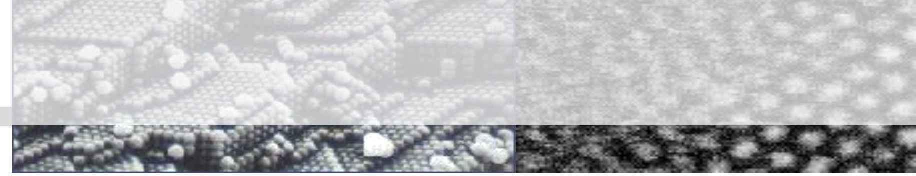
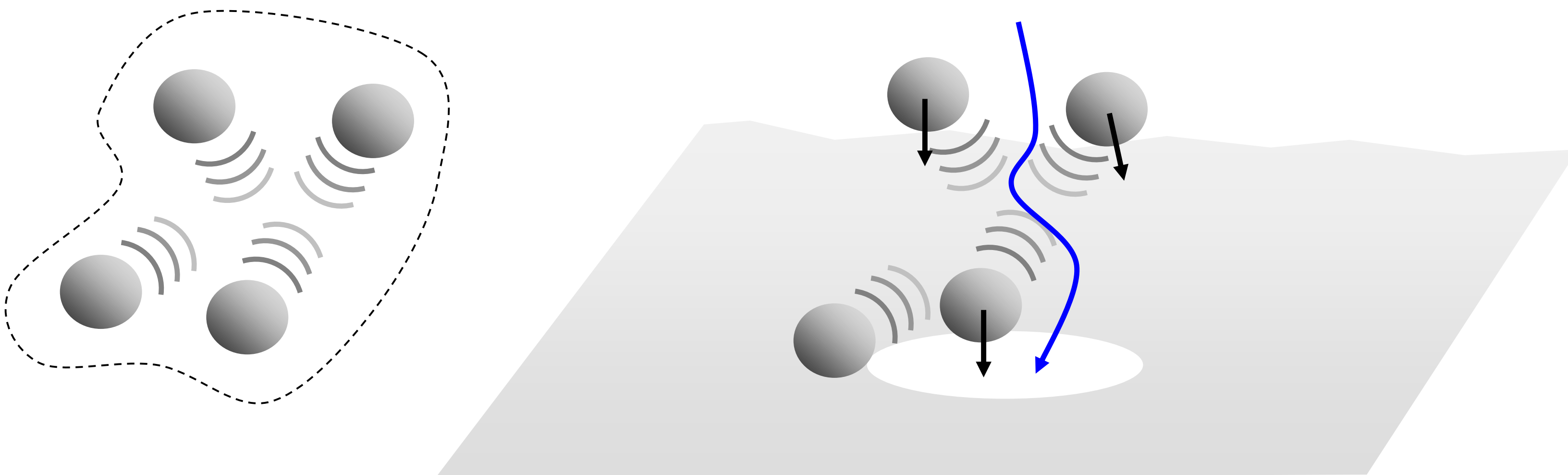


From colloidal interactions …

… to transport phenomena in processes



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Interfacial phenomena

1

Problematic
- How to model colloid transport in a process ?

Introduction
- What are colloids ?
- Problematic

From causes….

Electrostatic charges
- Origin
- Charge distribution at an interface (Gouy-Chapman theory)

Interactions between interfaces
- van der Waals attraction
- Electrostatic repulsion
- Interparticles interactions (DLVO theory)

… to consequences.

Electrokinetic phenomena
- Electrophoresis
- electro-osmosis
- Streaming potential
- Settling potential

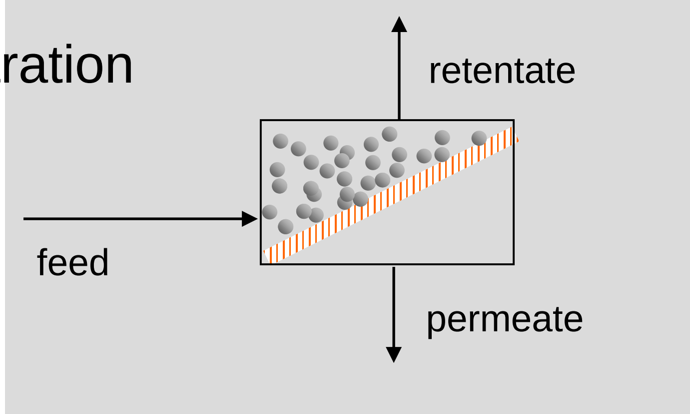
Aggregation
- Orthokinetic aggregation : slow or rapid ?
- Perikinetic Aggregation
- Population balance -> E. Climent course

Transport phenomena
- Osmotic pressure
- mobility
- diffusion
- settling
- filtration …

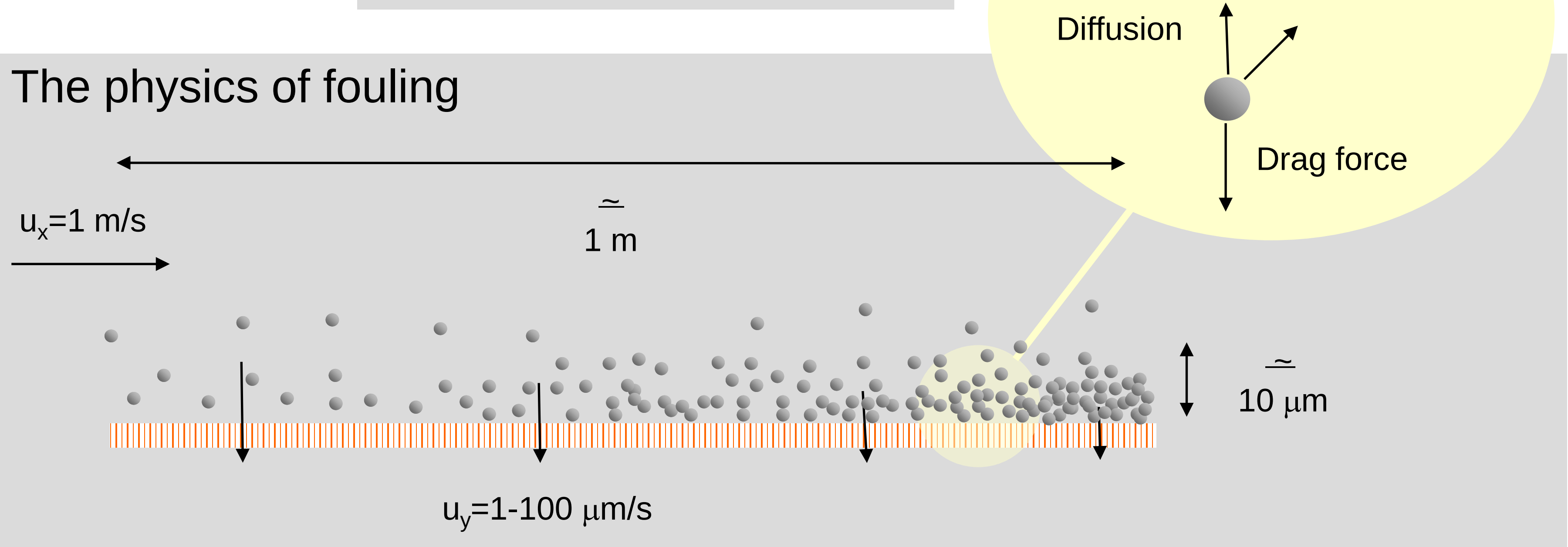
Viscosity et rheology
-> C. Xuereb course

A new kind of complexity in a process

Example with filtration

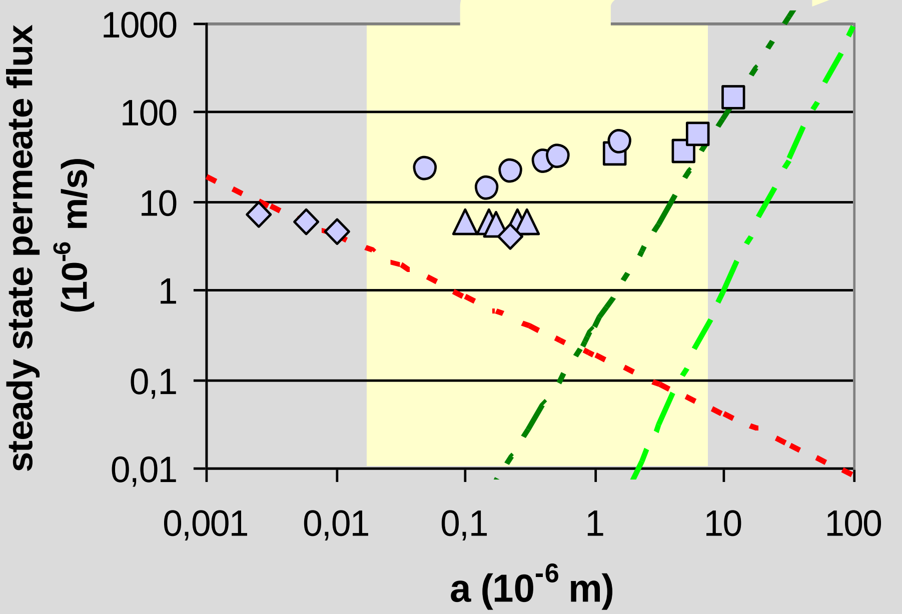


The physics of fouling



A new kind of complexity in a process (2)

Colloids



Permation flux can not be predicted by :

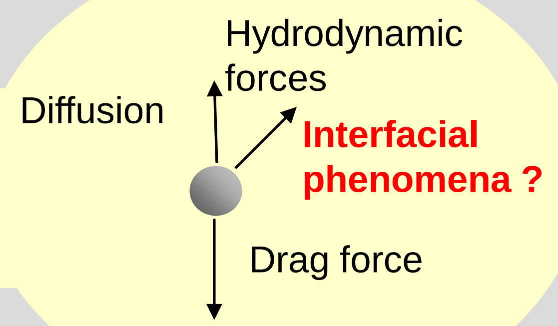
- - - **Diffusion**

Hydrodynamic phenomena

- — · — Lateral migration
- — · · · Shear induced diffusion

« Colloid flux paradox »

How to model colloids transport in a process ?



What are colloids?

Solutions

- *Brownian diffusion*
- *Stable solubilised state*

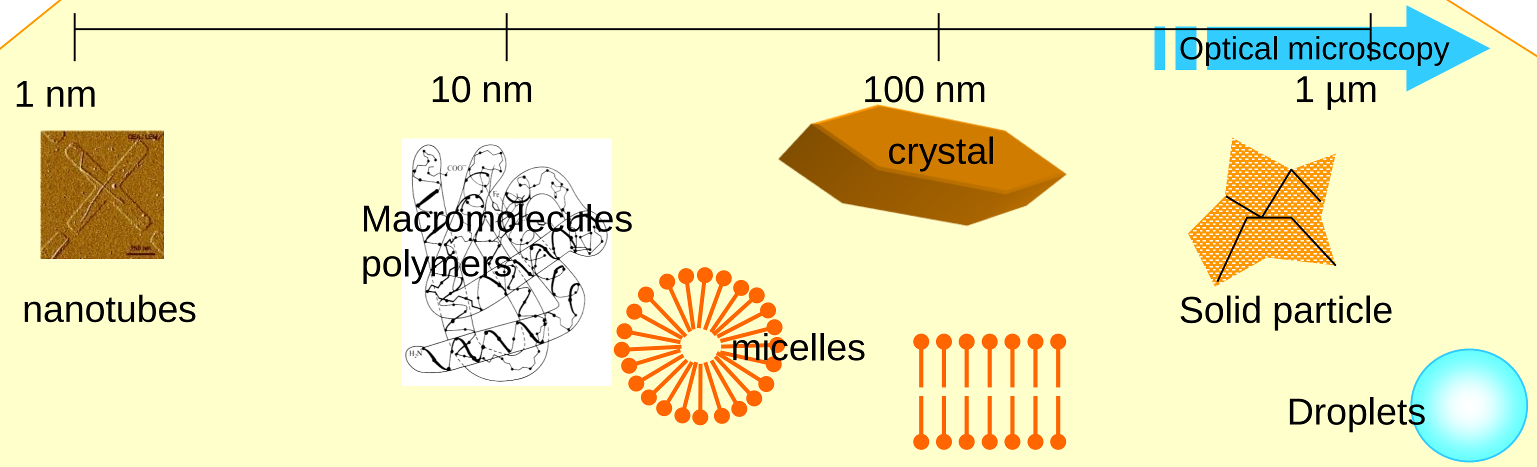
Colloidal dispersions

- *Brownian diffusion > Gravity*
- *Dispersed state = metastable*

Suspensions

- *Settling under gravity*
- *Suspended by mixing to be dispersed*

Interfacial area= 100 m^2/g



According IUPAC* : *the supramolecular entities whose extension in at least one spatial direction lies between 1 nm and 1 µm*

* International Union of Pure and Applied Chemistry

Un univers de taille et de forme !

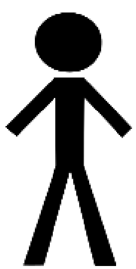
L'échelle des colloïdes …

1 nm — 10 nm — 100 nm — 1 µm

… à l'échelle humaine

1 m — 10 m — 100 m — 1 km

Eau



Une grande variété de taille et de volume

Il y a 1 milliards de nm^3 dans 1 µm^3

What are colloids?

Media	Particle	Type	Natural	Technique
liquid	solid	sol	superficial water	ink, paint
liquid	liquid	emulsion	milk	oil
liquid	gas	foam	sparkling water	Fire extinguishers
Gas	solid	aerosol	smoke	Pharmaceutical to inhale
Gas	liquid	aerosol	cloud	insecticide
solid	solid	alloy	wood, bone	Composite materials
solid	liquid	porous media	petrol, opal	Polymeric membrane
solid	gas	solid foam	snakestone	zeolite

Colloids are found in a **lot of processes**.

What are colloids?

A small volume with a large interfacial area

$$\frac{A}{V}=\frac{\text{surface des particules}}{\text{volume de la suspension}}=\overbrace{\frac{4\pi a^{2}}{\frac{4}{3}\pi a^{3}}}^{\text{spheres}}\phi=\frac{6\phi}{d_p}$$

d_p	*area*
1 µm	300 m^2
100 nm	3000 m^2
10 nm	3 10^4 m^2
1 nm	3 10^5 m^2

Colloids are controled by the **interfacial properties and the interactions between interfaces** (rather than by the chemical composition).

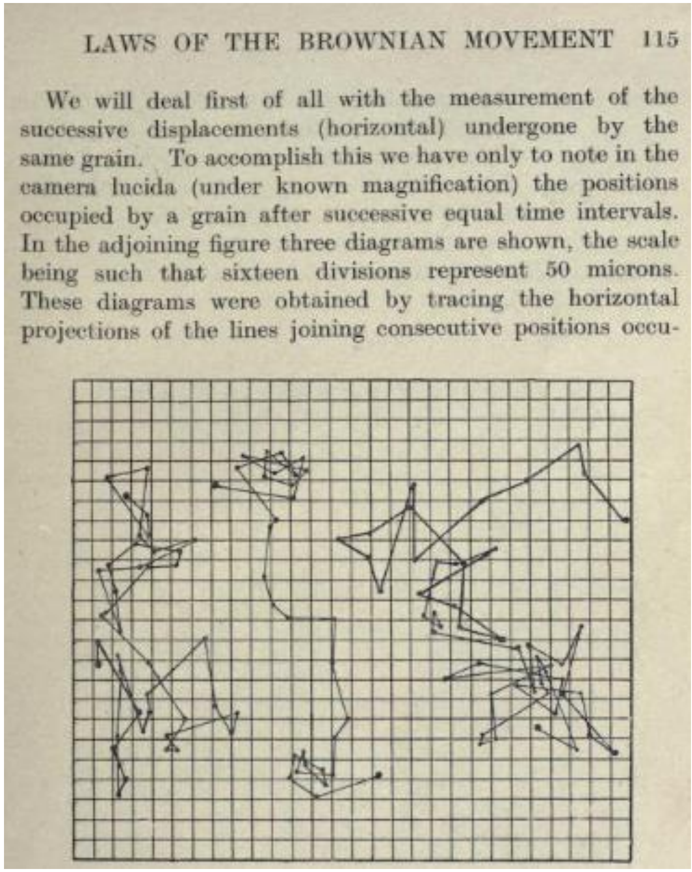
Perpétuellement en mouvement

Un colloïde : ça diffuse

$$D = \frac{kT}{6\pi\mu R}$$

2R	***distance moyenne parcourue en 1 min***
1 µm	5 µm
100 nm	16 µm
10 nm	50 µm
1 nm	0.16 mm

$$d = \sqrt{Dt}$$



LAWS OF THE BROWNIAN MOVEMENT 115

We will deal first of all with the measurement of the successive displacements (horizontal) undergone by the same grain. To accomplish this we have only to note in the camera lucida (under known magnification) the positions occupied by a grain after successive equal time intervals. In the adjoining figure three diagrams are shown, the scale being such that sixteen divisions represent 50 microns. These diagrams were obtained by tracing the horizontal projections of the lines joining consecutive positions occu-

Mouvement de colloïdes de 0.53 µm de rayon observé sous microscope à intervalle de 30 seconds (taille d'un carré 3.2 µm)
Jean Baptiste Perrin, Atoms, 1914

Colloids and soft matter

Soft matter
Systèmes moléculaires organisés
Matière mal condensée
Objets fragiles

Entities that interact weakly (compared with the chemical reaction)
But on important distance range (the colloid size increased by a factor of 10)

The properties are then controlled by these weak interactions:
a small change in these interactions (low energy is required)
can lead to substantial modification.

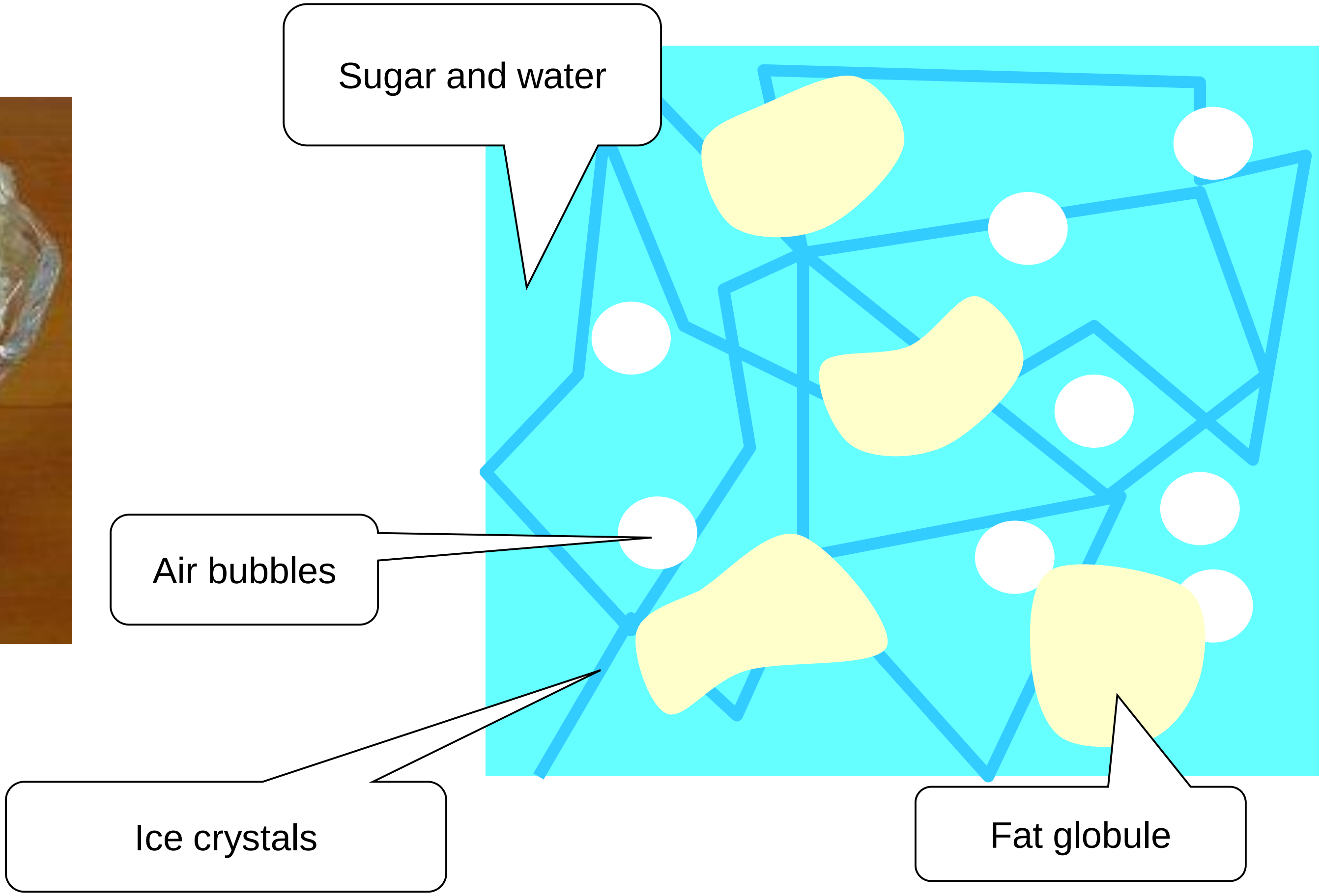
Physique de la matière
Mécanique
Physico-Chimie
Physique statistique

… on peut transformer la matière avec des actions extérieures faibles …
Voilà la définition centrale de la matière molle.
Pierre Gilles de Gennes et Jacques Badoz, Les objets fragiles

To watch the video - Physique des tas de sable et de la matière molle GUYON Etienne
Université de tous les savoirs sur canal U

Colloid and sof matter

Ice cream



Problematic

Les interactions (…) entraînent un accroissement de complexité source de l'émergence de performances inattendues.

Albert Jacquard, L'équation du nénuphar

… Important areas of physical chemistry such as interfacial phenomena, colloids, clusters and, more generally, De Gennes "soft matter" should be revisited using the system approach and chemical engineering methods.

Jacques Villermaux, Future challenges for basic research in chemical engineering
Chemical Engineering Science,48 (1993)

…mais totalement ignorante de la " matière molle ". Nous souffrons en France d'une certaine spécialisation du génie chimique. On n'y trouve pas toujours la variété de culture exhibée par les départements américains de Chemical Engineering.

Pierre Gilles de Gennes, Chimistes et physiciens : synergies et lacunes
L'actualité chimique, 258 (2005)

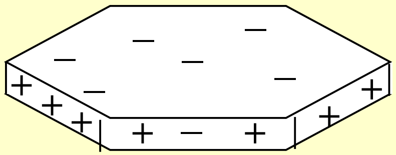
Electrostatic charge

The main part of macromolecules and particles are charged:

Structural origin

Substitution of ions : Si^{4+} by Al^{3+} or Mg^{2+}

Clay charges

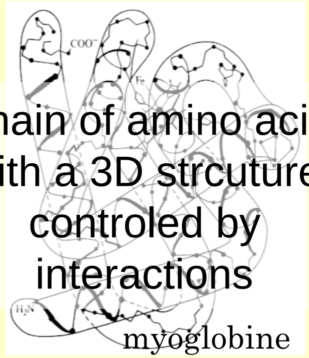


Ionisable group at the surface

Amphoteric group

Silica
Protein
Oxide

$\equiv$ Si — OH



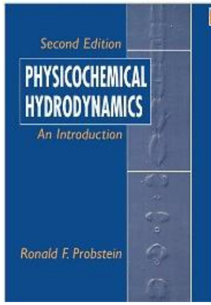
Chain of amino acid with a 3D strcuture controled by interactions

Selective ionic adsorption

Adsorption of anions (less hydrated)

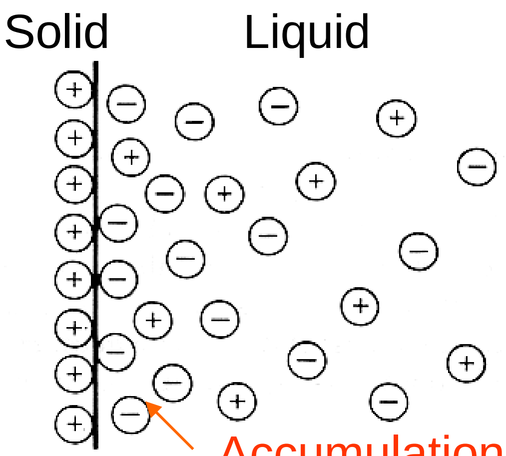
AgI

Electrostatic charges



Co-ions and counter-ions distribution near a charged surface:

The electrostatic double layer



Accumulation of counter-ions near the interface

Distribution of electrostatic potential :

Poisson equation
(charge distribution -> electrostatic potential)

$$\nabla^2 \psi = -\frac{\rho'}{\varepsilon}$$

$$\rho' = F \sum_i z_i c_i$$

$$\frac{c_i}{c_{i0}} = \exp\left(\frac{-z_i e \psi}{k_B T}\right)$$

Boltzmann equation
(electrostatic potential → ions distribution)

Electrostatic chagres

Electrostatic potential distribution (*Gouy-Chapman* theory)

Assumptions: - plane surface

- *Debye-Hückel* approximation $z_i e\psi << k_B T$ $\psi < 25{,}7\ \mathrm{mV}$

$$\psi = \psi_w \ e^{(-\frac{x}{\lambda_D})} \qquad \text{(I)}$$

Exact solution :

$$\tanh(z\hat{\psi}/4) = \tanh(z\hat{\psi}_0/4)\exp(-\kappa_D x)$$

avec $\hat{\psi} = e\psi / kT$

With the Debye lenght

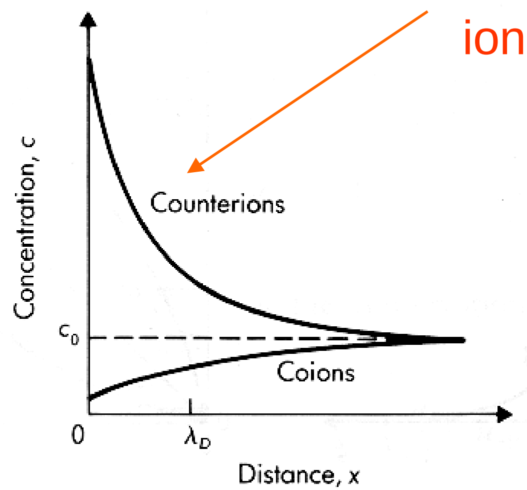
$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2F^2 \sum z_i^2 c_i}} = \frac{3.07\ 10^{-10}}{\sqrt{I}}$$

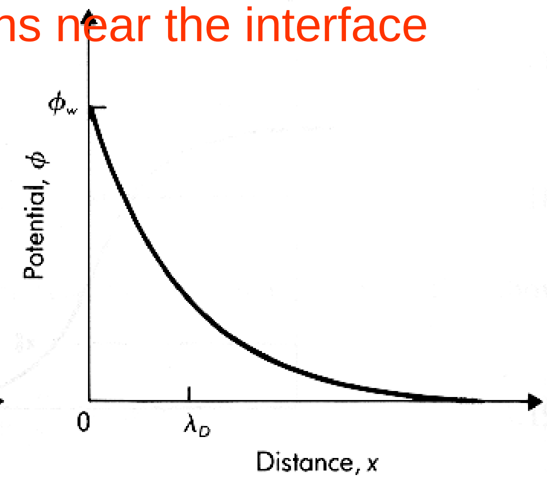
λ_D → m ; I → mol/l

Force ionique : $I = \frac{1}{2}\sum_i z_i^2 c_i$

$$\lambda_D = \frac{1}{\kappa_D}$$

Accumulation of counter – ions near the interface





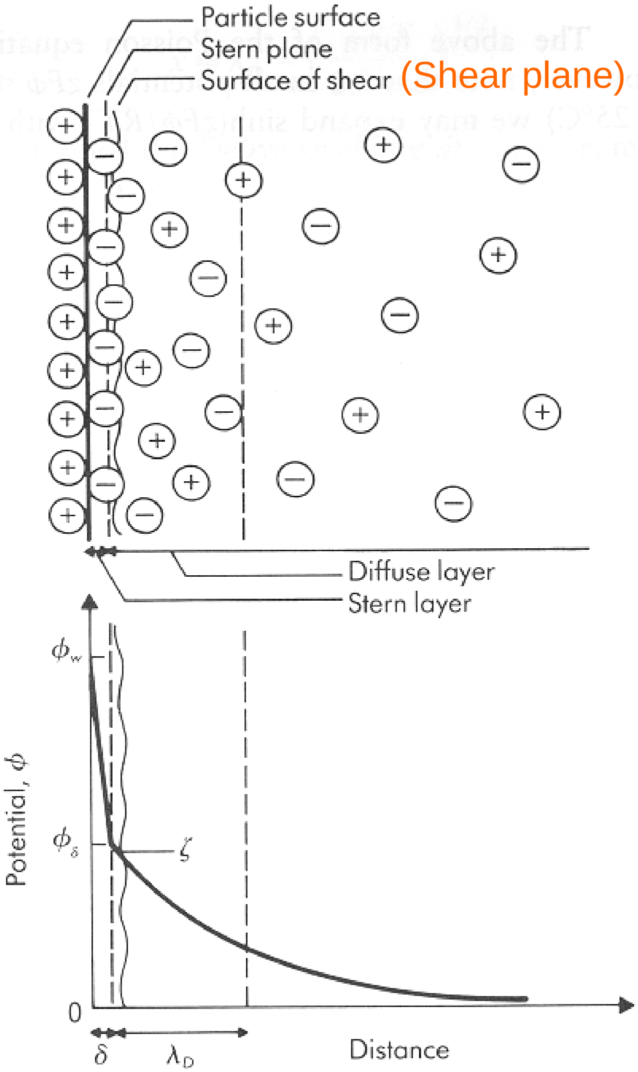
Electrostatic double layer et Stern internal plane

The zéta potential (ζ) is defined as the potential at the shear plane.
(experimentaly reachable)

As $\delta << \lambda_D$ **the equation (I)**

can be written with

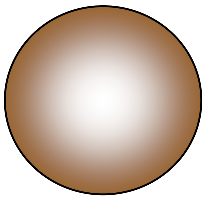
$$\psi_w = \zeta$$



Electrostatic double layer around a sphere

Poisson-Boltzmann equation around a sphere

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{F}{\varepsilon}\sum_i z_i c_{i0}\exp\left(\frac{-z_i e\psi}{k_B T}\right)$$



No analytical solution !

With the *Debye-Hückel* approximation :

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \kappa_D^2\psi$$

$$\psi = \psi_w a\frac{\exp\left[-\kappa_D(r-a)\right]}{r}$$

Electrostatic double layer around a sphere

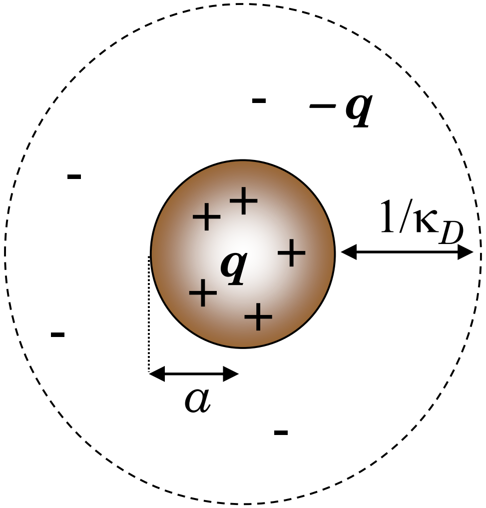
Electroneutrality

charge on the particule = charge in the double layer

$$q = -\int_a^\infty 4\pi r^2 \rho' dr$$

$$= 4\pi\varepsilon\kappa_D^2 \int_a^\infty r^2 \psi dr$$

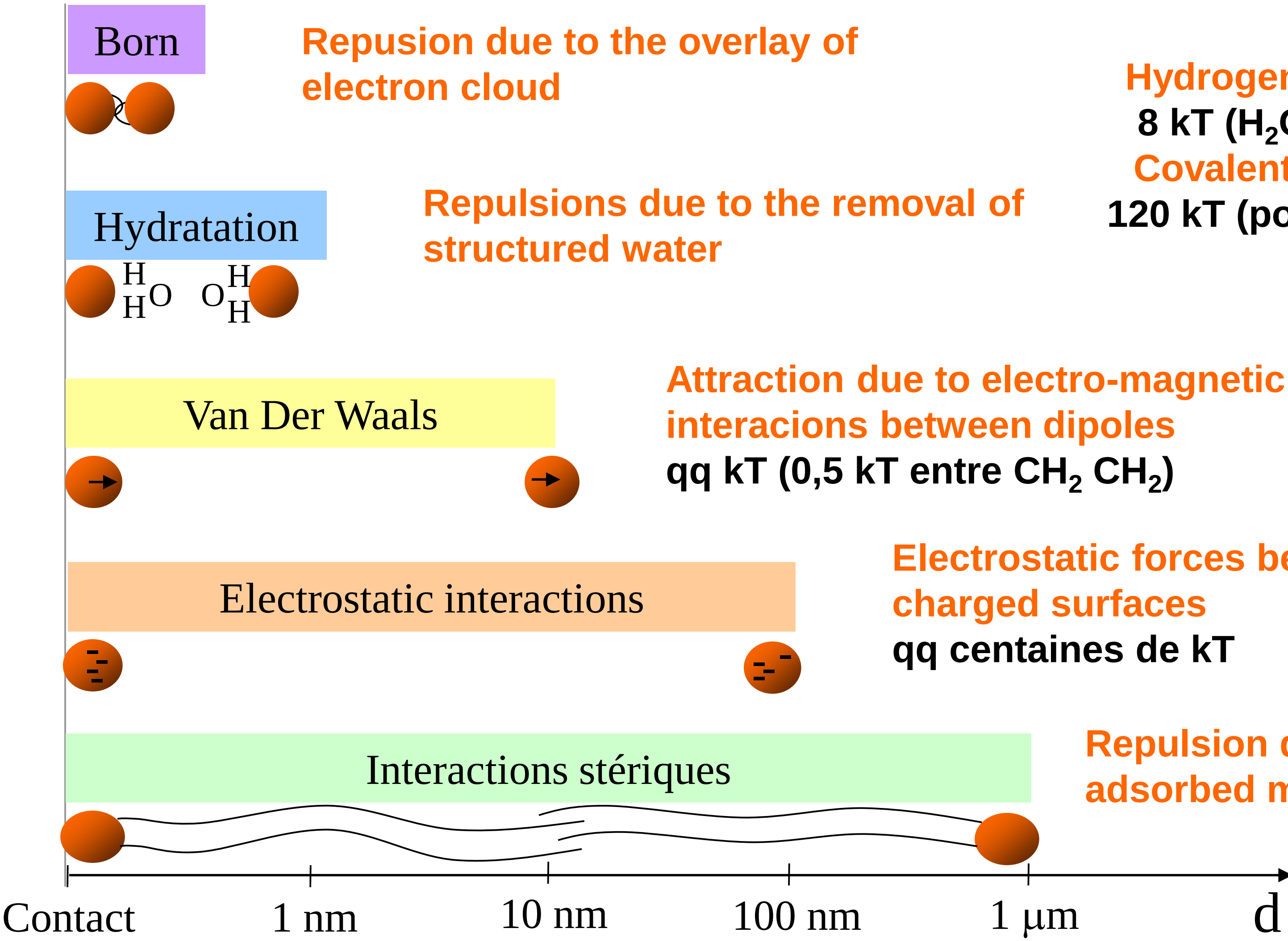
$$= 4\pi\varepsilon a(1+\kappa_D a)\psi_0$$



If *a* is the radius until the shear plane:

$$q = 4\pi\varepsilon a(1+\kappa_D a)\zeta$$

Interfacial Interactions



Born: Repusion due to the overlay of electron cloud

Hydratation: Repulsions due to the removal of structured water

Hydrogen bond
8 kT (H_2O-H_2O)
Covalent bond
120 kT (pour C-C)

Van Der Waals: Attraction due to electro-magnetic interacions between dipoles
qq kT (0,5 kT entre CH_2 CH_2)

Electrostatic interactions: Electrostatic forces between charged surfaces
qq centaines de kT

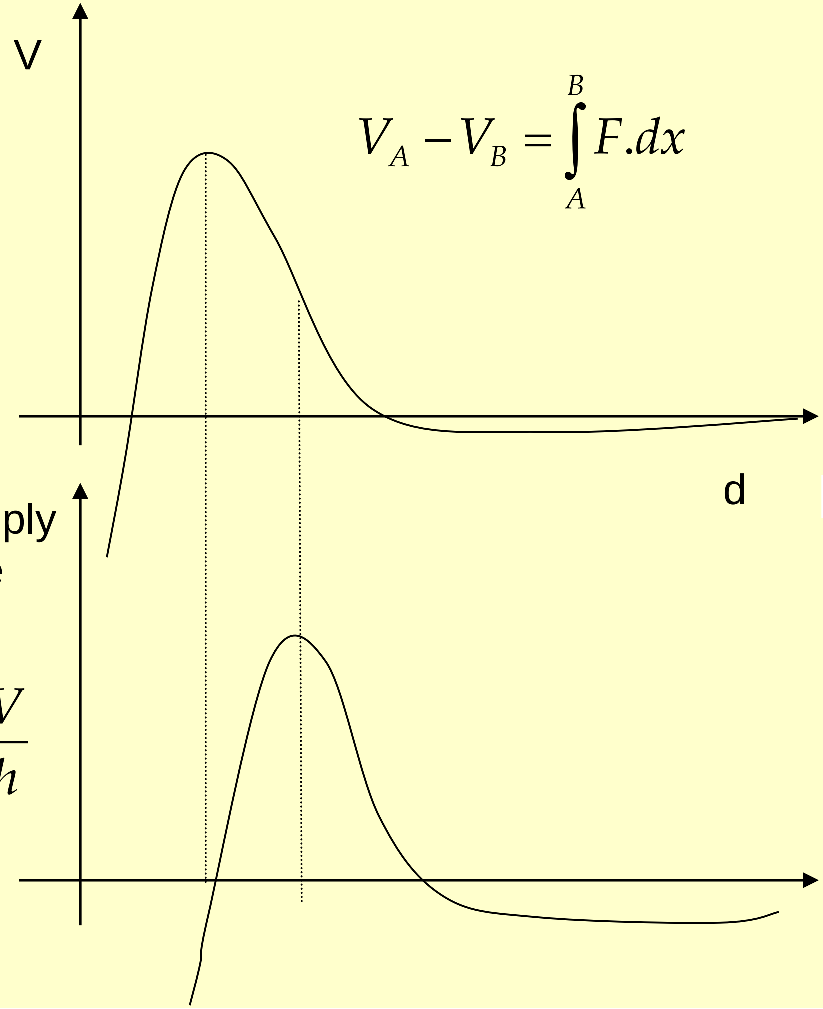
Interactions stériques: Repulsion due to the overlay of adsorbed molecules

distance between interacting bodies

Definition : the potentiel energy of interaction

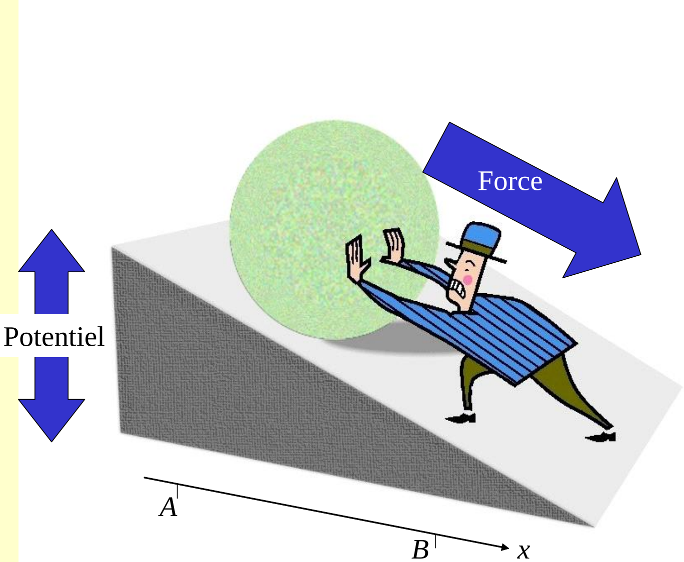
Energy, V, required to approach two surfaces infinitively separated until a distance d

$$V_A - V_B = \int_A^B F.dx$$



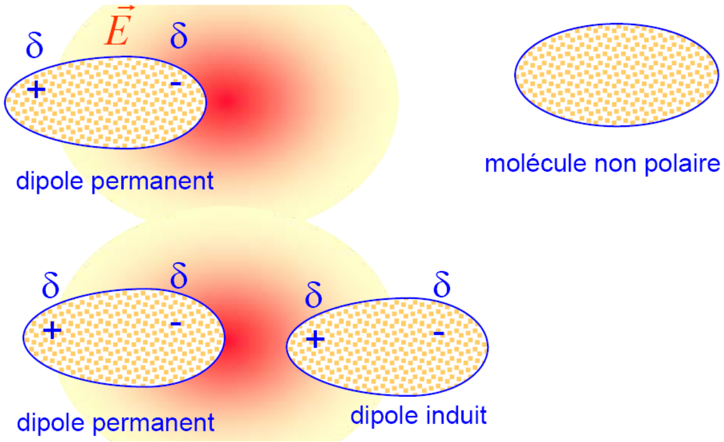
Force, F, to supply to approach the two surfaces

$$F = -\frac{dV}{dh}$$



Van der Waals interactions

Attractive force between permanent dipoles (KEESOM 1915) } Polar forces
permanent dipole–induced dipole (DEBYE 1921)

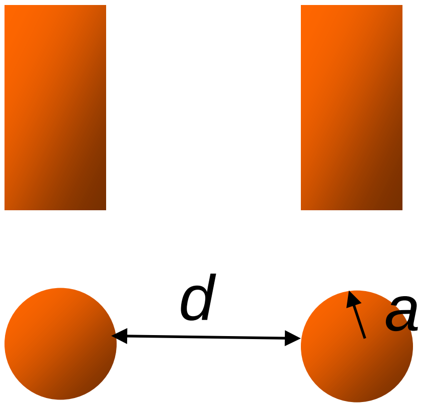


induced dipoles (LONDON 1930) } Dispersive force

Consequences

- **between atoms**
  gap to ideal gas law
- **between molecules**
  superfical tension
- **between macromolecules or particles**
  attractive potential énergy

Attractive potential of *van der Waals*



- between two infinite plate :

$$V_A = -\frac{A}{12\pi} d^{-2}$$

J/m^2

- between two identical spheres

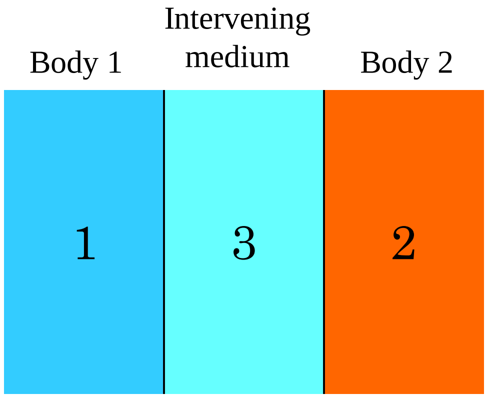
$$V_A = -\frac{A}{6}\left[\frac{2a^2}{d^2+4ad} + \frac{2a^2}{d^2+4ad+4a^2} + \ln\left(\frac{2a^2}{d^2+4ad+4a^2}\right)\right]$$

Si a >>d $\quad V_A = -\frac{Aa}{12d}$ $\quad$ J

- between two spheres with different radius :

Si a_1 >>d $\quad$ et $\quad$ a_2 >>d $\quad V_A = -\frac{Aa_1a_2}{6d(a_1+a_2)}$ $\quad$ J

Hamaker constant



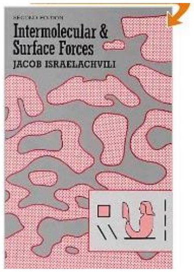
$$A_{132} \approx \pm\sqrt{A_{131}A_{232}}$$

If the intervening medium is vaccum: $A_{12} \approx \sqrt{A_{11}A_{22}}$

$$A_{131} \approx A_{313} \approx A_{11} + A_{33} - 2A_{13} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2$$

$$A_{132} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right)$$

Israelachvili 1991



A
Hamaker constant
10^{-19} - 10^{-20} J

A / 10^{-20} J		
Materials	**Vacuum**	**Water**
Polystyrene	7.9	1.3
Hexadecane	5.4	-
Gold	40	30
Silver	50	40
Al_2O_3	16.75	4.44
Copper	40	30
Water	4.0	-

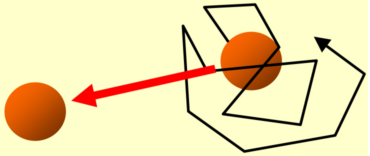
AN : Estimate A for polystyrene / eau / or

VdW energy and force ranges:

200 nm spheres of polystyrene (latex) dispersed in water

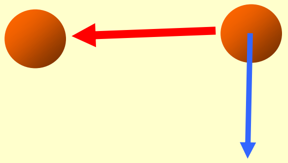
VdW compared with the diffusion :

d	1 nm	10 nm
$V_{A\ vdw}/kT$	-26	-2.6



VdW compared with the drag force (induced by a velocity of 1 mm/s) :

d	10 nm
$F_{A\ vdw}$	$-1.1\ 10^{-12}$ N
F_{Drag}	$1.9\ 10^{-12}$ N

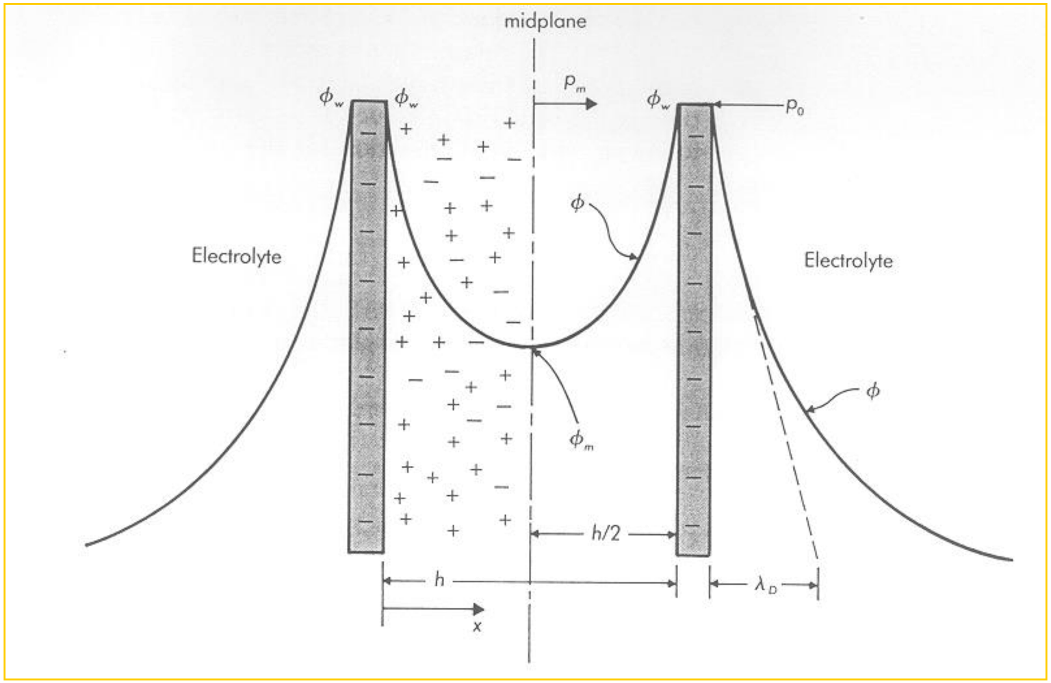


Electrostatic forces between two charged surfaces

Double layer superposition

↓

Repulsion between the surfaces



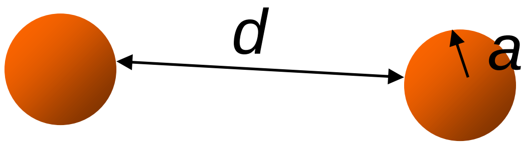
This force is often called ionic repulsion to underline its difference with a pure Coulombian repulsion

Repulsion potentiel energy

for a symetric electrolyte z:z

Between two plates:

$$V_R = \frac{64 n_0 k_B T}{\kappa_D} \Upsilon_0^2 \exp(-\kappa_D d)$$



Between two spheres:

$$V_R = \frac{64 \pi a n_0 k_B T}{\kappa_D^2} \Upsilon_0^2 \exp(-\kappa_D d)$$

$$\Upsilon_0 = \tanh\left(\frac{z \psi_0 e}{4 k_B T}\right)$$

DLVO theory: *Deryaguine, Landau* (1941), *Verwey, Overbeek* (1948)

Total potentiel energy of interaction, V :

Electrostatic repulsion

van der Waals attraction

$$V = V_R + V_A$$

Between two spheres :

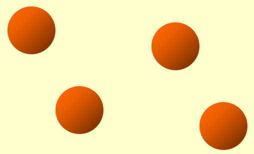
$$= \frac{64\pi a n_0 k_B T}{\kappa_D^2} \Upsilon_0^2 \exp(-\kappa_D d) - \frac{Aa}{12d}$$

- The estimation of *A* is imprecise.
- The zêta potential gives a minimal value of ψ_0
- The ionic strength control the value of κ_D.

DLVO theory and colloids stability

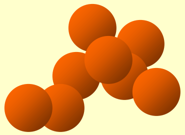
if V_{max}>kT

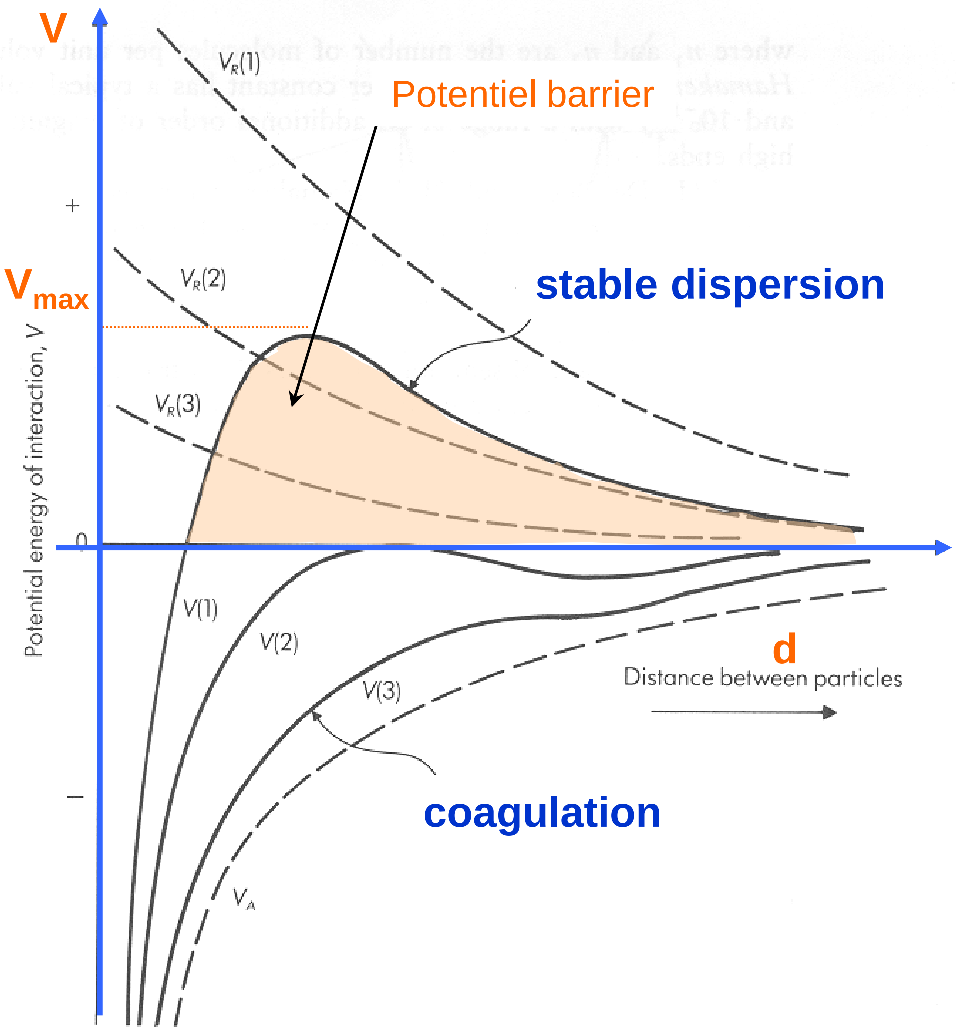
stable dispersion



if V_{max}<kT

coagulation





Critical Concentration in electrolyte for the Coagulation (c.c.c.)

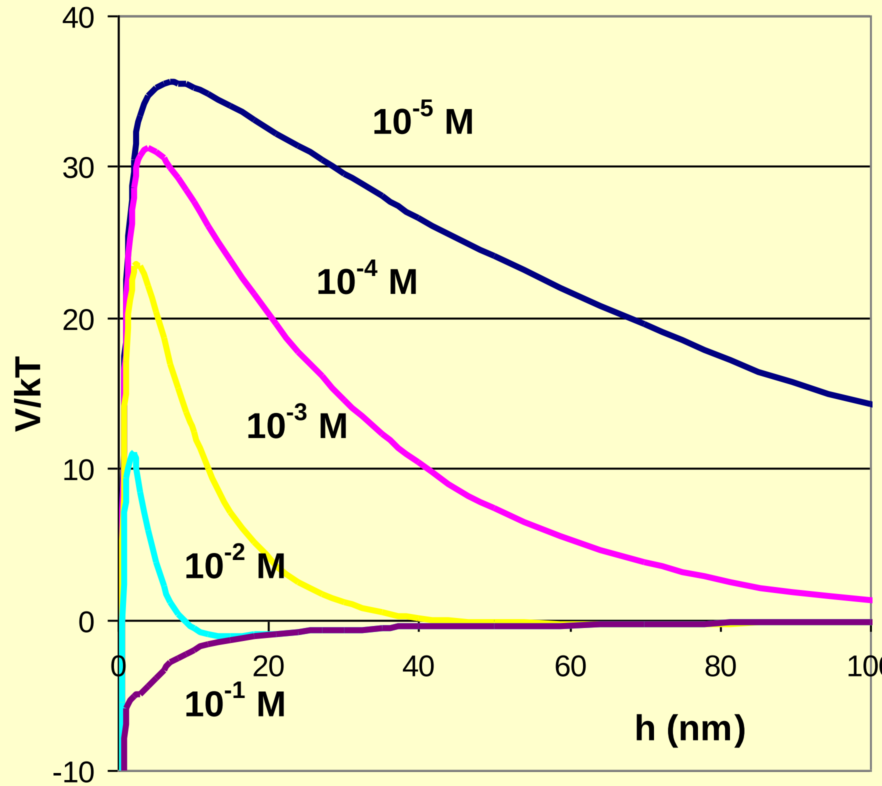
Schulze-Hardy rule

$$c_{crit} \text{ tel que et } \left.\frac{dV}{dh}\right|_{h_{max}} = 0 \text{ et } V(h_{max})=0$$

$$C_{crit} = 3{,}8.10^{-36}\,\frac{\gamma^4}{A^2 z^6} \quad \text{mol/m}^3$$

Variation of the c.c.c. with the valency[6]

Na^{+}	Ca^{2+}	Al^{3+}
100	1,56	0,137



Potentiel energy of interaction as a fonction of the body-body distance for 200 nm spheres with a zeta potentiel of 20 mV ($A=1.10^{-20}$ J)

https://hub.gke.mybinder.org/user/bacchin-chemica-ineering_python-0lqp3di1/notebooks/Colloid_DLVO.ipynb

Interfacial phenomena

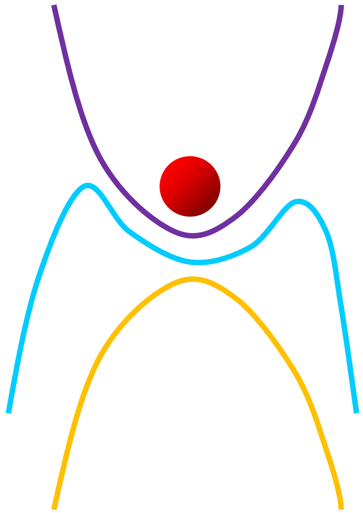
```
k=1.38064852e-23 #m2 kg s-2 K-1
T=298
avo=6.02214076e23
kT=k*T
e=1.6e-19
#colloids
a=1e-7
A=1e-20
zeta=-0.02
#solution
c0=[0.00001,0.0001,0.001, 0.01,0.1] #mol/L
z=1.
#allocation variable
maxi=np.zeros(len(c0))
print ('c0 \t V_max')

#Fonctions pour le calcul de VR -repulsion- et VA -attraction-
def VR(d,zeta,c):
    I=z**2*c
    n0=c*1e3*avo
    lamD=3.07e-10/np.sqrt(I)
    gam0=np.tanh(z*zeta*e/(4*kT))
    return 64*np.pi*a*n0*kT*(lamD**2)*(gam0**2)*np.exp(-d/lamD)
def VA(d):
    return -A*a/(12*d)
```

Stability, instability and metastability

Stable state (at equilibrium)

Pure liquid
Solution of hydrophilic or ionic molecules
Solution of hydrophobic molecules
Solution and association of amphiphilic molecule

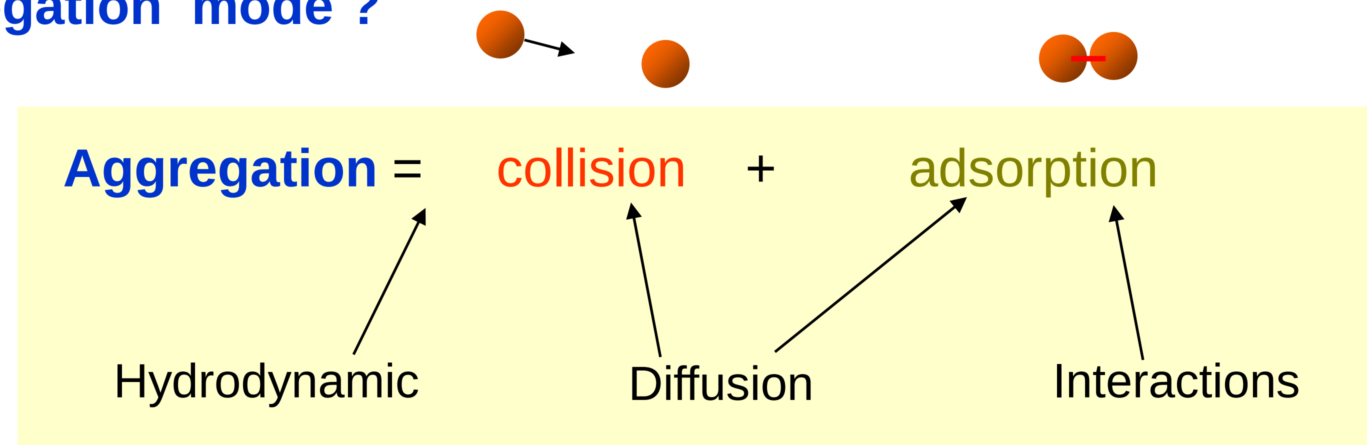


Metastable state (colloidal state)
(the evolution towards the equilibrium is blocked)

Solid/liquid dispersion
emulsion
gel

Instable state
Immiscible solvant

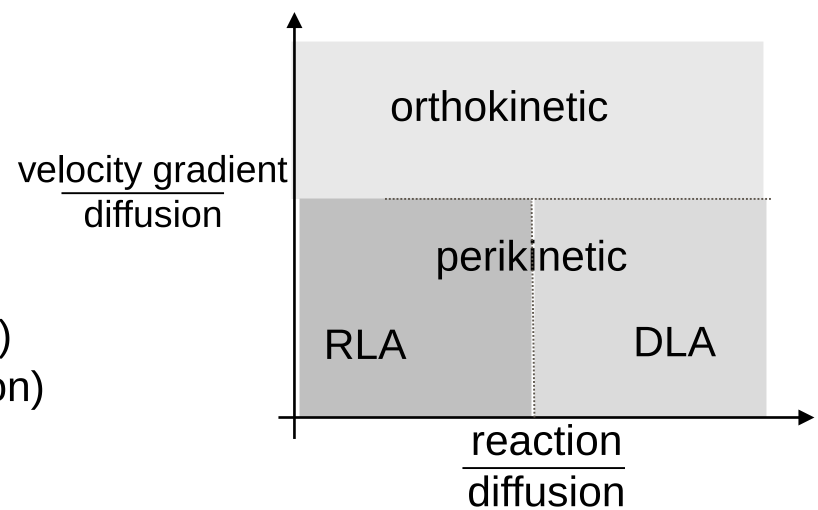
Aggregation mode ?



The Aggregation is controled by :

the collision mechanisms :
- Brownian diffusion (perikinetic aggregation)
- Velocity gradient (orthokinetic aggregation)

the adsorption :
- Brownian diffusion (Diffusion Limited Agregation)
- Surface interactions (Reaction Limited Agregation)



Aggregation kinetics

Number of interparticle collisions $= k_a n^2$

Kinetic of particle loss
(n particles per unit volume)

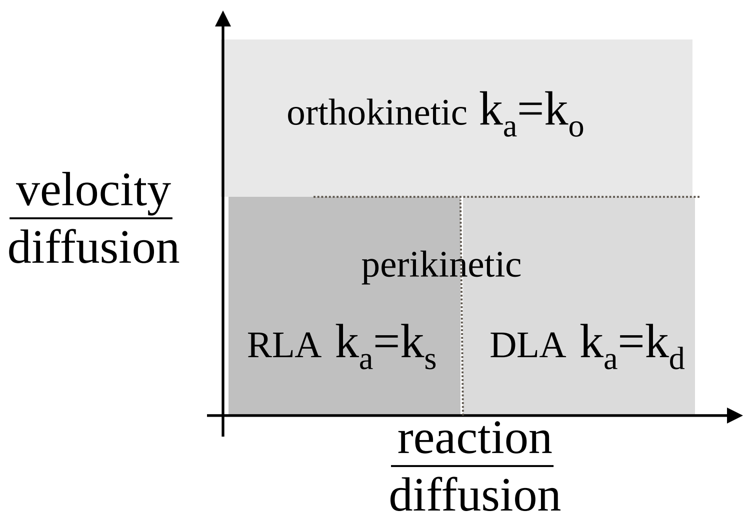
$$\frac{dn}{dt} = -k_a n^2$$

order of reaction : 2

$$n = \frac{n_0}{1 + k_a n_0 t}$$

$$n_0 = \frac{\phi}{\frac{4}{3}\pi a^3}$$

initial particle size



Perikinetic aggregation

$$k_s = \frac{8\pi D a}{W} = \frac{1}{W} k_D$$

constant for Brownian aggregation

collision efficiency

$$k_D = \frac{4kT}{3\mu} = 6.10^{-18}\, m^3.s^{-1}$$

constant for rapid aggregation (DLA)
(Smoluchosky 1917)

k_s constant for slow aggregation (RLA)
(Verwey et Overbeek 1948)

stability ratio

$$W = 2a\int_{2a}^{\infty} \exp\left(V / k_B T\right) r^{-2} dr$$

$$= 2a\int_{2a}^{\infty} \exp\left(V / k_B T\right) \frac{dh}{(h+2a)^2}$$

DLVO: $W \approx \frac{1}{\kappa_D 2a} \exp\left(\frac{V_{max}}{k_B T}\right)$

Arrhenius like equation

https://hub.gke.mybinder.org/user/bacchin-chemica-ineering_python-0lqp3di1/notebooks/Colloid_DLVO.ipynb

Slow or rapid aggregation ?

Half life time

$$t_{1/2} = \frac{1}{k_s n_0} = \frac{W}{8\pi D a n_0}$$

Characteristic time for the aggregation

$$t_{1/2} = \frac{W}{6D\phi} a^2$$

AN : Half life times for 200 nm particles at a volume fraction of *10^{-4}*

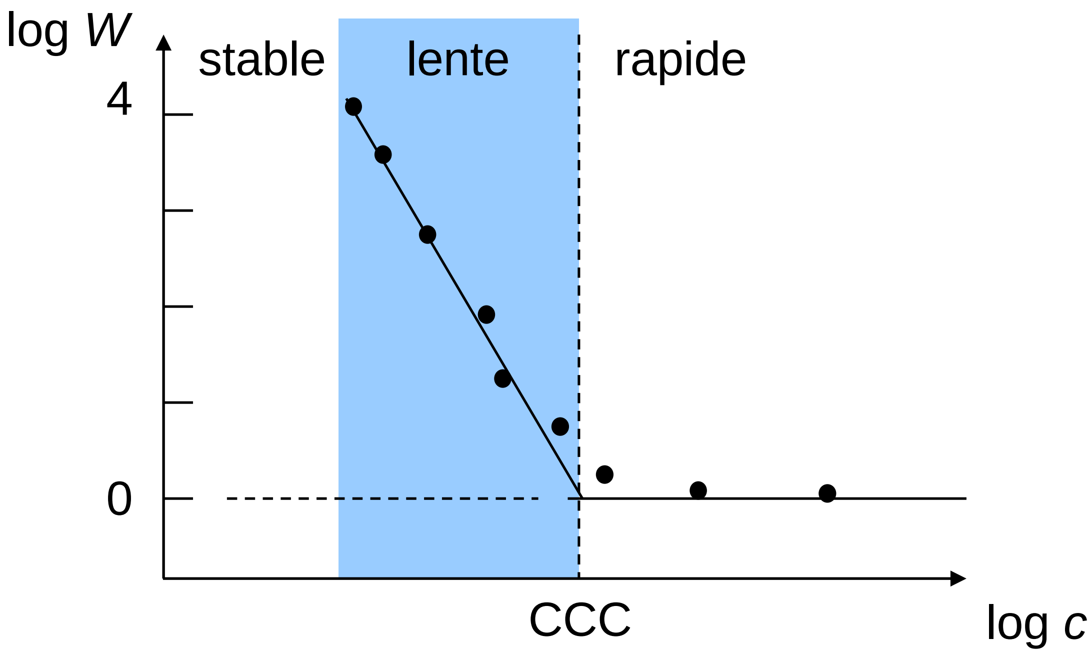
I (M)	10^{-3}	10^{-2}	0.05
K_d (nm)	9.7	3.1	1.4
V_{max}	23	10	0
W	5.10^{+8}	300	1
$t_{1/2}$ (s)	4.10^{+9}	$2.6\ 10^{+3}$	7.6
	1.1 siècle	43 min	7.6 s
	metastable	slow	rapid

Slow or rapid aggregation

For a coagulant at a concentration *c* (mol/dm³) :

$$\log_{10} W \approx K_1 \log_{10} c + K_0$$

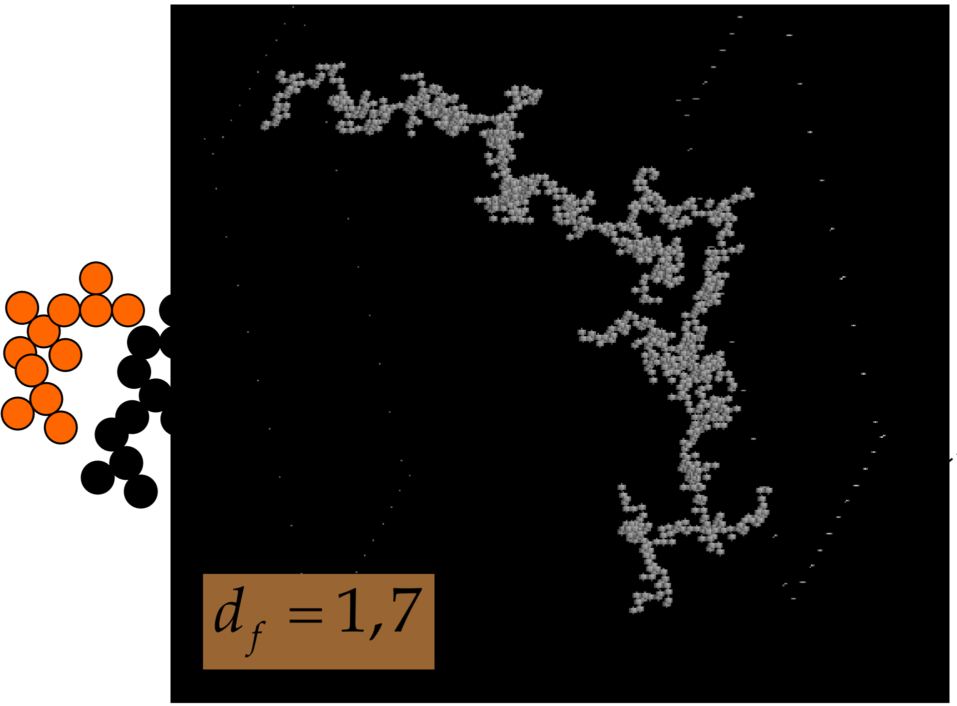
$$K_1 \approx -2 \times 10^9 \frac{\Upsilon_0^2 a}{z^2}$$



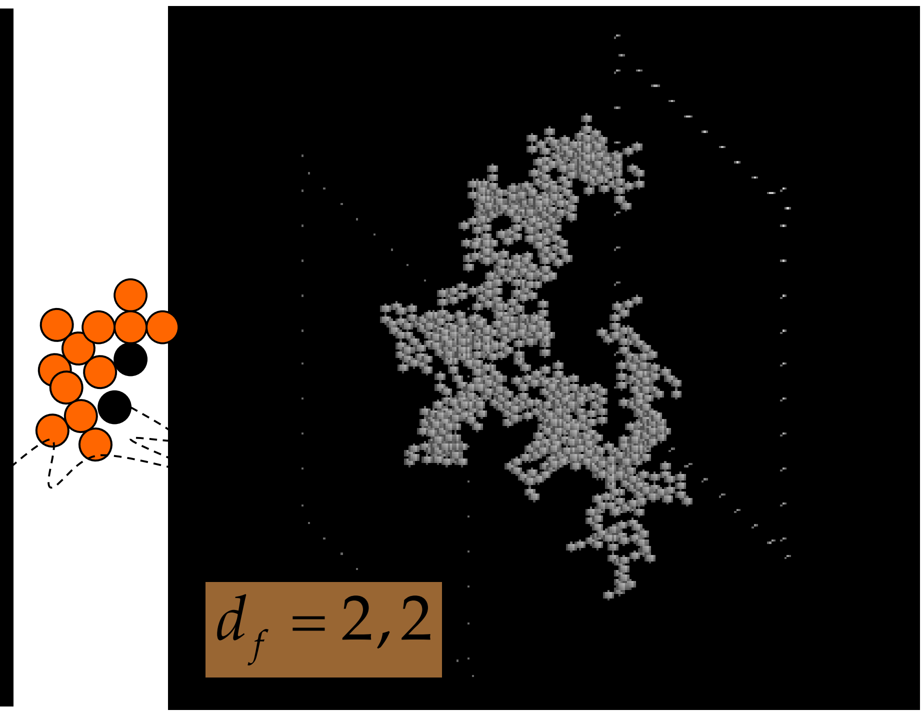
Slow coagulation when log *W* < 4 ($W < 10^4$) : $V_{max} \sim 15k_BT$

Stability conditions : **$V_{max} > 15k_BT$**

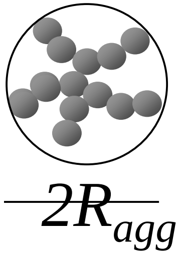
Perikinetic aggregation and fractal dimension



rapid aggregation =
limited by the diffusion



slow aggregation :
limited by interactions



$$N_{agg} = \left(\frac{R_{agg}}{a} \right)^{d_f}$$

$$\phi_{agg} = \left(\frac{R_{agg}}{a} \right)^{d_f - 3}$$

$$\rho_{agg} = \rho_s \phi_{agg} + (1 - \phi_{agg}) \rho$$

Exercise

Particles of 100 nm in size (diameter) are aggregated. The size of aggregates is 10 μm and the fractal dimension is 2.3.

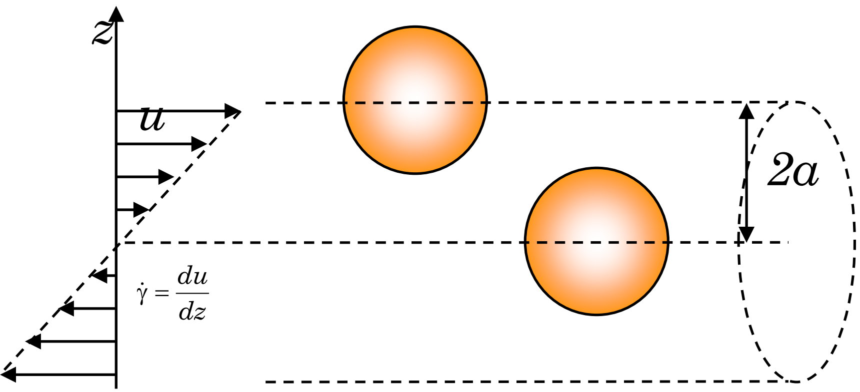
Conclude on the aggregation regime.

Compute the density of aggregate and the number of primary particles in an aggregate.

Compare the settling velocities for primary particles and aggregates. Discuss the assumptions made to compute the settling velocities.

Données : *masse volumique des particules primaires : 1500 kg/m3*

Orthokinetic aggregation



Orthokinetic constant

$$k_o = \frac{16}{3}\,\dot{\gamma}\,a^3$$

For primary particles :

$$\frac{dn}{dt} = -\frac{4\dot{\gamma}\phi}{\pi}n$$

$$\frac{n}{n_0} = \exp\left(-\frac{4\dot{\gamma}\phi}{\pi}t\right)$$

For a given volue fraction, the aggregate growing kinetics is a function of
$\dot{\gamma}t$ « *Camp number*"

Thomas et Camp (1953)

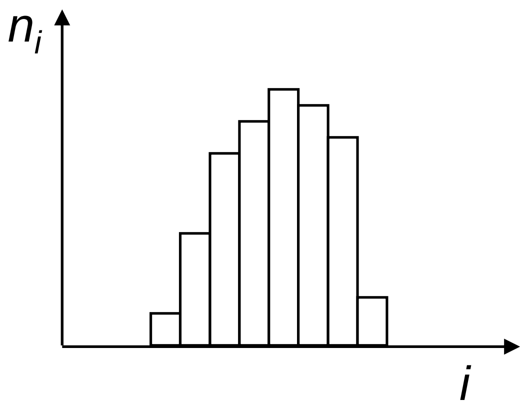
For a turbulent mixing

Camp & Stein, 1943 $\langle\dot{\gamma}\rangle = \sqrt{\rho\frac{\varepsilon}{\mu}}$

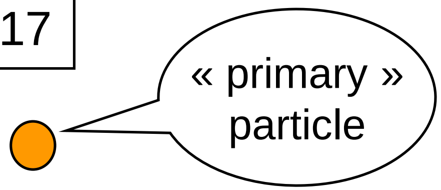
mixing power
per unit of fluid mass

Aggregation and population balances

But: the size distribution changes with time
(previous approaches are valid only for the fist aggregation time)

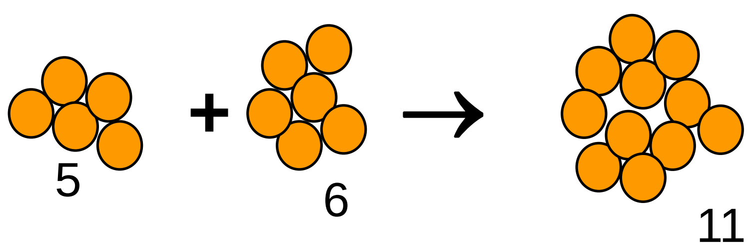


Smoluchowski 1917



n_i = number of particles containing i primary particles

Aggregation of aggregates have to be accounted !



constante de cinétique de 2e ordre

Number of collisions between particules of population i and particles of population j (m^{-3} s^{-1})

$$\dot{n}_{ij} = k_{ij} n_i n_j$$

Population balance equations

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{\substack{i+j=k \\ i=1}}^{i=k-1} k_{ij} n_i n_j - n_k \sum_{k=1}^{\infty} k_{ik} n_i$$

Birth

Death

$$\frac{dn_1}{dt} = -k_{11} n_1^2 - k_{12} n_1 n_2 - k_{13} n_1 n_3 \ldots$$

$$\frac{dn_2}{dt} = \frac{1}{2} k_{11} n_1^2 - k_{12} n_1 n_2 - k_{23} n_2 n_3 \ldots$$

$$\frac{dn_3}{dt} = \frac{1}{2} k_{12} n_1 n_2 - k_{13} n_1 n_3 - k_{23} n_2 n_3 \ldots$$

Total particles concentration :

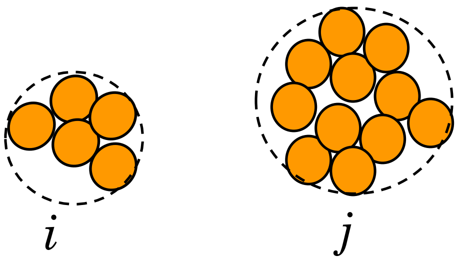
$$\frac{dn}{dt} = -k_a n^2$$ if $k_{ij} = k_{11} = 2k_a$

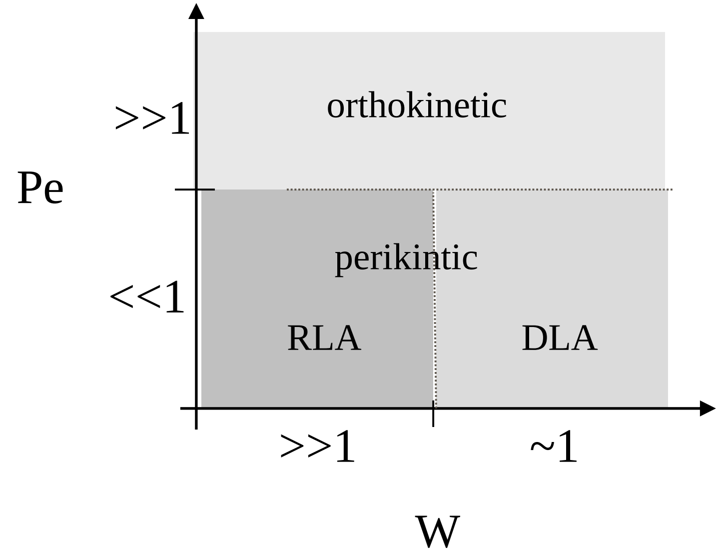
$$n = \frac{n_0}{1 + k_a n_0 t}$$ at $t = 0$: $n = n_1 = n_0$

Estimation of aggregation modes

$$Pe = \frac{F_{hydr}}{F_{br}} = \frac{6\pi\mu_w \dot{\gamma}\, a_i^3}{kT}$$

$$= 4.6.10^{18}\, \dot{\gamma}\, a_i^3$$





•Brownian diffusion (perikinetic aggregation), Pe <<1

$$k_{ij} = \frac{1}{W}\frac{2k_BT}{3\mu}\frac{(a_i + a_j)^2}{a_i a_j}$$

• Velocity gradient (orthokinetic aggregation), Pe>>1

$$k_{ij} = \frac{4}{3}\dot{\gamma}\left(a_i + a_j\right)^3$$

• Differential settling

$$k_{ij} = \left(\frac{2\pi g}{9\mu_w}\right)(\rho_s - \rho)\left(a_i + a_j\right)^3\left(a_i - a_j\right)$$

Application : coagulation/flocculation of waste water (1)

To treat water, the aggregation processus occurs in two steps

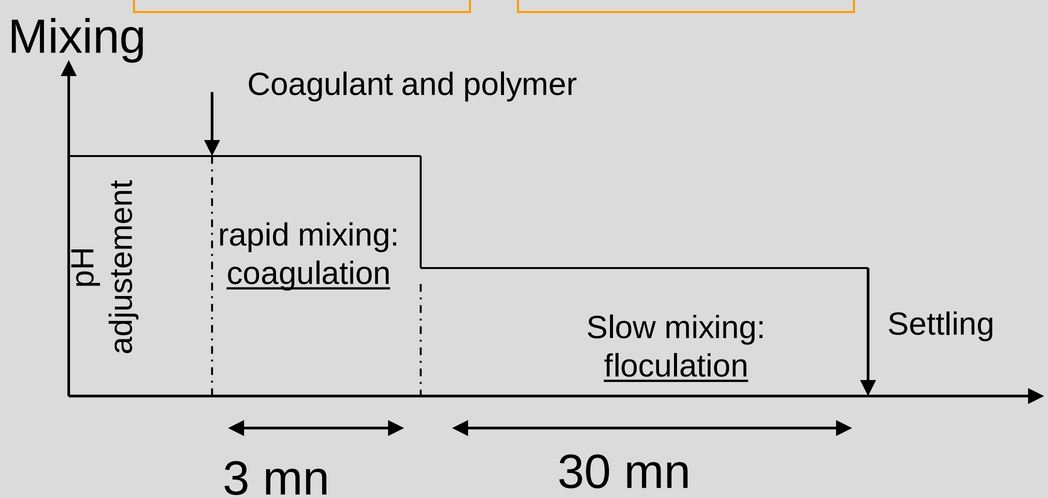
coagulation

destabilisation of colloidal particles -> aggregate by adding in a rapid mixing zone a coagulant (salt with high valency) to screen charges

floculation

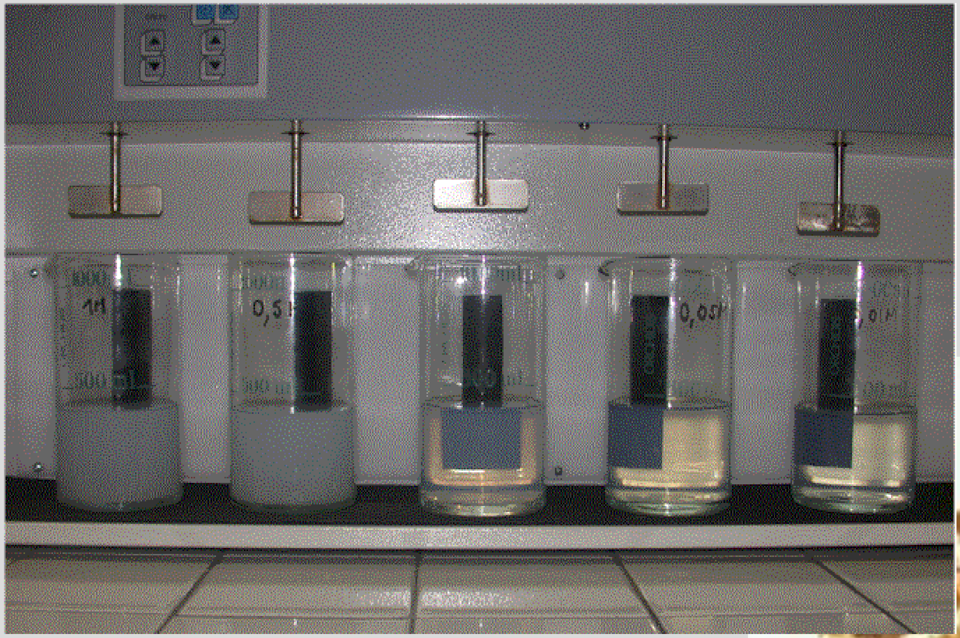
reversible formation of flocs between coagulat particles in a slow mixing zone by inter-particle ponting with polymer

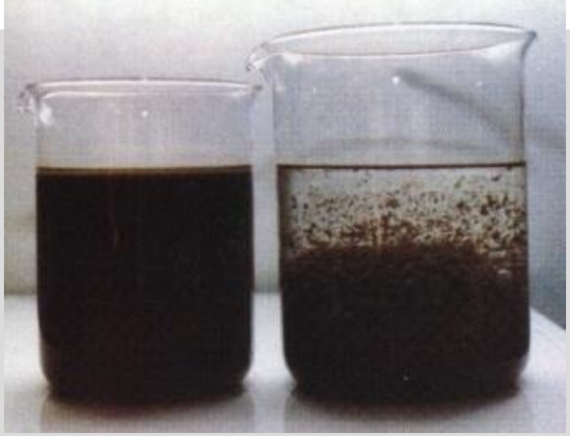
coagulation **flocculation**

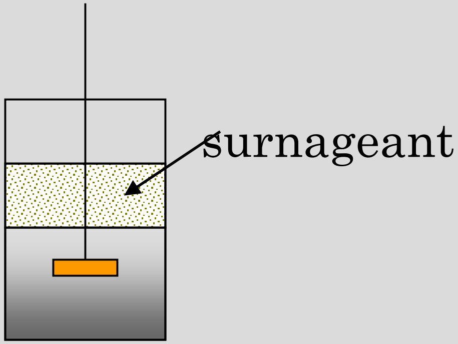


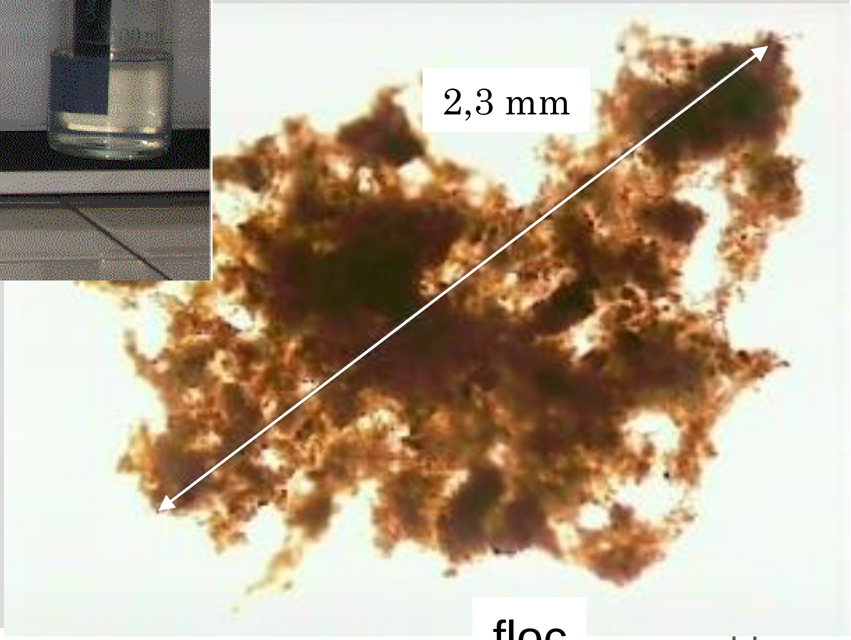
Application : coagulation/floculation in the lab

Jar test









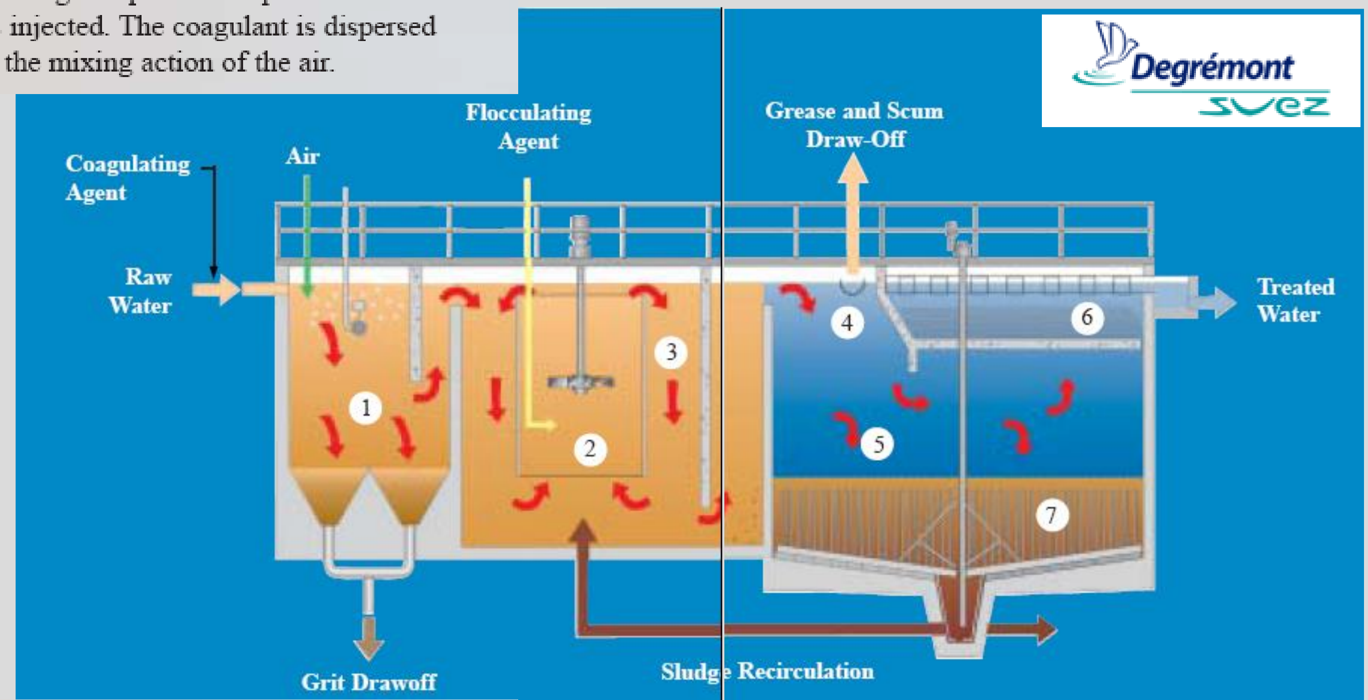
floc

Application : coagulation/floculation at industrial level

Operating Diagram

Zone 1: Grit removal/coagulation The raw water enters an air-mixing zone where grit separation is performed and a coagulating agent is injected. The coagulant is dispersed in the storm water by the mixing action of the air.

A l'échelle industrielle : Densadeg Degrémont

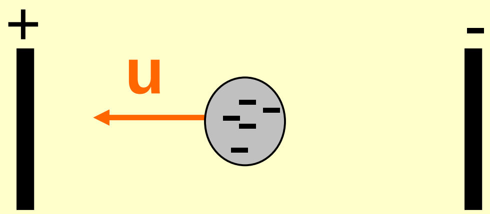


Zone 2: Flocculation, first stage
The water then flows into a second zone for intense internal recirculation and mixing by an axial-flow turbine. Here, a flocculating agent is added, together with thickened sludge recirculated through an external system. The recirculated sludge accelerates the flocculation process and ensures the formation of dense floc particles of homogeneous size.

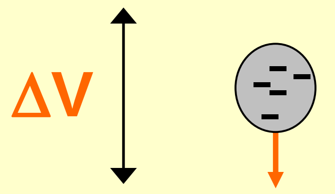
Zone 3: Flocculation, second stage
The transition to the settling settling stage is accomplished in this zone. The process is a plug-flow reactor where the flocculation process continues and the grease and scum start to separate out.

Electrokinetic phenomena

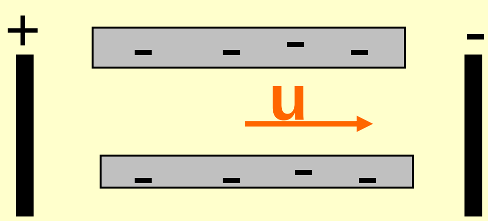
When the motion of an electrostatic double layer and an electric field interplay ...



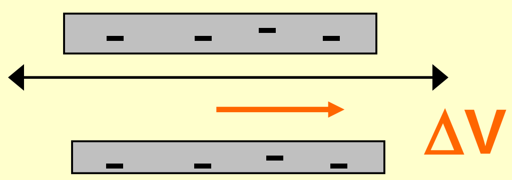
Electrophoresis :
motion of a charged interface in a stationary liquid induced by an electric field



Settling potential :
electric field induced by the motion of a charged interface in a stationary liquid



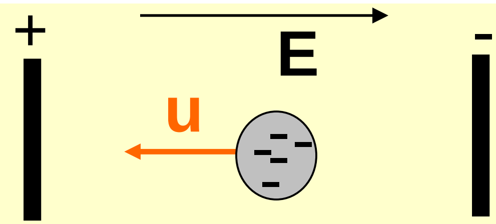
Electro-osmosis :
motion of liquid relatively to a charged interface induced by an electric field



Steaming potential :
electric field induced by the motion of a liquid relatively to a charged interface

Electrokinetic phenomena

Electrophoresis :



u : electrophoretic velocity

u/E : electrophoretic mobility

$\lambda_D >> a$ Assumption of a ponctual charge

Force balance :

$$u = \frac{qE}{6\pi\mu a}$$

With: $\zeta = \dfrac{q}{4\pi\varepsilon a}$

$$u = \frac{2\varepsilon\zeta E}{3\mu}$$

Hückel equation

Applications : separation, particle and macromolecule charge analysis

$\lambda_D << a$ Assumption of a plane double layer

Momentum transport equation :

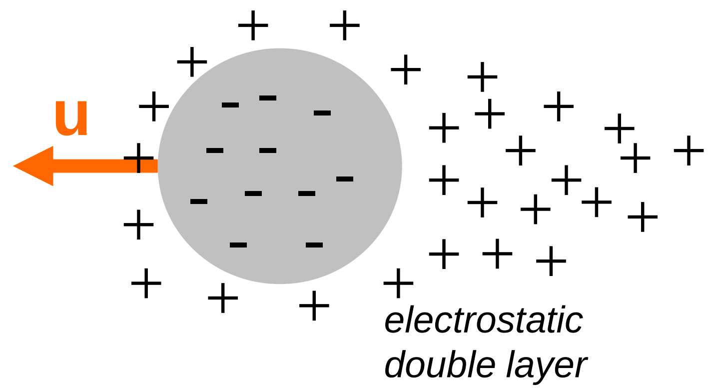
$$u = \frac{\varepsilon\zeta E}{\mu}$$

Helmholtz-Smoluchowski equation

Electrokinetic phenomena

finite λ_D → Electrophoretic retardation

The counter-ions of the double-layer move in the opposite direction (electro-osmosis) and slow down the electrophoresis



$$u = \frac{2\varepsilon\zeta E}{3\mu} f\left(\frac{a}{\lambda_D}\right)$$

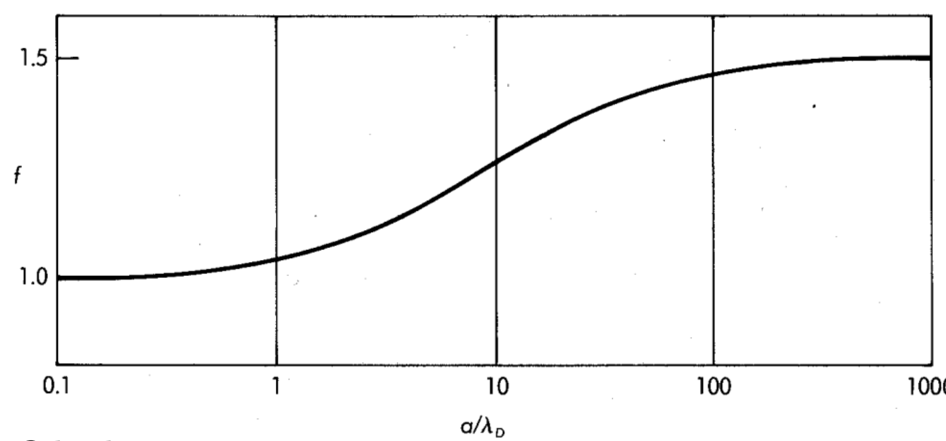
Henry equation function (1931)

→ $\frac{a}{\lambda_D} \to 0 \qquad f\left(\frac{a}{\lambda_D}\right) \to 1$

(small particle, dilute solution)

→ $\frac{a}{\lambda_D} \to \infty (>100) \qquad f\left(\frac{a}{\lambda_D}\right) \to 1{,}5$

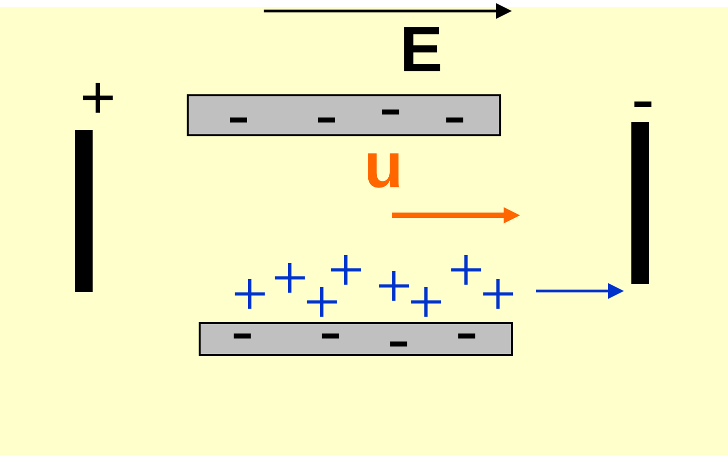
$$f(x) \approx 1 + 0{,}5 \Big/ \left[1 + \left\{\frac{5}{2x}\left(1 + 2e^{-x}\right)\right\}\right]^3$$



Ohshima 1994

Electro-osmosis (discovered by F.F. Reuss 1809) :

Under an electric field, the counter-ions (in the double layer near the surface) migrate and due to viscous drag the water is drawn by the ions and flows.



u : electro-osmotic velocity

if the porous radius >> 1/κ $f(\kappa a) \rightarrow 1{,}5$

$$u = -\frac{\varepsilon \zeta E}{\mu}$$

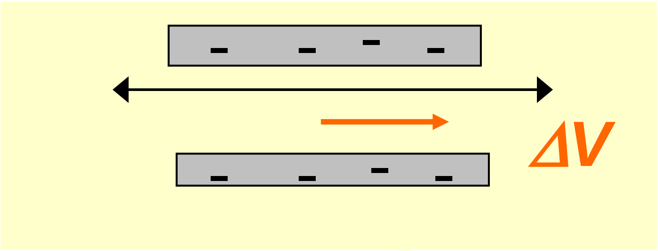
Applications : dewatering, transfer in biological membrane

AN : ζ=100 mV
E=1000 $V.m^{-1}$
u=10^{-4} $m.s^{-1}$

Electrokinetic phenomena

Streaming potentiel :

Charge transport → Streaming current → potential difference



$$\Delta V = \frac{\varepsilon\zeta}{\mu k}\Delta p$$

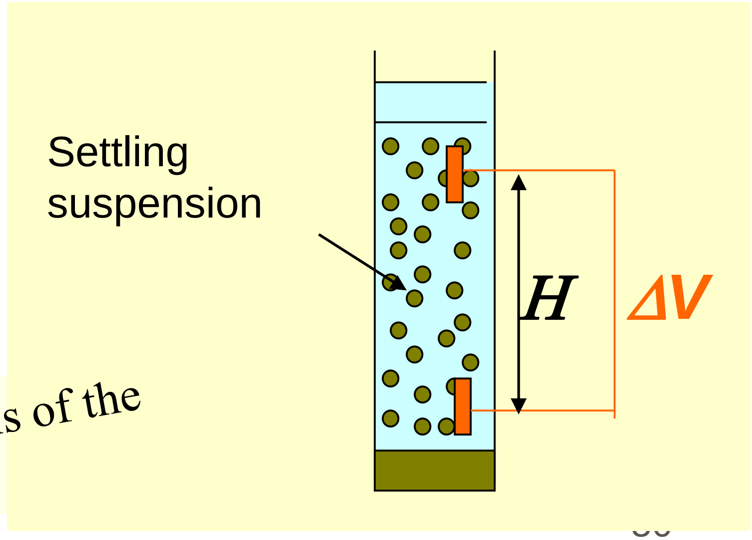
k conductivity of the bulk solution

Applications : analysis of surface charge

Settling potential :

$$\frac{\Delta V}{H} = -\frac{6\pi nUa\varepsilon\zeta}{k}$$

U : particle fall speed
n : particles per unit volume



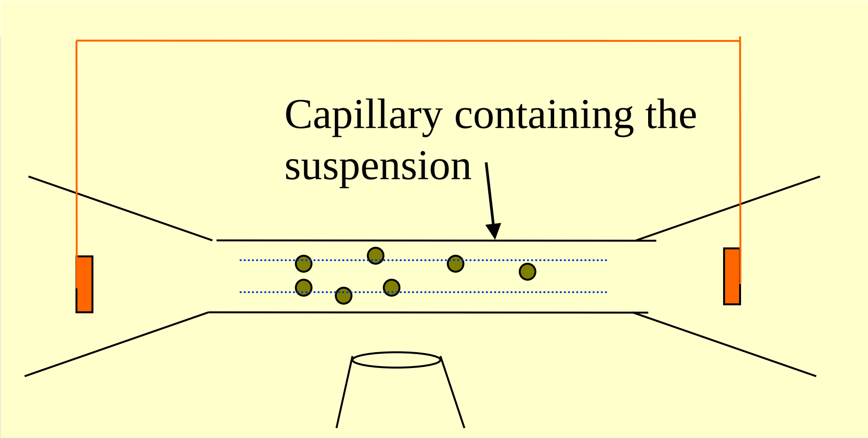
Applications : analysis of the particle charge ?

Applications (1)

Microelectrophoresis

Measurement of the motion of charged particles or macromolecules under microscopy (when size is > 1 μm) or by laser interferometer

velocity → **zéta potential**



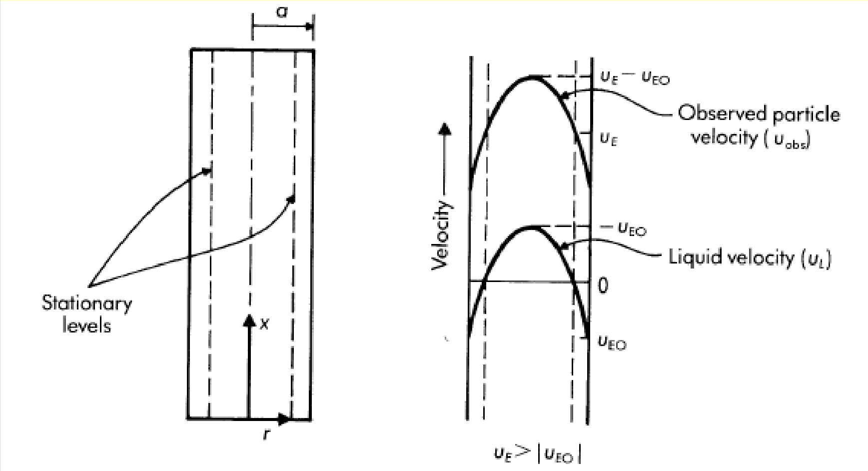
Problem :

The charge of the capillary leads to an electro-osmosis phenomena that modify the motion of particles

Solution :

Measurement of the electrophoretic velocity at stationary plane

$$u_L = u_{EO}\left(2\frac{r^2}{a^2} - 1\right) \rightarrow \frac{r_{stat}}{a} = \frac{1}{\sqrt{2}}$$



Physicochemical hydrodynamics : An introduction, *Wiley Inter Science*, R. F. Probstein (1994)

No slipping conditions are still existing in microfluidic?

E. Lauga et al. *Springer Handbook of Experimental Fluid Mechanics* (2007)

Applications (2)

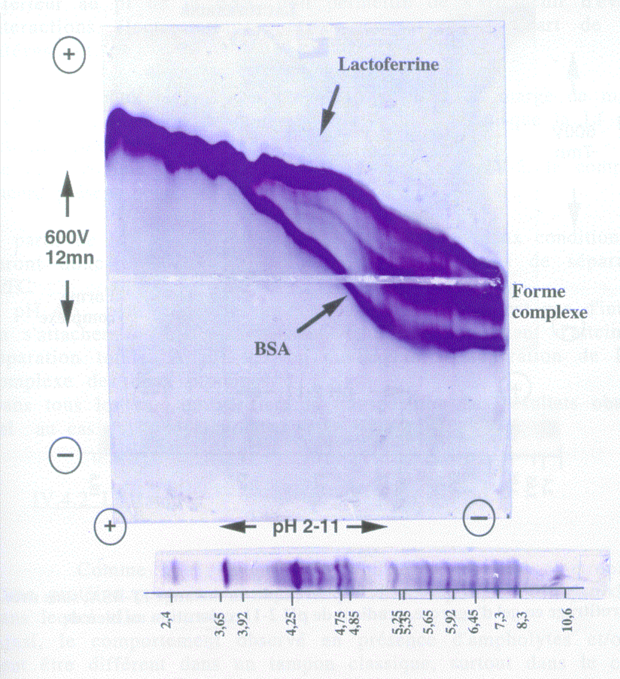
zone electrophoresis

Migration of charged solutes in a gel

\+ *reduction of convection* *(due to Joule effect)*

\- *electroosmosis and capilarity make the estimation of the solute charge impossible*

Use for qualitative analysis



Electrotitring curve in an agarose gel with a pH gradient

L'ÉLECTROPHORÈSE SÉPARE LE BON DU MAUVAIS

Qu'elle soit endogène ou exogène, l'EPO se présente sous plusieurs « isoformes ». Celles-ci diffèrent légèrement les unes des autres au niveau de groupements chimiques qui se fixent sur la molécule après sa « transduction », c'est-à-dire sa fabrication dans la cellule suivant les instructions du code génétique. Or l'EPO exogène recombinante, fabriquée par des cellules animales génétiquement modifiées, n'a pas le même « spectre » d'isoformes que la molécule 100 % humaine, et on peut le voir par séparation électrophorétique. La méthode consiste à faire migrer les molécules à l'intérieur d'un gel déposé sur une plaque, par application d'un champ électrique. Les isoformes n'ayant pas la même charge électrique migrent à des vitesses différentes et se séparent. Le résultat se présente, après révélation de la plaque, sous forme d'un spectre de taches. Or le spectre de l'EPO recombinante diffère nettement de celui de la molécule endogène. Le Laboratoire national de dépistage du dopage a testé sa méthode sur 102 échantillons urinaires prélevés lors du Tour de France 1998 et conservés par congélation. Sur 28 échantillons, dont une analyse préalable avait révélé une teneur anormalement élevée d'EPO, 14 ont été soumis au test par électrophorèse et ont révélé la présence d'EPO exogène.

Applications (3)

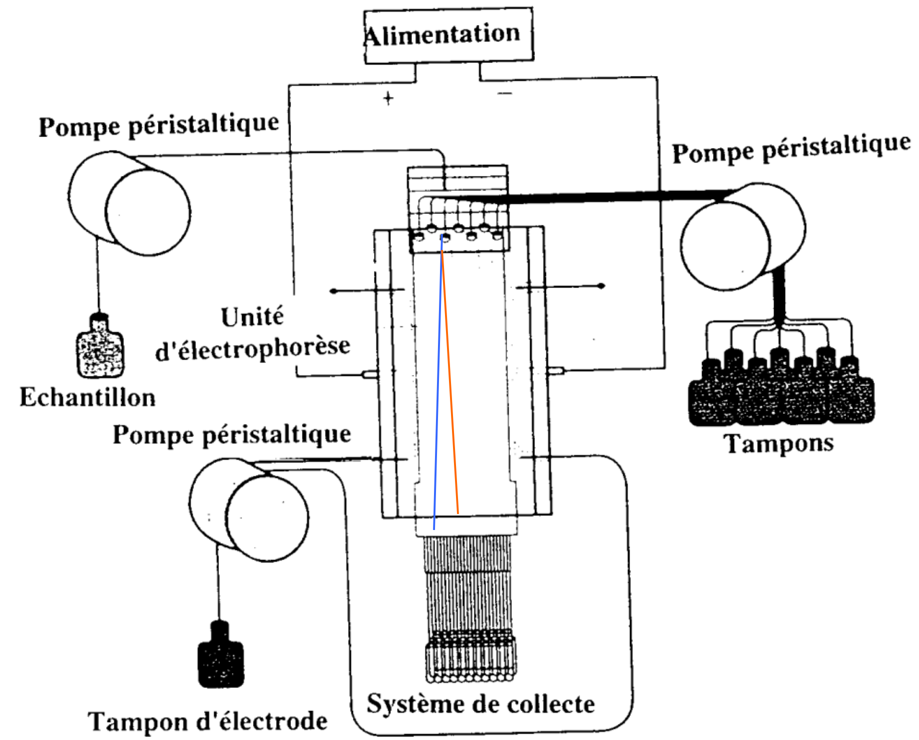
Continuous electrophoresis

Electrophoresis during the liquid streaming

\+ *important separation*

\- *Joule effect*

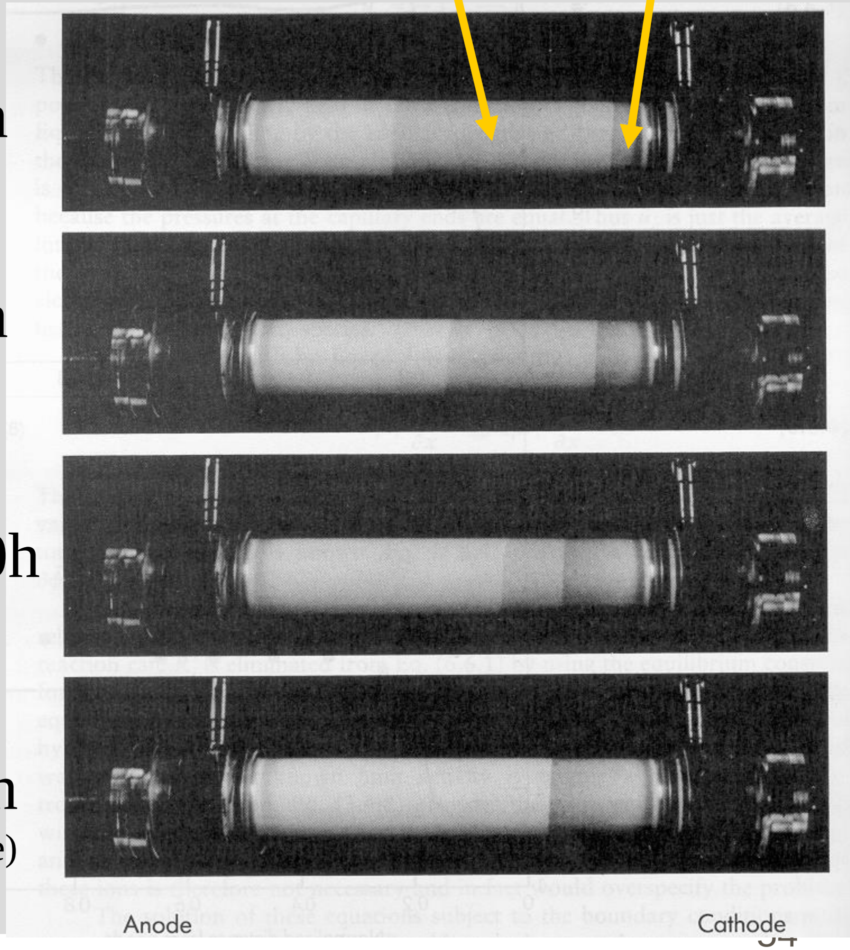
Use for the purification of biochemical product



Applications (4)

Electroosmosis for the removal of contaminants from soils

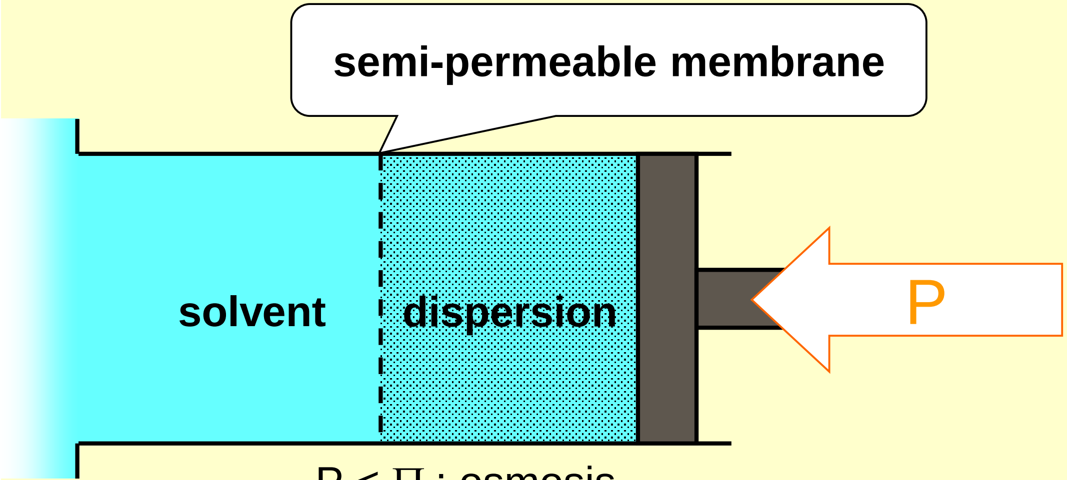
Zinc (8 mol/m^3) removal from a cylindrical clay sample 0.2 m long across which 8 V is applied.



Osmotic pressure and a_w

Chemical potentiel :

$$\mu_i = \mu_i^0 + V_i P + RT \ln a_i$$



P < Π : osmosis

P = Π : equilibrium

P > Π : reverse osmosis

(i) solvent extraction

(ii) compression

of the particles cloud

At equilibrium :

$$\mu_w^s = \mu_w^d$$

$$V_w P_0 = V_w \left(P_0 + \Pi\right) + RT \ln a_w$$

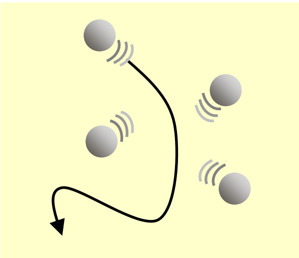
$$\boxed{V_w \Pi = -RT \ln a_w}$$

→ water activity : represent the water availibility “free water” and then the interactions between particles

Repulsion between particles	↗	a_w ↘	Π ↗
Attraction between particles	↗	a_w ↗	Π ↘
Attraction solvent-particles ↗	Repulsion ↗	a_w ↘	Π ↗

Osmotic pressure and interactions

Gas and ideal solution:



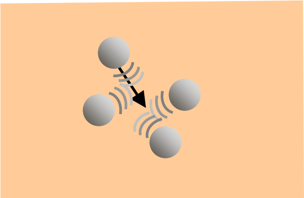
$$\ln a_w \approx \ln x_w = \ln(1 - x_p) \approx -x_p - \frac{x_p^2}{2} - \ldots$$

$$\Pi = \frac{x_p}{V_w} RT \approx CRT = nk_B T$$

C: mol/m3 $\quad n$: m^{-3}

van't Hoff law

Non-ideal solution and dispersion of interacting particules or macromolecules :



$$\Pi = nk_B T - \frac{2\pi}{3} n^2 \int_0^\infty r^3 g(r) \frac{dV_T}{dr} dr$$

Theoretical relationship

V_T: **colloïdal interactions (DLVO)**

$$\frac{\Pi \langle M \rangle_n}{cRT} = 1 + \Gamma_2 c + \Gamma_3 c^2 + \ldots$$

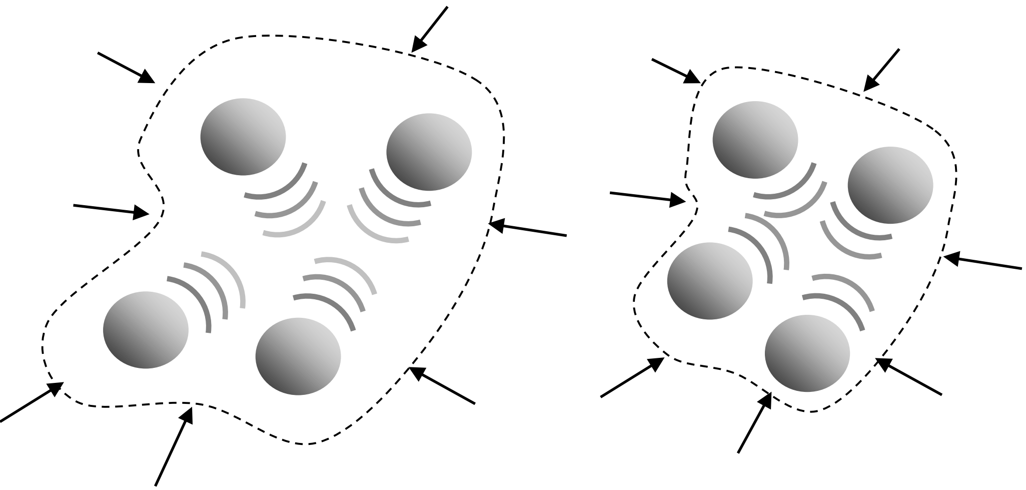
Semi-empirical relationship for macromolecules

$\langle M \rangle_n$: Averaged molecular mass

c: Mass concentration in g/m³

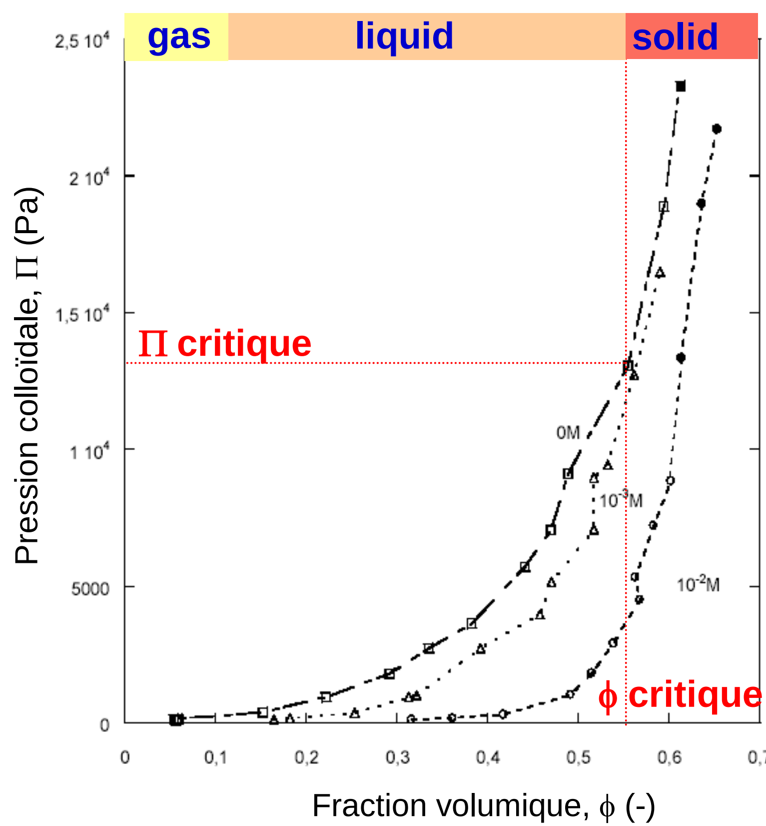
Γ_2, Γ_3: Virial coefficient **function of colloidal interactions, hydratation …**

Experimental highlights



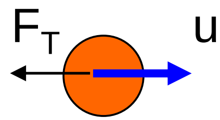
The osmotic pressure
is dependent of the ionic strenght

I ↗
repulsion ↘
Π ↘
compression resistance ↘
Φ ↗ (for an applied pressure)



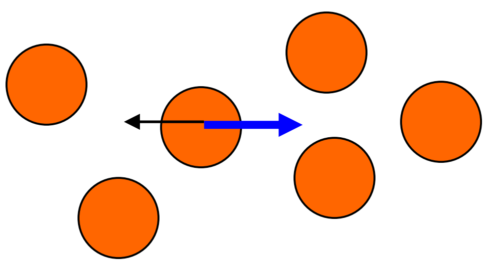
Mobility, m, of a dispersion

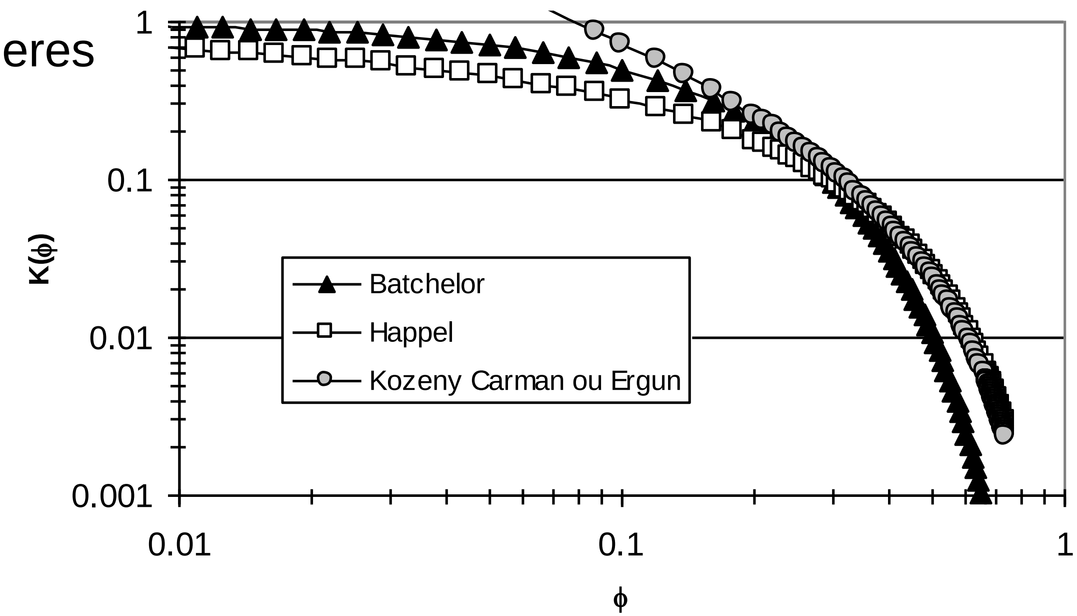
Diluted suspension of sphères



Stokes law $F_T = 6\pi\mu a u$ $m = \dfrac{1}{6\pi\mu a}$

Concentrated suspension of spheres





$$F_T = \frac{6\pi\mu a u}{K(\phi)}$$ $$m(\phi) = \frac{K(\phi)}{6\pi\mu a}$$

hydrodynamique coefficient (settling coefficient)

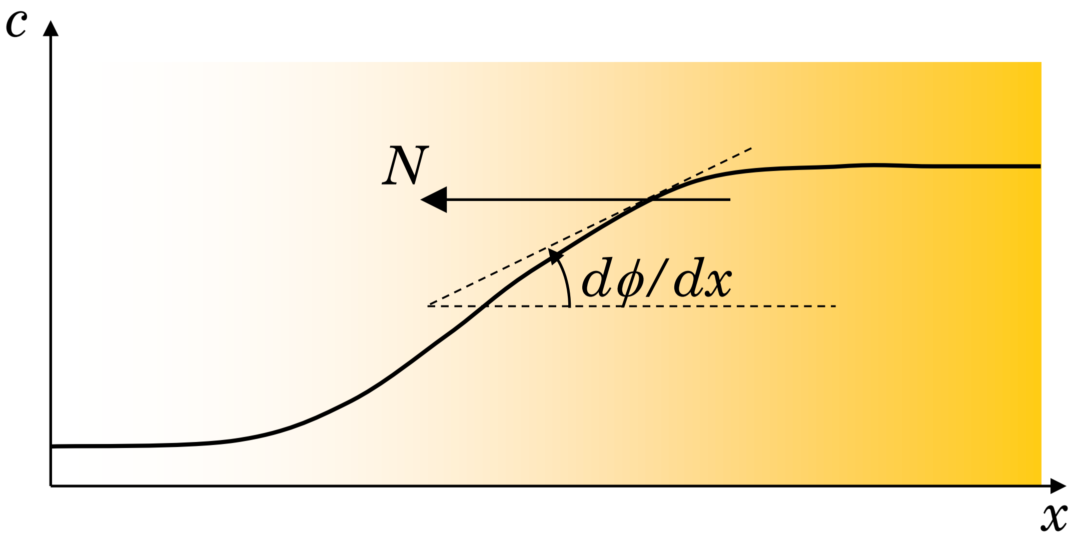
$$K(\phi) = \frac{u_{sed}(\phi)}{u_{sed_0}}$$

Happel function

$$H(\phi) = \frac{1}{K(\phi)} = \frac{6 + 4\phi^{\frac{5}{3}}}{6 - 9\phi^{\frac{1}{3}} + 9\phi^{\frac{5}{3}} - 6\phi^2}$$

Fickian diffusion

Transport of mass
from concentrated to diluted zones :



Mission :
Back to equilibrium

Means :
Brownian motion

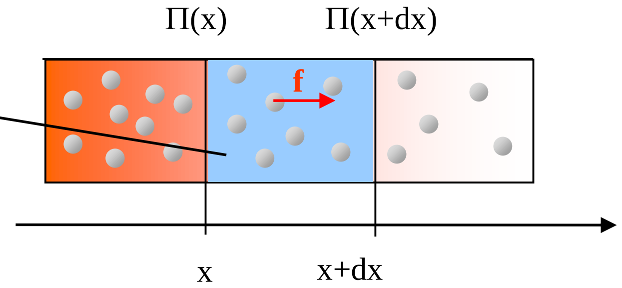
D : diffusion coefficient

$$N = -D\frac{d\phi}{dx}$$

The key : a link between diffusion, mobility and osmotic pressure

Number of particles per volume

$$\frac{\phi A dx}{V_p}$$



Force induced by the osmotic pressure

$$(\Pi(x)-\Pi(x+dx))A$$

Force per particle $$f=-\frac{V_p}{\phi}\frac{\partial\Pi}{\partial x}=-\frac{V_p}{\phi}\left(\frac{\partial\Pi}{\partial\phi}\right)\left(\frac{\partial\phi}{\partial x}\right)$$ inducing a x velocity $$u=m(\phi)\,f$$

Mass flux $$N=u\phi=-m(\phi)V_p\left(\frac{\partial\Pi}{\partial\phi}\right)\left(\frac{\partial\phi}{\partial x}\right)$$

Generalised Stokes Einstein law

Collective diffusion (in a gradient)

$$D=\frac{K(\phi)}{6\pi\mu a}V_p\frac{d\Pi}{d\phi}$$

$$D\xrightarrow[\phi\to 0]{}\frac{kT}{6\pi\mu a}$$

hydrodynamic & colloidal interactions colloïdales

Application to the filtration (1)

Permeability coefficient (m2)

$$J = -\frac{k_p}{\mu}\frac{dP}{dx}$$

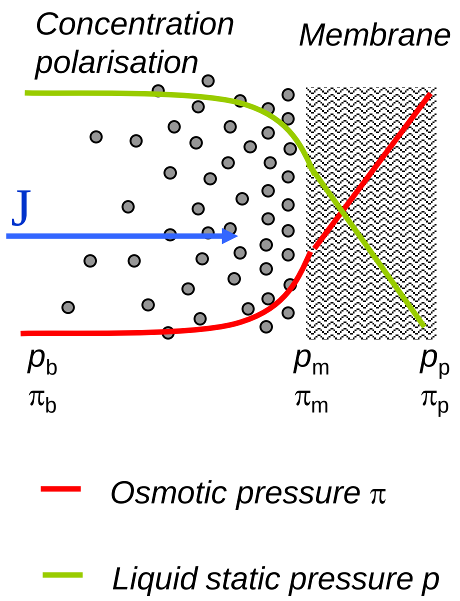
Darcy law

Integration over the thickness, e, of the membrane

Permeability (m)

$$J = \frac{k_p}{\mu}\frac{\Delta P}{e} = \frac{L_p}{\mu}\Delta P = \frac{\Delta P}{\mu R_m}$$

Hydraulic resistance (m-1)



with accumulation at the membrane

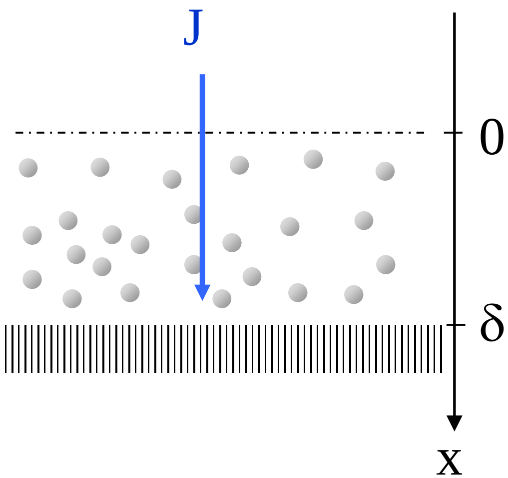
$$J = \frac{\Delta P - \left(\Pi_m - \Pi_p\right)}{\mu R_m}$$

Application to the filtration (2)

In permanent regime:
mass transport by convection is counterbalanced by diffusive transport

Effect of interfacial phenomena

$$N = J\phi - \frac{K(\phi)}{6\pi\mu a} V_p \frac{d\Pi}{dx} = 0$$



In cross flow filtration (accumulation in a boundary layer δ)

<u>Without interactions</u>

$$\frac{Jdx}{D_0} = \frac{d\phi}{\phi} \qquad Pe = \frac{J\delta}{D_0} = \ln\left(\frac{\phi_m}{\phi_b}\right)$$

<u>With interactions</u>

$$Pe = \frac{V_p}{kT} \int_{\Pi_b}^{\Pi_m} \frac{K(\phi)}{\phi} d\Pi$$

Application to the settling (1)

Archimeda

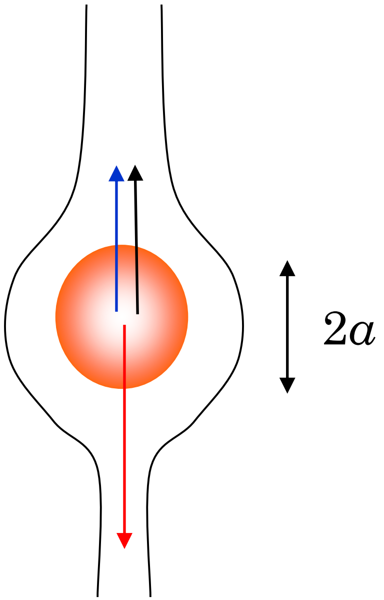
drag

Gravity

$$V_p\left(\rho_p - \rho_w\right)g = \frac{6\pi\mu a}{K(\phi)}u$$

For diluted suspension of spheres:

$$u = \frac{2}{9}\frac{a^2\left(\rho_p - \rho_w\right)g}{\mu}$$

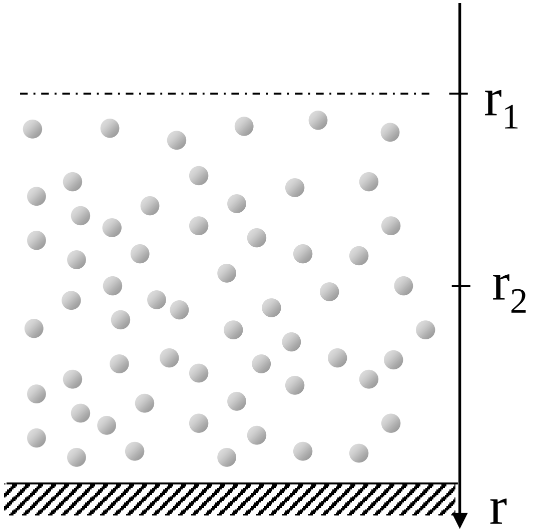


Application to the settling (2)

$$N = u_{sed}\phi - D(\phi)\frac{d\phi}{dx} = 0$$

Effect of interfacial phenomena

$$(\rho_p - \rho_w)g\phi - \frac{d\Pi}{dr} = 0$$



Without interactions

$$\ln\left(\frac{\phi_2}{\phi_1}\right) = \frac{V_p\left(\rho_p - \rho_w\right)g}{kT}(r_2 - r_1)$$

With interactions

$$(\rho_p - \rho_w)g\left(r_2 - r_1\right) = \int_{\Pi_1}^{\Pi_2}\frac{d\Pi}{\phi}$$

Application to the centrifugation (2)

Effect of interfacial phenomena

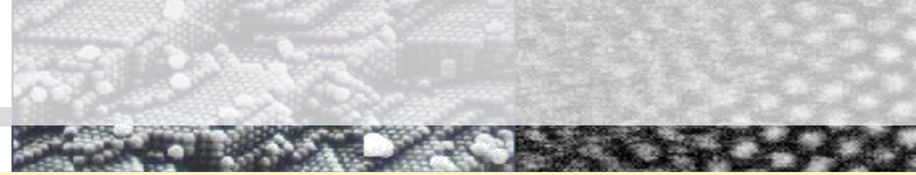
$$(\rho_p - \rho_w)\omega^2 r\phi - \frac{d\Pi}{dr} = 0$$

<u>Without interactions</u>

$$\ln\left(\frac{\phi_2}{\phi_1}\right) = \frac{V_p\left(\rho_p - \rho_w\right)}{kT}\omega^2\left(r_2^2 - r_1^2\right)$$

<u>With interactions</u>

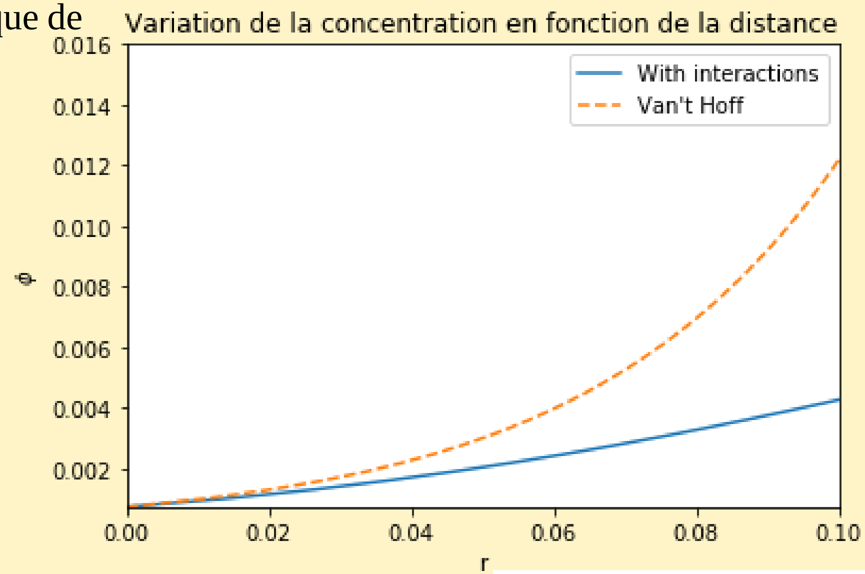
$$\frac{V_p\left(\rho_p - \rho_w\right)}{kT}\omega^2\left(r_2^2 - r_1^2\right) = \frac{V_p}{kT}\int_{\Pi_1}^{\Pi_2}\frac{d\Pi}{\phi}$$



Interfacial phenomena

Un récipient contient une suspension à 1 g/L de particules à une hauteur de 10 cm. A 25 °C, l'équilibre s'établit entre la diffusion et la sédimentation sous l'effet de la gravité terrestre (g = 9,8 m s–2).

Quel est la concentration en bas du récipient, si ces particules sphériques ont un diamètre de 40 nm et une masse volumique de 1,35 g/mL en l'absence d'interactions ?



Vitesse de sédimentation : = 3,05 10–10 m/s

Coefficient de diffusion : = 1,09 ×10–11 m2/s

$$\ln\left(\frac{\phi_2}{\phi_1}\right) = \frac{u_{sed}}{D}(r_2 - r_1)$$

C_2=16.4 g/L

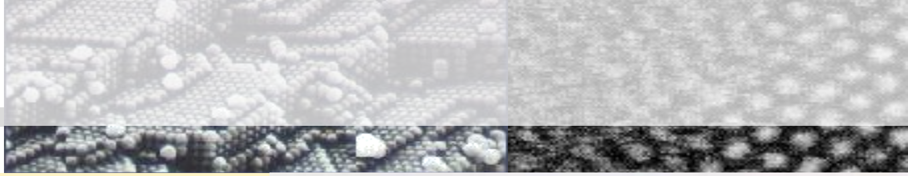
On considère maintenant, qu'en présence d'interactions répulsives entre les particules, la pression osmotique ne varie plus de façon linéaire avec la concentration mais se traduit par un second coefficient de Viriel de 0,01 Pa/(g/L)^2.

Recalculer alors la concentration au fond du récipient. Conclure.

$$\Pi = kT\frac{\phi}{V_p} + 0{,}01\left(\rho_p\phi\right)^2$$

C_2=5.7 g/L

Interfacial phenomena



On filtre la même dispersion sur une membrane tubulaire

diamètre 6 mm Longueur 1,2 m
Vitesse tangentielle 0,05-0,1 m/s } Re= 360-720

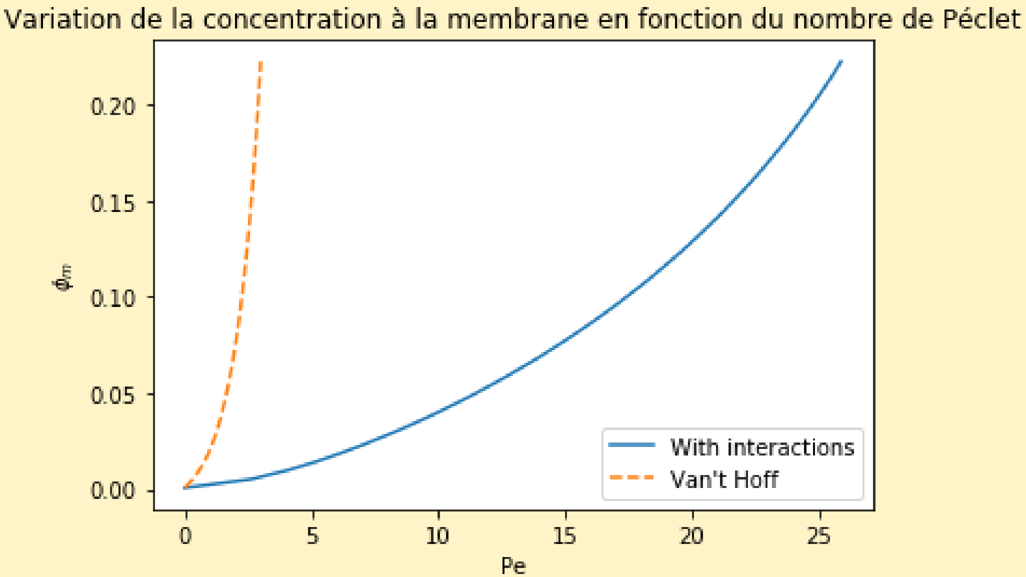
Physico-chimie Sc=xxx

Re et Sc } Couche limite

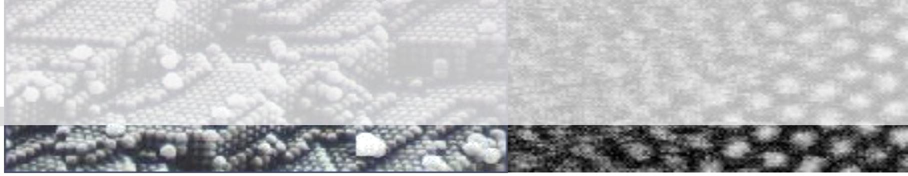
Couche limite et Flux de filtration } Péclet

$$Pe = \frac{V_p}{kT} \int_{\Pi_b}^{\Pi_m} \frac{K(\phi)}{\phi} d\Pi$$

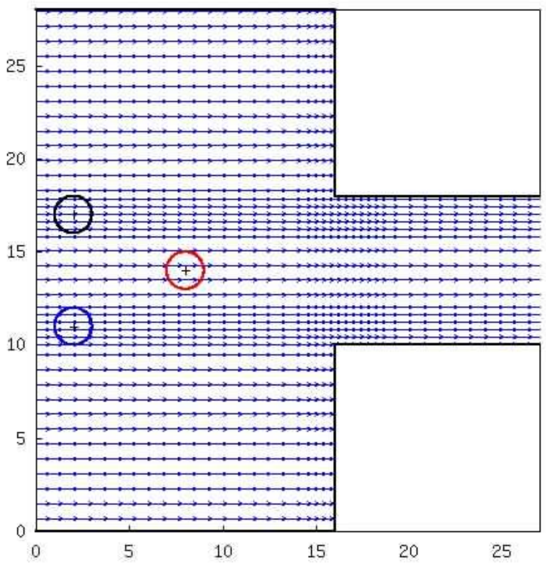
En présence de répulsions, la dispersion résiste mieux à la compression induite par la force de traînée liée à la filtration : l'accumulation est moins importante



Ce type de modèle peut permettre de déterminer quand un gel va se former à la surface d'une membrane ou d'une goutte qui sèche



- Exemples :
  - at hollow fiber scale
  - at pore scale



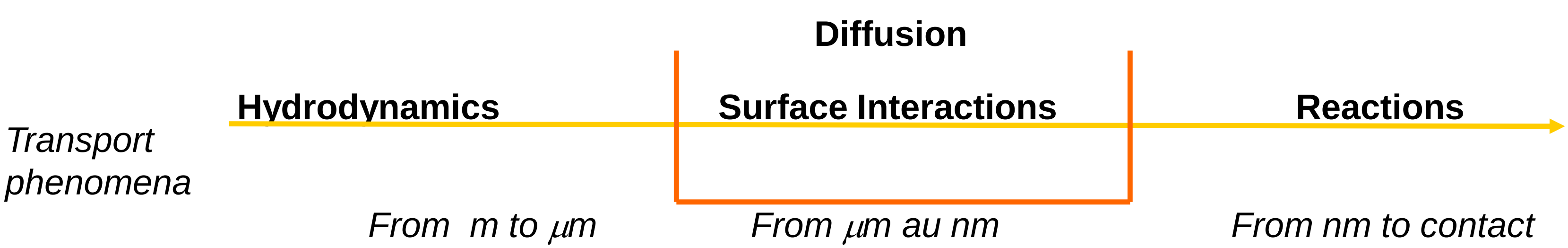
Conclusions

… Important areas of physical chemistry such as interfacial phenomena, colloids, clusters and, more generally, De Gennes "soft matter" should be revisited using the system approach and chemical engineering methods.

Jacques Villermaux, Future challenges for basic research in chemical engineering
Chemical Engineering Science,48 (1993)

Physico-chemical hydrodynamics of colloids
can
- open problems in processes
- be the source of new processes

when surface **interactions** are controled (and well known)…



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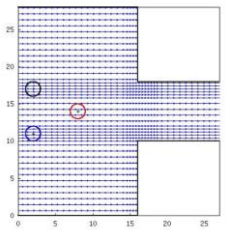
Interfacial phenomena

Interfacial phenomena

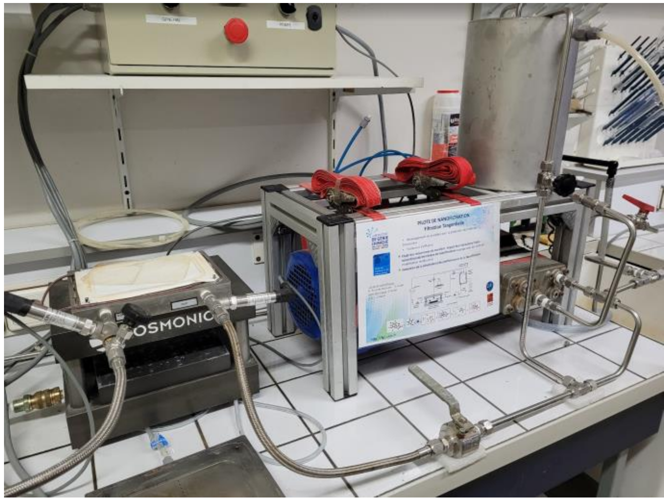
Visite virtuelle

Filtration à multi-échelle

De l'échelle d'un pore



Au pilote

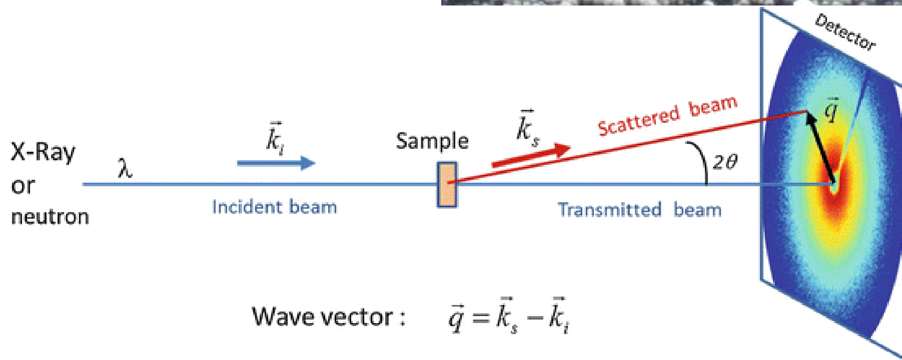


Interfacial phenomena

Interfacial phenomena

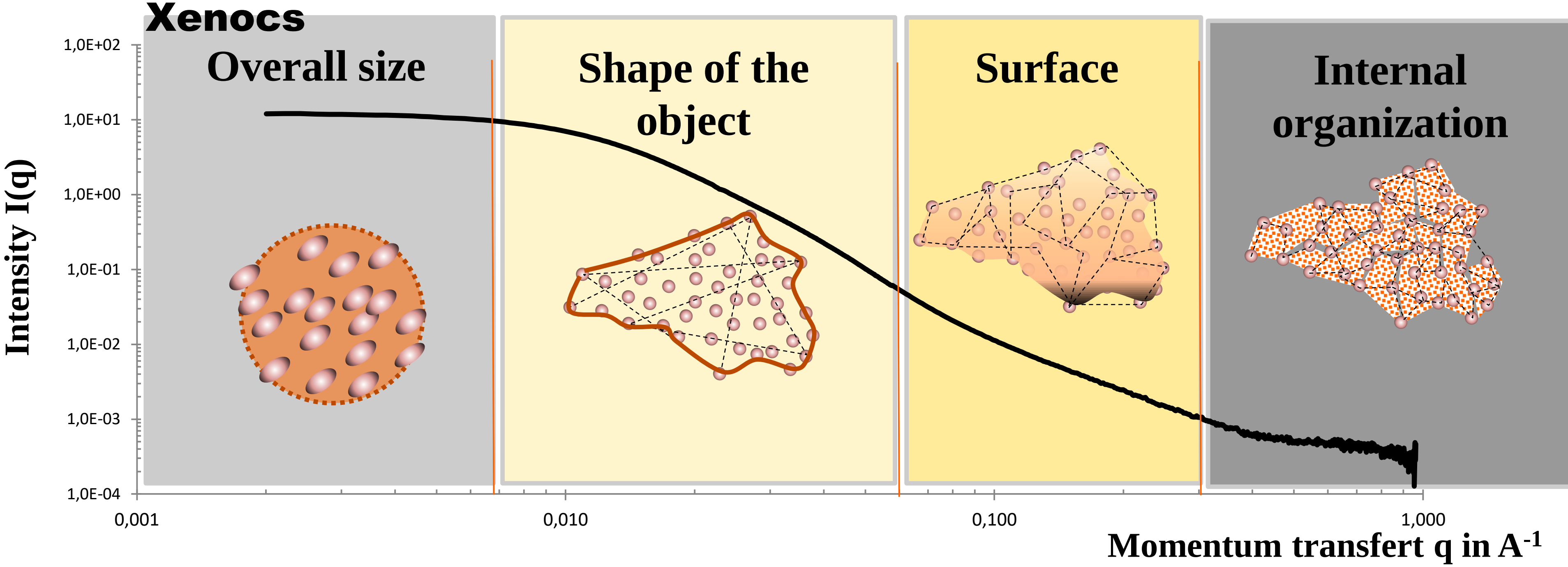
Caractérisation de la structure

SAXS



$$q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

From Xenocs



➕ Sonde l'organisation de la matière sur une grande gamme d'échelle de taille jusqu'à la centaine de nm

⚠ Analyse et modélisation des courbes de diffraction délicate

Interfacial phenomena

SAXS : Small Angle X ray Scaterring

Toulouse Occitanie

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