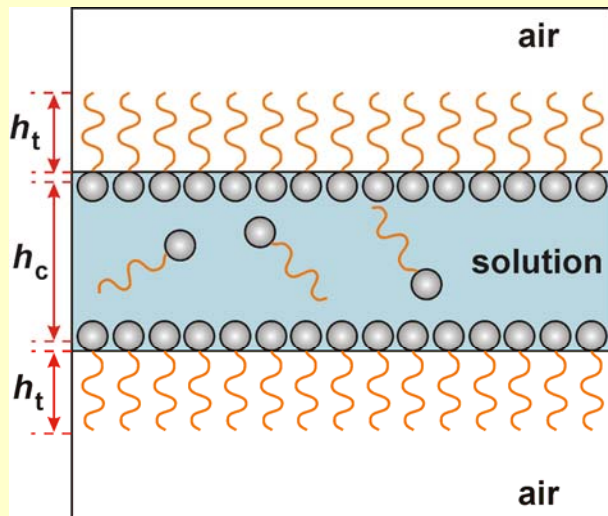# Forces between Surfaces

Peter A. Kralchevsky

Laboratory of Chemical Physics and Engineering, Faculty of Chemistry

Sofia University, Sofia, Bulgaria

Lecture at COST D43 School *Interfacial engineering in nanotechnology*

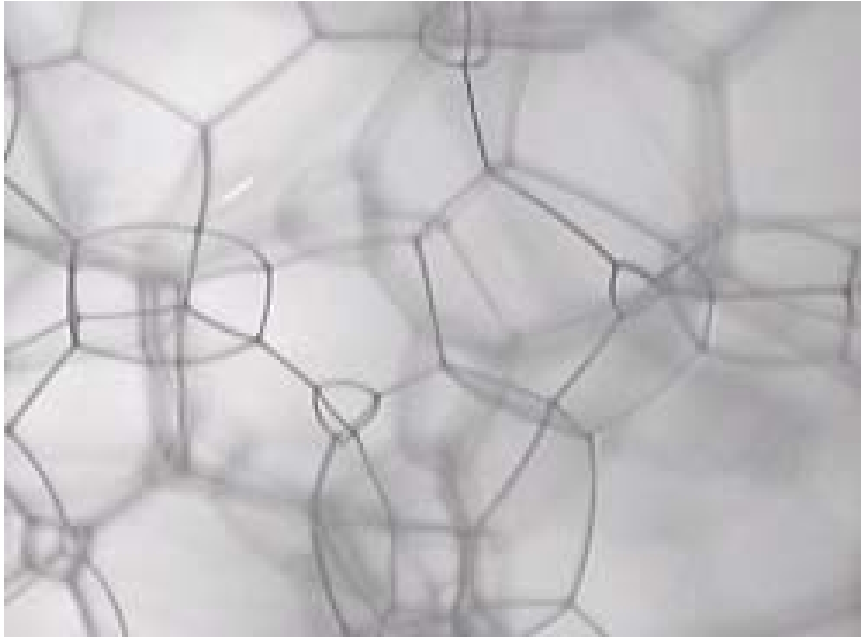**Leibniz Institute of Polymer Research, Dresden, Germany**

31 March – 3 April, 2009

Example:
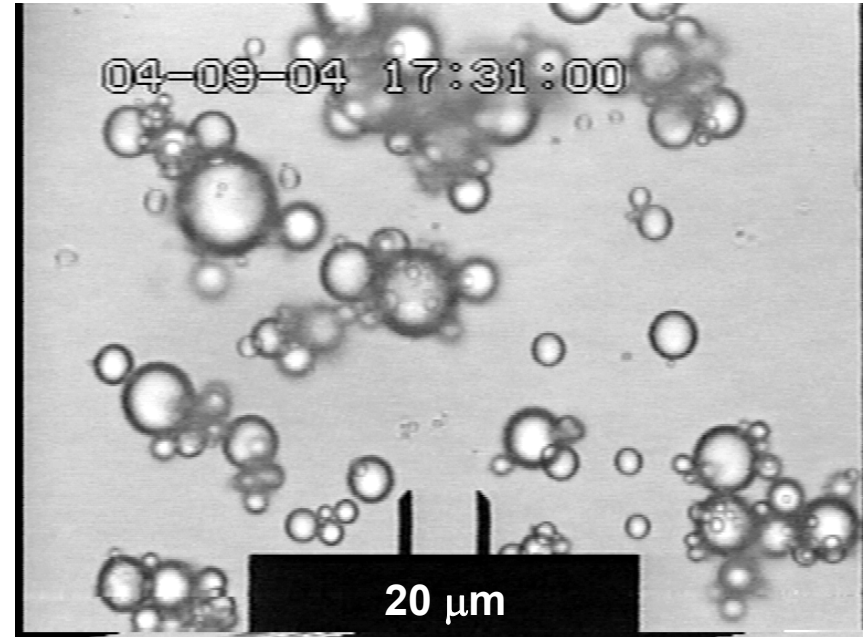
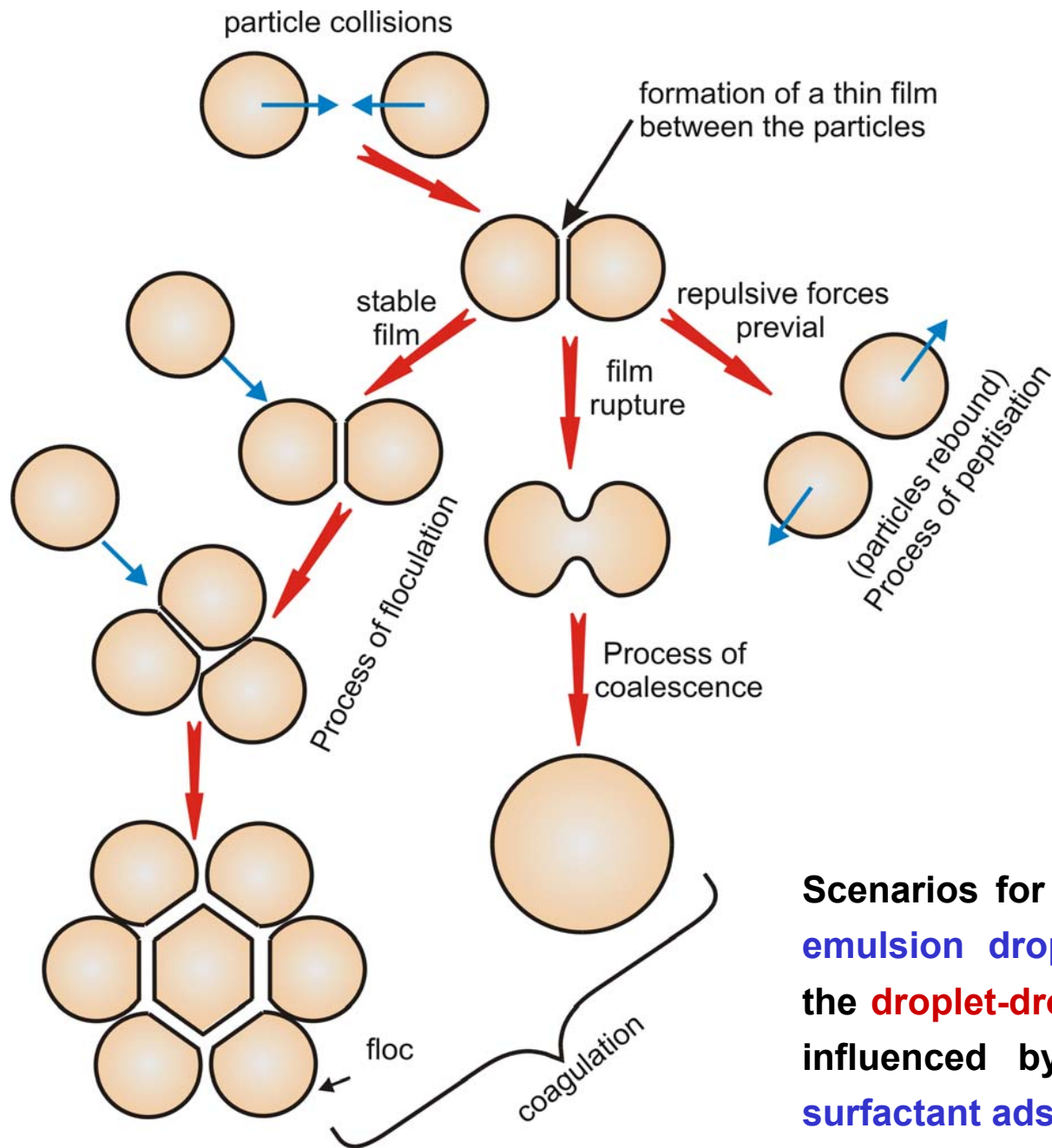**foam film stabilized by surface forces**

Sofia University

The Surface Forces Determine the Stability and Properties of Colloidal Dispersions (Examples)


Stability of foams
(gas-in-liquid dispersions)

04–09–04 17:31:00

20 μm

Flocculation in emulsions
(oil-in-water dispersions)

particle collisions

formation of a thin film between the particles

repulsive forces previal

stable film

film rupture

(particles rebound) Process of peptisation

Process of floculation

Process of coalescence

floc

coagulation

Scenarios for the behavior of colliding **emulsion droplets** in connection with the **droplet-droplet interaction**, which is influenced by the properties of the **surfactant adsorption monolayers**.
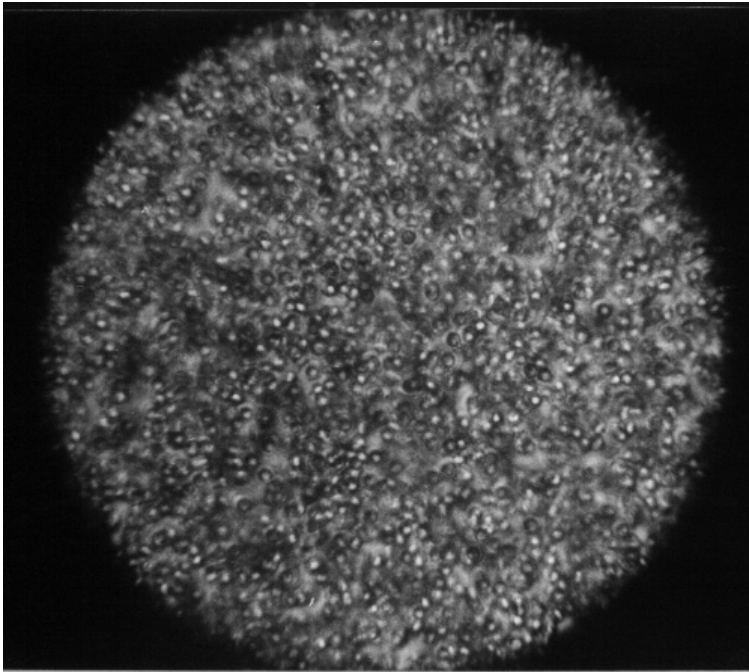
Particle coagulation in suspensions (solid-in-liquid dispersions)

Strongly dependent on the electrolyte concentration and counterion valence
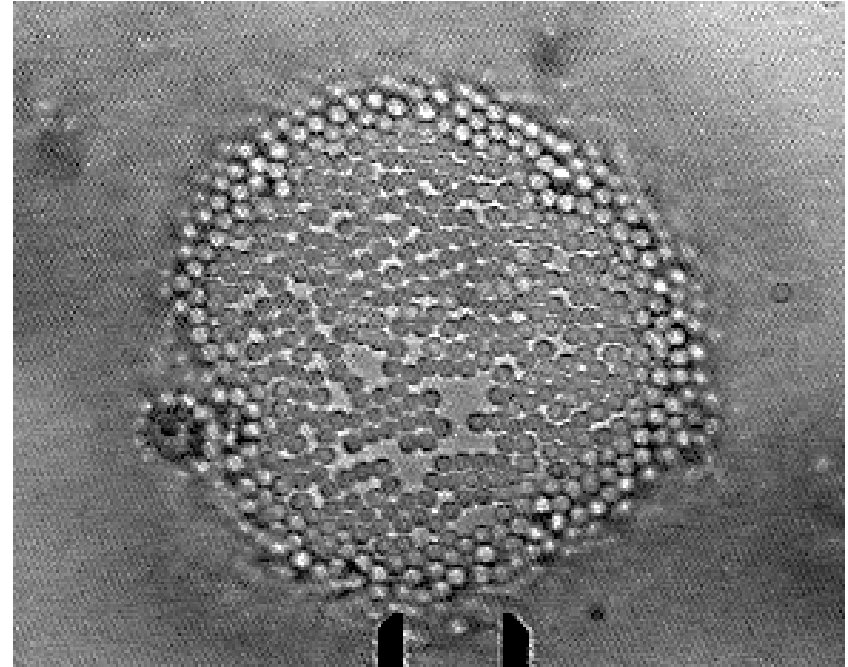
Emulsion drop covered by particles

The particles provide steric stabilization of the drops in Pickering emulsions
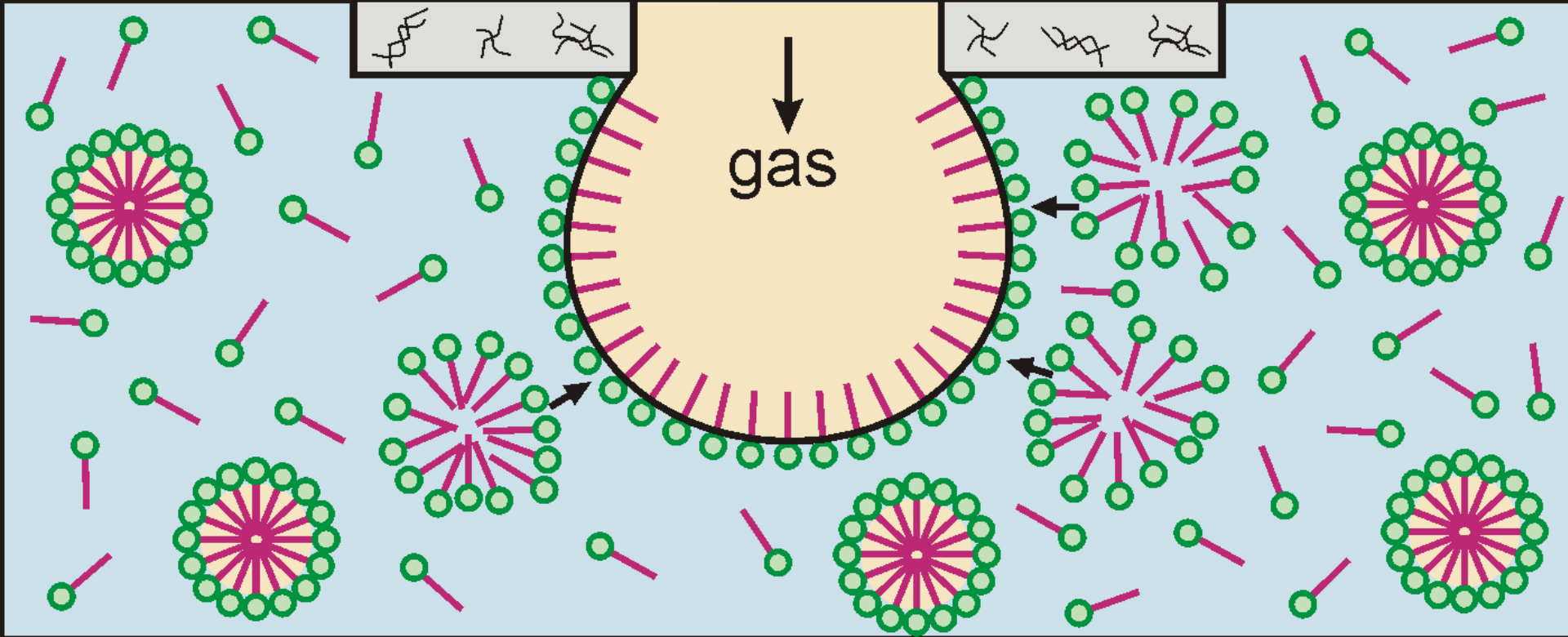
Interactions between the aggregates (micelles) in surfactant solutions, and of the micelles with interfaces during the process of washing.

In summary: The surface forces determine the stability and properties of various colloidal dispersions: foams, emulsions, suspensions, micellar and protein solutions, biological systems, etc.

Surface Force & Disjoining Pressure
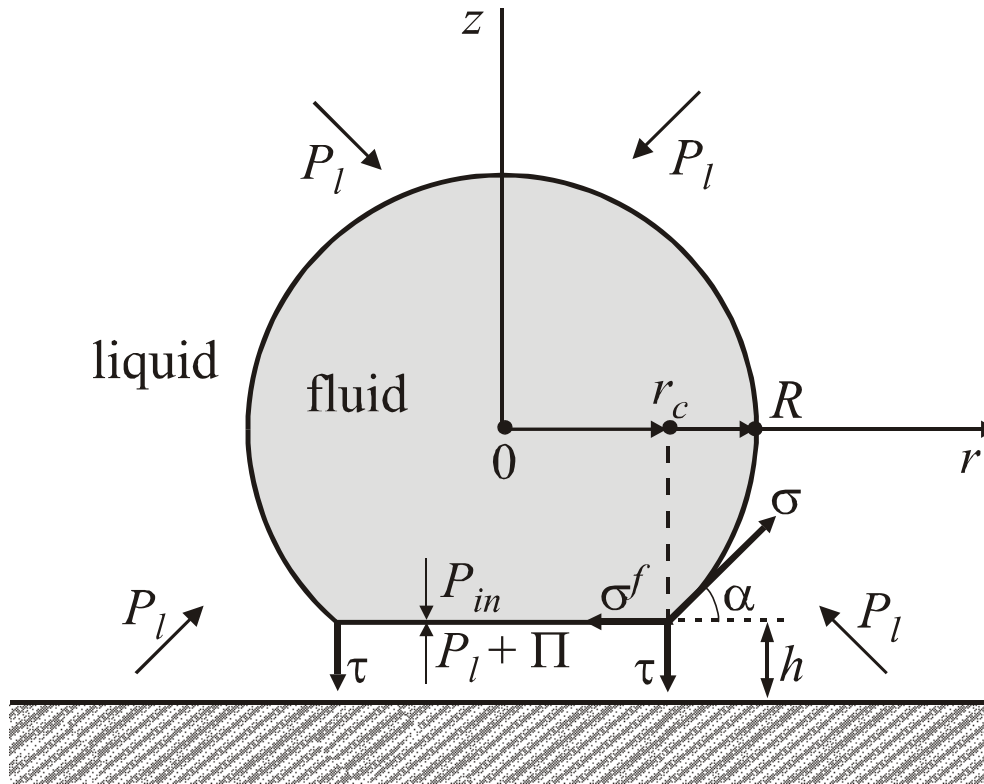
Surface force = Force of interaction between two bodies (two phases) when the distance *h* between their surfaces is relatively small.
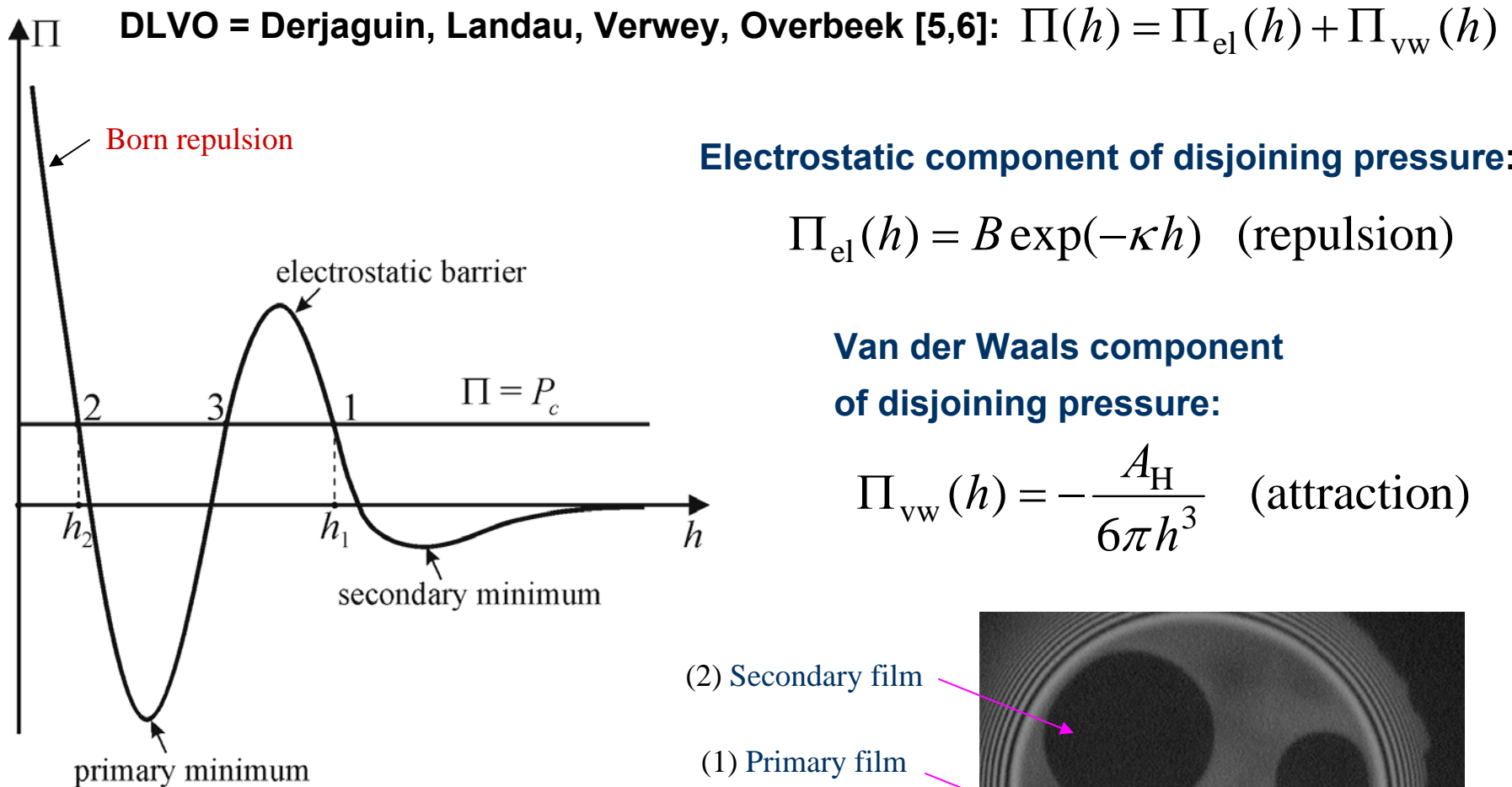
Typically, *h* < 100 nm.

Disjoining pressure, Π(*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)

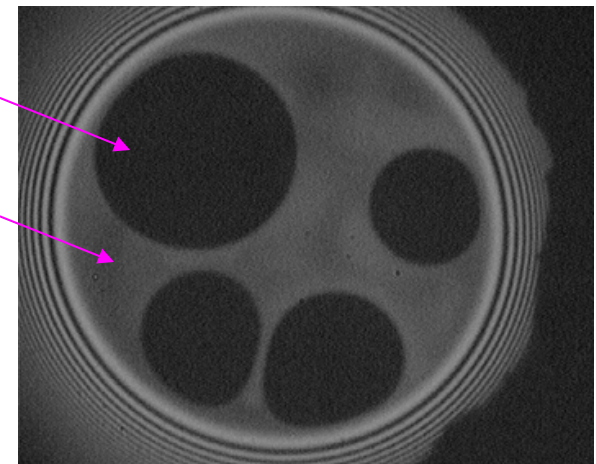**Force balance per unit area of the film surface: $P_l + \Pi = P_{in}$**

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

DLVO Theory: Equilibrium states of a free liquid film

DLVO = Derjaguin, Landau, Verwey, Overbeek [5,6]: $\Pi(h) = \Pi_{el}(h) + \Pi_{vw}(h)$

Born repulsion

electrostatic barrier

$\Pi = P_c$

secondary minimum

primary minimum

Electrostatic component of disjoining pressure:

$$\Pi_{el}(h) = B \exp(-\kappa h) \quad \text{(repulsion)}$$

Van der Waals component of disjoining pressure:

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

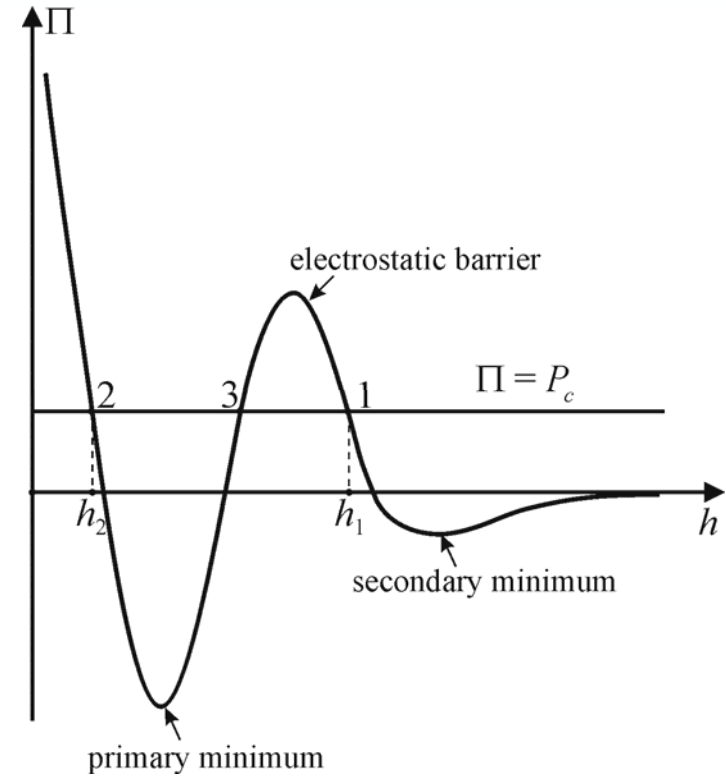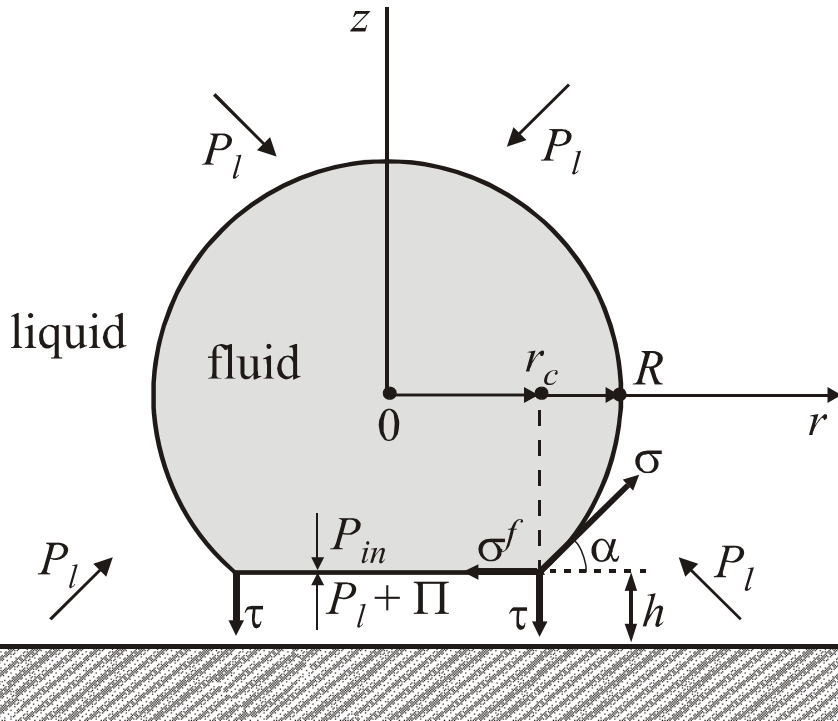

(2) Secondary film

(1) Primary film

h – film thickness; A_H – Hamaker constant;

κ – Debye screening parameter

Surface Forces and Contact Angles of Liquid films

film surface tension : $\sigma^f = \sigma \cos \alpha$

transversal tension : $\tau = \sigma \sin \alpha$ [9]

thermodynamics : $\dfrac{\partial \sigma^f}{\partial h} = -\Pi$

$$\sigma - \sigma^f = -\int_h^\infty \Pi(h)\,\mathrm{d}h \qquad \Rightarrow \qquad \cos \alpha = 1 + \frac{1}{\sigma}\int_h^\infty \Pi(h)\,\mathrm{d}h \qquad [10]$$
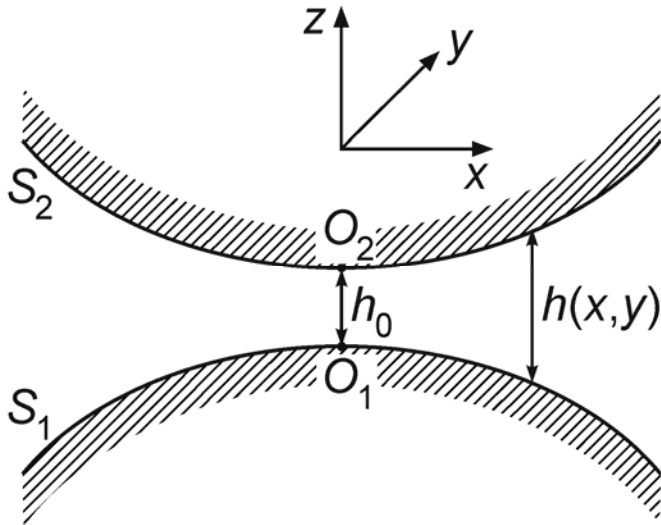
Derjaguin's Approximation (1934):

The energy of interaction, *U*, between two bodies across a **film of uneven thickness**, *h(x,y)*, is [11]:
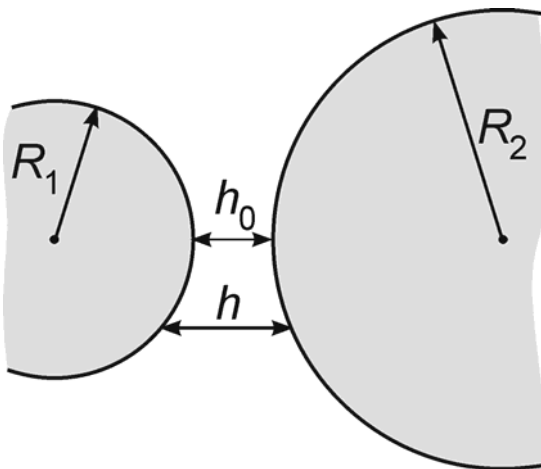
$$U = \iint f(h(x, y))\ dxdy$$

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

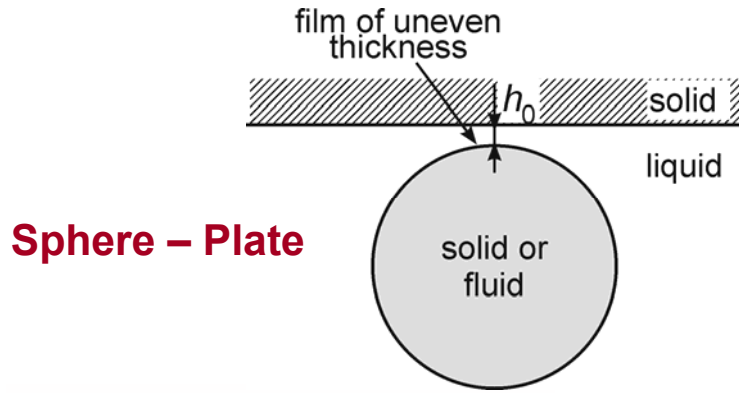$$f(h) = \int_{h}^{\infty} \Pi(\tilde{h})\, d\tilde{h}$$

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 *R₁* and *R₂*, 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 [1-3,12]:

Sphere – Plate

$$U(h_0) = 2\pi R_c \int_{h_0}^{\infty} f(h)\,dh$$
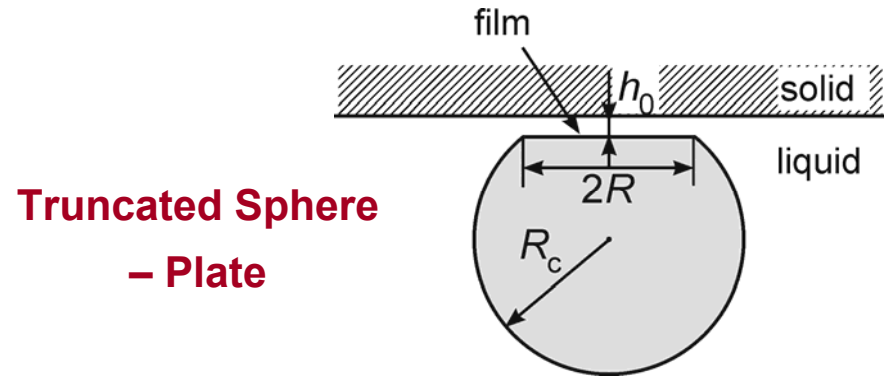
Truncated Sphere – Plate

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

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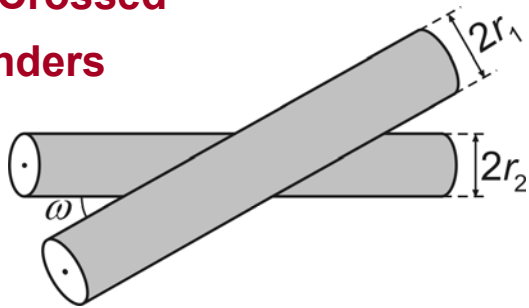
$$U(h_0) = \frac{2\pi\sqrt{r_1 r_2}}{\sin\omega} \int_{h_0}^{\infty} f(h)\,dh$$

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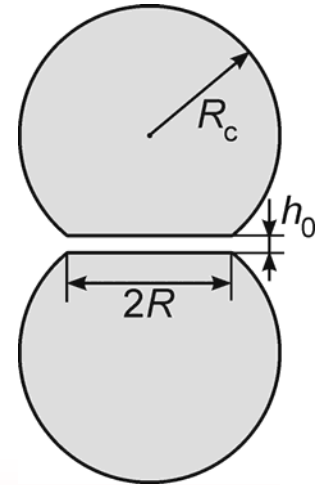
$$U(h_0) = \pi R_c \int_{h_0}^{\infty} f(h)\,dh + \pi R^2 f(h_0)$$

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 forces between molecules [13]: $u_{ij}(r) = -\dfrac{\alpha_{ij}}{r^6}$

Dipole – dipole interaction: The electric field of each dipole induces preferential **antiparallel orientation** of the other dipole. **Sum of three contributions**:

Two permanent dipoles:
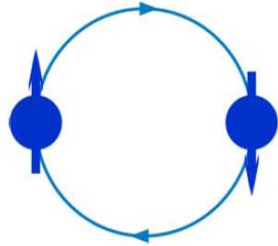
(1) Orientation interaction between two permanent dipoles (Keesom, 1912) **[14]**

(electrostatic effect)

permanent dipole   induced dipole

(2) Induction interaction between one permanent dipole and one induced dipole (Debye, 1920) **[15]**

(electrostatic effect)

e^-

$h\nu$

$h\nu$

e^-
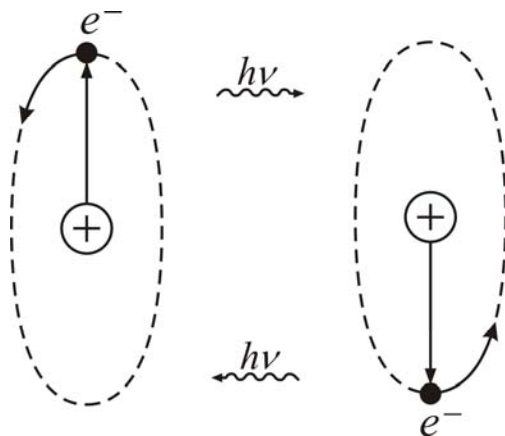
(3) Dispersion interaction between two induced dipoles (London, 1930) **[13]**

(quantum electrodynamic effect)

Van der Waals surface forces:
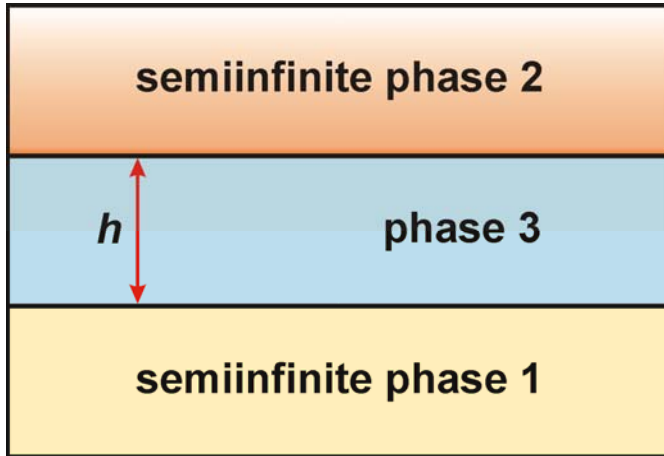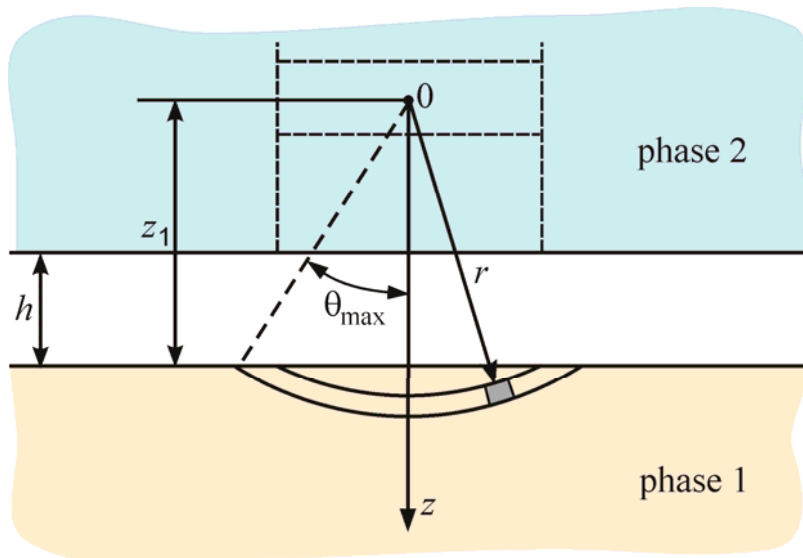
$$\Pi_{vw}(h) = -\frac{A_H}{6\pi h^3}$$

A_H – Hamaker constant

Hamaker's approach [16]

The interaction energy is **pair-wise additive**:
Summation over all couples of molecules.
Result [16,17]:

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

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

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

Symmetric film: phase 2 = phase 1

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

For symmetric films: always attraction!

Van der Waals repulsion:

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

semiinfinite phase 2

h phase 3

semiinfinite phase 1

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

Consider the case: $\qquad A_{11} > A_{33} > A_{22}$

For simplicity, let is set $\rho_2 = 0$ (gas); then:

$$A_H = -A_{31} + A_{33} = -A_{33}^{1/2}(A_{11}^{1/2} - A_{33}^{1/2}) < 0$$

Negative $A_H \Rightarrow$ repulsive van der Waals surface force

Helium vapor

h

H

Liquid Helium

Classical example: Liquid Helium climbs up the walls of the container [1].

Explanation: the repulsive van der Waals disjoining pressure across the adsorbed film balances the gravitational hydrostatic pressure:

$$\frac{|A_H|}{6\pi h^3} = \rho g H$$
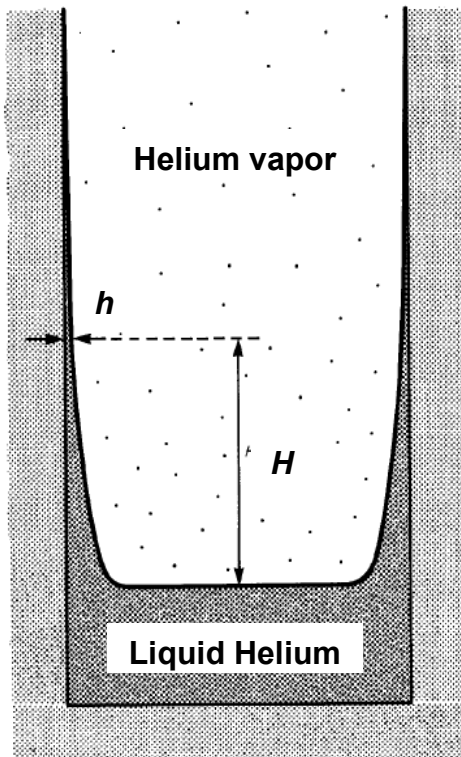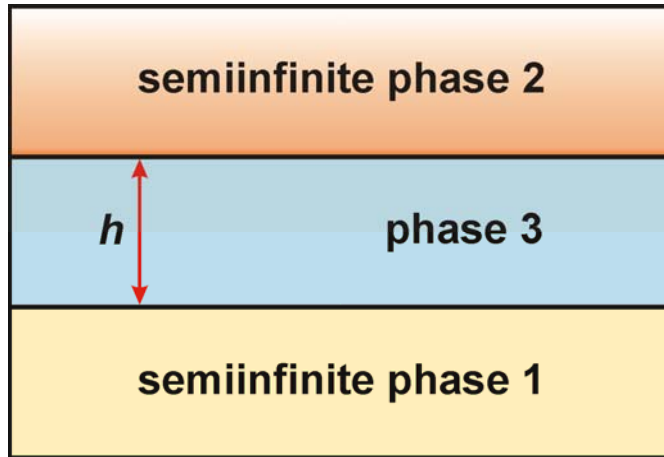
Van der Waals interaction in the presence of adsorption layers
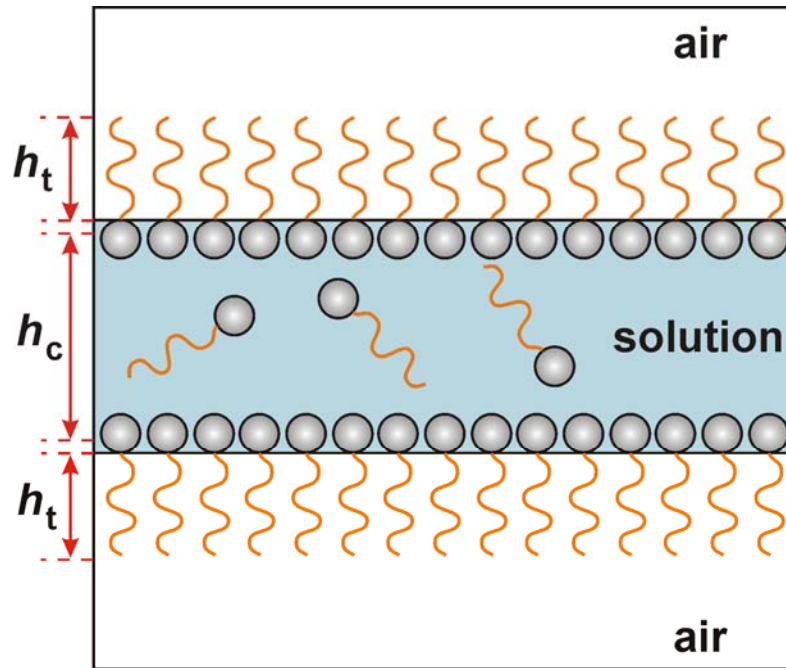
Example: Foam film stabilized
by surfactant

h_c – thickness of the <u>water core</u>;

h_t – thickness of layer of <u>surfactant tails</u>.

The integration over all couples of molecules belonging to the three layers yields [18]:

Free energy per unit area:

$$f_{vw} = -\frac{1}{12\pi}[\frac{A_{cc} - 2A_{ct} + A_{tt}}{h_c^2} + \frac{2(A_{ct} - A_{tt})}{(h_c + h_t)^2} + \frac{A_{tt}}{(h_c + 2h_t)^2}]$$

Disjoining pressure: $\Pi_{vw} = -\frac{\partial f_{vw}}{\partial h} = -\left(\frac{\partial f_{vw}}{\partial h_c}\right)_{h_t}$ $h = h_c + 2h_t$

Van der Waals interaction in a multilayered system
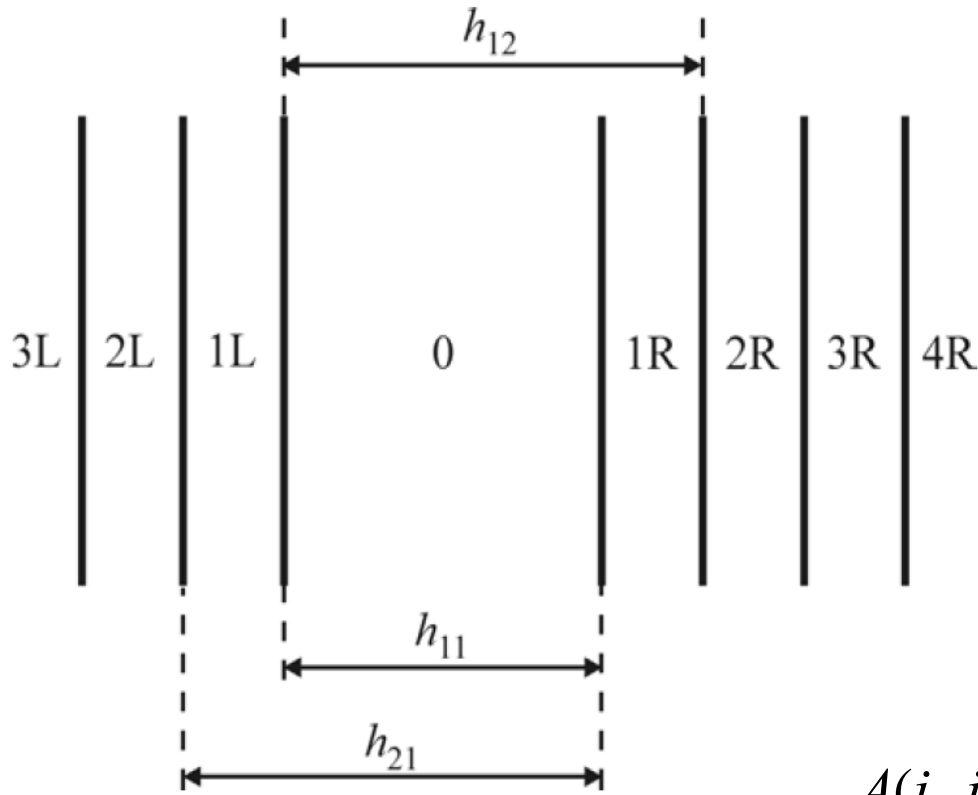
Case of two multilayered bodies interacting across a **medium 0**;

the layers are counted from the **central film 0** outward to the **left (L)** and **right (R)** [18].

$$f_{\text{vw}} = -\sum_{i=1}^{N_L}\sum_{j=1}^{N_R}\frac{A(i,j)}{12\pi h_{ij}^2}$$

$$A(i,j) = A_{i,j} - A_{i,j-1} - A_{i-1,j} + A_{i-1,j-1}$$

In the special case $N_L = N_R = 1$, we obtain the expression for symmetric film from phase "0" sandwiched between two phases "1":

$$A(1,1) = A_{1,1} - 2A_{1,0} + A_{0,0}$$

$$f_{\text{vw}} = -\frac{A(1,1)}{12\pi h_{11}^2}$$

Lifshitz approach to the calculation of Hamaker constant

semiinfinite phase 2

h phase 3

semiinfinite phase 1

E. M. Lifshitz (1915 – 1985) [19] took into account the **collective effects** in condensed phases (solids, liquids). (The total energy is **not** pair-wise additive over al pairs of molecules.)
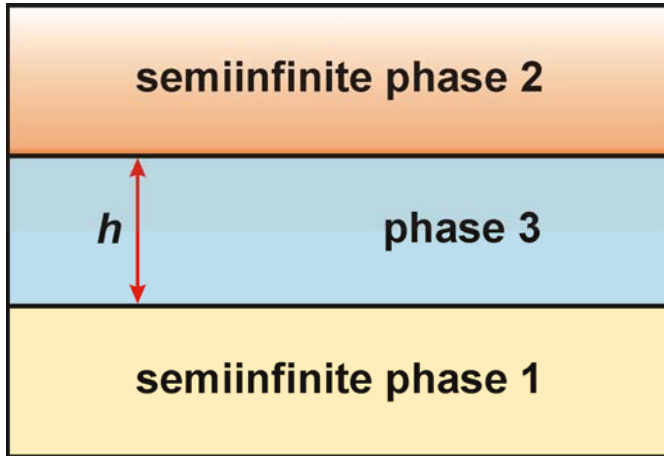
Lifshitz used the **quantum field theory** to derive <u>accurate</u> expressions in terms of:

(i) <u>Dielectric constants</u> of the phases: ε_1, ε_2 and ε_3 ;

(ii) <u>Refractive indexes</u> of the phases: n_1, n_2 and n_3:

$$A_{\mathrm{H}} \equiv A_{132} \approx \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h_{\mathrm{P}}\nu_e\left(n_1^2 - n_3^2\right)\left(n_2^2 - n_3^2\right)}{16\sqrt{2}\left(n_1^2 + n_3^2\right)^{3/4}\left(n_2^2 + n_3^2\right)^{3/4}}$$
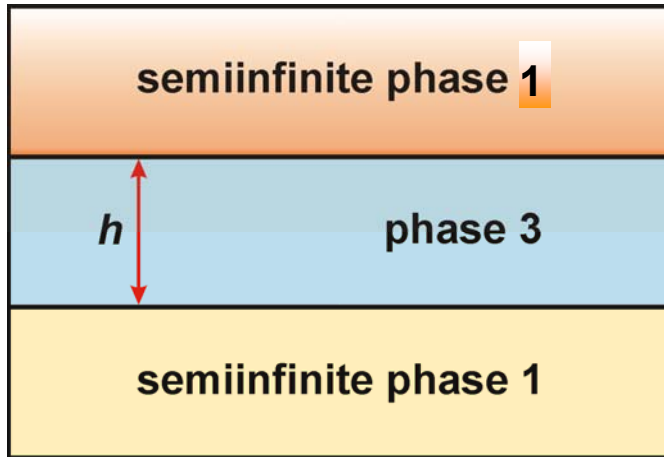
Zero-frequency term: $A_{132}^{(\nu=0)}$

orientation & induction interactions;

kT – thermal energy.

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

ν_e = 3.0 x 10^{15} Hz – main electronic absorption frequency;

h_{P} = 6.6 x 10^{-34} J.s – Planck's const.

Hamaker constant for symmetric films

semiinfinite phase 1

h phase 3

semiinfinite phase 1

$$A_{\mathrm{H}} \equiv A_{131} = A_{131}^{(\nu=0)} + A_{131}^{(\nu>0)}$$

$$= \frac{3}{4}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)^2 + \frac{3h_{\mathrm{P}}\nu_e\left(n_1^2 - n_3^2\right)^2}{16\sqrt{2}\left(n_1^2 + n_3^2\right)^{3/2}}$$

$$\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)^2 < 1 \quad \Rightarrow \quad A_{131}^{(\nu=0)} < \frac{3}{4}kT \approx 3\times10^{-21}\,\mathrm{J}$$

(i) For two bodies interacting across vacuum (or gas):
(ii) For a free-standing liquid or solid film (e.g. foam film): $A_{\mathrm{H}} = 10^{-19} - 10^{-20}\,\mathrm{J}$
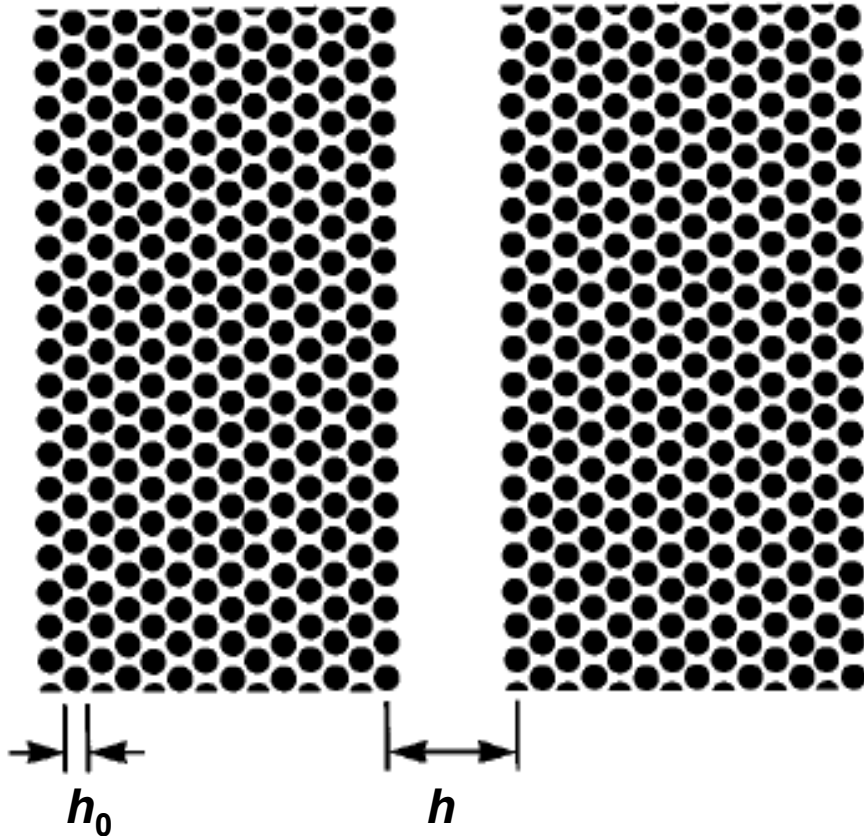
Hence, for such configurations the
dispersion interaction is predominant: $A_{131}^{(\nu=0)} << A_{131}^{(\nu>0)} \approx A_{\mathrm{H}}$

The zero-frequency term becomes comparable to the
dispersion term when n_1 is close to n_3 (e.g. emulsion systems): $A_{131}^{(\nu=0)} \approx A_{131}^{(\nu>0)}$

Determination of the **Hamaker constant** from the **surface tension**

$$f_{vw}(h_0) = \int_{h_0}^{\infty} \Pi_{vw}(\tilde{h})\,d\tilde{h} = \frac{A_H}{12\pi h_0^2} = 2\gamma$$

If h_0 is the center-to-center distance between two molecules, then $f_{vw}(h_0)$ is the work of adhesion, which for liquids equals **2γ** (where **γ** is the surface tension):

$$\gamma = \frac{A_H}{24\pi h_0^2}$$

With h_0 = 0.165 nm – good comparison theory-experiment for nonpolar liquids [1]:

Material	Theoretical A_H (10^{-20} J)	$\gamma = A_H/(24\pi h_0^2)$ (mN/m)	γ experimental (mN/m)
n-Octane	4.5	21.9	21.6
Cyclohexane	5.2	25.3	25.5
Water	3.7	18.0	73.0 (20 ºC)

Electromagnetic Retardation **Effect on Dispersion Force** [20]
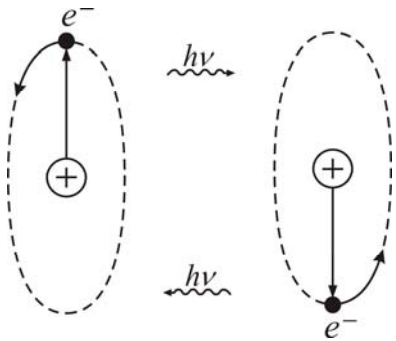
C = 3 x 10^8 m/s; v_e = 3 x 10^{15} s^{-1} $\Rightarrow$ $L = C/v_e$ = 100 nm

For $L \geq$ 50 nm the dipole – dipole correlation is suppressed

$$\Rightarrow \quad u_{ij}(r) \rightarrow -\frac{\alpha_{ij}}{r^7}$$

$$A_{131}^{(v>0)}(h) = \frac{3h_P v_e}{16\sqrt{2}} \frac{\left(n_1^2 - n_3^2\right)^2}{\left(n_1^2 + n_3^2\right)^{3/2}} \left[1 + (\pi h_d / \sqrt{32})^{3/2}\right]^{-2/3} \quad \textbf{Russel et al. [21]}$$

$$\Rightarrow \quad A_{131}^{(v>0)} \propto \frac{1}{h} \quad (h \rightarrow \infty) \qquad h_d = n_3 \left(n_1^2 + n_3^2\right)^{1/2} \frac{2\pi v_e h}{c}$$
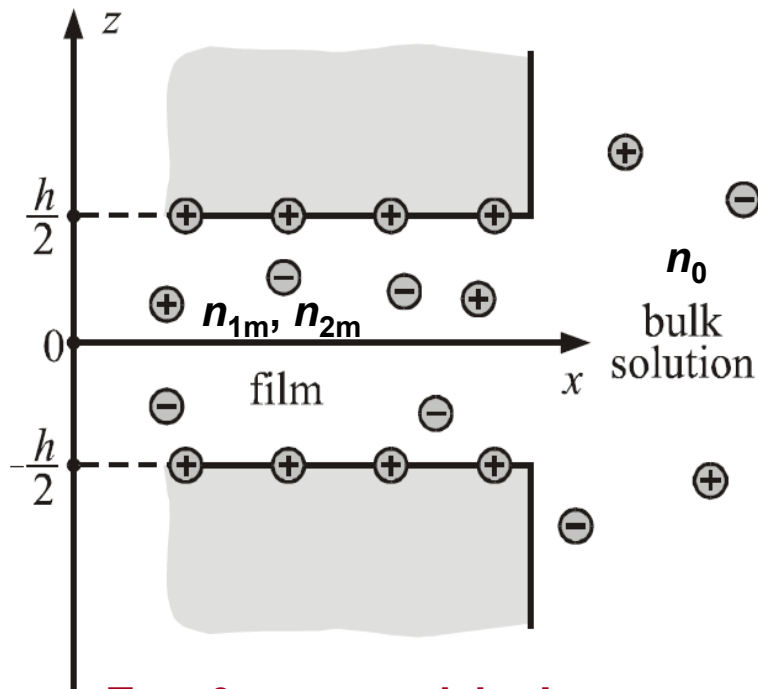
Dimensionless

$\leftarrow$ **thickness**

Suppression of **Orientation** & **Induction** Interactions by **Electrolyte** [22]

$$A_H(h) = 2\kappa h\, A_0^{(v=0)}\, e^{-2\kappa h} + A^{(v>0)} \quad \text{for} \quad \kappa h > 2; \qquad \kappa = \frac{2e^2 I}{\varepsilon\varepsilon_0 kT}$$

I is the ionic strength of solution

Electrostatic (Double Layer) Surface Force

$\frac{h}{2}$

0

n_{1m}, n_{2m}

film

$-\frac{h}{2}$

z

x

n_0

bulk
solution

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

Π_{el} = **excess osmotic pressure** of the ions **in the midplane** of a symmetric film (**Langmuir, 1938**) [23]:

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

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.

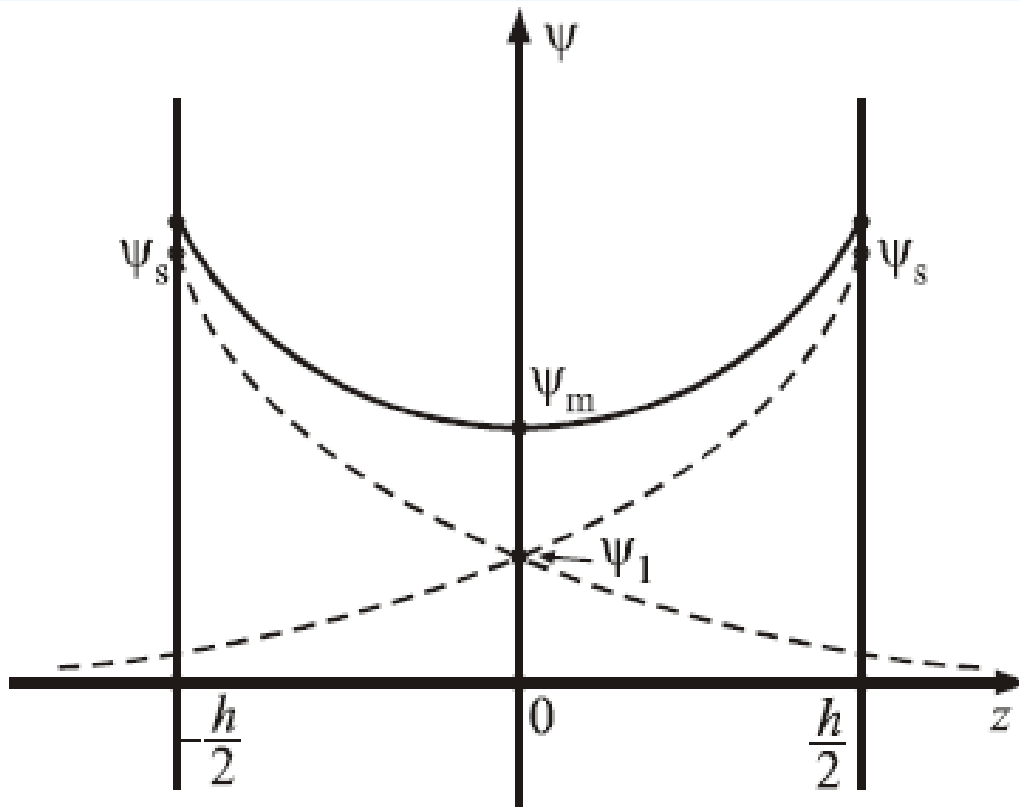For solution of a symmetric electrolyte: $Z_1 = -Z_2 = Z$; Z is the valence of the coions. Boltzmann equation; Φ_m – dimensionless potential in the midplane ($\Phi_m \ll 1$).

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

$$\Pi_{el} = 2n_0 kT\left[\cosh(\Phi_m) - 1\right] \approx n_0 kT \Phi_m^2 > 0 \qquad \cosh(\Phi_m) = 1 + \frac{\Phi_m^2}{2} + O(\Phi_m^4)$$

More general definition of Π_{el}

In the midplane **z = 0**,
the potential has a minimum
and we have:

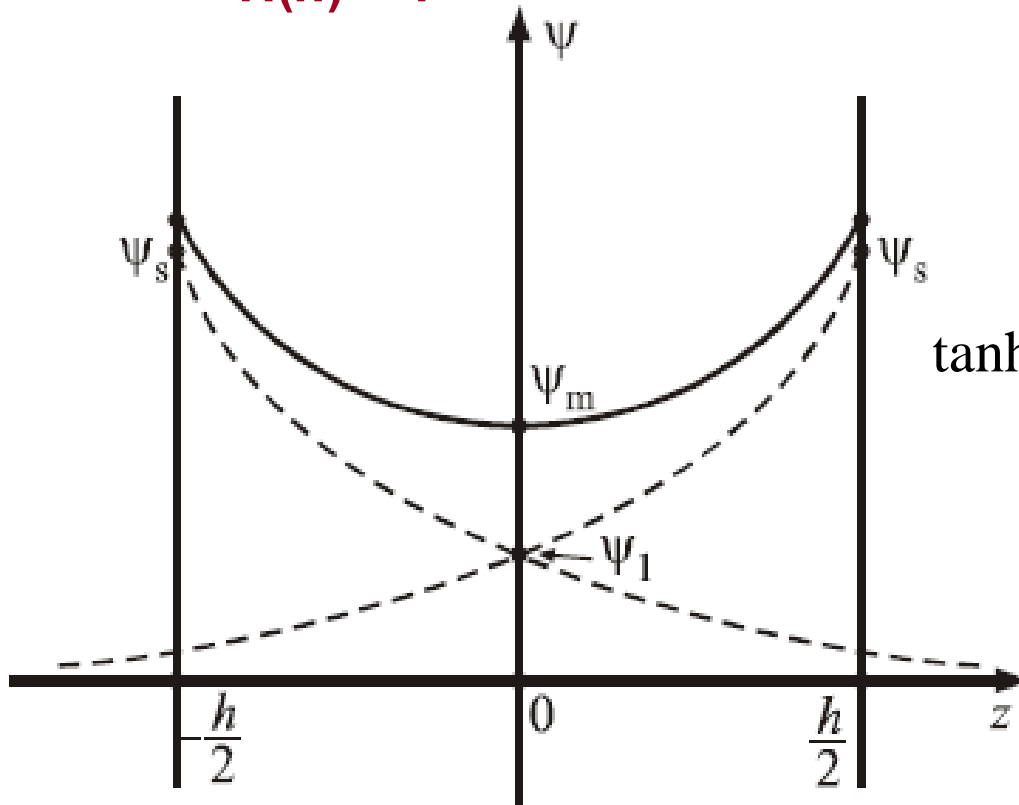$$\left(\frac{d\psi}{dz}\right)^2_{z=0} = 0$$

and in addition :

$$n_1\big|_{z=0} = n_{1m}$$

$$n_2\big|_{z=0} = n_{2m}$$

In each plane **z = const.**,
not necessarily the midplane,
we have [2]:

$$\Pi_{el} = kT[n_1(z) + n_2(z) - 2n_0] - \frac{\varepsilon_0 \varepsilon}{2}\left(\frac{d\psi}{dz}\right)^2$$

$$= kT(n_{1m} + n_{2m} - 2n_0) = \text{const.}$$

Π(h) = ?   Verwey – Overbeek Formula (1948)

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

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

Superposition approximation in the midplane: $\psi_{\mathrm{m}} = 2\psi_1$ [6]:
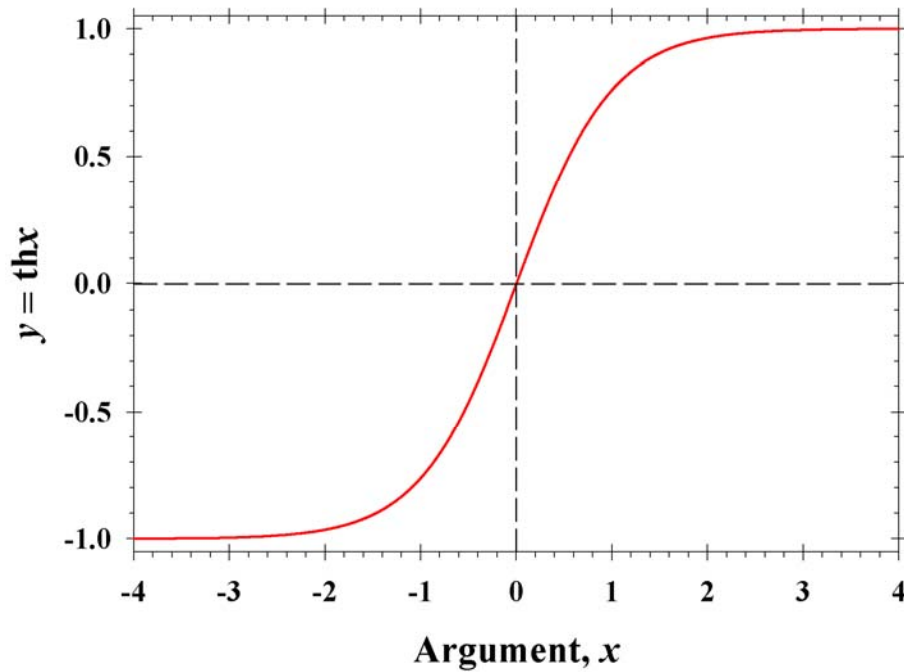
In the midplane $\dfrac{Ze\psi_1}{4kT} \ll 1$

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

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

$$\boxed{\Pi_{\mathrm{el}}(h) \approx n_0 kT\Phi_{\mathrm{m}}^2 \approx 64n_0 kT\gamma^2\exp(-\kappa h)}$$

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

$y = \text{th}x$ vs Argument, x

tanh(*x*) ≈ 1 for x ≥ 1.5

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

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

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

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

Debye screening length, κ^{-1}: $\quad \kappa^2 = \dfrac{2e^2 I}{\varepsilon\varepsilon_0 kT} \;\; ; \;\; I = \dfrac{1}{2}\sum_i Z_i^2 c_i \;\;$ (ionic strength)

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

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

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

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

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

$\Pi_{el}(h)$ in the case of **asymmetric** electrolytes **2:1** or **1:2**

2:1 electrolyte = **divalent counterion** and **monovalent coion**;

1:2 electrolyte = **monovalent counterion** and **divalent coion.**

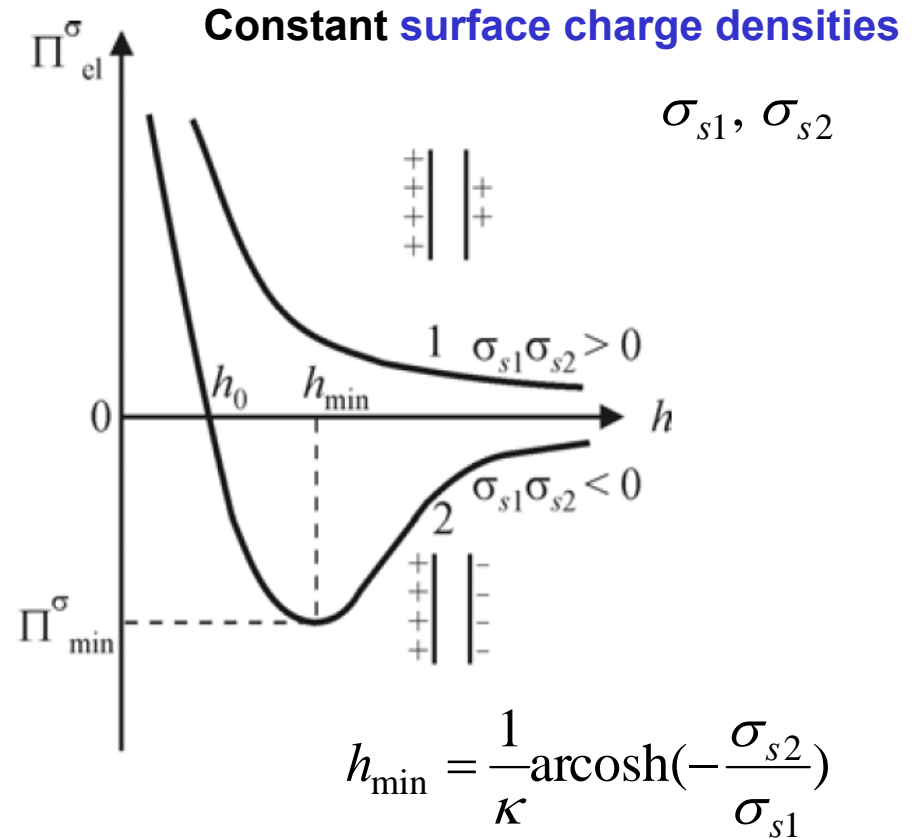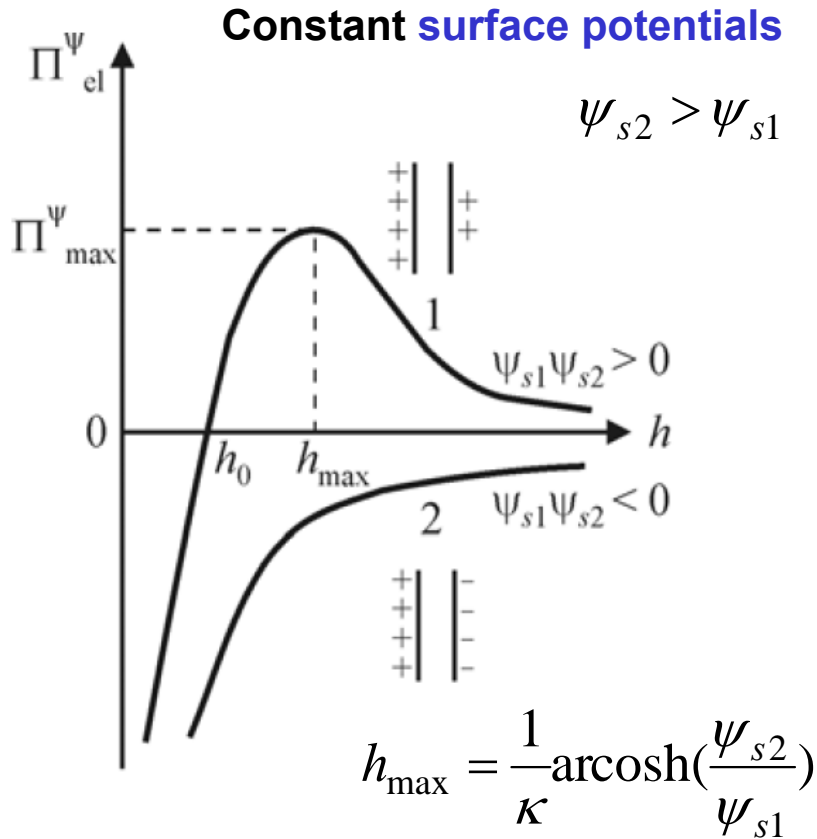$$\Pi_{el}(h) = 432 n_{(2)} kT \left(\tanh \frac{v_{i:j}}{4} \right)^2 \exp(-\kappa h)$$

derived in refs. [24,12]

$n_{(2)}$ is concentration of the divalent ions;

the subscript "$i{:}j$" takes value "2:1" or "1:2"

$$v_{2:1} = \ln\left[3 \bigg/ \left(1 + 2\exp\left(-\frac{e\psi_s}{kT} \right) \right) \right], \qquad v_{1:2} = \ln\left[\left(2\exp\left(\frac{e\psi_s}{kT} \right) + 1 \right) \bigg/ 3 \right]$$

$\Pi_{el}(h)$ in the case of nonidentically charged planes [12]

Constant surface potentials

$$\psi_{s2} > \psi_{s1}$$

Constant surface charge densities

$$\sigma_{s1}, \sigma_{s2}$$

$$h_{\max} = \frac{1}{\kappa}\text{arcosh}(\frac{\psi_{s2}}{\psi_{s1}})$$

$$h_{\min} = \frac{1}{\kappa}\text{arcosh}(-\frac{\sigma_{s2}}{\sigma_{s1}})$$

Asymptotic expression for not-too-small h [6]:   **(Z:Z – electrolyte)**

$$\Pi_{el}(h) = 64 n_0 kT \gamma_1 \gamma_2 e^{-\kappa h}, \qquad \gamma_k \equiv \tanh(\frac{Ze\psi_{sk}}{4kT}), \ k = 1,2$$

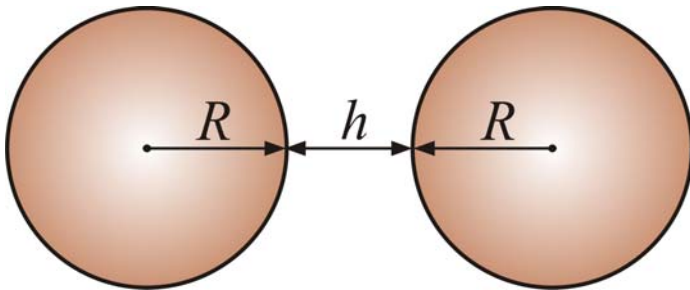# Derjaguin – Landau – Verwey – Overbeek (DLVO) Theory [5,6]

Disjoining pressure:

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

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

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

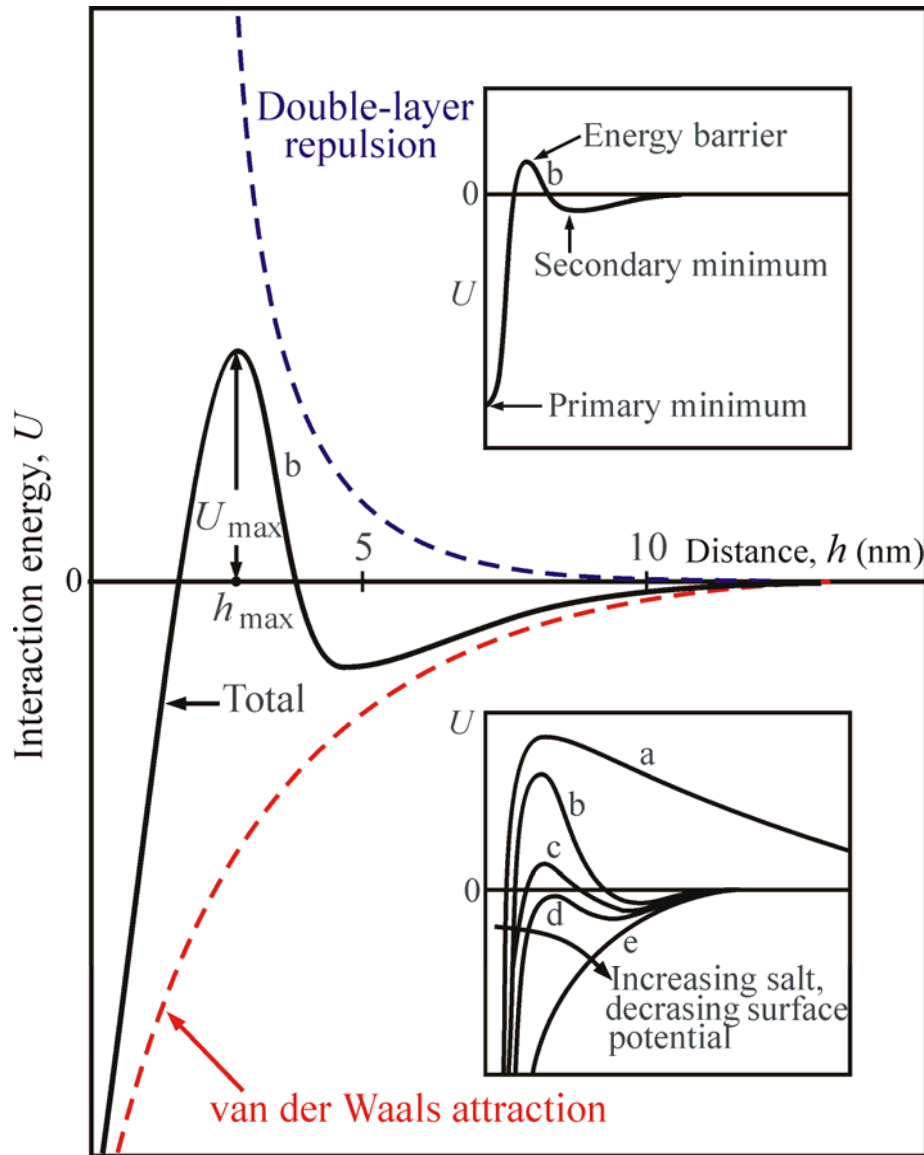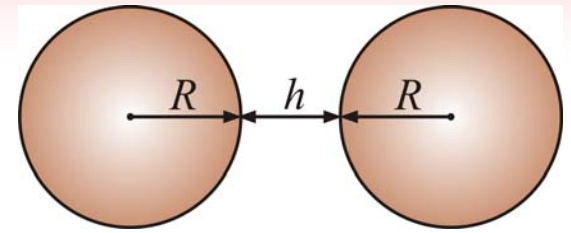**Energy of interaction between two identical spherical particles (Derjaguin approximation):**

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

$$B = 64 n_0 kT\gamma^2, \qquad \gamma \equiv \tanh\left(\frac{Ze\psi_{\mathrm{s}}}{4kT} \right)$$

$$(e - \text{electronic charge};\ \mathrm{e} = 2.71828...)$$

DLVO Theory: **The electrostatic barrier**

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

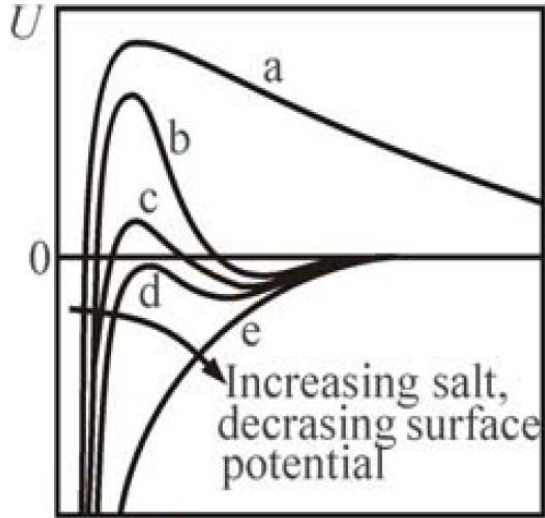The **secondary** minimum could cause coagulation only for big (1 μm) particles.

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

Condition for coagulation: $U_{max} = 0$

(zero height of the barrier to coagulation)

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

The Critical Coagulation Concentration (*ccc*) [5,6]

U vs *h* plot with curves a, b, c, d, e. "Increasing salt, decreasing surface potential"

$$U(h_{\max}) = 0 \quad \Rightarrow \quad \frac{B}{\kappa^2}e^{-\kappa h_{\max}} = \frac{A_H}{12\pi h_{\max}} \quad \times \quad \frac{1}{\kappa}$$

$$\left.\frac{dU}{dh}\right|_{h=h_{\max}} = 0 \quad \Rightarrow \quad \frac{B}{\kappa}e^{-\kappa h_{\max}} = \frac{A_H}{12\pi h_{\max}^2}$$

$$\Rightarrow \boxed{\kappa h_{\max} = 1} \quad \Rightarrow \quad \frac{B}{\kappa^3}e^{-1} = \frac{A_H}{12\pi}$$
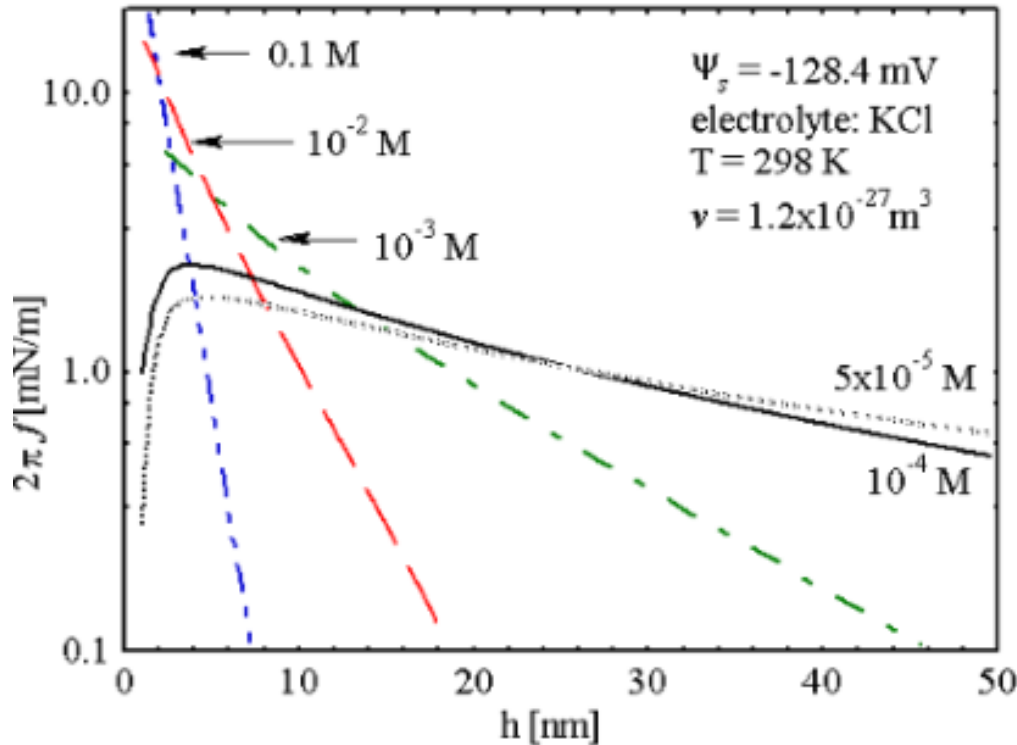
$$\Rightarrow \quad \frac{B^2}{\kappa^6} = \left(\frac{A_H e}{12\pi}\right)^2 \quad \Rightarrow \quad \frac{(64kT\gamma^2 n_0)^2}{\left(\dfrac{2Z^2 e^2}{\varepsilon_0 \varepsilon kT}\right)^3 n_0^3} = \left(\frac{A_H e}{12\pi}\right)^2$$

$$ccc \propto \frac{1}{Z^6} \quad \text{Rule of Schulze (1882) [25] and Hardy (1900) [26]}$$

$$(B = 64 n_0 kT\gamma^2)$$

$$\Rightarrow ccc \equiv n_0 = \frac{(64 \times 12\pi)^2}{2^3 e^2}\frac{\gamma^4 (\varepsilon_0 \varepsilon)^3 (kT)^5}{A_H^2 (Ze)^6} \approx 9.85 \times 10^4 \frac{\gamma^4 (\varepsilon_0 \varepsilon)^3 (kT)^5}{A_H^2 (Ze)^6}$$

Non-DLVO Surface Forces: Hydration Repulsion

At $C_{el} < 10^{-4}$ M (NaCl, KNO$_3$, 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, 27].

Empirical expression [1] for the interaction free energy per unit area:
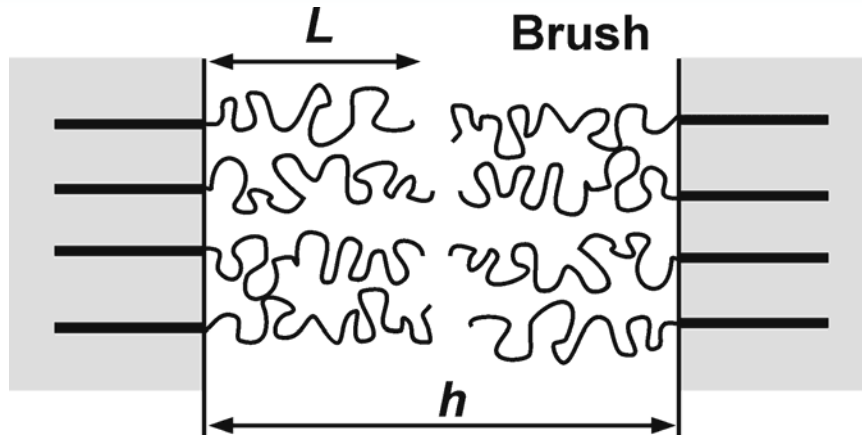
$$f_{\text{hydr}} = f_0 \exp(-h / \lambda_0)$$

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

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

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 [28].

Steric interaction due to adsorbed polymer chains

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

l – the length of a segment;

N – number of segments in a chain;

In a good solvent L > L₀, whereas

in a poor solvent L < L₀.

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

L depends on adsorption of chains, Γ

[1,21].

$$\text{for } h < 2L_{\mathrm{g}}; \quad L_{\mathrm{g}} = N\left(\Gamma l^5\right)^{1/3}$$
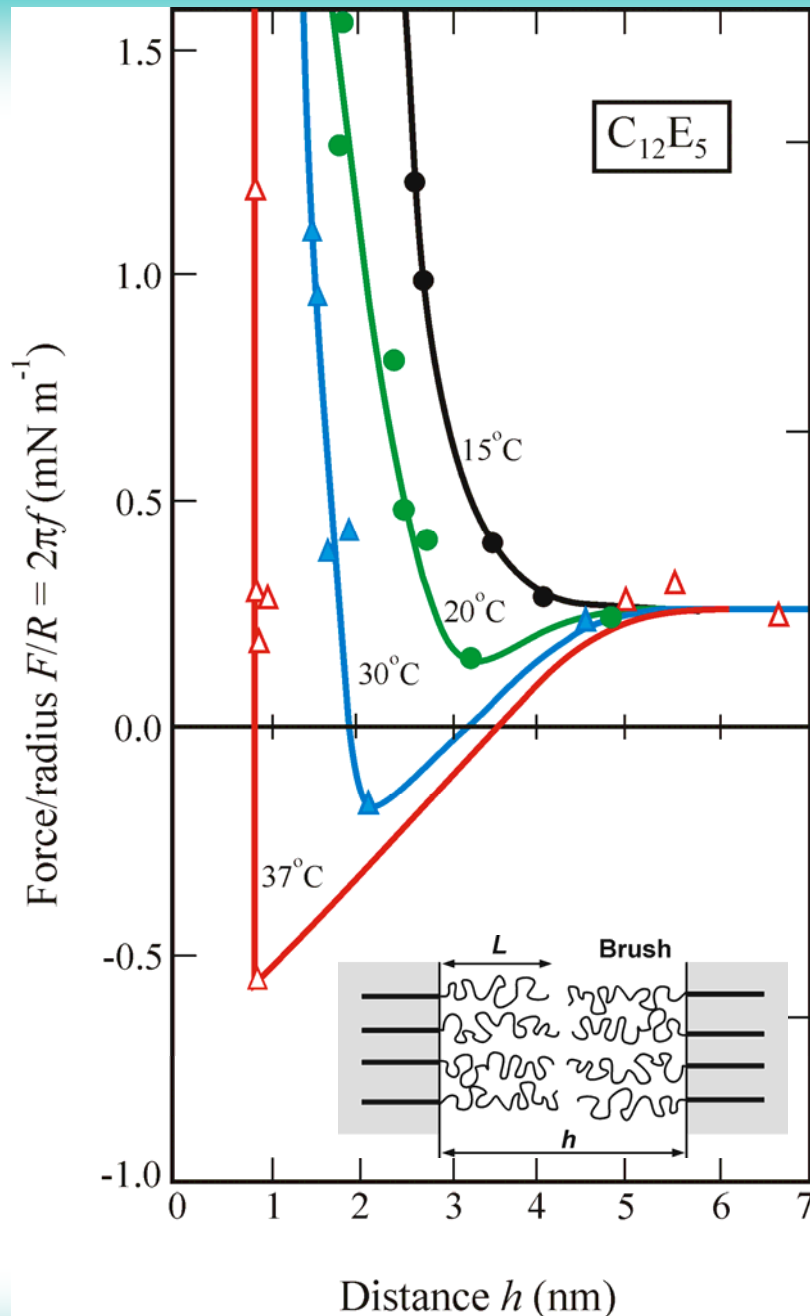
← Alexander – de Gennes theory

for the case of good solvent [29,30]:

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].**

Steric interaction – poor solvent

Plot of experimental data for measured forces, $F/R \equiv 2\pi f$ vs. h, between two surfaces covered by adsorption monolayers of the **nonionic surfactant $C_{12}E_5$** for various temperatures.

The **appearance of minima** in the curves indicate that the water becomes a **poor solvent** for the polyoxyethylene chains with the increase of temperature; from Claesson et al. [31].

Oscillatory–Structural Surface Force

For details – see the book by Israelachvili [1]
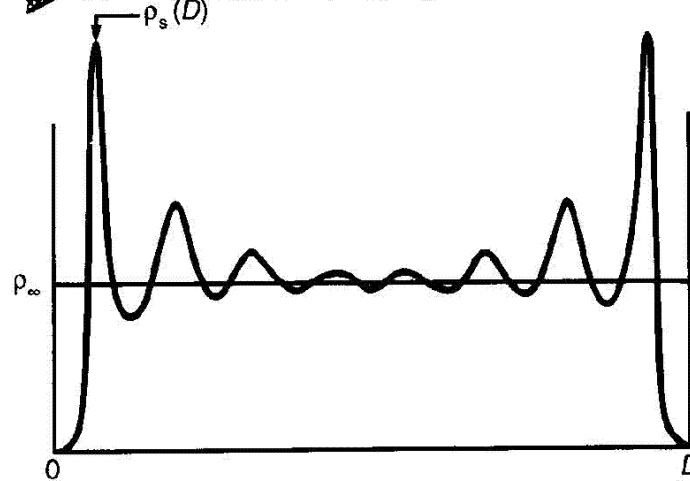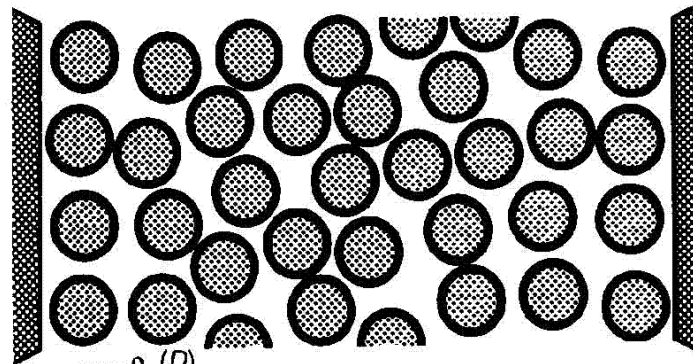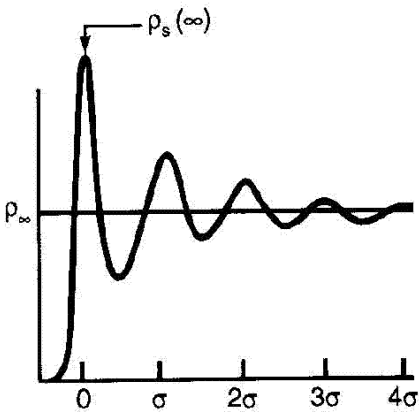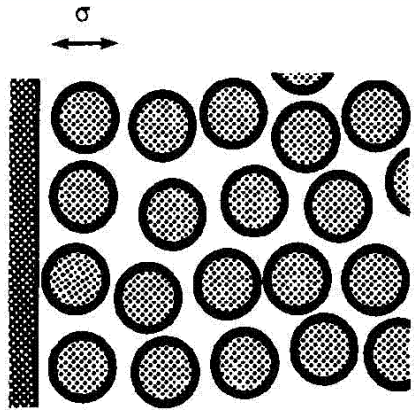
A planar phase boundary (wall) induces ordering in the adjacent layer of a hard-sphere fluid.

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**.

Oscillatory structural forces were observed in liquid films containing colloidal particles, e.g. latex & surfactant micelles; Nikolov et al. [32,33].
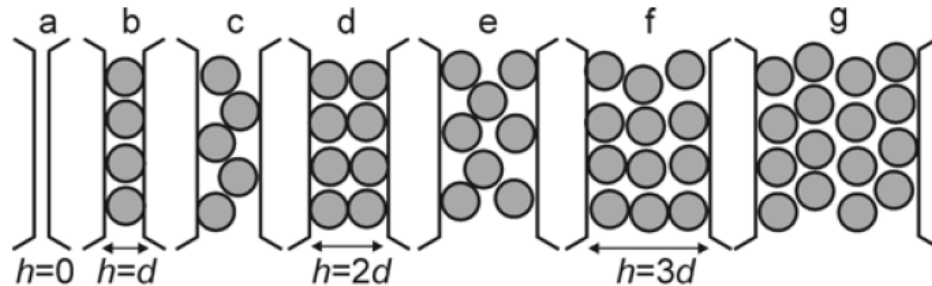
(a)
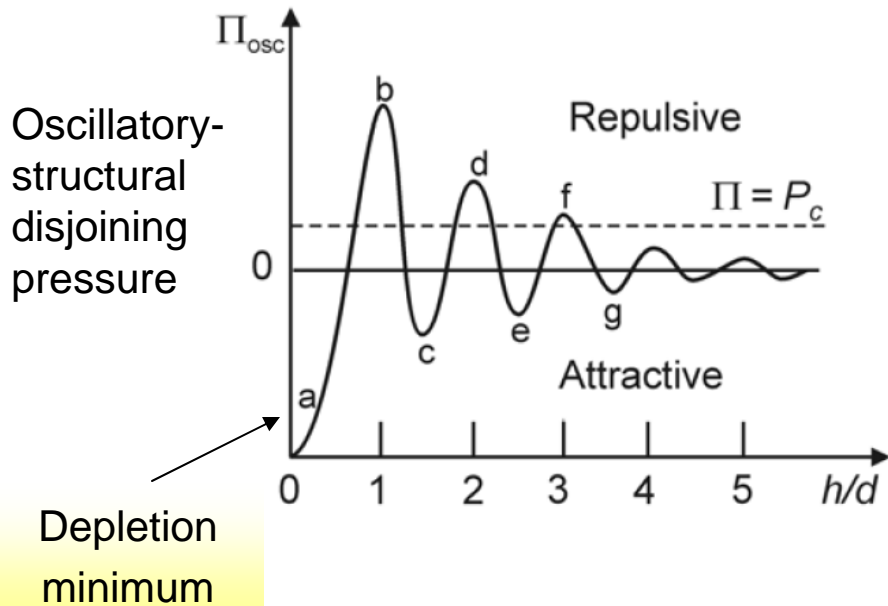
The maxima of the oscillatory force could stabilize colloidal dispersions.

Oscillatory-structural disjoining pressure

Depletion minimum

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 Solvent Molecules
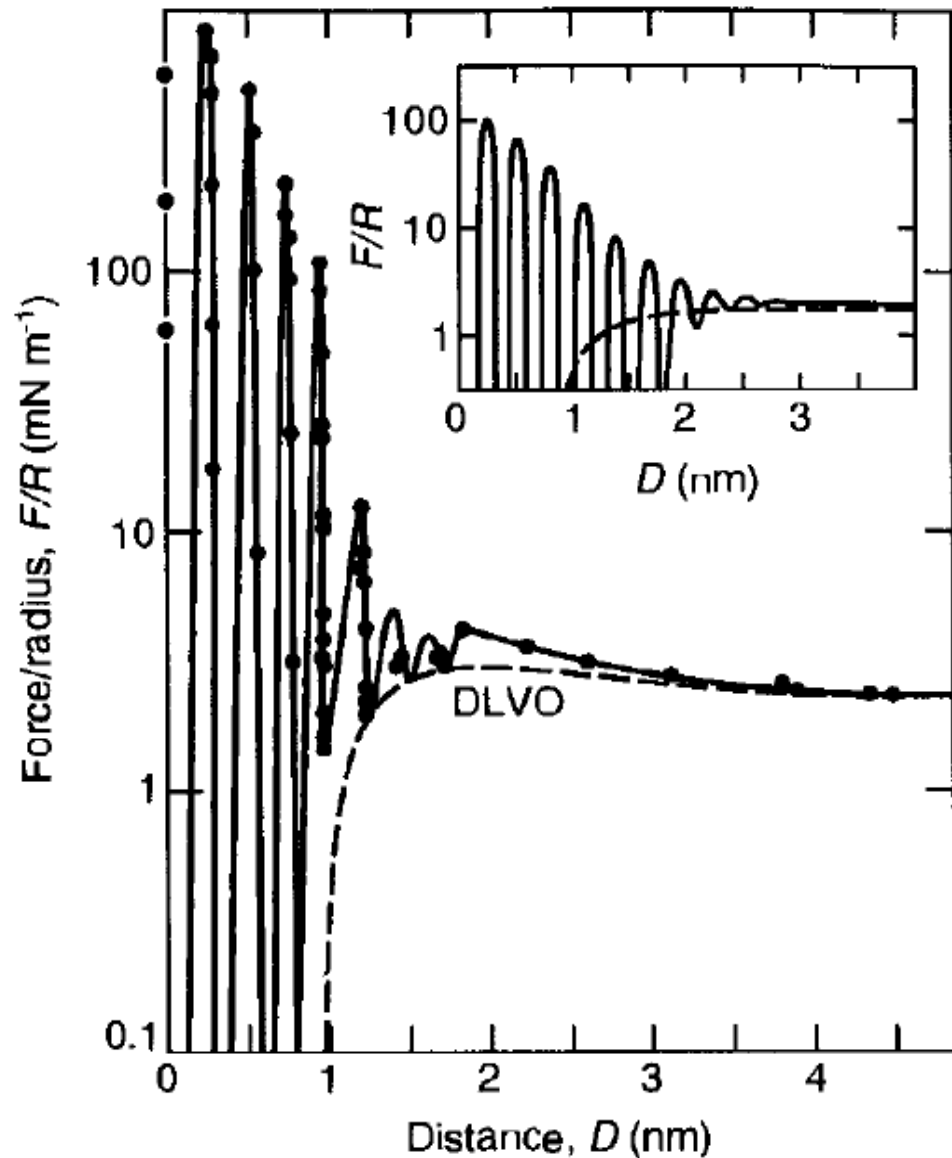
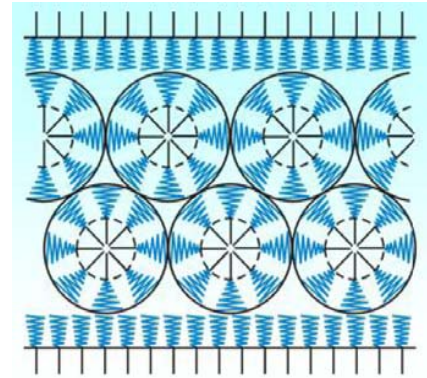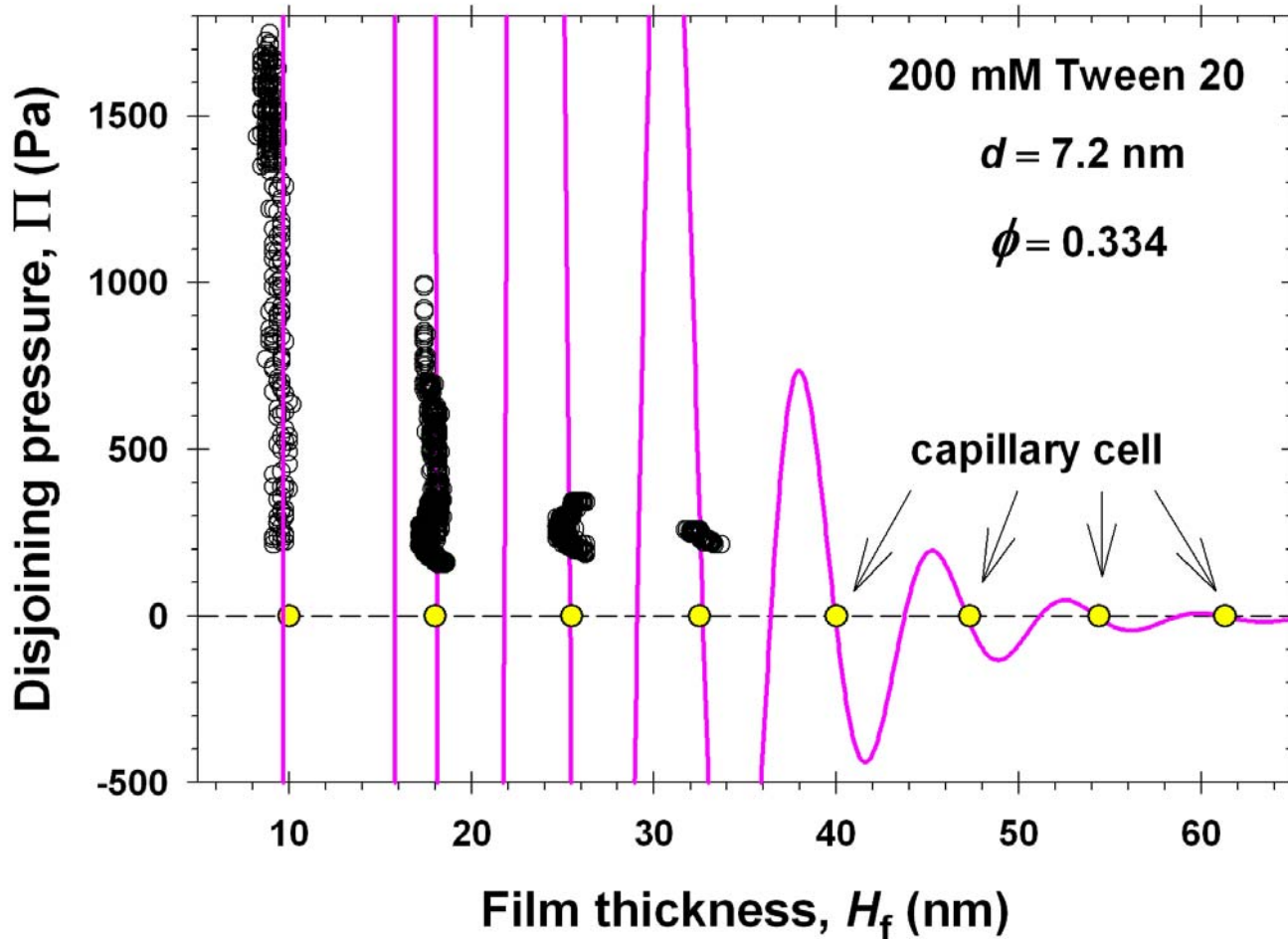Measured short-range force between two cylindrical mica surfaces of radii R = 1 cm in 10^{-3} M KCl solution.

The dashed line shows the expected DLVO interaction.

The oscillatory force has a period of 0.22 − 0.26 nm, about the diameter of the water molecule (oscillatory hydration force)

Theoretical computations are shown in the inset.

(Experimental results from Israelachvili and Pashley, 1983 [34].

Oscillatory–Structural Surface Force Due to Colloid Particles

200 mM Tween 20

$d = 7.2$ nm

$\phi = 0.334$

capillary cell

Disjoining pressure, Π (Pa) (y-axis: 1500, 1000, 500, 0, -500)

Film thickness, H_f (nm) (x-axis: 10, 20, 30, 40, 50, 60)

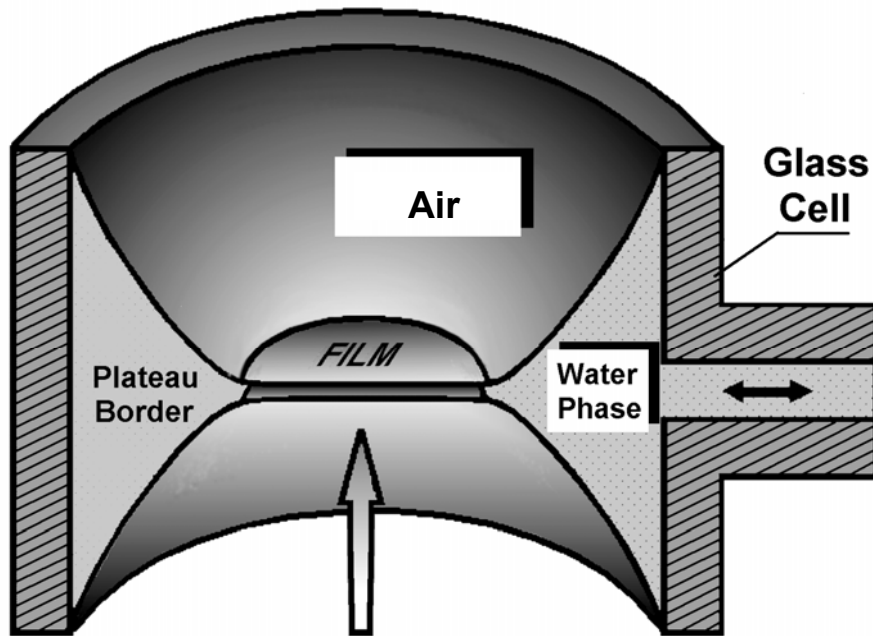Ordering of **micelles** of the nonionic surfactant Tween 20 [36].

Methods: Mysels' porous plate cell and Scheludko capillary cell [7,8]

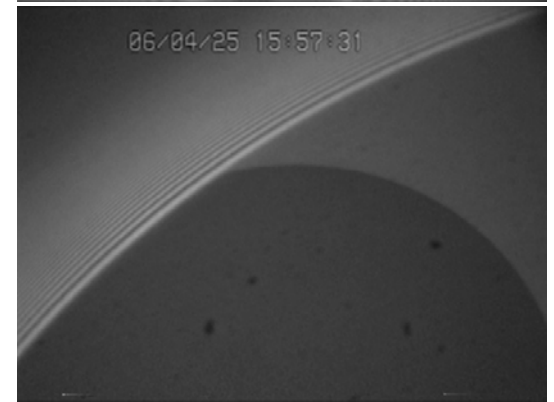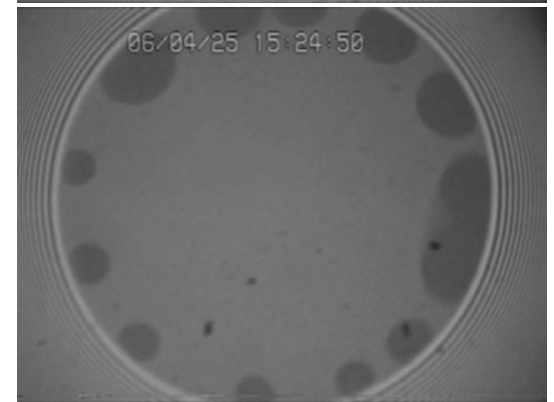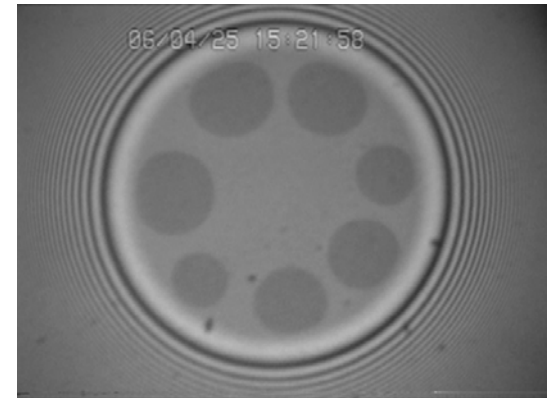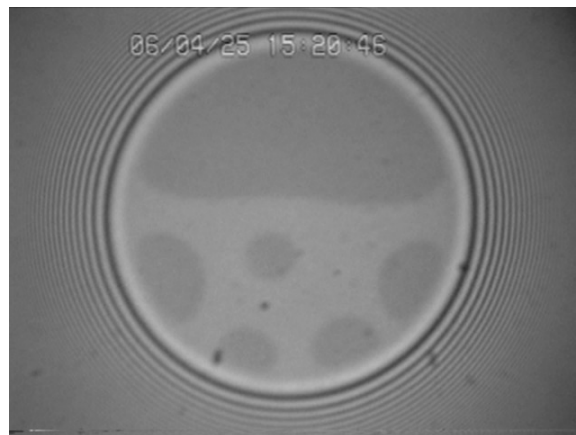**Theoretical curve** – by means of the **Trokhimchuk formulas** [35].
The micelle aggregation number, N_{agg} = 70, is determined [36].

Foam Film Stratification by the Scheludko Capillary Cell

Stepwise thickness transitions: 0.1 M Brij 35 + 0.1 M NaCl
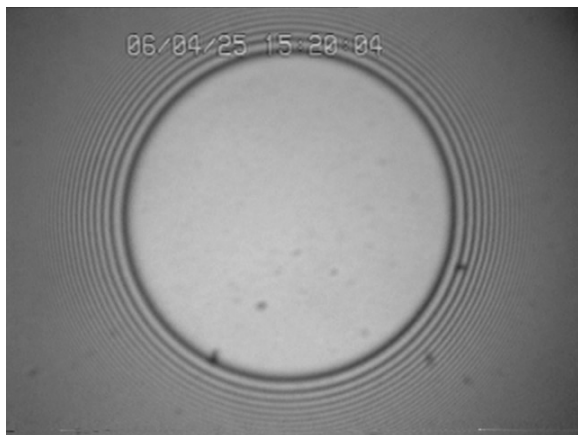
Decaying Oscillations

Semiempirical expression [37]:

$$\Pi_{\text{ocs}} = P_{\text{hs}} \cos\left(\frac{2\pi h}{d_1}\right)\exp\left(\frac{d^3}{d_1^2 d_2} - \frac{h}{d_2}\right), \quad \text{for } h > d$$

$$\Pi_{\text{ocs}} = -P_{\text{hs}}, \quad \text{for } 0 < h < d$$

d – **particle diameter; (hard spheres)**

d_1 – period; d_2 – decay length :

$$\frac{d_1}{d} = \sqrt{\frac{2}{3}} + 0237\,\Delta\phi$$

$$\frac{d_2}{d} = \frac{0.487}{\Delta\phi} - 0.420$$

ϕ – **particle volume fraction,** $\Delta\phi = 0.74 - \phi$
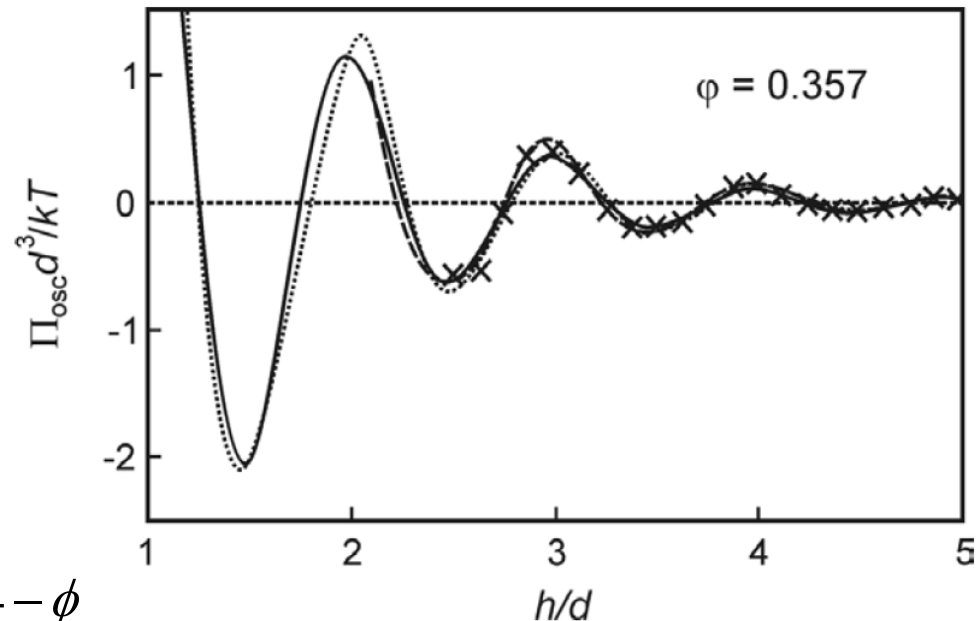
The above expression for $\Pi_{\text{osc}}(h)$ works well at all distances, **except** in the region of the first (the highest) maximum. **For all h, use the Trokhimchuk formulas [35].**

(P_{hs} – osmotic pressure of a hard-sphere fluid: Carnahan–Starling formula)

Depletion Attraction

Depletion minimum

$\rho\sigma^3 = 0.8$

$d/2$

$D/2$ h_0 $D/2$

d
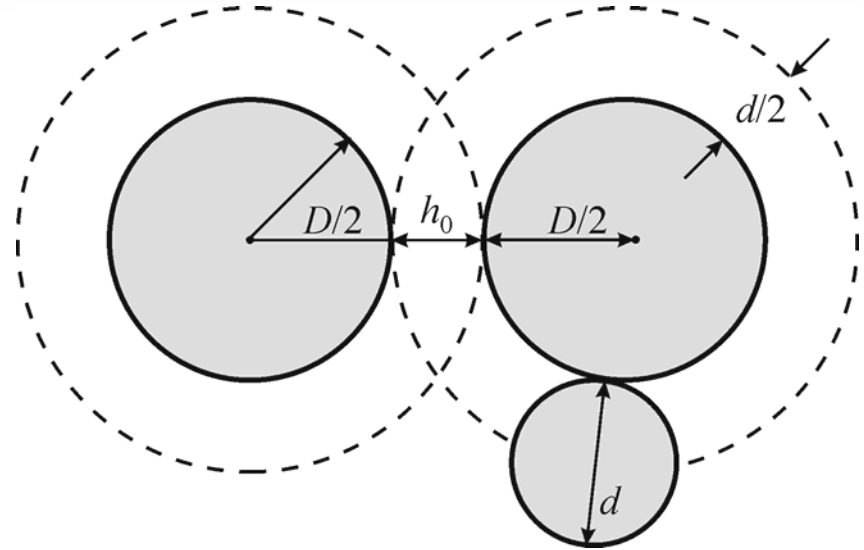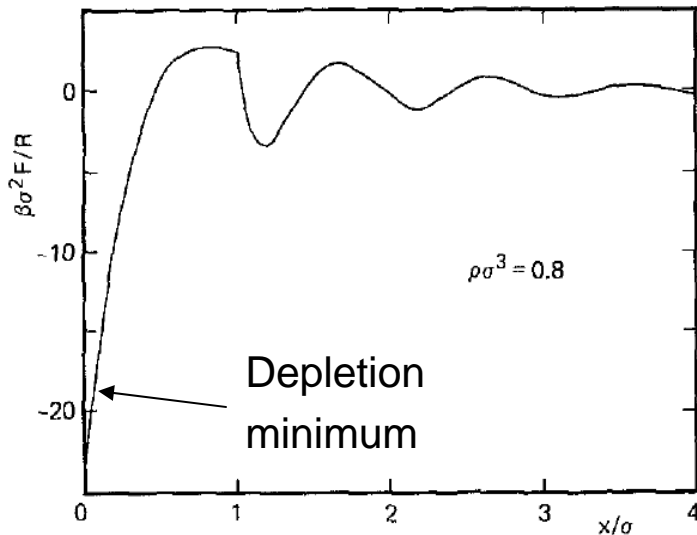
At low particle volume fractions, the oscillations disappear and **only the first "depletion" minimum remains**. The oscillatory force degenerates into the "**depletion attraction**". It leads to **coagulation** in colloidal dispersions by **smaller particles**, e.g. polymer coils [38].

The depletion attraction is due to the **osmotic pressure of the smaller particles**, which cannot penetrate in a certain "depletion zone" between the two bigger particles. **Depth of the depletion minimum (0 ≤ h_0 ≤ d) [1]:**

$$U_{dep}(h_0)/kT \approx -\frac{3}{2}\phi\frac{D}{d^3}(d-h_0)^2$$

$$D/d = 50; \quad \phi = 0.10; \quad U_{dep}(0) = 7.5kT$$

The total energy of interaction between two particles , $U(h)$, includes contributions from all surface forces:
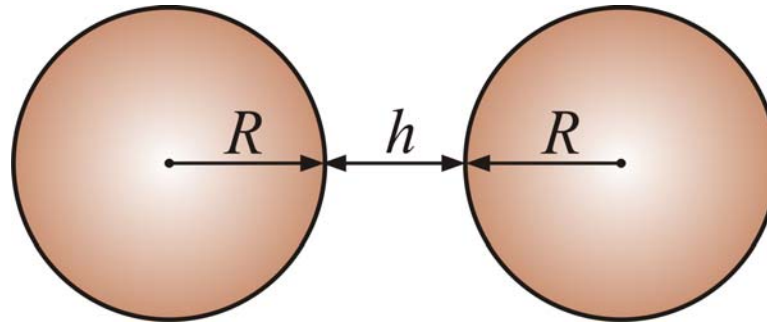
$$U(h) = U_{vw}(h) + U_{el}(h) + U_{hydr}(h) + U_{st}(h) + U_{osc}(h) + \ldots$$

DLVO forces

Non-DLVO forces

(The depletion force is included in the expression for the oscillatory-structural force, U_{osc})

Basic References

1. J.N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1992.

2. P.A. Kralchevsky, K. Nagayama, *Particles at Fluid Interfaces and Membranes*, Elsevier, Amsterdam, 2001; Chapter 5.

3. P.A. Kralchevsky, K.D. Danov, N.D. Denkov. Chemical physics of colloid systems and Interfaces, Chapter 7 in *Handbook of Surface and Colloid Chemistry",* (Third Edition; K. S. Birdi, Ed.). CRC Press, Boca Raton, 2008; pp. 197-377.

Additional References

4. B.V. Derjaguin, M.M. Kussakov, *Acta Physicochim. USSR* 10 (1939) 153.

5. B.V. Derjaguin, L.D. Landau, Theory of Stability of Highly Charged Lyophobic Sols and Adhesion of Highly Charged Particles in Solutions of Electrolytes, *Acta Physicochim. USSR* 14 (1941) 633-652.

6. E.J.W. Verwey, J.Th.G. Overbeek, *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.

7. A. Scheludko, Über das Ausfließen der Lösung aus Schaumfilmen. *Colloid Polymer Sci.*, 1957, 155, 39-44.

8. A. Scheludko, Thin Liquid Films, *Adv. Colloid Interface Sci.* 1 (1967) 391-464.

9. P.A. Kralchevsky, I.B. Ivanov, On the Mechanical Equilibrium between a Film of Finite Thickness and the External Meniscus, *Chem. Phys. Lett.* 121 (1985) 111-115 & 116-121.

10. I.B. Ivanov, B.V. Toshev, Thermodynamics of Thin Liquid Films. II. Film Thickness and its Relations to the Surface Tension and the Contact Angle, *Colloid Polym. Sci.*, 253 (1975) 593-599.

11. B.V. Derjaguin, Friction and Adhesion. IV. The Theory of Adhesion of Small Particles, *Kolloid Zeits*. 69 (1934) 155-164.

12. B.V. Derjaguin, N.V. Churaev, V.M. Muller, *Surface Forces,* Plenum Press: Consultants Bureau, New York, 1987.

13. F. London, Zur Theorie und Systematik der Molekularkräfte, *Z. Phys.* 63 (1930) 245-279.

14. W.H. Keesom, On the Deduction from Boltzmann's Entropy Principle of the Second Virial-coefficient for Material Particles (in the Limit Rigid Spheres of Central Symmetry) which Exert Central Forces Upon Each Other and For Rigid Spheres of Central Symmetry Containing an Electric Doublet at Their Centers, *Communications Physical Laboratory University of Leiden Supplement*, Ed. By H. Kamerlingh Onnes, Eduard Ijdo Printer, Leiden, Supplement 24b to No. 121-132, pp. 23-41 (1912).

15. P. Debye, Van der Waals Cohesive Forces, *Physikalische Zeitschrift* 21 (1920) 178-187.

16. H.C. Hamaker, The London – Van der Waals Attraction Between Spherical Particles *Physica* 4(10) (1937) 1058-1072.

17. B.V. Derjaguin, *Theory of Stability of Colloids and Thin Liquid Films*, Plenum Press: Consultants Bureau, New York, 1989.

18. S. Nir, C.S. Vassilieff, Van der Waals Interactions in Thin Films" in: *Thin Liquid Films,* I.B. Ivanov (Ed.), Marcel Dekker, New York, 1988; p.207.

19. E.M. Lifshitz, The Theory of Molecular Attractive Forces between Solids, *Soviet Phys. JETP* (English Translation) 2 (1956) 73-83.

20. H.R. Casimir, D. Polder, The Influence of Retardation on the London – van der Waals Forces, *Phys. Rev*. 73 (1948) 360-372.

21. W.B. Russel, D.A. Saville, W.R. Schowalter, *Colloidal Dispersions*, Cambridge Univ. Press, Cambridge, 1989.

22. J. Mahanty, B.W. Ninham, *Dispersion Forces,* Academic Press, New York, 1976.

23. I. Langmuir, The Role of Attractive and Repulsive Forces in the Formation of Tactoids, Thixotropic Gels, Protein Crystals and Coacervates. *J. Chem. Phys.* 6 (1938) 873-896.

24. V.M. Muller, *Kolloidn. Zh*. 38 (1976) 704-709.

25. H. Schulze, Schwefelarsen im wässeriger Losung, *J. Prakt. Chem*. 25 (1882) 431-452.

26. W.B. Hardy, A Preliminary Investigation of the Conditions, Which Determine the Stability of Irreversible Hydrosols, *Proc. Roy. Soc. London* 66 (1900) 110-125.

27. R.M. Pashley, Hydration Forces between Mica Surfaces in Electrolyte Solutions, *Adv. Colloid Interface Sci.* 16 (1982) 57-62.

28. V.N. Paunov, R.I. Dimova, P.A. Kralchevsky, G. Broze and A. Mehreteab. The Hydration Repulsion between Charged Surfaces as Interplay of Volume Exclusion and Dielectric Saturation Effects, *J. Colloid Interface Sci*. 182 (1996) 239-248.

29. S.J. Alexander, Adsorption of Chain Molecules with a Polar Head: a Scaling Description, *J. Phys. (Paris)* 38 (1977) 983-987.

30. P.G. de Gennes, Polymers at an Interface: a Simplified View, *Adv. Colloid Interface Sci*. 27 (1987) 189-209.

31. P.M. Claesson, R. Kjellander, P. Stenius, H.K. Christenson, Direct Measurement of Temperature-Dependent Interactions between Non-ionic Surfactant Layers, *J. Chem. Soc., Faraday Trans. 1*, 82 (1986), 2735-2746.

32. A.D. Nikolov, D.T. Wasan, P.A. Kralchevsky, I.B. Ivanov. Ordered Structures in Thinning Micellar and Latex Foam Films. In: *Ordering and Organisation in Ionic Solutions* (N. Ise & I. Sogami, Eds.), World Scientific, Singapore, 1988, pp. 302-314.

33. A. D. Nikolov, D. T. Wasan, et. al. Ordered Micelle Structuring in Thin Films Formed from Anionic Surfactant Solutions, *J. Colloid Interface Sci.* 133 (1989) 1-12 & 13-22.

34. J.N. Israelachvili, R.M. Pashley, Molecular Layering of Water at Surfaces and Origin of Repulsive Hydration Forces, *Nature* 306 (1983) 249-250.

35. A. Trokhymchuk, D. Henderson, A. Nikolov, D.T. Wasan, A Simple Calculation of Structural and Depletion Forces for Fluids/Suspensions Confined in a Film, *Langmuir* 17 (2001) 4940-4947.

36. E.S. Basheva, P.A. Kralchevsky, K.D. Danov, K.P. Ananthapadmanabhan, A. Lips, The Colloid Structural Forces as a Tool for Particle Characterization and Control of Dispersion Stability, *Phys. Chem. Chem. Phys.* 9 (2007) 5183-5198.

37. P.A. Kralchevsky, N.D. Denkov, Analytical Expression for the Oscillatory Structural Surface Force, *Chem. Phys. Lett.* 240 (1995) 385-392.

38. S. Asakura, F. Oosawa, On Interaction between Two Bodies Immersed in a Solution of Macromolecules, *J. Chem. Phys.* 22 (1954) 1255-1256.