Plan du cours

III.   Forces Interparticulaires et Stabilité Colloïdales

a.   Introduction, définitions

b.   Interaction de van der Waals

c.   Interaction électrostatique

d.   Energie totale d'interaction

e.   Concentration critique de coagulation

f.   Limites de la théorie DLVO

g.   Interactions de solvatation

-         Solvatation des ions

-         Forces répulsives d'hydratation

-         Forces attractives hydrophobes

h.   Interactions stériques

Forces Interparticulaires et Stabilité Colloïdale

a. Stabilité des systèmes colloïdaux: Introduction, définitions

Stabilité d'une dispersion de particules colloïdales par rapport à quoi? : par rapport à leur propension a s'agglomérer ou a coaguler.

Dispersion stable: les particules restent des entités individuelles
Dispersion instable: les particules forment des entités plus grosses appelées agglomérats ou aggrégats.

Objectif: comprendre les facteurs qui déterminent la stabilité d'une suspension de particules colloïdales

Forces Répulsives

Interaction électrostatique

Forces d'hydratation

Interaction stérique

Forces Attractives

Interaction de van der Waals

Forces hydrophobes

Théorie DLVO

Dipole Moments

The polarity of a molecule is described by its dipole moment, *u*, given as:
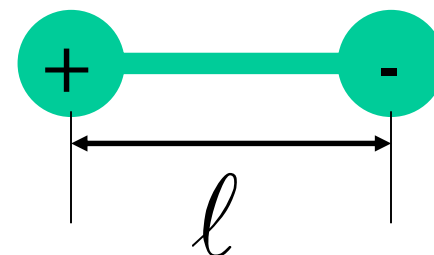
$$\vec{u} = q\vec{\ell}$$

where charges of **+q** and **-q** are separated by a distance ℓ .

Typically, **q** is the charge of the electron: 1.602×10^{-19} C and the magnitude of ℓ is on the order of $1\text{Å} = 10^{-10}$ m, giving **u** $= 1.602 \times 10^{-29}$ Cm.

A "convenient" (and conventional) unit for polarity is called a Debye:
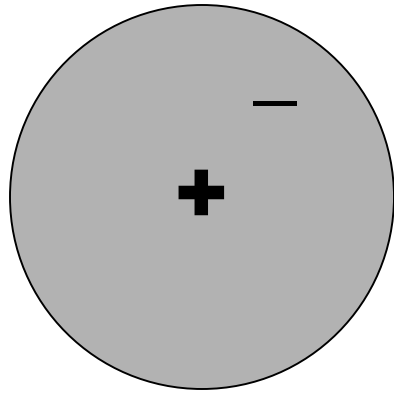
1 D = 3.336 x 10^{-30} Cm

Polarisability

All molecules can have a dipole induced by an external electromagnetic field, $\vec{E}$

The strength of the **induced** dipole moment, $|u_{ind}|$, is determined by the polarizability, α, of the molecule:
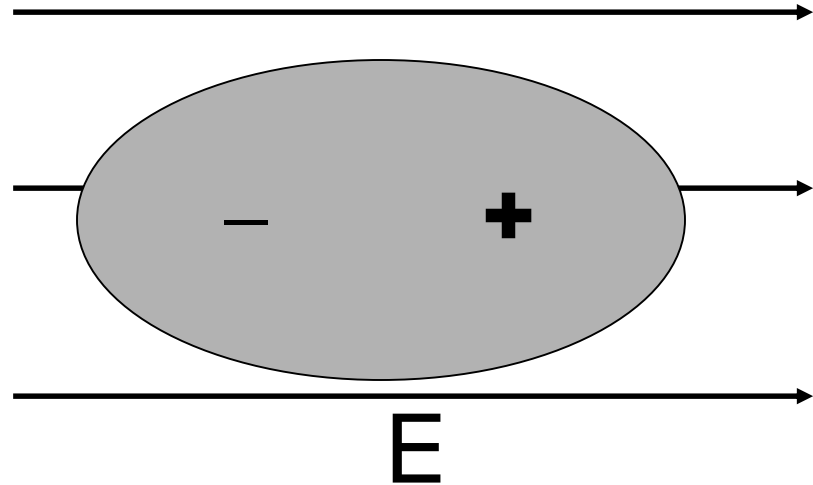
$$\alpha = \frac{\vec{u}_{ind}}{\vec{E}}$$

Units : $C^2 \, m^2 / J$

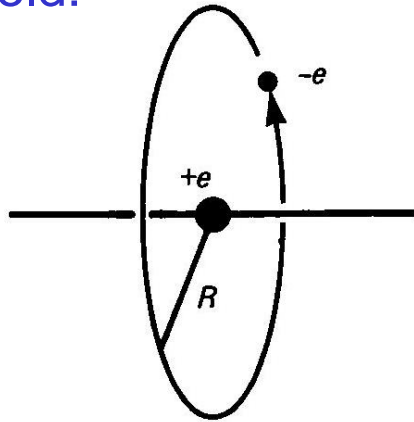An electric field will shift the **electron** cloud of a molecule.

Initial state

In an electric field

E
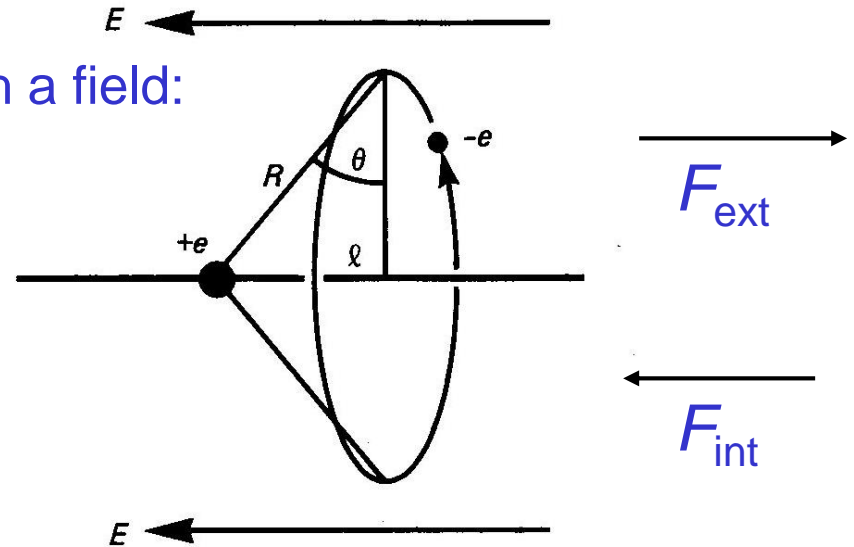
The extent of polarisation is determined by its **electronic** polarizability, α_o.

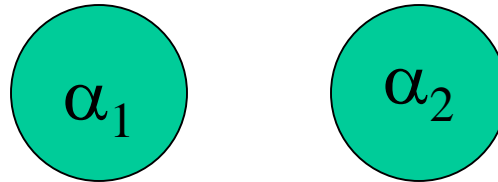# Simple Illustration of e⁻ Polarizability
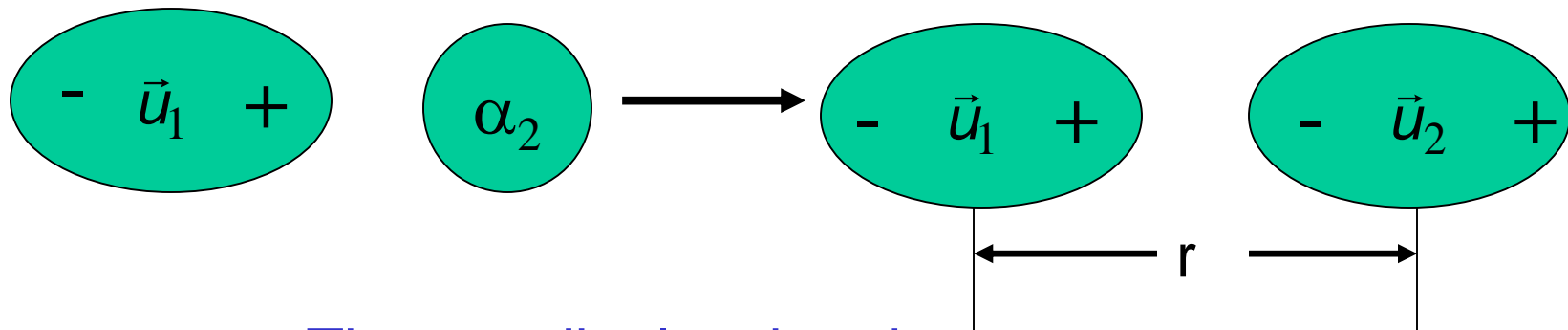
Without a field:

With a field:

Interaction permanent dipole-induced dipole

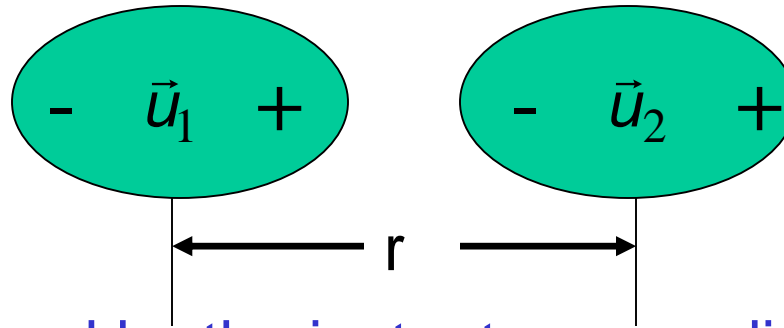The dispersive energy is quantum-mechanical in origin, but we can treat it with electrostatics.

An **instantaneous** dipole, resulting from fluctuations in the electronic distribution, creates an electric field that can polarise a neighbouring molecule.
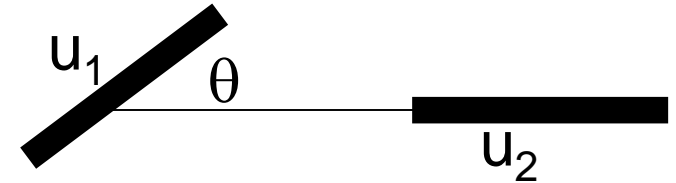
The two dipoles then interact.

Interaction permanent dipole-induced dipole

- $\vec{u}_1$ +   - $\vec{u}_2$ +

$\longleftarrow$ r $\longrightarrow$

The field produced by the instantaneous dipole is:

$$\vec{E} = \frac{\vec{u}_1}{4\pi\varepsilon_o r^3}(1+3\cos^2\theta)^{1/2}$$

u_1 $\quad\theta$
$\quad u_2$

So the induced dipole moment in the neighbour is:

$$\vec{u}_{ind} = \vec{u}_2 = \alpha_o\vec{E} = \frac{\alpha_o\vec{u}_1}{4\pi\varepsilon_o r^3}f(\theta)$$

We can now calculate the interaction energy between the two dipoles (using equations for permanent dipoles):

$$w(r) = \frac{\vec{u}_1\vec{u}_2}{4\pi\varepsilon_o r^3}f(\theta_1,\theta_2,\phi) = \frac{\vec{u}_1\left(\dfrac{\alpha_o\vec{u}_1}{4\pi\varepsilon_o r^3}\right)}{4\pi\varepsilon_o r^3} = \frac{\alpha_o\vec{u}_1^{\,2}}{(4\pi\varepsilon_o)^2 r^6}$$

van der Waals Forces

The three components that constitute van der Waals Forces

Interaction Component	Origin of Interactions	Equation
Keesom	Dipole-dipole	$w(r) = -\dfrac{u_1^2 u_2^2}{3(4\pi\varepsilon_o\varepsilon_r)^2 k_B T}\dfrac{1}{r^6}$
Debye	Dipole – induced dipole	$w(r) = -\dfrac{u^2\alpha_o}{(4\pi\varepsilon_o\varepsilon_r)^2}\dfrac{1}{r^6}$
London (Dispersion)	Induced Dipole – Induced Dipole	$w(r) = -\dfrac{3}{2}\dfrac{\alpha_{o1}\alpha_{o2}}{(4\pi\varepsilon_o)^2}\dfrac{I_1 I_2}{(I_1+I_2)}\dfrac{1}{r^6}$

The London component is the most dominant.
n = 6 indicates van der Waals forces are short range

Interactions between Surfaces and Particles
- Microscopic Approach -

1937: Hamaker calculated the total interaction between two spherical particles by adding contributions for each atom in the solid

$$F(H) = -\frac{AR}{12H^2}$$

F = van der Waals Force

R = particle radii

H = separation distance

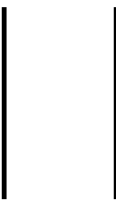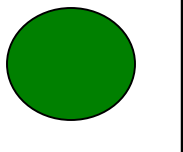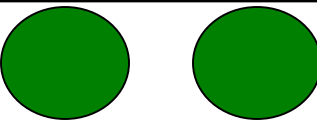A = Hamaker Constant (Material property)

Note that the Hamaker constant may be defined as

$$A = \pi^2 C \rho_1 \rho_2$$

Where ρ_1 and ρ_2 are the number of atoms per unit volume in the two bodies.

van der Waals Interaction Potential for various configurations

Configuration	Schematic	Expression for van der Waals force potentials
Molecule - Molecule		$V_A = -\dfrac{C}{r^6}$
Plate – Plate		$V_A = -\dfrac{A}{12\pi H^2}$
Sphere - Plate		$V_A = -\dfrac{AR}{6H}$
Sphere - Sphere		$V_A = -\dfrac{AR}{12H}$

c. Electrostatic Interaction
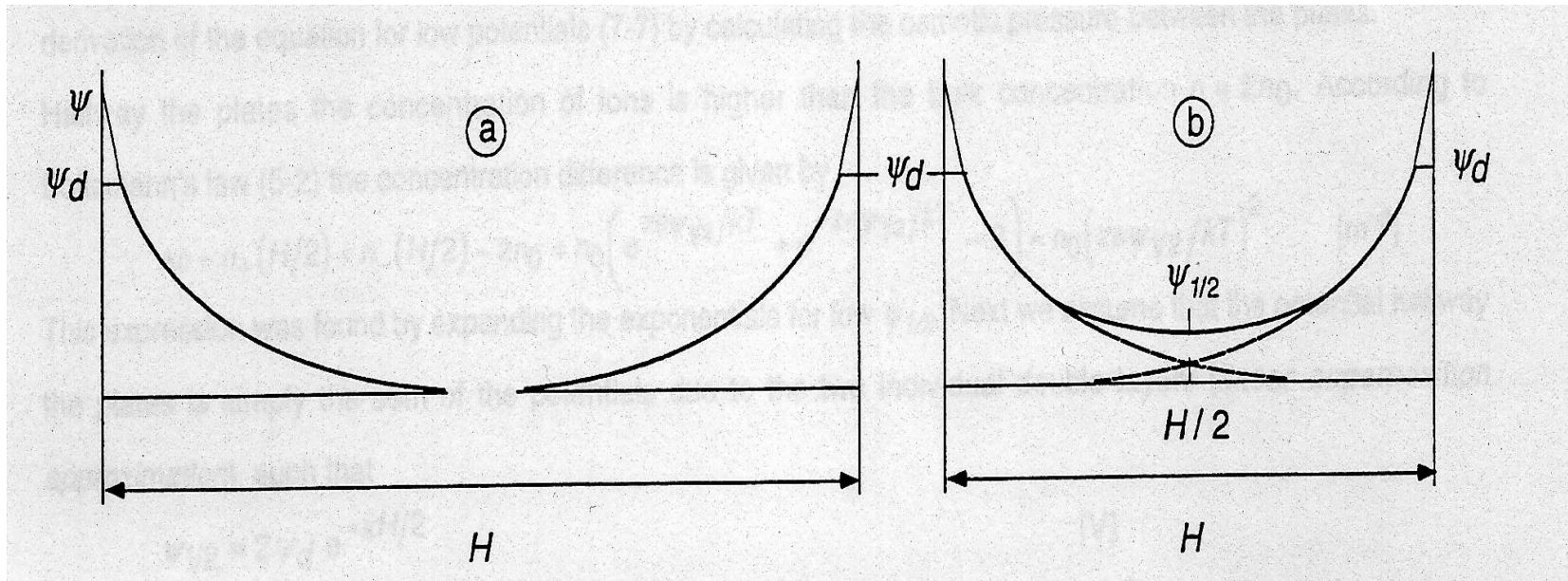
To keep the plates at distance H in mechanical equilibrium upon an infinitesimal displacement, the change in pressure dp plus the change in the electrical pressure, written as $\rho d\psi$, must be zero. Therefore we have :

$$dp = - \rho d\psi$$

We define the disjoining pressure Π_{el} by $\Pi_{el} = p(h)-p(\infty)$ and obtain
$$\Pi_{el}(H) = 4cRT\sinh^2(zy_m/2) \text{ with } y_m = F\Psi_{1/2}RT$$
$(N\ m^{-2})$

The mid-way potential may be obtained by LSA and we have

$$zy_m = 8\tanh(zy^d/4)e^{-\kappa H/2} \text{ (valid for low } y_m)$$

Thus, it comes

$$\Pi_{el}(H) = 64cRT(\tanh(zy^d/4))^2 e^{-\kappa H} \quad (N\ m^{-2})$$

The energy associated to the double layer interactions is

$$V_R(H) = -\int_{\infty}^{H} \Pi_{el}(H)dH$$

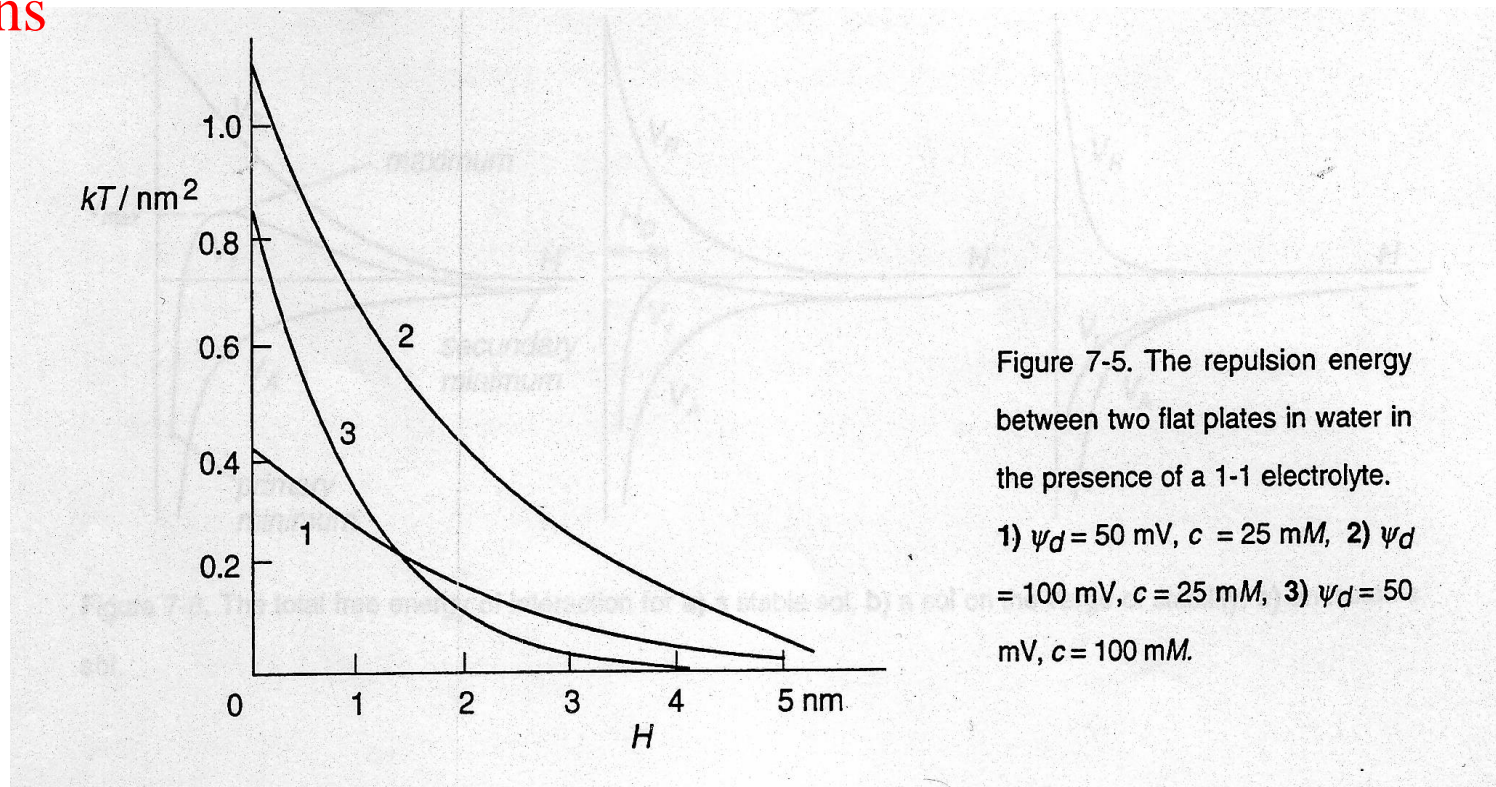After calculation we get

$$V_R(H) = 64cRT\kappa^{-1}(\tanh(zy^d/4))^2 e^{-\kappa H} \quad (J\ m^{-2})$$
(limit weak double layer overlap)

Limit low y^d : $V_R(H) = 2\varepsilon\kappa(\Psi^d)^2 e^{-\kappa H} \quad (J\ m^{-2})$

Figure 7-5. The repulsion energy between two flat plates in water in the presence of a 1-1 electrolyte.

1) $\psi_d = 50$ mV, $c = 25$ mM, 2) $\psi_d = 100$ mV, $c = 25$ mM, 3) $\psi_d = 50$ mV, $c = 100$ mM.

Following the same methodology, one can show that the interaction NRJ between two spheres is given by

$$V_R(H) = 64\pi c R T a \kappa^{-2}(\tanh(zy^d/4))^2\, e^{-\kappa H} \quad (J)$$

and for low potentials y^d

$$V_R(H) = 2\pi\varepsilon a(\Psi^d)^2\, e^{-\kappa H} \quad (J)$$
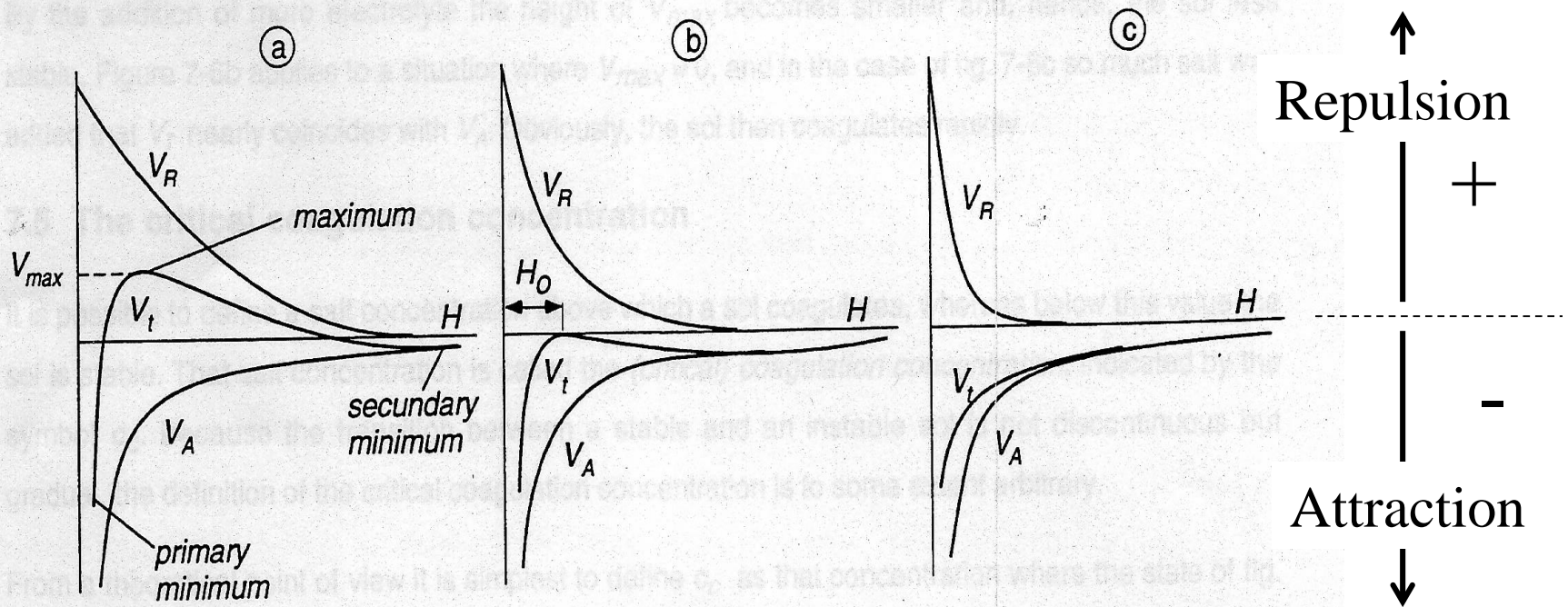
d. Total Interaction Energy

$$V_t = V_A + V_R$$

Figure 7-6. The total free energy of interaction for **a)** a stable sol, **b)** a sol on the verge of stability, **c)** an instable sol.

$V_{max} > 5\text{-}10 \text{ kT} \Longleftrightarrow$ Stable Dispersion

(to compensate for the thermal NRJ of two approaching particles, figure a)

e. Critical concentration coagulation c_c (or n_c)

C_c is defined as the electrolyte concentration at which the dispersion is about to coagulate, that is when :

$$V_t = V_A + V_R = 0$$
$$dV_t/dH = dV_A/dH + dV_R/dH$$

(conditions of figure b, previous slide)

After computation, one obtains

$$n_c = 2.13 \times 10^5 \, \varepsilon^3 \, (kT)^5 \, (\tanh(zy^d/4))^4 \, (A)^{-2} \, (ze)^{-6} \quad (m^{-3})$$

(valid for weak overlap and the interaction between two plates)

Application : water purification by flotation
delta formation
paint industry …

f. Limites de la théorie DLVO

Formes géométriques définies

Objets « dures » non perméables aux ions

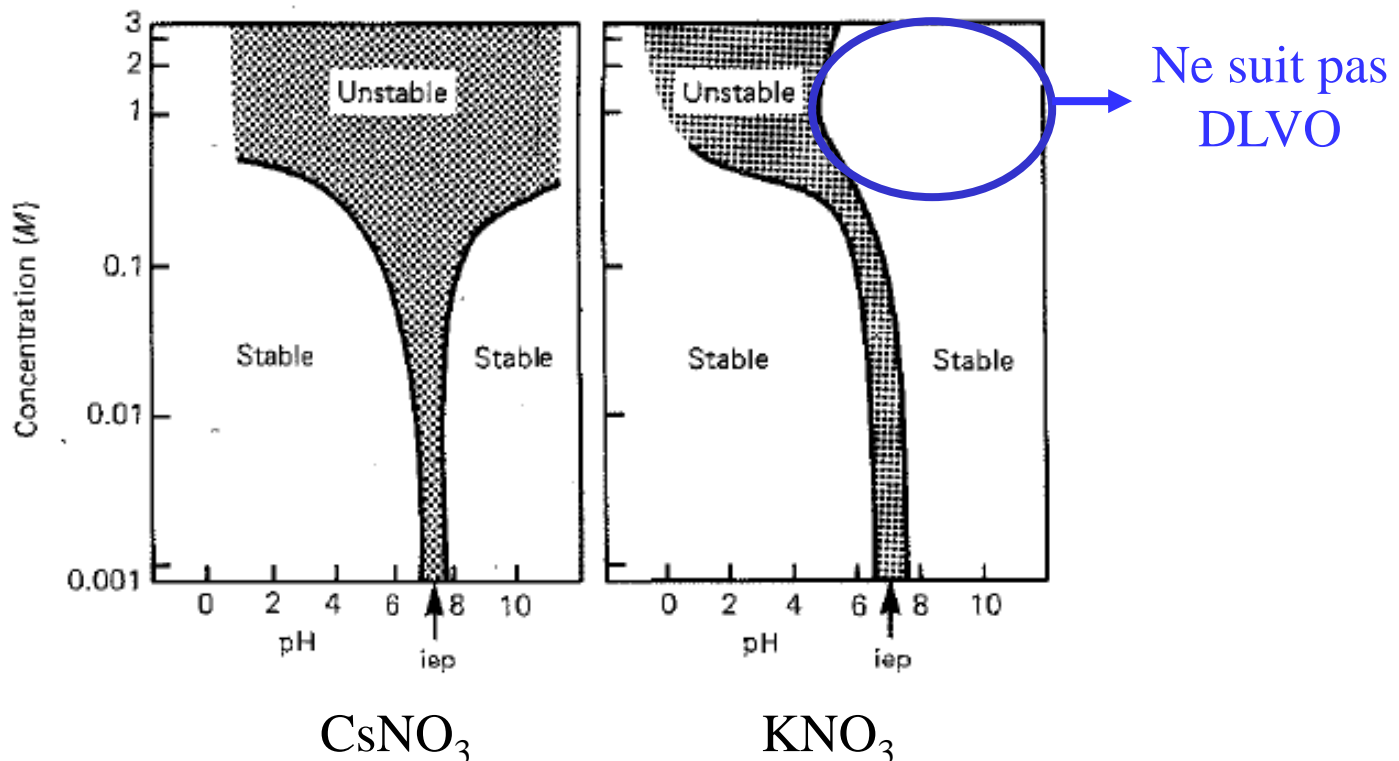Potentiel constant lors du rapprochement des objets

Potentiel = somme des potentiels de chaque objet (LSA)

Milieu continu

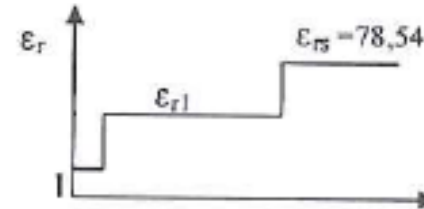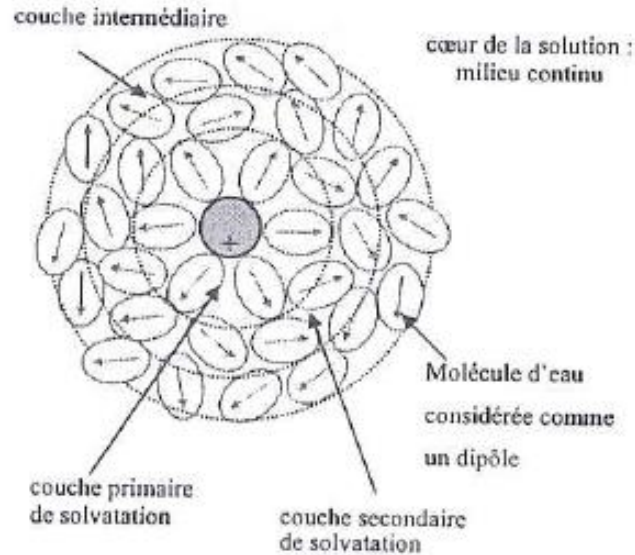Adsorption de molécules et nature du solvant non pris en compte

Particules de latex amphotères ($-COOH$ et $-NH_3^+$)

Ne suit pas DLVO

$CsNO_3$ KNO_3

g. Interactions de solvatation

- **Solvatation des ions**

couche intermédiaire

cœur de la solution : milieu continu

Molécule d'eau considérée comme un dipôle

couche primaire de solvatation

couche secondaire de solvatation

ε_r

ε_{r1}

$\varepsilon_{rs} = 78,54$

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

Solvatation

- **Notion de surfaces hydrophobes / hydrophiles**

    Mesure de l'angle de contact

Internal contact angle

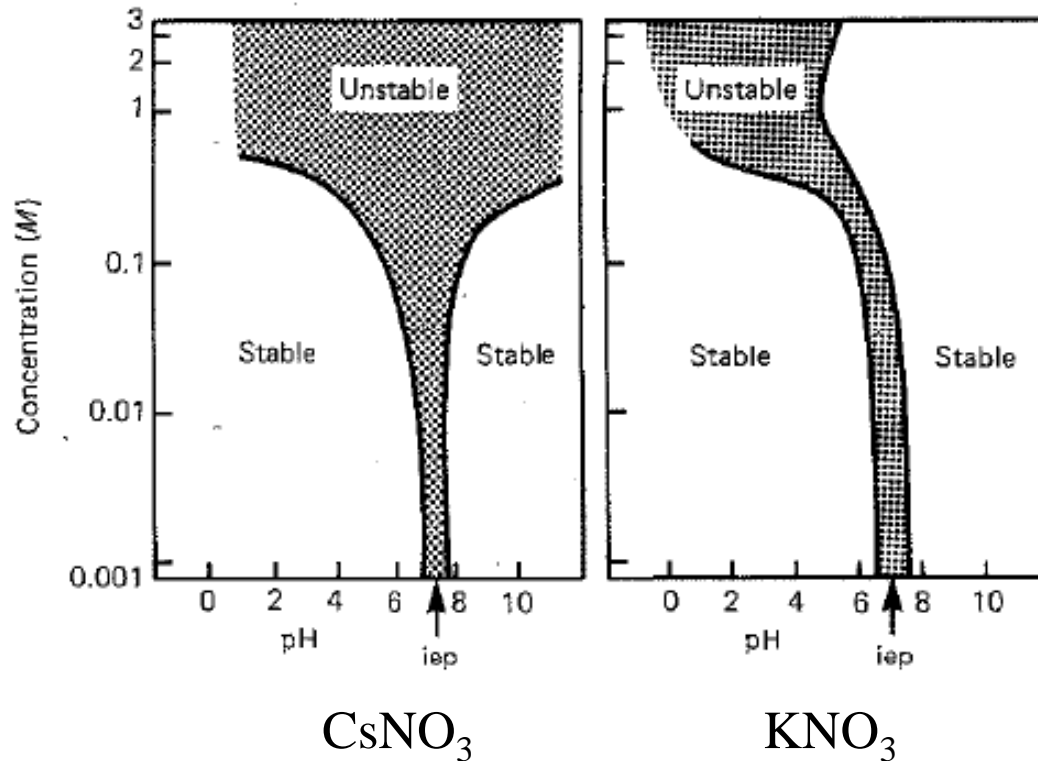Normal surface
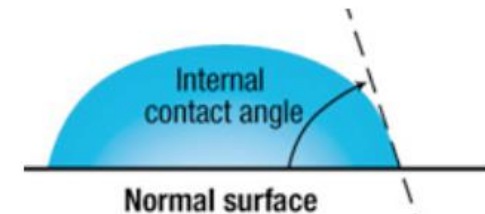
- **Forces répulsives d'hydratation**

  Force répulsive additionnelle à la force décrite par DLVO
  Origine: présence de molécules d'eau fortement liées à la surface
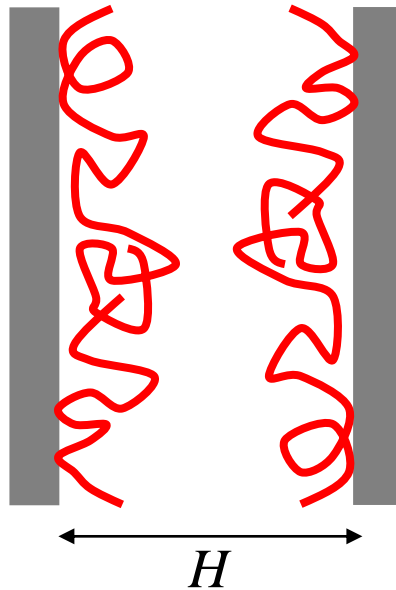 => interaction à faible portée

$$CsNO_3 \qquad\qquad KNO_3$$

$$\overleftarrow{Li^+ > Na^+ > K^+ > Rb^+ > Cs^+}$$

Solvatation

- **Forces attractives hydrophobes**

  Interaction à longue portée entre particules / surfaces non polaires (hydrophobes)
  Forte attraction des deux objets hydrophobes avec expulsion d'eau

h. Interactions Stériques

Macromolécules liées à la surface => Encombrement stérique

Forces stériques répulsives + pression osmotique

Double-layer repulsion

Interaction energy W

O

Distance (nm)

5

10

W_s

Total

van der Waals attraction

b

b

Energy barrier

O

b

W

Secondary minimum (W_s)

Primary minimum (W_p)

W

a

b

c

d

e

O

Increasing salt, decreasing surface potential