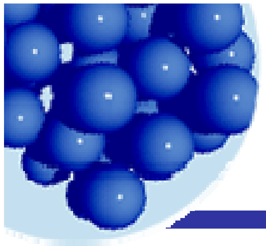
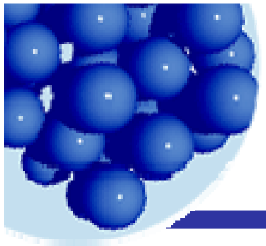


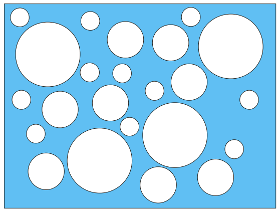
The stability of thin (soft) films

Lecture 2 – Thermodynamics and stability

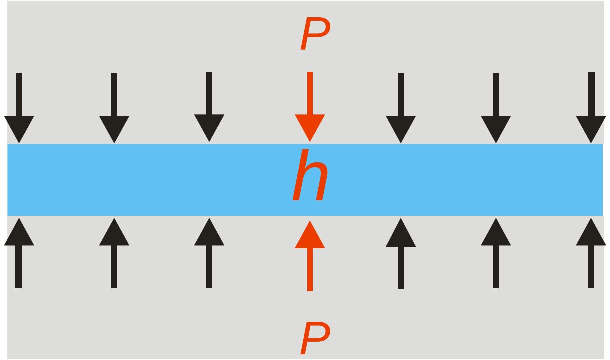
October 30, 2009



Review of Lecture 1



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



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

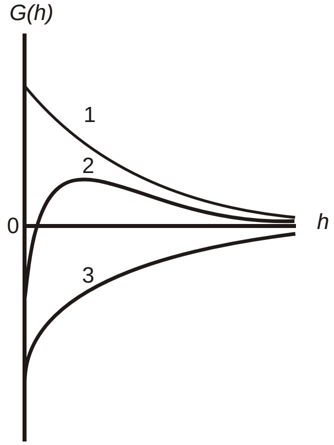
Force between 2 spheres:

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

$$\Pi(h) = -\frac{\partial G(h)}{\partial h}$$

$$G(0) = \sigma_{s0} - \sigma_{sl} - \sigma_{lv} = S$$

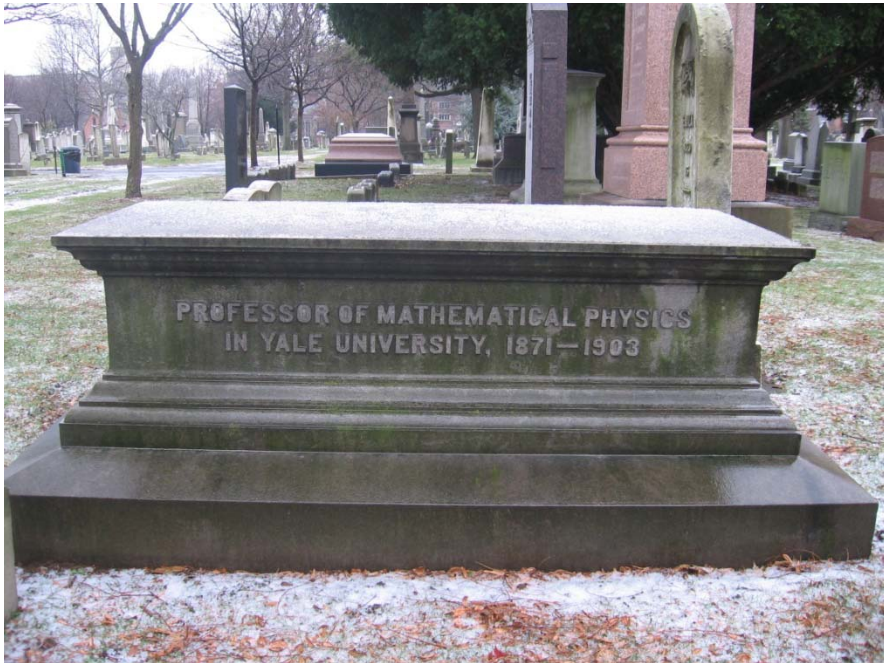
$$G(\infty) = 0$$



Curve 1 – Stable
Curve 2 – Metastable
Curve 3 - Unstable

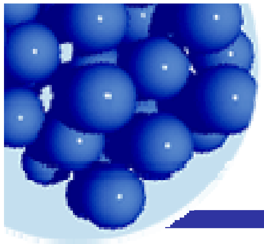
Josiah Willard Gibbs

JOSIAH WILLARD GIBBS
Born Feb. 11, 1839 – Died Apr. 22, 1903

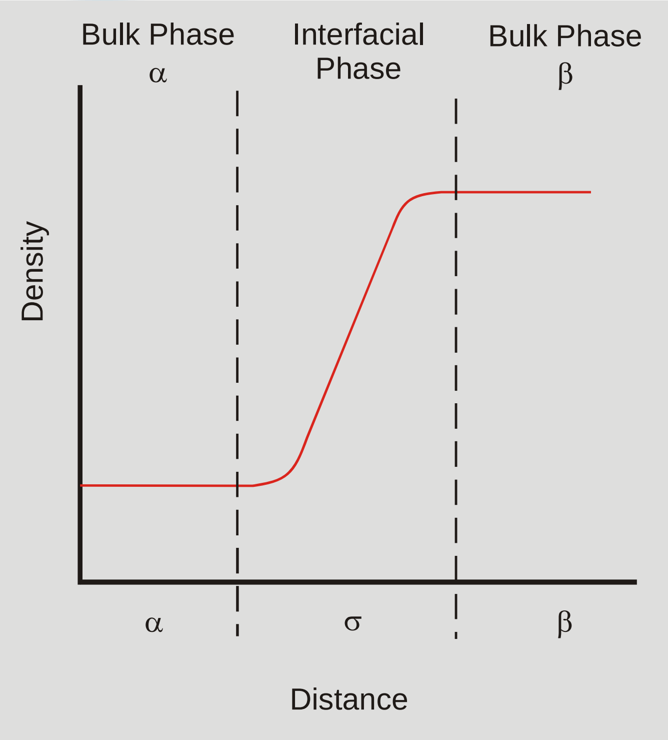


PROFESSOR OF MATHEMATICAL PHYSICS
IN YALE UNIVERSITY, 1871 - 1903

11-30-08



Gibbs' interfacial phase



$dU = TdS - pdV + \sigma dA + \sum \mu_i dn_i$ Differential of total energy

$U = TS - pV + \sigma A + \sum \mu_i n_i$ Total energy

$SdT - Vdp + Ad\sigma + \sum n_i d\mu_i = 0$ Gibbs-Duhem equation

$S^{\alpha} dT - V^{\alpha} dp + \sum n_i^{\alpha} d\mu_i^{\alpha} = 0$

$S^{\beta} dT - V^{\beta} dp + \sum n_i^{\beta} d\mu_i^{\beta} = 0$

For each bulk phase

$d\mu_i = d\mu_i^{\alpha} = d\mu_i^{\beta}$ At equilibrium

$$\left(S - S^{\alpha} - S^{\beta}\right) dT - \left(V - V^{\alpha} - V^{\beta}\right) dp + Ad\sigma + \sum \left(n_i - n_i^{\alpha} - n_i^{\beta}\right) d\mu_i = 0$$

$S^{\sigma} = S - S^{\alpha} - S^{\beta}$ $V^{\sigma} = V - V^{\alpha} - V^{\beta}$ $n_i^{\sigma} = n_i - n_i^{\alpha} - n_i^{\beta}$

$Ad\sigma + S^{\sigma} dT - V^{\sigma} dp + \sum n_i^{\sigma} d\mu_i = 0$ Subtracting and renaming.

Gibbs adsorption isotherm:

$$-d\sigma = \sum \frac{n_i^{\sigma}}{A} d\mu_i = \sum \Gamma_i d\mu_i$$

Surface concentrations:

$$\Gamma_i = \frac{n_i^{\sigma}}{A} \quad \text{mol m}^{-2}$$

$$F = C - P + 2$$

Gibbs' surface phase

Gibbs adsorption isotherm:

$$-d\sigma = \sum \frac{n_i^\sigma}{A} d\mu_i = \sum \Gamma_i d\mu_i$$

The surface excess:

$$\Gamma_i = \frac{n_i^\sigma}{A} \quad \text{mol m}^{-2}$$

For a 2-component system:

$$-d\sigma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2$$

with the Gibbs-Duhem relation

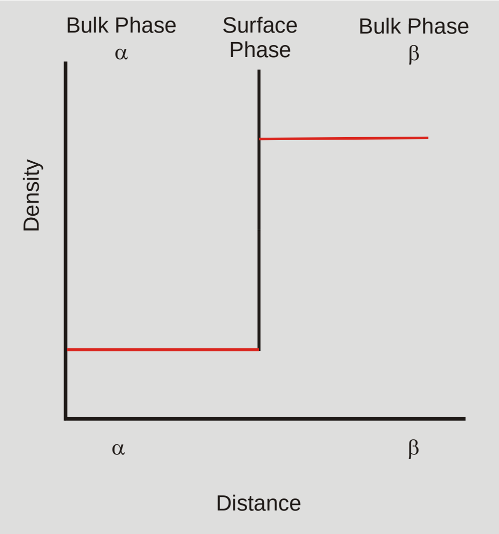
$$X_1 d\mu_1 + X_2 d\mu_2 = 0$$

gives $-d\sigma = \Gamma_2^G d\mu_2$

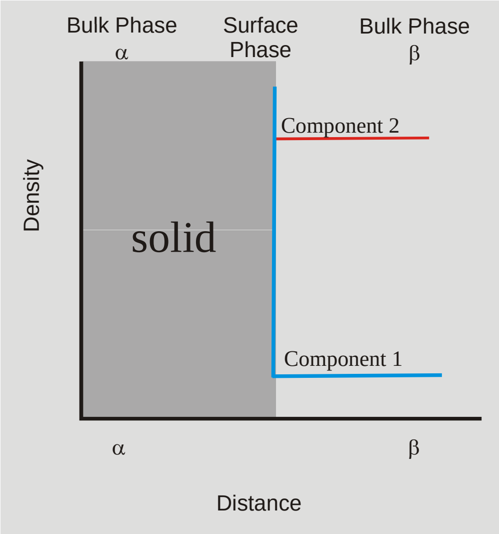
and the surface-excess concentration

$$\Gamma_2^G = \Gamma_2 - \frac{X_2}{X_1}\Gamma_1$$

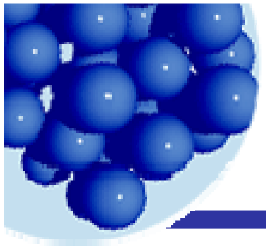
is independent of the dividing surface.

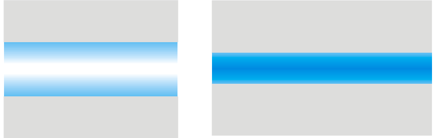


2 components,
2 phases

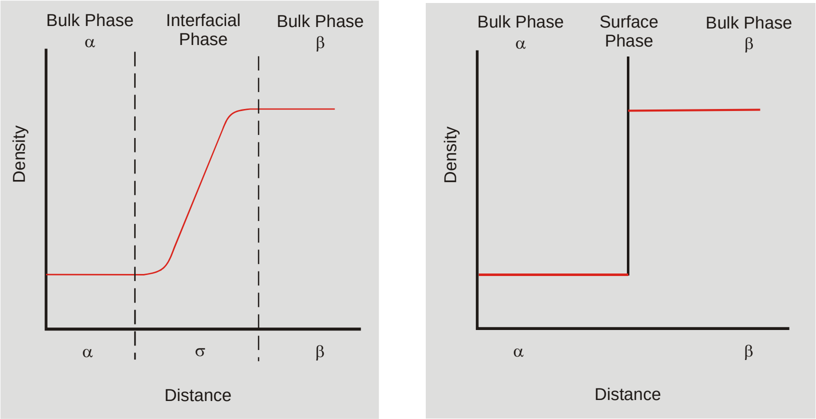


2 components,
1 phase

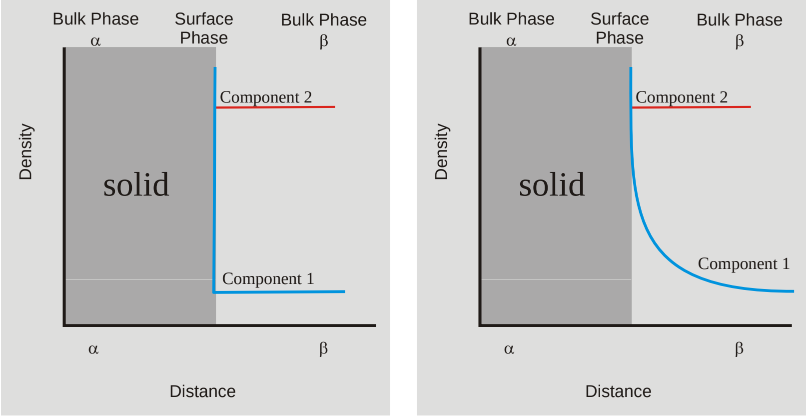




Interacting adsorption layers?



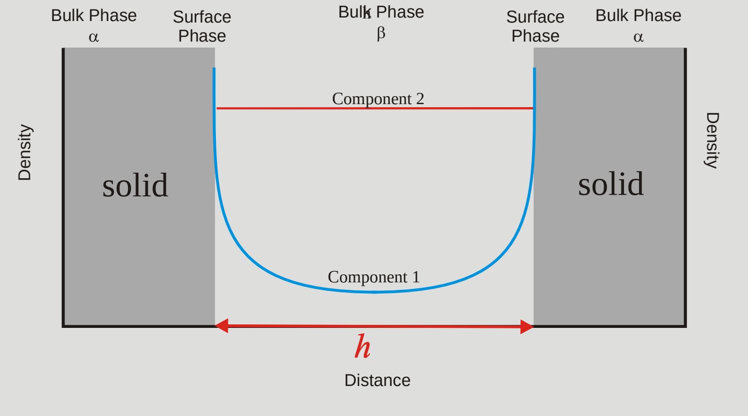
2 phases, 2 components



1 phase, 2 components

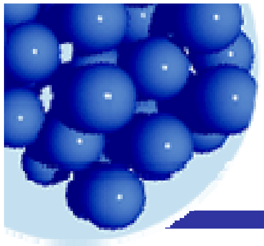
$$\Gamma_2^G = \Gamma_2 - \frac{X_2}{X_1}\Gamma_1$$

X_1 and X_2 are no longer constant. They depend on *h*.



1 liquid phase, 2 components

h is a new degree of freedom



$$dU = TdS - pdV + \sum_i \mu_i \cdot dn_i \qquad G = U - TS + pV\,{}^{**}$$

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

Thermodynamics of thin films* - 1

$$dG = -SdT + VdP + \sum_{i=1}^{r} \mu_i dN_i + A\sum_{j}^{plates} \Psi_j d\sigma_j - A\Pi dh \qquad \sum_{j}^{plates} \Psi_j d\sigma_j = \Psi_1 d\sigma_1 + \Psi_2 d\sigma_2$$

$$G(T,P,N_i,\sigma_1,\sigma_2,h) = A\int_h^\infty \Pi(T,P,N_i,\sigma_1,\sigma_2,k)\,dk + G_{h=\infty}$$

$G_{h=\infty}$ is the free energy of Gibbs' model including the adsorption at surfaces.

$$dG' = d\left(G - \sum_{i=1}^{r} \mu_i dN_i - \Psi_1 d\sigma_1 - \Psi_2 d\sigma_2\right) = -SdT + VdP + \sum_{i=1} N_i d\mu_i + A(\sigma_1 d\Psi_1 + \sigma_2 d\Psi_2) - A\Pi dh$$

As Gibbs did, we shall do, subtract the uniform properties of the bulk:

$$V = \sum_k V_k$$

$$S^s = S - \sum_k S_k = S - \sum_k V_k s_k$$

$$N_i^s = N_i - \sum_k N_k = N_i - \sum_k V_k n_{i,k}$$

$$\boxed{dG' = -S^s dT - \sum_{i=1,r} N_i^s d\mu_i - A(\sigma_1 d\Psi_1 + \sigma_2 d\Psi_2) - A\Pi dh}$$

**Rowlinson and Widom, Appendix 1 - Thermodynamics

* Parallel plates.

$$dG' = -S^s dT - \sum_{i=1,r} N_i^s d\mu_i - A\left(\sigma_1 d\Psi_1 + \sigma_2 d\Psi_2\right) - A\Pi dh = 0$$

Thermodynamics of thin films - 2

Since the LHS is a total differential, so is the RHS, so …

$$\frac{1}{A}\left(\frac{\partial N_i^s}{\partial h}\right)_{\mu_i,\ldots,\Psi_1,\Psi_2} = \left(\frac{\partial \Pi}{\partial \mu_i}\right)_{h,\mu_i,\ldots,\Psi_1,\Psi_2}$$

$$\Pi = \frac{1}{A}\int_h^\infty \left(\left(\frac{\partial N_i^s}{\partial h}\right)_{\mu_i,\ldots,\Psi_1,\Psi_2}\right) d\mu_i$$

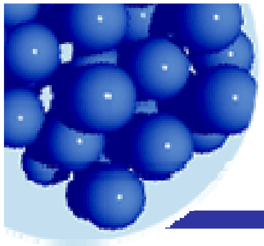
is a ‘modified” Gibbs equation.

$$\left(-d\sigma = \sum \frac{n_i^\sigma}{A} d\mu_i = \sum \Gamma_i d\mu_i\right)$$

$$\frac{N_i^s}{A} - \Gamma_i = A\int_h^\infty \left(\frac{\partial \Pi}{\partial \mu_i}\right)_{h,\ldots} dh$$

is the excess adsorption due to disjoining pressure. Note that we do not know how much excess is on either plate!

$$dG' = -S^s dT - \sum_{i=1,r} N_i^s d\mu_i - A\left(\sigma_1 d\Psi_1 + \sigma_2 d\Psi_2\right) - A\Pi dh = 0$$



Thermodynamics of thin films - 3

$$\frac{1}{A}\left(\frac{\partial S^s}{\partial h}\right)_{\mu_i,\ldots,\Psi_1,\Psi_2} = \left(\frac{\partial \Pi}{\partial T}\right)_{h,\mu_i,\ldots,\Psi_1,\Psi_2}$$

$$\frac{1}{A}\left(S^s - S^s_{h=\infty}\right) = \int_h^\infty \left(\frac{\partial \Pi}{\partial T}\right)_{h,\ldots} dh$$

is the excess entropy due to disjoining pressure.

If we know $\Pi = \Pi\left(h, T, \Psi_1, \Psi_2, \mu_i\right)$

We have

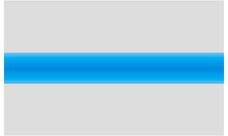
$$G\left(T, P, N_i, \sigma_1, \sigma_2, h\right) = A\int_h^\infty \Pi\left(T, P, N_i, \sigma_1, \sigma_2, k\right) dk + G_{h=\infty}$$

$$S = S^s + \sum_k V_k s_k$$

So all the thermodynamic functions can be calculated.
The rest is statistical mechanics, soft matter scaling, etc…

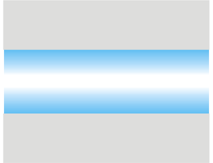
Stability of films between parallel plates

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



$$\frac{\partial^2 G}{\partial h^2} > 0$$

$$\Pi(h) = -\frac{1}{A}\frac{\partial G}{\partial h}$$



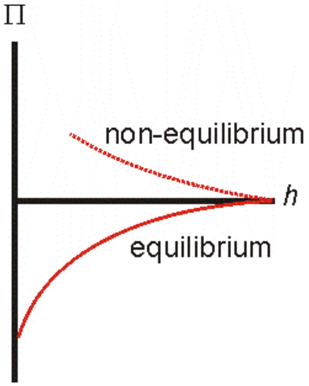
Unstable: $\frac{d\Pi(h)}{dh} = \frac{d(P-P_0)}{dh} = 0$

Stable when $\frac{\partial \Pi(h)}{\partial h} < 0$ Assuming all other thermodynamic values RTS.

If the change in thickness is not by a reversible path, then the (non-equilibrium) state is at a higher free energy so that:

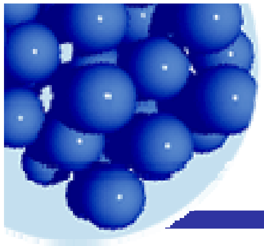
$$\frac{\partial \Pi(h)}{\partial h}\bigg|_{non-eq} < \frac{\partial \Pi(h)}{\partial h}\bigg|_{eq}$$

Some unstable films will be stable to fast perturbations:



e.g. Gibbs-Marangoni stability – a increase in liquid surface tension with expansion because surfactant adsorption is slow.

Not presented during Lecture 2.



$$F_{s-p}\left(y\right)\cong 2\pi R\int_y^{\infty}\Pi\left(h\right)dh \qquad F_{s-s}\left(y\right)\cong \frac{2\pi R_1R_2}{R_1+R_2}\int_y^{\infty}\Pi\left(h\right)dh \qquad F_{r-r}\left(y\right)\cong \frac{2\pi\sqrt{R_1R_2}}{\sin\Omega}\int_y^{\infty}\Pi\left(h\right)dh$$

Stability of films between convex bodies

The change in force with distance is:

$$\frac{\partial F}{\partial y}=-g\Pi\left(y\right)$$

Stability of the equilibrium is:

$$\frac{dF}{dy}<0$$

Hence:

$$\Pi\left(y\right)>0$$

If the change in thickness is not by a reversible path, then the (non-equilibrium) state is at a higher force so that:

$$\frac{dF\big|_{non-eq}}{dy}<\frac{dF\big|_{eq}}{dy} \quad \text{or} \quad \frac{dF\big|_{non-eq}}{dy}>-g\Pi\left(y\right)$$

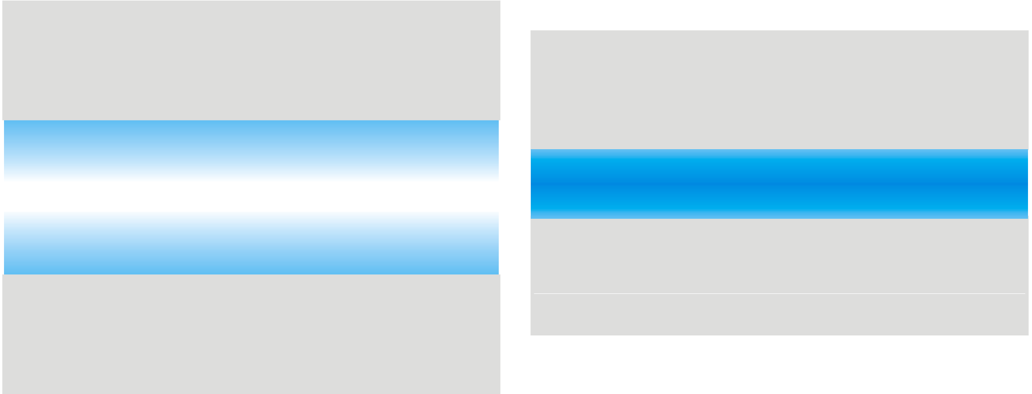
e.g. If the collision of charged particles is more rapid than the time for the surface charge to equilibrate, the dispersion may appear to be more stable than it really is.

But, interactions between convex surfaces are more likely to be at equilibrium than parallel plates.

Not presented during Lecture 2.

Components of disjoining pressure

What overlaps?

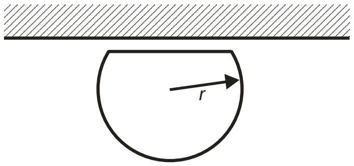


- Electromagnetic fields from the random, quantum fluctuations of electrons in all the three phases. (Dispersion forces.)
- Static electric fields from charged surfaces.
- Interactions between molecules or polymers adsorbed on the surface.
- Layered structuring of solvent molecules, solute molecules or dispersed phases.

Not presented during Lecture 2.

Experimental evidence

Derjaguin, B.V.; Rabinovich, Y.I.; Churaev, N.V. "Direct measurement of molecular forces" *Nature*, *272*, 313 – 318, **1978**.



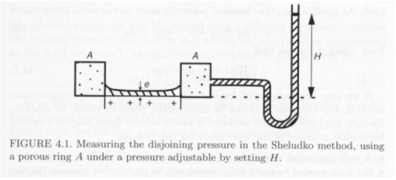
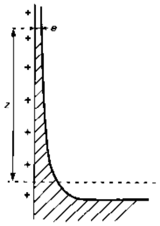


FIGURE 4.1. Measuring the disjoining pressure in the Sheludko method, using a porous ring A under a pressure adjustable by setting H.

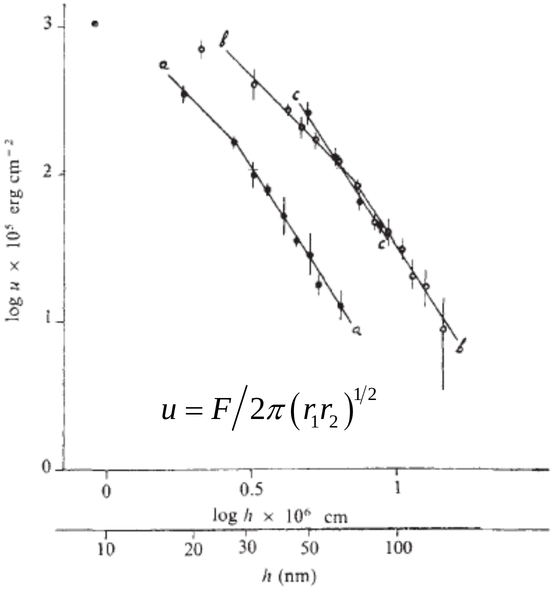


First direct measurements were reported in 1951. First English report in 1954.

Quartz, platinum, gold in air.

Glass threads in water.

Glass threads in water.



$$u = F/2\pi(r_1 r_2)^{1/2}$$

Fig. 3 Dependence of the energy of molecular attraction per unit area of plane-parallel surface on the gap h in the air. Quartz filaments: a; platinum filaments: b; gold filaments: c.

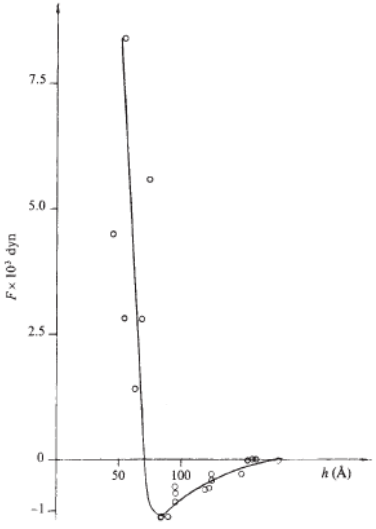


Fig. 7 Dependence on gap h of the interaction force F of crossed threads (1.0 and 1.2 mm in diameter) in KCl solution ($c = 0.1$ mol l⁻¹).

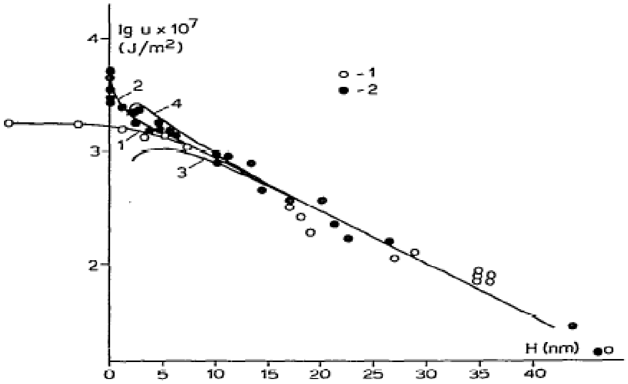


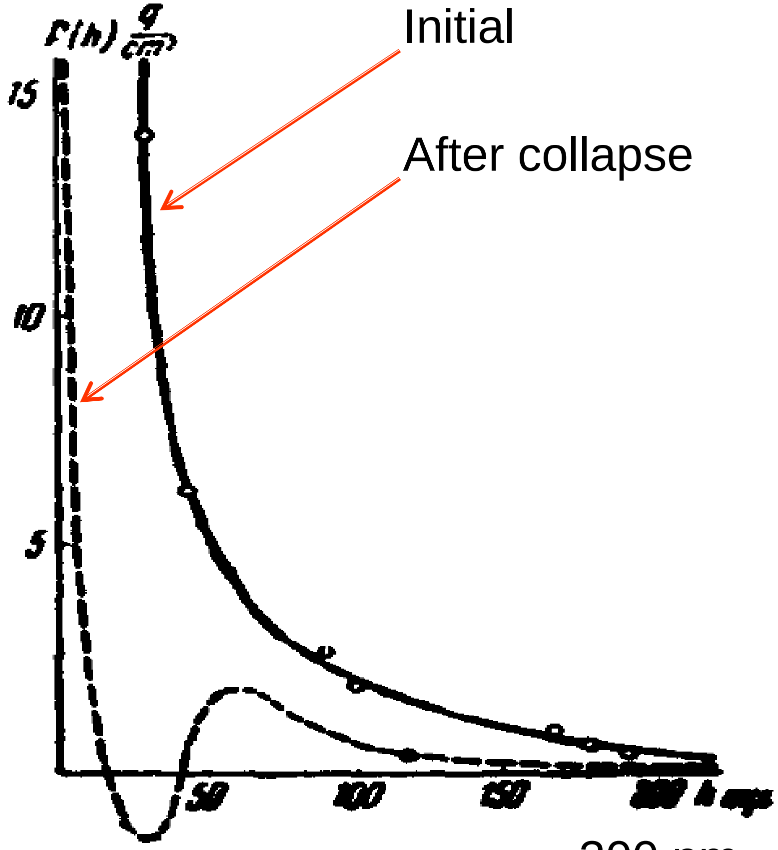
Fig. 2. Specific interaction energy between flat glass samples as a function of gap width H obtained in a KCl solution; $C = 1.1 \cdot 10^{-3}$ mole/liter.

Rabinovich, Ya.I.; Derjaguin, B.V.; Churaev, N.V. Direct measurements of long-range surface forces in gas and liquid media. *Adv. Colloid Interface Sci.*, *16*, 63 – 78, **1982**.

Not presented during Lecture 2.

Polymolecular adsorbed layers?

Water on mica



Initial

After collapse

300 nm

“These distances are much larger than Debye lengths. For example: 0.1 N LiCl on polished diamond was 75 nm at 900 dynes/cm^2. The Debye length should be about 1 nm. Nor is it van der Waals forces because of the extreme sensitivity to the dissolved components.”

Derjaguin, B.; Kussakov, M.; Lebedva. Range of molecular action of surfaces and polymolecular solvate (adsorbed) layers. C.R. Acad. Soc. URSS, **1939**, *23*(7), 671-673.

Not presented during Lecture 2.

“Polywater”

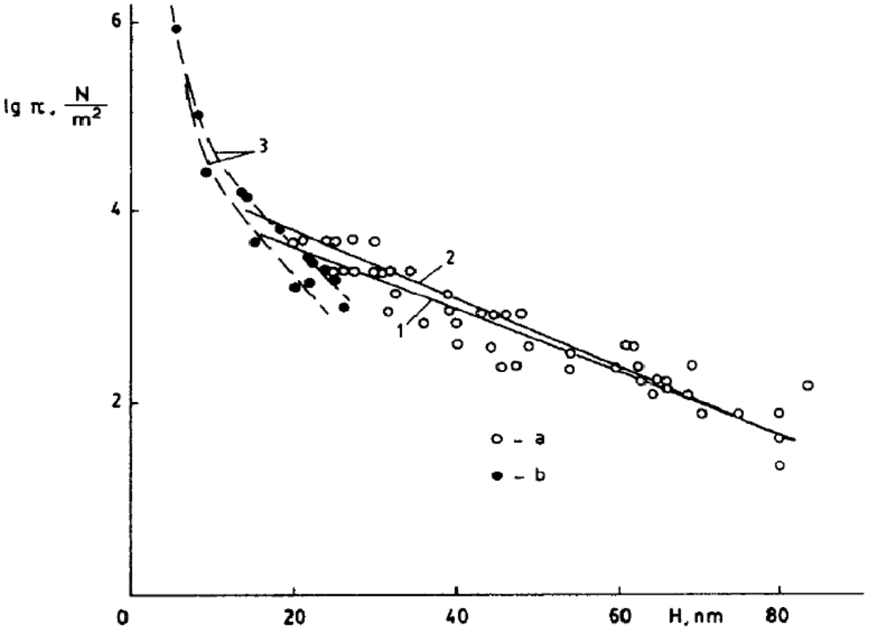


Fig. 2. Dependence of disjoining pressure on the thickness of the aqueous interlayer between hydrophobized silica filaments (before contact). “a” indicates our results; “b”, the results of Claesson's study [11]; “1” is Eqn (4); “2” is Eqn (6) [differentiation of the dependence $(F/R)-(H)$, of the straight line 1 in Fig. 1, in accordance with Eqn (5)]; “3” is the sum of two exponents with decay lengths of 1.2 and 5 nm [11].

Rabinovich, Y.I.; Derjaguin, B.V. Interaction of hydrophobized filaments in aqueous-electrolyte solutions. *Colloids Surf*., *30*, 243 – 251, **1988**.

Not presented during Lecture 2.

Polywater – “Ice-nine”

Ice-nine is a fictional material conceived by writer Kurt Vonnegut in his novel Cat's Cradle. It is supposed to be a more stable polymorph of water than common ice (Ice I_h) which instead of melting at 0° Celsius (32° Fahrenheit), melts at 45.8°C (114.4°F). When ice-nine comes into contact with liquid water below 45.8°C (which is thus effectively supercooled), it acts as a seed crystal, and causes the solidification (freezing) of the entire body of water which quickly crystallizes as ice-nine. A global catastrophe involving freezing the Earth's oceans by simple contact with ice-nine is used as a plot device in Vonnegut's novel. (wikipedia.com)

“Future observers will chuckle quietly over Derjaguin’s discomfiture…scientific history will see Derjaguin as a great physical chemist who has dominated theory and experiment in surface and colloid science for fifty years... Let the last words on polywater be those of Derjaguin: ‘It was not a matter of belief, it was a matter of performing better experiments.’”

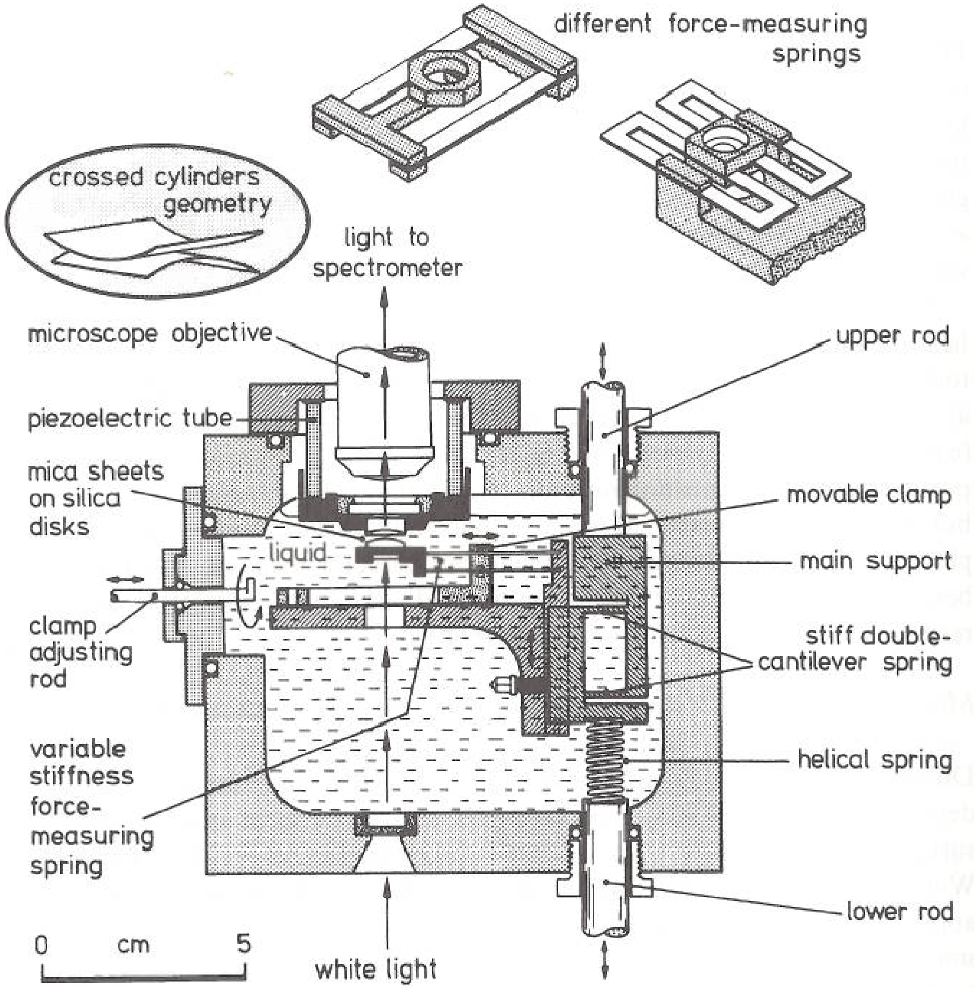
Pethica, B.A. Book review: *Polywater* by F. Franks, MIT Press: **1981**. *J. Colloid Interface Sci., 21*, 607, **1982**.

Boris Vladimirovich Derjaguin, 1902 – 1994.

Not presented during Lecture 2.

Israelachvili, J. *Intermolecular and surface forces*, 2nd ed.; Academic Press: Amsterdam; **1985**.

Jacob’s box



Surface forces apparatus: Two mica surfaces, atomically smooth, accuracy to 1 Å. At the 10 Å scale fluid properties, such as relaxation times, can be 10^{10} times greater than in the bulk.

Disjoining pressure is only mentioned twice in this (terrific) book, once with negative Hamaker constants and once with electrostatic repulsion.)

Not presented during Lecture 2.