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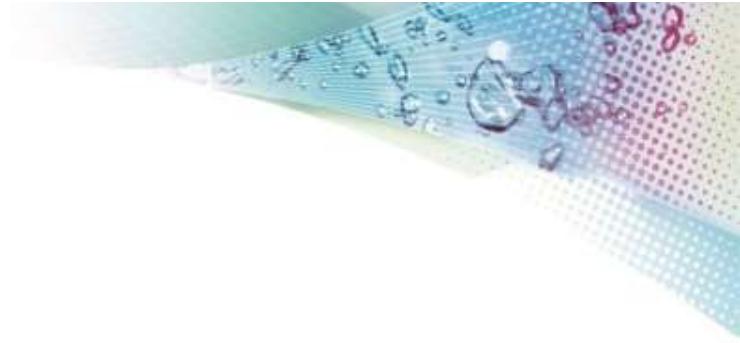
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PAUL SABATIER

# **Physicochemical hydrodynamics: colloidal suspensions and separation processes**

Yannick Hallez & Patrice Bacchin (LGC-UT3)

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[patrice.bacchin@univ-tlse3.fr](mailto:patrice.bacchin@univ-tlse3.fr)



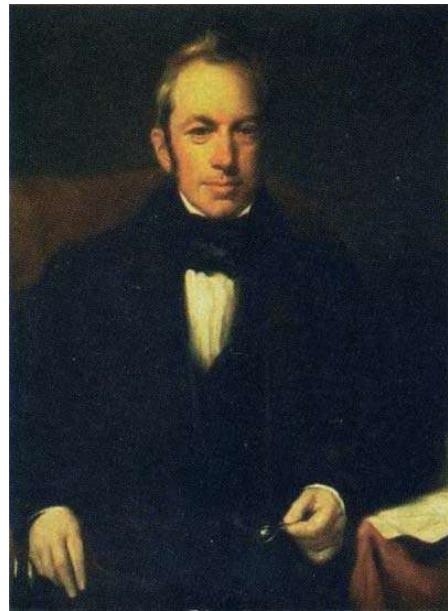
# CHAPTER 1

## What are colloids?

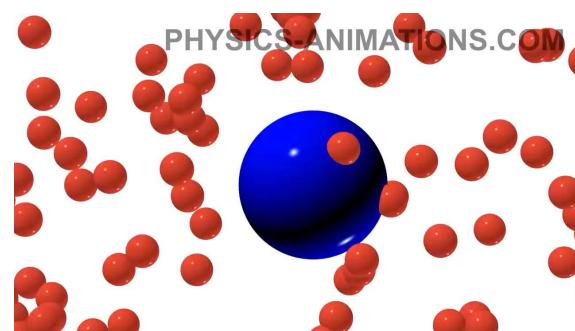
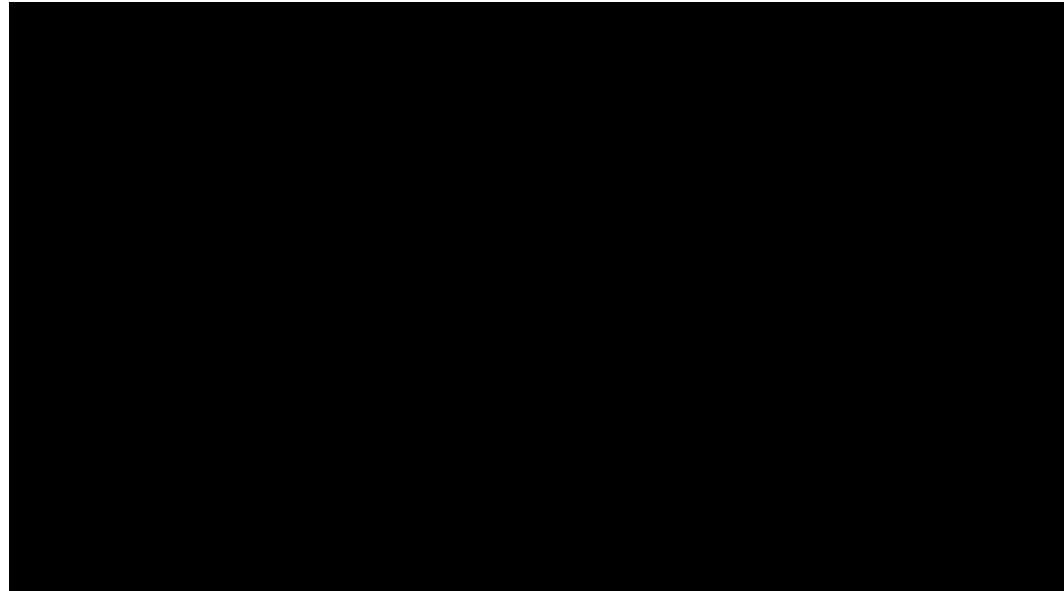


# Diffusion

Microscopic mechanism: thermal agitation also called « Brownian motion »

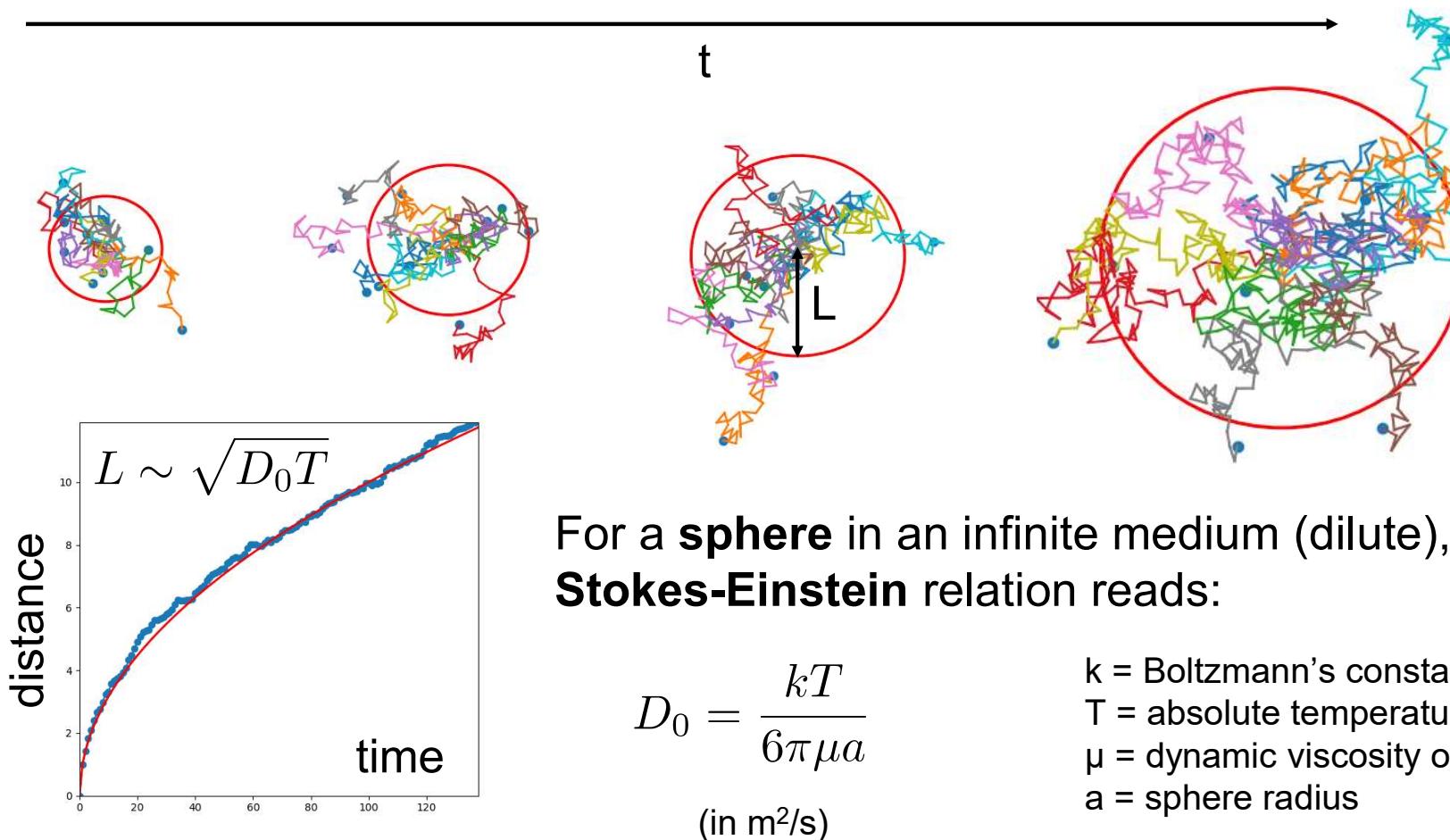


Robert Brown  
(1773-1858)



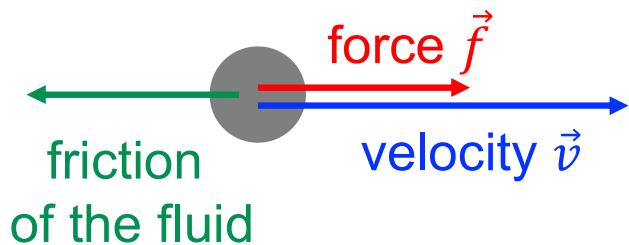
# (Self-) Diffusion in the dilute regime

A simple microscopic model: the random walk (drunkard's walk)



# Migration

Matter can move because of an external force field.



$$\vec{v} = \gamma \vec{f}$$

$\gamma$  = mobility, depends on the size and shape of the object, of the fluid viscosity...

For a **small or slow sphere of radius  $a$**  (actually, for  $\text{Re} < 1$ )

$$\gamma = \frac{1}{6\pi\mu a}$$

Example 1: electrophoresis

$$f = qE \longrightarrow v = \frac{qE}{6\pi\mu a}$$

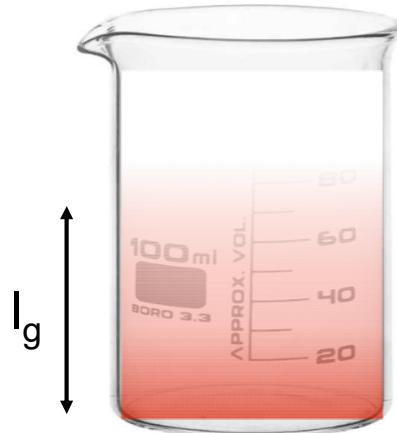
Electrophoretic drift velocity

Example 2: sedimentation

$$f = \frac{4}{3}\pi a^3 \Delta\rho g \longrightarrow v = \frac{2a^2 g \Delta\rho}{9\mu}$$

Stokes sedimentation velocity

# (Self-) Diffusion Vs. sedimentation



Particles experiences sedimentation with a flux

$$j_{\text{sed}} = -n v_{\text{sed}}$$

where  $n$  is the particle number density (number / m<sup>3</sup>). So a concentration gradient tends to form. Diffusion thus sets in with a flux

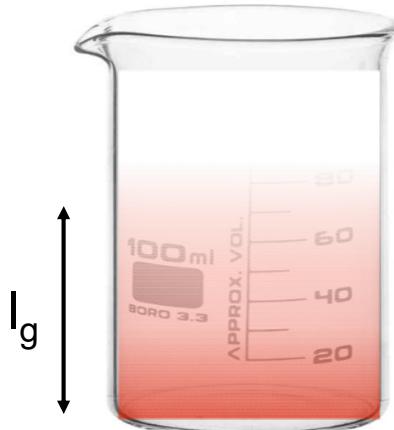
$$j_{\text{diff}} = -D_0 \frac{dn}{dz}$$

At equilibrium, fluxes are equal and opposite. The solution is

$$n(z) = n_0 e^{-z/l_g} \quad \text{where } l_g = \frac{kT}{V_p \Delta \rho g} \quad \text{is the sedimentation length}$$

(Jean Baptiste Perrin's Nobel prize in 1926)

# (Self-) Diffusion Vs. sedimentation

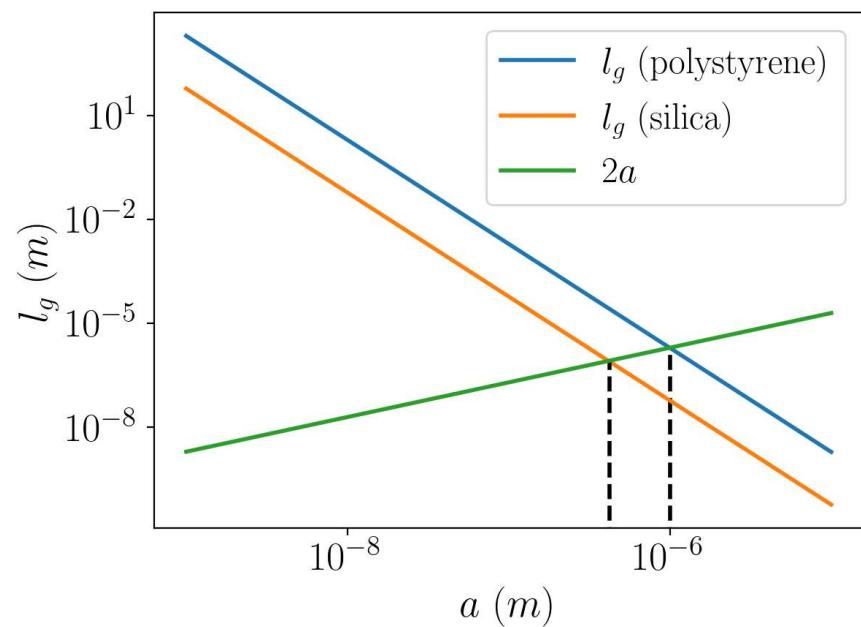


$$l_g = \frac{kT}{V_p \Delta \rho g}$$

Very small/light objects have a large sedimentation length. In order to observe equilibrium,  $l_g$  must be at least a few particle diameters.

Comparison between  $l_g$  and  $2a$  for polystyrene ( $\rho=1050 \text{ kg/m}^3$ ) and silica ( $\rho=2650 \text{ kg/m}^3$ ) spheres in water ( $\rho=1000 \text{ kg/m}^3$ ).

**Sedimentation-diffusion equilibrium exists only for objects smaller than  $\sim 1 \mu\text{m}$ , so-called colloids.**



# What are colloids?

## What is a colloid?

IUPAC (International Union of Pure and Applied Chemistry): *supramolecular entities whose extension in at least one spatial direction lies between 1 nm and 1 μm.*

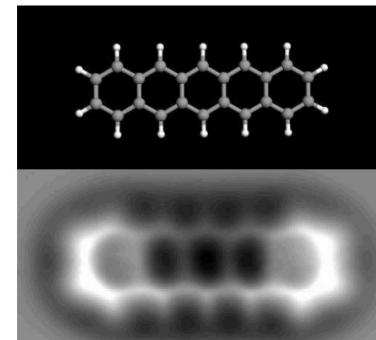
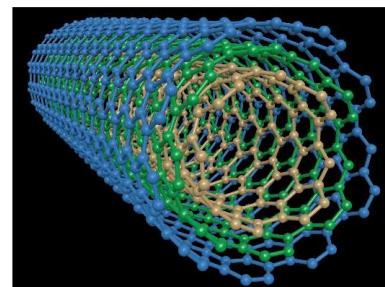
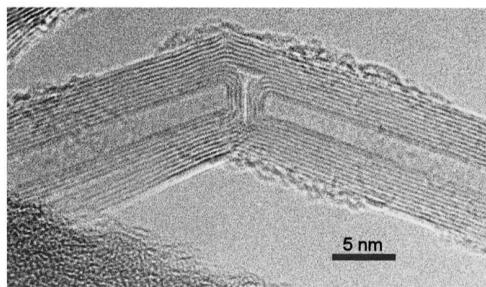
They are objects large enough not to be considered as molecules, but small enough to feel thermal agitation.

## What is *not* a colloidal dispersion or suspension?

- A solution: molecules in a liquid state, feel thermal agitation, not large enough to be considered continuous objects.
- A (non-colloidal) suspension: objects are large enough for thermal forces to be negligible compared to other forces (size  $> 1 - 10 \mu\text{m}$ ).

# Quiz

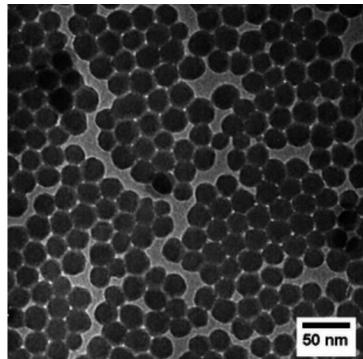
Carbon nanotubes



Pentacene  
molecule  
( $C_{22}H_{14}$ )

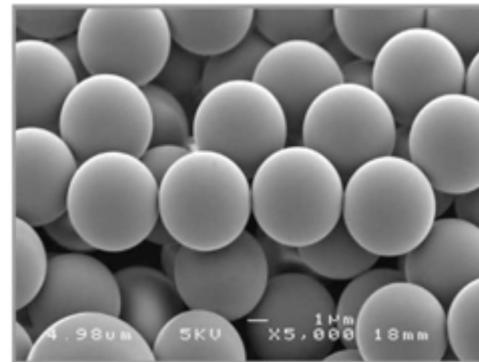
(AFM image from IBM)

Silica spheres



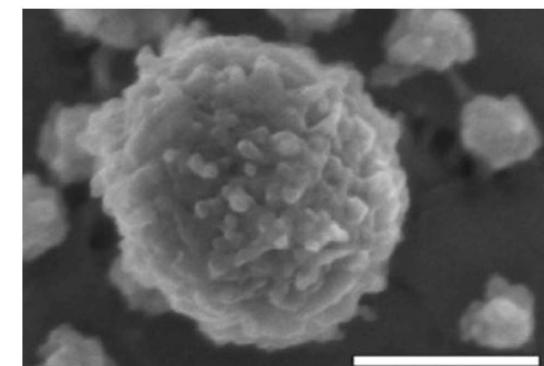
Jang & Lim. Chemical Communications (2006)

Latex microspheres



(Thermo Scientific)

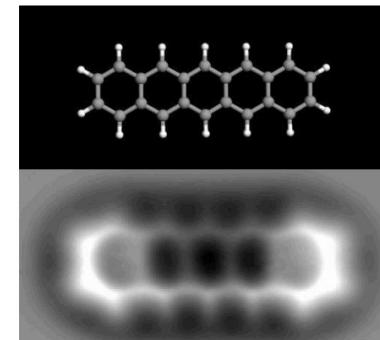
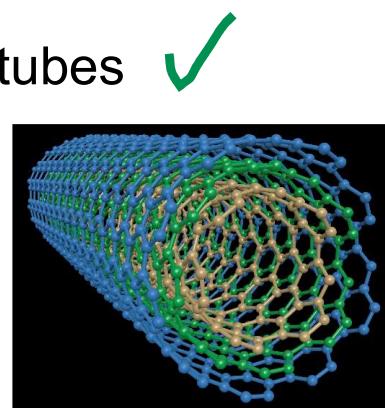
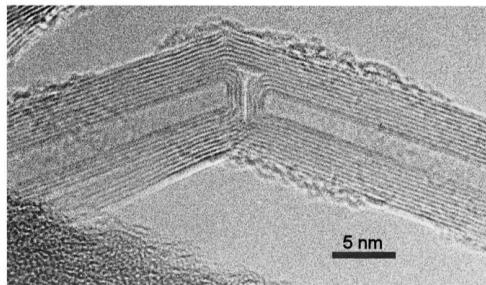
Casein micelle (50-600 nm)



(Hristov et al., Milk Proteins - From Structure  
to Biological Properties and Health Aspects, 2016)

# Quiz

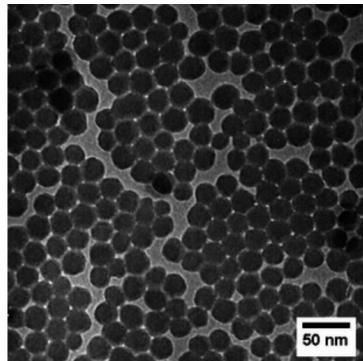
Carbon nanotubes ✓



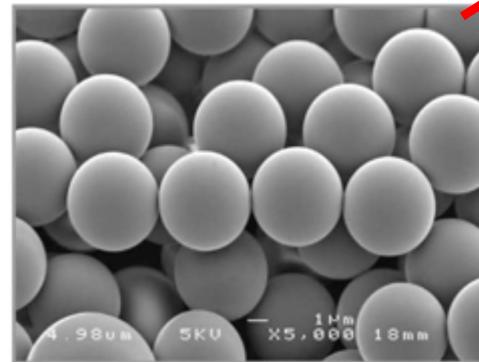
Pentacene  
molecule  
( $C_{22}H_{14}$ ) ✗

(AFM image from IBM)

Silica spheres ✓



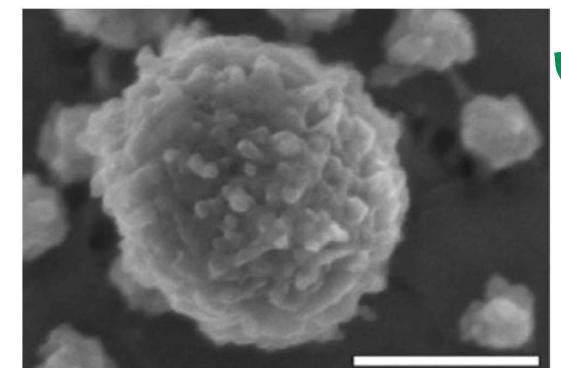
Latex microspheres ✗



(Thermo Scientific)

Jang & Lim. Chemical Communications (2006)

Casein micelle (50-600 nm) ✓



(Hristov et al., Milk Proteins - From Structure  
to Biological Properties and Health Aspects, 2016)

# Different natures of colloids

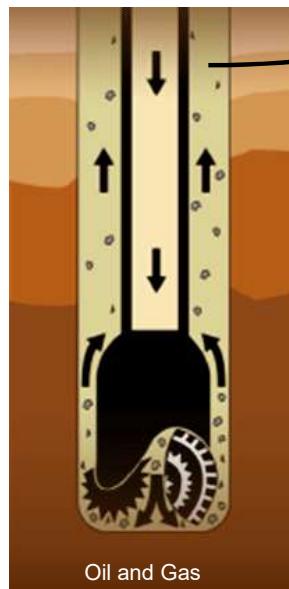
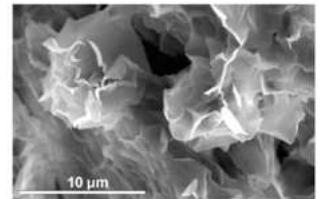
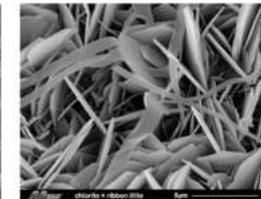
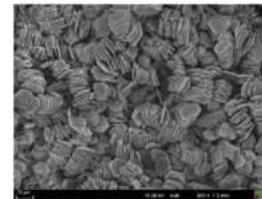
Media	Particle	Type	Natural	Technique
liquid	solid	sol	superficial water	ink, paint
liquid	liquid	emulsion	milk	oil
liquid	gas	foam	sparkling water	Fire extinguishers
Gas	solid	aerosol	smoke	Pharmaceutical to inhale
Gas	liquid	aerosol	cloud	insecticide
solid	solid	alloy	wood, bone	Composite materials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

Colloids are involved in a lot of natural and industrial processes

# Engineering w/ colloids examples: drilling fluids



kaolinite, chlorite-illite, and smectite (montmorillonite)

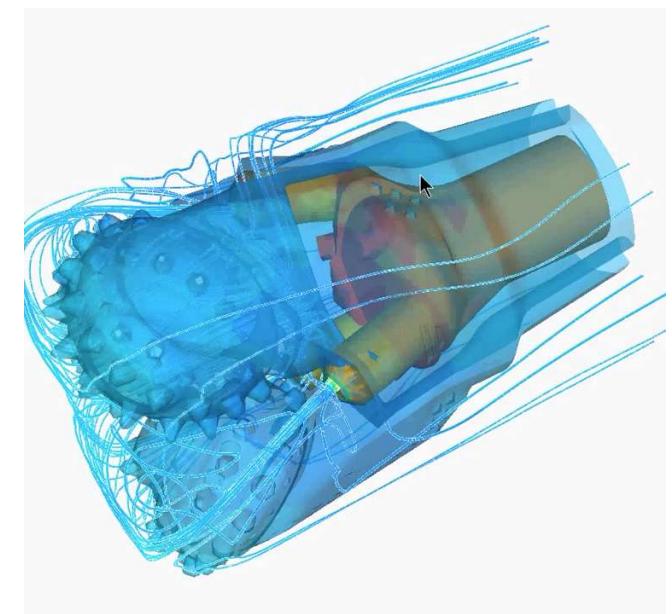
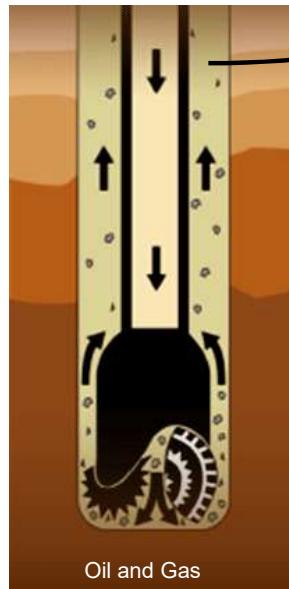
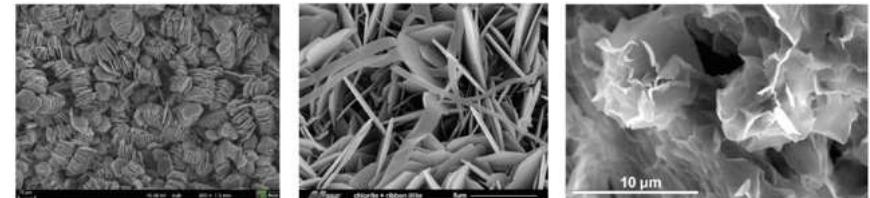


Drilling fluids can represent from  
15 to 18% of the total cost  
of well drilling but may cause  
100% of drilling problems  
[Alcazar-Vara Cortes-Monroy]

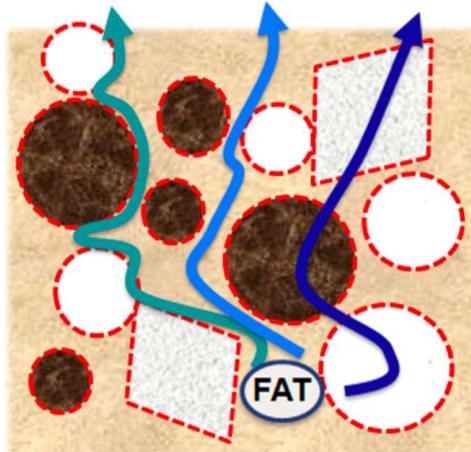
# Engineering w/ colloids examples: drilling fluids



kaolinite, chlorite-illite, and smectite (montmorillonite)



# Engineering w/ colloids examples: chocolate tempering



Continuous network  
of particles:

- Cocoa solids
- Sucrose
- Milk powder
- Lecithin

Continuous fat phase:



Cocoa butter

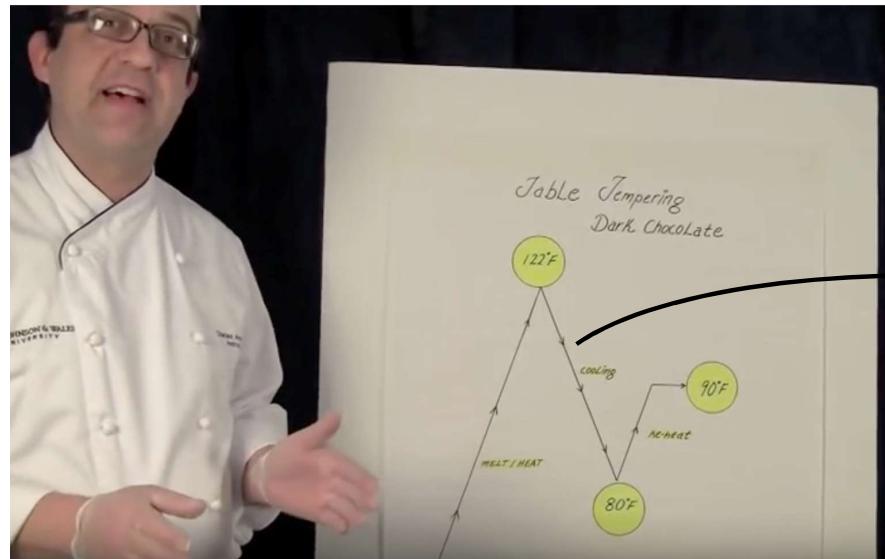
Reinke et al., ACS applied materials & interfaces, 2015

- Change of visual aspect
- Change of internal structure
- Change of melting temperature
- Change of rheological properties



Fat blooming

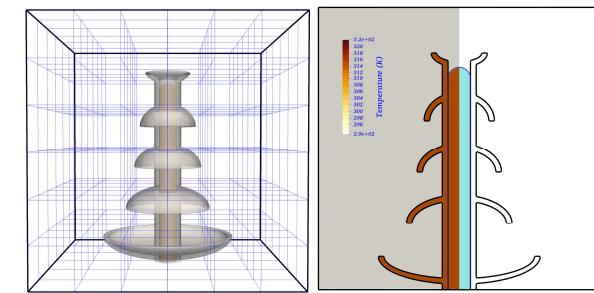
# Engineering w/ colloids examples: chocolate tempering



Chocolate tempering



Change of visual aspect  
Change of internal structure  
Change of melting temperature  
Change of rheological properties



# Engineering w/ colloids examples: water filtration

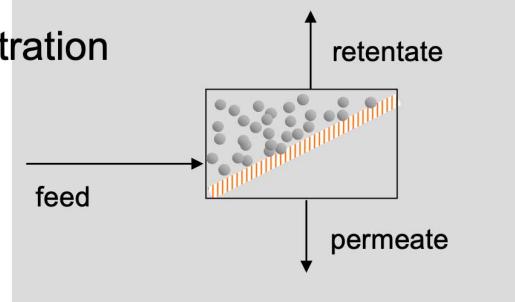
Fluides et Procédés /A7N7 / P. Bacchin

## Interfacial phenomena

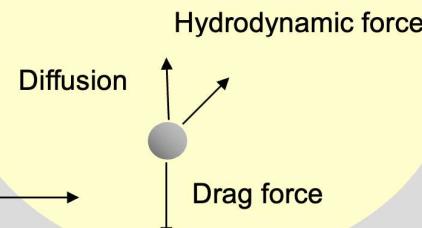


A new kind of complexity in a process

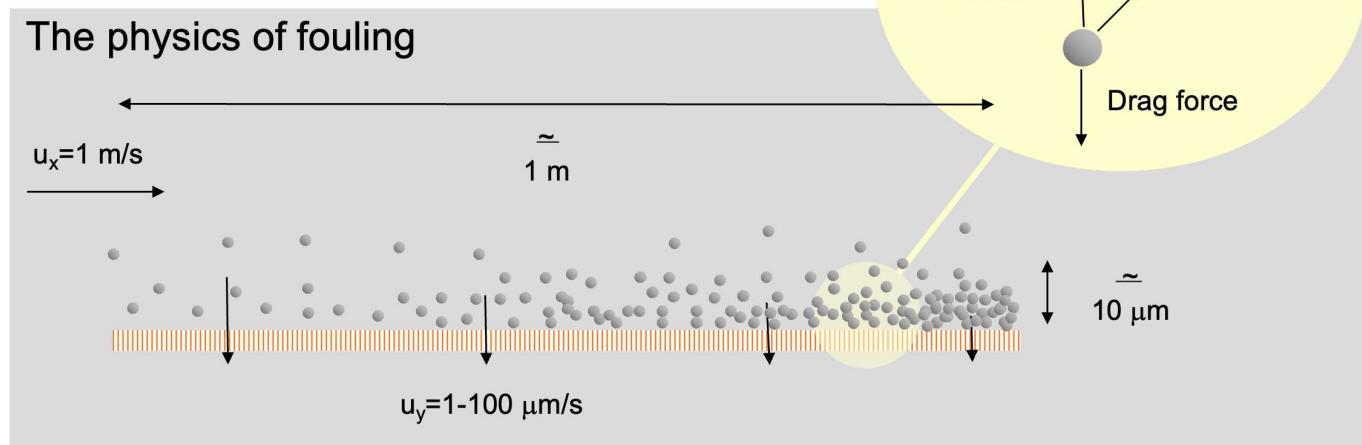
Example with filtration



Classically a force balance between :



The physics of fouling

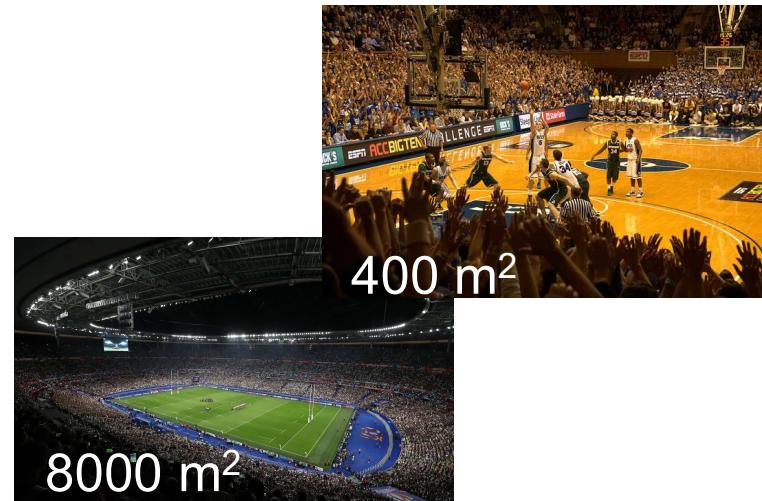


## OK but what's new! 😊

Let's compute the quantity of interface in 1L of colloidal suspension. Assume 1% volume fraction, and sphere radii 1  $\mu\text{m}$ , 100 nm, and 10 nm.



Radius	Surface area
1 $\mu\text{m}$	30 $\text{m}^2$
100 nm	300 $\text{m}^2$
10 nm	3000 $\text{m}^2$

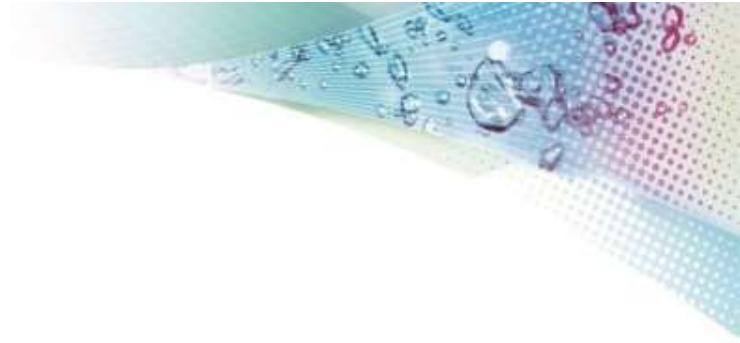


### ⚠ Specific colloidal characteristic ⚠

Intercolloidal forces are often mediated by their surface and the surface area per unit volume is very large, so the macroscopic suspension properties (structure, thermodynamics, rheology...) depend strongly on colloidal interactions.



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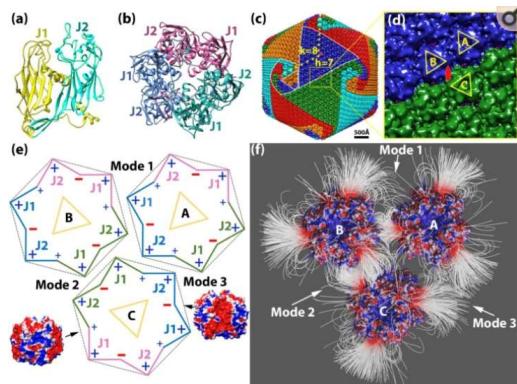
## CHAPTER 2

# Electrostatic interactions



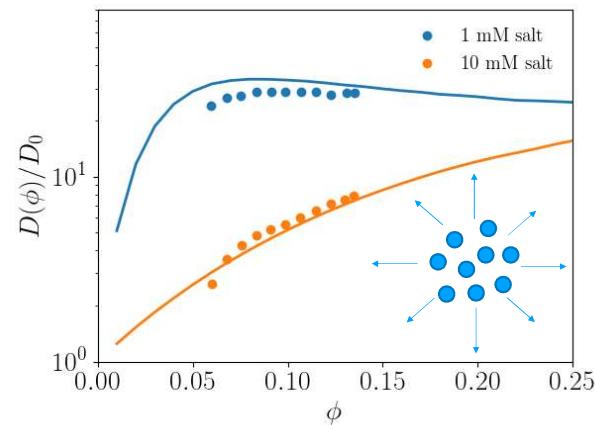
# Large scale signature of electrostatic interactions

Biophysics: protein recognition,  
viral capsid self-assembly...



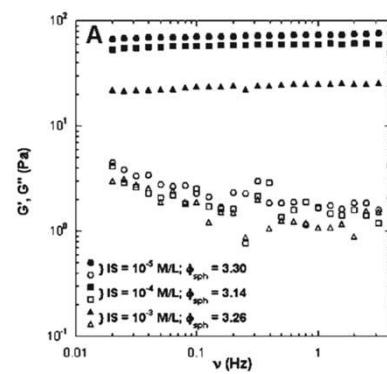
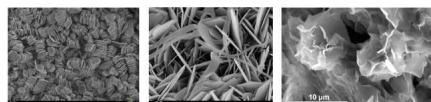
Xian et al., Int. J. Mol. Sci. 2019

Transport properties:  
collective diffusion coefficient...

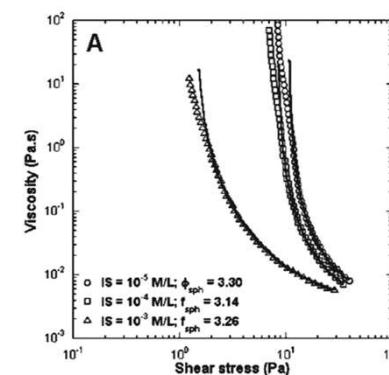


Keita et al., PRE, 2021

Rheology:  
viscosity, yield stress...



Paineau et al,  
Langmuir, 2011



# Where do electric charges come from?

## Origin of the surface charge

- Structural charges: uncompensated charges at boundaries and isomorphic substitution (e.g.  $\text{Si}^{4+} \longleftrightarrow \text{Al}^{3+}$ ). Example: Laponite (synthetic clay)
- Ionizable group whose form depends on the pH (charge regulation). Example: e.g.  $-\text{OH}$  can become  $-\text{OH}_2^+$  or  $-\text{O}^-$ .
- Specific ion adsorption on the surface, leading to inner sphere complexes (no water between ion and colloid surface) or outer sphere complexes (ion keeps some water from its hydration shell).

# Where do electric charges come from?

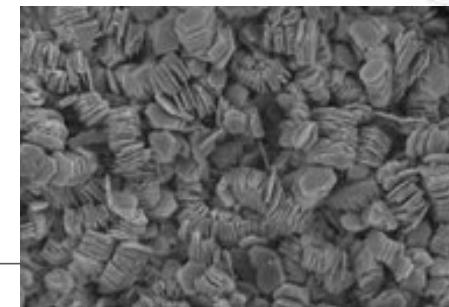
Example of structural charge and ionizable groups:



www.MaterialsViews.com

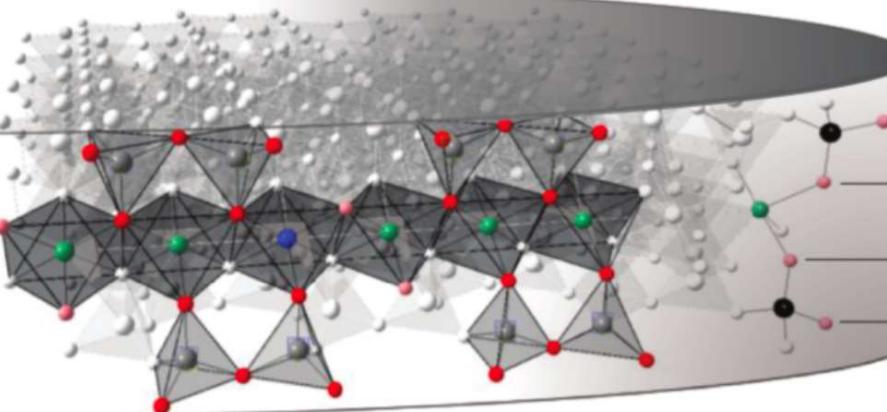
## Clay: New Opportunities for Tissue Regeneration and Biomaterial Design

Jonathan I. Dawson\* and Richard O. C. Oreffo\*



Permanent negative surface charge

6O <sup>2-</sup>	-12
4Si <sup>4+</sup>	16
8O <sup>2-</sup>	-16
5Mg <sup>2+</sup> , 1Li <sup>1+</sup>	11
4OH <sup>-</sup>	-4
4Si <sup>4+</sup>	16
6O <sup>2-</sup>	-12
<b>Net</b>	<b>-1</b>



pH dependent edge charge  
(positive <pH9)

- OH
- OH<sup>1/2+</sup>
- OH<sup>1/2+</sup>
- OH

**Figure 3.** a) Smectites (here, the synthetic hectorite Laponite,  $[(\text{Si}_8 \text{Mg}_{5.5} \text{Li}_{0.3}) \text{O}_{20}(\text{OH})_4]^{-0.7}$ ) possess a permanent negative surface charge arising from isomorphic substitutions in the crystal structure and a pH dependent edge charge from unsatisfied valences in the disrupted crystal lattice.

# Where do electric charges come from?

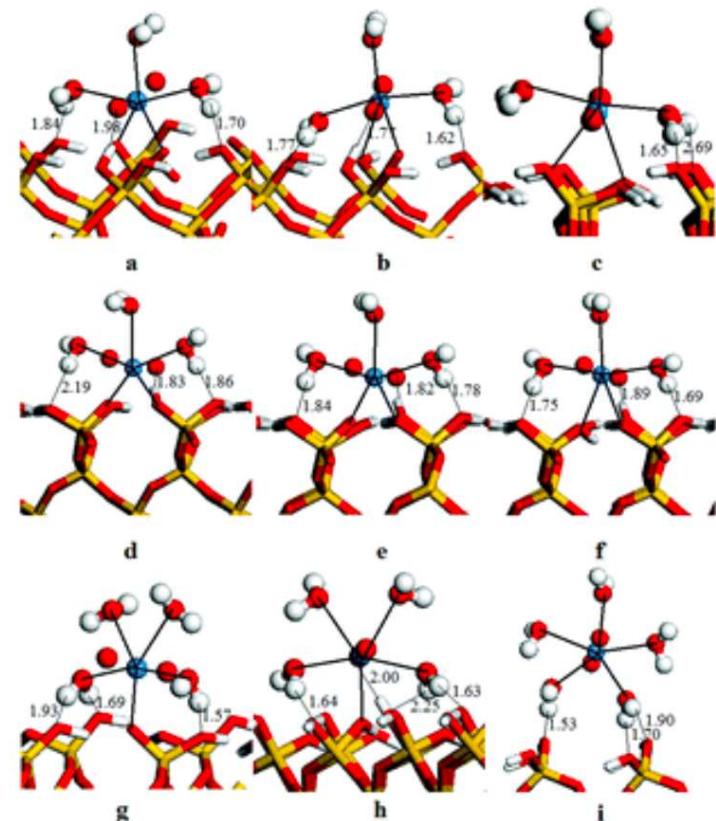
Example of ion adsorption ( $\text{UO}_2^{2+}$  on silica):

DOI: [10.1039/C4DT02872D](https://doi.org/10.1039/C4DT02872D) (Paper) *Dalton Trans.*, 2015, 44, 1646-1654

## Adsorption of uranyl on hydroxylated $\alpha\text{-SiO}_2(001)$ : a first-principle study†

Hui Wang <sup>a</sup>, Zhifang Chai <sup>ab</sup> and Dongqi Wang <sup>\*a</sup>

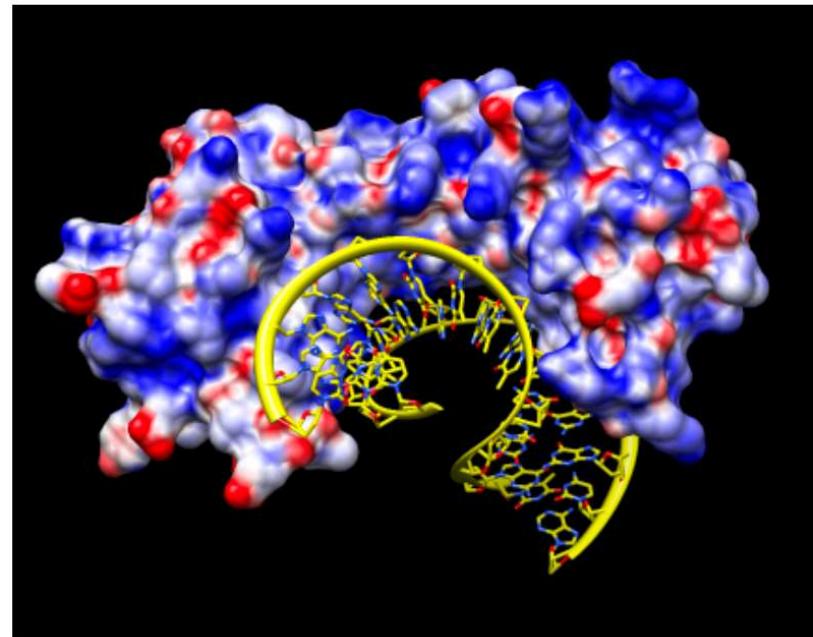
Fig. 1 Optimized adsorption structures of uranyl adsorbed on the hydroxylated  $\alpha\text{-SiO}_2(001)$  surface. Inner-sphere: bidentate complex (a)  $\text{SiOO}$ , (b)  $\text{SiOOH}$ , (c)  $\text{SiOHOH}$ , (d)  $\text{SiO-SiO}$ , (e)  $\text{SiO-SiOH}$ , (f)  $\text{SiOHSiOH}$ ; monodentate complex (g)  $\text{SiO}$ , (h)  $\text{SiOH}$ . Outer-sphere complex (i). Color scheme: U (blue), O (red), Si (orange), H (white).



# Where do electric charges come from?

Surface charges are not always uniform.

Example of the DNA binding protein 1qna:

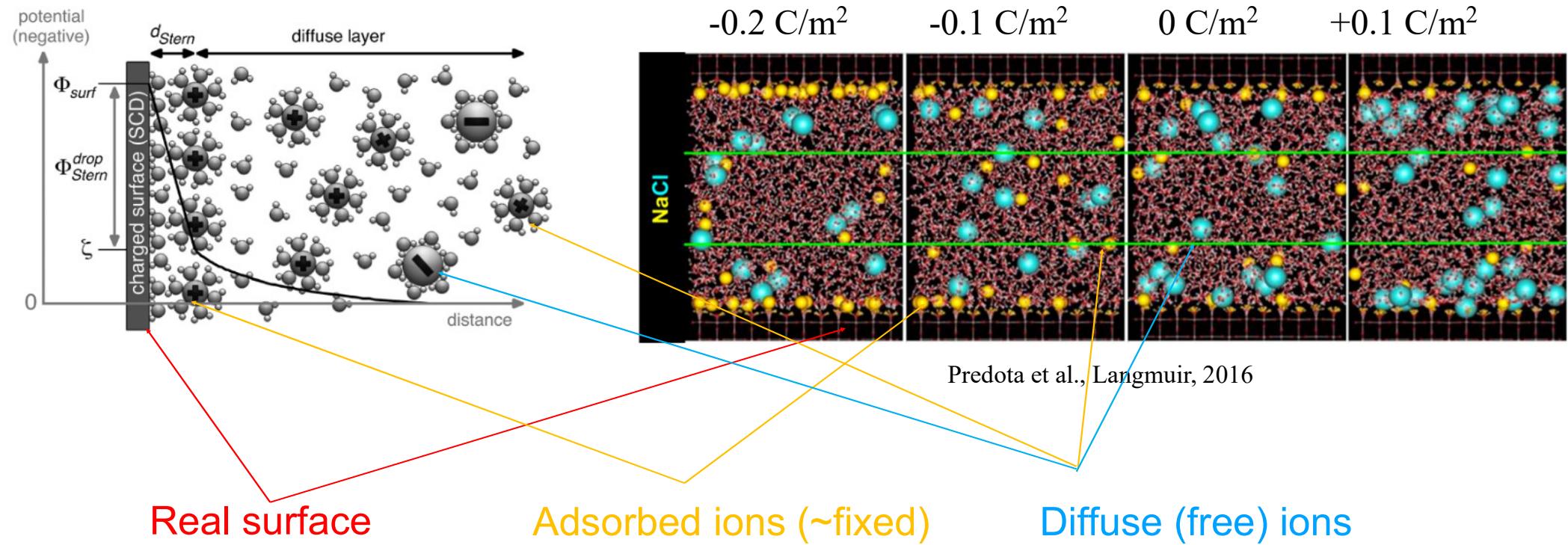


Blue for positive potential, red for negative potential.

<https://www.cgl.ucsf.edu/chimera/data/tutorials/maps08/exercises.html>

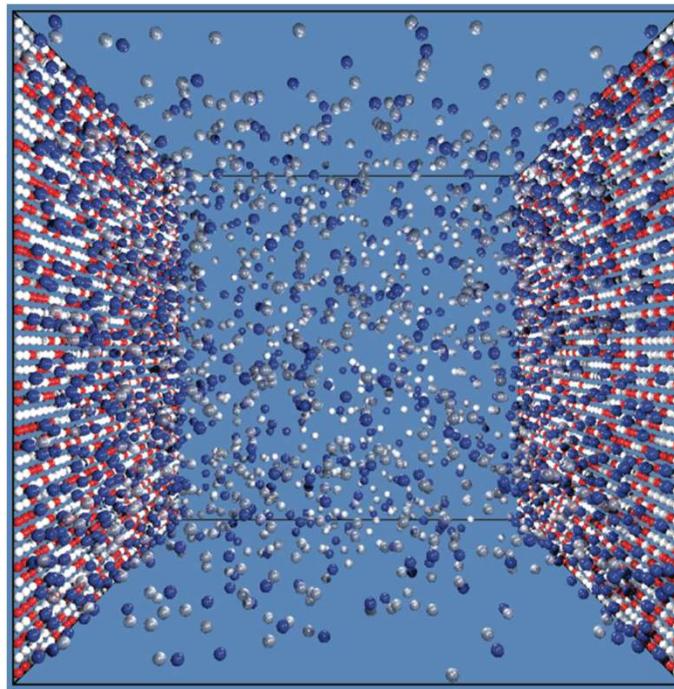
# The smallest scale: surfaces, solvent, charged species

## The electrical double layer (EDL)



For all practical purposes, this requires simplification !

## The primitive model: get rid of the solvent



Labbez et al., Langmuir, 2009

The primitive model: solvent is a continuous medium with permittivity  $\varepsilon$ .

# Electrostatics in the primitive model

The electric field is given by the Poisson equation:

$$\nabla \cdot (\epsilon \mathbf{E}) = \rho_f \longrightarrow \left\{ \begin{array}{l} \text{“fixed” surface charges} \\ \text{and} \\ \text{mobile ions} \end{array} \right.$$

It derives from a potential:

$$\mathbf{E} = -\nabla \Phi$$

$$\rho_f(\mathbf{x}, t) \quad !$$
$$\Phi(\mathbf{x}, t)$$

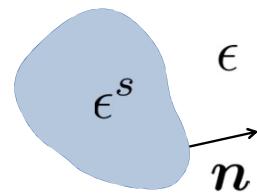
so

$$\nabla \cdot (\epsilon \nabla \Phi) = -\rho_f$$

A priori  $\epsilon$  and the charge density can vary in space, be discontinuous...

At an interface between two continuous media:

$$(\epsilon \mathbf{E} - \epsilon^s \mathbf{E}^s) \cdot \mathbf{n} = \sigma$$



## Electrostatics in the primitive model

Exercise:

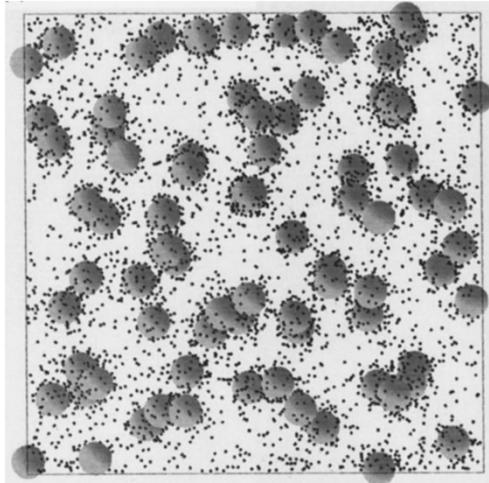
Compute the potential field generated by a charge  $Q$  located at  $r=0$ .

# The primitive model in practice

Well known Coulomb interactions

⚠️ Multiple species, so a lot of degrees of freedom

## Computer simulations



Linse & Lobaskin,  
PRL 1999, J. Chem. Phys. 2000

Can we simplify again?

Yes and No

## Theory

Statistical physics, multicomponent  
Ornstein-Zernike equation...

$$Z = \int_{r_\alpha}^{r_\beta} \int \int \dots \int_{2N} \exp\left[-\left(\sum_i u_{pi} + \sum_{i>j} u_{ij}\right)/kT\right] d\mathbf{r}_1 \dots d\mathbf{r}_N$$

$$h_{i,j}^s(r) = c_{i,j}^s(r) + \sum_{k=1}^n c_{i,k}^s(r) * h_{k,j}^s(r)$$

often needs further approximations,  
not unlikely to end up on a computer

## Electrostatics in the weak coupling limit: the idea

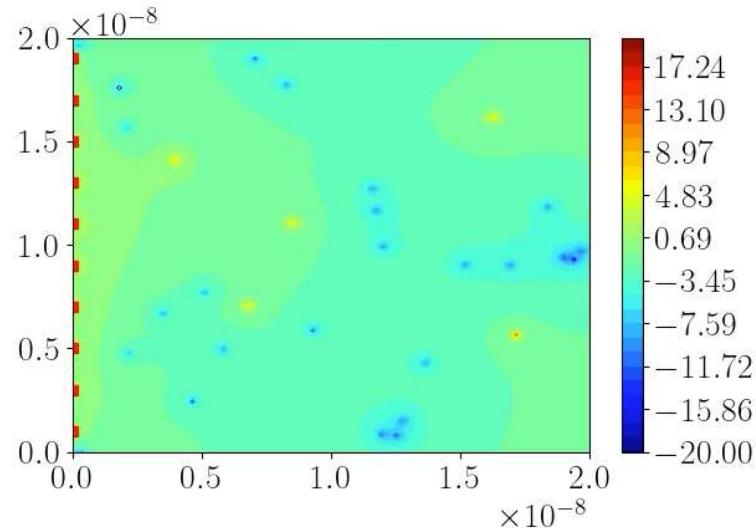
Ions are dilute, so they respond to the **mean electrostatic potential** and not to direct pair interactions

$$\mu^\pm(\mathbf{x}) = kT \ln n^\pm(\mathbf{x}) \pm e\Psi(\mathbf{x})$$

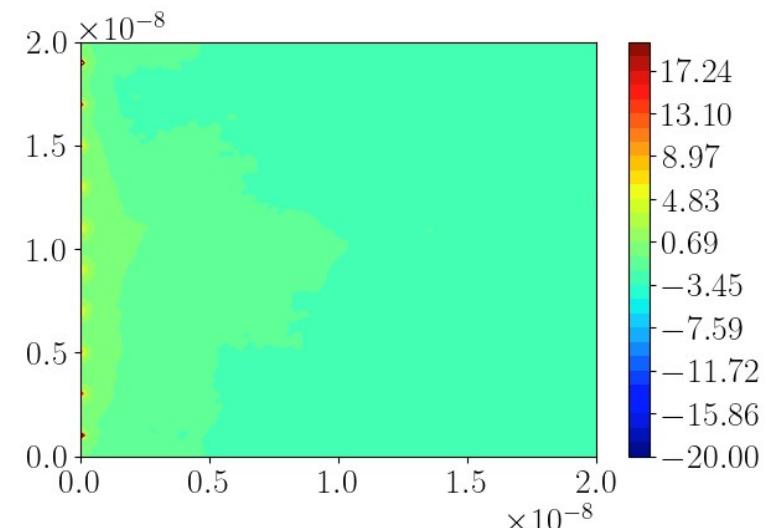
$$\Psi(\mathbf{x}) = \langle \Phi(\mathbf{x}, t) \rangle_t$$



Instantaneous potential  $\Phi(\mathbf{x}, t)$



Mean potential  $\Psi(\mathbf{x})$



## Electrostatics in the weak coupling limit: the idea

Ions are dilute, so they respond to the **mean electrostatic potential** and not to direct pair interactions

$$\mu^\pm(\mathbf{x}) = kT \ln n^\pm(\mathbf{x}) \pm e\Psi(\mathbf{x})$$

$$\Psi(\mathbf{x}) = \langle \Phi(\mathbf{x}, t) \rangle_t$$



Adiabatic hypothesis: ions are always in thermodynamic equilibrium  $\longrightarrow \nabla \mu^\pm = \mathbf{0}$

Define some reference ion density as

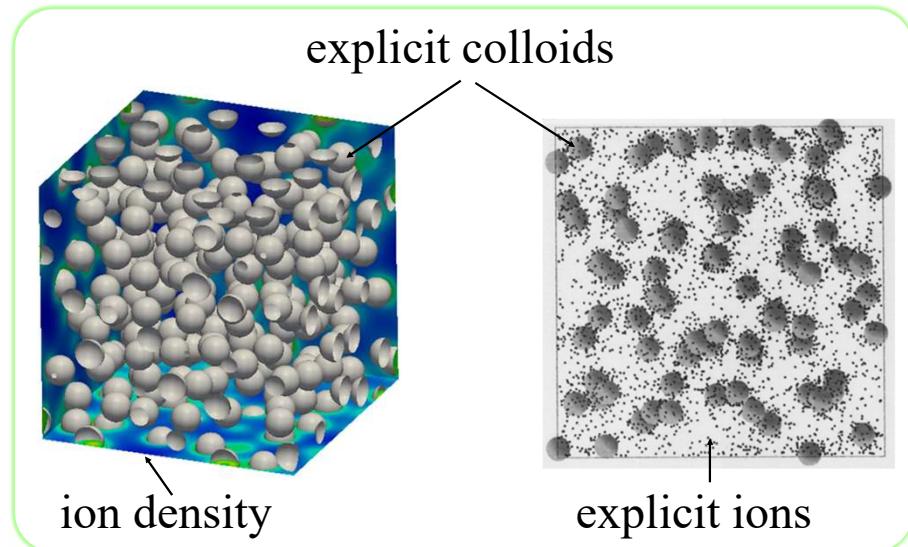
$$\mu^\pm = kT \ln n_0 \pm e \times 0$$

so we get the Boltzmann distribution:

$$n^\pm = n_0 e^{\mp\psi}$$

with

$$\psi = \frac{e\Psi}{kT}$$



# The Poisson-Boltzmann theory

Volume charge density in the fluid:  $\rho_f = en^+ - en^- = -2n_0e \sinh \psi$

The Poisson equation becomes the Poisson-Boltzmann (PB) equation:

$$\nabla \cdot (\epsilon \nabla \Psi) = 2n_0e \sinh \psi$$

Assuming uniform dielectric constant in the fluid...

$$\nabla \cdot (\nabla \psi) = \frac{2n_0e^2}{\epsilon kT} \sinh \psi$$

Length scale of potential gradients (Debye length):

$$\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon kT}{2n_0e^2}}$$

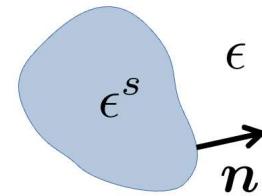
PB equation:

$$\Delta \psi = \kappa^2 \sinh \psi$$

# Boundary conditions

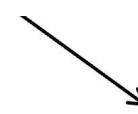
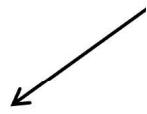
Possible boundary conditions:

$$(\epsilon \mathbf{E} - \epsilon^s \mathbf{E}^s) \cdot \mathbf{n} = \sigma$$



in general

$$(\epsilon \nabla \psi - \epsilon^s \nabla \psi^s) \cdot \mathbf{n} = \sigma(\psi)$$



Constant Charge (CC)

$\sigma \sim \text{const.}$  from weak chemistry-electrostatics coupling.

Constant Potential (CP)

$\sigma(\psi)$  from chemistry-electrostatics coupling such that  $\psi \sim \text{const.}$  on the surface.

Charge Regulation (CR)

$\sigma(\psi)$  from chemistry-electrostatics coupling

# Calculation of the Debye length for monovalent salts

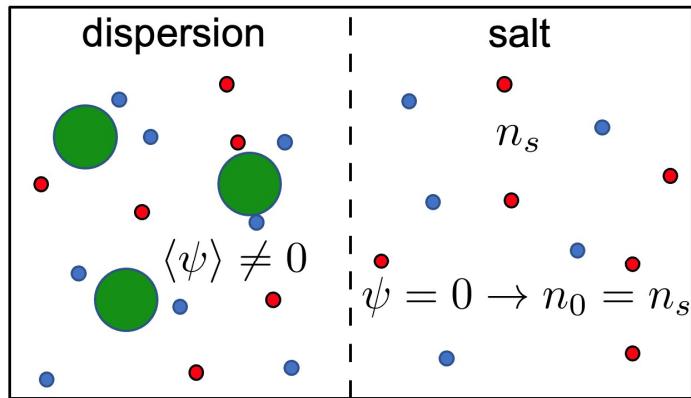
Different expressions for the Debye length?

$$\Delta\psi = \kappa^2 \sinh \psi$$

with

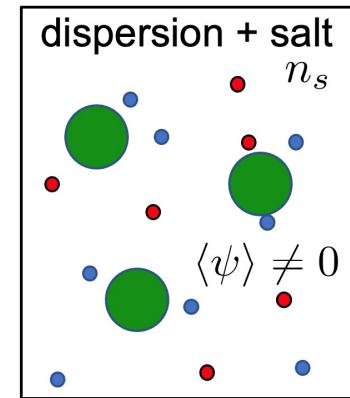
$$\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon kT}{2n_0 e^2}}$$

Donnan equilibrium



$$\lambda_D = \sqrt{\frac{\epsilon kT}{2n_s e^2}}$$

Closed suspension



$$\lambda_D = \sqrt{\frac{\epsilon kT(1 - \phi)\langle\cosh\psi\rangle_e}{(\rho Z_c + 2n_s)e^2}}$$

## Calculation of the Debye length for multivalent salts

For multiple ion species  $i$ , with valency  $z_i$  and concentration at zero potential  $c_i$  (mol/L):

Compute the **ionic strength**:  $I = \frac{1}{2} \sum_i z_i^2 c_i$

**Generalization of the Debye length** is  $\lambda_D = \sqrt{\frac{\epsilon k T}{2 \times 1000 N_a I \times e^2}}$



Valid only in dilute suspensions, Valid only for monovalent counterions

Exercise:

1. Compute  $\lambda$  for 0.01 mol/L solutions of 1:1, 2:1, and 3:1 electrolytes in the salt reservoir.
2. Suggest how these values can be adapted to other temperatures or media without complete recalculation.
3. In water at room temperature, a useful formula is  $\lambda = 0.304/\sqrt{I}$ , where  $\lambda$  will be in nm and  $I$  must be given in mol/L. Prove this formula from the most general one above.

## Example of Poisson-Boltzmann solution for a flat plate

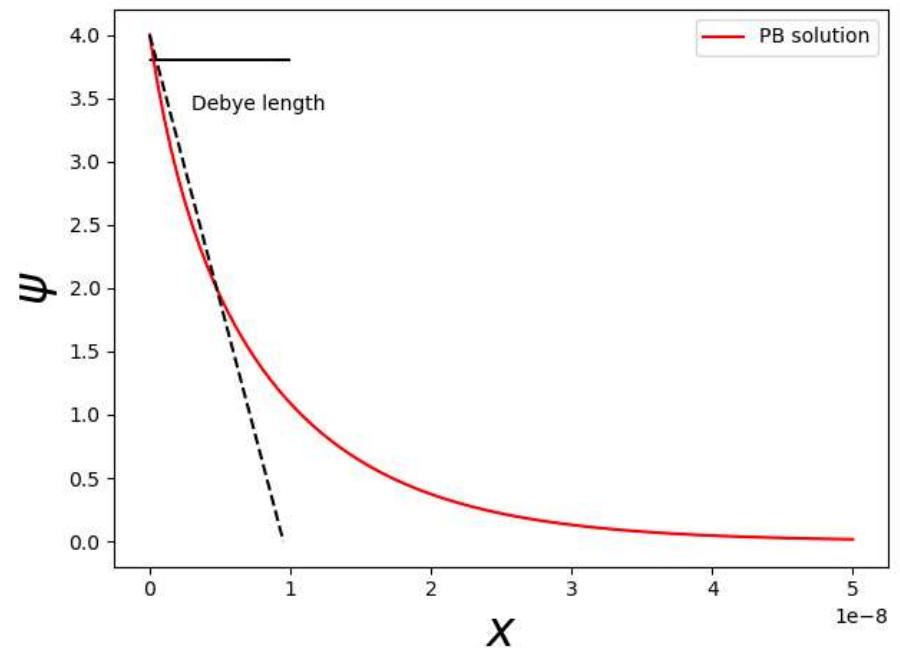
Solution for a flat plate with surface potential  $\psi_s$ :

$$\psi(x) = 2 \ln \left\{ \frac{1 + e^{-\kappa x} \tanh(\frac{\psi_s}{4})}{1 - e^{-\kappa x} \tanh(\frac{\psi_s}{4})} \right\}$$

And the surface charge density – surface potential relation is:

$$\sigma = 2\sqrt{2n_0\epsilon kT} \sinh(\psi_s/2)$$

(Grahame equation)



# The Debye-Hückel theory

Poisson-Boltzmann theory:

$$\Delta\psi = \kappa^2 \sinh \psi$$

$$\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon kT}{2n_0 e^2}}$$

Debye and Hückel proceeded to linearize this equation. Technically, linearization is only valid if  $\psi \ll 1$ , however, being practically minded Debye and Hückel linearized first and worried about the consequences later.

Yan Levin, in Braz. J. Phys. 2004

At low potentials...  $\sinh \psi \simeq \psi + \dots$

The Debye-Hückel (DH) equation:

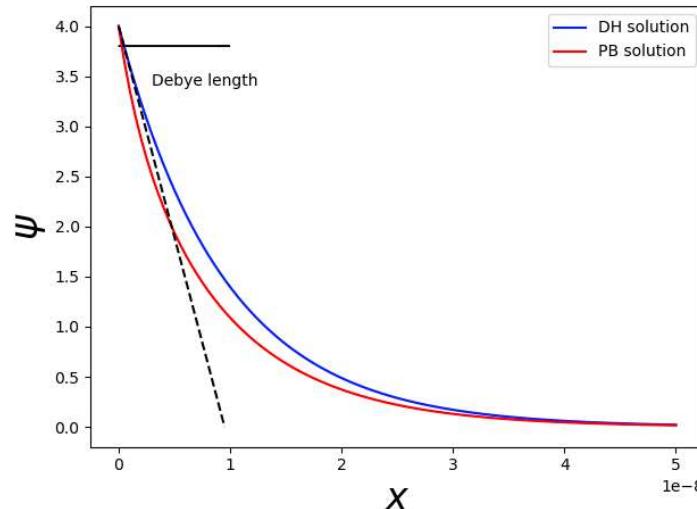
$$\Delta\psi = \kappa^2 \psi$$

$$n^\pm \simeq n_0(1 \mp \psi)$$

# The Debye-Hückel theory

Exercise:

Compute the DH solution for the potential field generated by a flat plate with fixed potential or fixed surface charge density.

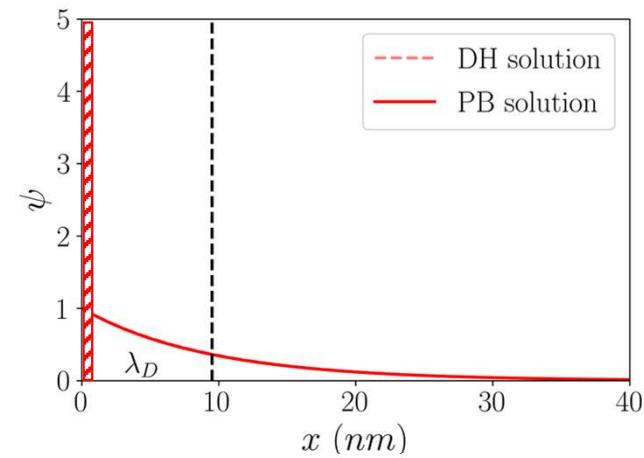


Exercise:

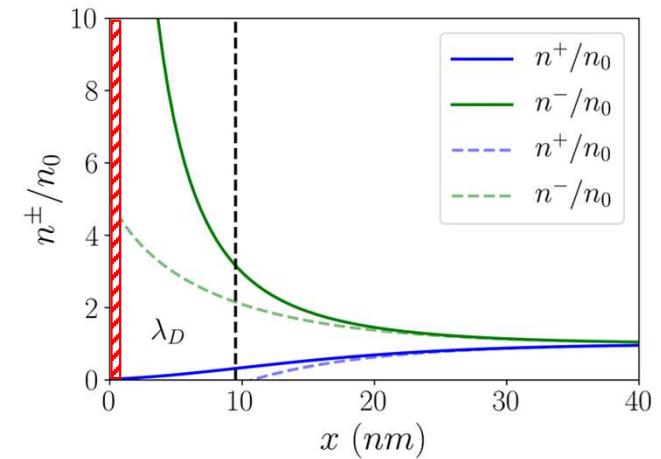
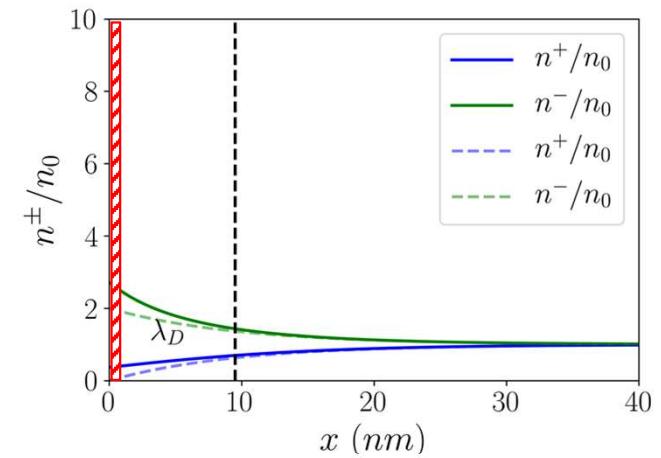
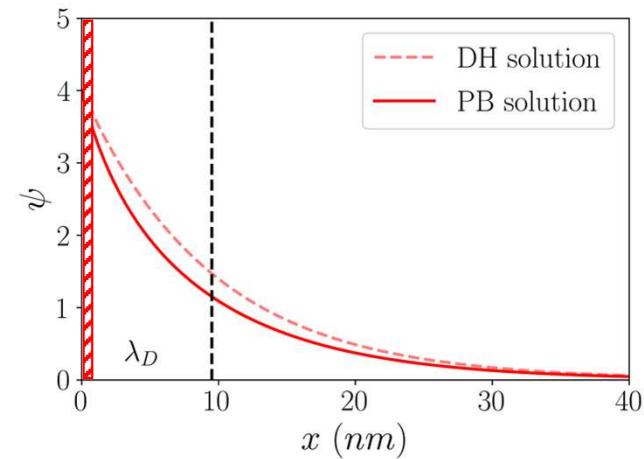
Compute the DH solution for the potential field generated by a sphere with fixed potential or fixed surface charge density. (Hint: replace  $f=r\psi$ )

# Poisson-Boltzmann theory Vs. Debye-Hückel theory

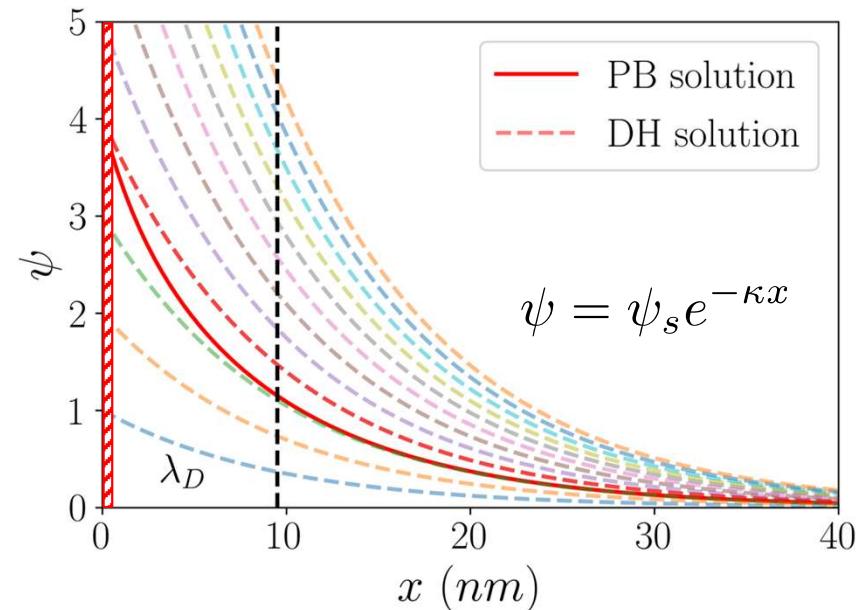
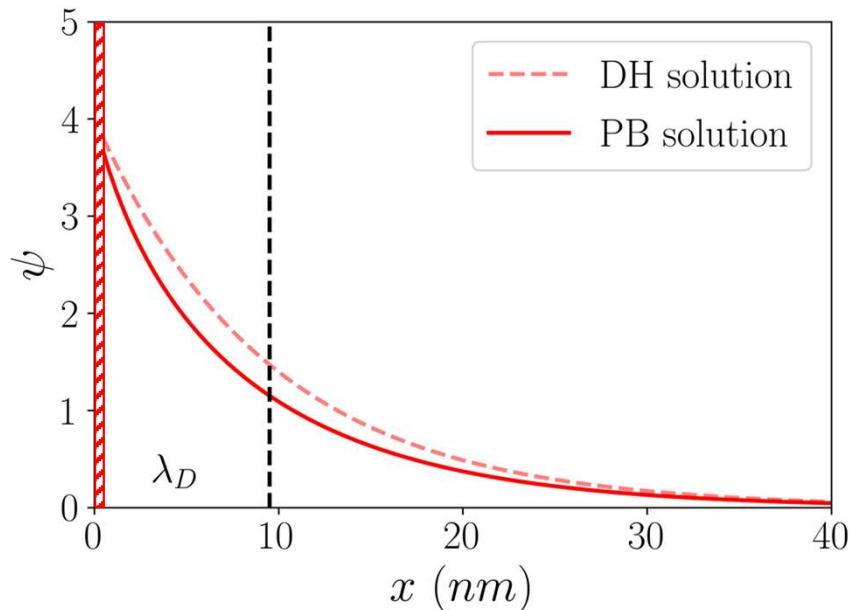
$$\Psi_s = 25 \text{ mV}$$



$$\Psi_s = 100 \text{ mV}$$



# Renormalization and effective charges or potentials



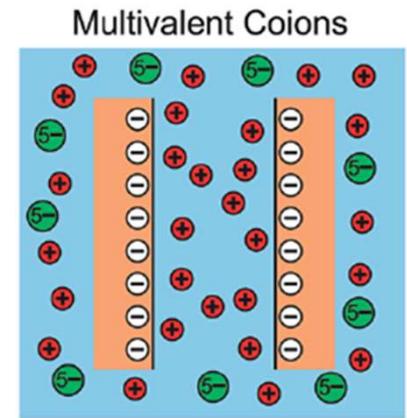
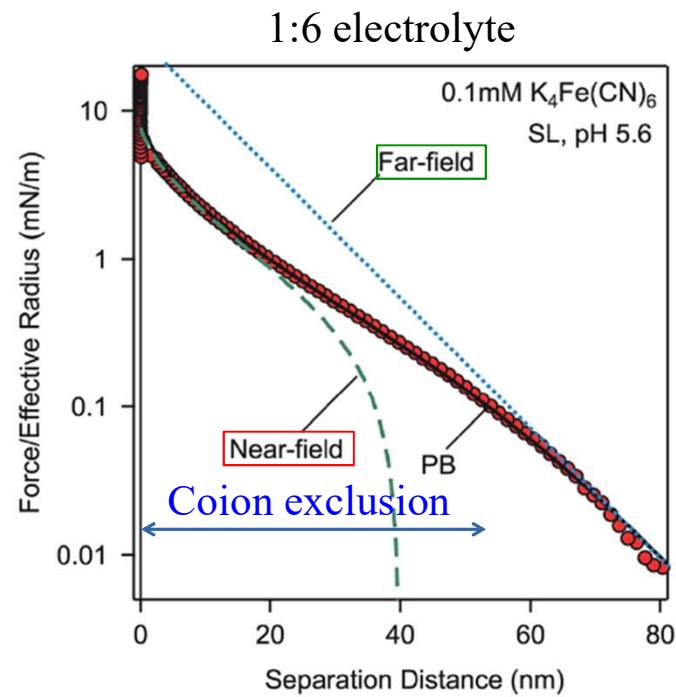
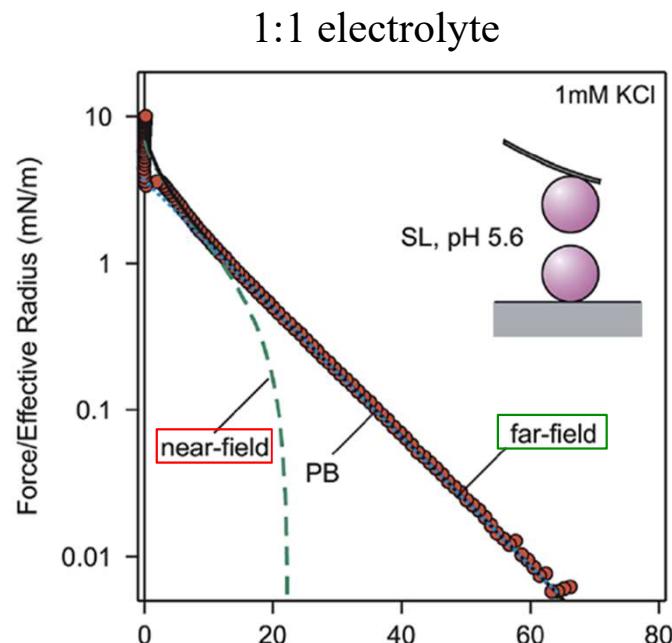
## Renormalization: PB → DH\* mapping

- Redefine boundary conditions:  
**Effective surface charge/potential**
- Redefine screening length if  $\langle \psi \rangle \neq 0$   
**Effective screening length**

**Example: pressure between 2 flat plates at distance  $h \gg \lambda_D$**

$$\left. \begin{aligned} \psi(h/2) &\simeq 2\psi_{\text{eff}} e^{-\kappa h/2} \\ \Pi &\simeq 4n_0 kT \psi_{\text{eff}}^2 e^{-\kappa h} \end{aligned} \right\} \text{from DH theory}$$

# Interaction potentials at arbitrary charge (PB): renormalization



Far field, weak overlap (DH\*)

$$\Pi \simeq 4n_0 kT \psi_{\text{eff}}^2 e^{-\kappa h}$$

$$\psi_{\text{eff}} = \begin{cases} \psi_s & \text{for } \psi_s \ll 1 \\ \alpha & \text{for } \psi_s \gg 1 \end{cases}$$

Near field, salt free behavior (PB)

$$\Pi \simeq \frac{2\pi^2 \epsilon}{\beta^2 e^2} \frac{1}{h^2} \quad (\text{at high charge and large separation})$$

Ruiz-Cabello et al., Soft Matter 2015

# True or Effective surface charge/potentials: summary

At **low true** surface potential ( < 50 mV, almost never happens ):      true = effective

At **high true** surface potential ( > 50 mV, almost always the case ):

- Use **true** surface charge/potential with the **PB theory**
- Use **effective** surface charge/potential with the **DH theory**

## Measurement

**True surface charge density** is measured by titration with an acid / a base.

**True surface potential** is measured by electrophoresis using the Smoluchowski model (equivalent to PB theory).

**Effective surface potential** is measured by electrophoresis using the Debye model (equivalent to DH theory).

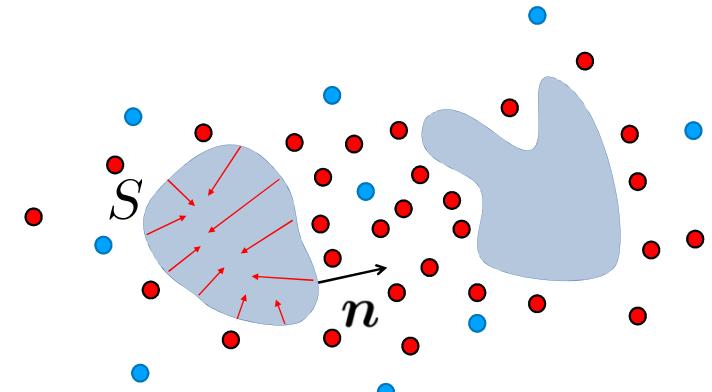
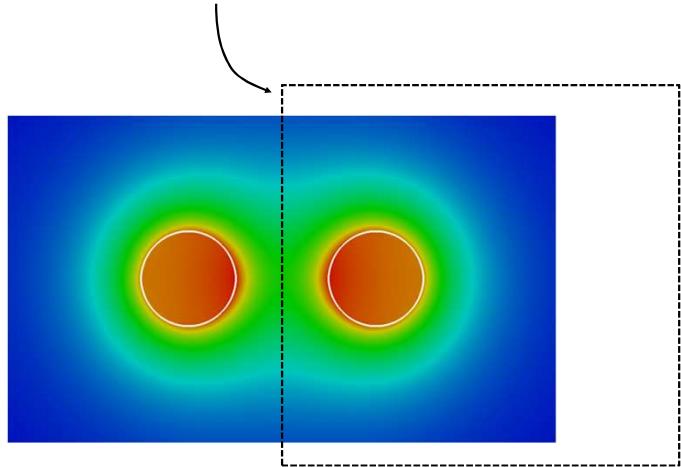
# From electric potential (in V) to interaction potential (in J).

From the excess osmotic stress tensor

$$\tau = -2n_0 kT (\cosh \psi - 1) \mathbf{I} + \epsilon \left[ \mathbf{E} \otimes \mathbf{E} - \frac{1}{2} \mathbf{E}^2 \mathbf{I} \right]$$

Forces are obtained by integration

$$\mathbf{F} = \int_{\tilde{S}} \tau \cdot \mathbf{n} dS$$



Obtaining  $\psi$  analytically is impossible with PB

If we linearize PB, we can get the DLVO model at large distance:

$$\beta u(r) \simeq Z^2 l_B \left( \frac{e^{-\kappa a}}{1 + \kappa a} \right)^2 \frac{e^{-\kappa r}}{r}$$

## Electrostatic interactions between spheres: the Linear Superposition Approximation (LSA)

### Hypotheses

- Dilute suspension (EDL not overlapping too-much, only pair interactions).
- Based on DH theory, so use it only for low surface charge density or potential ( $\psi_s < 2$ , or  $\Psi_s \approx \zeta \lesssim 50\text{mV}$ ).

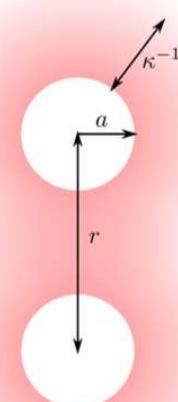
Interaction potential:

$$V = \epsilon \left( \frac{kT}{ze} \right)^2 4\pi \psi_s^2 a^2 \frac{e^{-\kappa(r-2a)}}{r} \quad \text{or} \quad V = 4\pi \frac{\sigma^2 a^4}{\epsilon(1+\kappa a)^2} \frac{e^{-\kappa(r-2a)}}{r}$$

Interaction force:

$$F = \epsilon \left( \frac{kT}{ze} \right)^2 4\pi \psi_s^2 \frac{1+\kappa r}{r^2} a^2 e^{-\kappa(r-2a)} \quad \text{or} \quad F = 4\pi \frac{\sigma^2 a^4}{\epsilon(1+\kappa a)^2} \frac{1+\kappa r}{r^2} e^{-\kappa(r-2a)}$$

$\psi_s$  is dimensionless,  $a$  is in  $m$ ,  $\sigma$  is in  $C/m^2$ ,  $V$  is in  $J$ ,  $F$  is in  $N$ .



## Electrostatic interactions between spheres: the Derjaguin approximation

Hypotheses (useful for any big colloid  $a > 100\text{ nm}$  in water at reasonable ionic force)

- Dilute suspension (EDL not overlapping too-much, only pair interactions).
- Thin EDL compared to the particle size ( $\kappa a \gg 1$ ).
- Small separation distance compared to particle size ( $r - 2a \ll a$ ).
- No restriction on the surface charge density or potential.

Interaction potential:

$$V = \epsilon \left( \frac{kT}{ze} \right)^2 32\pi a \tanh^2 \left( \frac{\psi_s}{4} \right) e^{-\kappa(r-2a)}$$

Interaction force:

$$F = \epsilon \left( \frac{kT}{ze} \right)^2 32\pi \kappa a \tanh^2 \left( \frac{\psi_s}{4} \right) e^{-\kappa(r-2a)}$$

