

Colloid and Surface Engineering

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Plan

1 Colloids

2 Aggregation

3 Electrokinetics

4 Operators

1 Colloids

- Introduction
- Colloidal interactions: electrostatics
- Van der Waals interactions

2 Aggregation

3 Electrokinetics

4 Operators

Definition

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.

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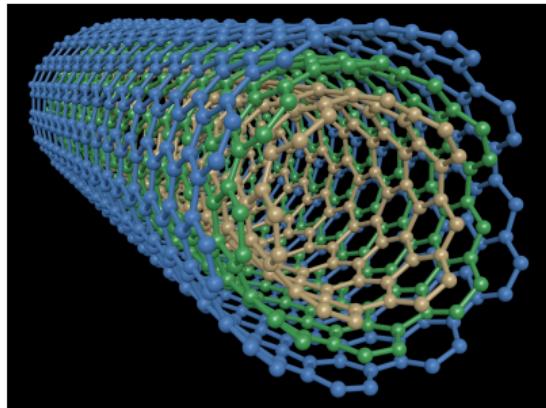
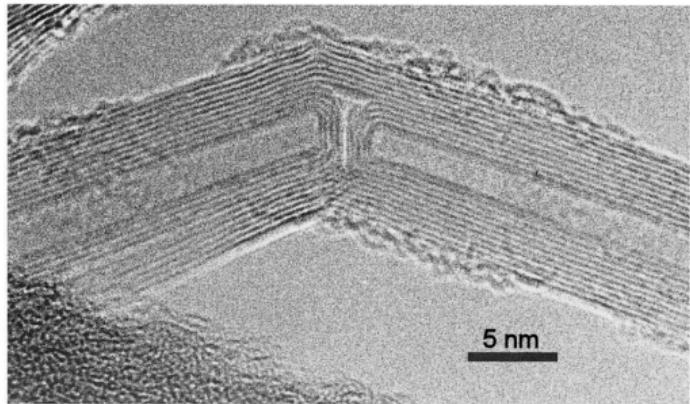
They are objects large enough not to be considered as molecules, but small enough to feel thermal agitation.

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 $> 1 - 10 \mu\text{m}$).

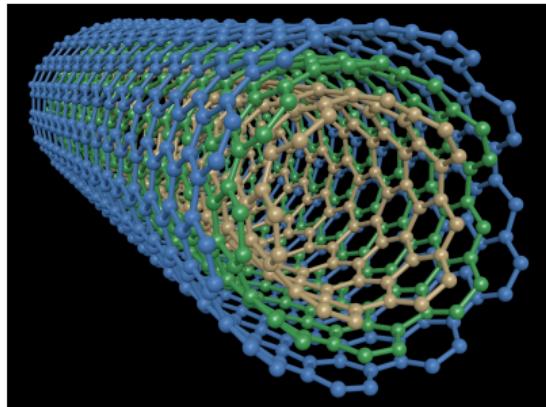
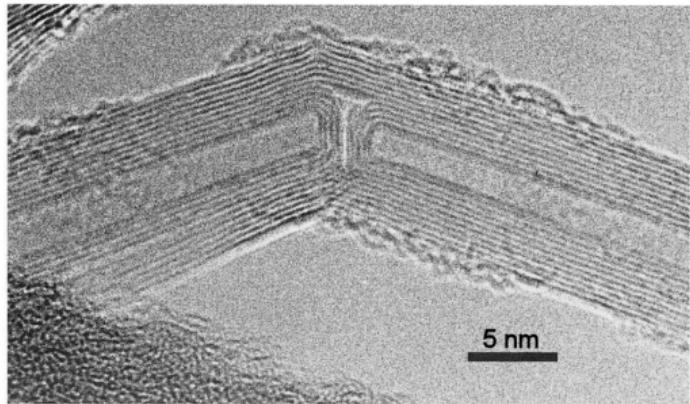
Examples

A carbon nanotube



Examples

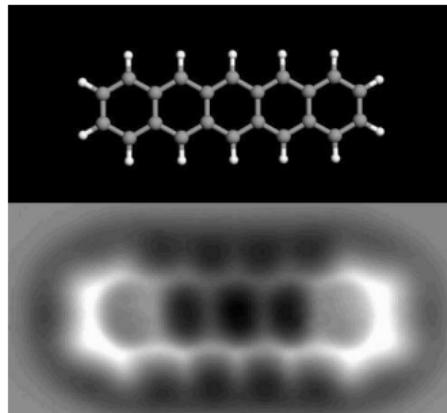
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Colloid !

Examples

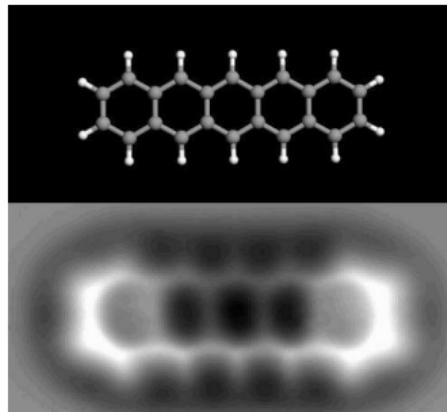
A pentacene ($C_{22}H_{14}$) molecule



(AFM image from IBM)

Examples

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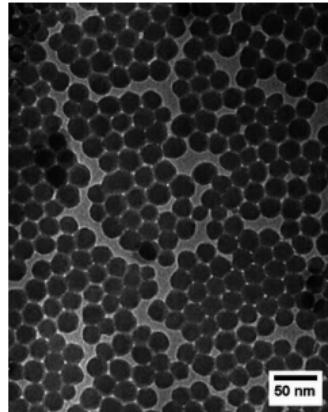


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Not colloid !

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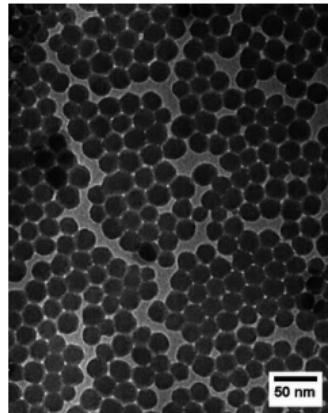
Silica particles grafted with polymers



Jang & Lim. Chemical Communications (2006)

Examples

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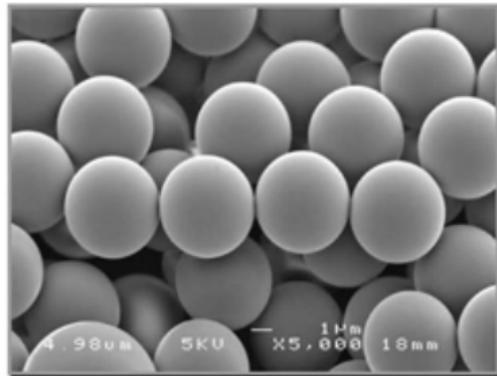


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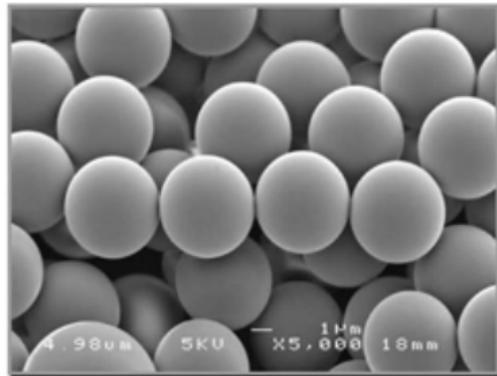
Latex micro-spheres



(Thermo Scientific)

Examples

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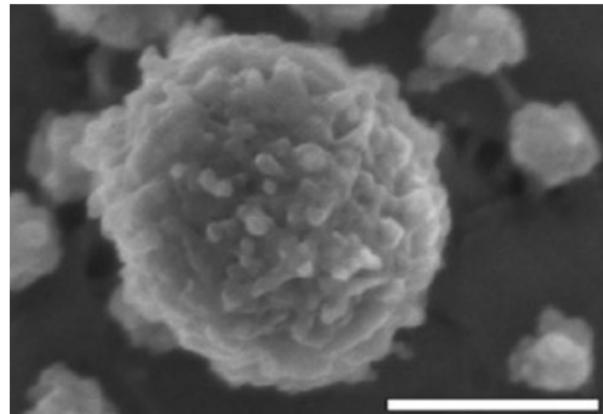


(Thermo Scientific)

Not colloid !

Examples

Casein micelle ($50 - 600 \text{ nm}$)

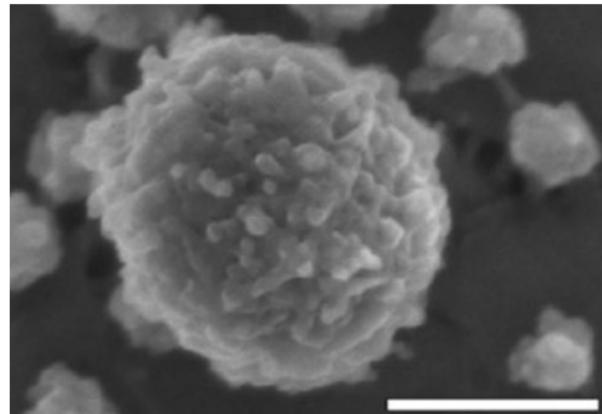


(Hristov et al., Milk Proteins - From Structure

to Biological Properties and Health Aspects, 2016)

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Colloid !

Remarkable properties

Their organization is very sensitive to interparticle forces, that are often surface forces

- electrostatic interactions
- van der Waals interactions
- solvent mediated interactions (hydrophilic/phobic)
- hydrodynamic interactions

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The colloid surface area per unit volume of suspension is huge!

- size $a \sim 10\text{ nm}$ induces a particle volume $V_p = (4/3)\pi a^3 \sim 10^3 \text{ nm}^3$
- consider a dilute dispersion with volume fraction $\phi = \frac{\text{colloid volume}}{\text{total volume}} = \frac{NVp}{V} \sim .001$
- the colloid number in one liter is then $N \sim 10^{18}$
- the total colloidal surface in one liter (specific surface area) is $S = 4\pi a^2 N \sim 100 \text{ m}^2 !$

Remarkable properties

Examples of specific surface area for $\phi = 1\%$ (still quite dilute):

Size	Specific surface area
$1 \mu m$	$10 m^2/L$
$100 nm$	$100 m^2/L$
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⚠ 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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Colloids often carry surface charges

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)

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- 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).

Colloids often carry surface charges

Example of structural charge and ionizable groups:

Materials
Views

www.MaterialsViews.com

ADVANCED
MATERIALS

www.advmat.de

Clay: New Opportunities for Tissue Regeneration and Biomaterial Design

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

Permanent negative
surface charge

6O ²⁻	-12	●
4Si ⁴⁺	16	●
8O ²⁻	-16	●
5Mg ²⁺ , 1Li ¹⁺	11	●
4OH ⁻	-4	●
4Si ⁴⁺	16	●
6O ²⁻	-12	●
Net	-1	

pH dependent edge charge
(positive <pH9)

- OH
- OH^{1/2+}
- OH^{1/2+}
- OH

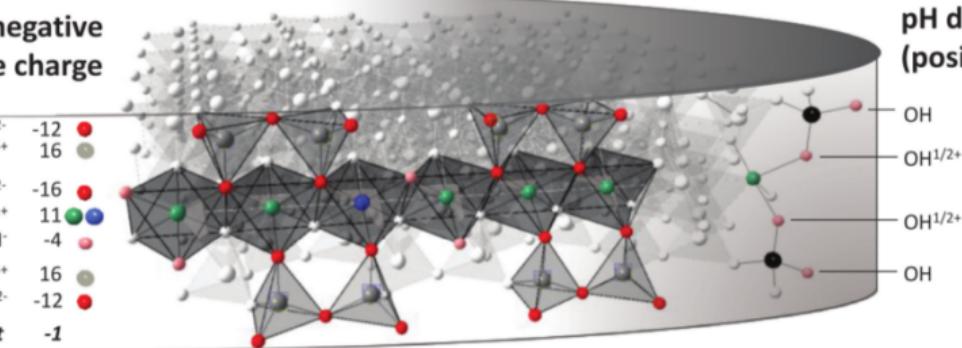


Figure 3. a) Smectites (here, the synthetic hectorite Laponite, $[(\text{Si}_8 \text{Mg}_{5.5} \text{Li}_{0.3}) \text{O}_{20}(\text{OH})_4]^{-0.7}$) possess a permanent negative surface charge arising from isomorphic substitutions in the crystal structure and a pH dependent edge charge from unsatisfied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

Colloids often carry surface charges

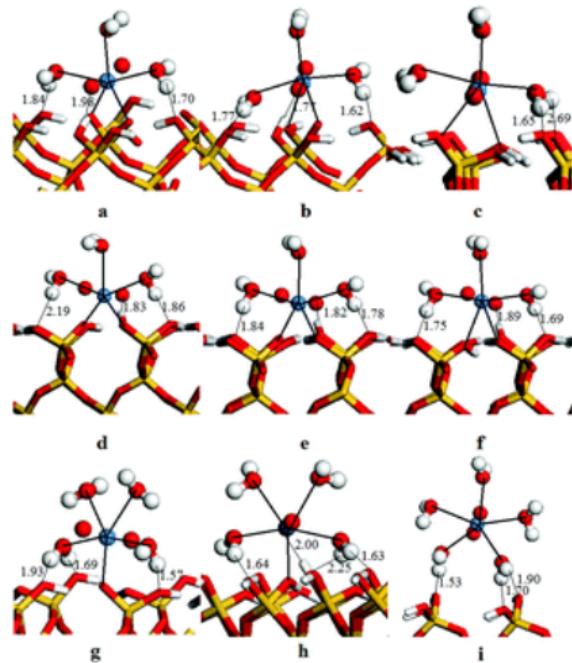
Example of ion adsorption (UO_2^{2+} on silica):

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 ^a, Zhifang Chai ^{ab} and Dongqi Wang ^{*a}

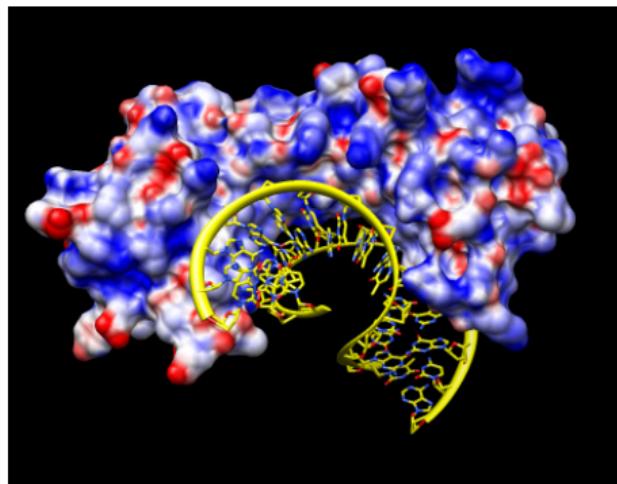
Fig. 1 Optimized adsorption structures of uranyl adsorbed on the hydroxylated $\alpha\text{-SiO}_2(001)$ surface. Inner-sphere: bidentate complex (a) SiOO , (b) SiOOH , (c) SiOHOH , (d) SiO-SiO , (e) SiO-SiOH , (f) SiOHSiOH ; monodentate complex (g) SiO , (h) SiOH . Outer-sphere complex (i). Color scheme: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



Colloids often carry surface charges

Surface charges are not always uniform.

Example of the DNA binding protein 1qna:



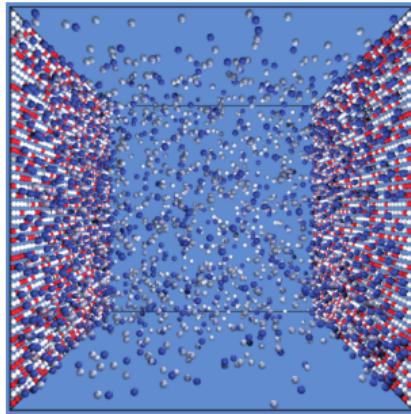
Blue for positive potential, red for negative potential.

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

Structure of the Electrical Double Layer (EDL)

Since objects are charged, there are also free charges in the fluid phase that globally neutralize the total suspension charge. These are called counterions. Moreover, if a salt is added and dissociates, ions with charges of both signs are introduced. All these ions have trajectories resulting from a balance between electrostatic forces and thermal motion.

Ion distribution near a charged surface: the electrical “double” layer (EDL).



Labbez et al., Langmuir, 2009.

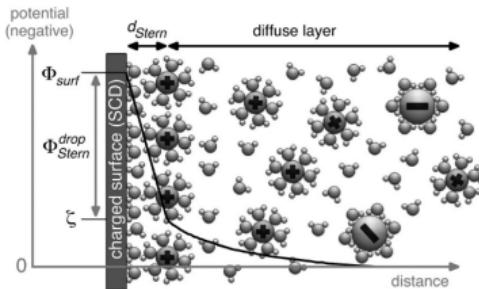
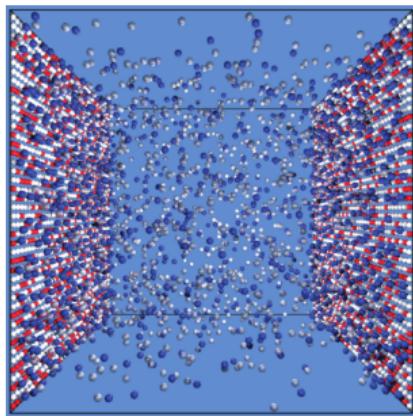
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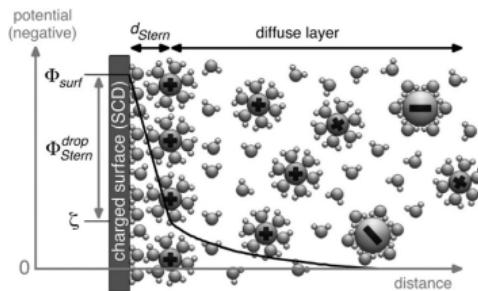
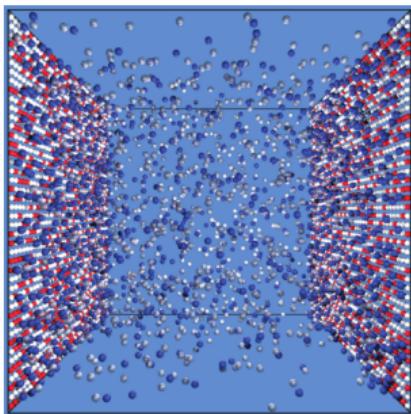


Brown et al., Angewandte Chemie, 2016.

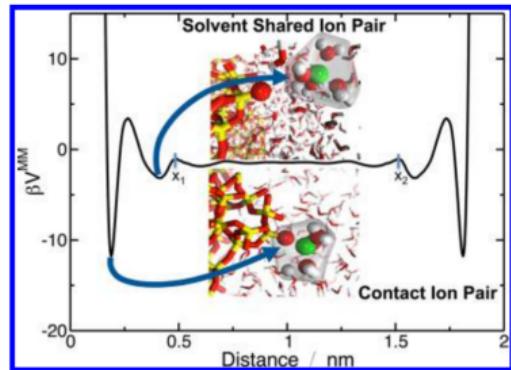
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Hocine et al., J. Phys. Chem. C, 2015.

Electrostatics in a continuous medium

Permittivity

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- The lowest permittivity is that of vacuum $\epsilon_0 = 8.854187817\dots \cdot 10^{-12} F/m$.
- The permittivity of other media ϵ is often given as a relative permittivity $\epsilon_r = \epsilon/\epsilon_0$.

medium	relative permittivity (room temperature)
vacuum	1
air	1.0006
polystyrene	2.4 – 2.7
SiO_2	3.9
Methanol	30
water	78
TiO_2	86 – 173
...	> 1000

Electrostatics in a continuous medium

The Poisson equation

The electric field \mathbf{E} (electrostatic force in Newtons exerted on a charge divided by the charge in Coulombs) is the solution of the Poisson equation

$$\nabla \cdot (\epsilon \mathbf{E}) = \rho_f, \quad (1)$$

where $\nabla \cdot$ is the divergence and ρ_f is the charge density.

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When plugged into Eq. (1), if ϵ is uniform we obtain the Poisson equation for Ψ

$$\boxed{\Delta \Psi = -\frac{\rho_f}{\epsilon}} \quad (3)$$

Electrostatics in a continuous medium

The Poisson equation

Thanks to the divergence theorem, one can show the Poisson equation is also the Gauss' law

$$\int_S \mathbf{E} d\mathbf{S} = \frac{Q}{\epsilon}, \quad (4)$$

where S is any surface enclosing a total charge Q and a volume V .

Electrostatics in a continuous medium

The Poisson equation

This is a second order partial differential equation (PDE), so it needs 2 boundary conditions.
Common boundary conditions are

- Vanishing potential at infinity $\Psi(x \rightarrow \infty) = 0$.
- Constant surface potential: $\Psi = \Psi_s$ on a surface
- Constant surface charge density σ (in C/m^2): $\epsilon_{\text{solid}} \frac{\partial \Psi}{\partial n} \Big|_{\text{solid}} - \epsilon_{\text{solvent}} \frac{\partial \Psi}{\partial n} \Big|_{\text{solvent}} = \sigma$
- Mixed condition (charge regulation): $f(\Psi, \nabla \Psi) = 0$ on a surface.

Electrostatics in a continuous medium

Example: field generated by an isolated point charge q in vacuum.

Consider a point charge q at $\mathbf{x} = 0$. Let's imagine a sphere of radius r around it. Gauss' law reads

$$\int_S \mathbf{E} d\mathbf{S} = \int_S \mathbf{E} \cdot \mathbf{n} dS = \frac{Q}{\epsilon_0} = \frac{q}{\epsilon_0}$$

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where \mathbf{n} is a unit vector pointing out of the sphere: $\mathbf{n} = \mathbf{e}_r$. By spherical symmetry, the field depends only on r and the surface integral is just the integrand multiplied by the surface, so

$$4\pi r^2 E(r) = \frac{q}{\epsilon_0}$$

and the solution is

$$E(r) = \frac{q}{4\pi\epsilon_0 r^2} \quad (5)$$

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Since $E(r) = -d\Psi/dr$, the electrostatic potential is (assuming a vanishing potential at infinity)

$$\Psi(r) = \frac{q}{4\pi\epsilon_0 r} \quad (6)$$

Electrostatics in electrolytes

The problem with electrolytes

The previous example was in vacuum and we considered a unique point charge with known position. In an electrolyte, charges contributing to ρ_f are the colloidal surface charges (assumed to be known) and the ions in the electrolyte. These ions experience electrostatic forces but they also move all the time and in every direction due to the thermal agitation. The charge density ρ_f is thus unknown a priori. It is determined by the solution of the Poisson equation. We need a second equation relating the electrostatic potential to the charge density.

Assuming ions are point charges (valency z) independent of each other but feeling the mean electrostatic potential field Ψ (in practice, valid for a 1:1 electrolyte at an ion concentration $< 0.1 M$), the (electro)chemical potential of ion species i with valence z_i (positive or negative) is

$$\mu_i = kT \ln(n_i) + z_i e \Psi \quad (7)$$

where e is the elementary charge, k is Boltzmann's constant, and T is the absolute temperature. The first term is the ideal contribution and the second one is the electrostatic energy per ion in the field Ψ .

Electrostatics in electrolytes

At equilibrium, no gradient in chemical potential can exist, so the chemical potential is the same everywhere. In particular, we can define a (maybe fictitious) place where $\Psi = 0$ and we call the ion density at this position $n_{i,0}$.

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This is called a Boltzmann distribution.

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The total charge density is the sum of the charge densities of each species $\rho_f = \sum_i z_i e n_i$. Using the previous result, the charge density in the electrolyte is

$$\rho_f(\mathbf{x}) = \sum_i z_i e n_{i,0} e^{-\frac{z_i e \Psi(\mathbf{x})}{kT}}$$

Electrostatics in electrolytes

The Poisson-Boltzmann equation (PBE)

The Poisson equation for electrostatics in the electrolyte then becomes the **Poisson-Boltzmann** equation

$$\Delta\Psi = -\frac{e}{\epsilon} \sum_i z_i n_{i,0} e^{-\frac{z_i e \Psi(\mathbf{x})}{kT}} \quad (10)$$

This is a non-linear PDE, so there is an analytical solution only in extremely simple geometries. Due to the approximations involved in its derivation, the Poisson-Boltzmann is valid for low electrostatic couplings, which means in practice...

- Ion concentrations below around $0.1 M$ (to neglect their finite size and correlations).
- 1:1 electrolytes (monovalent ions) (to neglect their electrostatic correlations).

There are more elaborate/complex theories to deal with this issue (modified PB theory, DFT...)

Electrostatics in electrolytes

The Poisson-Boltzmann equation for 1:1 electrolytes

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In this course, we focus on 1:1 electrolytes. If there are several ion species, the PB theory does not distinguish them so there are only two effective species with $z_1 = 1$ and $z_2 = -1$. At the place where $\Psi = 0$ electroneutrality says that $n_{1,0} = n_{2,0} = n_0$.

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$$\boxed{\kappa = \sqrt{\frac{2n_0e^2}{\epsilon kT}}} \quad \text{or in water } \lambda \approx \frac{0.307 \text{ (nm)}}{\sqrt{I \text{ (mol/L)}}} \text{ where } I = \frac{1}{2} \sum_i z_i^2 c_i \quad (13)$$

Electrostatics in electrolytes

⚠ How do I compute the Debye length ? ⚠

It is no always easy because n_0 may be unknown. In particular, n_0 is NOT the density of added salt in a beaker unless the dispersion is very dilute. There are 2 cases.

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Easy case: Donnan equilibrium/dialysis

The colloidal dispersion is in contact with a large reservoir of ions through a membrane blocking colloids but letting ions pass. The electrolyte is in equilibrium with the ion reservoir. In this reservoir, the PB equation applies, the potential is $\psi = 0$ and thus n_0 is the prescribed and constant ion density in the reservoir.

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Difficult case: a dispersion in a beaker

There may be no points where $\psi = 0$, especially in concentrated suspensions. But, we could design a dialysis experiment with a membrane on the side of the beaker and in which the total number of ions in the beaker is the same as in the original experiment, and then "close" the membrane. To achieve this, the value of the reservoir ion density n_0 would have to be adjusted. This is the density to be used in the Debye length. The value of n_0 can be computed numerically.

Electrostatics in electrolytes: low surface charges of potentials

The Debye-Hückel theory

For weakly charged surfaces, the dimensionless surface potential is small everywhere so we can use the Taylor expansion around $\psi = 0$: $\sinh \psi \sim \psi + \frac{1}{6}\psi^3 + O(\psi^5)$.

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$$\Delta\psi = \kappa^2\psi \tag{14}$$

This equation is now a linear PDE and there are various techniques to solve it in more or less simple geometries. This approximation is often used for this reason, but remember it is valid in practice only for $\psi \lesssim 2$, or $\Psi \lesssim 50\text{ mV}$.

Electrostatic interactions

Interaction potential $V(r)$ between two objects

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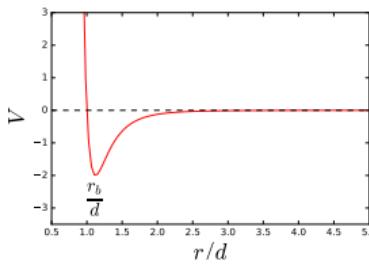
$$V(r) - V(r \rightarrow \infty) = \int_r^{\infty} F(r) dr$$

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Example: the Lennard-Jones potential

$$V(r) = 4\epsilon \left[\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^6 \right]$$



Electrostatic interactions

Warning !

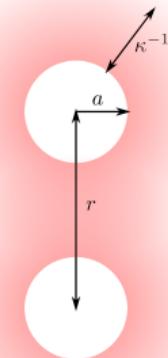
The method for computing true electrostatic interactions between two objects is known, but there is no general explicit relation for arbitrary distances, volume fractions, or surface charge density / potential.

Here, two models useful in different situations will be reported : the Derjaguin approximation and the Linearized Superposition Approximation (LSA).

Pay attention to the hypotheses !

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

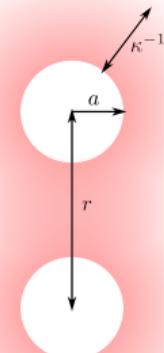
Hypotheses



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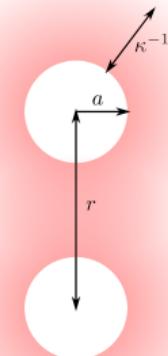
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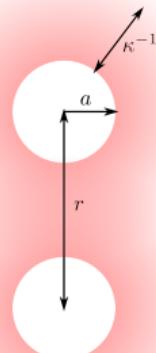
Interaction potential:

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

Interaction force:

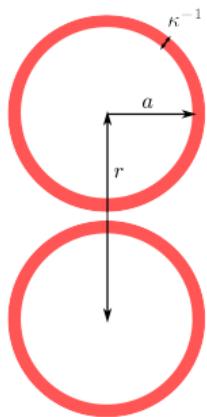
$$F = \epsilon \left(\frac{kT}{ze} \right)^2 4\pi \psi_s^2 \frac{1+\kappa r}{r^2} a^2 e^{-\kappa(r-2a)} \quad \text{or} \quad F = 4\pi \frac{\sigma^2 a^4}{\epsilon(1+\kappa a)^2} \frac{1+\kappa r}{r^2} e^{-\kappa(r-2a)}$$

ψ_s is dimensionless, a is in m , σ is in C/m^2 , V is in J , F is in N .



Electrostatic interactions between spheres: the Derjaguin approximation

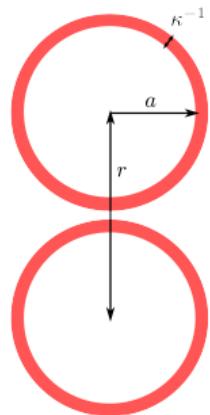
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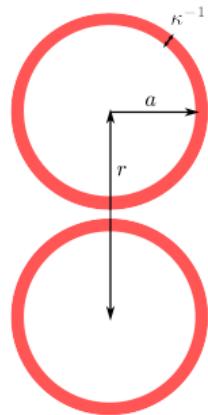
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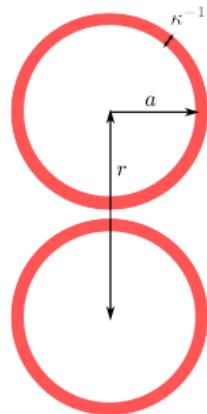
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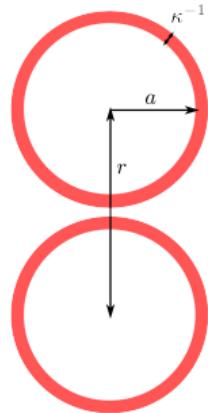
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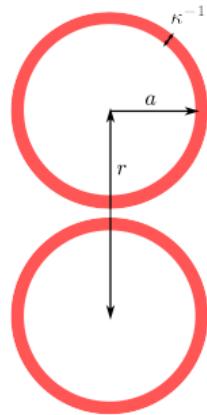
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$$V = \epsilon \left(\frac{kT}{ze} \right)^2 32\pi a \tanh^2 \left(\frac{\psi_s}{4} \right) e^{-\kappa(r-2a)}$$

Interaction force:

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



Getting values for κ , ψ_s , or σ

In the interaction models give previously, different quantities have to be specified and so they have to be measured. What are the available measurement methods ?

The surface potential ψ_s

The surface potential is measured classically with electrophoresis. An electric field is applied on the sample, which makes the colloids move with some velocity that is measured with optical methods. In order to relate this velocity to a surface potential, some models are used. To make a long story short, these models can be based on a linearized electrokinetic theory (DH) or on a non-linear one (PB). The non-linear theory is called Smoluchowski theory and gives a potential to be used in the (non-linear) Derjaguin approximation. Both Smoluchowski and Derjaguin models rely on the assumption of small EDL compared to the particle size. The linear electrokinetic theory corresponds to the DH model on the apparatus and the resulting surface potential should be used in the LSA interaction model (comming from DH).

Getting values for κ , ψ_s , or σ

The surface charge density σ

The surface charge density can be measured by titration. If it is high enough to generate surface potentials $> 50mV$, it should **not** be used in the LSA model as is because this model is valid for low surface potentials. Instead, the renormalization procedure described hereafter should be used to obtain an effective surface potential or an effective surface charge.

The inverse screening length κ

- In an electrostatically dilute suspension, i.e. EDL do not overlap on average, κ can be approximated with the formula given previously using the bulk ion concentration for $2n_0$.
- In an electrostatically concentrated suspension, i.e. EDL do overlap on average, the best is to obtain an effective κ from the renormalization procedure.

Electrostatic interactions between spheres

There are several other models with various hypotheses. Always try to understand if they are based on a linearization hypothesis (DH theory), and in this case use either low true charge/potential or renormalized ones. If there is no linearization involved (Derjaguin theory), use the real surface charge/potential, without renormalization.

What is the idea of renormalization ?

Renormalization is a procedure to be used only for highly charged or electrostatically concentrated systems. In this case, the LSA interaction model should not be used.

However, it is possible to find so-called **effective** or **renormalized** surface charge/potential or screening length that will lead to good estimates of interaction potentials or forces when used in the LSA formula.

The next slides are aimed at showing why and how this can be done.

Solutions of the PB equation

Potential generated by a flat, weakly charged, surface in an infinite medium.

The Linearized PB equation is 1D and reads $\psi''(x) = \kappa^2\psi$. Characteristic equation $r^2 - \kappa^2 = 0$, so there are 2 real roots $\pm\kappa$ and the general solution is $\psi(x) = Ae^{\kappa x} + Be^{-\kappa x}$. Since we want ψ to be finite at $x \rightarrow \infty$, $A=0$. If the surface potential is given (ψ_s), then the boundary condition is $\psi(0) = \psi_s = Be^0$ so $B = \psi_s$ and

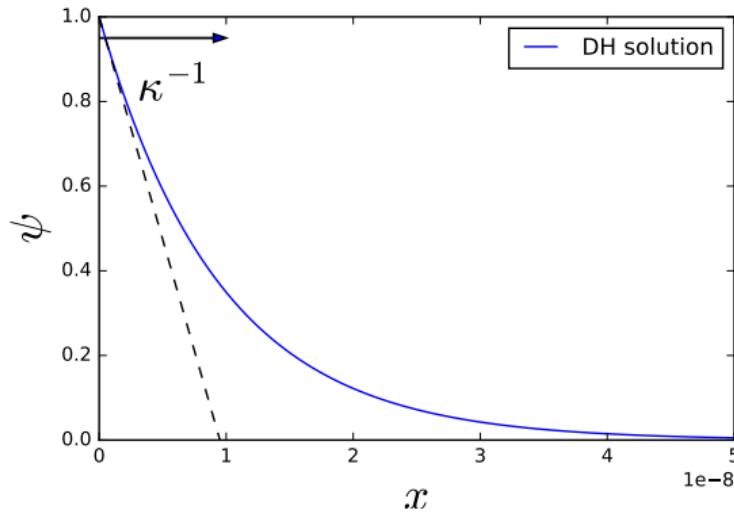
$$\psi(x) = \psi_s e^{-\kappa x}$$

If the surface charge density is given, the Laplace equation on the left says $\psi(x < 0) = constant$, so $\psi'(x < 0) = 0$. Then the constant charge BC reads $0 - \epsilon\Psi'(0) = \sigma$. We have shown $\Psi' = -\kappa\Psi$ everywhere so it is true at $x=0$ and $\epsilon\kappa\Psi(0) = \sigma$ or in dimensionless potential: $\psi(0) = \Psi(0)e/kT = \sigma e/(\kappa\epsilon kT)$ so the solution is

$$\psi(x) = \frac{\sigma e}{\kappa\epsilon kT} e^{-\kappa x}$$

Solutions of the PB equation

Potential generated by a flat, weakly charged, surface in an infinite medium.



Solutions of the PB equation

Potential generated by a flat, fully charged, surface in an infinite medium.

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Potential generated by a flat, fully charged, surface in an infinite medium.

The non-linear PB equation is 1D and reads $\psi''(x) = \kappa^2 \sinh \psi$. For a constant surface potential ψ_s , the solution is

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

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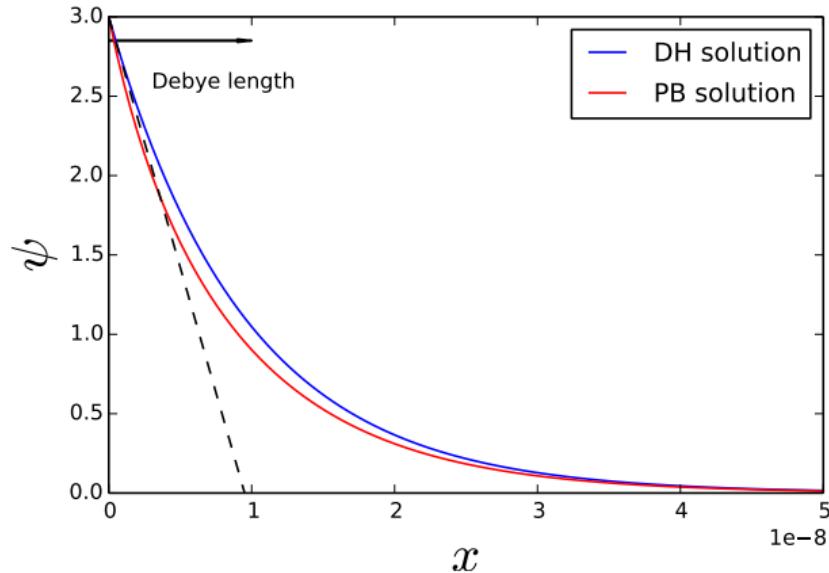
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From this and the constant charge density BC, we obtain the **Grahame equation**

$$\sigma = 2 \sqrt{2 n_0 \epsilon k T} \sinh \left(\psi_s / 2 \right)$$

Solutions of the PB equation

Potential generated by a flat surface in an infinite medium.



Solutions of the PB equation

Potential generated by a flat, fully charged, surface in an infinite medium.

If the surface has a **high potential**, $\tanh \psi_s / 4 \rightarrow 1$ and $\psi \approx 2 \ln \left\{ \frac{1+e^{-\kappa x}}{1-e^{-\kappa x}} \right\}$. The potential field becomes independent of the surface potential !!! Far from the surface, $e^{-\kappa x}$ is small so $\psi(\kappa x \gg 1) \approx 4e^{-\kappa x}$. This formula looks like the DH solution with a surface potential which would be 4.

Using the DH theory with a fake value of the surface potential instead of the PB theory with the real surface potential is very common. The fake surface potential is called an **effective potential** and the process of replacing the real potential by the effective one is called **charge renormalization**. Remember that this trick is valid only if the surfaces are separated by at least about one Debye length.

For a flat plate, the dimensionless effective potential is smaller than the real potential and saturates at a value of 4 ($\sim 100mV$ in water at room temperature) if the real potential is too high. This is the phenomenon of **effective potential saturation**.

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The DH equation in spherical coordinates gives

$$\psi(r) = A \frac{e^{-\kappa r}}{r}$$

and A is fixed by BC.

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and if $\Psi'(a) = -\sigma/\epsilon$ (constant charge BC; beware $\psi = \Psi e/kT$)

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It shows that for an isolated sphere, the surface charge - potential relation is

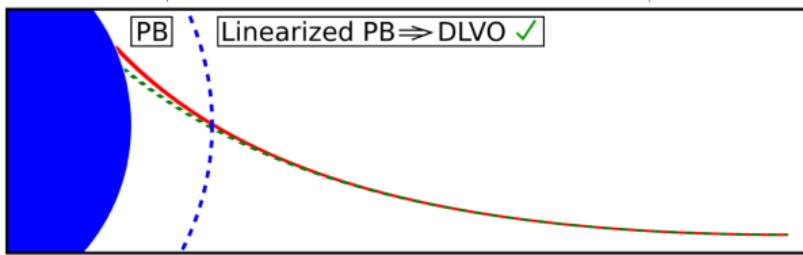
$$\boxed{\psi_s = \frac{\sigma a}{\epsilon(1 + \kappa a)}}$$

and the full charge is

$$\boxed{Q = 4\pi a^2 \sigma = 4\pi a \epsilon \psi_s (1 + \kappa a)}$$

Effective surface charge density and potential: renormalization

Idea of surface charge renormalization:



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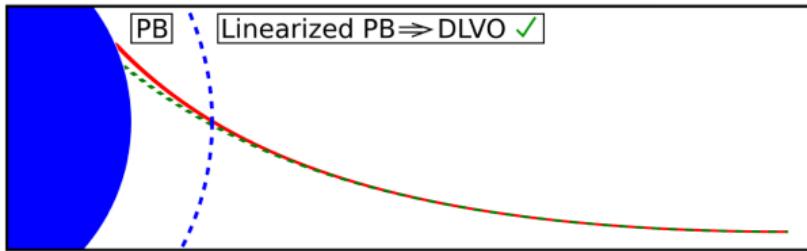
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Effective surface charge density and potential: renormalization

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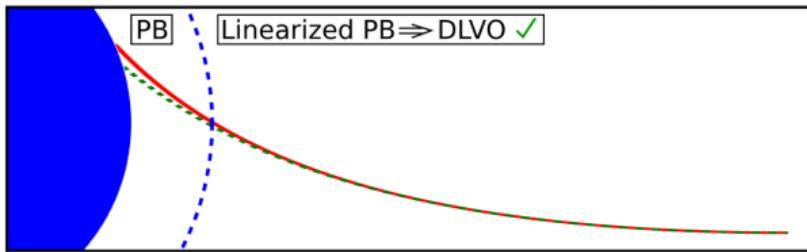
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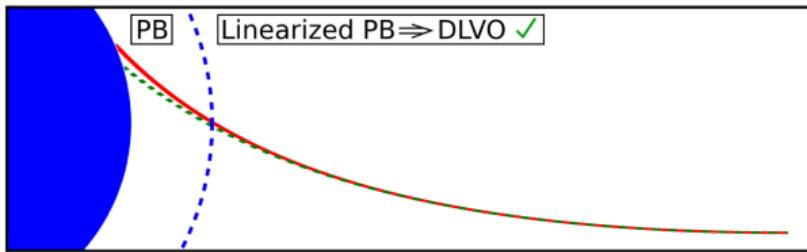
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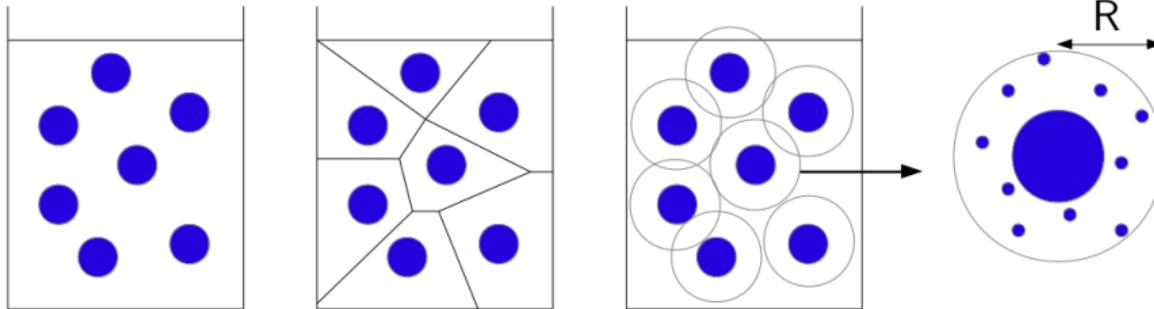
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- The effective surface potential is generally close to the ζ potential, although a factor of 2 is sometimes found between the two.



Effective surface charge density and potential: renormalization

A common simplified geometry: the cell model

- Split the solution in electro-neutral cells containing each one colloid (of radius a).
- Assume the cells are identical and spherical for simplicity, with a radius $R = a\phi^{-1/3}$.
- Solve the PB equation numerically in this spherically symmetrical geometry.



Surface charge density and surface potential

Summary (see scheme on the next slide at the same time)

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Surface charge density and surface potential

Summary (see scheme on the next slide at the same time)

- The real (bare) surface charge density is measured by titration and corresponds to the real surface.
- The real surface potential is measured experimentally only with the Smoluchowski theory for electrophoresis.
- The ζ (zeta) potential is measured with the DH theory for electrophoresis. Its physical significance and the location where it is realized are not very clear. It is generally assumed to be found just outside the Stern "layer". It is therefore some kind of effective surface potential.

Surface charge density and surface potential

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Surface charge density and surface potential

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- It is possible to switch from real surface properties to effective ones by matching the results of the PB theory with real parameters to those of the DH theory with fitted parameters in a simple geometry. These fitted parameters are called effective parameters.

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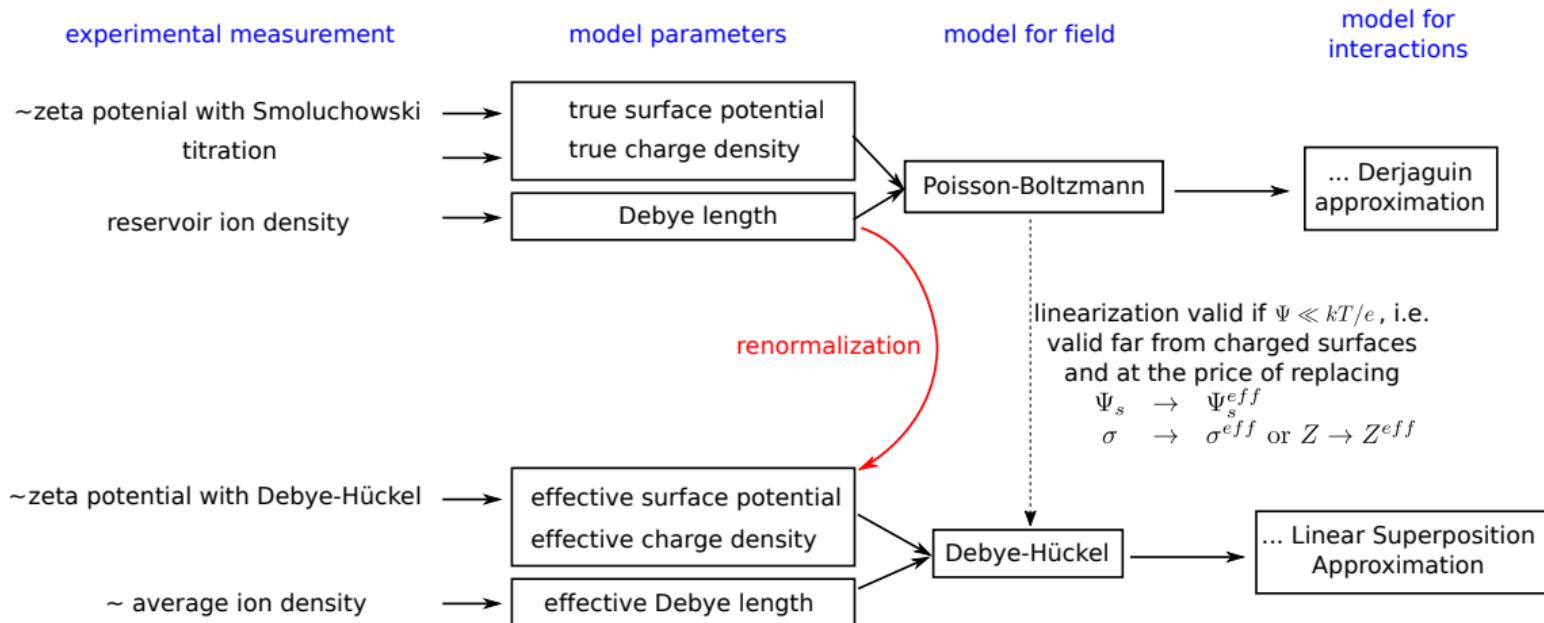
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- The Debye-Hückel theory can quite give qualitatively correct results with an effective or ζ potential as boundary condition.
- The Poisson-Boltzmann theory can give quantitatively correct results with the bare surface charge density or the surface potential from Smoluchowski theory for electrophoresis as boundary conditions.
- The DH theory must not be used with the bare charge - and the PB theory must not be used with the effective/ ζ potential - unless the surface charge density and potential are very low so that both theories coincide.

Summary on electrostatics



1 Colloids

- Introduction
- Colloidal interactions: electrostatics
- Van der Waals interactions

2 Aggregation

3 Electrokinetics

4 Operators

Origin of van der Waals forces: gas picture

Electrodynamic interactions between atoms/molecules in dilute gases (1930s)

- Keesom, or dipole-dipole, interactions: $V(r) = -\frac{C_{\text{Keesom}}}{r^6}$
- Debye, or dipole-induced-dipole, interactions: $V(r) = -\frac{C_{\text{Debye}}}{r^6}$
- London, or induced-dipole-induced-dipole, interactions: $V(r) = -\frac{C_{\text{London}}}{r^6}$

So the interaction between two atoms or molecules is $V(r) = -\frac{C}{r^6}$.



Origin of van der Waals forces: gas picture

Contribution of dispersion (London) forces.

Molecule pair	% of the total energy of interaction
Ne-Ne	100
CH ₄ -CH ₄	100
HI-HI	99
HCl-HI	96
HBr-HBr	96
H ₂ O-CH ₄	87
HCl-HCl	86
CH ₃ Cl-CH ₃ Cl	68
NH ₃ -NH ₃	57
H ₂ O-H ₂ O	24

Origin of van der Waals forces: gas picture

Electrodynamic interactions between solids/liquids (Hamaker, 1937)

Sum by pairs the atom/molecule interactions over the atom/molecules constituting the solids/liquids.

$$E = -\frac{A}{\pi^2} \int_{V_1} \int_{V_2} \frac{1}{r^6} dV_1 dV_2$$

As a result, the interaction energy between flat plates varies like $1/r^2$ and that between two spheres varies like $1/r$: they are much longer-ranged than the atom/molecule interactions ! As a consequence, the van der Waals forces enter in competition with electrostatic forces.

Origin of van der Waals forces: gas picture

Problem 1: solids and liquids are not gases !

Hamaker's idea of pairwise summation is correct only if 2 dipoles do not see any third dipole in their vicinity. Otherwise, the $1/r^6$ pair potentials are not correct.

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Problem 1: solids and liquids are not gases !

Hamaker's idea of pairwise summation is correct only if 2 dipoles do not see any third dipole in their vicinity. Otherwise, the $1/r^6$ pair potentials are not correct.

Problem 2: retardation effects

The $1/r^6$ interaction energy between 2 (isolated) dipoles assumes that they react to each other's electric field instantaneously. But the speed of light being finite, it takes a certain amount of time for the fluctuating field of one dipole to reach the second one. Then the second one can adapt to this field and generate its own influenced field, which will take some time to propagate back to the first dipole. The $1/r^6$ interaction potential is obtained if the speed of light is considered infinite. Otherwise, the interaction energy will fall to $1/r^7$ because the dipoles cannot correlate their orientations.

Origin of van der Waals forces: gas picture

Interaction between planar surfaces (no retardation)

If d , is the distance between walls, the interaction energy per unit surface area is

$$V(d) = -\frac{A}{12\pi d^2}$$

and the force is

$$F(d) = -\frac{A}{6\pi d^3}$$

Origin of van der Waals forces: gas picture

Interaction between identical spheres (no retardation).

$$V_{vdw}(r) = -\frac{A}{3} \left[\frac{a^2}{r^2 - 4a^2} + \frac{a^2}{r^2} + \frac{1}{2} \ln \left(1 - \frac{4a^2}{r^2} \right) \right]$$
$$F_{vdw}(r) = -\frac{32Aa^6}{3r^3(r^2 - 4a^2)^2}$$

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Limiting laws at large and small distance.

From very far away:

$$V_{vdw}(r) \sim -1/r^6$$

$$F_{vdw}(r) \sim -1/r^7$$

so the gas result is recovered.

At close distance ($h = r - 2a \ll a$):

$$V_{vdw}(r) \simeq -\frac{Aa}{12h}$$

$$F_{vdw}(r) \sim -\frac{Aa}{12h^2}$$

The Hamaker “constant”

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- The Hamaker constant A_{132} depends on the dielectric properties of the two interacting objects (say indices 1 and 2) and of the medium containing them (say index 3).

$$A_{132} = \frac{3}{4} kT \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} + \frac{3h}{4\pi} \int_{v_1}^{\infty} \frac{\epsilon_1(iv) - \epsilon_3(iv)}{\epsilon_1(iv) + \epsilon_3(iv)} \frac{\epsilon_2(iv) - \epsilon_3(iv)}{\epsilon_2(iv) + \epsilon_3(iv)} dv + \dots$$

where the first term (“zero frequency”) represents the effects of permanent dipoles (Keesom/Debye) and the second one represent the effect of fluctuating dipoles (London/dispersion). The $\epsilon(iv)$ are real functions of the material, can be measured, and found in the literature.

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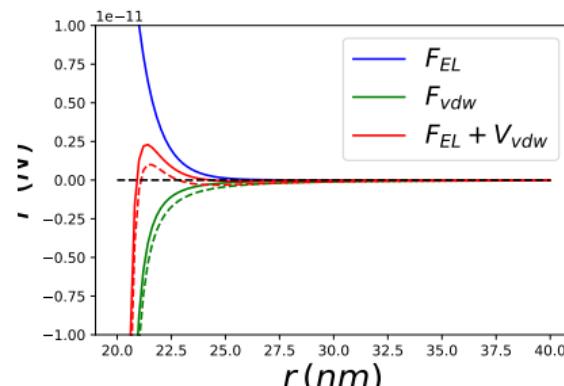
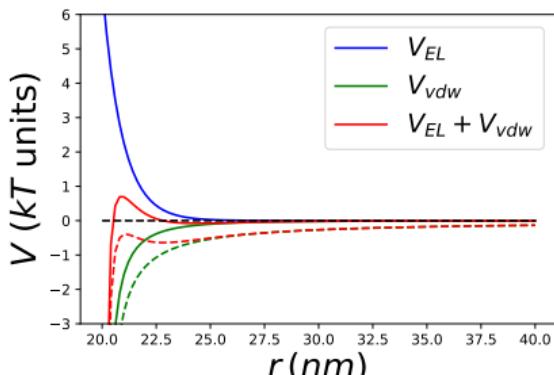
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- Van der Waals forces are often attractive but can also be repulsive.
- This sort of approximate formula gives vdW forces with an accuracy of $\sim 10 - 20\%$.
- Better treatment (especially at long distance) Lifschitz theory (see, e.g., the book “Van der Waals forces” by Parsegian). In particular, the Hamaker constant actually depends on the distance if retardation is included.

Surface interactions: the DLVO theory

In the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the interaction potential between two objects is supposed to be the sum of the electrostatic V_{EL} and the van der Waals V_{vdW} contributions presented in this chapter:

$$V_{DLVO}(r) = V_{EL}(r) + V_{vdW}(r)$$



Stability of a colloidal suspension

Stability of a suspension

A colloidal suspension is said to be **unstable** if the colloids tend to form aggregates (in a moderate period of time) due to the attractive (vdW) forces exerted between them. These forces are always present in real systems, and their effect is most significant at short distances. However, repulsive electrostatic interactions can prevent colloids from coming too close to each other, which prevents vdW forces from having any strong effect. The colloids then remain suspended (for a “long” time) and the suspension is said to be **stable**.

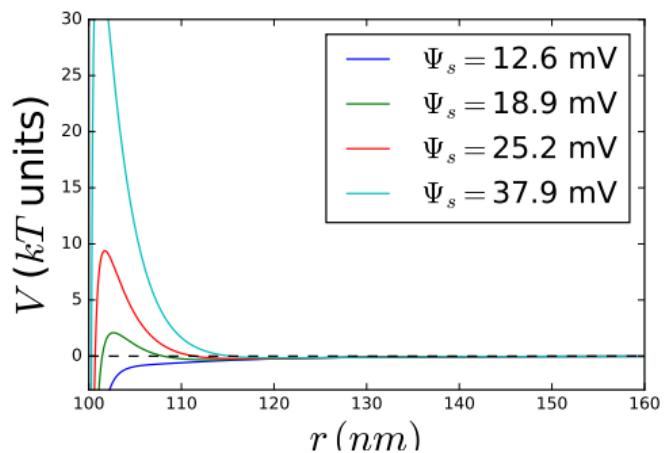
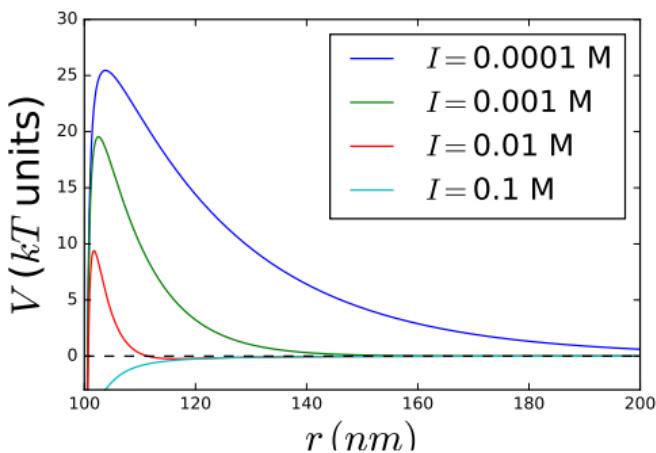
Coagulation and flocculation

- **Coagulation** is mentioned when a suspension becomes unstable due to an ionic strength increase.
- **Flocculation** is mentioned when a suspension becomes unstable due to adsorption on polymers on the surfaces of the colloids.

Stability of a colloidal suspension

Stability can be estimated from the maximum value of the DLVO potential V_{max} as follows:

Potential value	Behavior
$V_{max} > 15kT$	stable
$0 < V_{max} < 15kT$	slow, irreversible aggregation
$V_{max} < 0$	rapid, irreversible aggregation



The Critical Coagulation Concentration (CCC)

The CCC can be given by the Schulze-Hardy rule, given here for highly charged surfaces in water, with thin EDL compared to the particle size, and a z:z electrolyte.

$$CCC = 3.8 \cdot 10^{-36} \frac{\gamma_0^4}{A^2 z^6} \text{ mol/m}^3$$

where $\gamma_0 = \tanh\left(\frac{\psi_s}{4}\right)$ and A is Hamaker's constant.

Sixth power of the ion valency !

Plan

1 Colloids

2 Aggregation

3 Electrokinetics

4 Operators

Aggregation kinetics

To obtain aggregation, you need 2 things:

- ① Particle encounters
- ② No release after encounter

Aggregation kinetics

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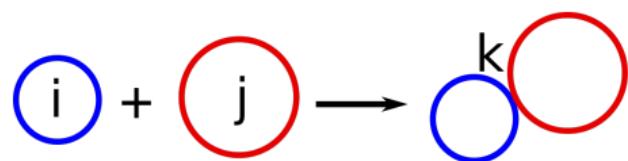
Aggregation kinetics

To obtain aggregation, you need 2 things:

- ① Particle encounters → driven by particle transport processes
- ② No release after encounter → determined by particle-particle interactions

Smoluchowski theory (1917)

Assume the aggregation can be treated as a chemical reaction.



The rate of collision J_{ij} (number of collisions per unit time per unit volume) between species i and j is a second order process so

$$J_{ij} = k_{ij} n_i n_j$$

where n_i and n_j are the number densities of species i and j , and k_{ij} is a second order reaction rate constant depending on the transport mechanism leading to particle encounters.

Smoluchowski theory (1917)

So an encounter between species i and j has 2 effects:

- ① create species k with a rate $\frac{dn_k}{dt} = J_{ij} = k_{ij}n_i n_j$
- ② destroy species i and j with a rate $\frac{dn_i}{dt} = \frac{dn_j}{dt} = -J_{ij} = -k_{ij}n_i n_j$

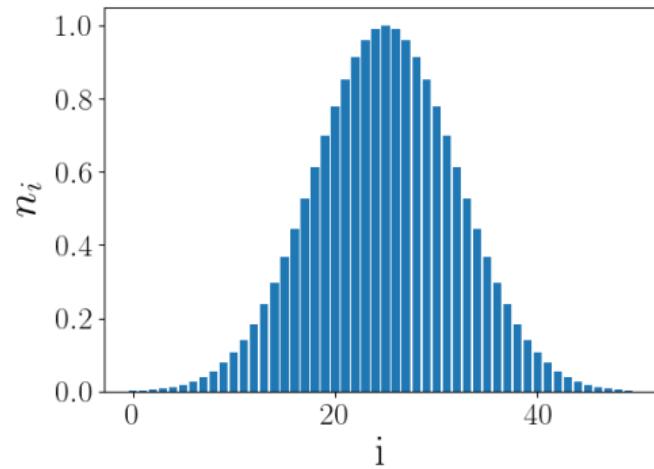
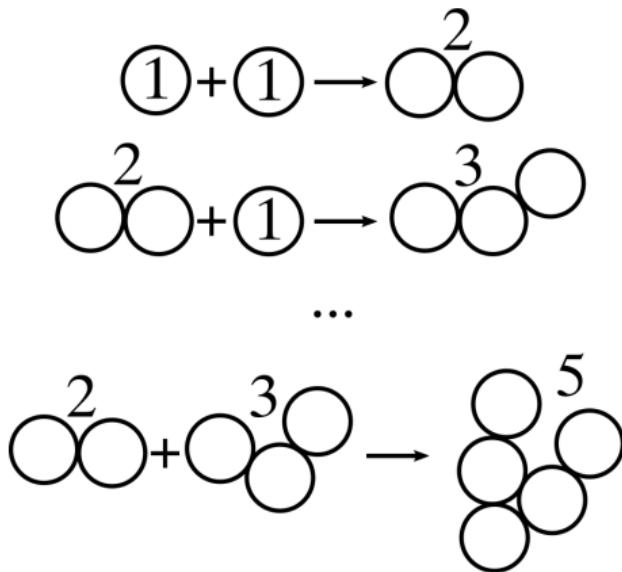
Writing these equations for all possible i, j, k we get

$$\forall l, \frac{dn_l}{dt} = \frac{1}{2} \sum_{\text{all } i+j=l} k_{ij}n_i n_j - \sum_{\text{all } i} k_{il}n_i n_l \quad (15)$$

NB: Here we assumed any collision leads to irreversible aggregation, but this is not always the case.

Smoluchowski theory (1917)

A succession of aggregation events between different species (or sizes) leads to the formation of a wealth of new species (or sizes) so, unlike bimolecular reactions, there is a growth process leading to a size *distribution*.



Calculating the "reaction" rates k_{ij}

The rate constants k_{ij} depend on the transport mechanism. There are 3 classical cases:

- ① Transport by diffusion (Brownian motion): perikinetic aggregation
- ② Transport by a shear flow: orthokinetic aggregation
- ③ Transport by sedimentation: differential settling

Perikinetic aggregation

For dilute spheres of radius a_i , transport by diffusion means that the rate at which particles i are brought to contact with one particle of type j is

$$J = 4\pi(a_i + a_j)D_i n_i$$

so the rate at which type- i collides with type- j is $4\pi(a_i + a_j)D_i n_i n_j$. As particles j also diffuse toward type- i , we also have a collision rate $4\pi(a_i + a_j)D_j n_j n_i$ and the total collision rate is

$$J_{ij} = 4\pi(a_i + a_j)(D_i + D_j)n_i n_j$$

The Stokes-Einstein diffusion coefficient is $D_i = kT/(6\pi\eta a_i)$ so after simplification and identification we get

$$k_{ij}^{peri} = \frac{2}{3} \frac{kT}{\eta} \frac{(a_i + a_j)^2}{a_i a_j}$$

Perikinetic aggregation

For very short times, and if it can be assumed that $k_{ij} = \bar{k}$ is independent of i and j , we have

$$\bar{k}^{peri} = \frac{8}{3} \frac{kT}{\eta}$$

and so summing the Smoluchowski equations for all species,

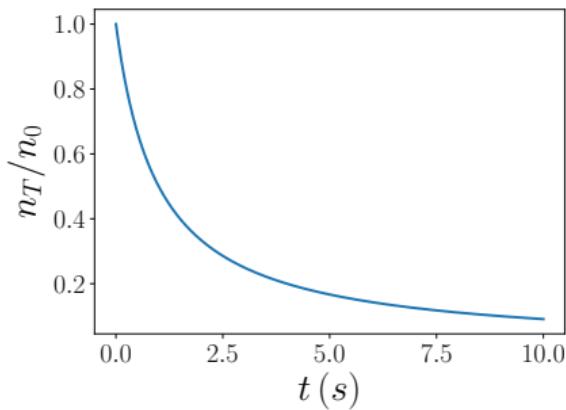
$$\frac{dn_T}{dt} = -\frac{1}{2} \bar{k}^{peri} n_T^2$$

where n_T is the sum of all n_i , i.e. the number density of particles irrespective of their size. The solution is, with n_0 the initial number of particles,

$$n_T(t) = \frac{n_0}{1 + \frac{1}{2} \bar{k}^{peri} n_0 t}$$

Perikinetic aggregation

$$n_T(t) = \frac{n_0}{1 + t/\tau} \quad \text{with} \quad \tau = \frac{2}{\bar{k}^{peri} n_0}$$



Some numbers (water, room temperature):

n_0	τ
1.0×10^{17}	$1.85 s$
1.0×10^{15}	$185 s$
1.0×10^{11}	$18500 s$

But remember, this is true for short times, particle sizes differing by a factor 2 maximum, and we supposed every particle collision leads to capture.

Perikinetic aggregation

Remark: considering relation $n_T(t) = \frac{n_0}{1+t/\tau}$ and the fact that n_0/n_T is the average number of small spheres per aggregate, we see that

$$n_0/n_T = 1 + t/\tau \propto t/\tau$$

at not too short times. Since $n_0/n_T = V(t)/V_0 = R(t)^3/a^3$, with $V(t)$ and $R(t)$ the average aggregate volume and radius at time t , we see that the **size of aggregates increases as $t^{1/3}$ at long times ($R/a \approx (t/\tau)^{1/3}$)**. This is very slow, so perikinetic aggregation is not efficient to obtain big aggregates.

Perikinetic aggregation

Exercise:

We want to aggregate a dispersion of nanometric particles prior to decantation. $T = 25^\circ C$, $\eta = 1 \text{ mPa.s}$, $a = 100 \text{ nm}$, initial particle density $n_0 = 33.5 \times 10^5 \text{ m}^{-3}$, fluid density $\rho_f = 1000 \text{ kg/m}^3$, particle density $\rho_p = 2200 \text{ kg/m}^3$. We try to add KCl electrolyte to destabilize the suspension. We record the following aggregation times:

$[KCl] (\text{mM})$	$n_0 (\text{m}^{-3})$	$\tau (\text{s})$
20	33.5×10^5	no aggregation
30	33.5×10^5	no aggregation
65	33.5×10^5	360
80	33.5×10^5	19.5
100	33.5×10^5	20.3
200	33.5×10^5	20.7

Perikinetic aggregation

- ① Can you tell what is the CCC and why ?
- ② If we increase the initial particle concentration by a factor 10 and keep the salt concentration at the CCC, do we expect a slower or faster decrease of particle concentration ? Why ?
- ③ What is the mean aggregate size after 15min?
- ④ What is the corresponding sedimentation rate, using the Stokes formula

$$V = \frac{2g(\rho_p - \rho_f)R^2}{9\eta}$$

- ⑤ What is the time required for these aggregates to sediment over 1m.

Perikinetic aggregation

- ① Can you tell what is the CCC and why ? 80 mM because from this point τ does not vary anymore, in agreement with the theory we've written for collisions always leading to aggregation.
- ② If we increase the initial particle concentration by a factor 10 and keep the salt concentration at the CCC, do we expect a slower or faster decrease of particle concentration ? Why ? Faster decrease since $\tau = 2/(\bar{k}^{\text{peri}} n_0)$
- ③ What is the mean aggregate size after 15min? $R \approx a(t/\tau)^{1/3} \approx 360\text{ nm}$
- ④ What is the corresponding sedimentation rate, using the Stokes formula

$$V = \frac{2g(\rho_p - \rho_f)R^2}{9\eta}$$

About $0.34\mu\text{m/s}$

- ⑤ What is the time required for these aggregates to sediment over 1m. About $2.95 \times 10^6\text{ s} \approx 1\text{ month}$

Perikinetic aggregation

Summary about perikinetic aggregation

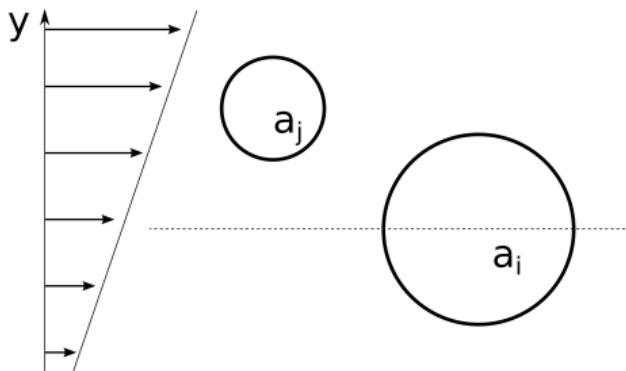
The formula we used are very approximate because

- They assume $k = \text{const}$ which is true for size differences < 2 .
- They are valid at short times and we used them at long times.
- They neglect hydrodynamic interactions
- They assume every collision results in an aggregation event
- They assume aggregates are roughly spherical

BUT they show one universal thing : perikinetic aggregation, due to Brownian motion alone, is very *inefficient* to form large aggregates. An therefore, sedimentation of the aggregates formed this way can take a very, very long time (days to years). To overcome this limit, we can use a flow as explained hereafter.

Orthokinetic aggregation

In a simple shear flow, the shear rate is $\dot{\gamma} = du/dy$. Assuming particles are transported horizontally with velocity $\dot{\gamma}y$, neglecting hydrodynamic interactions, the rate of collision of particles i with one particle j is



$$J = (4/3)n_i\dot{\gamma}(a_i + a_j)^3$$

and thus the global collision rate between i and j species is

$$J_{ij} = (4/3)\dot{\gamma}(a_i + a_j)^3 n_i n_j \equiv k_{ij} n_i n_j$$

so the rate constant for orthokinetic aggregation is

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

Orthokinetic aggregation

Comparison with the perikinetic case

- In the perikinetic case, for nearly identical particles, the k_{ij}^{peri} is almost constant (bigger particles are more likely to touch others but they diffuse more slowly also). In the orthokinetic case, k_{ij}^{ortho} grows like the cube of the particle size (bigger particles swipe more other particles than small particles). So as aggregation proceeds, the rate of aggregation increases ! This is much more efficient.
- In the orthokinetic case it's much less justified to assume k_{ij}^{ortho} is independent of ij since it depends much on the size ! but let's do it for sake of comparison with the perikinetic case.

Orthokinetic aggregation

Focusing on the very initial stage where we have only some primary particles forming 'dimers', assuming the total number of particles is approximately the number of primary particles, we have

$$\frac{dn_T}{dt} = -\frac{1}{2} k_{11}^{ortho} n_T^2$$

with

$$k_{11}^{ortho} = \bar{k}^{ortho} \simeq \frac{32}{3} \dot{\gamma} a^3$$

and the solution at short times

$$n_T(t \rightarrow 0) = \frac{n_0}{1 + \frac{16}{3} a^3 n_0 \dot{\gamma} t} = \frac{n_0}{1 + \frac{4}{\pi} \phi \dot{\gamma} t}$$

where ϕ is the volume fraction. So here the characteristic time scale for aggregation is $\tau^{ortho} = \pi / (4\phi\dot{\gamma})$. It shows that aggregation can be sped up by using a high shear rate (stirring) or a high volume fraction, which is used in practice.

Orthokinetic aggregation

In the ideal conditions of very short times, we can compare

$$\frac{\bar{k}^{ortho}}{\bar{k}^{peri}} = \frac{4\eta\dot{\gamma}a^3}{kT}$$

which is close to 1 for particles with size $1\mu m$ and a shear rate of $1 s^{-1}$ (very mild stirring). So in practice, stirring (typically $100 s^{-1}$) leads to dominance of orthokinetic aggregation.

Orthokinetic aggregation

We used a simple shear flow in the present lesson. In practice, we use **turbulent flows**. In the latter, the power per unit volume injected in the flow ϵ is transferred to smaller and smaller flow structures, the smallest ones being of size $\eta_K \simeq (\nu^3/\epsilon)^{1/4}$ where $\nu = \eta/\rho_f$ is the kinematic viscosity. It can be assumed that the flow is roughly a simple shear flow with average shear rate $\langle \dot{\gamma} \rangle = (\epsilon/\nu)^{1/2}$ **for particles smaller than η_K** . This leads to

$$k_{ij}^{ortho} \simeq \frac{4}{3} \left(\frac{\epsilon}{\nu} \right)^{1/2} (a_i + a_j)^3$$

This is fine for sub micron particles.

Differential sedimentation

From Stokes law for sedimentation, we can compute an aggregation rate due to the difference in fall velocity between aggregates/particles of different sizes

$$J_{ij} = \frac{2\pi g(\rho_p - \rho_f)}{9\eta} (a_i + a_j)^3 (a_i - a_j) n_i n_j$$

so the rate constant is

$$k_{ij}^{\text{sedim}} = \frac{2\pi g(\rho_p - \rho_f)}{9\eta} (a_i + a_j)^3 (a_i - a_j)$$

It often happens in later stages of flocculation when larger aggregates have formed and fall through smaller aggregates or particles.

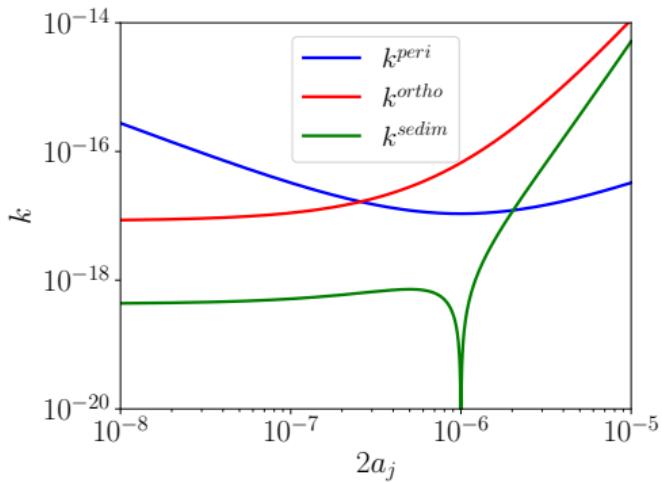
Comparison of the 3 types of aggregation mechanisms

Reminder

$$k_{ij}^{peri} = \frac{2}{3} \frac{kT}{\eta} \frac{(a_i + a_j)^2}{a_i a_j}$$

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

$$k_{ij}^{sedim} = \frac{2\pi g(\rho_p - \rho_f)}{9\eta} (a_i + a_j)^3 (a_i - a_j)$$



For a $1 \mu m$ diameter particle i and various sizes of particles j , aqueous suspension at 25 degrees C, $\dot{\gamma} = 50 s^{-1}$, $\rho_s = 2000 kg/m^3$.

What about interactions ?

Up to this point, we always supposed "collisions" lead to aggregation but in practice this is not true. Colloidal interactions may prevent aggregation. Imagine repulsive electrostatic forces deflecting a particle to the side of a target particle before they have a chance to come into contact in a shear flow. To account for these effects, we define either a **collision efficiency α** or the **stability ratio $W = 1/\alpha$** .

- If $\alpha \rightarrow 0$ or $W \gg 1$, collisions are not efficient (as in the example) and the suspension is called "stable".
- If $\alpha \rightarrow 1$ or $W \sim 1$, collisions perfectly efficient (as in the previous section of the course) and the suspension is generally not "stable".

If $W = 1000$, then 1 collision out of 1000 collisions lead to aggregation.

The Smoluchowski theory of the previous part must then be corrected with:

$$J_{ij} = k_{ij}^* n_i n_j \quad \text{where} \quad k_{ij}^* = \alpha k_{ij} = \frac{k_{ij}}{W}$$

Computing the stability ratio W : perikinetic case

In the perikinetic case, Fuchs (1934) has shown that

$$W = 2 \int_0^\infty \frac{e^{V/kT}}{(u+2)^2} du$$

where

$$u = \frac{2d}{a_i + a_j}$$

or for equal particles $u = d/a$, and V is the interaction potential between particles i and j (for example the DLVO potential). This has to be computed numerically in general. However since V has some maximum (energy barrier) the integral can be approximated by a simpler version and we get (Reerink and Overbeek 1954)

$$W \simeq \frac{1}{\kappa(a_i + a_j)} e^{\frac{V_{max}}{kT}}$$

Computing the stability ratio W : perikinetic case

Exercise: compute the stability ratio for $1\mu m$ diameter particles in 100 mM 1-1 electrolyte and for a potential barrier height of $10kT$ and $20kT$ and 25 degrees C.

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In water at room temperature the Debye length is $\lambda = 0.304/\sqrt{I} \approx 0.96\text{ nm}$ so $\kappa = 1/\lambda = 1.04 \times 10^9$. The simplified formula leads to $W(10kT) \approx 21$ (one collision out of 21 is effective) and $W(20kT) \approx 4.66 \times 10^5$ (one collision out of one million is effective).

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Remarks:

- Even a modest barrier can be very efficient
- Stability is extremely sensitive to details of the potential, which we don't know that precisely, so all these W computations are very, very, very approximate !

Plan

- 1 Colloids
- 2 Aggregation
- 3 Electrokinetics
- 4 Operators

Introduction

Electrokinetics: Combination of electrical effects and motion of the fluid

- A particle and its ion cloud are moving relative to the surrounding fluid: electrophoresis, sedimentation potential
- An electrolyte is moving relative to a stationary charged wall: electro-osmosis, streaming potential

Electrophoresis

Debye-Hückel approximation ($\zeta < 25 \text{ mV}$ and $\kappa a < 1$)

We have already shown that the particle charge Q is, for low surface potentials,

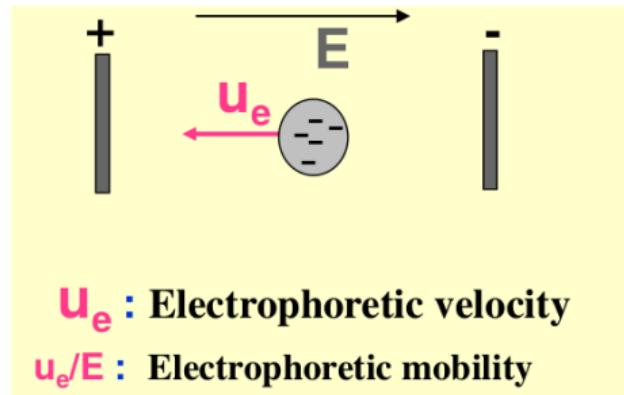
$$Q = 4\pi\epsilon a(1 + \kappa a)\Psi_s$$

If the particle is like a point charge ($\kappa a \ll 1$) and we assume $\Psi_s \approx \zeta$,

$$Q \approx 4\pi\epsilon a\zeta$$

and a force balance on the particle yields

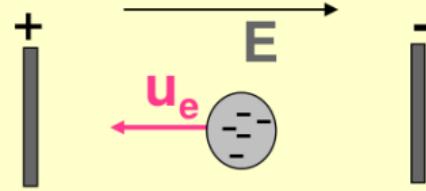
$$u_e = \frac{2\epsilon\zeta E}{3\mu} \text{ and } \mu_e = \frac{2\epsilon\zeta}{3\mu}$$



Electrophoresis

Smoluchowski approximation ($\kappa a \gg 1$)

$$u_e = \frac{\epsilon \zeta E}{\mu} \text{ and } \mu_e = \frac{\epsilon \zeta}{\mu}$$



u_e : Electrophoretic velocity

u_e/E : Electrophoretic mobility

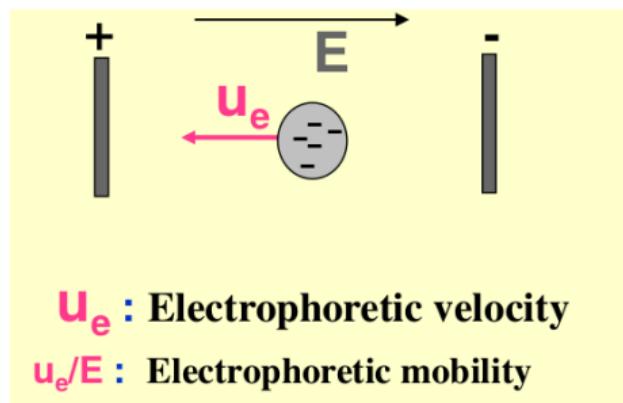
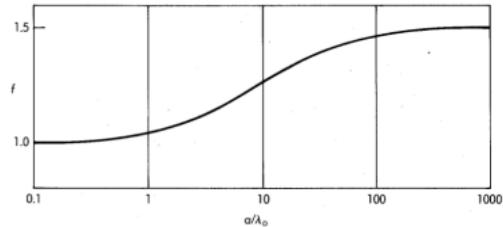
Electrophoresis

At intermediate κa

$$u_e = \frac{2 \epsilon \zeta E}{3 \mu} f(\kappa a) \text{ and } \mu_e = \frac{2 \epsilon \zeta}{3 \mu} f(\kappa a)$$

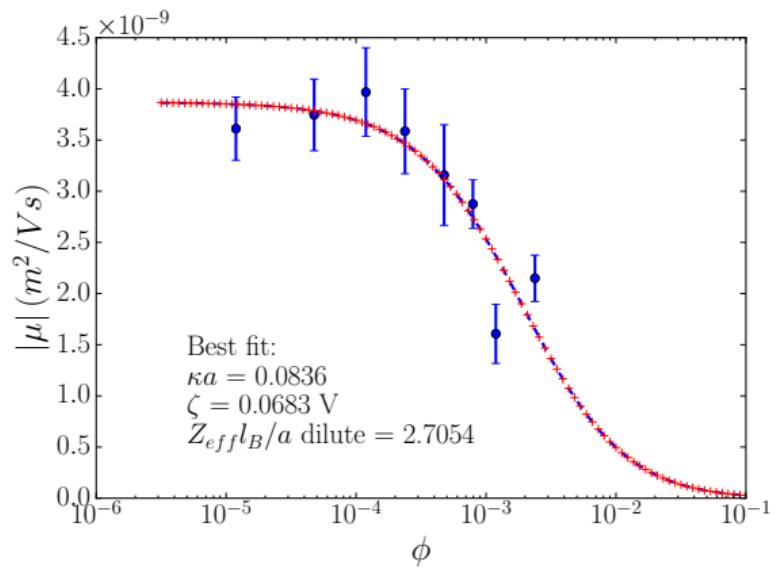
where f is Henry's function (1931)

$$f(\kappa a) = 1 + \frac{1}{2} \left[1 + \frac{5}{2\kappa a} (1 + 2e^{-\kappa a}) \right]^{-3}$$



Electrophoresis

Beware ! These theories are for dilute suspensions (dilute enough so that colloids do not interact hydrodynamically or electrostatically). For more sophisticated models: see e.g. Ohshima's work in the 90's and after.



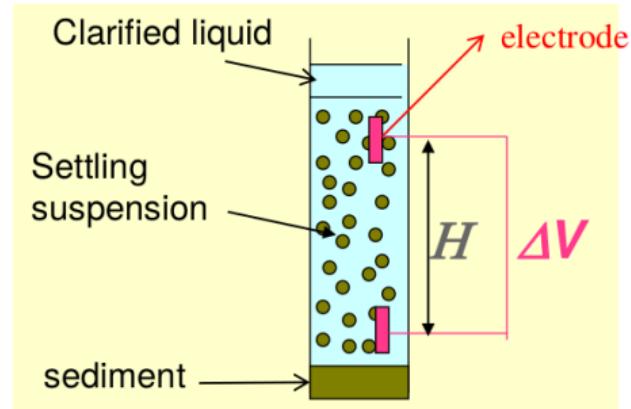
Sedimentation potential

This is basically the same as electrophoresis, but the particles move because of gravity and not due to an applied electric field. As a result

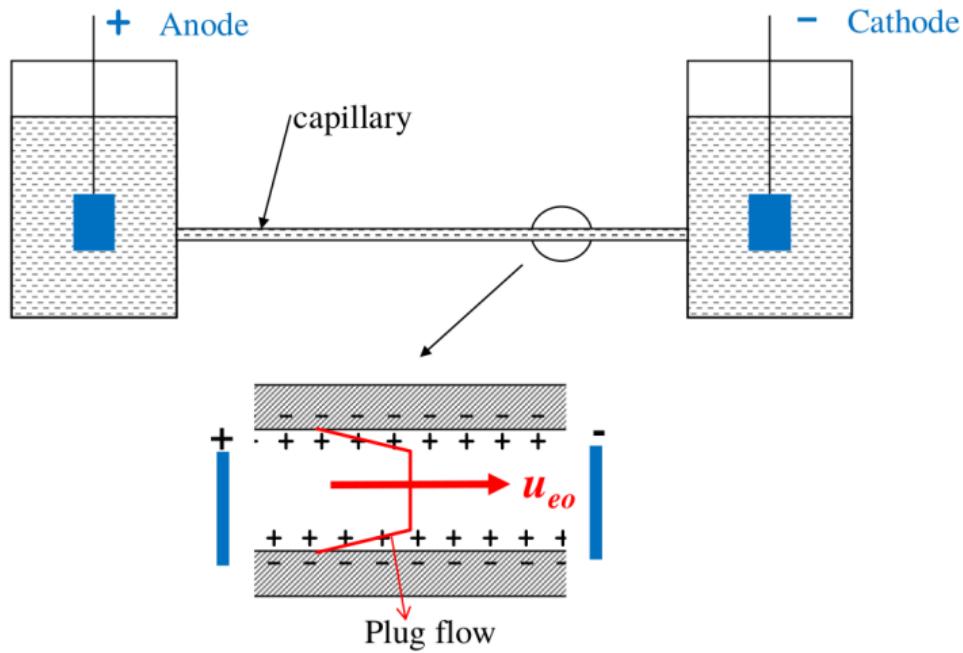
$$\frac{\Delta V}{H} = E' = -\frac{6\pi\rho_c U a \epsilon \zeta}{\chi}$$

where ρ_c is the colloid density (number per unit volume), U is the colloid sedimentation velocity, and χ is the electric conductivity of the medium.

Application: analyze the surface charge of particles.



Electro-osmosis



Electro-osmosis

Form an electrical double layer much smaller than the capillary radius R , Smoluchowski relation for the electroosmotic velocity

$$u_{eo} = -\frac{\epsilon \zeta E}{\mu}$$

where μ is the dynamic viscosity of the fluid. The electroosmotic mobility is

$$\mu_{eo} = -\frac{\epsilon \zeta}{\mu}$$

Example: $\mu = 0.001 \text{ Pa.s}$ (water), $\zeta = -100 \text{ mV}$, $E = 1000 \text{ V/m}$ gives $u_{eo} = 0.1 \text{ mm/s}$.

Streaming potential

Basically the same as electroosmosis, but instead of applying E and measuring a flow, we apply a flow by imposing a pressure difference and we measure E . For a capillary radius R much larger than the EDL,

$$\Delta V = \frac{\epsilon\zeta}{\mu\chi} \Delta P$$

where ΔV is the potential difference and χ is the electric conductivity of the medium. This is used to analyze the surface charge of planar surfaces.

Exercises: electrophoresis

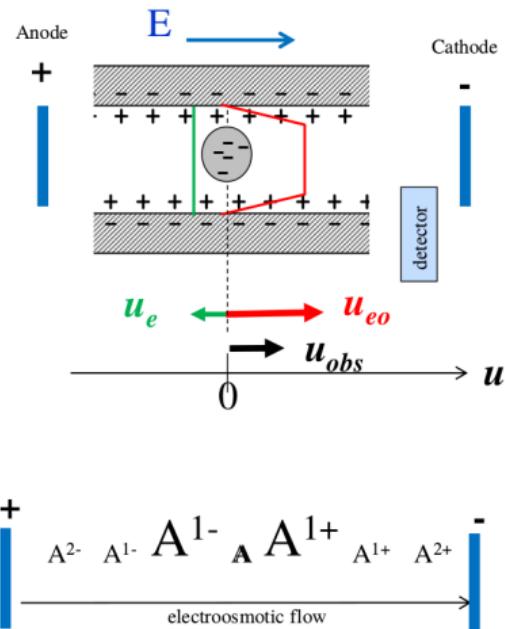
A protein (ovalbumine) is mixed in a 0.118 M NaCl solution. A capillary is filled with this solution and an electric field of +1.50 V/cm is applied between the entrance and the exit of the capillary, the protein then migrates at the velocity $-1.20 \mu\text{m/s}$. The particle diameter is simultaneous measured: 53.4 Angstroms. The temperature of the experiment is 25°C . Calculate the following parameters:

- ① The electrophoretic mobility of the protein
- ② κa
- ③ The zeta potential of the protein (in mV)
- ④ The number of charges carried by the protein ($=Q/e$)

Exercises: capillary electrophoresis

The separation of compounds is dependent on (i) the differential migration of analytes in an applied electric field and, (ii) the rate of electroosmotic flow of the buffer.

In a typical system, the electroosmotic flow is directed toward the negatively charged cathode so that the buffer flows through the capillary from the source vial to the destination vial. Since the electroosmotic flow of the buffer solution is generally greater than that of the electrophoretic flow of the analytes, all analytes are carried along with the buffer solution toward the cathode. Even small, triply charged anions can be redirected to the cathode by the relatively powerful electroosmotic flow of the buffer solution. Negatively charged analytes are retained longer in the capillary due to their conflicting electrophoretic mobilities. The order of migration seen by the detector is: small multiply charged cations migrate quickly and small multiply charged anions are retained strongly.



Exercises: capillary electrophoresis

An equipment of capillary electrophoresis is used to measure the electrophoretic mobility of 2 proteins in mixture. The capillary tube used in this device is not closed at ends, its total length is $L = 50 \text{ cm}$ and its internal radius 50 mm . Under the effect of an electric field of 10 kV applied between 2 electrodes located at the entrance and exit of the tube, the proteins move with a velocity: $u_{obs} = u_e + u_{eo}$ At a distance $L_d = 43 \text{ cm}$ from the entrance of the capillary is located a UV detector which allows to measure the elution time of each species present in the mixture. This elution time t is expressed by

$$t = \frac{L_d}{u_{obs}}$$

- ① What condition must satisfy u_{eo} so that analysis is feasible knowing that proteins are negatively charged. BSA radius: 3.61 nm . α -lactalbumin radius : 2.06 nm . Electrolyte concentration (1:1) $C = 10^{-3} M$. $T=25$ degrees C. $\mu = .001 \text{ Pa.s}$
- ② A neutral standard (glucose) is first injected. Its elution time at pH 6.2 being 8.53 min, calculate u_{eo} .

Exercises: capillary electrophoresis

- ③ The mixture of BSA and α -lactalbumin dissolved in a buffer at pH 6.2 is then analyzed. Knowing that the electrophoretic mobilities of these proteins are at this pH: BSA: $-19.7 \cdot 10^{-9} m^2/(Vs)$; α -lactalbumin: $-10.2 \cdot 10^{-9} m^2/(Vs)$; Calculate the elution time expected for each protein. Deduce the value of their Zeta potential at this pH.
- ④ When the pH is changed, glucose and BSA elution times are:

pH 7.15

pH 4.56

$$t(\text{glucose}) = 8.74 \text{ min} \quad t(\text{glucose}) = 9.19 \text{ min}$$

$$t(\text{BSA}) = 25.59 \text{ min} \quad t(\text{BSA}) = 9.12 \text{ min}$$

Re-calculate for pH 7.15 and 4.56 the electrophoretic mobilities and the zeta potential of BSA.

- ⑤ Deduce the isoelectric point of this protein.

Plan

1 Colloids

2 Aggregation

3 Electrokinetics

4 Operators

Notations

Vectors are underlined (ex : \underline{A}) and second order tensors are double-underlined (ex : $\underline{\underline{T}}$).

In a cartesian frame of reference, the components will be denoted by $\underline{A} = (A_x, A_y, A_z)$. In a cylindrical frame of reference $\underline{A} = (A_r, A_\theta, A_z)$. The expressions of each operator in what follows are given in the order cartesian-cylindrical. The expressions in spherical coordinates are not used in this lesson but can be found on the internet.

Einstein's notation

A vector \underline{A} is written as its “i” component A_i . A second order tensor $\underline{\underline{T}}$ is represented by T_{ij} , its component at row “i” and column “j”. Einstein’s convention considers that there is implicit summation on all the possible values of any index that is repeated twice in a multiplicative group. For example, the scalar product of \underline{A} and \underline{B} is written :

$$\underline{A} \cdot \underline{B} = A_x B_x + A_y B_y + A_z B_z = A_i B_i \quad (16)$$

When summation occurs, the index is “mute” (the result does not depend on this index). $A_i B_j$ has the dimension of a second order tensor (it depends on two indices).

The “nabla” operator ∇

∇ is basically the gradient operator (it is not really a vector) :

$$\nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} \quad (17)$$

In cartesian coordinates, the “scalar product” of ∇ with a vector corresponds to the divergence of this vector. For example, the divergence of the gradient of a scalar function (in other words the laplacian) can be written $\Delta = \nabla \cdot (\nabla f)$, or also denoted $\nabla^2 f$.

Gradient of a scalar

$$\text{grad}(f) = \nabla f = \frac{\partial f}{\partial x_i} = \begin{pmatrix} \frac{\partial f}{\partial x} \\ \frac{\partial f}{\partial y} \\ \frac{\partial f}{\partial z} \end{pmatrix} \text{ in cartesian coordinates}$$

or

$$= \begin{pmatrix} \frac{\partial f}{\partial r} \\ \frac{1}{r} \frac{\partial f}{\partial \theta} \\ \frac{\partial f}{\partial z} \end{pmatrix} \text{ in cylindrical coordinates.}$$

Gradient of a vector

$$\nabla \underline{A} = \frac{\partial A_i}{\partial x_j} = \begin{pmatrix} \frac{\partial A_1}{\partial x} & \frac{\partial A_1}{\partial y} & \frac{\partial A_1}{\partial z} \\ \frac{\partial A_2}{\partial x} & \frac{\partial A_2}{\partial y} & \frac{\partial A_2}{\partial z} \\ \frac{\partial A_3}{\partial x} & \frac{\partial A_3}{\partial y} & \frac{\partial A_3}{\partial z} \end{pmatrix} \text{in Cartesian coordinates}$$

or

$$= \begin{pmatrix} \frac{\partial A_1}{\partial r} & \frac{1}{r} \frac{\partial A_1}{\partial \theta} - \frac{A_2}{r} & \frac{\partial A_1}{\partial z} \\ \frac{\partial A_2}{\partial r} & \frac{1}{r} \frac{\partial A_2}{\partial \theta} + \frac{A_1}{r} & \frac{\partial A_2}{\partial z} \\ \frac{\partial A_3}{\partial x} & \frac{1}{r} \frac{\partial A_3}{\partial \theta} & \frac{\partial A_3}{\partial z} \end{pmatrix} \text{in cylindrical coordinates}$$

Divergence of a vector

$$\begin{aligned} \operatorname{div} \underline{A} = \nabla \cdot \underline{A} &= \frac{\partial A_i}{\partial x_i} = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z} \text{ (Cartesian)} \\ \text{or} \\ &= \frac{1}{r} \frac{\partial r A_r}{\partial r} + \frac{1}{r} \frac{\partial A_\theta}{\partial \theta} + \frac{\partial A_z}{\partial z} \text{ (cylindrical)} \end{aligned}$$

Divergence of a symmetric second order tensor (ex: stress tensor)

$$\operatorname{div} \underline{\underline{T}} = \frac{\partial T_{ij}}{\partial x_j} = \begin{pmatrix} \frac{\partial T_{11}}{\partial x} + \frac{\partial T_{12}}{\partial y} + \frac{\partial T_{13}}{\partial z} \\ \frac{\partial T_{21}}{\partial x} + \frac{\partial T_{22}}{\partial y} + \frac{\partial T_{23}}{\partial z} \\ \frac{\partial T_{31}}{\partial x} + \frac{\partial T_{32}}{\partial y} + \frac{\partial T_{33}}{\partial z} \end{pmatrix} \text{ (Cartesian)}$$

or

$$= \begin{pmatrix} \frac{\partial T_{11}}{\partial r} + \frac{1}{r} \frac{\partial T_{12}}{\partial \theta} + \frac{\partial T_{13}}{\partial z} + \frac{T_{11} - T_{22}}{r} \\ \frac{\partial T_{21}}{\partial r} + \frac{1}{r} \frac{\partial T_{22}}{\partial \theta} + \frac{1}{r} \frac{\partial T_{23}}{\partial z} + \frac{2T_{12}}{r} \\ \frac{\partial T_{31}}{\partial x} + \frac{1}{r} \frac{\partial T_{32}}{\partial \theta} + \frac{\partial T_{33}}{\partial z} + \frac{T_{31}}{r} \end{pmatrix} \text{ (cylindrical)}$$

Laplacian

$$\Delta f = \nabla^2 f = \frac{\partial^2 f}{\partial x_k \partial x_k} = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \text{ (Cartesian)}$$

or

$$= \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial f}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 f}{\partial \theta^2} + \frac{\partial^2 f}{\partial z^2} \text{ (cylindrical)}$$