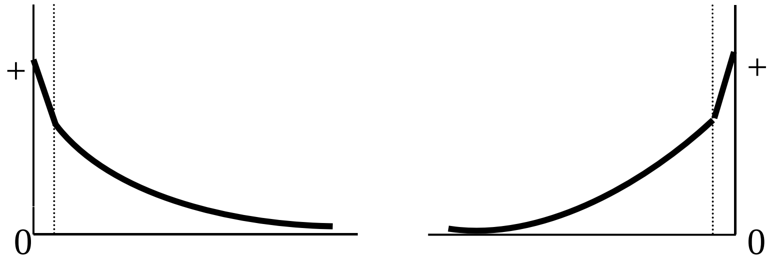
Lecture 6

Surface Forces II:
Double Layer Force,
DLVO theory and beyond

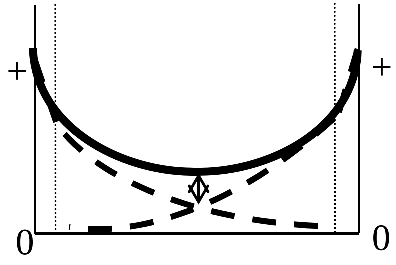
The electrostatic double layer force

- When electric double layers of two surfaces overlap a force will arise.

far away



close to each other



- we expect this force to be a repulsive one as the surface charge is not completely screened.

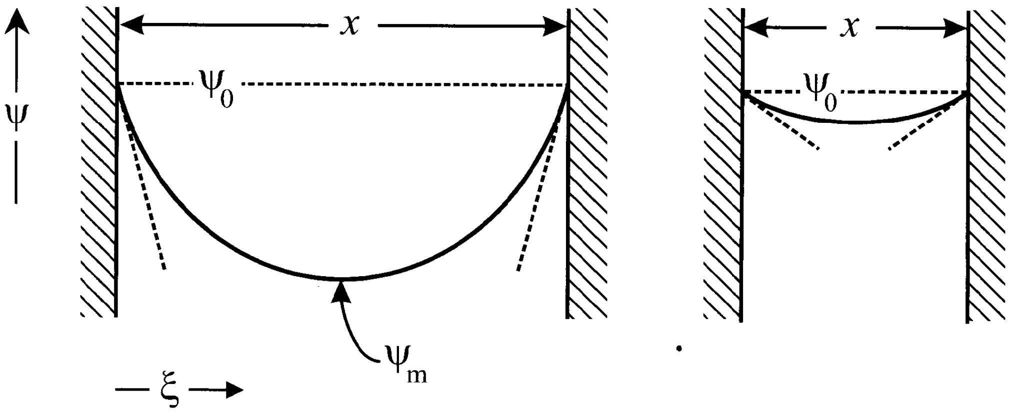
Equation for DL-force

- Gibbs free energy (per unit area) of two infinitely separated double layers:

$$g^{\infty} = -2\int_{0}^{\varphi_0} \sigma' d\varphi_0'$$

- if the surface are at a distance ***x*** from each other both surface charge and potential depend on ***x***.

$$g(x) = -2\int_{0}^{\varphi_0(x)} \sigma'(x) d\varphi_0'$$



- the interaction energy

$$w(x) = \Delta g = g(x) - g^{\infty}$$

- the interaction force: $\Pi = -\dfrac{d\Delta g}{dx}$

Equation for DL-force

- Poisson-Boltzmann equation:

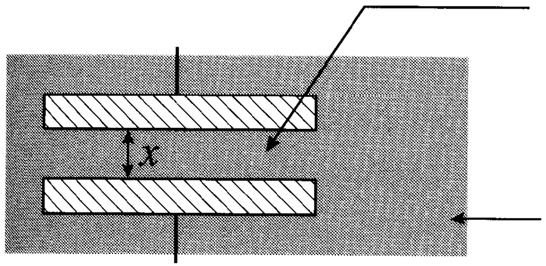
$$ec_0\left(e^{\frac{e\varphi}{kT}} - e^{\frac{-e\varphi}{kT}}\right) - \varepsilon\varepsilon_0 \frac{d^2\varphi}{dx^2} = 0$$

- after first integration:

$$c_0 kT\left(e^{\frac{e\varphi}{kT}} - e^{\frac{-e\varphi}{kT}}\right) - \frac{\varepsilon\varepsilon_0}{2}\left(\frac{d\varphi}{dx}\right)^2 = P$$

Equation for DL-force

- The disjoining pressure:



Pressure in the film
$P = P_0 + \Pi$

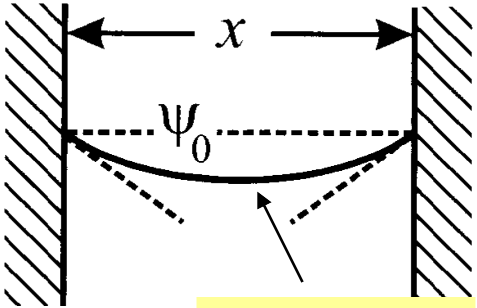
Pressure P_0 of the bulk phase

$$\Pi = P - 2kTc_0 = c_0 kT\left(e^{\frac{e\varphi}{kT}} - e^{\frac{-e\varphi}{kT}} - 2\right) - \frac{\varepsilon\varepsilon_0}{2}\left(\frac{d\varphi}{d\xi}\right)^2$$

Electrostatic interaction between identical surfaces

- As at the equilibrium the pressure is the same everywhere, we calculate it in the middle of the gap:

$$\Pi = c_0 kT\left(e^{\frac{e\varphi_m}{kT}} - e^{\frac{-e\varphi_m}{kT}} - 2\right)$$



$$\frac{d\varphi}{dx} = 0;\ \varphi = \varphi_m$$

- for low potentials:

$$\Pi = \frac{c_0 e^2}{kT} kT\varphi_m{}^2 = \frac{\varepsilon\varepsilon_0}{2\lambda_D{}^2} kT\varphi_m{}^2$$

$$\lambda_D = \sqrt{\frac{\varepsilon\varepsilon_0 kT}{2c_0 e^2}}$$

if we have and expression for the potential we can calculate the pressure

Electrostatic interaction between identical surfaces

- for a slight overlap of DLs we can assume

$$\varphi_m = 2\varphi'(x/2)$$

- for low potentials

$$\Pi = \frac{2\varepsilon\varepsilon_0}{\lambda_D{}^2}\varphi_0{}^2 e^{-x/\lambda_D}$$

$$w(x) = -\int_{\infty}^{x} \Pi(x')dx' = -\frac{2\varepsilon\varepsilon_0\varphi_0{}^2}{\lambda_D} e^{-x/\lambda_D}$$

- for high potentials

$$w(x) = 64c_0 kT\lambda_D \tanh^2\left(\frac{e\varphi_0}{4kT}\right) e^{-x/\lambda_D}$$

The DLVO theory

- The theory explains why dispersions aggregate when salt concentration is increased

Derjaguin-Landau-Verwey-Overbeek

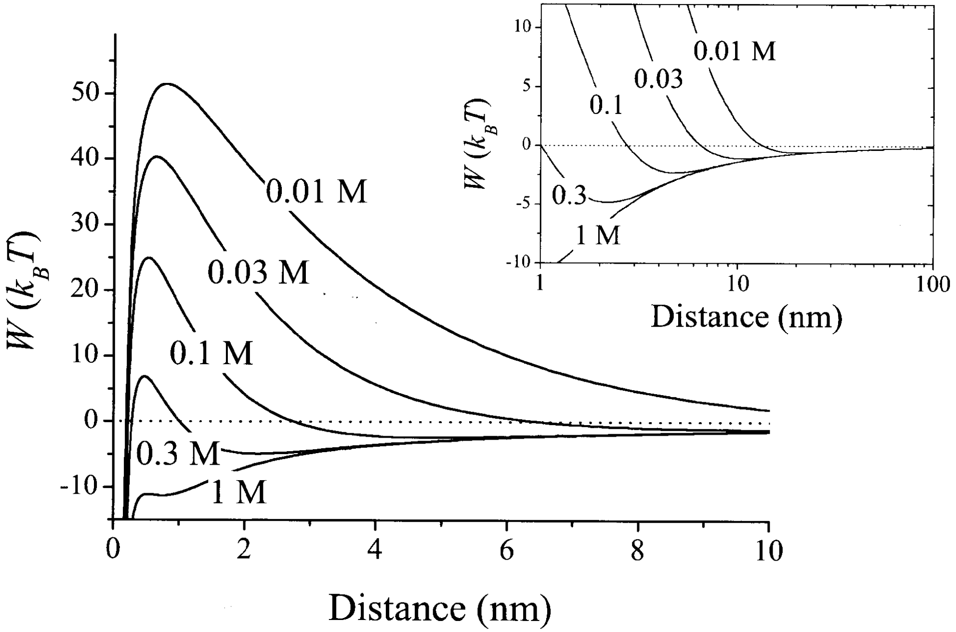
Derjaguin B.V. and Landau L.D., 1941. “Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solutions of electrolytes”. Acta Physicochimica URSS **14**, 633-662.

Verwey E.J.W. and Overbeek J.Th.G., 1948. “Theory of the Stability of Lyophobic Colloids”. Elsevier, New York

The DLVO theory

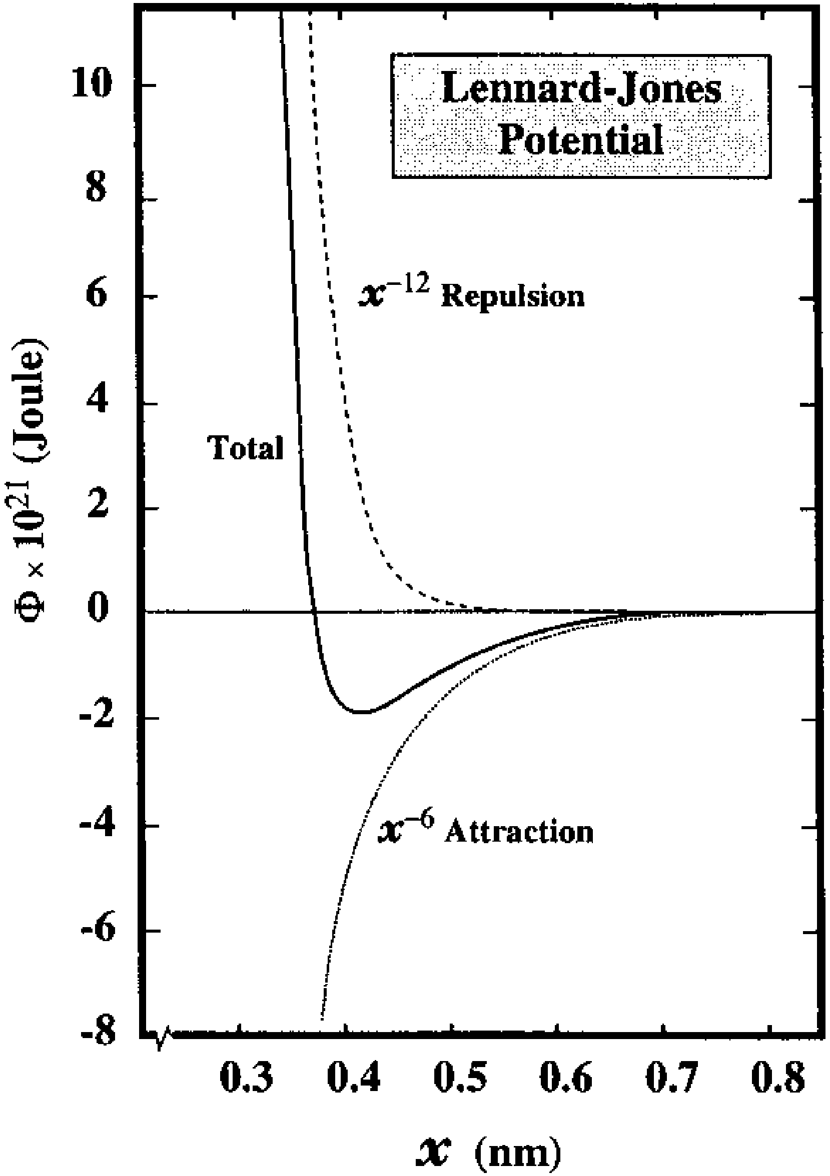
- Coagulation of dispersed particles is explained by the interplay of two forces: van der Waals and double-layer force (DLVO forces)

$$w(x) = 64 c_0 kT \lambda_D \left(\frac{\exp\left(e\varphi_0 / 2kT\right) - 1}{\exp\left(e\varphi_0 / 2kT\right) + 1} \right)^2 \exp\left(-x/\lambda_D\right) - \frac{A_H}{12\pi x^2}$$



Non-DLVO forces

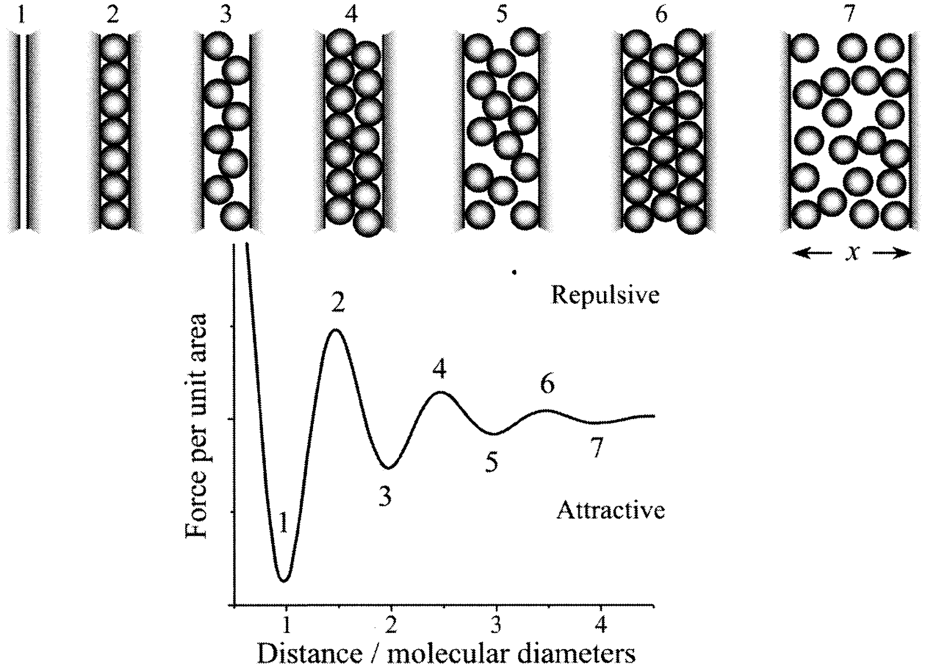
- Born repulsion
    - origin in same *interatomic potential* as van der Waals
    - repulsion from overlap of electron shells
    - very short range force
    - prevents contact between attached particles
    - provides finite depth to primary minimum



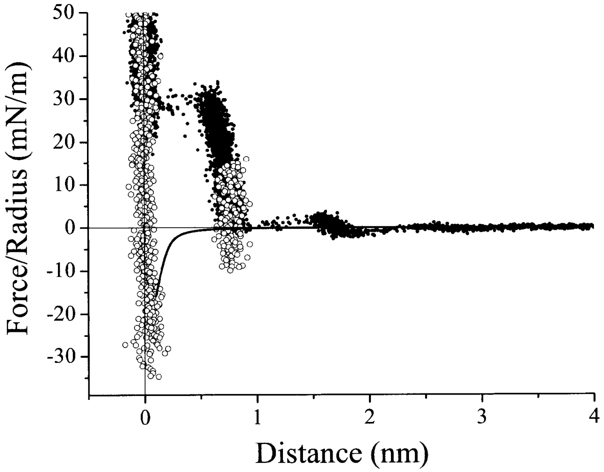
Non-DLVO forces

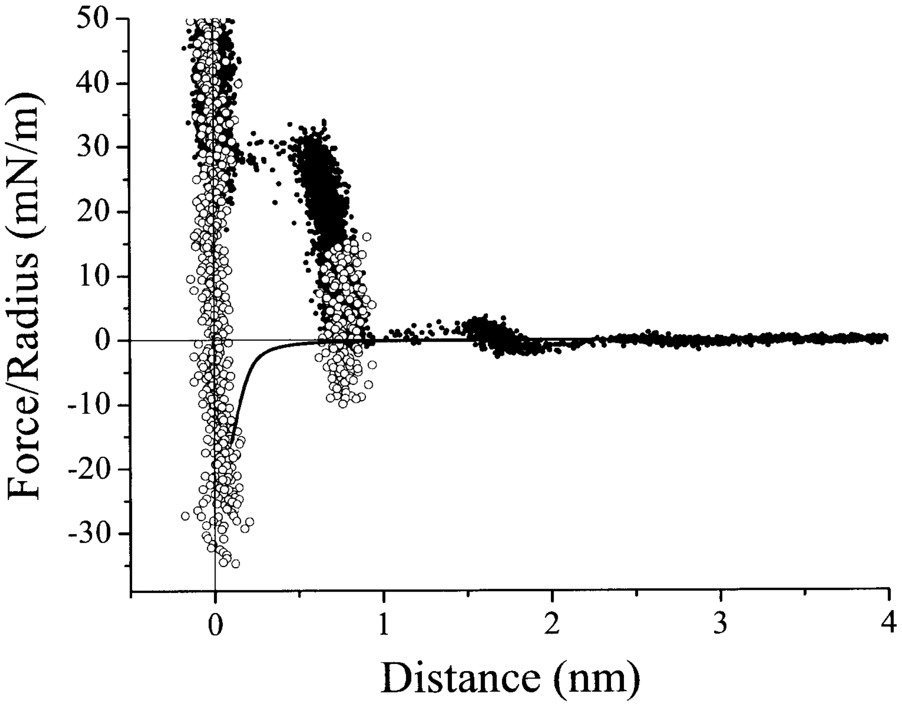
- Solvation forces:

$$f(x) = f_0 \cos\left(\frac{2\pi x}{d_0}\right) e^{-x/x_0}$$



Experimentally measured force between a SiN tip and mica in 1-propanol

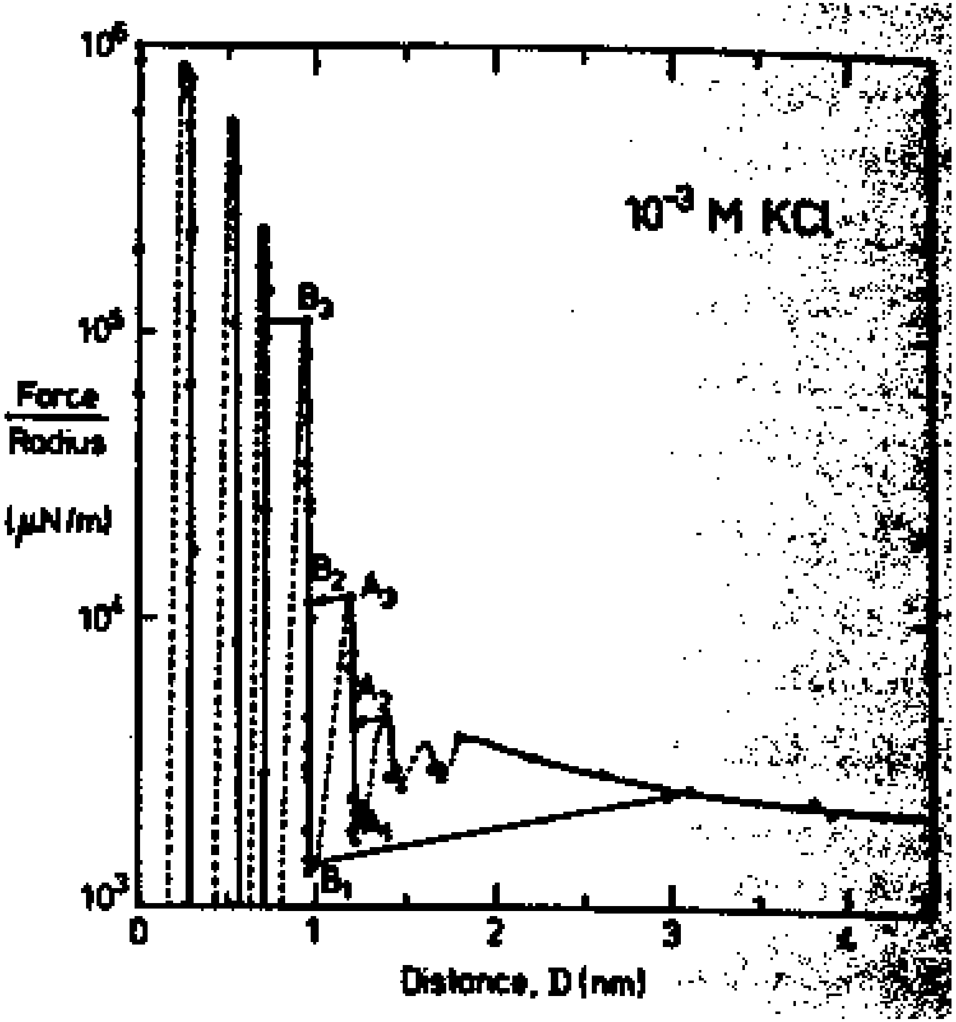




Force/Radius (mN/m)
50
40
30
20
10
0
-10
-20
-30
0
1
2
3
4
Distance (nm)

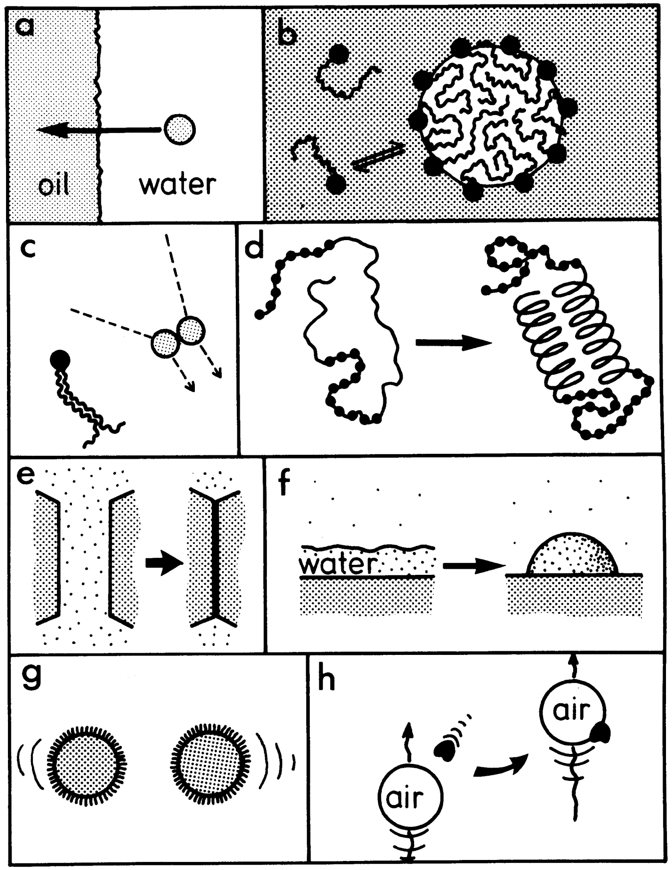
Non-DLVO forces

- **Hydration**
  - “vicinal” water structure
  - repulsive force
  - corresponds to layer-by-layer removal of vicinal water
  - effect of ionic strength, cation
    - Li^+, $Na^+ > K^+ > Cs^+$



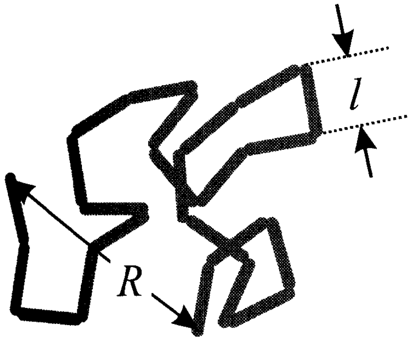
Non-DLVO forces

- **Hydrophobic interaction**
  - attractive force
  - exponentially decaying
  - stronger than vdWaals forces
  - usually two component assumed:
    - short-range (1-2nm) due to change in water structure:
    - long-distance (up to 200nm) due to spontaneously formed gas bubbles



examples of hydrophobic interaction

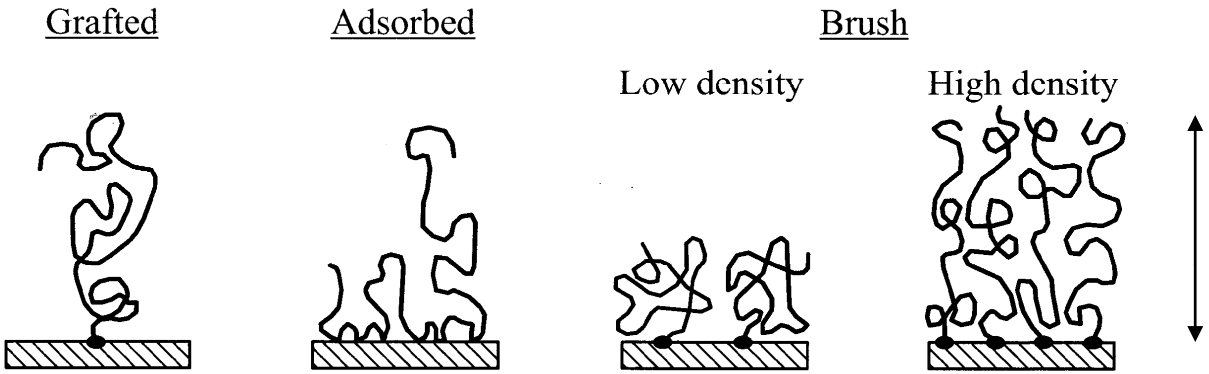
Non-DLVO forces: Steric force



- A macromolecule in solution:
- for a freely jointed segment chain model:
  - Rms of the end-to-end distance: $R_0 = l\sqrt{n}$
  - radius of gyration: $R_0 = \dfrac{l\sqrt{n}}{\sqrt{6}}$
- Solvent influence
  - ideal solvent: interaction between the monomers is the same as with the solvent
  - good solvent: repulsive interaction between monomers, Rg increases
  - bad solvent: attraction between the monomers, Rg decreases

Steric force

- The force between two surface coated by a polymer is determined by:
  - the nature of solvent
  - the way the polymer is deposited and its density



$$L_0 = nl^{5/3}\Gamma^{1/3}$$

$$\Gamma < 1/R_g{}^2 \qquad \Gamma \gg 1/R_g{}^2$$

Steric force

- Repulsive force caused by:
  - Entropic factor (reduced configuration entropy)
  - osmotic pressure in the gap
  - intersegment force

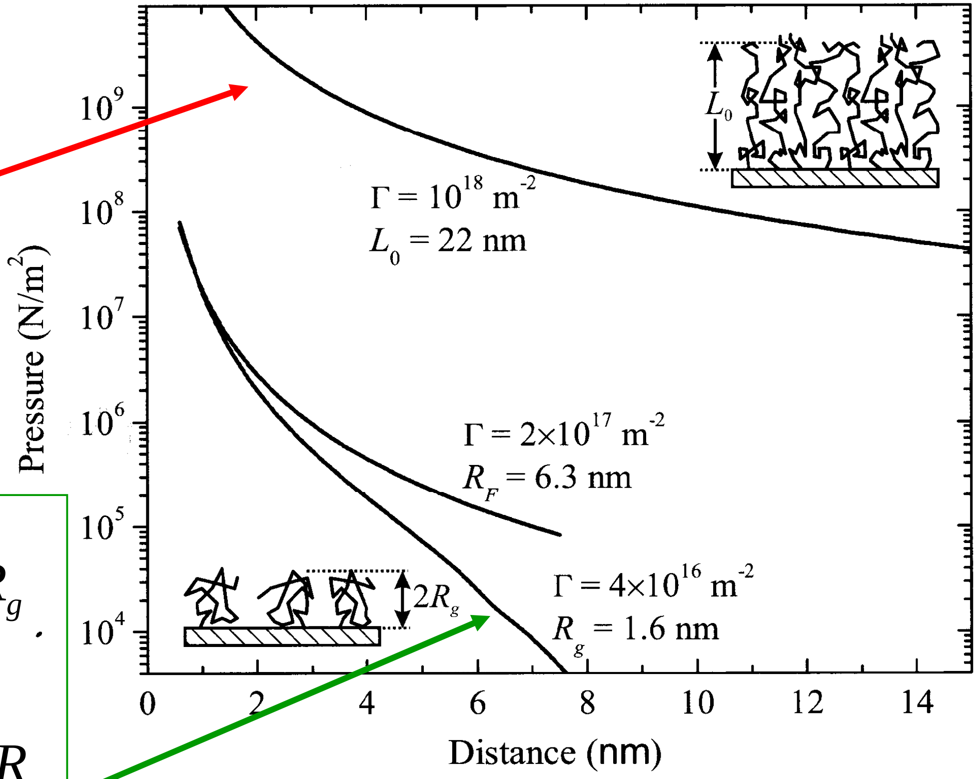
- High density brush

$$\Pi(x) = kT\Gamma^{3/2}\left[\left(\frac{2L_0}{x}\right)^{\frac{9}{4}} - \left(\frac{x}{2L_0}\right)^{\frac{3}{4}}\right]$$

- Low density brush

$$\Pi(x) = \frac{kT\Gamma}{x}\left(\frac{2\pi^2 R_g{}^2}{x^2} - 1\right) \quad \text{for } x \le 3\sqrt{2}R_g,$$

$$\Pi(x) = \frac{kT\Gamma x}{R_g}\exp\left(-\frac{x}{2R_g}\right)^2 \quad \text{for } x > 3\sqrt{2}R_g$$

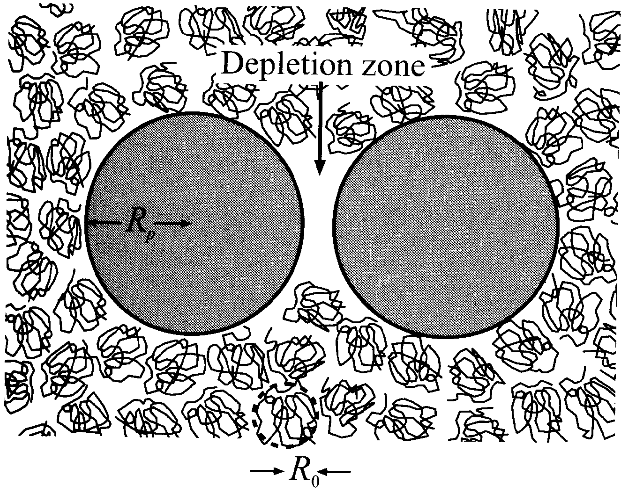


Depletion forces

- Attractive force between two particles in solution of macromolecules will arise due to osmotic pressure

- Asakura-Oosawa theory:

$$\begin{cases} W(D) \approx \dfrac{\pi}{2} ckTR_p \left(2R_0 - D\right)^2 & D \leq 2R_0 \\ W(D) = 0 & D > 2R_0 \end{cases}$$



- Alternatively could be explained due increase of total free volume available to macromolecules

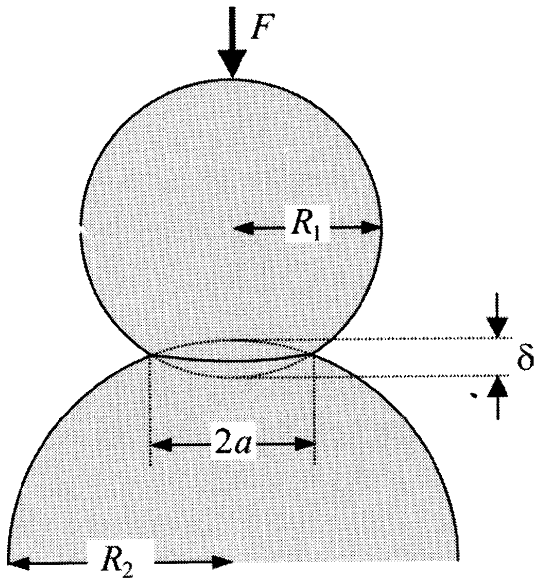
Contact forces and adhesion

- Hertz theory
  - If two spheres having Young moduli E_1, and Poisson ratios n_1, n_2 are pressed together:

effective radius

$$a^3 = \frac{3R^*}{4E^*}F \qquad \delta = \frac{a^2}{R^*}$$

reduced Young modulus



  - where:

$$R^* = \frac{R_1 \cdot R_2}{R_1 + R_2} \qquad \frac{1}{E^*} = \frac{1-\nu_1^{\,2}}{E_1} + \frac{1-\nu_2^{\,2}}{E_2}$$

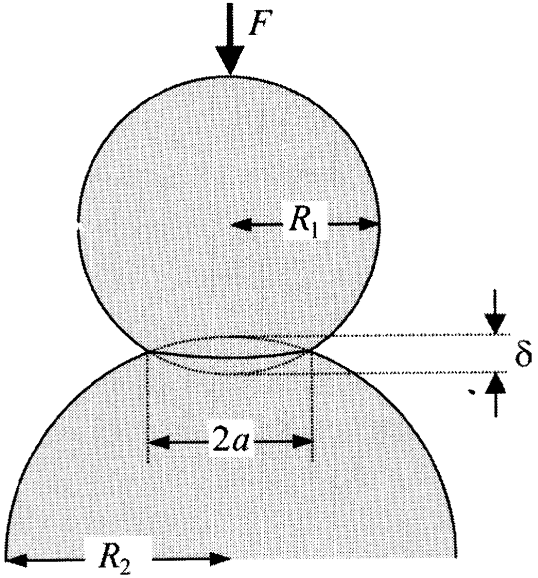
Contact forces and adhesion

- Johnson, Kendall and Roberts (JKR theory)
  - additionally the work of cohesion is taken into account

$$a^3 = \frac{3R^*}{4E^*}\left(F + 3\pi WR^* + \sqrt{6\pi WR^* F + \left(3\pi WR^*\right)^2}\right)$$

  - so, a force is required to separate two solids

$$F_{adh} = \frac{3\pi}{2} WR^*; \quad W = 2\gamma_s$$



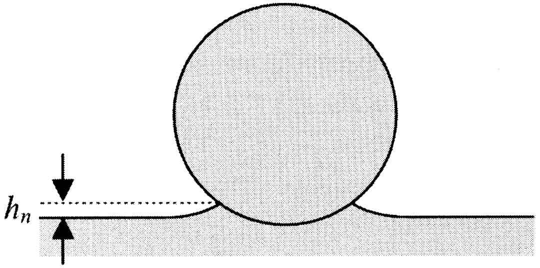
- Derjagin, Muller, Toropov (DMT theory)
  - van der Waals forces are taken into account

$$F_{adh} = 4\pi\gamma_s R^*$$

Contact forces and adhesion

- Criterion:
  - if size of the neck is larger than interatomic distance – JKR, otherwise DMT

$$h_n \approx \left(\frac{\gamma_s^2 R^*}{E^{*2}} \right)^{1/3}$$



Problems

End of chapter problems:

- ch.6.8
- ch.6.9