

Soft matter and complex fluids The stability of thin (soft) films

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The disjoining pressure is a jump in pressure at the boundary. It does not vary between the plates.

$$\Pi(h) = -\frac{1}{A} \frac{\partial G}{\partial h}\Big|_{T,P,\sigma_1,\sigma_2,N_i}$$



"The disjoining pressure of a thin plane-parallel layer of liquid separating two bodies is equal to the pressure *P* with which (in addition to the "normal" hydrostatic pressure in the layer) the liquid layer acts in a state of equilibrium on the adjacent bodies, tending to force them apart."

Derjaguin, B.V." Definition of the concept of, and the magnitude of the disjoining pressure and its role in the statics and kinetics of thin layers of liquids." *Kolloidnyi Zhurnal*, *17*, 191 – 197, **1955**.

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The Derjaguin approximation



Let the force per unit area between two flat plates be:

$$\Pi(h)$$

Force between sphere and plate:

$$F_{s-p}(y) = \int_{S} \Pi(h) dS$$
$$\cong 2\pi R \int_{y}^{\infty} \Pi(h) dh$$

A sphere against a flat surface.

$$dS = 2\pi r dr$$
$$\frac{dr}{dh} \cong \frac{R}{r}$$
$$dS \cong 2\pi R dh$$

Similarly, the force between two spheres:

$$F_{s-s}(y) \cong \frac{2\pi R_1 R_2}{R_1 + R_2} \int_{y}^{\infty} \Pi(h) dh$$

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The overlap energy is not a simple combination of the isolated layers.

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Fig. 13.5. Measured force laws between mica surfaces across straight-chained liquid alkanes such as *n*-tetradecane and *n*-hexadecane (molecular width $\sigma \approx 0.4$ nm), and across the branched alkane (iso-paraffin) 2-methyloctadecane. The dotted line is the theoretical continuum van der Waals interaction. (From Christenson *et al.*, 1987; Gee and Israelachvii, 1990.)



If the film remains unchanged then the film is at equilibrium and the disjoining pressure exists. The Laplace pressure measures the disjoining pressure in the thin film between the bubble and the solid.



FIGURE 4.1. Measuring the disjoining pressure in the Sheludko method, using a porous ring A under a pressure adjustable by setting H.

The thin film acts as if it is under pressure. The chemical potential of the thin film is equal to the chemical potential of liquid in the column at the same level:

$$\mu_0 - v_0 \Pi(h) = \mu_0 + v_0 p_H$$

$$\therefore \quad \Pi(h) = -p_H$$
The "disjoining" pressure is negative.

When an external pressure is applied, $\Pi(h)$ can be measured.

de Gennes, 2002, pp. 88f



$$\Pi(h) = -\frac{1}{A} \frac{\partial G}{\partial h}\Big|_{T,P,\sigma_1,\sigma_2,N_i}$$



The chemical potential of liquid at any height above the liquid surface equals the chemical potential of the liquid in the bath:

$$\mu_0 - v_0 \Pi(h) + mgz = \mu_0$$

$$\Pi(h) = \frac{m}{v_0} gz = \rho gz$$



$$\sigma_{s0}$$
 σ_{sl} h

$$\frac{Energy}{m^2} = \sigma_{sl} + \sigma_{lv} + P(h)$$

as $h \to 0$ $\frac{Energy}{m^2} \to \sigma_{s0}$
as $h \to \infty$ $\frac{Energy}{m^2} \to \sigma_{sl} + \sigma_{lv}$

 $\Pi(h) = -\frac{1}{A} \frac{\partial G}{\partial h} \bigg|_{T,P,\sigma_1,\sigma_2,N_i}$

Range of P(h): Between surfaces: $1/h^2$ For polymers: size of coils Electrostatics: 10's nm in water 100's nm in oil $P(0) = \sigma_{s0} - \sigma_{sl} - \sigma_{lv} = S$ $P(\infty) = 0$



$$\frac{Energy}{m^2} = \sigma_{sl} + \sigma_{lv} + P(h) \qquad \Pi(h) = -\frac{1}{A} \frac{\partial G}{\partial h}\Big|_{T,P,\sigma_1,\sigma_2,N_i}$$

Disjoining pressure is (i) a definite and quantitative concept; (ii) connected to the question of colloidal stability; (iii) measurable; (iv) thermodynamic and (v) a measure of the intensity of molecular attraction between solvated and solvating phases.

$$\Pi(h) = -\frac{\partial P(h)}{\partial h}$$
$$P(0) = \sigma_{s0} - \sigma_{sl} - \sigma_{lv} = S$$
$$P(\infty) = 0$$



Derjaguin, B. (with Obuchov, E.) "Ultramicrometric analysis of solvate layers and elementary expansion effects". *Acta Phys.-Chim.*, **1936**, *5*(1), 1-22.