1 — Surface free energy and disjoining pressure

Consider two planar surfaces separated by distance h. The free energy per unit area is

$$w(h).$$

Tasks

1. Show that the **disjoining pressure**

$$\Pi(h) = -\frac{dw}{dh}$$

is the force per unit area between the surfaces.

2. Show that the mechanical equilibrium of a thin film requires

$$P_{inside} = P_{outside} + \Pi(h).$$

3. Discuss the relation between disjoining pressure and **thin film stability**.

2 — Derjaguin approximation as a curvature expansion

Two curved surfaces interact via an interaction density $w(h)$. Let the local surface separation be

$$h(x, y) = h_0 + \frac{x^2}{2R_1} + \frac{y^2}{2R_2}.$$

Tasks

1. Show that the total interaction energy is

$$U = \int w(h(x, y))\, dA.$$

2. Expand the integral for small curvature $h_0 \ll R$.
3. Show that the leading contribution gives

$$U(h_0) = 2\pi R_{\mathrm{eff}} \int_{h_0}^{\infty} w(h)\, dh.$$

4. Identify

$$R_{\mathrm{eff}} = \frac{R_1 R_2}{R_1 + R_2}.$$

This is the **Derjaguin approximation**.

3 — van der Waals attraction from pair potentials

Assume molecules interact via

$$V(r) = -\frac{C}{r^6}.$$

Consider two semi-infinite media separated by distance h.

Tasks

1. Compute the interaction energy by integrating over both half spaces.
2. Show that the result has the form

$$w(h) = -\frac{A_H}{12\pi h^2}.$$

3. Derive the expression for the **Hamaker constant**

$$A_H \propto C n_1 n_2$$

where n_i are molecular densities.

4 — Derjaguin + van der Waals forces

Using

$$w(h) = -\frac{A_H}{12\pi h^2},$$

apply the Derjaguin approximation.

Tasks

1. Derive the interaction energy between spheres

$$U(h) = -\frac{A_H R}{12h}.$$

2. Derive the force

$$F(h) = -\frac{A_H R}{12h^2}.$$

3. Discuss the scaling with particle size.

5 — Debye screening

In electrolyte solutions the electrostatic potential satisfies

$$\nabla^2\psi = \kappa^2\psi.$$

Tasks

1. Solve the equation for a planar charged surface.
2. Show that the potential decays exponentially.
3. Derive the Debye length

$$\lambda_D = \sqrt{\frac{\varepsilon k_B T}{2ne^2}}.$$

4. Estimate λ_D for a 1 mM salt solution.

6 — DLVO theory

The DLVO interaction between colloidal particles is

$$U(h) = U_{vdW} + U_{elec}.$$

Tasks

1. Combine the expressions

$$U_{vdW} = -\frac{A_H R}{12h}$$

and

$$U_{elec} = U_0 e^{-\kappa h}.$$

2. Determine the condition for the existence of an **energy barrier**.
3. Show how increasing salt concentration affects stability.

7 — Depletion attraction from the grand canonical ensemble

Consider large colloidal spheres in a solution of small polymers. Polymers are ideal and excluded from a layer near the surface.

Tasks

1. Show that the polymer free energy is

$$F = -\Pi V_{free}.$$

2. Show that overlap of depletion zones increases V_{free}.

3. Derive the depletion potential

$$U = -\Pi V_{overlap}.$$

4. Interpret the result physically.

8 — Scaling of depletion force

Consider polymer radius R_p and colloids of radius R.

Tasks

1. Estimate the overlap volume for $h < 2R_p$.
2. Show that the depletion energy scales as

$$U \sim -\Pi R R_p^2.$$

3. Discuss dependence on polymer concentration.

9 — Polymer brush repulsion

Consider surfaces grafted with polymer chains of length N. The brush thickness scales as

$$L \sim N\sigma^{1/3}$$

where σ is grafting density.

Tasks

1. Estimate the free energy cost of compressing two brushes.
2. Show that the interaction is strongly repulsive.
3. Discuss how this stabilizes colloids.

10 — Langmuir adsorption isotherm

Assume adsorption obeys

$$\Gamma = \frac{\Gamma_\infty c}{K + c}.$$

Tasks

1. Show that adsorption saturates at large c.
2. Combine with the Gibbs equation to obtain

$$\gamma(c).$$

3. Suppose surface tension depends on surfactant concentration:

$$\gamma = \gamma_0 - \alpha c.$$

a. Show that gradients in concentration generate surface stresses.
b. Explain why fluid flows toward regions of **higher surface tension**.
c. Relate this to detergent spreading on water.