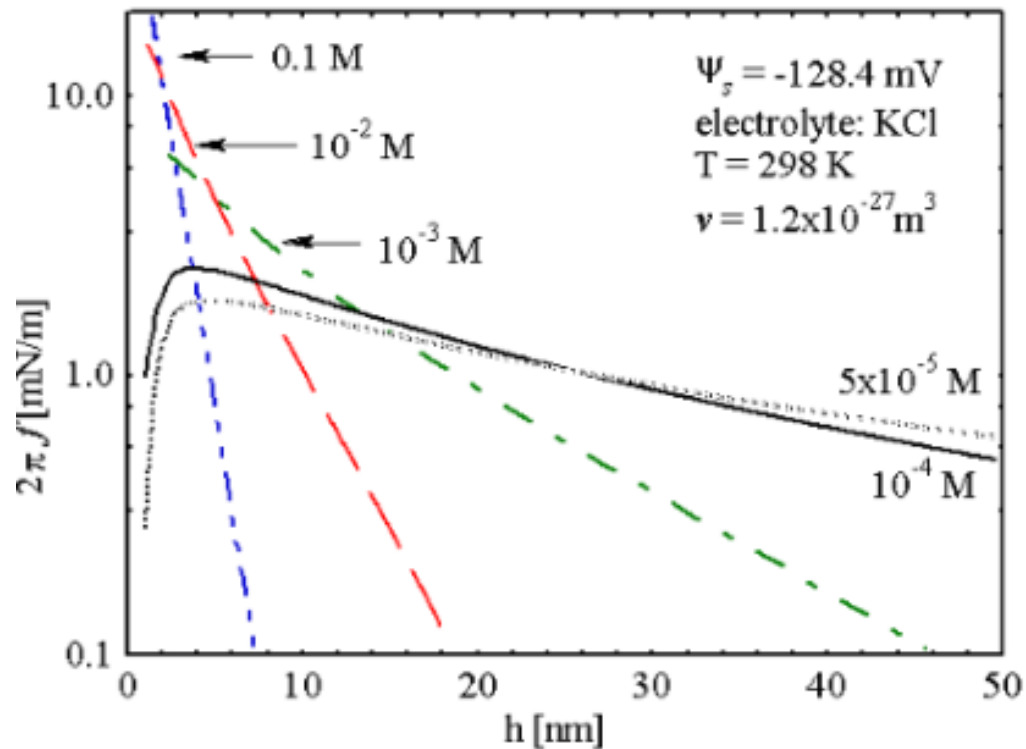
The **secondary** minimum could cause coagulation only for big (1 μm) particles.

The **primary** minimum is the reason for coagulation in most cases.

Condition for coagulation: $U_{max} = 0$
(zero height of the barrier to coagulation)

$$U(h_{max}) = 0; \quad \left. \frac{dU}{dh} \right|_{h=h_{max}} = 0$$

Hydration Repulsion



At $C_{el} < 10^{-4}$ M (NaCl, KNO₃, KCl, etc.), a typical DLVO maximum is observed.

At $C_{el} \geq 10^{-3}$ M, a strong short-range repulsion is detected by the surface force apparatus – the **hydration repulsion** [1, 16].

Empirical expression [1] for the interaction free energy per unit area:

Important: f_{el} **decreases**, whereas f_{hydr} **increases** with the rise of electrolyte concentration!

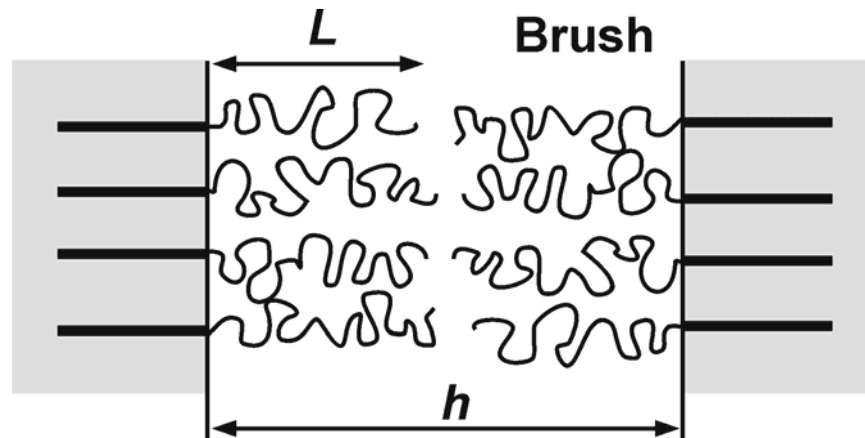
Explanation: The hydration repulsion is due mostly to the finite size of the hydrated counterions [17].

$$f_{hydr} = f_0 \exp(-h / \lambda_0)$$

$$\lambda_0 = 0.6 - 1.1 \text{ nm}$$

$$f_0 = 3 - 30 \text{ mJ/m}^2$$

Steric interaction due to adsorbed polymer chains



$$L \approx L_0 \equiv lN^{1/2} \text{ (ideal solvent)}$$

l – the length of a segment;

N – number of segments in a chain;

In a **good** solvent $L > L_0$, whereas
in a **poor** solvent $L < L_0$.

L depends on adsorption of chains, Γ
[1,21].

← **Alexander – de Gennes theory**

for the case of **good** solvent [18,19]:

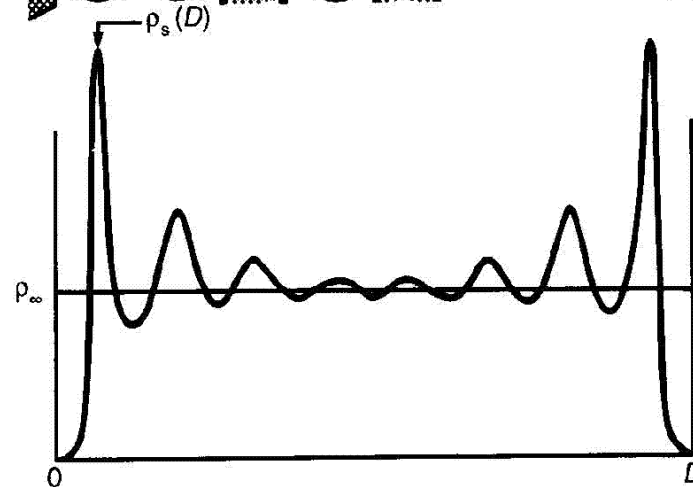
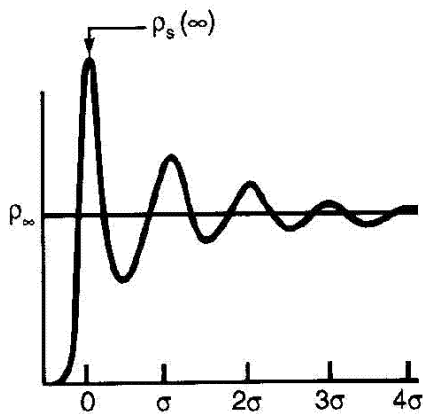
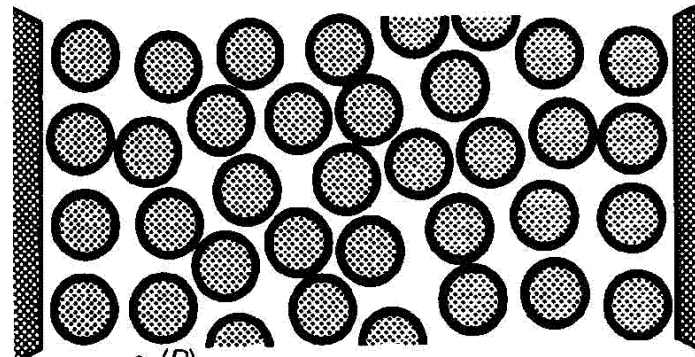
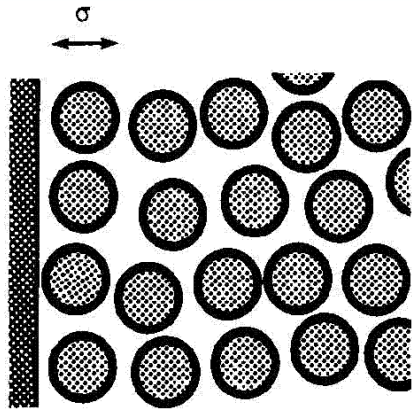
$$\Pi_{\text{st}}(h) = kT\Gamma^{3/2} \left[\left(\frac{2L_g}{h} \right)^{9/4} - \left(\frac{h}{2L_g} \right)^{3/4} \right]$$

for $h < 2L_g$; $L_g = N(\Gamma l^5)^{1/3}$

The positive and the negative terms in the brackets in the above expression correspond to **osmotic repulsion** and **elastic attraction**.

The validity of the Alexander – de Gennes theory was **experimentally confirmed**; see e.g. Ref. [1].

Oscillatory–Structural Surface Force

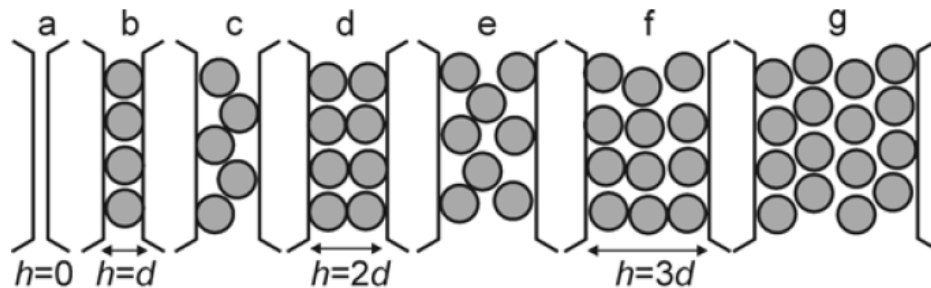


A planar phase boundary (wall) induces ordering in the adjacent layer of a hard-sphere fluid.

The **overlap of the ordered zones** near two walls **enhances the ordering** in the gap between the two walls and **gives rise to the oscillatory-structural force**.

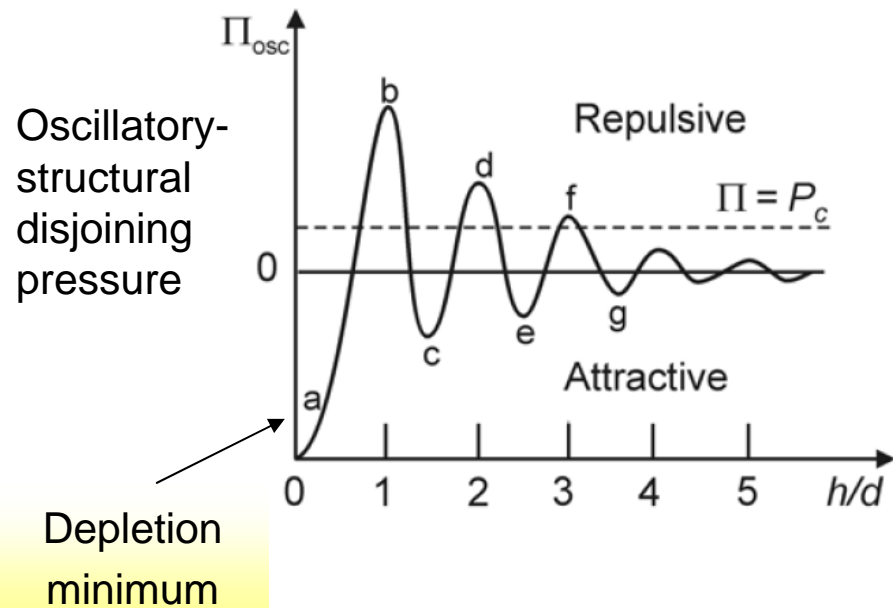
For details – see the book by Israelachvili [1]

Oscillatory structural forces [1,20] were observed in liquid films containing **colloidal particles**, e.g. latex & surfactant micelles; Nikolov et al. [21,22].



(a)

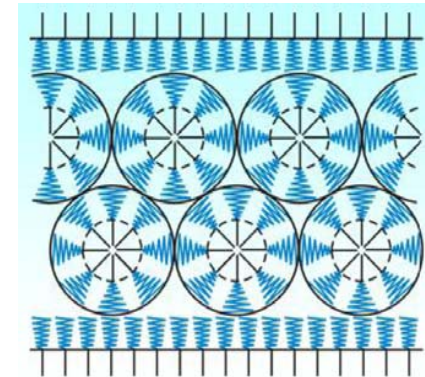
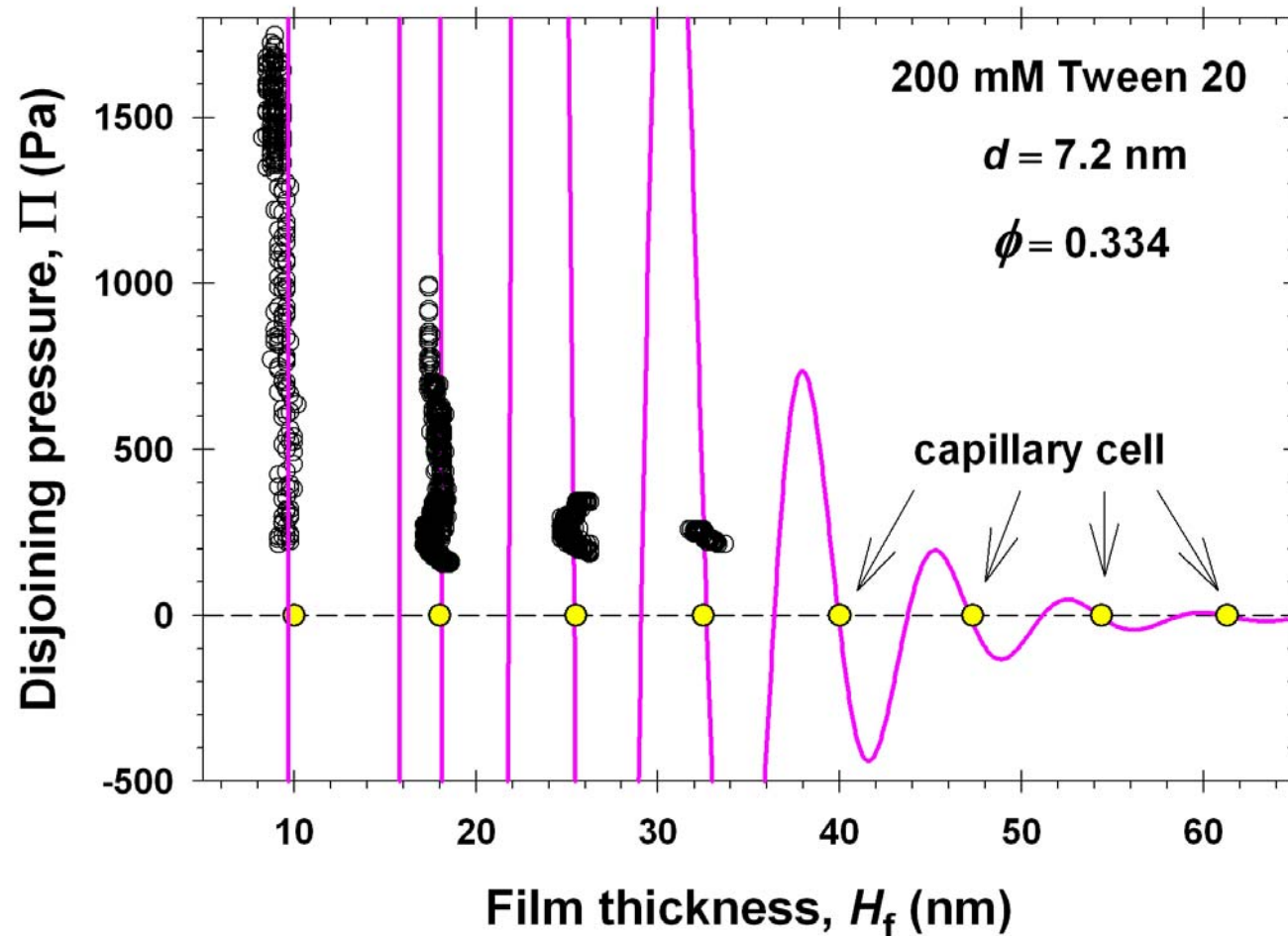
The maxima of the oscillatory force could stabilize colloidal dispersions.



The **metastable states** of the film correspond to the intersection points of the oscillatory curve with the horizontal line $\Pi = P_c$.

The **stable branches** of the oscillatory curve are those with $\partial\Pi/\partial h < 0$.

Oscillatory–Structural Surface Force Due to Colloid Particles



Ordering of micelles of the nonionic surfactant Tween 20 [24].

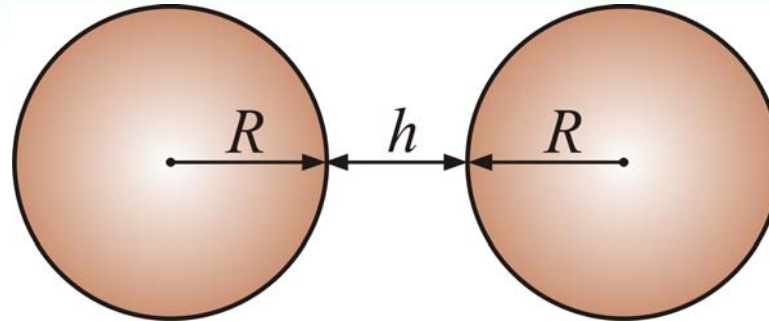
Methods:

Mysels' porous plate cell and

Scheludko-Exerowa capillary cell [7,8]

Theoretical curve – by means of the Trokhimchuk formulas [23].
The micelle aggregation number, $N_{\text{agg}} = 70$, is determined [24].

The total energy of interaction between two particles , $U(h)$, includes contributions from all surface forces:



Disjoining pressure (force per unit area of a plane parallel film):

$$\Pi(h) = \Pi_{vw}(h) + \Pi_{el}(h) + \Pi_{hydr}(h) + \Pi_{st}(h) + \Pi_{osc}(h) + \dots$$

Energy of interaction between two particles: $U(h) \approx \pi R \int_h^\infty d\tilde{h} \int_{\tilde{h}}^\infty d\hat{h} \Pi(\hat{h})$

$$U(h) = U_{vw}(h) + U_{el}(h) + U_{hydr}(h) + U_{st}(h) + U_{osc}(h) + \dots$$

DLVO forces

Non-DLVO forces

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