Surfaces of biomaterials

Three lectures:

1.23.06 – Surface Properties of Biomaterials
1.25.06 – Surface Characterization
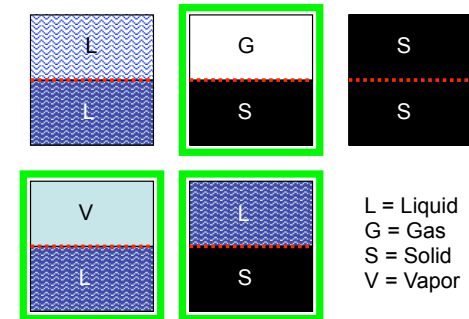1.27.06 – Surface and Protein Interactions

Three points:

1 – Surfaces have unique properties
2 – We can (and do) measure these properties
3 – Because they affect biocompatibility
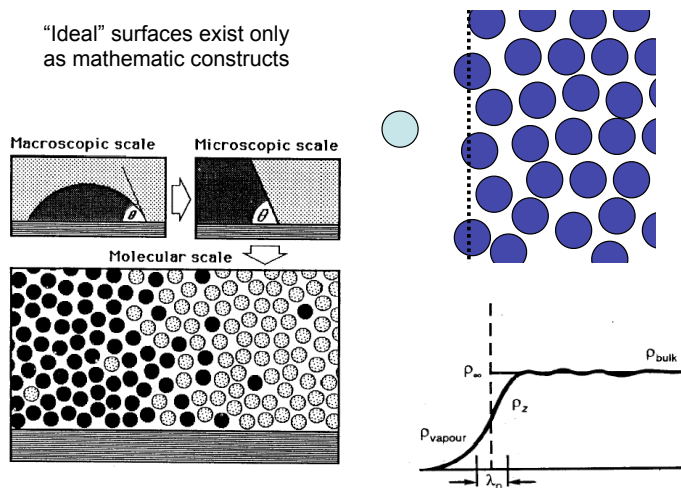

What constitutes a surface?

An interface is the boundary region between two adjacent bulk phases

L = Liquid
G = Gas
S = Solid
V = Vapor

We recognize (S/G), (S/L), and (L/V) as surfaces

Surfaces are (not) smooth (pure 2D)

"Ideal" surfaces exist only
as mathematic constructs

Macroscopic scale   Microscopic scale

Molecular scale

ρ_∞
ρ_z
ρ_{vapour}
ρ_{bulk}
λ_0

Physical description of biomaterial surfaces

Biomaterial surfaces exhibit remarkable heterogeneity in physical structure:

Material dependant: Metals vs. Polymers vs. Ceramics vs. Gels
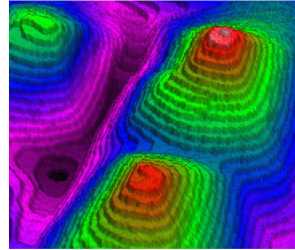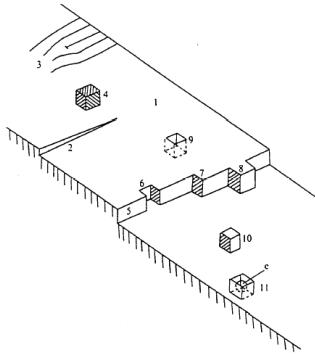Chemistry: Polar vs. Apolar, Charge, Reactivity, Patterned
Morphology: Smooth, Rough, Stepped, Patterned, Diffuse
Order: Crystalline, Amorphous, Semi-Crystalline, Phases
Environment: Hydration, Solvent Quality

Bumpy   with   Phases   Glassy

Hydration
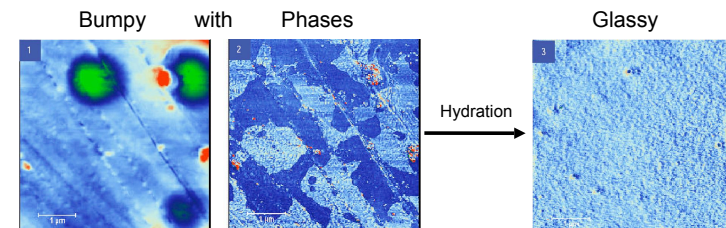
Crystal surface defects dominate

10 µm x 10 µm GaSb screw dislocations (3 Å high steps)

FIG. 5.4. Some simple defects that are often found on a low-index crystal face. 1. The perfect flat face itself – a terrace; 2. an emerging screw dislocation; 3. the intersection of an edge dislocation with the terrace; 4. an impurity adatom (adatoms are discussed in Chapter 6); 5. a monatomic step in the surface – a ledge; 6. a vacancy in the ledge; 7. a step in the ledge – a kink; 8. an adatom of the same kind as the bulk atoms situated upon the ledge; 9. a vacancy in the terrace; 10. an adatom on the terrace; 11. a vacancy in the terrace where an electron is trapped – in an alkali halide this would be an F-centre.

Crystal surfaces are dynamic

Selvedge

Relaxation

Selvedge
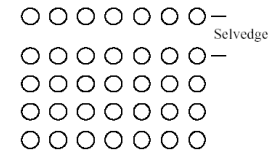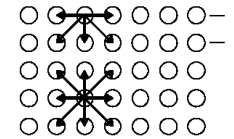
Reconstruction
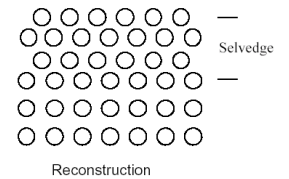
Polymer surface dynamics

Given sufficient mobility, polymer surfaces will reorient or restructure in response to their local micro-environment so as to minimize their interfacial free energy with the surrounding phase.

Polar Solvent

Apolar Solvent / Air

OH   OH   OH   OH

CH_3 CH_3 CH_3 CH_3

Bulk

CH_3 CH_3 CH_3 CH_3

OH   OH   OH   OH

Bulk

Biological surfaces (cell membranes) "flow"

see next page

Surface energetics is different from bulk

Molecules in the bulk of a material (e.g. crystal lattice) have a low relative energy state due to nearest neighbor interactions (e.g. bonding).
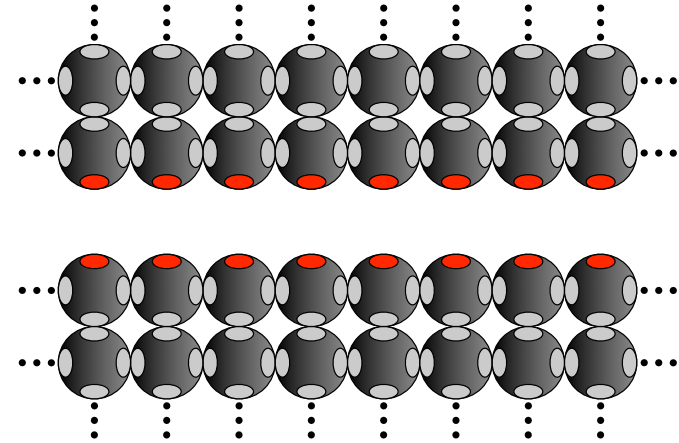
Performing sufficient work on the system to create an interface can disrupt this harmony...
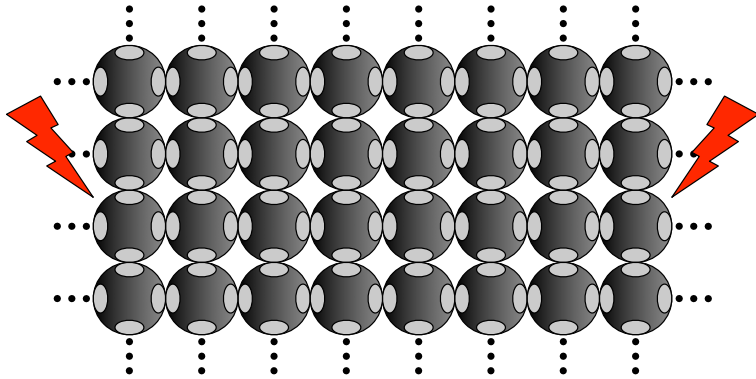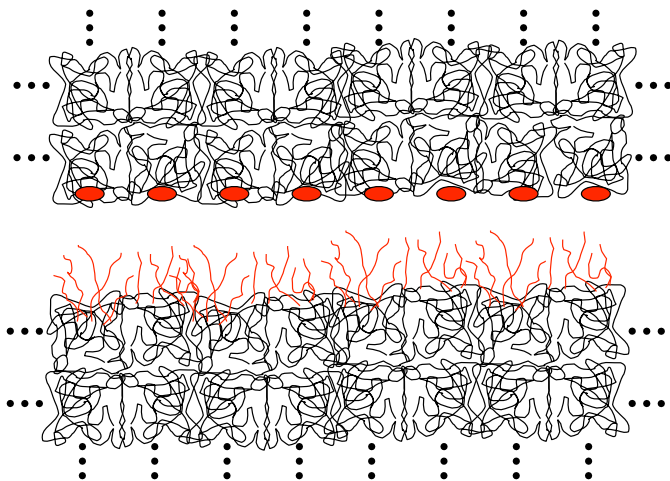

(Excess) surface free energy

Molecules at a surface are in a state of higher free energy (why "FREE" energy"?) than those in the bulk. This is in large part due to the lack of nearest neighbor interactions at a surface.

(Excess) surface free energy

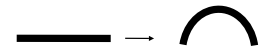The same thing occurs regardless of material (e.g. polymers).

Important point: free energy goes to minimum at equilibrium

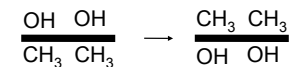Systems move toward lowering their free energy

Surfaces do so by:

Geometric changes (minimizing area if possible)

Binding (adsorption interactions)

Dynamic rearrangement

Surface energy and tension in liquids

In order to develop some concepts related to surfaces we will first look at the surface properties of liquids.

The work (*w*) required to create a new surface is proportional to the # of molecules at the surface, hence the area (*A*):

$$\delta w = \gamma \times \delta A$$

Where γ is the proportionality constant defined as the specific <u>surface free energy</u>. It has units of (force/length, mN/m) or (energy/area, mJ/m^2).

γ acts as a restoring force to resist any increase in area, for liquids it is numerically equal to the <u>surface tension</u>.

Surface tension acts to decrease the free energy of the system by minimizing the area, hence some observed effects:

- liquid droplets form spheres
- meniscus effects in capillaries

Surface energy and tension of solids

Problem:

Solid surfaces have well defined surface free energy, however, the surface tension of solids is experimentally inaccessible (or very difficult to measure).

Why?

Creation of new area in a solid is not reversible – you end up stretching or cleaving the sample. Interfacial stress during elastic enlargement can be measured and related to interfacial tension only if the relationship of interfacial tension as a function of strain is independently known.

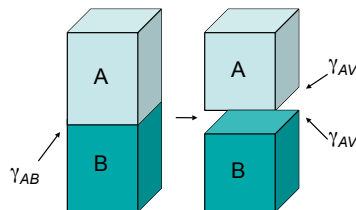## Works of cohesion and adhesion

For a single type of material (cohesion):

$$W_{AA} = 2\gamma_{AV}$$
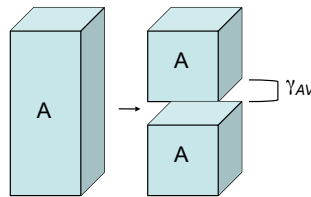
For two different materials (adhesion):

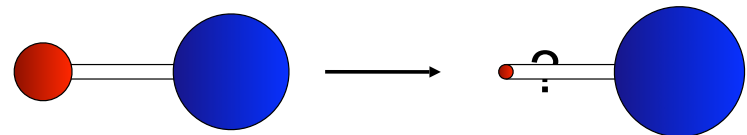$$W_{AB} = \gamma_{AV} + \gamma_{BV} - \gamma_{AB}$$

(V = vapor)

The Young-Laplace equation

The pressure difference (Δp) across the surface of a liquid is related to the surface curvature:

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$

for the radius of curvature in directions 1/(R$_1$) and 2/(R$_2$). Hence γ is balanced by Δp, or the surface tension tends to compress the droplet, increasing the internal pressure.

An interesting consequence:

Gibbs-Kelvin equation

One can relate the change in pressure due to surface tension to thermodynamic properties in order to obtain:

$$RT\ln\left(\frac{p}{p_o}\right) = \gamma V_L\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Where R is the gas constant, T is the absolute temperature, V_L is the molar volume of the liquid (weight divided by density), p is the vapor pressure at curved interfaces and p_o is the vapor pressure at flat interfaces respectively.
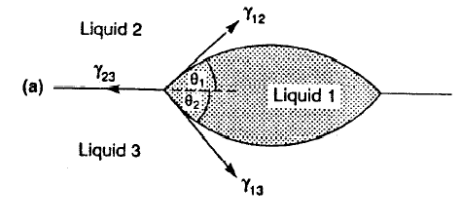
One consequence of G-K equation is that small liquid droplets evaporate faster (because higher vapor pressure) than flat liquid surface.

Young-Dupre equation

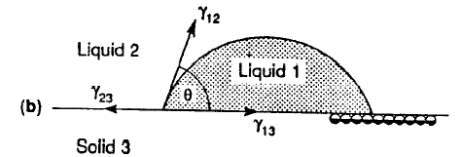For a small droplet of a liquid (1) on a solid or liquid (3) in the presence of vapor or liquid (2).

From a balance of forces:

$$\gamma_{23} = \gamma_{12}\cdot\cos\theta_1 + \gamma_{13}\cdot\cos\theta_2 \qquad \text{(a)}$$
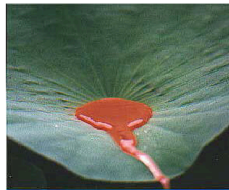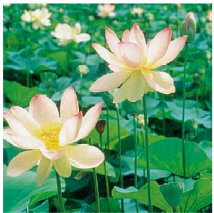
or, when the surface is rigid:

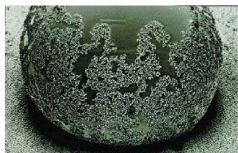$$\gamma_{23} = \gamma_{12}\cdot\cos\theta_1 + \gamma_{13} \qquad \text{(b)}$$

Measurement of contact angles is a useful tool for probing surface energetics. More on this in Lecture 2.

Super-hydrophobicity

The **surface** of plant **leafs**, especially of the **lotus** flower, can show **extreme hydrophobicity** to water (large water contact angles > 150°C).

Such **hydrophobic surfaces** also show a remarkable **self-cleaning** effect.

explanation:
- hydrophobic material
- surface structure (20-100µm)
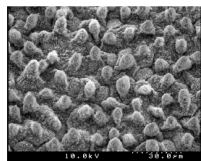
What is keeping the "stuff" together?

Intermolecular forces

- the **strong interaction**
- the **weak interaction**

- the **electromagnetic interaction**

- gravitation

- the **super-strong interaction**
- the **super-weak interaction**

$$w = \frac{X}{r^n}$$

$$w = \frac{X}{r^n}$$

strong — weak — long-range — short-range — w

(w = energy)

Strong intermolecular forces

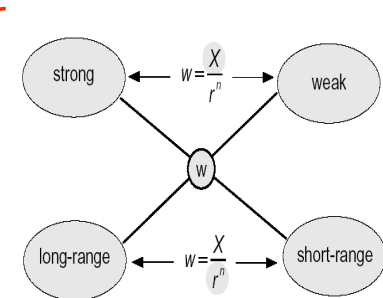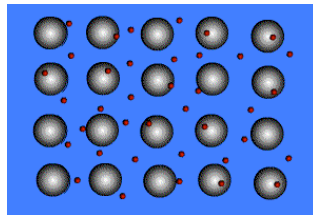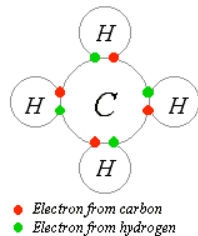Strong intermolecular forces arise from the sharing of electrons between two or more atoms as typified by covalent and metallic bonds. They have the following characteristics:

- valency
- directionality
- short in range (1 – 2 Å)
- relatively strong (100 – 300 kT/bond) (why do we use kT here?)

- ● Electron from carbon
- ● Electron from hydrogen

Charge-charge interaction

Ionic bonds are an example of the interaction of permanent charges. The force (F) resulting from two point charges is given by Coulomb's Law:

$$F(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_o \varepsilon r^2}$$

where point charges Q_1 and Q_2 are separated by distance r in a medium of dielectric permittivity ε. The interaction energy is:

$$U(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_o \varepsilon r}$$

Coulombic forces are very long ranged ($1/r^2$), however they are usually screened by closely associated ions of opposite charge. They can also be relatively strong bonds (200 kT in ionic crystal such as NaCl)

Charge - dipole interactions

Electrostatic interaction also result from charge sharing of permanent charges with dipoles. Assuming a fixed point dipole approximation, the interaction energy (U) resulting from this case is:

$$U(r) = \frac{Qp\cos\theta}{4\pi\varepsilon_o \varepsilon r^2}$$
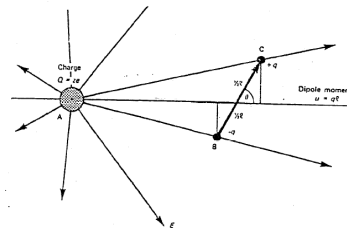
where point charge Q and dipole p (p=dipole moment) are separated by distance r in a medium of dielectric permittivity ε and the dipole is oriented at an angle of incidence θ.

Note that the charge – dipole interaction force falls off $\propto 1/r^3$ for the fixed case and $\propto 1/r^5$ for the rotating case.

Dipole - dipole interactions

The interaction between dipoles is of short range:

$$U(r) \propto \frac{1}{r^3} \; to \; \frac{1}{r^6}$$

The case of two freely rotating dipoles is known as *Keesom energy*. These energies are in the range of kT and fall-off with $1/(r^6)$ power of distance (often called "orientation energies or forces".)

$$u(+) = -p_1 p_2 \left[2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi \right] / 4\pi\varepsilon_o \varepsilon r^3$$
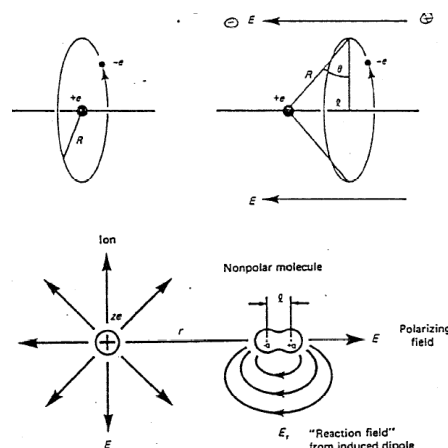
$$u(+) = -p_1^2 p_2^2 / 3(4\pi\varepsilon_o \varepsilon)^2 kT r^6$$

Induced dipoles

Even non-polar molecules are polarizable (what does it mean?) !
Displacement of the electron cloud in the presence of an electric field leads to polarization.

$$U(r) \propto \frac{1}{r^4} \text{ to } \frac{1}{r^6}$$

These interactions lead to attractive energies of forces, called "induction energies or forces."
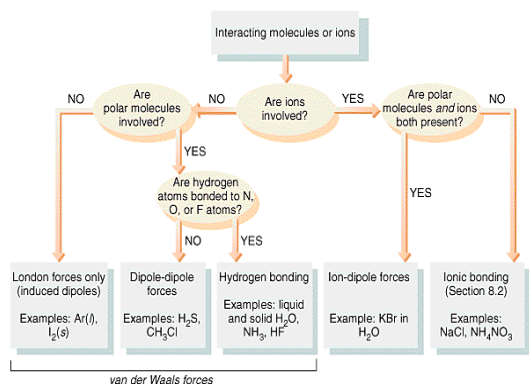

London ("dispersion") interactions

These are long range forces arising between non-polar molecules that are quantum mechanical in origin. At any moment there is a finite dipole moment derived from the instantaneous position of the electrons around the nucleus. Two neighboring electron clouds thus "feel" each other at any instant of time. This leads to an ATTRACTIVE force! The time-average of this force is finite. Like "orientation" and "induction" energies , the "dispersion" interaction ennergies also fall off with the inverse 6th power of distance.

It seems counterintuitive, but London forces dominate for large molecule / surface interactions. Why are they called "dispersion energies of "???

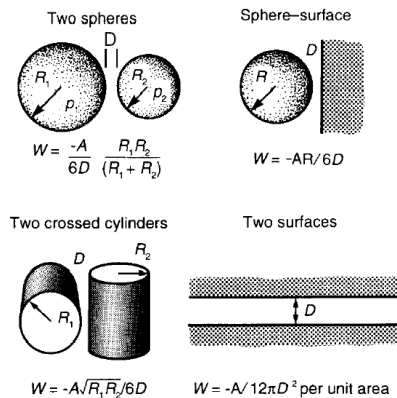## Summary of intermolecular forces: they are all, in fact, Coulombic!

???

THIS IS INCORRECT: VdW forces include dispersion, induction, and orientation interactions (all scale with r^(-6) power)

## VdW interactions (energies or forces) between objects

These are found by integrating the VdW atom-atom interactions between two bodies.

Two spheres

$$W = \frac{-A}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$$

Sphere–surface

$$W = -AR/6D$$

Two crossed cylinders

$$W = -A\sqrt{R_1 R_2}/6D$$

Two surfaces

$$W = -A/12\pi D^2 \text{ per unit area}$$

$A = \pi^2 \, C \, \rho_1 \rho_2 \sim 10^{-19}$ J (in vacuum)   Hamaker constant

Attractive and repulsive forces

example: Lennard Jones 6-12 Pair Interaction (like, between two uncharged atoms)
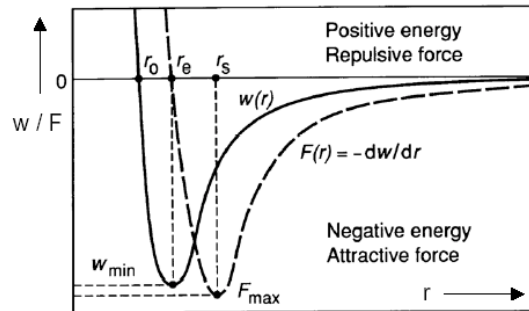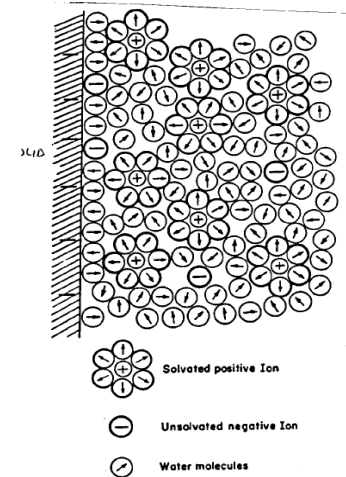

$$w(r)=-\frac{A}{r^6}+\frac{B}{r^{12}}$$

very short-range "hard sphere" repulsion

long-range attractive van der Waals interaction
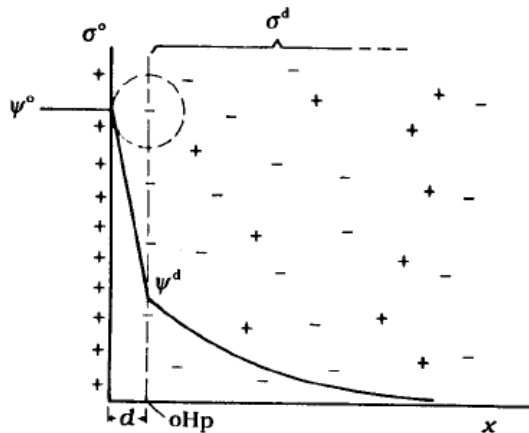
Important: $F(r) = - dW/dr$

Water and ionic solutions

The presence of water changes quite a lot:

- "Hydrophobic effect"
- Ion shielding (screening)
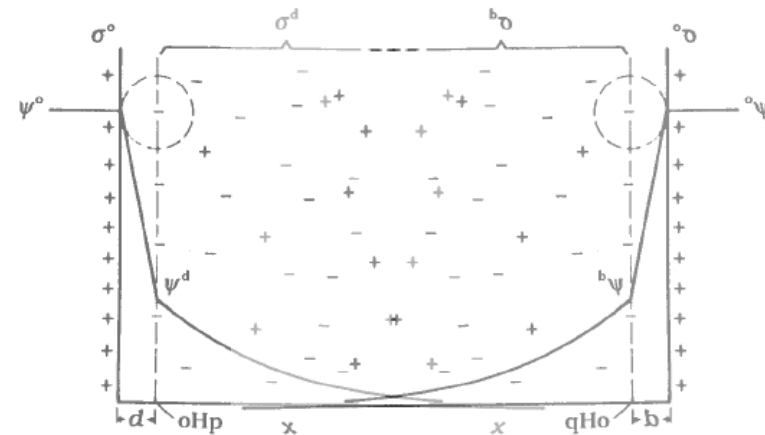- Charged surfaces --> double elec. layer

Electrical charges at interfaces lead to a electrical double layer formation

There is an electrical potential difference between solid surface and far solution, psi

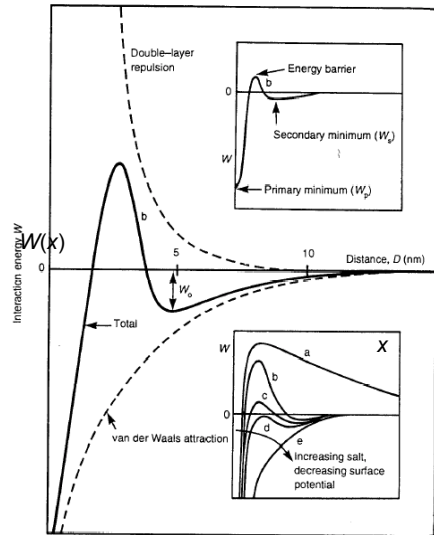## Two double layers repel each other

DLVO theory combines vdW attraction and double layer repulsion

a variety of phenomena will occur due to the features present in the resulting interaction energy profile: $W(x)$

Fig. **12.12.** Schematic energy versus distance profiles of DLVO interaction. (a) Surfaces repel strongly; small colloidal particles remain 'stable'. (b) Surfaces come into stable equilibrium at secondary minimum if it is deep enough; colloids remain 'kinetically' stable. (c) Surfaces come into secondary minimum; colloids coagulate slowly. (d) The 'critical coagulation concentration'. Surfaces may remain in secondary minimum or adhere; colloids coagulate rapidly. (e) Surfaces and colloids coalesce rapidly.