Forces between Surfaces

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Example:
foam film stabilized by surface forces
The Surface Forces Determine the Stability and Properties of Colloidal Dispersions (Examples)

- Stability of foams (gas-in-liquid dispersions)
- Flocculation in emulsions (oil-in-water dispersions)
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 = Force of interaction between two bodies (two phases) when the distance \( h \) between their surfaces is relatively small.

Typically, \( h < 100 \text{ nm} \).

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

Capillary (Laplace) pressure: \( P_c = P_{in} - P_l = \frac{2\sigma}{R} \)  (\( \sigma \) – 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]: \[ \Pi(h) = \Pi_{el}(h) + \Pi_{vw}(h) \]

Electrostatic component of disjoining pressure:
\[ \Pi_{el}(h) = B \exp(-\kappa h) \] (repulsion)

Van der Waals component of disjoining pressure:
\[ \Pi_{vw}(h) = -\frac{A_H}{6\pi h^3} \] (attraction)

\( h \) – film thickness; \( A_H \) – Hamaker constant;
\( \kappa \) – 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]

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

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

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

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

$$f(h) = \int_0^\infty \Pi(\tilde{h}) \, d\tilde{h}$$

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 [1-3,12]:

**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]:

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

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

1. **Orientation interaction** between two permanent dipoles (Keesom, 1912) [14]
   (electrostatic effect)

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

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]:

\[ A_H = A_{12} - A_{23} - A_{31} + A_{33} \]

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

Symmetric film: phase 2 = phase 1

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

For symmetric films: **always attraction**!
Van der Waals repulsion:

\[ A_H = A_{12} - A_{23} - A_{31} + A_{33} \]

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

Consider the case:

\[ A_{11} > A_{33} > A_{22} \]

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 \( A_H \) ⇒ repulsive van der Waals surface force

**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 water core;

\( h_t \) – thickness of layer of surfactant tails.

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

Free energy per unit area:

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

Disjoining pressure:

\[
\Pi_{vw} = -\frac{\partial f_{vw}}{\partial h} = -\left( \frac{\partial f_{vw}}{\partial h_c} \right)_{h_t} \quad h = h_c + 2h_t
\]
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].

\[
A(i, j) = A_{i,j} - A_{i,j-1} - A_{i-1,j} + A_{i-1,j-1}
\]

In the special case \(N_L = N_R = 1\), we obtain the expression for symmetric film from phase “0” sandwiched between two phases “1”:

\[
A(1,1) = A_{1,1} - 2A_{1,0} + A_{0,0}
\]

\[
f_{vw} = - \frac{A(1,1)}{12\pi h_{11}^2}
\]
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 all pairs of molecules.)

Lifshitz used the quantum field theory to derive accurate expressions in terms of:

(i) **Dielectric constants** of the phases: $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_3$;

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

$$A_H \equiv A_{132} \approx \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right) + \frac{3h_P \nu_e (n_1^2 - n_3^2)(n_2^2 - n_3^2)}{16\sqrt{2}(n_1^2 + n_3^2)^{3/4}(n_2^2 + n_3^2)^{3/4}}$$

**Zero-frequency term:** $A_{132}^{(\nu=0)}$

- orientation & induction interactions;
- $kT$ – thermal energy.

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

- $\nu_e = 3.0 \times 10^{15}$ Hz – main electronic absorption frequency;
- $h_P = 6.6 \times 10^{-34}$ J.s – Planck’s const.
Hamaker constant for symmetric films

\[ A_H \equiv A_{131} = A_{131}^{(v=0)} + A_{131}^{(v>0)} \]
\[ = \frac{3}{4} kT \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 + \frac{3h_p\nu_e (n_1^2 - n_3^2)^2}{16\sqrt{2}(n_1^2 + n_3^2)^{3/2}} \]
\[ \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right)^2 < 1 \quad \Rightarrow \quad A_{131}^{(v=0)} < \frac{3}{4} kT \approx 3 \times 10^{-21} \text{ J} \]

(i) For two bodies interacting across vacuum (or gas):
(ii) For a free-standing liquid or solid film (e.g. foam film):

\[ A_H = 10^{-19} - 10^{-20} \text{ J} \]

Hence, for such configurations the dispersion interaction is predominant:

\[ A_{131}^{(v=0)} << A_{131}^{(v>0)} \approx A_H \]

The zero-frequency term becomes comparable to the dispersion term when \( n_1 \) is close to \( n_3 \) (e.g. emulsion systems):

\[ A_{131}^{(v=0)} \approx A_{131}^{(v>0)} \]
**Determination of the Hamaker constant from the surface tension**

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 \( 2\gamma \) (where \( \gamma \) is the surface tension):

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

With \( h_0 = 0.165 \text{ nm} \) – good comparison theory-experiment for nonpolar liquids [1]:

<table>
<thead>
<tr>
<th>Material</th>
<th>Theoretical ( A_H \left(10^{-20} \text{ J}\right) )</th>
<th>( \gamma = \frac{A_H}{24\pi h_0^2} ) (mN/m)</th>
<th>( \gamma ) experimental (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Octane</td>
<td>4.5</td>
<td>21.9</td>
<td>21.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>5.2</td>
<td>25.3</td>
<td>25.5</td>
</tr>
<tr>
<td>Water</td>
<td>3.7</td>
<td>18.0</td>
<td>73.0 ( \text{(20 °C)} )</td>
</tr>
</tbody>
</table>
Electromagnetic Retardation Effect on Dispersion Force [20]

C = \(3 \times 10^8\) m/s; \(v_e = 3 \times 10^{15}\) s\(^{-1}\) \(\Rightarrow\) \(L = C/v_e = 100\) nm

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

\[\Rightarrow u_{ij}(r) \rightarrow -\frac{\alpha_{ij}}{r^7}\]

\[
A_{131}^{(v>0)}(h) = \frac{3h_p v_e}{16\sqrt{2}} \frac{(n_1^2 - n_3^2)^2}{(n_1^2 + n_3^2)^{3/2}} \left[1 + \left(\frac{\pi h}{\sqrt{32}}\right)^{3/2}\right]^{-2/3}
\]

\[\Rightarrow A_{131}^{(v>0)} \propto \frac{1}{h} \quad (h \to \infty)\]

\[h_d = n_3 \left(n_1^2 + n_3^2\right)^{1/2} \frac{2\pi v_e h}{c}\]

Russel et al. [21]

Suppression of Orientation & Induction Interactions by Electrolyte [22]

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

\(I\) is the ionic strength of solution
Electrostatic (Double Layer) Surface Force

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

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

\( n_0 \) – concentration of the ions in the bulk solution; \( \psi_m \) potential in the midplane.

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

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

\[ \Pi_{el} \approx n_0 kT \Phi_m^2 > 0 \]

\[ \cosh(\Phi_m) = 1 + \frac{\Phi_m^2}{2} + O(\Phi_m^4) \]
More general definition of $\Pi_{el}$

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

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

and in addition:

$$n_1|_{z=0} = n_{1m}$$
$$n_2|_{z=0} = n_{2m}$$

In each plane $z = \text{const.}$, not necessarily the midplane, we have [2]:

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

$$= kT (n_{1m} + n_{2m} - 2n_0) = \text{const.}$$
\[ \Pi(h) = ? \]

**Verwey – Overbeek Formula (1948)**

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

\[
\tanh \left( \frac{Z e \psi_1}{4kT} \right) = \tanh \left( \frac{Z e \psi_s}{4kT} \right) \exp \left( -\kappa z_w \right)
\]

Superposition approximation

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

In the midplane \( \frac{Z e \psi_1}{4kT} \ll 1 \)

\[
\Phi_m = 2\psi_1 \frac{Z e}{kT} = 8 \tanh \left( \frac{Z e \psi_s}{4kT} \right) \exp \left( -\frac{\kappa h}{2} \right)
\]

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

\[
\gamma = \tanh \left( \frac{Z e \psi_s}{4kT} \right)
\]
Debye screening length, $\kappa^{-1}$:

$$\kappa^{-1} = \frac{0.304}{\sqrt{[\text{NaCl}]}}, \quad \kappa^{-1} = \frac{0.176}{\sqrt{[\text{CaCl}_2]}}, \quad \kappa^{-1} = \frac{0.152}{\sqrt{[\text{MgSO}_4]}} \text{ nm}$$

$$\kappa^2 = \frac{2e^2 I}{\varepsilon \varepsilon_0 kT} \quad ; \quad I = \frac{1}{2} \sum_i Z_i^2 c_i \quad \text{(ionic strength)}$$

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

<table>
<thead>
<tr>
<th>$I$ for 1:1 el. (M)</th>
<th>$10^{-7}$ pure water</th>
<th>$10^{-5}$</th>
<th>$10^{-3}$</th>
<th>$10^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa^{-1}$ (nm)</td>
<td>960</td>
<td>96</td>
<td>9.6</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Π_{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**.

\[
Π_{el}(h) = 432n_{(2)}kT\left(\tanh\frac{\nu_{i:j}}{4}\right)^2 \exp(-\kappa h)
\]

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

the subscript "i:j" takes value "2:1" or "1:2"

\[
\nu_{2:1} = \ln\left[\frac{3}{1 + 2 \exp\left(-\frac{e\psi_s}{kT}\right)}\right], \quad \nu_{1:2} = \ln\left[\frac{2\exp\left(\frac{e\psi_s}{kT}\right) + 1}{3}\right]
\]

derived in refs. [24,12]
\( \Pi_{\text{el}}(h) \) in the case of nonidentically charged planes \([12]\)

**Constant surface potentials**

\[ \psi_{s2} > \psi_{s1} \]

\[ h_{\text{max}} = \frac{1}{\kappa} \text{arcosh}\left(\frac{\psi_{s2}}{\psi_{s1}}\right) \]

**Constant surface charge densities**

\[ \sigma_{s1}, \sigma_{s2} \]

\[ h_{\text{min}} = \frac{1}{\kappa} \text{arcosh}\left(-\frac{\sigma_{s2}}{\sigma_{s1}}\right) \]

Asymptotic expression for not-too-small \( h \) \([6]\):  

\( \Pi_{\text{el}}(h) = 64n_0kT\gamma_1\gamma_2 e^{-\kappa h} \), \( \gamma_k \equiv \tanh\left(\frac{Ze\psi_{sk}}{4kT}\right), \ k = 1,2 \)
Derjaguin – Landau – Verwey – Overbeek (DLVO) Theory [5,6]

Disjoining pressure:

\[ \Pi = \Pi_{el} + \Pi_{vw} = Be^{-\kappa h} - \frac{A_H}{6\pi h^3} \]

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

\[ f(h) = \int_{h}^{\infty} \Pi(\tilde{h}) d\tilde{h} = \frac{B}{\kappa} e^{-\kappa h} - \frac{A_H}{12\pi h^2} \]

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

\[ U(h) \approx \pi R \int_{h}^{\infty} f(\tilde{h}) d\tilde{h} = \pi R \left( \frac{B}{\kappa^2} e^{-\kappa h} - \frac{A_H}{12\pi h} \right) \]

\[ B = 64n_0 kT \gamma^2, \quad \gamma \equiv \tanh \left( \frac{Ze\psi_s}{4kT} \right) \]

\( (e - \text{electronic charge}; \ e = 2.71828... ) \)
DLVO Theory: The electrostatic barrier

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:** \( U_{\text{max}} = 0 \)

(zero height of the barrier to coagulation)

\[
U(h) \approx \pi R \left( \frac{B}{\kappa^2} e^{-\kappa h} - \frac{A_H}{12\pi h} \right)
\]
The Critical Coagulation Concentration \((ccc)\) \([5,6]\)

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

\[
\frac{dU}{dh} \bigg|_{h=h_{\text{max}}} = 0 \quad \Rightarrow \quad \frac{B}{\kappa} e^{-\kappa h_{\text{max}}} = \frac{A_H}{12\pi h_{\text{max}}^2}
\]

\[
\Rightarrow \quad \kappa h_{\text{max}} = 1 \quad \Rightarrow \quad \frac{B}{\kappa^3} e^{-1} = \frac{A_H}{12\pi}
\]

\[
\Rightarrow \quad \frac{B^2}{\kappa^6} = \left(\frac{A_H e}{12\pi}\right)^2 \Rightarrow \quad \frac{(64kT\gamma^2 n_0)^2}{\left(\frac{2Z^2 e^2}{\varepsilon_0 \varepsilon kT}\right)^3 n_0^3} = \left(\frac{A_H e}{12\pi}\right)^2
\]

\[
B = 64n_0 kT\gamma^2
\]

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

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

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

$\lambda_0 = 0.6 - 1.1$ nm

$f_0 = 3 - 30$ 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

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

\( l \) – 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, \( \Gamma \) [1,21].

← Alexander – de Gennes theory for the case of good solvent [29,30]:

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

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

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].
Steric interaction – poor solvent

Plot of experimental data for measured forces, $F/R = 2\pi f$ 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

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 were observed in liquid films containing colloidal particles, e.g. latex & surfactant micelles; Nikolov et al. [32,33].

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 $\frac{\partial \Pi}{\partial h} < 0$. 

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Oscillatory-structural disjoining pressure

Depletion minimum
Measured short-range force between two cylindrical mica surfaces of radii $R = 1 \text{ cm}$ in $10^{-3} \text{ M KCl}$ solution.

The dashed line shows the expected DLVO interaction.

The oscillatory force has a period of $0.22 - 0.26 \text{ nm}$, 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

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

The micelle aggregation number, \( N_{\text{agg}} = 70 \), is determined [36].

Theoretical curve – by means of the Trokhimchuk formulas [35].

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

200 mM Tween 20
\[ d = 7.2 \text{ nm} \]
\[ \phi = 0.334 \]
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]:

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

\[ \Pi_{osc} = -P_{hs}, \quad \text{for} \ 0 < h < d \]

\( d_1 \) – period; \( d_2 \) – decay length:

\[ \frac{d_1}{d} = \sqrt{\frac{2}{3}} + 0237 \Delta \phi \]

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

\( \phi \) – particle volume fraction, \( \Delta \phi = 0.74 - \phi \)

The above expression for \( \Pi_{osc}(h) \) 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
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 \( 0 \leq h_0 \leq d \) [1]:

\[
U_{\text{dep}}(h_0) / kT \approx -\frac{3}{2} \phi \frac{D}{d^3} \frac{d}{2} \frac{1}{(d - h_0)^2}
\]

\[
D / d = 50; \quad \phi = 0.10; \quad U_{\text{dep}}(0) = 7.5kT
\]
The total energy of interaction between two particles, $U(h)$, includes contributions from all surface forces:

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

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


Additional References


