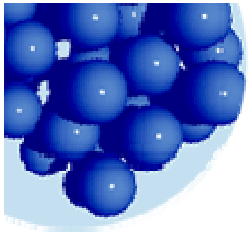
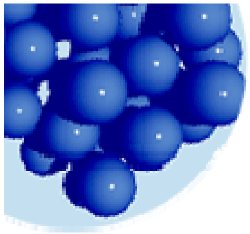


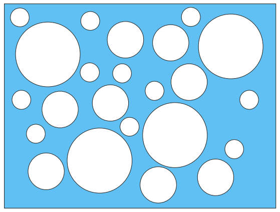
The stability of thin (soft) films

Lecture 5 – Stability of thin films
Long range forces*
November 20, 2009

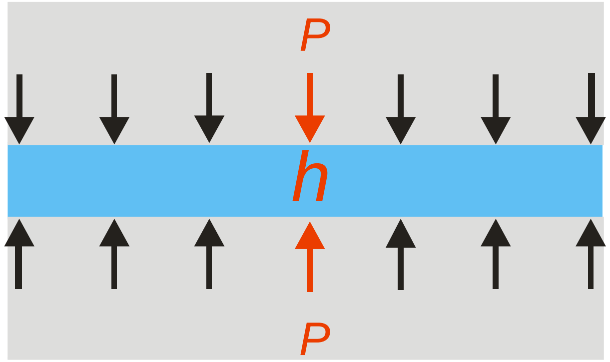
e.g. Dispersion, electrostatic, polymeric



Review of Lecture 1



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



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

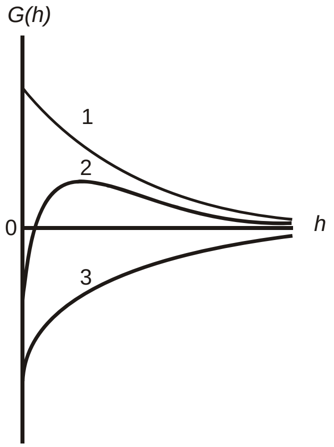
Force between 2 spheres:

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

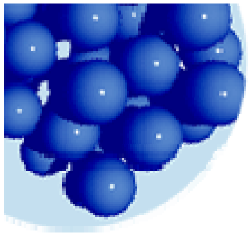
$$\Pi(h) = -\frac{\partial G(h)}{\partial h}$$

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

$$G(\infty) = 0$$



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



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

Review of Lecture 2

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

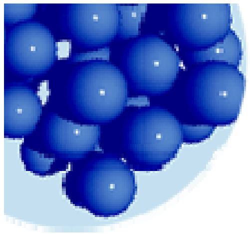
$$dG' = -S^s dT - \sum_{i=1,r} N_i^s d\mu_i - A\left(\sigma_1 d\Psi_1 + \sigma_2 d\Psi_2\right) - A\Pi dh$$

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

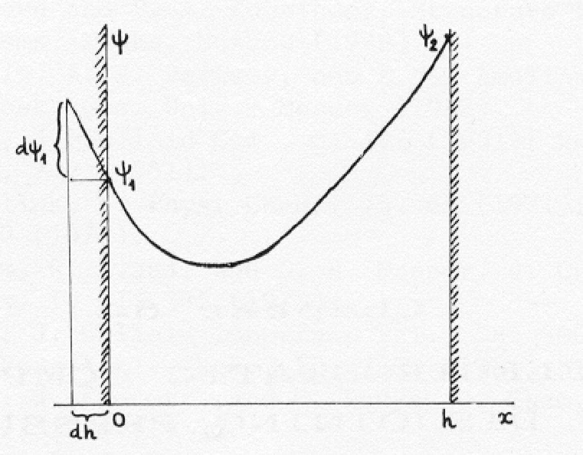
is a ‘modified” Gibbs equation. $\left(-d\sigma = \sum \frac{n_i^\sigma}{A} d\mu_i = \sum \Gamma_i d\mu_i\right)$

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

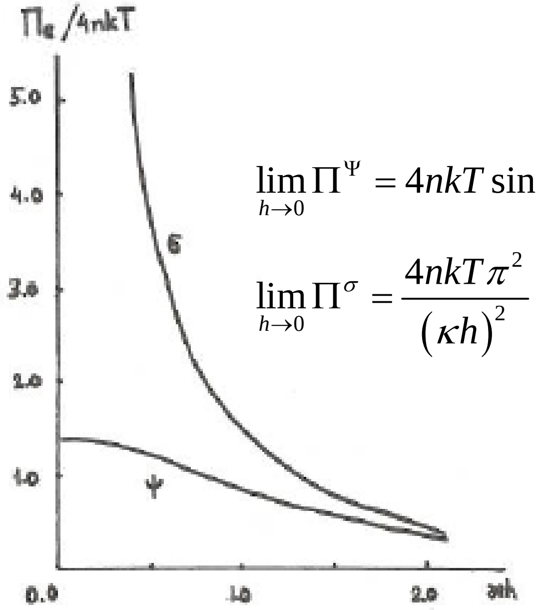
is the excess adsorption due to disjoining pressure. Note that we do not know how much excess is on either plate!



Review of Lecture 3



$$\Pi(h) = \frac{\varepsilon}{2}\left(E_h^2 - E_o^2\right)$$



$$\lim_{h\to 0} \Pi^{\Psi} = 4nkT\sinh^2\left(\frac{\Psi_0}{2}\right)$$

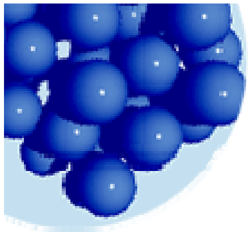
$$\lim_{h\to 0} \Pi^{\sigma} = \frac{4nkT\pi^2}{(\kappa h)^2}$$

$$\frac{\kappa h}{2} = \int_{\Phi_m}^{\Phi_0} \frac{d\Phi}{\sqrt{2\left(\cosh\Phi - \cosh\Phi_m\right)}}$$

For the approach of surfaces at constant potential, Φ_0 is constant.

For the approach of surfaces at constant surface charge density Φ_0 is:

$$\sigma_s = \frac{2zen}{\kappa}\sqrt{2\left(\cosh\Phi_0 - \cosh\Phi_m\right)}$$



$$\Delta G_{123} = -\frac{A_{123}}{12\pi H^2} \qquad A_{123} = \frac{3kT}{2}\sum_{n=0}^{\infty}{}' \Delta_{12}\Delta_{32} \times \mathrm{Rel}_n(l)$$

Review of Lecture 4

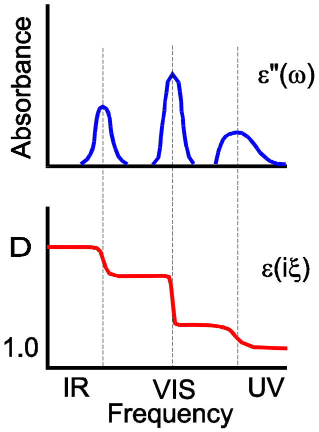
Lifshitz (1954) – The distance derivative of the standing, oscillatory EM waves between two flat plates is the force per area.

Convert optical data to dielectric data:

$$\varepsilon''(\omega) = 2n_{ref}\kappa_{abs}$$

$$\mathrm{Reflectivity}_{normal} = \frac{(n_{ref}-1)^2 + \kappa_{abs}^2}{(n_{ref}+1)^2 + \kappa_{abs}^2}$$

$$\varepsilon(i\xi) = 1 + \frac{2}{\pi}\int_0^{\infty}\frac{\omega\varepsilon''(\omega)}{\omega^2+\xi^2}\,d\omega$$



Fit dielectric data to empirical equation:

$$\varepsilon(i\xi_n) = 1 + \sum_j \frac{d_j}{1+\xi_n\tau_j} + \sum_j \frac{f_j}{\omega_j^2 + g_j\xi_n + \xi_n^2}$$

The Matsubara frequencies:

$$\xi_n = n\frac{4\pi^2 kT}{h}$$

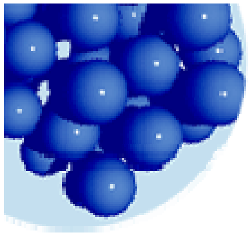
The dielectric differences:

$$\Delta_{12} = \frac{\varepsilon_1(i\xi_n) - \varepsilon_2(i\xi_n)}{\varepsilon_1(i\xi_n) + \varepsilon_2(i\xi_n)}$$

$$\Delta_{32} = \frac{\varepsilon_3(i\xi_n) - \varepsilon_2(i\xi_n)}{\varepsilon_3(i\xi_n) + \varepsilon_2(i\xi_n)}$$

The Lifshitz constant:

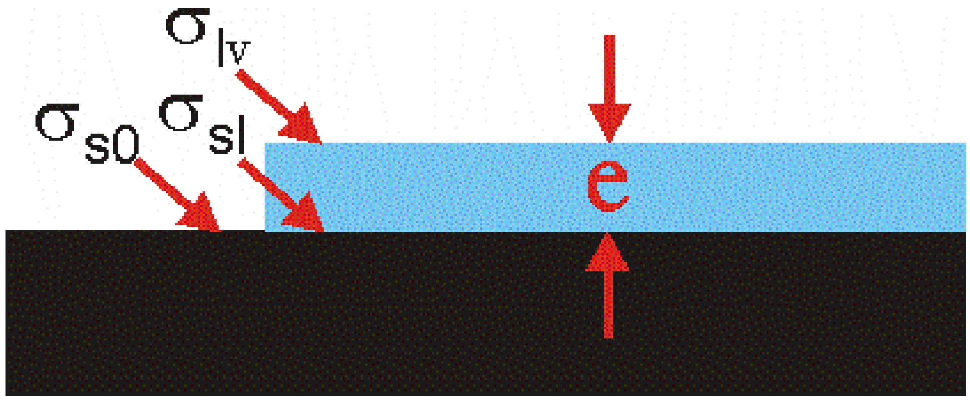
$$A_{123} = \frac{3kT}{2}\sum_{n=0}^{\infty}{}' \Delta_{12}\Delta_{32} \times \mathrm{Rel}_n(l)$$



From lecture 1.

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

Energy of thin liquid films



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

$$\text{as } e \to 0 \quad \frac{Energy}{m^2} \to \sigma_{s0}$$

$$\text{as } e \to \infty \quad \frac{Energy}{m^2} \to \sigma_{sl} + \sigma_{lv}$$

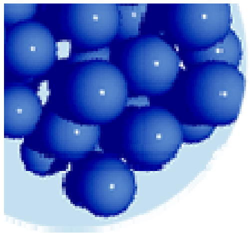
Range of *P*(*e*):

- Between surfaces: $1/e^2$
- For polymers: size of coils
- Electrostatics: 10’s nm in water
  100’s nm in oil

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

$$P(\infty) = 0$$

*de Gennes, P-G; Brochard-Wyart, F.; Quéré, D.
Capillarity and wetting phenomena: Drops, bubbles, pearls, waves.
Springer: New York; **2004**.



Energy at constant volume

$$\bar{E} = \frac{Energy}{m^2} = \sigma_{sl} + \sigma_{lv} + P(e) \qquad \text{or} \qquad E = \left[\sigma_{sl} + \sigma_{lv} + P(e)\right]A$$

Differentiating gives:

$$dE = \left[\sigma_{sl} + \sigma_{lv} + P(e)\right]dA + A\left(\frac{dP(e)}{de}\right)de$$

$$= \left[\sigma_{sl} + \sigma_{lv} + P(e)\right]dA - A\Pi de$$

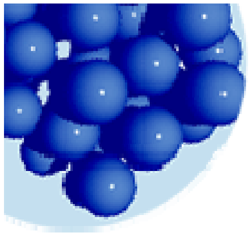
Consider changes at constant volume = Ae

$$Ade + edA = 0 \quad \text{or} \quad \frac{A}{dA} = -\frac{e}{de}$$

The surface tension of the film is the change in energy with area:

$$\sigma_{film} = \left(\frac{dE}{dA}\right)_{Ae=constant}$$

$$\sigma_{film} = \sigma_{sl} + \sigma_{lv} + P(e) + e\Pi(e)$$



dGBWQ, Fig. 4.3

Stability of thin films

The energy of a film at constant volume is:

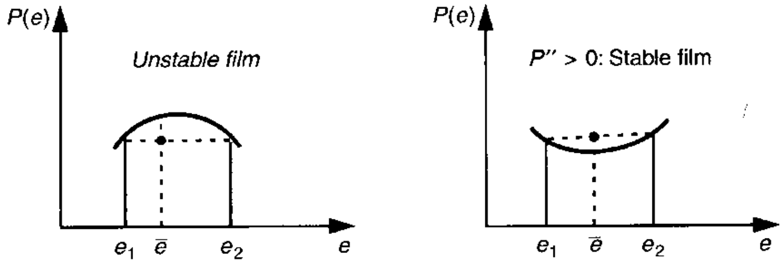
$$\sigma_{film} = \sigma_{sl} + \sigma_{lv} + P(e) + e\Pi(e)$$

The differential with respect to thickness is:

$$\frac{d\sigma_{film}}{de} = 0 + 0 - \Pi(e) + \Pi(e) + e\frac{d^2P(e)}{de^2} = e\frac{d^2P(e)}{de^2}$$

A film is stable (locally)only if:

$$\frac{d^2P(e)}{de^2} > 0$$



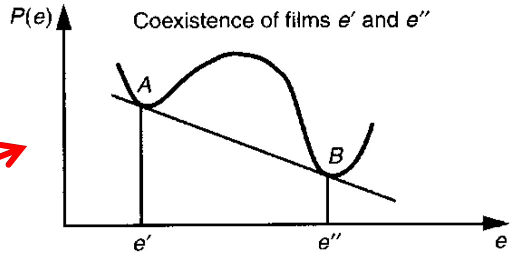
(a)

(b)

(c) represents the splitting of the film in (a) into two thickness of partial areas, α_1 and α_2

$$\alpha_1 P(e_1) + \alpha_2 P(e_2) < P(e)$$

$$\alpha_1 + \alpha_2 = 1$$



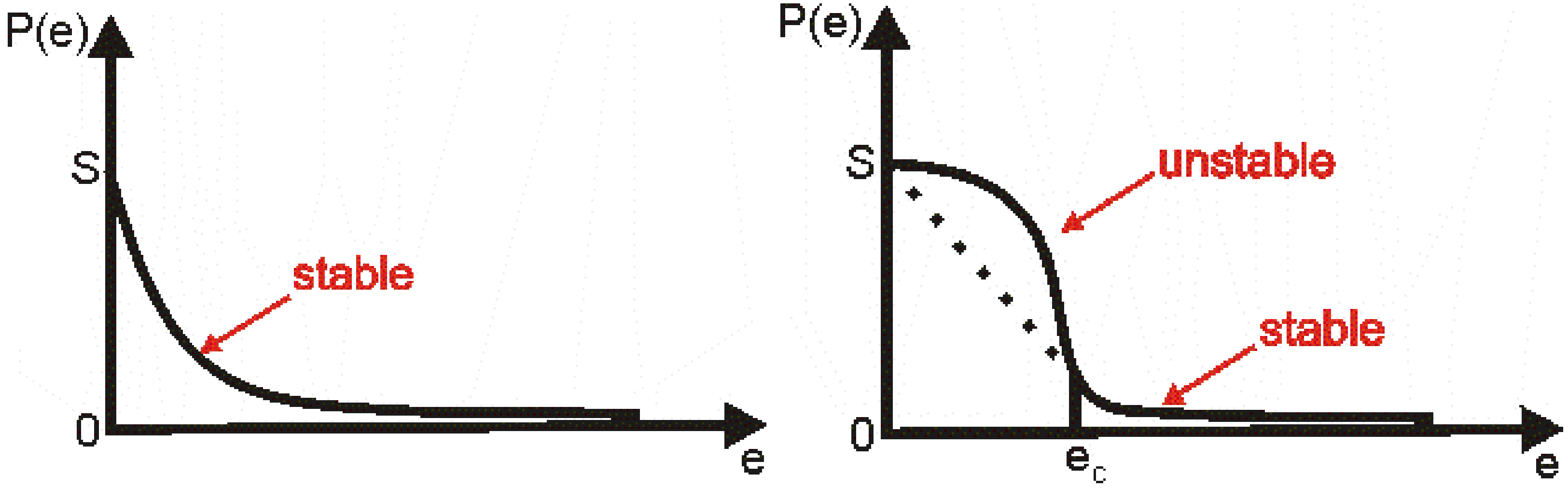
(c)

This is the energy at constant *Ae*!

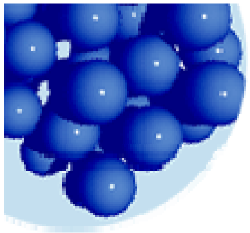
dGBWQ, Fig. 4.4

Total wetting

$$S = \sigma_{s0} - \sigma_{lv} - \sigma_{sl} > 0$$



Films greater than e_c are stable.



Thickness of a large drop.

Small drops are spherical segments. Large drops are flattened.

To “spread” the drop requires an force per unit length:

$$\sigma_{sv} - \left(\sigma_{lv} + \sigma_{sl}\right)$$

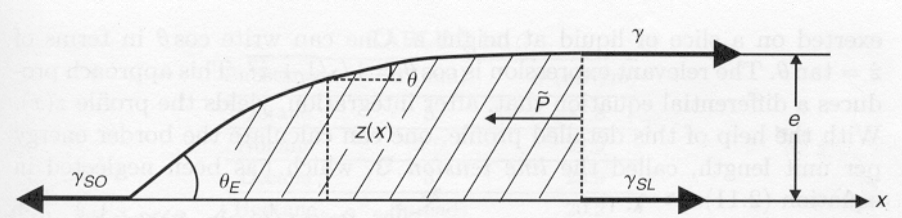


FIGURE 2.4. Equilibrium of the forces (per unit length of the line of contact) acting on the edge of a puddle. $\tilde{P} = \rho g e^2/2$ is the hydrostatic pressure.

The hydrostatic pressure integrated over the depth of the drop is a force per unit length pushing to “spread” the drop:

$$\tilde{P} = \int_0^e \rho g \left(e - \tilde{z}\right) d\tilde{z} = \frac{1}{2}\rho g e^2$$

At equilibrium the sum of the two is zero:

$$\sigma_{sv} - \left(\sigma_{lv} + \sigma_{sl}\right) + \frac{1}{2}\rho g e^2 = 0$$

Substituting the Young-Dupré equation:

$$\sigma_{lv}\left(1 - \cos\theta_e\right) = \frac{1}{2}\rho g e^2$$

Re-arranging gives:

$$e = 2\kappa^{-1}\sin\left(\frac{\theta_e}{2}\right)$$

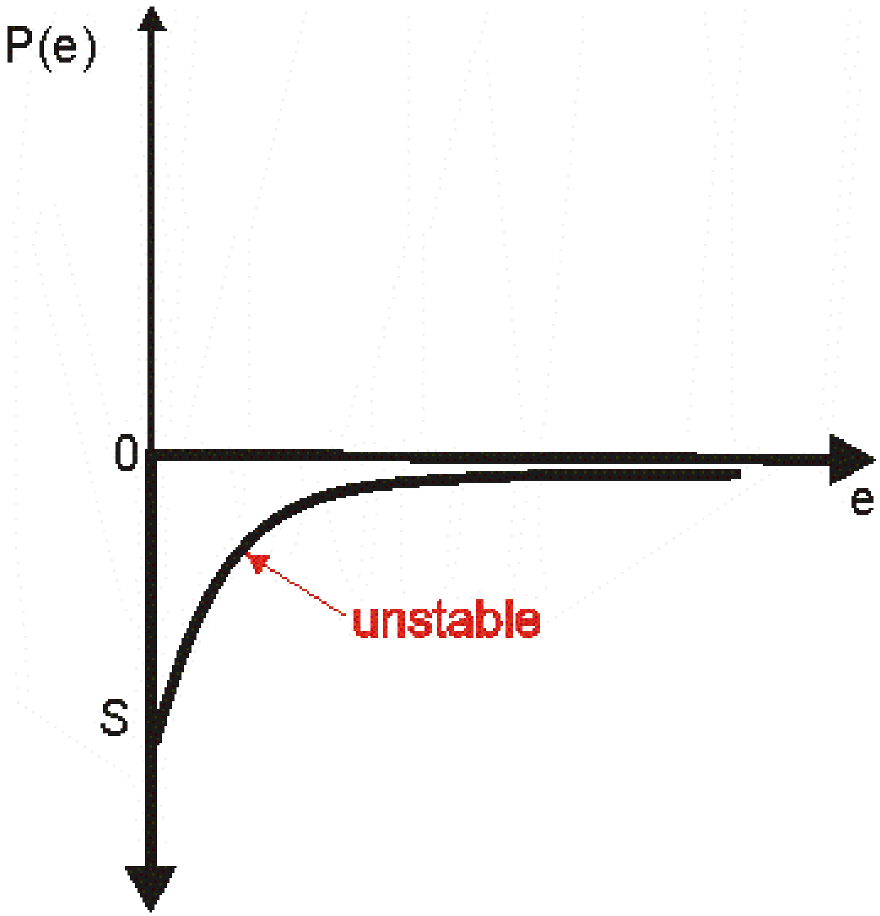
dGBWQ, Fig. 2.4

dGBWQ, Fig. 4.4

Partial wetting

$$S = \sigma_{s0} - \sigma_{lv} - \sigma_{sl} < 0$$

$$\sigma_{s0} = \sigma_{lv} \cos\theta + \sigma_{sl}$$

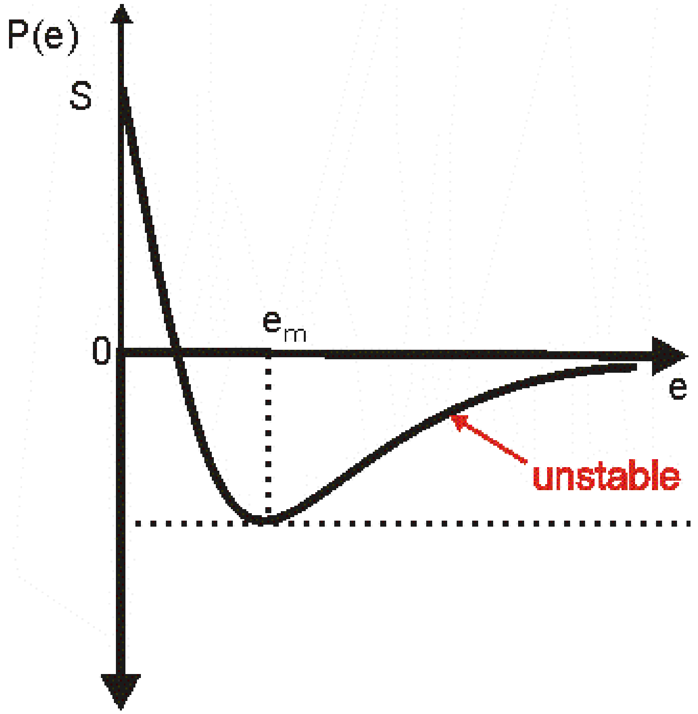


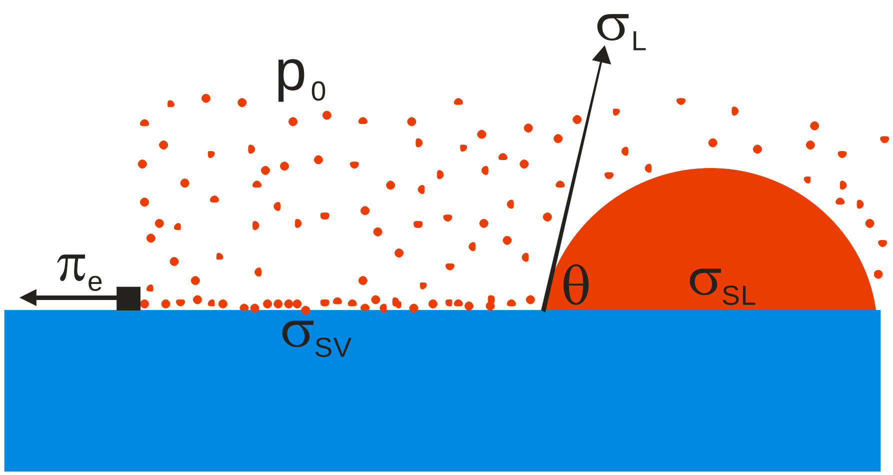
dGBWQ, Fig. 4.4

Pseudo-partial wetting

$$S = \sigma_{s0} - \sigma_{lv} - \sigma_{sl} < 0$$

$$\sigma_{s0} - \pi_e = \sigma_{sv} = \sigma_{lv} \cos\theta + \sigma_{sl}$$



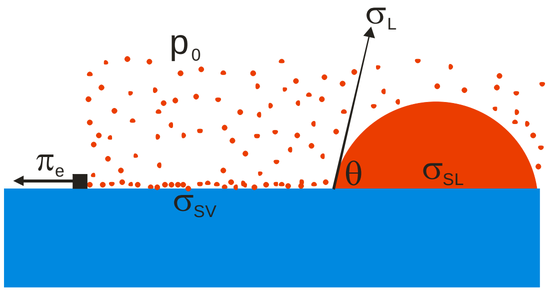


Gibbs' adsorption isotherm:

$$\pi_e = RT \int_0^{p_0} \Gamma d \ln p$$

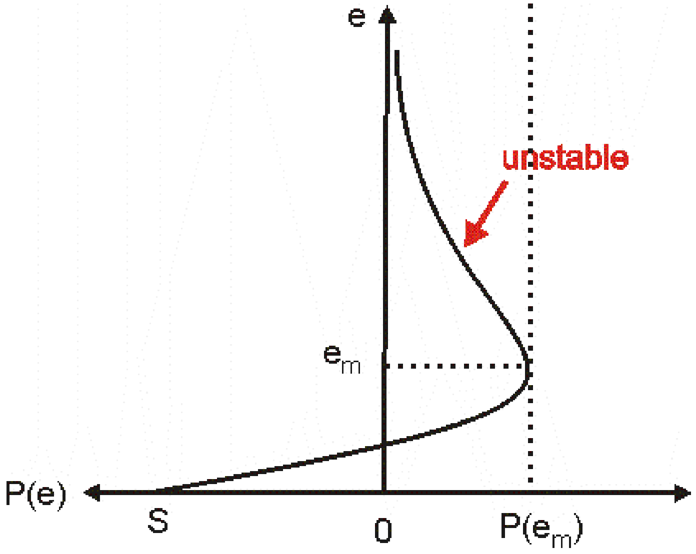
$$\sigma_{film} = \sigma_{sl} + \sigma_{lv} + P(e) + e\Pi(e)$$

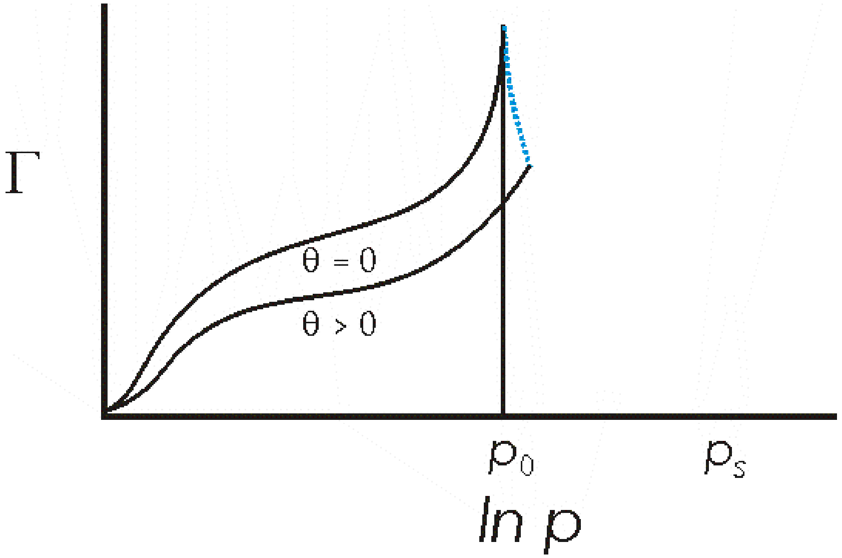
Wetting, gas adsorption, and contact angles



$$\sigma_{sv} = \sigma_{lv}\cos\theta + \sigma_{sl}$$

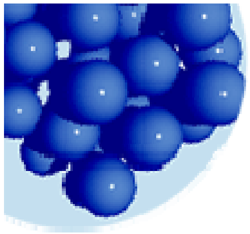
If the liquid has a finite contact angle, then gas adsorption is finite at p_0.





$$\frac{d\sigma_{film}}{de} = -e\ddot{P}(e)$$

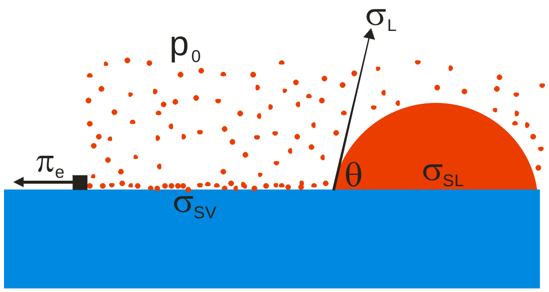
$$\pi(\Gamma) = RT\int_0^{p(\Gamma)} \Gamma \, d\ln p$$

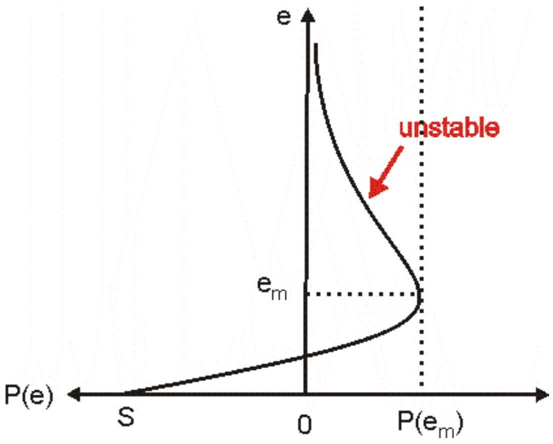


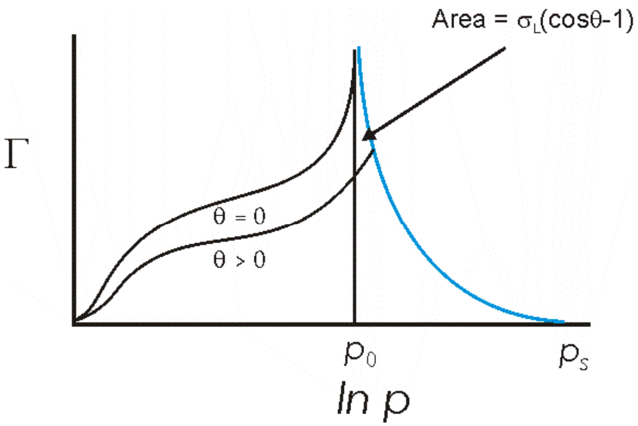
$$\sigma_{film} = \sigma_{sl} + \sigma_{lv} + P(e) + e\Pi(e)$$

$$P(e) = \frac{A_{121}}{12\pi e} = 2\sigma_{lv}(e = e_c)$$

Wetting – contact angles – gas adsorption







From a thermodynamic argument by deGennes et al:

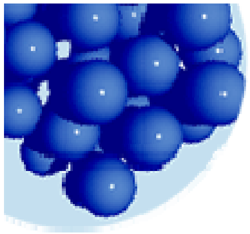
$$\sigma_{sl} + \sigma_{lv} + P(e_m) + e_m\Pi(e_m) = \sigma_{sl} + \sigma_{lv}\cos\theta$$

$$P(e_m) = \sigma_{lv}(\cos\theta - 1)$$

From a thermodynamic argument by Adamson:

$$Area = \sigma_{lv}(\cos\theta - 1)$$

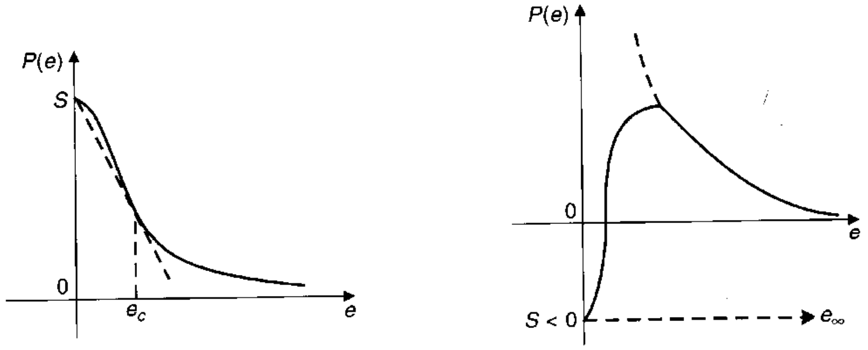
The contact angle on small particles!



Slabs of thickness *a*, separation *l*: $-\frac{A}{12\pi}\left[\frac{1}{l^2}-\frac{2}{(l+a)^2}+\frac{1}{(l+2a)^2}\right]$

Interactions on treated surfaces

Silane treatment of glass



Bare glass

(a)

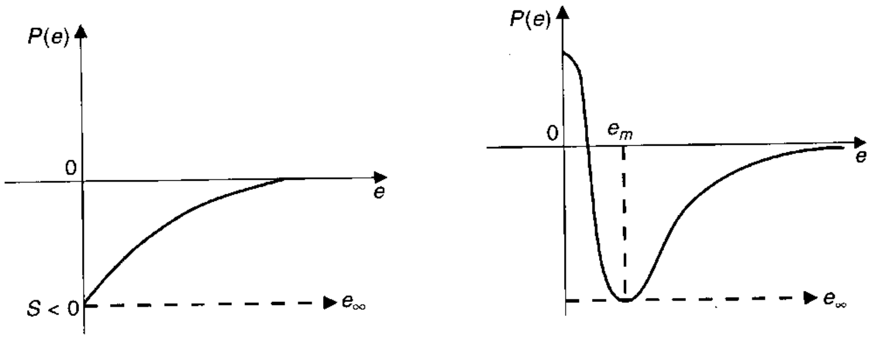
Silanized glass

(b)

(a) Water spreads on clean glass – thick films are stable.

(b) On thinly silanized glass, thick films or water are stable, thin films of water are unstable.

Gold films on plastic



(a)

(b)

(a) Thin films of water are unstable on plastic.

(b) Thin films of water are stable on gold-coated plastic.

dGBWQ, p. 98.