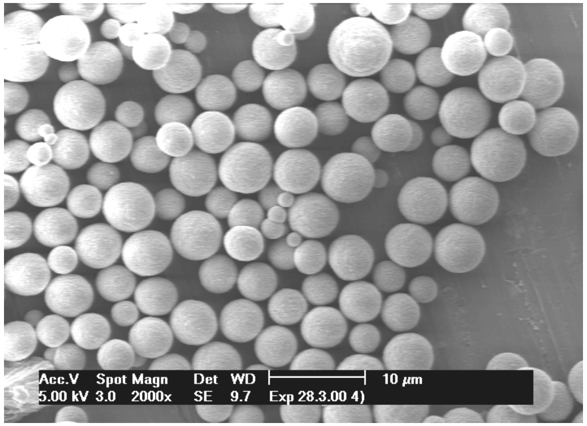
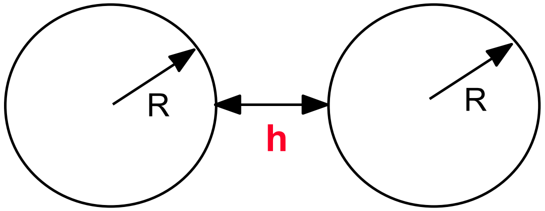
Week 8

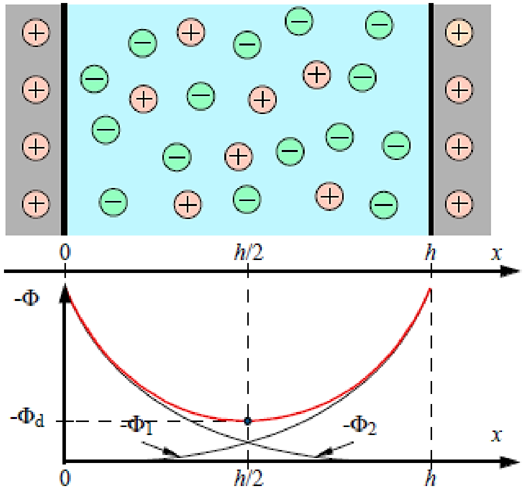
8. Powder Treatment (2)

Interaction between charged surfaces- electrostatic - Colloidal stability : DLVO model – aggregation kinetics.

A. Testino



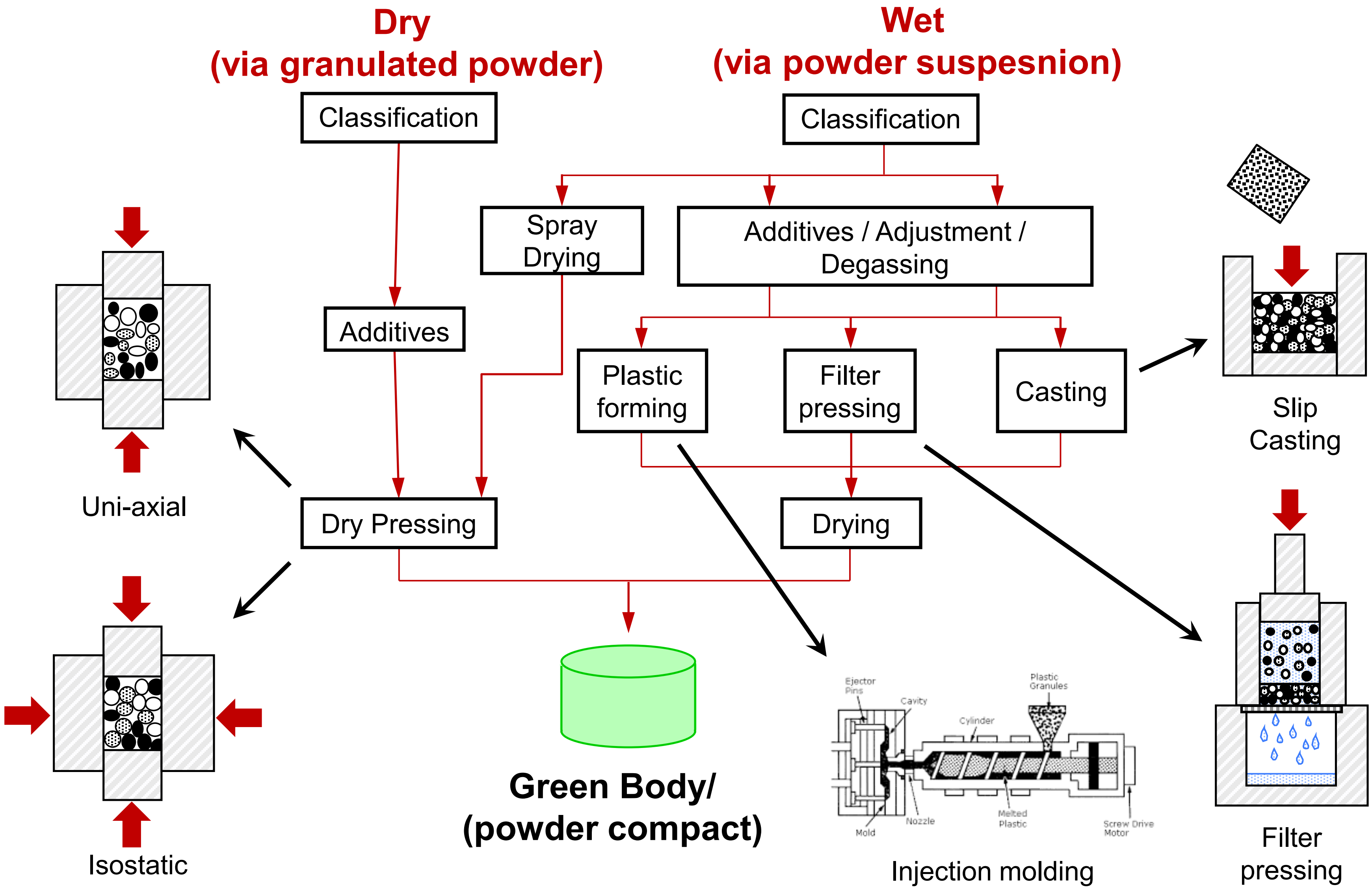




The Colloidal Domain - DF Evans & H. Wennerström, Wiley, 1999. (Chp. 3 & 5)

Les Céramiques, J. Barton, P. Bowen, C. Carry & J.M. Haussonne,
Les Traité des Matériaux, Volume 16, PPUR, 2005

Manufacture of Ceramics - Ceramic Processing



Dry
(via granulated powder)

Classification

Additives

Dry Pressing

Uni-axial

Isostatic

Wet
(via powder suspesnion)

Classification

Spray Drying

Additives / Adjustment / Degassing

Plastic forming

Filter pressing

Casting

Drying

Slip Casting

Green Body/
(powder compact)

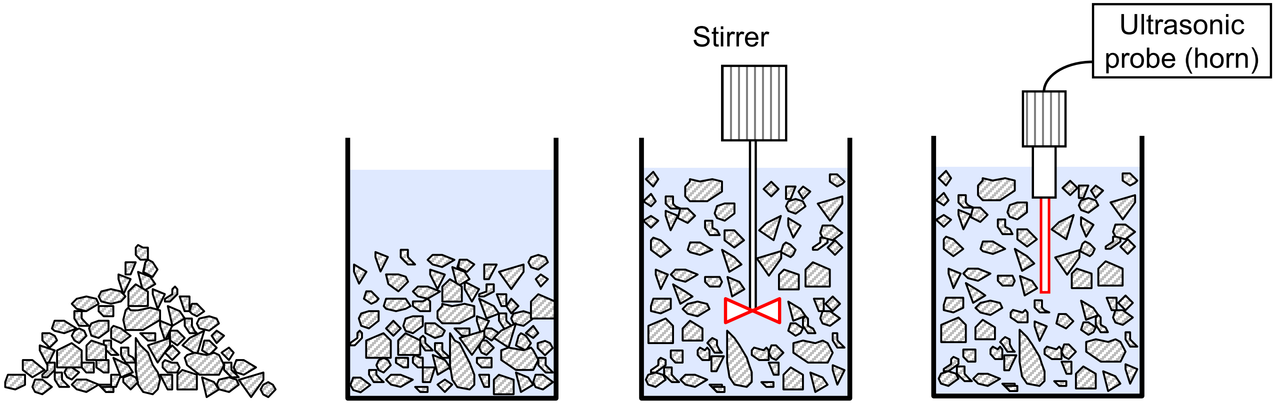
Injection molding

Filter pressing

Dispersion - Suspensions and Pastes

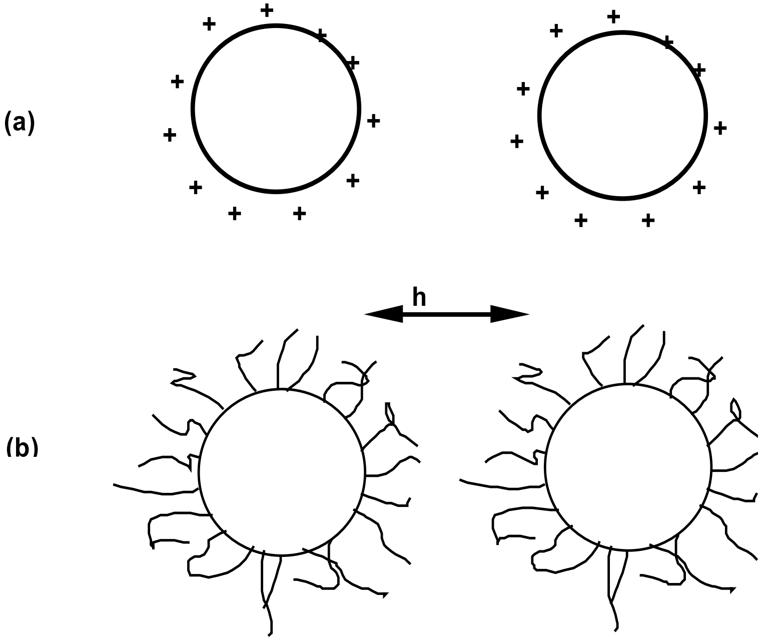
The key factors in producing a paste or dispersion are;

- wetting the surface of the powder with the liquid;
- the dispersion of the powder in the volume of this liquid by mixing or stirring;
- breaking up agglomerates (soft) or aggregates (hard) by ultrasonic treatment or by milling;
- the ability to keep the powder well dispersed and to avoid agglomeration or phase separation by sedimentation.
- agglomerates (soft) - no chemical bond
- aggregates (hard) - chemical bond



Interparticle forces

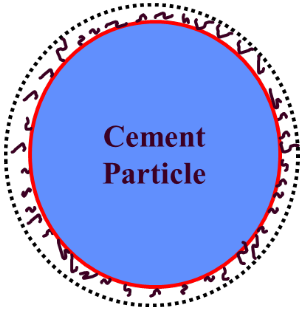
- Attractive *(last week)*
  - Van der Waals forces V_A



(distance h between particles)

Repulsive

- Electrostatic *(today)*
  - a dissociation of species at the surface
  - adsorption of charged species
  - dissociated ions, molecules or polymers
- Steric *(next week)*
  - molecules - often adsorbed polymers



Themes - this week

- Formation of charged interfaces
- Charged surface / dissolved electrolytes interaction
- Interaction forces in colloidal systems
- Interactions between charged surfaces
- Colloidal stability
- Theory of colloidal stability
- Aggregation of colloidal suspensions

*Chapter 3 & 5 - The Colloidal Domain – DF Evans & H. Wennerström, Wiley, 1999.

Summary

Formation of charged interfaces /dissolved electrolytes – double layer theory (9-27)

- Formation of charged interfaces (9)
- examples (10-11)
- distribution of ions in solution
  Poison Boltzmann Equation (12-15)
- Guoy Chapman model (15-16)
- Stern Model (17-18)
- Double layer thickness (19-20)
- Surface charge density (21)
- Linearized Poison Boltzman (22)
- Ionic conc - Surface Potential (23-26)

Zeta potential measurement (27-29)

- Constant charge or potential (30)

Interaction forces in colloidal systems (31)

Interaction between charged surfaces (32-41)

- Identically charged surfaces (33- 34)
- Surfaces of opposite sign (35)

Colloidal stability (36-41)

- DLVO theory (36-38)
- repulsion between charged surfaces (39-41)
- critical concentration of CCC coagulation (53)

Aggregation of colloidal suspensions (43-47)

- Hamaker program (44)

1

Formation of Charged Interfaces

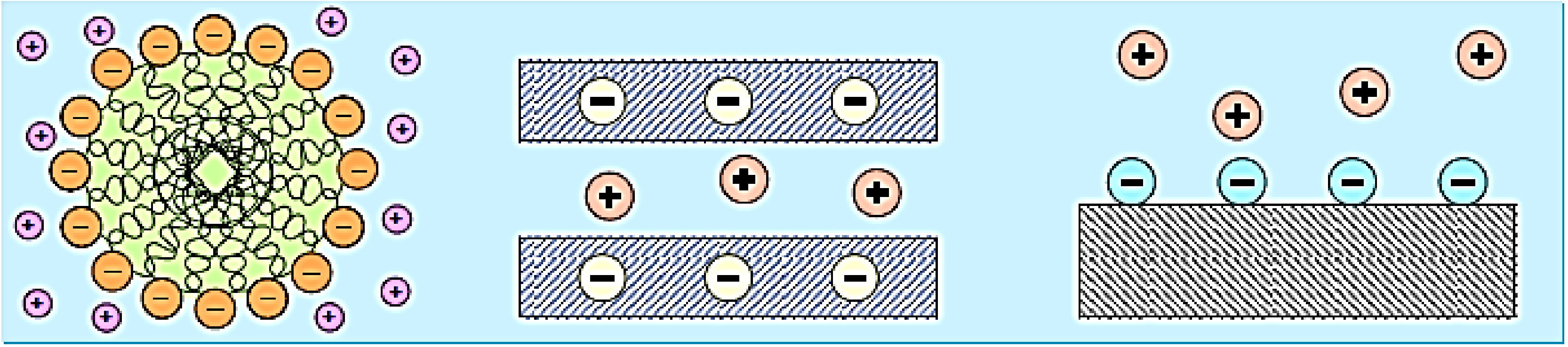
Ion adsorption at interfaces

– Mechanisms that can produce surface charges

- Colloidal particles formed from charged species: micelles of ionic surfactants (e.g. SDS); polyelectrolytes (e.g. polyacrylate, alginate, etc.)
- Defects in crystal structure (substitution of Si^{4+} by Al^{3+} in clays)
- Presence of surface functional groups… titratable :

  $–OH, –COOH, –NH_2, –SO_4H, –PO_4H_2$...
- Adsorption of charged species in solution (*Hofmeister* series):

$I^- > ClO_4^-$, $NO_3^- > Br^- > Cl^- > OH^- > F^-$, SO_4^{2-}



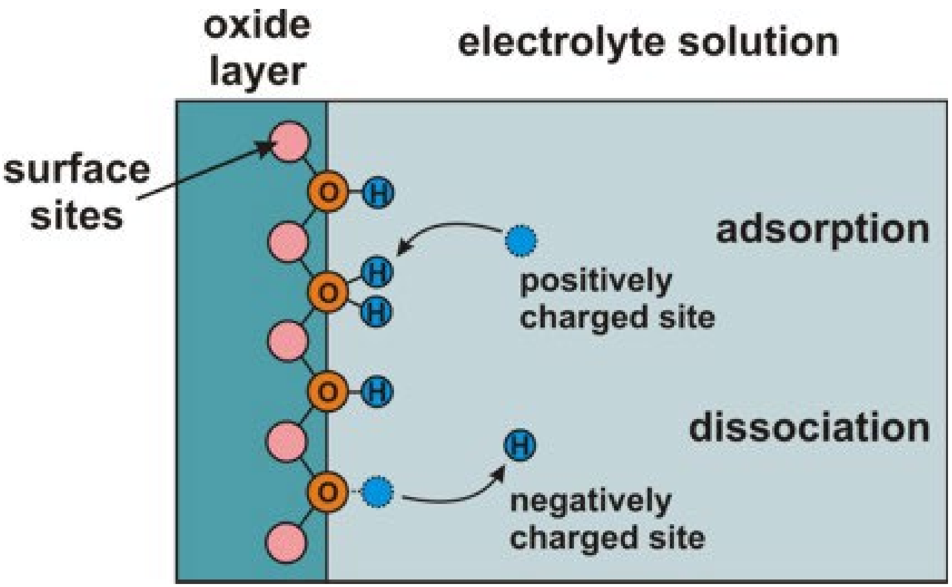
Micelle

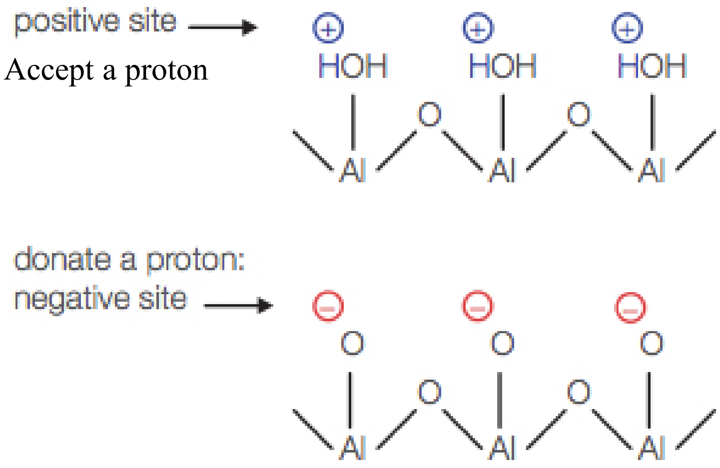
Clay sheet

Anion adsorption

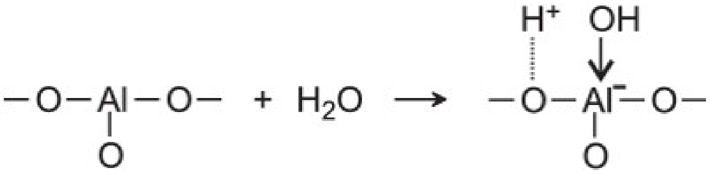
Surface charging - examples

- Surface of oxides in water often hydroxylated – termination metal-OH





Accept a proton



$$-\mathrm{O}-\underset{\mathrm{O}}{\underset{|}{\mathrm{Al}}}-\mathrm{O}- + H_2O \longrightarrow -\overset{\mathrm{H^+}}{\overset{\vdots}{\mathrm{O}}}-\underset{\mathrm{O}}{\underset{|}{\overset{\mathrm{OH}}{\overset{\downarrow}{\mathrm{Al}^-}}}}-\mathrm{O}-$$

Whether one has adsorption or dissociation depends on pH (concentrations of H + and OH- ions) and the chemistry of the metal-oxygen bond - hydroxide

Lewis acid: accepts a pair of electron   Lewis base: donates a pair of electron

Brønsted acid: releases a H^+ (donor)   Brønsted base: captures a H^+(acceptor)

Surface charging - Ion adsorption at interfaces

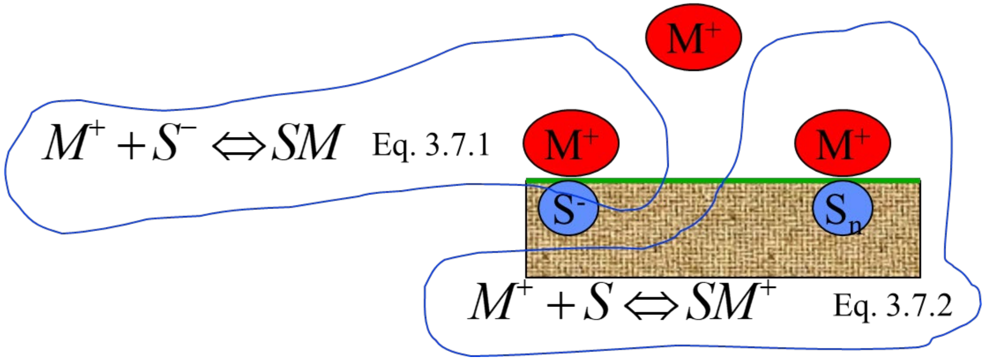
1

❖ "**potential determining ions** – pdi "- determines the potential of the surface

- e.g. Ca^{2+}… preferentially adsorbs on cement surface - surface charge changes from negative to positive
- NaCl… indifferent electrolyte … no specific adsorption…does not influence potential
- HCl… H^+ Cl^- - **H^+** determines the potential ...
- NaOH…Na^+ OH^- - **OH^-** - determines the potential
- H^+ and OH^- determines the potential as a **function of pH**….
- De-protonation of a silanol group $-SiOH \leftrightarrow -SiO^- + H^+$

❖ Charge often determined by equilibrium process - 3 Free energy contributions

- Chemical interactions – short range – promote adsorption
- Electrostatic – longer range – limits surface charge – ordered localised arrangement
- Entropy – tends towards desorption – random uniform distribution of ions

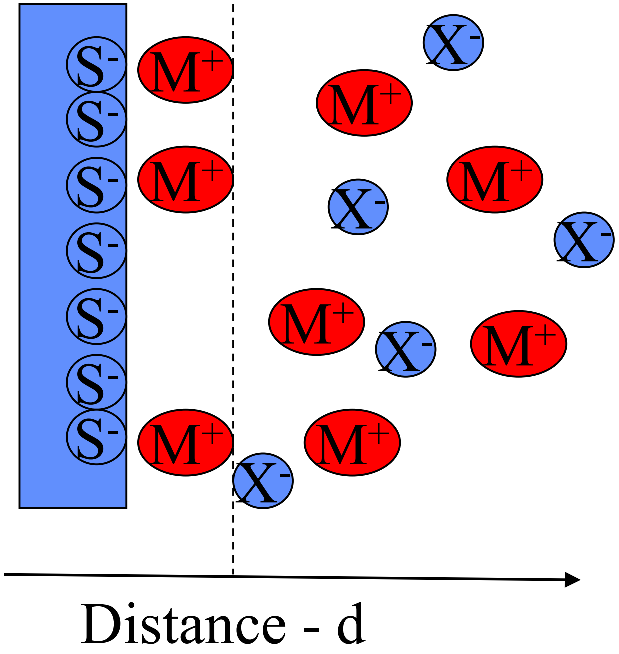


$$M^+ + S^- \Leftrightarrow SM$$ Eq. 3.7.1

$$M^+ + S \Leftrightarrow SM^+$$ Eq. 3.7.2

3.8 – Poisson Boltzmann equation – charged surface

- Describes surface potential (Φ), ionic concentration (c), vs distance (d) from surface
- Relationship between surface charge density (σ) and surface potential (Φ)



- Poisson equations –charge density (*ρ)*

$$\varepsilon_0 \varepsilon_r \vec{\nabla}^2 \Phi = \rho_{(free-ions)} \quad (3.5.13)$$

$$\rho_{(free-ions)} = e \sum_i z_i c_i^* (\vec{r}) \quad (3.8.1)$$

•Boltzmann distribution

$$c_i^*(\vec{r}) = c_{i0}^* \exp\left(\frac{-z_i e \Phi}{kT}\right) \quad (3.8.2)$$

c^*_{io} - bulk value far from surface (Φ=0)

* Indicate that concentration is expressed as no. of molecules per m^3.

$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$: Laplace operator; *e* is the electric charge

Boltzmann contribution – charged surface

- **Electrostatic** contribution tends to favour **ordered layer**
- **Entropy** tends to generate **random** uniform distribution
- Boltzmann distribution – effect of external field, Φ,
- cf gravitational field - m x g x h – density of air diminishes as we go up !!!

$$c_i^*(\vec{r}) = c_{i0}^* \exp\left(\frac{-z_i e\Phi}{kT}\right) \qquad (3.8.2)$$

- c^*_{io}, concentration at Φ=0 i.e. in bulk solution far from interface ***(no. of molecules per m^3)***
- Combine Poisson Equations with Boltzmann distribution

$$\varepsilon_0 \varepsilon_r \vec{\nabla}^2 \Phi = \rho_{(free-ions)} \qquad \rho_{(free-ions)} = e \sum_i z_i c_i^*(\vec{r})$$

ρ(r) volume charge density (C/m^3)

Poisson Boltzmann (PB) Equation – charged surface

- Ion distribution in an electrolyte outside a charged surface

$$\boxed{\rho_{(free-ions)} \approx e\sum_i z_i c_{i0}^* \exp\left(\frac{-z_i e\Phi}{kT}\right)} \qquad \text{Eq. 3.8.3}$$

$$\boxed{\varepsilon_0\varepsilon_r\nabla^2\Phi = -e\sum_i z_i c_{i0}^* \exp\left(\frac{-z_i e\Phi}{kT}\right)} \qquad \text{Eq. 3.8.4}$$

That is the PB equation describing the ion distribution in an electrolyte solution outside a charged particle

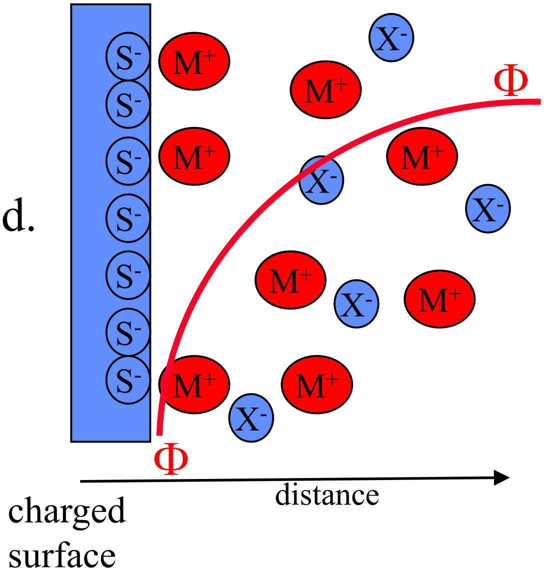
Assumptions made to arrive at PB – limitations

- Potential generated by External charge – but ions also contribute
- Ions are in motion dynamic – we take an average of many possible configurations to get an average potential
- **Mean Field Approximation** to get a mean electrostatic potential
- Approach can sometimes fail even qualitatively

Infinite plane solution – Guoy - Chapmann

- To solve PB need geometry – infinite plane ⇨ *d /dz*
- Model of *Gouy (1910) - Chapman (1913) – diffuse layer of counterions outside the charged surface*
  - *spatial distribution of* ions for an *infinite plane* evenly charged.
  - the *Poisson –Boltzmann* equation simplifies to linear form

$$\nabla^2\Phi \rightarrow \frac{d^2\Phi}{dz^2}$$

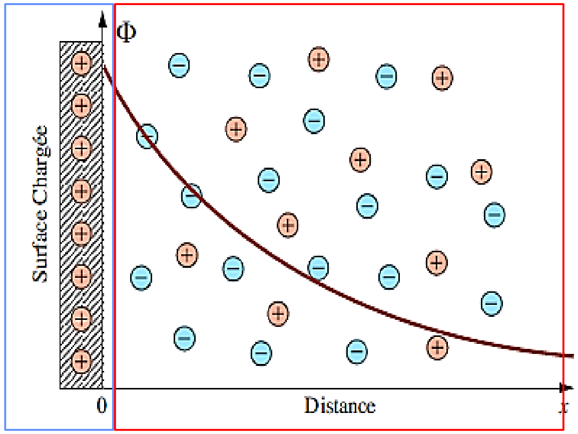


- Boundary conditions
  - Electroneutrality $d\Phi/dz = 0$ far from surface and
  - c^*_{io}, represents bulk electrolyte concentration (no. ions/m^3)
  - at surface behaves like capacitor $d\Phi/dz = -\sigma/\varepsilon_0\varepsilon_r$ (Eq 3.8.7)
  - no charged species below surface i.e. $z <= 0$, $d\Phi/dz = 0$

$$\left(\frac{d\Phi}{dz}\right)^2 = \frac{2kT}{\varepsilon_0\varepsilon_r}\sum_i c^*_{i0}\left[\exp\left(\frac{-z_i e\Phi}{kT}\right)-1\right] \qquad \text{Eq 3.8.10}$$

- Square root of LHS gives ± negative or positive surfaces

Diffuse layer of counterions



The charged surface, together with the diffuse layer of counterions forms an *electric double layer* .

Guoy Chapmann Theory – infinite plate

- For symmetric electrolyte e.g. NaCl (z=1) or $MgSO_4$ (z=2)

Eq. 3.8.11
$$\frac{d\Phi}{dz} = \left(\frac{8kTc_0^*}{\varepsilon_0\varepsilon_r}\right)^{1/2} \sinh\left(\frac{z_i e\Phi}{2kT}\right)$$

- On integration

Eq. 3.8.12
$$\Phi(z) = \frac{2kT}{z_i e}\ln\left\{\frac{1+\Gamma_0\exp(-\kappa z)}{1-\Gamma_0\exp(-\kappa z)}\right\}$$

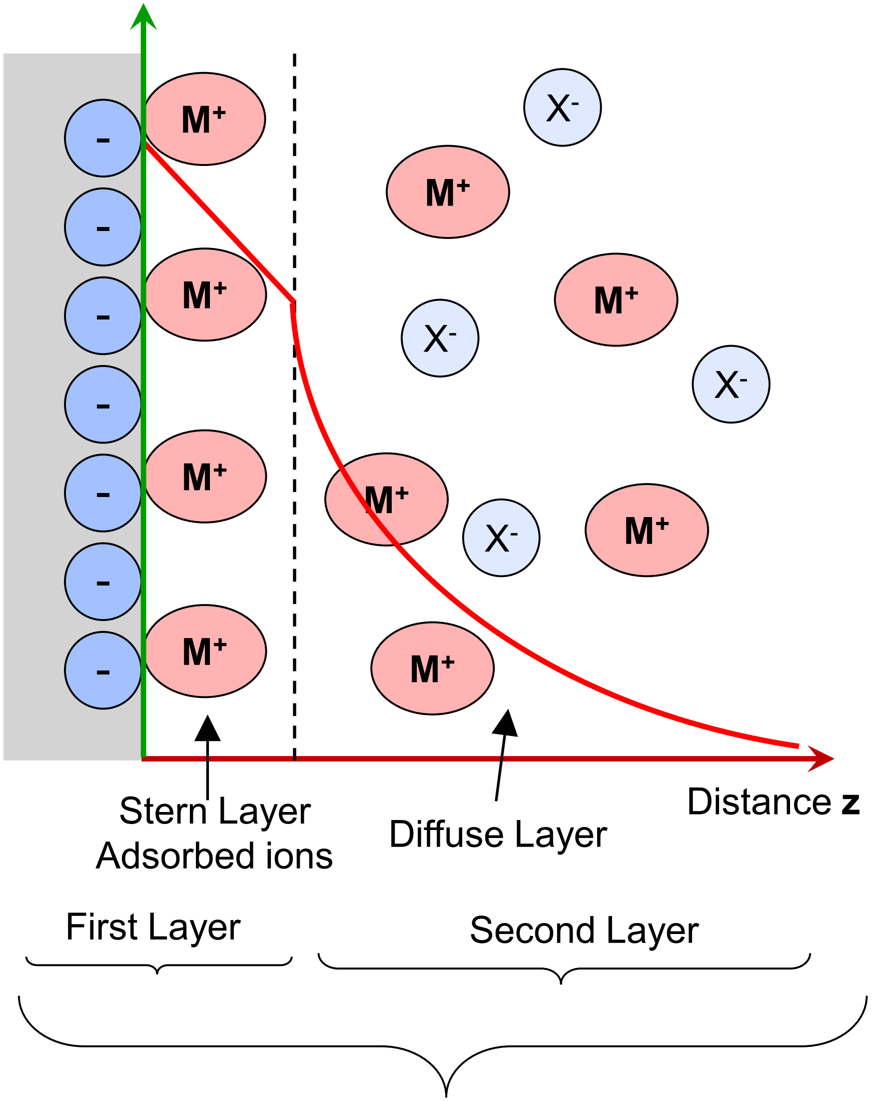
- Where κ^{-1} – known as the Debye screening length is

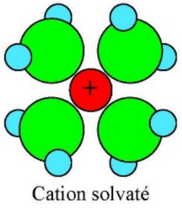
$$\frac{1}{\kappa} = \left(\frac{\varepsilon_0\varepsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^*}\right)^{1/2}$$
Eq. 3.8.13a

And
$$\Gamma_0 = \tanh\left(\frac{ze\Phi_0}{4kT}\right)$$

Dimensionless surface potential

Double layer - Gouy and Chapman – Stern model

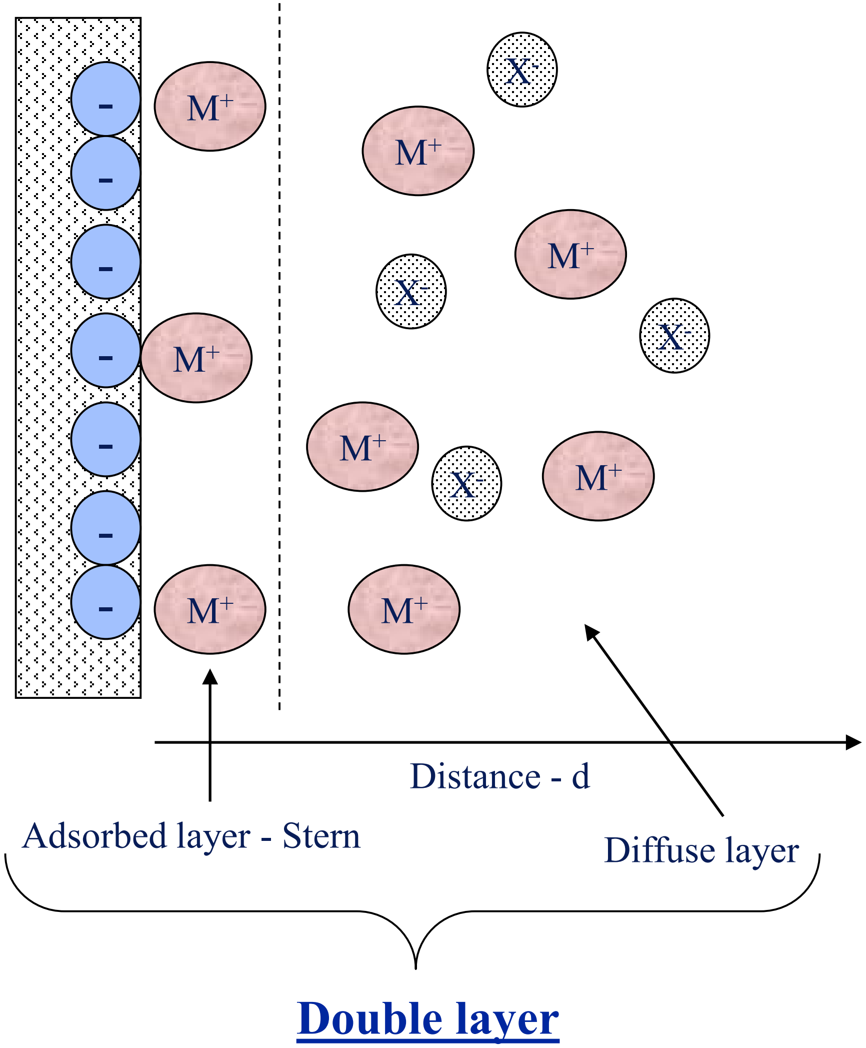




- Model of Gouy-Chapman -
- Treats ions as point charges…
- Hydrated ions can adsorb…(Helmholtz*)
- also water can adsorb – hydrogen bonding
- Layer close to the surface – combined the diffuse layer model of Guoy-Chapman and adsorbed ions of Helmholtz ⇨
- **Stern layer**.
- The limits of validity are for potentials of 200mV and ionic strengths of 1M.
- Surface and adsorbed layer – first layer
- - behaves as capacitor - linear decrease
- Exponential-like decrease of potential in diffuse layer

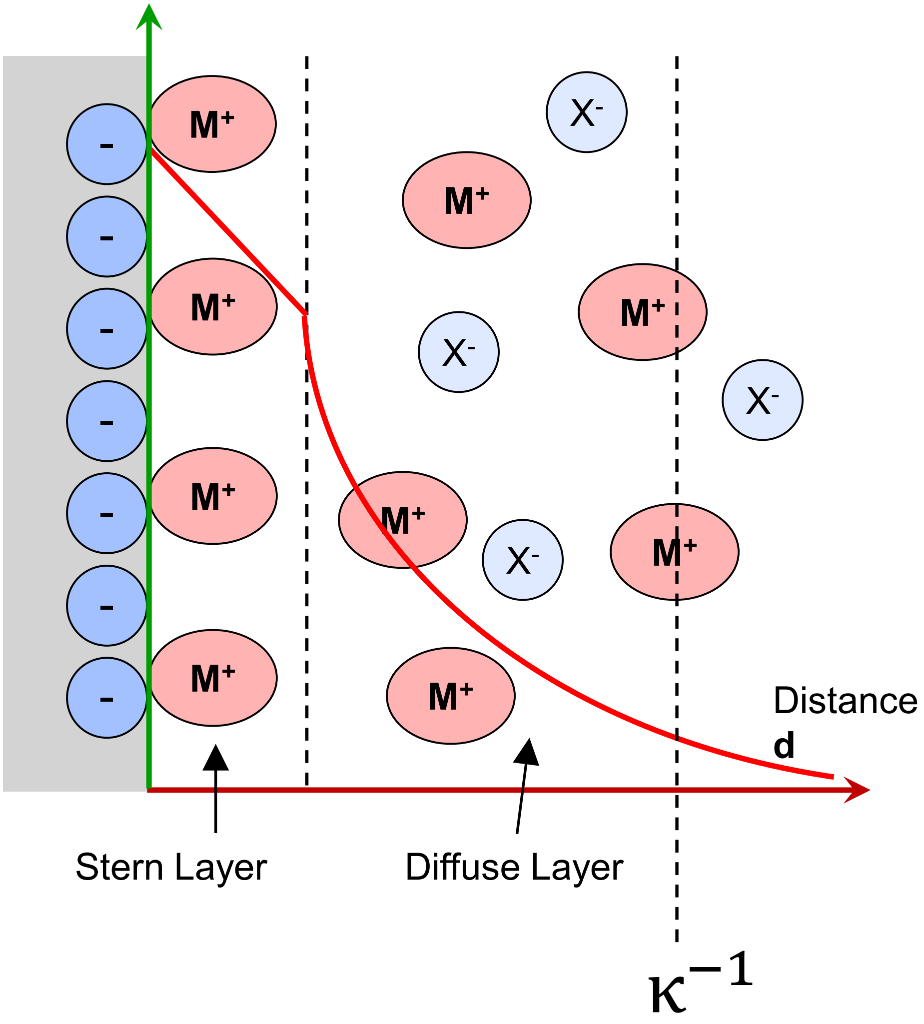
*https://en.wikipedia.org/wiki/Double_layer_(surface_science)

Double layer - Gouy and Chapman – Stern model



- Mean field approximation - i.e. average of many configurations of moving ions
- Limitations
  1. Ion-correlation effects due to highly polarizable layers - attractive
  2. Finite ion size - excluded volume effect - repulsive
  3. Image forces - "reflected" charge by surface gives "image in surface" - repulsive
  4. Surface charges discreet - not averaged as above - attractive
  5. Solvation forces - displacement / ordering of solvent - attractive, repulsive, oscillatory
- Details Chp. 5 Colloidal Domain

Double Layer Thickness – Debye Length - κ^{-1}



$$\frac{1}{\kappa} = \left(\frac{\varepsilon_0 \varepsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^*}\right)^{1/2}$$

- distance form the surface where the potential drops **by 1/e**
- Debye Length or
- Double layer (DL) thickness.

Debye length vs. ionic strength

- κ^{-1}
- Debye screening length or
- Double Layer thickness
- Effect size and rheology

$$\frac{1}{\kappa} = \left(\frac{\varepsilon_0 \varepsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^{*}} \right)^{1/2}$$

	Electrolyte – Thickness (nm)					
Conc. (M)	*1:1*	*1:2*	*1:3*	*2:2*	*3:3*	
0.001	9,6	7,9	6,8	4,8	3,2	
0.01	3,0	2,5	2,2	1,5	1,0	
0.1	0,96	0,79	0,68	0,48	0,32	

Surface Charge density

- Combining Eq. 3.8.7 and 3.8.11 (Gouy – Chapman Theory)
  - surface charge density, σ (C/m^2), as fn of surface potential, Φ,

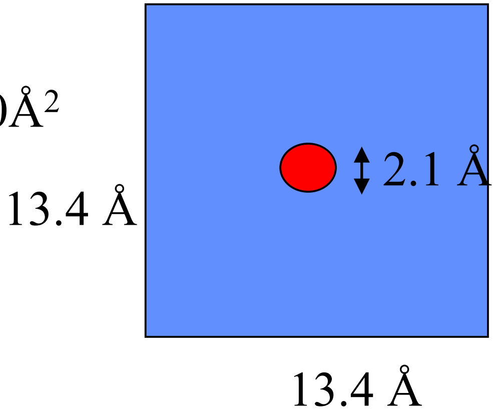
$$\sigma = \left(8kTc^{*}_{i0}\varepsilon_0\varepsilon_r\right)^{1/2}\sinh\left(\frac{z_i e\Phi_0}{2kT}\right) \qquad \text{Eq. 3.8.15}$$

Boundary conditions for integration Eq 3.8.10, slide 15

$$\left.\frac{d\Phi}{dz}\right|_{z\to\infty} = 0 \qquad \text{Eq. 3.8.6}$$

$$\left.\frac{d\Phi}{dz}\right|_{z=0} = \frac{-\sigma}{\varepsilon_0\varepsilon_r} \qquad \text{Eq. 3.8.7}$$

- Example
  - $\Phi_0 = -75$ mV, c = 0.15M, NaCl, 25°C
  - $\sigma = 0.09$ C/m^2 means 1 unit charge per 180Å^2
  - Na$^+$ ~ 1 Å (radius) (+ solvation 2.1 Å)



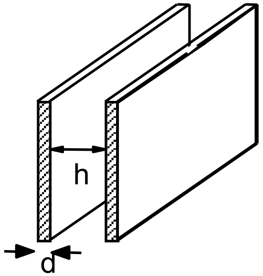
(NB - c_{i0} - in number of molecules or ions / m^3)

See Z-pot later, which is bit smaller than Φ_0, and measurable. A suspension of alumina in HNO$_3$ 5 mM ≈ Z-pot 55 mV.

Linearised Poisson Boltzmann

- Analytical solution of the PB equation – only for very few special cases
- Guoy-Chapmann linearized to give analytical solution for **planar surface**
- Further simplification
- Weakly charged surfaces
- < 25 mV gives

$$\frac{d^2\Phi}{dz^2} = \kappa^2\Phi$$ Eq.3.8.18



- Potential $$\Phi(z) = \Phi_0 e^{-\kappa z}$$ Eq.3.8.19
- Surface charge dens. $$\sigma = \varepsilon_0\varepsilon_r\kappa\Phi_0$$ Eq.3.8.20
- Capacitance of surface at Stern layer $$C = \frac{\sigma}{\Phi_0} = \frac{\varepsilon_0\varepsilon_r}{1/\kappa}$$ Eq.3.8.21

- Spherically symmetrical case – Debye-Hückel theory for electrolyte solutions

Ionic concentration and surface potential (1)

- Total ion surface concentration from Eq. 3.8.10 (infinite plane)

$$\left(\frac{d\Phi}{dz}\right)^2 = \frac{2kT}{\varepsilon_0\varepsilon_r}\sum_i c_{i0}^*\left[\exp\left(\frac{-z_i e\Phi}{kT}\right)-1\right]$$ Eq. 3.8.10, PB eq.

- with boundary condition of 3.8.7
  - surface behaves like capacitor

$$\left.\frac{d\Phi}{dz}\right|_{z=0} = \frac{-\sigma}{\varepsilon_o\varepsilon_r}$$ Eq. 3.8.7

- Using 3.8.7 in 3.8.10 gives - Graham Eq. 3.8.26 – takes into account both ions and counter-ions

$$\sum_i c_i^*(0) = \frac{\sigma^2}{2kT\varepsilon_0\varepsilon_r} + \sum_i c_{i0}^* = \frac{\sigma^2}{2kT\varepsilon_0\varepsilon_r} + \frac{\Pi_{osm}}{kT}$$ Eq. 3.8.26

Concentration of ions fn surface charge density and ionic conc. at bulk, which is correlated to the osmotic pressure

3

Ionic concentration and surface potential (2)

$$\sum_i c_{i0}^* = \frac{\Pi_{osm}}{kT}$$ Definition of osmotic pressure in an ideal solution (Eq. 1.5.11)

(c_{i0} - in molecules / m^3)

From Thermodynamics course - definition of osmotic pressure in an ideal solution

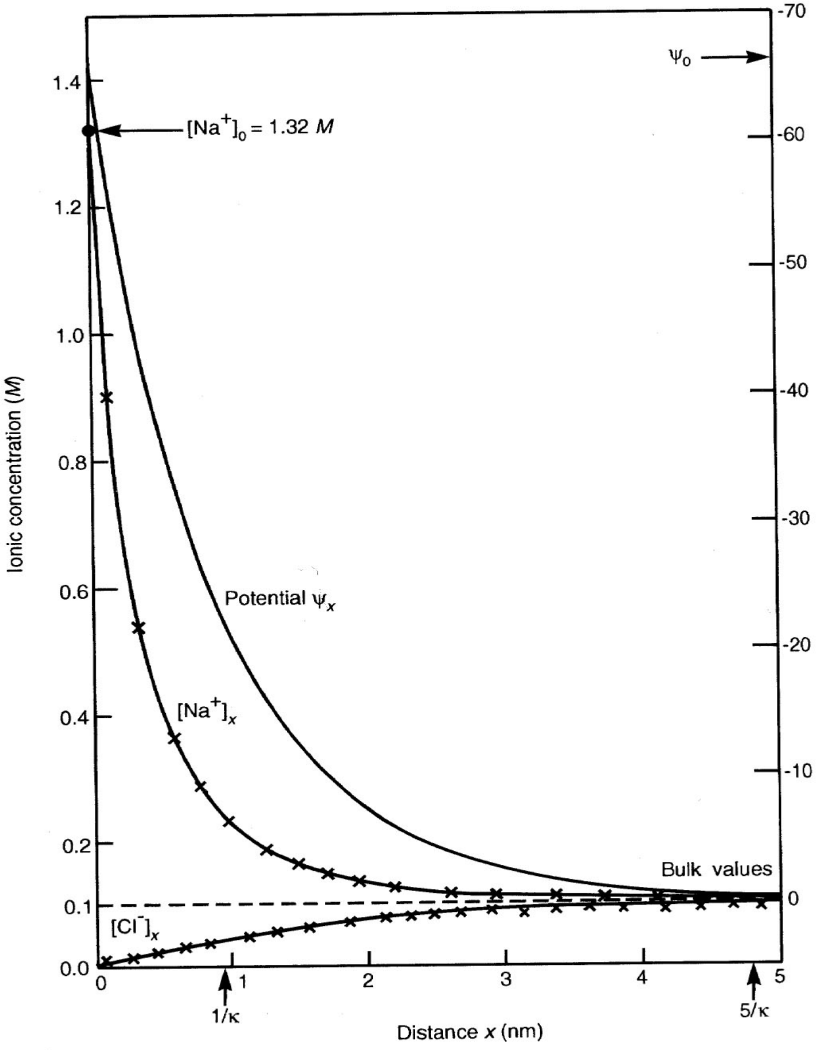
$$\Pi_{osm} = \frac{n_{solute}RT}{V_{solvent}} = \frac{n_{solute}k_B N_A T}{V_{solvent}}$$

$$\frac{n_{solute}N_A}{V_{solvent}} = \frac{\Pi_{osm}}{k_B T} \qquad \frac{n_{solute}N_A}{V_{solvent}} = \sum_i c_{i0}^* = \frac{\Pi_{osm}}{k_B T}$$

n_{solute} – mole fraction of solute, $V_{solvent}$ – volume of solvent (total)

gives concentration – number of molecules per unit volume (m^3)

Ionic concentration and surface potential



- Example –NaCl (0.1 M)-from Israelachvili*
  - $\sigma = 0.0621\ C/m^2$ ($1e/2.6nm^2$)
  - Φ_0= -66.2 mV (from Graham Eq. 3.8.26)
  - **x** Monte Carlo simulation
- Counterion concentration very near surface (84% within 3Å) according to this Gouy–Chapman double layer approach
- Concentration of ions at surface ~1-3M!
- such high concentrations raise questions about assumptions for linearised Poisson- Boltzman approach (see slide 19)
- Molecular modelling and numerical simulations (Monte Carlo) – show limitations – e.g.
- Kerisit S, Cooke DJ, Marmier A, Parker SC , CHEMICAL COMMUNICATIONS (24): 3027-3029 (2005)

*J. Israelachvili – Intermolecular & Surface Forces, 2nd edition, Academic Press, London, 1992

Dependance on valence, z

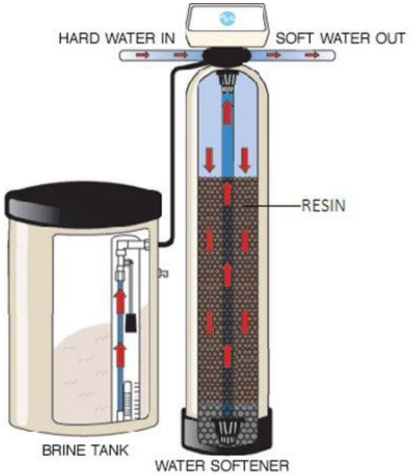
- Surface concentration of ion attracted electrostatically – Boltzmann distribution Eq. 3.8.2

$$c_i^*(0) = c_{i0}^* \exp\left(\frac{-z_i e\Phi}{kT}\right)$$

- when $e\Phi \geq kT$ valence effect z_i becomes more pronounced

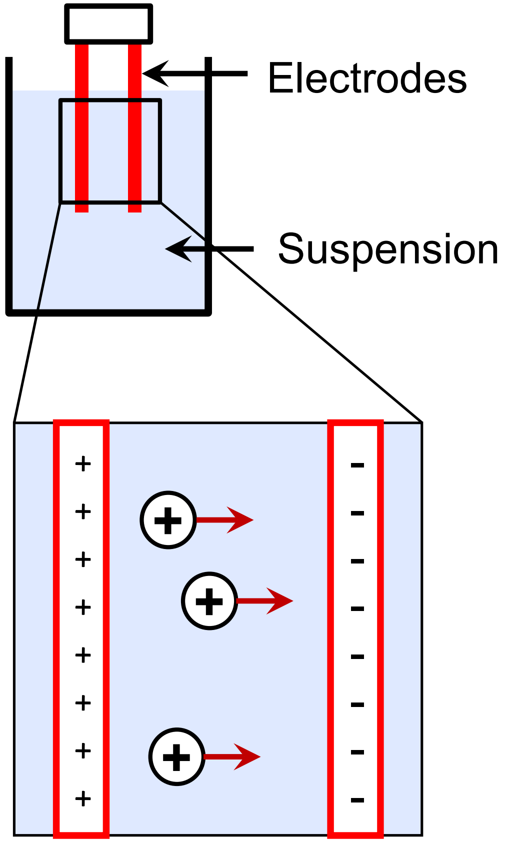
Example

- Clays or resins used in ion exchangers to soften water by removing divalent ions
  - surfaces are preloaded with Na^+ and then exchange for divalent ions eg Ca^{2+}
  - because of valence effect
- Ca^{2+} surface concentration enhanced by 50 times for surface potentials of 100 mV (low electrolyte concentrations) because of these electrostatic interactions
- dishwasher salt works by providing Na^+ for the dishwasher's 'ion exchange resins' in the softener unit - regenerated by Na^+, these attract and trap the magnesium and calcium ions that cause hard water and streaks on plates and glasses…



Surface potential measurement – zeta potential

- The experimentally determined surface potential is
- The zeta potential, ζ,
- Often calculated from a measure of electrophoretic mobility* (velocity per unit electric field) or
- Acoustophoretically$^{\$}$ by inducing a distortion of double layer, in an electric or acoustic field, leading to a differential movement between the charged particles and the continuous medium.
- The **zeta potential** thus determined does not correspond to the actual surface potential of the particles,
- but to the potential of an ill-defined plane beyond which the ions are not permanently bound to the particle.
- Called the Slip plane.
- The pH at which the zeta potential is zero is called the isoelectric point **(iep)**
- The pH when the surface potential is zero is called the point of zero charge **(pzc)**



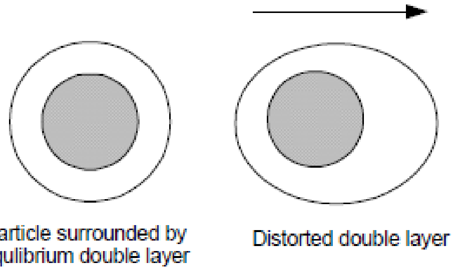


Figure 3: Distortion of double layer by applied electric field

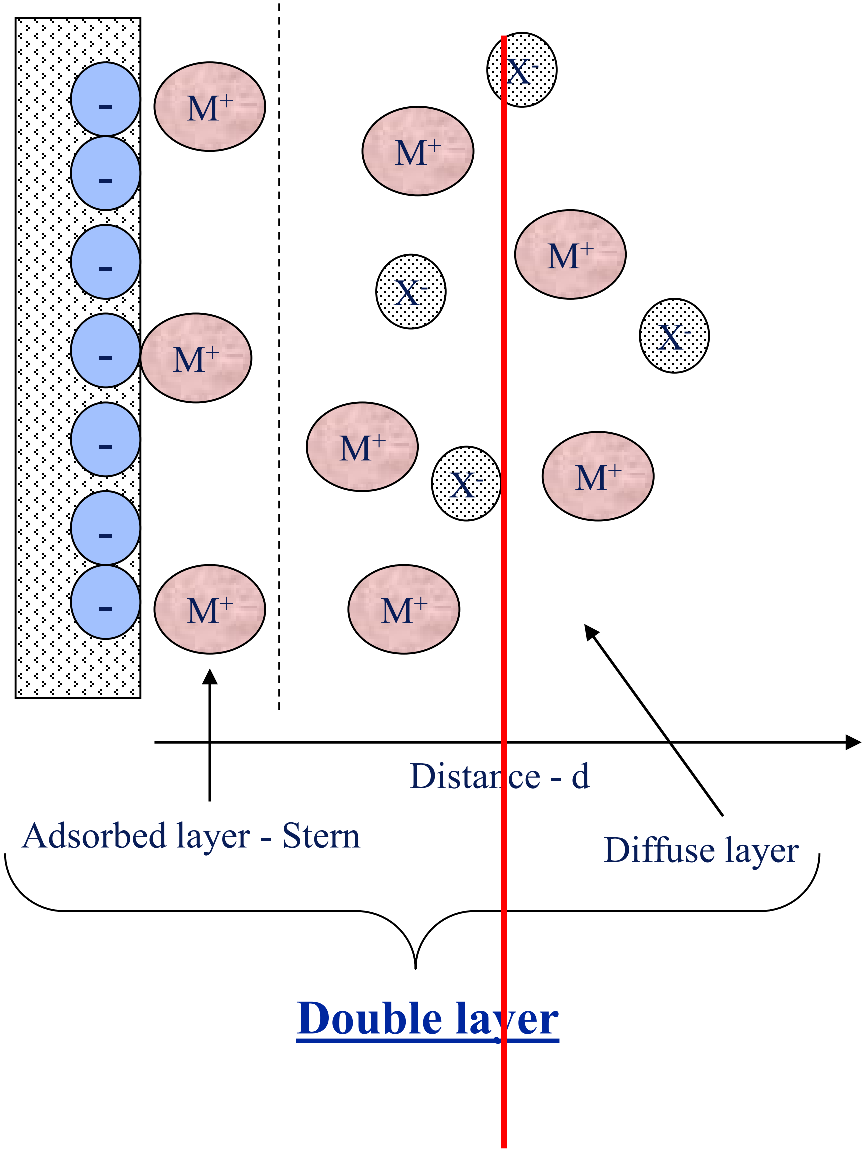
40 nm Al_2O_3 particle speed ≈ 2 m/s

---

* O'Brien, R.W. White, L.R. -J. Chem. Soc. Faraday Trans. 2, 74 1607 (1978)

$ O'Brien et al J.Coll.Inter.Sci., 173 406-418 (1995).

Double layer - Gouy and Chapman – Stern model



Slip plane – zêta plane

- Mean field approximation - i.e. average of many configurations of moving ions
- Limitations
  1. Ion-correlation effects due to highly polarizable layers - attractive
  2. Finite ion size - excluded volume effect - repulsive
  3. Image forces - "reflected" charge by surface gives "image in surface" - repulsive
  4. Surface charges discreet - not averaged as above - attractive
  5. Solvation forces - displacement / ordering of solvent - attractive, repulsive, oscillatory
- Details Chp. 5 Colloidal Domain

Surface potential measurement – zeta potential

Zeta potential as a function of pH with and ionic concentration for a TiO_2

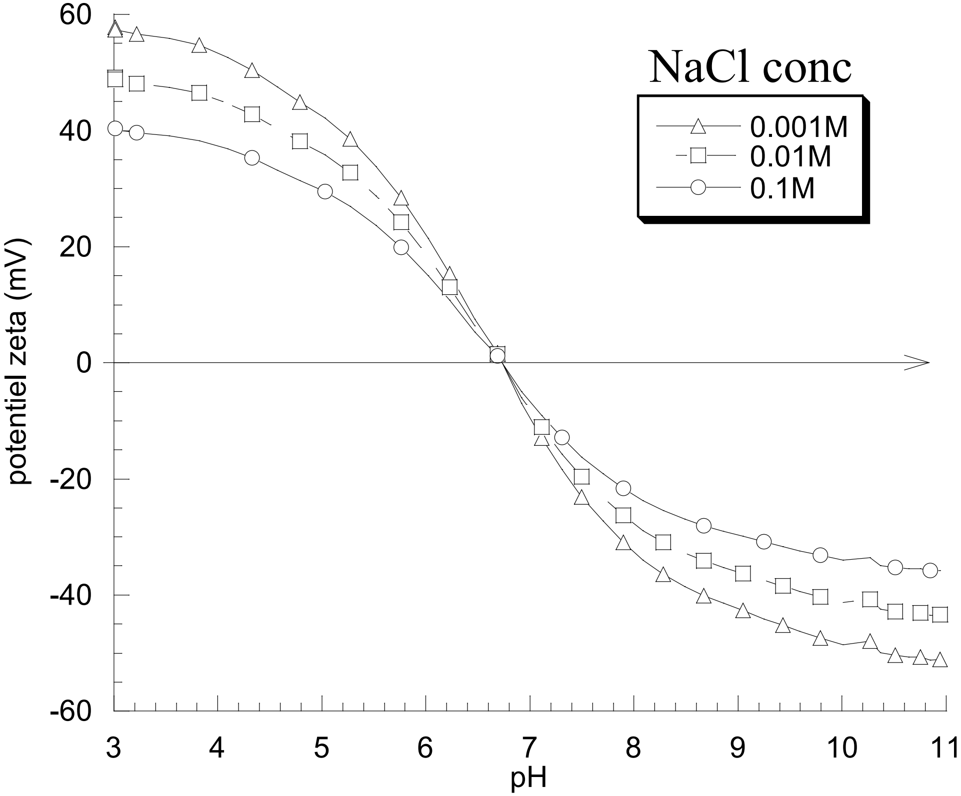


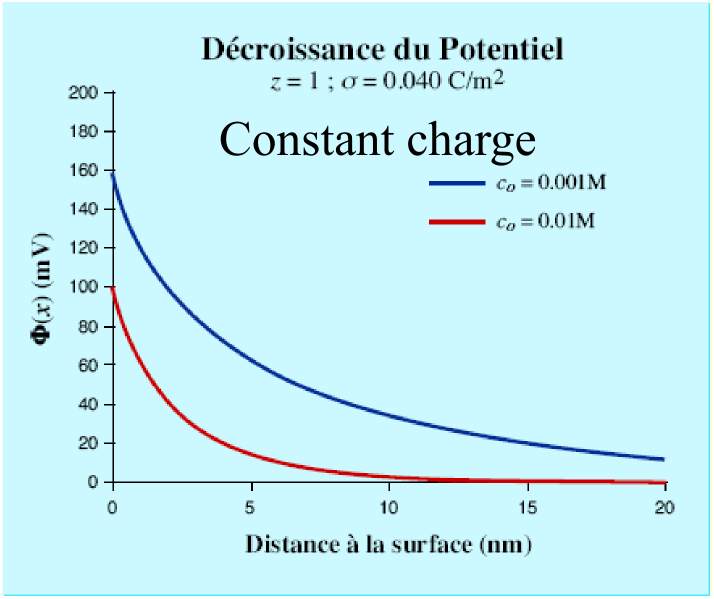
Table 2.13 p155 - Ceramics and glasses, The Treaties of Materials, Volume 16, PPUR, 2005

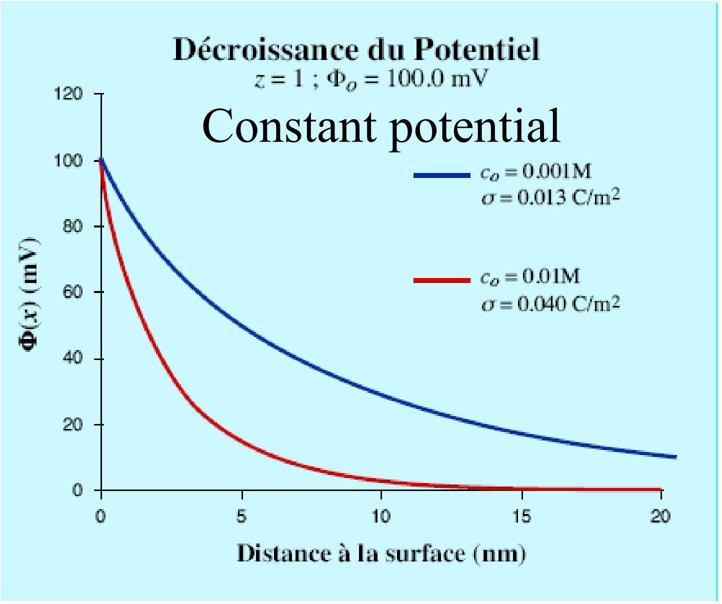
Powder	SiO_2	ZrO_2	TiO_2 rutile	TiO_2 anatase	Kaolin (edges)	Fe_3O_4	Fe_2O_3	Al_2O_3	ZnO_2	MgO
pH (iep)	2-3	4-5	4-5	6-7	5-7	6-7	6-9	8.5-9.5	≈9	12-13

Constant charge – Constant potential*

- Constant charge when charged species fixed at surface
- Constant potential when species can desorb within time scale of a collision

- Discussed in more detail in Chp. 5 – Force calculations*
- >30 nm identical vg results
  - theory vs experiment - planar surfaces





- Recent work at Geneva University – suggests charge regulation model needed for accurate DLVO predictions (depends on adsorption equilibria of pdi's)
- F. Javier Montes Ruiz-Cabello, Plinio Maroni, and Michal Borkovec. J.CHEM.PHYS. 138, 234705 (2013)

*Chp. 5 – The Colloidal Domain–D. F. Evans & H. Wennerström, Wiley, 1999

Interaction Forces in Colloidal Systems

Interaction force

- The *interaction force* between two colloidal particles expresses the variation of their *interaction potential G* according to their *distance* of separation *h* :

$$F = -\left(\frac{\partial G}{\partial h}\right)_T = -\left(\frac{\partial H}{\partial h}\right)_T + T\left(\frac{\partial S}{\partial h}\right) \qquad (5.1.1)$$

- The sign "-" is chosen so as to give a sign *positive* to a *repulsive force*.

Osmotic pressure

- A particle in a solution undergoes a *force* linked to the *osmotic pressure* of the solution:

$$\frac{F}{Area} = -\frac{1}{Area}\left(\frac{\partial G}{\partial h}\right)_T = -\left(\frac{\partial G}{\partial V}\right)_T = -\frac{1}{V_{solute}}\left(\frac{\partial G}{\partial n_{solute}}\right)_T = \Pi_{osm} \qquad (5.1.2)$$

"Area" is the surface of the particle (see also slide 24) .

Interactions between colloidal particles

- The attractive / repulsive interactions between particles of a colloidal suspension in an electrolyte result from an *osmotic pressure difference* between the solution located *between* particles and *bulk* of the solution.
- A direct effect of the formation of the double layer at a charged surface

Interaction Between Charged Surfaces

1

Identically charged surfaces

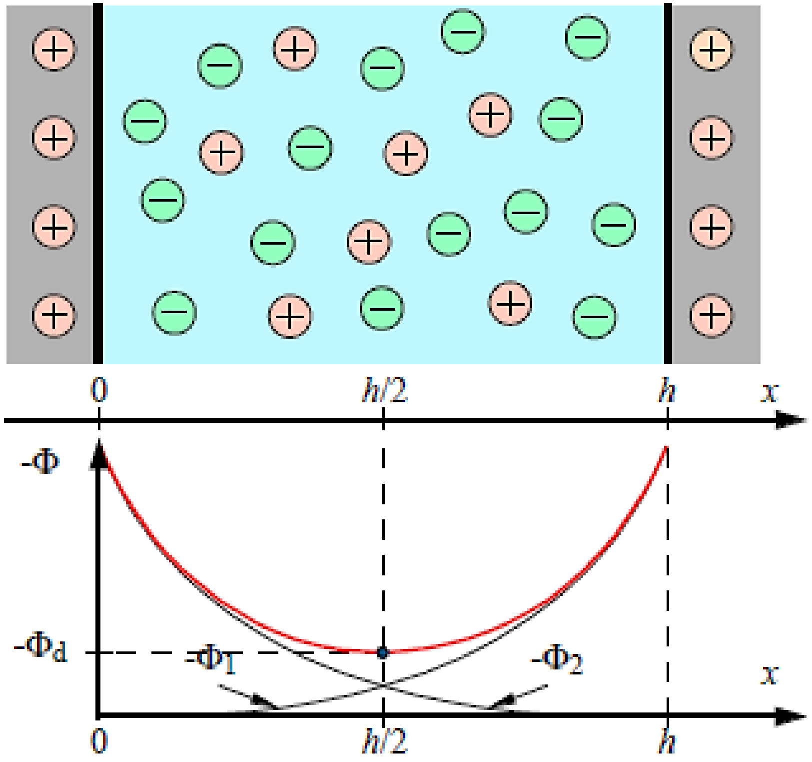
- Semi-infinite plates separated by an electrolyte solution
- When we bring together two identical charged surfaces, separated by an electrolyte solution
- **the overlap of their double layers produces a *repulsive* interaction.**

For reasons of symmetry, we have:

$$\frac{d\Phi}{dx}\Big|_{h/2} = 0; \Phi(h/2) = \Phi_d \qquad (5.1.23)$$

The ionic distribution between each charged surface and the mid-plane (h/2) is identical giving :

$$\frac{F}{Area} = \Pi_{osm} = kT \sum_i c_i(h/2) \qquad (5.1.24)$$



This equation also applies to *swelling of charged layered crystals such as clays* (e.g. montmorillonites see slides week 3 – 16 &17).

2

Interaction Between Charged Surfaces

- **Identically charged surfaces**
- Semi-infinite plates separated by an electrolyte solution

- We consider charged surfaces immersed in a solution of average concentration c_{io}.

- The **net interaction force** per unit area between surfaces is then the *difference* between osmotic pressure *between* the surfaces and the average osmotic pressure of the solution:

$$\frac{F}{Area} = \Pi_{osm}(h/2) - \Pi_{osm}(bulk) = kT\left[\sum_i c_i(h/2) - \sum_i c_{io}\right] \qquad (5.1.26)$$

- The average solution fixes the chemical potential of the dissolved species, as well as the reference level of the electrostatic potential.

The composition of the pore solution halfway between the surfaces is therefore:

$$c_i(h/2) = c_{io}\exp\left(-\frac{z_i e\Phi_d}{kT}\right) \qquad (5.1.27)$$

Therefore, the net force is:

$$\frac{F}{Area} = kT\sum_i c_{io}\left[\exp\left(-\frac{z_i e\Phi_d}{kT}\right) - 1\right] \qquad (5.1.28)$$

Interaction between Charged Surfaces

2

- **Identically charged surfaces**
- **Semi-infinite plates separated by an electrolyte solution**
- At long interaction distances the mid-distance potential $\Phi_d \rightarrow 0$ when $h \rightarrow \infty$.
- In this case, we can approximately solve the Eq. (5.1.28) by keeping only the first two terms of the Φ series expansion of the exponential function:

$$\frac{F}{Area} \cong \frac{1}{2} \sum_i \frac{c_{i0}(z_i e)^2 \Phi_d^2}{kT} = \frac{\varepsilon_o \varepsilon_r \kappa^2 \Phi_d^2}{2} \qquad (5.1.29)$$

Assuming that the potential Φ_d is simply the sum of the *Gouy-Chapman* potentials of the two surfaces taken separately one obtains, ***for a symmetrical electrolyte (z : z):***

$$\Phi_d(h/2) = \frac{8kT}{ze} \Gamma_0 \exp(-\kappa\, h/2)) \qquad (5.1.30)$$

or $\Gamma_0 = \tanh\,(ze\Phi_0/\,4kT)$ as in Eq. (3.8.14). The repulsive force between the surfaces is then:

$$\frac{F}{Area} \cong 32(kT)^2 \frac{\varepsilon_o \varepsilon_r}{(ze)^2} \kappa^2 \Gamma_0^2 \exp(-\kappa h) = 64kT c_o \Gamma_0^2 \exp(-\kappa h)) \qquad (5.1.31)$$

Γ_0 : see slide 16, dimensionless surface potential

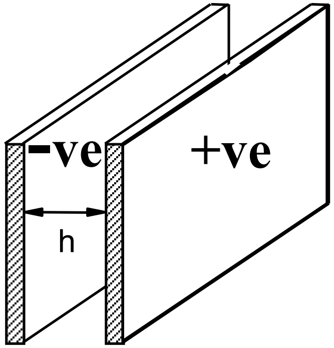
κ: see slide 19, Debye length

Interaction Between Charged Surfaces

♦ Surfaces of opposite signs

Such surfaces are *attractive* at *long* distance.

- **As there is no intermediate point where the electric field is canceled,**
- the interaction force can then be shown to be (see book, eq. 5.1.22):



$$\frac{F}{Area} = -\frac{\sigma^2}{2\varepsilon_o\varepsilon_r} + kT\sum_i [c_i(wall) - c_{io}] \qquad (5.1.38)$$

- As the two surfaces neutralize each other, their approach the counterions are *forced out* into the bulk of the solution**. (see slides 15 &27, concentration of counterions inverted for a surfaces of opposite charge)**

If $\sigma_2 = -\sigma_1$, the attraction *persists* until *contact** between surfaces, where it is:

$$\frac{F}{Area} = -\frac{\sigma^2}{2\varepsilon_o\varepsilon_r} \qquad (5.1.38b)$$

If $|\sigma_2| \neq |\sigma_1|$, the interaction becomes *repulsive* at a very short distance.

* but water can be there anyway, difficult to be removed, crystallographic match may not be achieved.

Colloidal Stability - DLVO Theory

Theory *DLVO* *

- The total interaction potential $V(h)$ is the algebraic sum of the repulsive potentials $V_R(h)$ (electrostatic) and attractive $V_A(h)$ (from *van der Waals*).

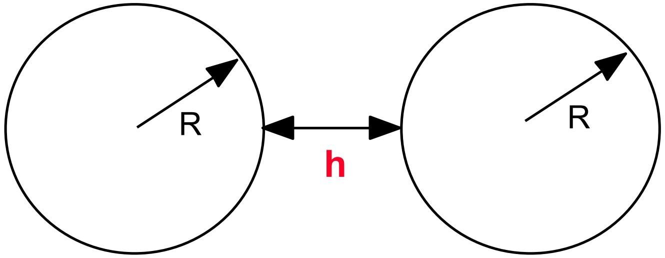
$$V(h) = V_R(h) + V_A(h)$$

- The corresponding interaction force is therefore:

$$F = -\frac{dv}{dh} = -\frac{dv_A}{dh} - \frac{dv_R}{dh} \quad (8.2.1)$$

- Theory developed by *B. Derjaguin* & *L. Landau*, and *E. Verwey* & *T. Overbeek*. 2 independent groups at the same time…. 1940's

Colloidal Stability - DLVO Theory



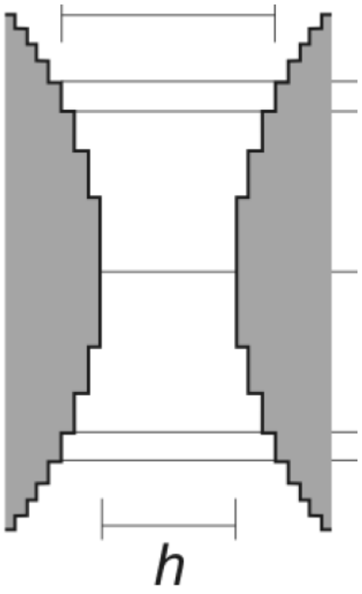
- Interaction between two identical **spheres**

When the radius R of the spheres is large enough to use the approximation of *Derjaguin* (Eq. 5.2.31), we find that ***for a symmetrical electrolyte (z : z)***:

$$F(h) = -\pi R\left\{\underbrace{\frac{H_{121}}{12\pi h^2}}_{\text{Last week, attr.}} - \underbrace{\frac{64kTc_O\Gamma_O^2}{\kappa}\exp(-\kappa h)}_{\text{Today, slide 34, repul.}}\right\} \quad (8.2.8)$$

- After integration of $F(x)$ dx for $x = \infty \rightarrow h$, this gives :

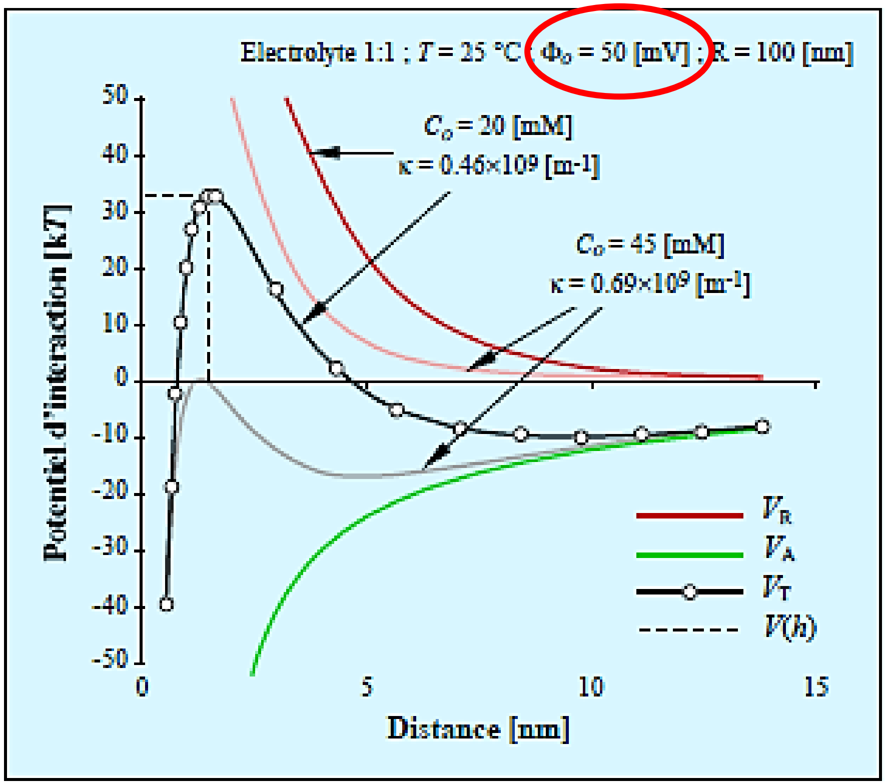
$$V(h) = -\pi R\left\{\frac{H_{121}}{12\pi h} - \frac{64kTc_O\Gamma_O^2}{\kappa^2}\exp(-\kappa h)\right\} \quad (8.2.9)$$

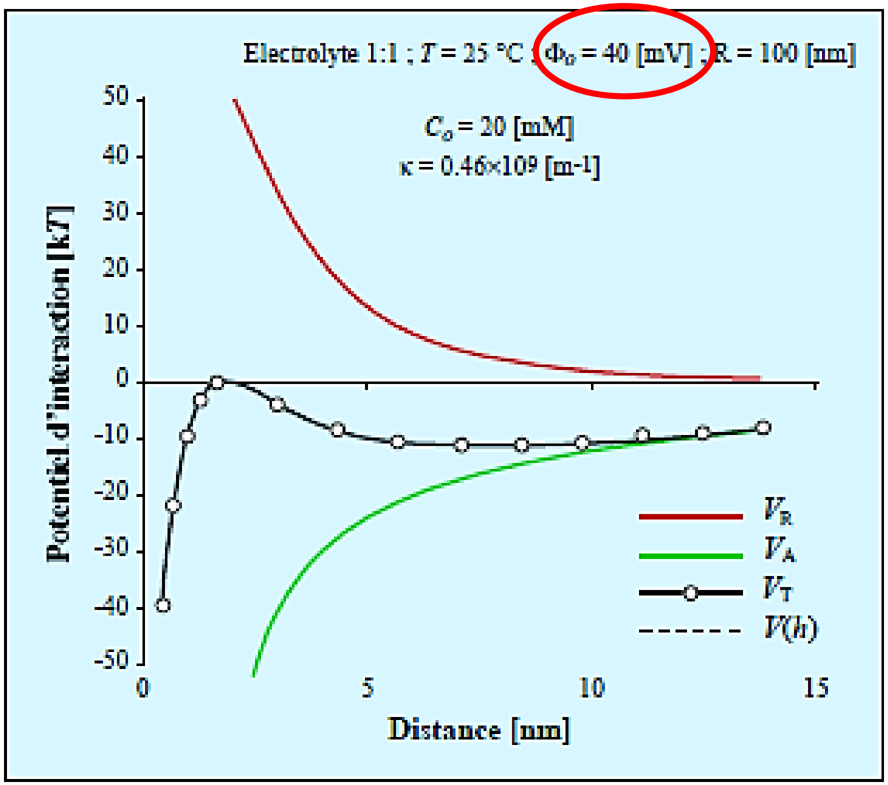


Derjaguin Approx.

Colloidal Stability - DLVO Theory

- Interaction between two identical **spheres** ***for a symmetrical electrolyte (1: 1) e.g. NaCl***
- The “electrostatic repulsion” component
- **decreases with increasing concentration** in the electrolyte of the solution;
- it is **very sensitive to the magnitude of the surface potential Φ_o**.
- Barrier decreases from 33 kT to 0 as potential decreases from 50 to 40 mV.





Repulsion Between Charged Surfaces - Summary

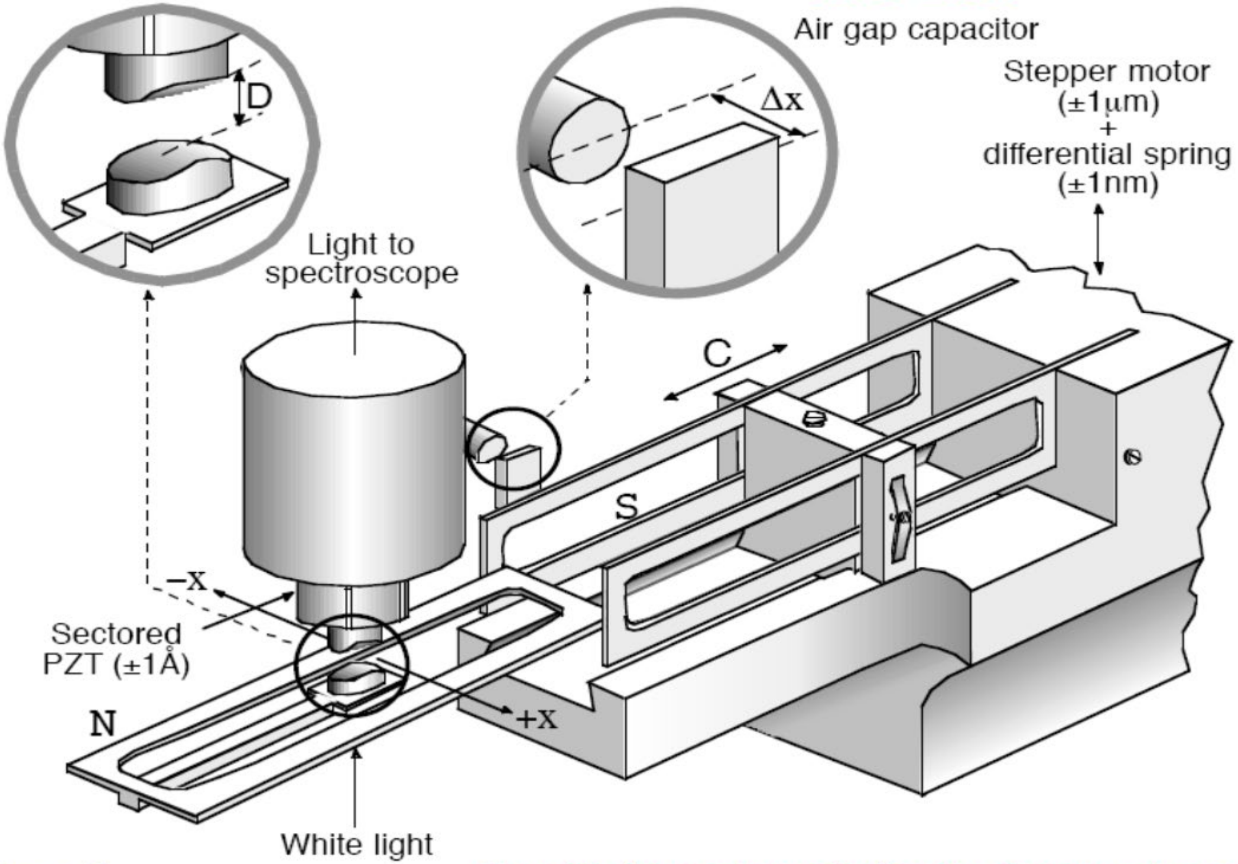
- Origin - osmotic pressure associated with entropy that promotes ion dissociation (number of configurations)
- Enthalpy - promotes association - adsorption
- Repulsion – function of surface charge and ionic concentrations

Geometry	Interaction energy
Parallel flat plates - (semi-infinite), constant potential	$64k_BTc_0^b\kappa^{-1}\tanh^2\left(\frac{\Psi}{4}\right)e^{-\kappa h}$
Identical spheres, constant potential	$2\pi\varepsilon_0\varepsilon\left(\frac{k_BT}{ze}\right)^2 a\Psi^2\ln\left(1+e^{-\kappa h}\right)$
Identical spheres, constant charge	$-2\pi\varepsilon_0\varepsilon\left(\frac{k_BT}{ze}\right)^2 a\sigma_0^2\ln\left(1-e^{-\kappa h}\right)$

Atomic Force Apparatus

D & ΔD to ±1-2Å

Δx to ± 2Å

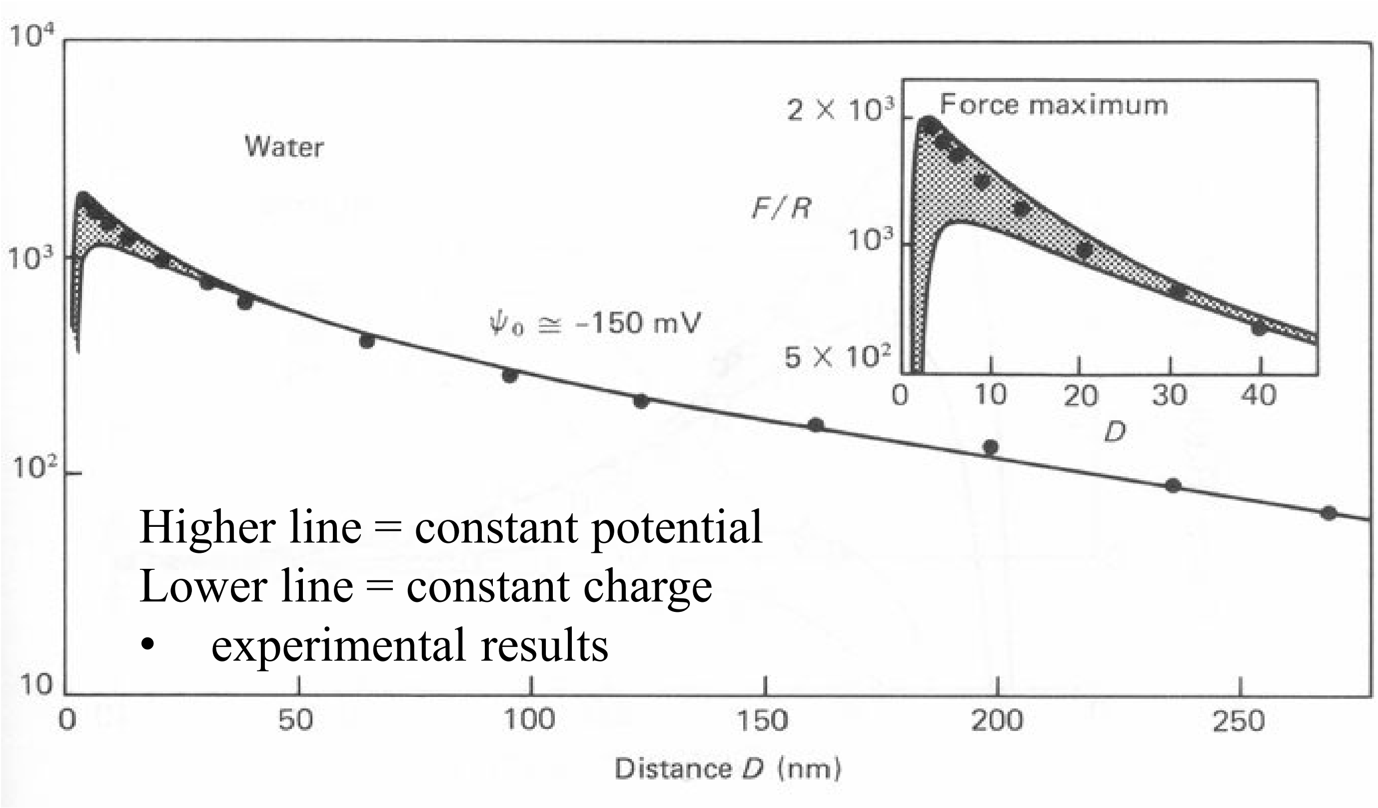


J. Phys. Chem. B
105, 8125 (2001)

Sensitivity and resolution in shear and normal stress is ca. 5-10,000-fold that of tipped AFM, STM

Repulsion between charged surfaces

- **Electrostatic repulsion – from overlap over double layers it is not a coulombic type** interaction like – point charges in vacuum –double layer depends on surface potential (surface charge density) and ionic concentration



Higher line = constant potential
Lower line = constant charge
- experimental results

Repulsive forces measured with the atomic force apparatus for ***two charged mica surfaces*** the points are the experimental data and the lines are the predictions of the DLVO theory (Israelachvili, 1992)

Colloidal Stability - Coagulation

Critical coagulation concentration (*CCC*) – controlled agglomeration of particles by increasing salt concentration (e.g. waste water treatment)

- The *critical coagulation concentration* (*CCC*) is the electrolyte concentration such that

  $V(h_o) = 0$ and $F(h_o) = 0$ are approached simultaneously .

Calculation

- We calculate the *CCC* by introducing the condition $h_o = 1 / \kappa$ in the Eq. (8.2.9) and solving with respect to c_o.
- As c_o is in the expression of κ, we find an approximate expression of the *CCC* (in molecules / m^3) for identical spheres, and symmetrical electrolyte:

$$CCC = \frac{1}{2}\left(\frac{384\pi}{\exp(1)}\right)^2 \frac{(\varepsilon_o\varepsilon_r)^3 (kT)^5 \Gamma_O^5}{(ze)^6 H_{121}^2} \cong 10^5 \frac{(\varepsilon_o\varepsilon_r)^3 (kT)^5 \Gamma_O^5}{(ze)^6 H_{121}^2} \qquad (8.2.11)$$

- For a ***strongly* charged** surface , $\Gamma_o \rightarrow 1$ and the *CCC* varies proportionally **to 1 /*z*^{6}** known as *Schultze-Hardy* rule.
- For a ***weakly* charged** surface , $\Gamma_o \cong ze\Phi_o / 4kT$ and the Eq. (8.2.11) becomes:

$$CCC = \frac{1}{2\times 4^4}\left(\frac{384\pi}{\exp(1)}\right)^2 \frac{(\varepsilon_o\varepsilon_r)^3 kT \Phi_O^4}{(zeH_{121})^2} \cong 4\times 10^2 \frac{(\varepsilon_o\varepsilon_r)^3 kT \Phi_O^4}{(zeH_{121})^2} \qquad (8.2.12)$$

Only proportional **to 1 /*z*^{2}**

$$* \; \Gamma_O = \tanh\left(\frac{ze\Phi_O}{4kT}\right)$$

Aggregation of Colloidal Suspensions - Kinetics

Aggregation limited by *diffusion*

- When the interaction potential barrier Max [$V(h)$] **is negligible**, the speed of the ***aggregation kinetics are*** determined by the *speed of diffusion of particles* in suspension under the action of Brownian motion.

Aggregation limited by *interaction*

- Effect of the repulsive barrier. The ***aggregation kinetics*** are determined by the height of the repulsive barrier, when $V_{\mathrm{max}} >> \mathrm{k}T$. This is taken into account by introducing a factor expressing the influence of the repulsive potential.

Solids concentration

- The number of collisions per unit of time is also dependent on the concentration of particles in the suspensions.

See aggregation/agglomeration kernel, week 4, slide 7

Aggregation of Colloidal Suspensions - Kinetics

- **Open access software - EPFL website - HAMAKER or PTG**

- *http://hamaker.epfl.ch*
- *or*
- PTG website (lmc.epfl.ch) - PTG - Research - Powder Processing - Colloidal Stability
- One can calculate the potential and the force of interaction and make an estimate of stability against agglomeration as a function of solids concentration and time.

FOR EXERCISE SESSIONS 9 -

- **Register (to get password),**
- **download and installation on your laptop ...Hamaker 2**
- **Need Java environment? OK ? ..**
- **Problems to be solved with software….**

Aggregation of Colloidal Suspensions - Hamaker[$]

- The stability of a colloidal suspension is evaluated according to the model published by Israelashvili*. A particle of diameter *d* and density ρ_p in a suspension at temperature *T* will have a mean Brownian velocity given by:

$$\frac{1}{2}mv^2 = \frac{1}{2}\left[\frac{4}{3}\pi\left(\frac{d}{2}\right)^3 \rho_p\right]v^2 \approx kT \Rightarrow v \approx \sqrt{\frac{12kT}{\pi d^3 \rho_p}} \qquad \text{Eq. H 3}$$

- At a given suspension concentration *c* (in wt.% s / l) the number of particles per unit volume N_p is given as a function of the densities of the particles ρ_p and the medium ρ_m as well as the particle diameter *d* by dividing the total mass of all particles m_{pT} by the mass of a single particle m_p.

$$N_p = \frac{m_{pT}}{m_p} = \frac{\frac{c}{100}\rho_m}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3 \rho_p} \qquad \text{Eq. H 4}$$

$ *http://hamaker.epfl.ch* - U. Aschaueret al J Dispersion Science Technology. 32 (4), 470 - 479 (2011)

* JN Israelashvili, *Intermolecular and Surface Forces*. Academic Press: San Diego, 1991.

Aggregation of Colloidal Suspensions - Hamaker

- For a binary system the number of particles per unit volume is given by the sum of the two particle contributions:

Eq. H 5

$$N_p = N_{p,1} + N_{p,2}$$

- The number of particles along one edge of the unit volume is given by the cubic root of N_p, the inverse of which finally gives the spacing between two particles along the edge. This is considered as the closest **interparticle spacing *ds*** at equilibrium.

$$ds = \frac{1}{\sqrt[3]{N_p}}$$

Eq. H 6

In order for two particles to collide, the particle has to travel the interparticle distance *ds* which as it's mean Brownian velocity *v* will require a time Δt, thus the time between collisions. The **collision frequency f_{vs}** is then given by the inverse of Δt.

$$f_c = \frac{1}{\Delta t} = \frac{v}{ds}$$

Eq. H 7

Aggregation of Colloidal Suspensions

- Where for a binary system the mean velocity is considered:

$$v = \frac{1}{2}\left(v_1 + v_2\right) \qquad \text{Eq. H 8}$$

- The probability *p* of two particles having a kinetic energy allowing them to overcome an energy barrier ΔW is given by

$$p = \exp\left(\frac{-\Delta W}{kT}\right) \qquad \text{Eq. H 9}$$

k being the Boltzmann constant and *T* the temperature.

- Within a time *t*, $t \cdot f_c$ collisions will occur, which means that for none of these collisions to be energetic enough to overcome the barrier there is a minimum value for ΔW in order to avoid such energetic collisions and thus the onset of agglomeration can be calculated as:

$$\left(\frac{\Delta W}{kT}\right)_{\min} = -\ln\left(\frac{1}{t \cdot f_c}\right) \qquad \text{Eq. H 10}$$

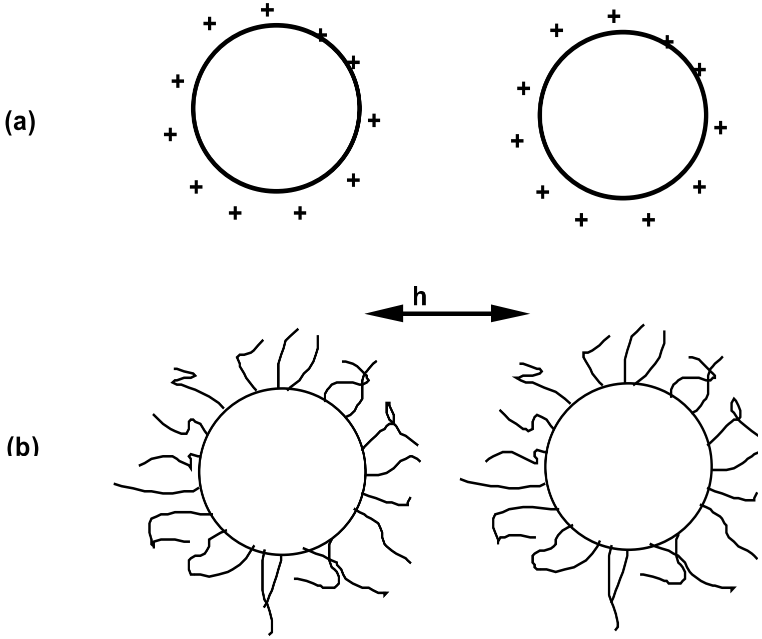
Which represent the minimum energy barrier needed to avoid (statistically, in the time t) that particles get over the barrier.

1

Repulsive forces

- Electrostatic *(today)*
  - a dissociation of species at the surface
  - adsorption of charged species
  - dissociated ions,

- Steric *(next week)*
  - molecules
  - often adsorbed polymers



(distance h between particles)