

Powder Technology

From Landslides and Avalanches to Concrete and Chocolate

Prof. P. Bowen (EPFL), (EPFL), Dr. P. Derlet (PSI)

3 Particle – Particle interactions (1)

File no.5

Course Contents - Plan

1. Introduction
 - general introduction to course
 - example transparent ceramics
2. Particle Packing and Powder Compaction
 - Theoretical and empirical models (PB)
 - Powder compaction (PD)
- 3 Particle-Particle Interactions (PB)
 - Colloidal Dispersions
 - DLVO –theory and limitations
 - non-DLVO and steric forces

Exercises – particle particle interactions and rheology – HAMAKER & YODEL
4. Introduction to Atomistic Scale Simulations (PD)
 - introduction to modeling of surfaces and interfaces at the atomic scale
 - defects in metals – towards sintering
5. Sintering mechanisms (PD)
 - metals, ceramics
 - influence of microstructure
 - simulation

Exercises – Atomistic modeling and DEM - LAMMPS
6. New Powder Processing Technologies (PB)
 - rapid prototyping
 - laser sintering, Spark Plasma Sintering

SiC - abrasive



« La neige » Snow ...



- The Colloidal Domain – D. F. Evans & H. Wennerström, Wiley, 1999,
 - Principles of Ceramic Processing – J.S.Reed , Wiley, 1995. English
 - Les Céramiques, J. Barton, P. Bowen, C. Carry & J.M. Haussonne, Les Traités des Matériaux, Volume 16, PPUR, 2005
- P. Bowen, EPFL.* *09/10/2018*

Teaching plan 2018

- Files of lectures and notes to be found on PTG website : <http://lmc.epfl.ch/PTG/Teaching>

Week-DATE	File. no.		Powder Technology – Wednesday 10.15-13.00 – MXG 110
1- sept 19	1&2	PB	Introduction – example rheology – Yodel - Powder packing and compaction – 1 (i) – (3hrs)
2 – sept 26	2&3	PB MS	Powder packing and compaction – 1(ii), 2- Examples and DEM guest lecturer – (3hrs)
3 – oct 3	4	PD	Powder packing and compaction -3 & 4(i) – (3hrs)
4 – oct 10	4&5	PD PB	Powder packing and compaction - 4 (ii) – (1hr) Particle – Particle Interactions 1 - 2hrs
5 – oct 17	6&7	PB	Particle – Particle Interactions 2 & 3(i) – (3hrs) – Download Hamaker
6 – oct 24	7	PB	Particle – Particle Interactions – 3(ii) YODEL-PB (1hr) Exercises – Intro to Hamaker & YODEL software & groups project (2hrs)
7 – Oct 30		AKM	Exercises - Hamaker and Yodel Modelling – group projects
8 – nov 7	8	PB PD	Exercises –presentation of interparticle project results (1 hr) Introduction to atomistic scale simulations – (2hrs)
9 – nov -14	9& 11	PD	Compaction, Sintering & Defects in metals at atomistic scale (2hrs) Sintering Mechanisms – 1(i) (1 hr)
10 – nov 21	11	PD	Sintering Mechanisms - 1 (ii) & 2 (3hrs)
11 -nov-28		PD	Exercises -Introduction to Molecular Dynamics Modelling using LAMMPS (3hrs) .
12 - dec 5		PD	Exercises - MD- DEM modelling exercise using LAMMPS –particle packing - Effect of parameters (3 hrs)
13 – dec 12	10	PB	New Technologies -1 Processing – Forming – Shaping (2hrs) & Exercises or invited lecture or visit
14 – dec 19	10	PB	New Technologies-2 – Sintering Methods & Exercises or invited lecture or visit & Exam method
			PB – Prof. Paul Bowen (EPFL), PD – Dr. Peter Derlet (PSI)
			MS- Dr. Mark Sawley (EPFL), AKM - Aslam Kuhni Mohamed (EPFL)

Today's Course (objectives)

- ◆ Aggregation/agglomeration effect – rheology – effective volume – maximum packing – hence ceramic microstructures – dispersion important – how to assure particles do not aggregate.....
- ◆ Introduction – Forces and colloidal stability, show a sinterable material (slides 5-12)
- ◆ Attractive forces – van der Waals – brief summary (treated in detail 3rd yr*) (13-16)
- ◆ Repulsive forces – electrostatic (17-42)
 - Poisson-Boltzmann Equation
 - Surface Potentials
 - Composition of double layer (double couche)
- ◆ Zeta potential measurement (43-47)
- ◆ Examples (48 -61)
- ◆ Real size of nanosized spherical silica particles
- ◆ Atomistic modelling of water-inorganic solid interface – particle size of nanosized iron oxides

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

Forces

- ◆ Four distinct forces in nature

- Strong interactions

- Weak interactions

- Electromagnetic forces

- Gravitational forces

} Very short range $< 10^{-5}$ nm

} Act between atoms and molecules from 0.1nm to end of galaxy... -

- ◆ Electromagnetic forces

- Source of all **intermolecular interactions** (solids, liquids, gases, chemistry, biology)

- ◆ Gravitational forces

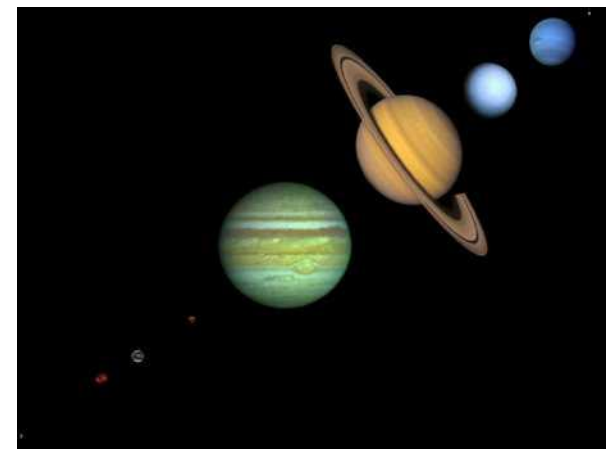
- Tidal motion

- Motion of planets

- ◆ Together

- capillary rise

- Avalanches



Avalanches – SLF

- ◆ SLF – www.slf.ch
- ◆ Eidgenössisches Institut für Schnee- und Lawinenforschung
- ◆ Institut Fédéral pour l'Etude de la Neige et des Avalanches

- ◆ **Adresse:**

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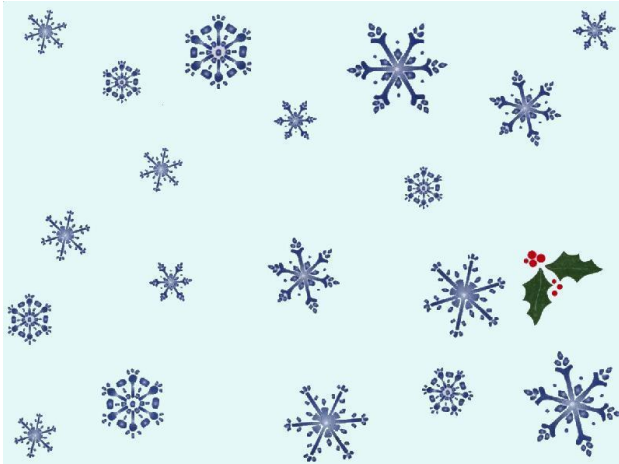
- ◆ www.slf.ch



Weissfluhjoch test site

Avalanches (2)

- ◆ Interparticle forces vs. Gravity
- ◆ Friction – entanglement between snow flakes
- ◆ Change of interparticle forces – solid bridges – sintering
- ◆ vapour phase transport with variation in temperature - sintering
- ◆ with and without densification – plate or « plaque » formation - dangerous
- ◆ If cold enough no change – just friction and interparticle forces - dangerous



P. Bowen, EPFL.

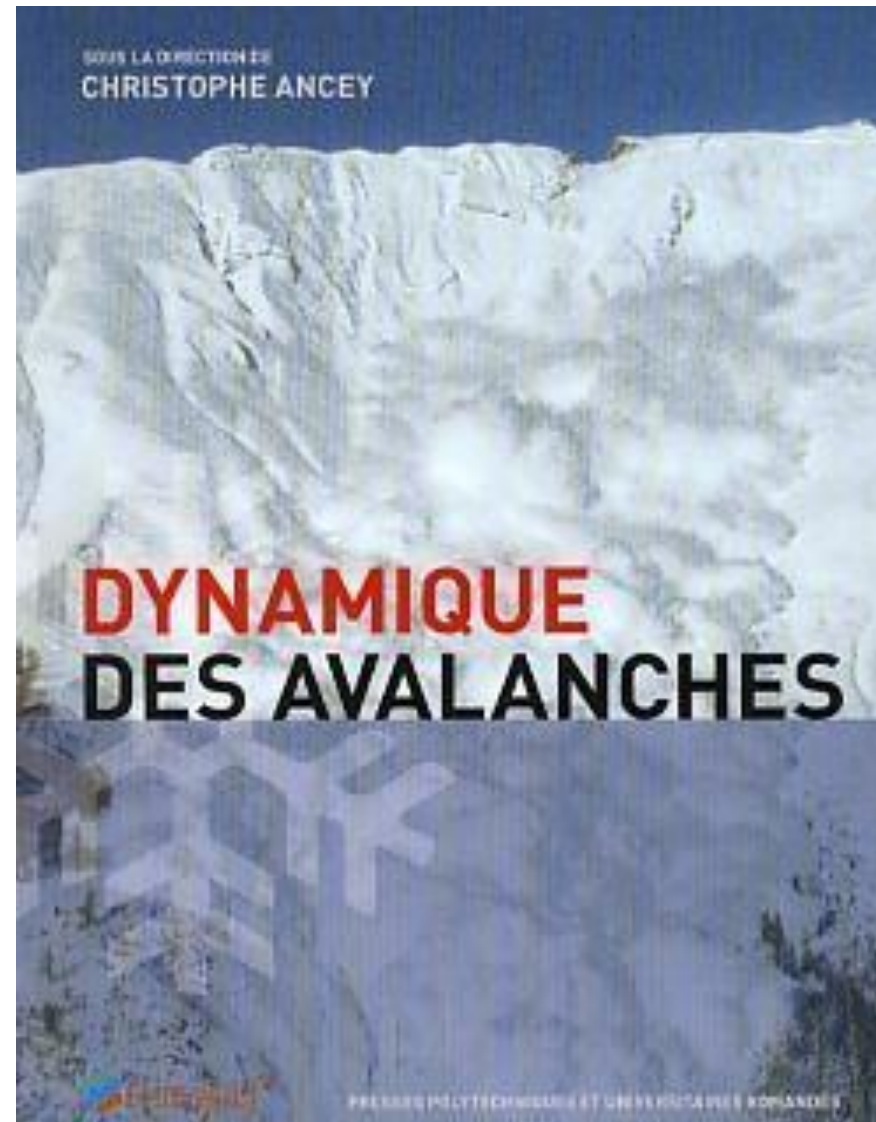
Computer tomography scans: evolution of a snow specimen in a constant ambient temperature of -3°C , from its original condition (left) to its condition after 23 weeks (right). The coarsening of the ice crystal structure is clearly visible.

Avalanches (3)



Avalanches 4

- ◆ Christophe Ancey's book (EPFL)
- ◆ **The rheophysical approach in the study of natural gravity-driven flows**
Environmental Hydraulics Laboratory
ENAC - Section de génie civil
Faculté de l'environnement naturel, architectural et construit , EPFL.
- ◆ Continuum mechanics and rheophysics
- ◆ Deducing the rheological properties from field measurements....
- ◆ Investigating granular flows in the laboratory as a prototypical example of gravity driven flows
- ◆ Towards a rheophysical analysis of the frictional-collisional regime.
- ◆ Landslides/Avalanches
- ◆ Eric Bardou- laves torrentielles,
- ◆ DEM - Mark Sawley, David Geissbühler

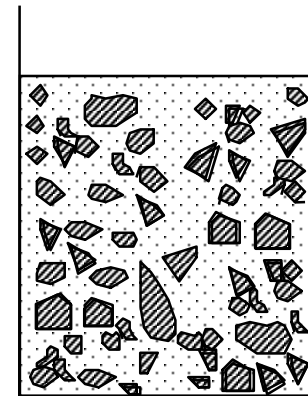


Dispersion

Chapter 2.4.3 Pastes and dispersion - (BAR 2005 - Vol. 16 Traité des matériaux)

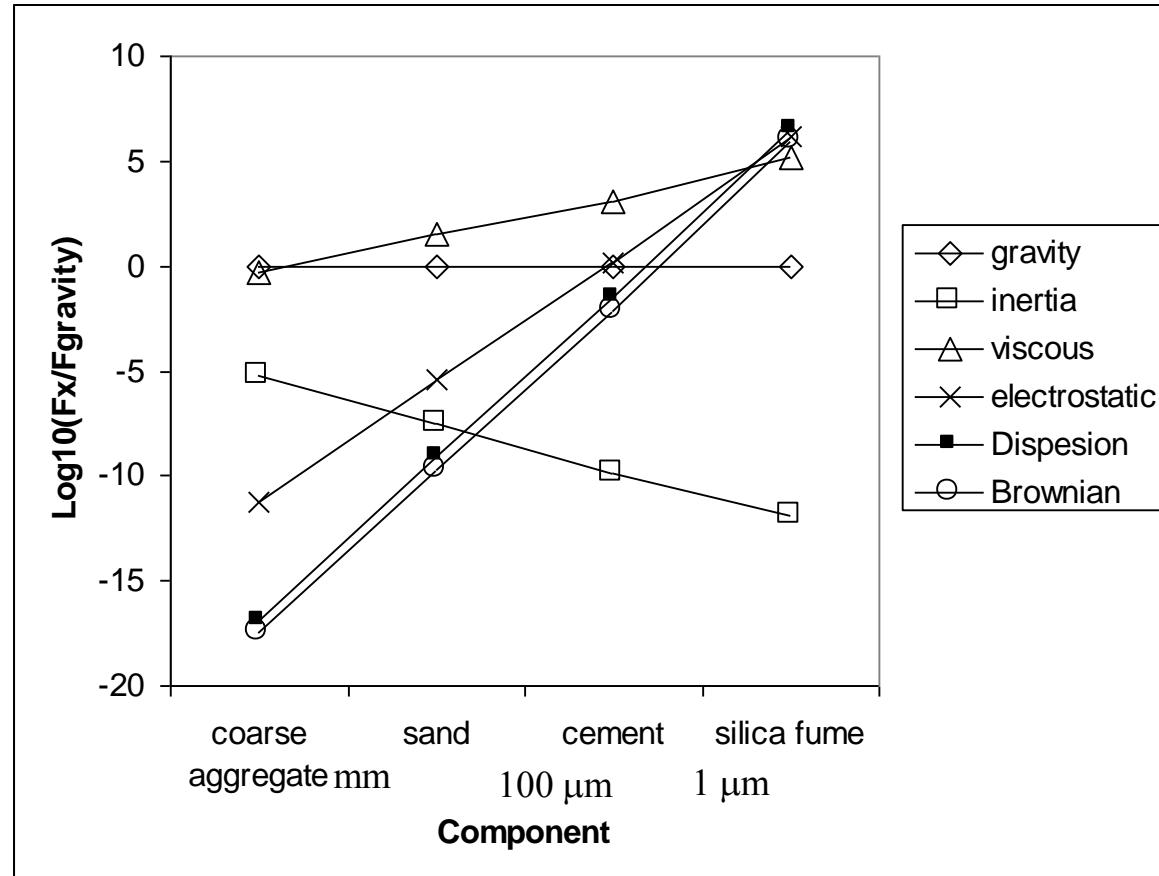
J.S. Reed Chp. 10, T.A.Ring Chp. 9&10

- ◆ The key factors in the production of a paste or dispersion are;
 - The powder surface needs to be wet by the liquid ;
 - The powder dispersion in this liquid volume by mixing or **agitation** ;
 - The agglomerate (soft) or aggregate (hard) rupture by an ultrasonic treatment or by milling;
 - The capacity to maintain the powder well dispersed and to avoid agglomeration or the separation of the phases by sedimentation.
- ◆ Agglomerates (soft) – no chemical bond
- ◆ Aggregates (hard) – chemical bond



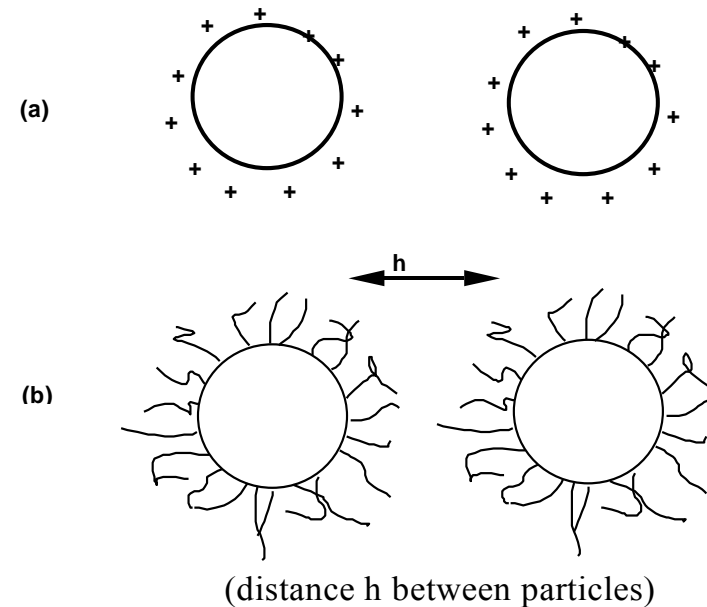
Colloidal stability - Dispersion

- ◆ Colloidal stabilisation is
 - the ability to avoid the creation of agglomerates.
- ◆ Often studied for colloidal systems,
 - Particles $< 0.5 \mu\text{m}$
 - kT dominates gravity.
- ◆ More general term is
 - Dispersion stability
- ◆ We are using the term
 - Colloidal stability
 - Even if the particles are not always in the colloidal domain.
 - Cement 1-150 microns



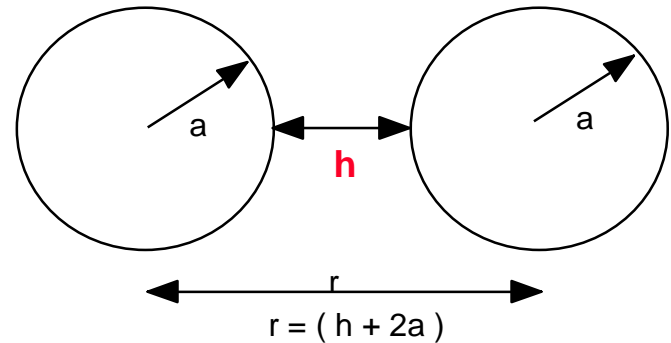
Colloidal stability or dispersion stability

- ◆ For the particles $> 1\mu\text{m}$,
 - Gravity can induce a relatively quick sedimentation.
- ◆ Interparticle forces
- ◆ Attractive
 - Van der Waals or magnetic
 - particles with opposite charges
- ◆ Repulsive -
 - Surface charges with the same sign or
 - Adsorbed molecules



Attractive forces

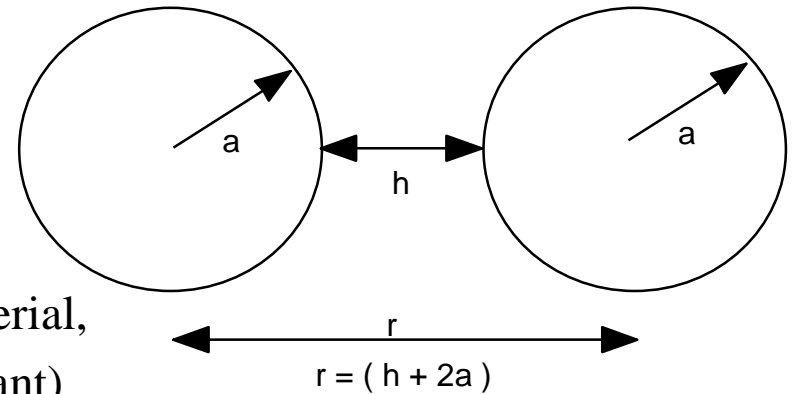
- ◆ Van der Waals
 - Always attractive between same nature particles
 - Result from a particle's dipoles fluctuations inducing a **correlated** response in the neighbouring particles
 - Permanent or induced dipoles from permanent dipoles
 - Instantaneous dipoles -London or dispersion force
 - Function of material **dielectric properties** and **geometry**
- ◆ Hamaker approach - **total** interaction energies of a particle's molecules with another particle.
- ◆ $V_A(h) = -A \cdot H(h, \text{shape})$
- ◆ A is the Hamaker's constant,
- ◆ H is the geometric factor and
- ◆ h is the separation distance between particles



Van der Waals*

- ◆ Hamaker constant – A - depends on the dielectric properties (~**polarisability**)
 - Of the continuous medium separating them (air, vacuum, liquid)
 - For the whole spectral domain of the electromagnetic waves.
- ◆ For particles of identical size and chemistry – in vacuum

$$A = \frac{3}{8} N^2 kT \sum_{n=0}^{\infty} \alpha^2 (i\xi_n)$$



N is the number of molecules **per unit volume** of the material,

α is the **polarisability** of these molecules (dielectric constant)

ξ_n is the electromagnetic frequency

Al_2O_3 in water is $\sim 36.7 \times 10^{-21}$ J, under vacuum 152×10^{-21} J,

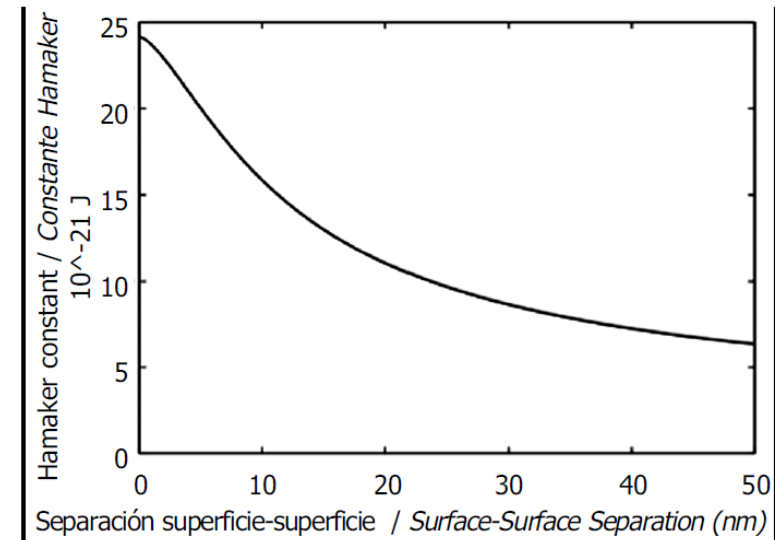
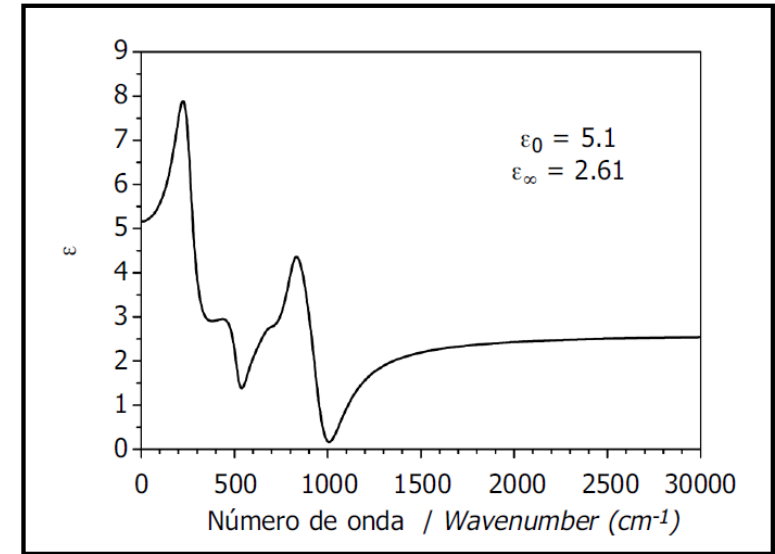
SiO_2 (silica) in water is $\sim 4.6 \times 10^{-21}$ J, under vacuum 65×10^{-21} J

For other powders see Bergström [Adv. Colloid Interface Sci. **70** (1997) 125-169]

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

Estimation of Hamaker constant for blast furnace slag*

- ◆ Used Spark Plasma sintering to produce Blast furnace slag dense sintered piece – polished and measured optical properties
- ◆ Knowing dielectric constant and
- ◆ refractive index - effective Hamaker constant as a function of the surface-surface separation d was determined using the equation §



$$A_{eff}(d) = \frac{3}{4} kT \left(\frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + \varepsilon_m} \right)^2 + \frac{3\hbar\omega(n_p^2 - n_m^2)^2}{16\sqrt{2}(n_p^2 + n_m^2)^{3/2}} \left\{ 1 + \left[\frac{\pi n_m}{4\sqrt{2}} \sqrt{n_p^2 + n_m^2} \frac{d\omega}{c} \right]^{3/2} \right\}^{-2/3}$$

Where k is the Boltzmann constant, T the temperature, h Planck's constant, c the speed of light and ε and n are the dielectric constant and the refractive index of the slag particles (subscript p) and the medium (subscript m) respectively, ω is the absorption frequency, which has been fixed at $2.01 \cdot 10^{16} \text{ s}^{-1}$ in the present case.

*M. Palacios, P. Bowen, M. Kappl, H-J. Butt, M. Stuer, C. Pecharromás, U. Aschauer, F. Puertas "Repulsion Forces of Superplasticizers on Alkali Activated Slag Pastes", Mat.Construcción, , 489-513, 62(308), 2012

§Russel, W. B.; Saville, D. A.; Schowalter, W. R.: Colloidal Dispersions. Cambridge Press, Cambridge, U.K., (1985).

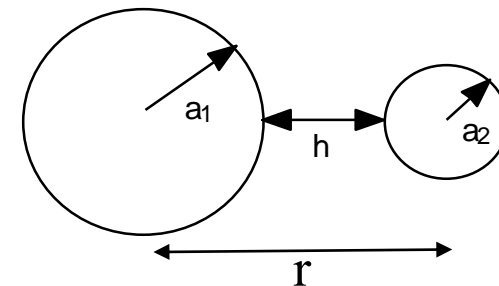
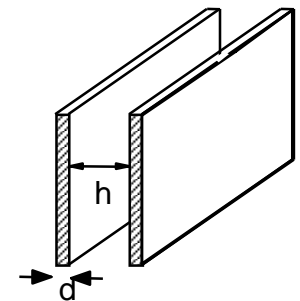
Van der Waals – Hamaker*

Limitations

$$V_A(h) = -A \cdot H(h, \text{shape})$$

- ◆ Retardation (slowing down) –
 - effects of several bodies – phase shift of the dipole correlation
- ◆ Screening
 - In presence of a high electrolyte concentration
- ◆ H, includes the particles' morphology, their size, their separation and the orientation

Shape	H - geometric factor*
Plain parallel plates - (semi- infinite)	$-\frac{1}{12\pi h^2}$
Identical spheres, radius a	$-\frac{1}{6} \left[\frac{2a^2}{r-4a^2} + \frac{2a^2}{r^2} + \ln \frac{r-4a^2}{r^2} \right]$
Spheres with radius, a ₁ et a ₂	$-\frac{1}{6} \left[\frac{2a_1 a_2}{r^2 - (a_1 + a_2)^2} + \frac{2a_1 a_2}{r^2 - (a_1 - a_2)^2} + \ln \frac{r^2 - (a_1 + a_2)^2}{r^2 - (a_1 - a_2)^2} \right]$



*Uses Derjaguin approximation for the curved surfaces a_1 et $a_2 \gg h$

Attractive Forces – magnetic*

- ◆ Materials with Fe, Ni, Co or Cr can have magnetic interparticular forces.
- ◆ For cubic particles (approx. Semi-infinite planes), the magnetic attraction energy is given by (Ozaki et al, 1988) :

$$V_m = - \frac{pM^2}{4\pi\mu_0(a+h)^3} \quad \text{Eq 3.4.12*}$$

p is a constant depending on the orientation of the magnetic moments (de -2 à $+2$),

M is the dipole of the magnetic moment,

μ_0 is the magnetic permeability,

h is the separation distance between particles

a is the size of the cube's edge

- ◆ When the particles are very small (10-15nm), they become superparamagnetic
- ◆ Many bio-medical applications – important research axis at LTP

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

Repulsives Forces – surface charges

- ◆ Chapter 3 & 5 of the book (Cours – 3eme année - céramiques et colloïdes)

THE COLLOID DOMAIN

Where Physics, Chemistry, Biology, and Technology Meet

D. Fennel Evans, Hakan Wennerström

(second Edition)

Wiley-VCH, New-York, 1999

- ◆ Use Poisson Equation Containing Solvent Averaged Properties to Describe Free Energy of Solvation – Poisson Boltzmann equation

3.6 Free energy of solvation (1)

- ◆ Powders in suspension in aqueous media – ions in solution important – energy of solvation of ions.
- ◆ Use continuum – mean field - dielectric model – Born model of solvation*
- ◆ Simple but qualitatively correct ($\pm 50\%$)
- ◆ Electric field outside spherically symmetrical charge
– eg atomic ion

$$E_r = \frac{q}{4\pi\epsilon_0} \frac{1}{r^2} \quad (3.6.1)$$

- ◆ To calculate a solvation free energy A_{sol}
- ◆ Take free energy in solvent subtract free energy in vacuum – constant temperature – liquid incompressible

$$A_{\text{sol}} = U_{\text{med}} - U_{\text{vac}} \quad (3.6.3)$$

* http://www.quimica.urv.es/~bo/MOLMOD/Mike_Colvin/solvation/solv.html

Free energy of solvation (2)

- ◆ For $r > R_{ion}$

$$U_{vac} = \frac{1}{2} \epsilon_0 \int_{R_{ion}}^{\infty} E^2 dV \quad (3.6.2a)$$

- ◆ Use E from 3.6.1 in 3.6.2 get

$$U_{vac} = \frac{1}{2} \epsilon_0 \int_{R_{ion}}^{\infty} \left(\frac{q}{4\pi\epsilon_0} \right)^2 \frac{1}{r^4} 4\pi r^2 dr = \frac{q^2}{8\pi\epsilon_0} \frac{1}{R_{ion}}$$

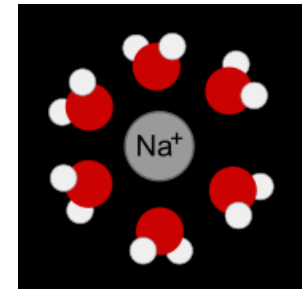
- ◆ To get free energy in the ionic medium – simply replace ϵ_0 with $\epsilon_0 \epsilon_r$

Free energy of solvation (3)

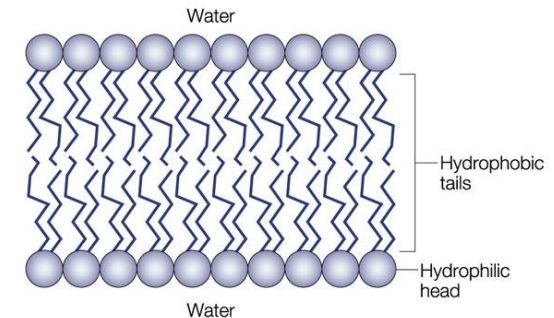
$$A_{sol} = U_{med} - U_{vac} = \frac{q^2}{8\pi\epsilon_r\epsilon_o} \frac{1}{R_{ion}} - \frac{q^2}{8\pi\epsilon_o} \frac{1}{R_{ion}}$$

$$A_{sol} = -\frac{q^2}{8\pi\epsilon_o} \frac{1}{R_{ion}} \left(\frac{\epsilon_r - 1}{\epsilon_r} \right)$$

- ◆ For monovalent ion, 1 Å radius – e.g Na⁺, in water ($\epsilon_r = 78.3$)
- ◆ solvation free energy $\Rightarrow -140\text{kT}$ (3.6 eV) ($5.8 \cdot 10^{-19}$ J)
- ◆ Solvated – hydrated radius 2.1 Å
- ◆ For low dielectric permittivity $\epsilon_r = 3$ (lipid membrane)
- ◆ solvation free energy $\Rightarrow +284 \text{ kT}$ – very low affinity for ions
- ◆ Accuracy of this Born approach depends strongly on radius used



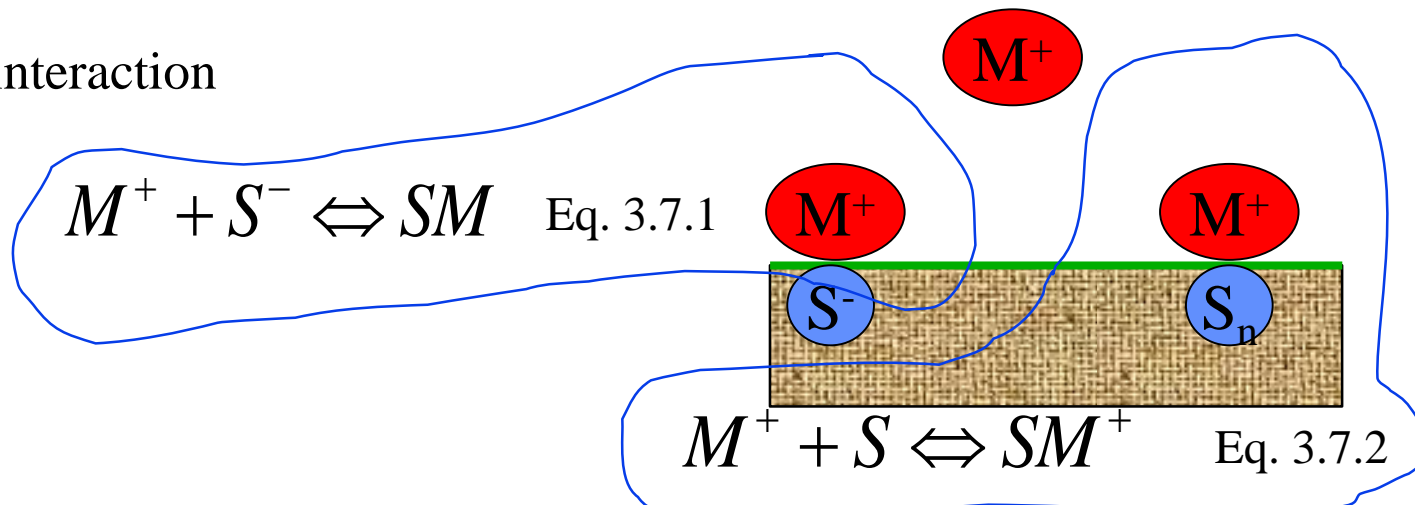
http://www.thefullwiki.org/Ethanol_precipitation



http://www.nature.com/horizon/livingfrontier/background/figs/membrane_f1.html

3.7 Charged Interfaces

- ◆ 3 mechanisms to charge an interface
 - Colloid is charged – e.g. latex has covalently bonded groups at surface
 - Adsorption of charged species – ions OH^- or polyelectrolytes
 - Titratable groups – i.e. dissociation of oxide surface $\text{MOH} \leftrightarrow \text{M}^+ + \text{OH}^-$
- ◆ Charge often determined by equilibrium process - 3 Free energy contributions
 - Chemical interactions – short range – promote adsorption
 - Electrostatic – longer range – limit to surface charge – ordered localised arrangement
 - Entropy – tends towards desorption – random uniform distribution of ions
- ◆ Short range chemical interaction



Chemical potential of surface

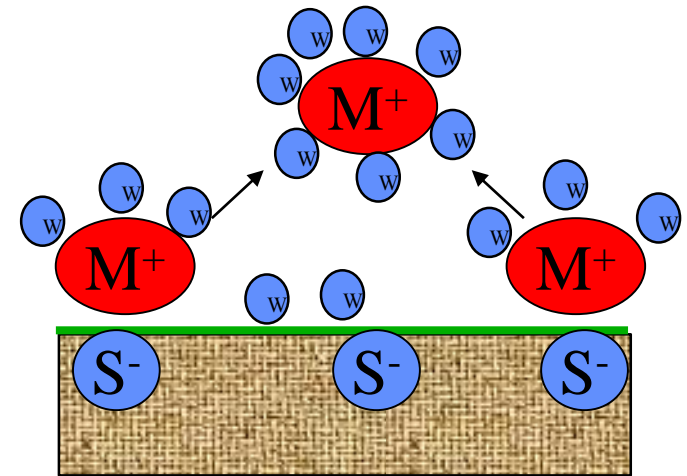
- ◆ Surface equilibrium – 2 extra points of bulk
 - Surface charge changes with association \Rightarrow ion-ion interaction
 - Entropic contribution from free energy of mixing \Rightarrow confined to surface
 - Energy of solvation also modified at surface (hydration shell no longer isotropic)

- ◆ Chemical potentials
 - Surface - solute - associated pair

$$\mu_S + \mu_M = \mu_{SM}$$

- ◆ K_S surface equilibrium constant

$$\frac{X_{SM}}{X_S C_M} = K_S \exp\left(\frac{-z_s e \Phi_0}{kT}\right)$$



Electrostatic interaction

$$X_{SM} - \text{mole fraction} = \frac{n_{SM}}{n_{SM} + n_S}$$

C_M solute concentration

z_s – valence, Φ_0 surface potential

Effects - Surface titration

- ◆ Form of surface titration not same sigmoidal as bulk because of surface charge
- ◆ Example of protein enzyme – ribonuclease (12,600- M_w)
 - Surface carboxylic groups (-COOH) and
 - amino groups (-NH₂)
 - pzc – point of zero charge
 - surface potential = 0
 - iep = isoelectric point
 - zeta potential = 0
 - high pH=9 for protein unusual
 - lots of amino groups

Gets more and more difficult to increase the number of charged groups because of increasing surface charge density

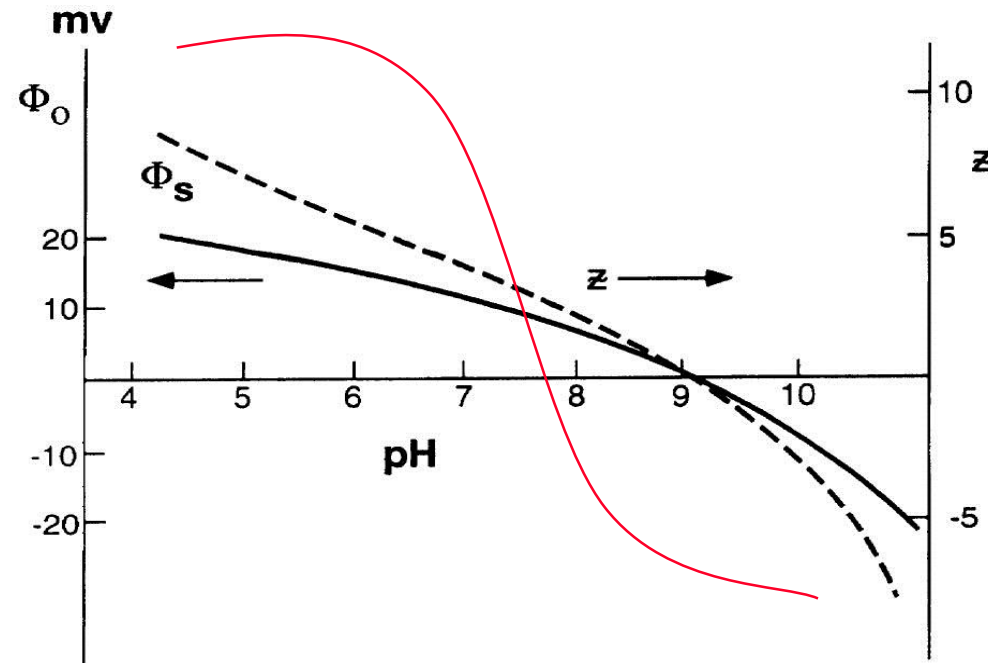
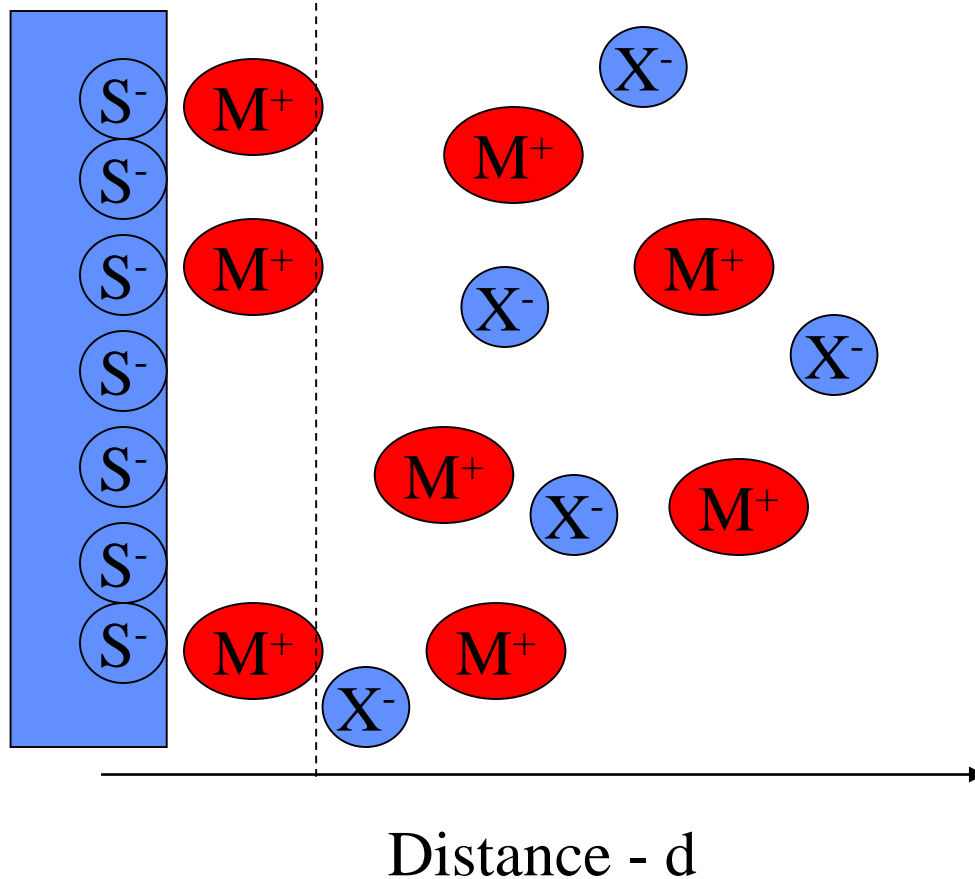


Fig 3.7 Φ surface potential , $z(e)$ net charge

3.8 – Poisson Boltzmann equation

- ◆ Describe, surface potential, Φ , ionic concentration C , vs distance from surface
- ◆ Relationship between surface charge density, σ and surface potential Φ



- ◆ Poisson equations – ρ charge density

$$\epsilon_0 \epsilon_r \nabla^2 \Phi = \rho_{(free-ions)}$$

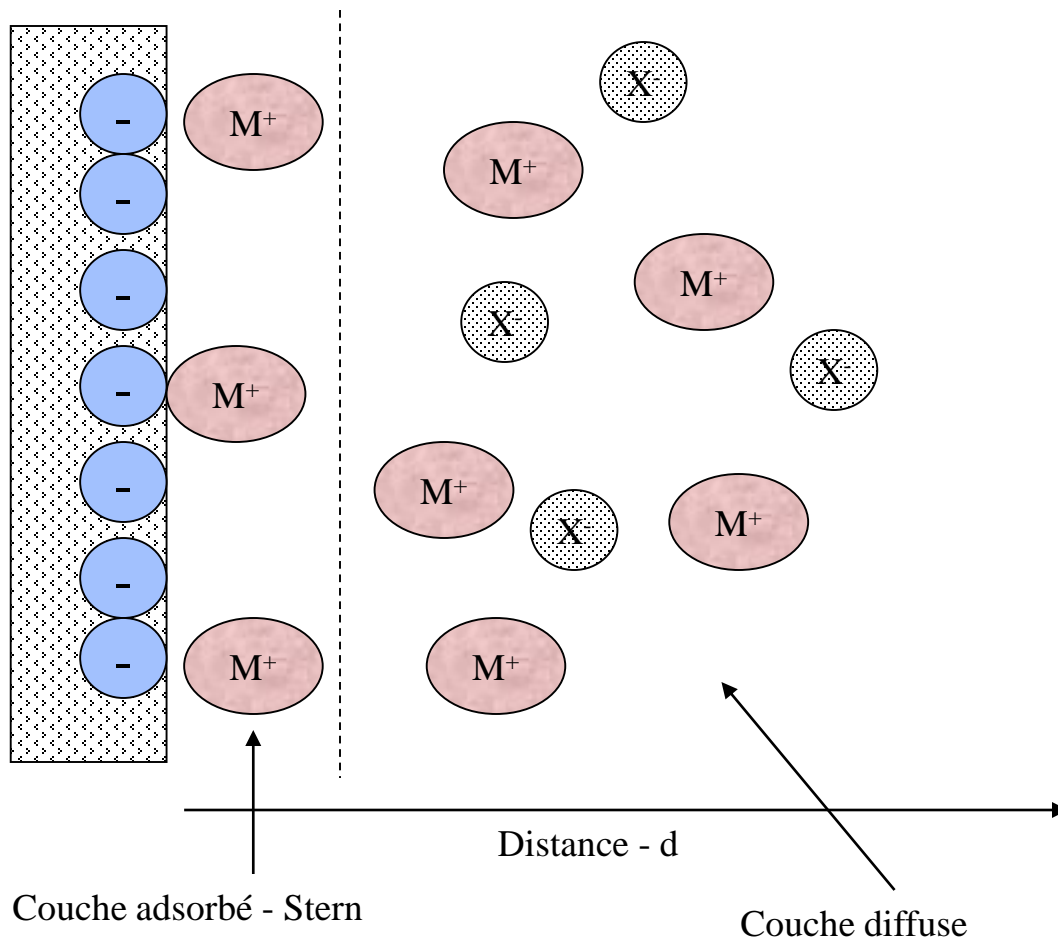
$$\rho_{(free-ions)} = e \sum_i z_i c_i^*(\vec{r})$$

• Boltzmann distribution

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

c_{i0}^* - bulk value far from surface ($\Phi=0$)

Double Layer



- Negative ions strong affinity for surfaces – Hofmeister series
- $I^- > ClO_4^-, NO_3^- > Br^- > Cl^- > OH^-, F^-, SO_4^{2-}$,
- Stern Layer – strongly attached
- Diffuse layer counter-ions
- Electrical DOUBLE LAYER

Boltzmann contribution

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

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

- ◆ c_{i0}^* , concentration at $\Phi=0$ ie in bulk solution far from interface (number of molecules per m^3)
- ◆ Combine Poisson Equations with Boltzmann distribution

$$\epsilon_0 \epsilon_r \nabla^2 \Phi = \rho_{(free-ions)} \quad \rho_{(free-ions)} = e \sum_i z_i c_i^*(\vec{r})$$

$\rho(r)$ volume charge density (C/m^3)

Poisson Boltzmann (PB) Equation

- ◆ Ion distribution in an electrolyte outside a charged surface

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

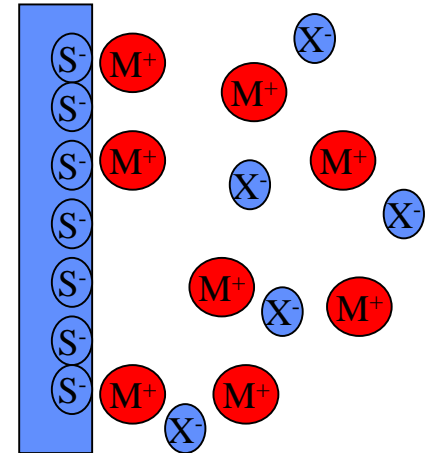
$$\epsilon_0 \epsilon_r \nabla^2 \Phi = -e \sum_i z_i c_{i0}^* \exp\left(\frac{-z_i e \Phi}{kT}\right) \quad \text{Eq. 3.8.4}$$

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

- ◆ To solve PB need geometry – infinite plane $\Rightarrow d/dz$
- ◆ Boundary conditions
 - Electroneutrality $d\Phi/dz = 0$ far from surface and
 - c_{i0}^* , represents bulk electrolyte concentration
 - At surface behaves like capacitor $d\Phi/dz = -\sigma/\epsilon_0\epsilon_r$ (Eq 3.8.7)
 - No charged species below surface ie $z <= 0$, $d\Phi/dz = 0$



$$\left(\frac{d\Phi}{dz} \right)^2 = \frac{2kT}{\epsilon_0\epsilon_r} \sum_i c_{i0}^* \left[\exp\left(\frac{-z_i e\Phi}{kT} \right) - 1 \right] \quad \text{Eq 3.8.10}$$

- ◆ Square root of LHS gives \pm negatively or positively charged surfaces

Guoy Chapman theory

- ◆ For symmetric electrolyte eg NaCl ($z=1$) or MgSO₄ ($z=2$)

Eq. 3.8.11

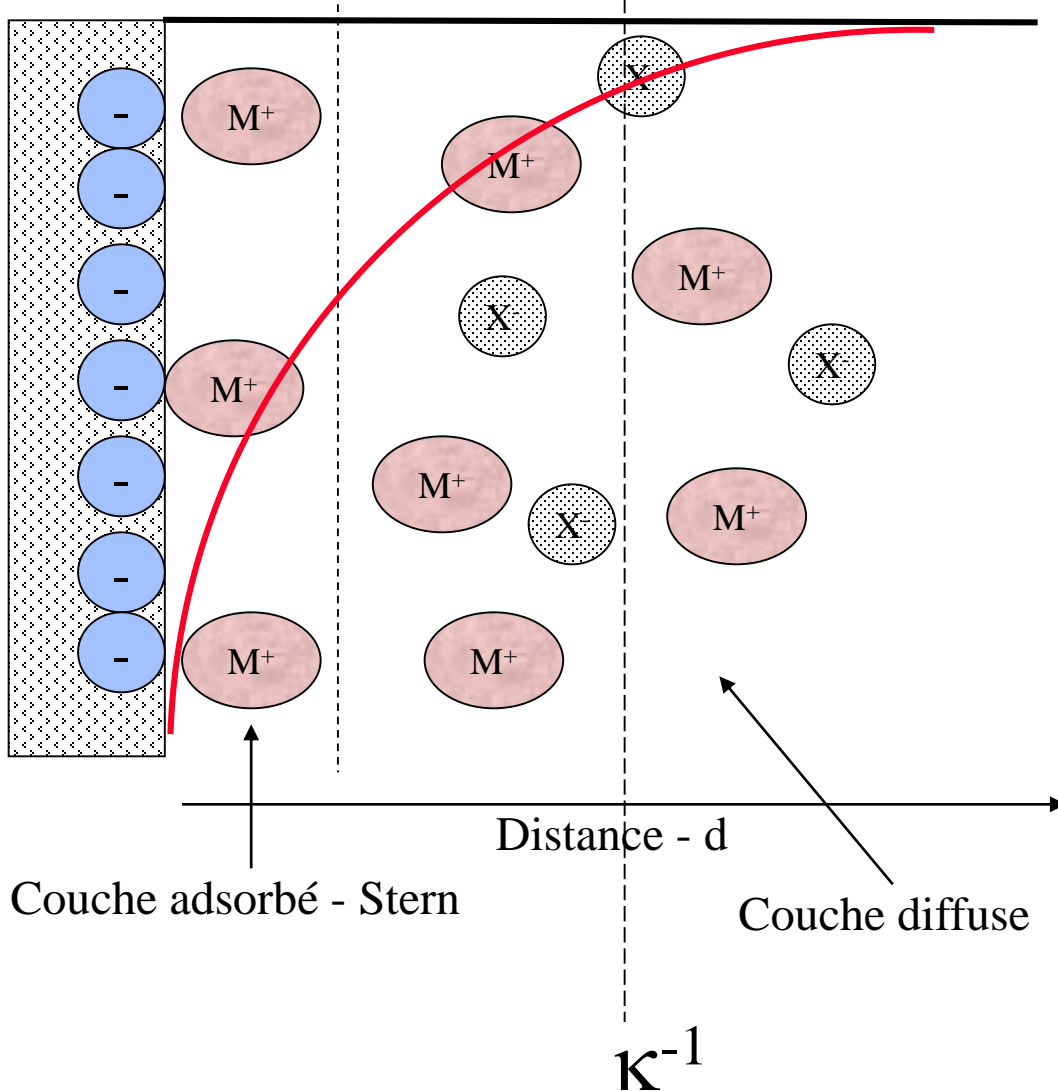
$$\frac{d\Phi}{dz} = \left(\frac{8kTc_0^*}{\epsilon_0\epsilon_r} \right)^{1/2} \sinh\left(\frac{z_i e \Phi}{2kT} \right)$$

- ◆ 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

$$\frac{1}{\kappa} = \left(\frac{\epsilon_0 \epsilon_r k T}{\sum_i (z_i e)^2 c_{i0}^*} \right)^{1/2} \quad \text{Eq. 3.8.13a} \quad \text{And} \quad \Gamma_0 = \tanh\left(\frac{ze\Phi_0}{4kT} \right)$$

Longueur de Debye - κ^{-1} -



$$\frac{1}{\kappa} = \left(\frac{\epsilon_0 \epsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^*} \right)^{1/2}$$

- ◆ La distance du potentiel de surface est $1/e$
- ◆ le « rayon » de l'atmosphère ionique κ^{-1} ,
- ◆ le longueur de Debye,
- ◆ épaisseur de la double couche.

Debye length vs. ionic strength

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

$$\frac{1}{\kappa} = \left(\frac{\epsilon_0 \epsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^*} \right)^{1/2}$$

	Electrolyte – Thickness (nm)					
Conc. (M)	<i>1:1</i>	<i>1:2</i>	<i>1:3</i>	<i>2:2</i>	<i>3:3</i>	
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

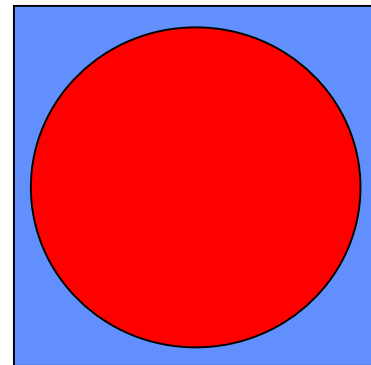
- ◆ Combining Eq. 3.8.7 and 3.8.11 (Gouy – Chapman Theory)
 - surface charge density, σ (C/m²), as fn of surface potential, Φ ,

$$\sigma = \left(8kTc_{i0}^* \epsilon_0 \epsilon_r \right)^{1/2} \sinh \left(\frac{z_i e \Phi_0}{2kT} \right) \quad \text{Eq. 3.8.15}$$

- ◆ Example

- $\Phi_0 = -75$ mV, $c = 0.15$ M, NaCl, 25°C
- $\sigma = 0.09$ C/m² means 1 unit charge per 180Å²
- Na⁺ ~ 1 Å (radius) (+ solvation 2.1 Å)

13.4 Å

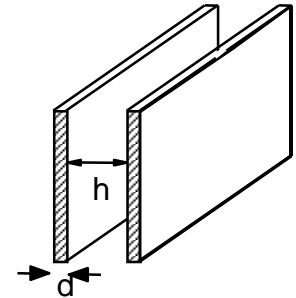


13.4 Å

Linearised Poisson Boltzmann

- ◆ Analytical solution of the PB equation – only for very few special cases
- ◆ Linearise to give analytical solution for **planar surface**
- ◆ Weakly charged < 25 mV

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



- ◆ Potential

$$\Phi(z) = \Phi_0 e^{-\kappa z} \quad \text{Eq.3.8.19}$$

- ◆ Charge

$$\sigma = \epsilon_0 \epsilon_r \kappa \Phi_0 \quad \text{Eq.3.8.20}$$

- ◆ Capacitance

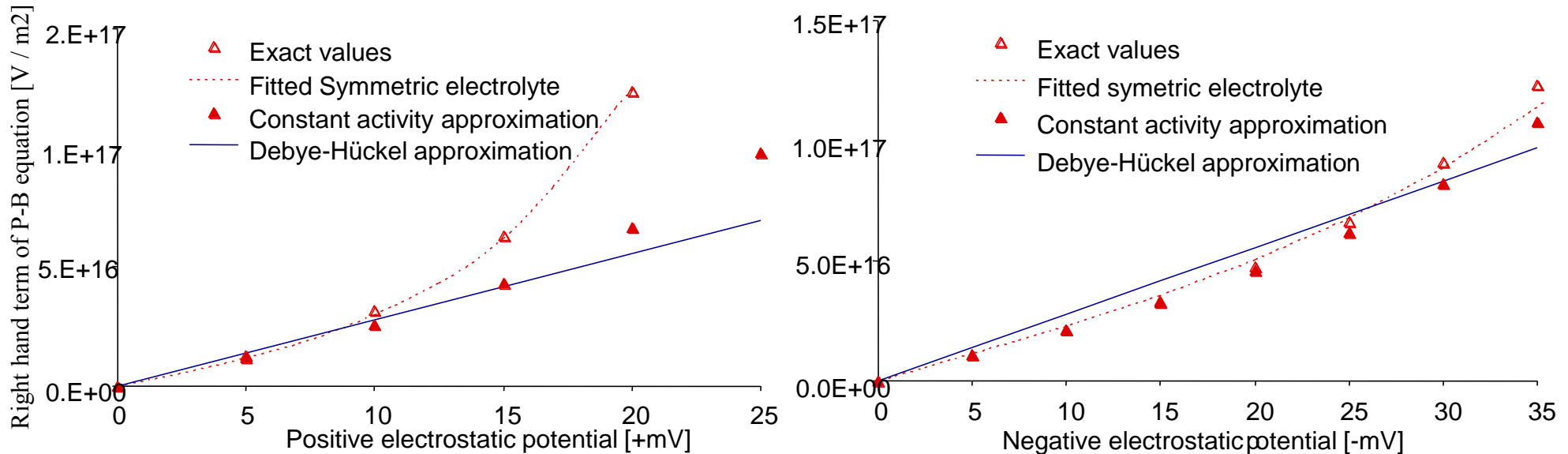
$$C = \frac{\sigma}{\Phi_0} = \frac{\epsilon_0 \epsilon_r}{1/\kappa} \quad \text{Eq.3.8.21}$$

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

Linearised Poisson Boltzmann - Debye Huckel - limits

- ◆ Work at LTP* on cement – mixture of 8 ions, K^+ , Na^+ , Ca^{2+} , SO_4^{2-} , Silicates, Mg^{2+} , Al^{3+} , OH^- - varied valence and 0.3 M
 - compared approximation with numerical solutions
- ◆ Showed linearised PB valid for 0.3M
 - can use a non-integer valence e.g. 1.16 (-ve surface) 3.52 (+ve surface)
 - -35mV to 10mV error less than 15% cf exact values from numerical solution

$$\frac{1}{\kappa} = \left(\frac{\epsilon_0 \epsilon_r kT}{\sum_i (z_i e)^2 c_{i0}^*} \right)^{1/2}$$

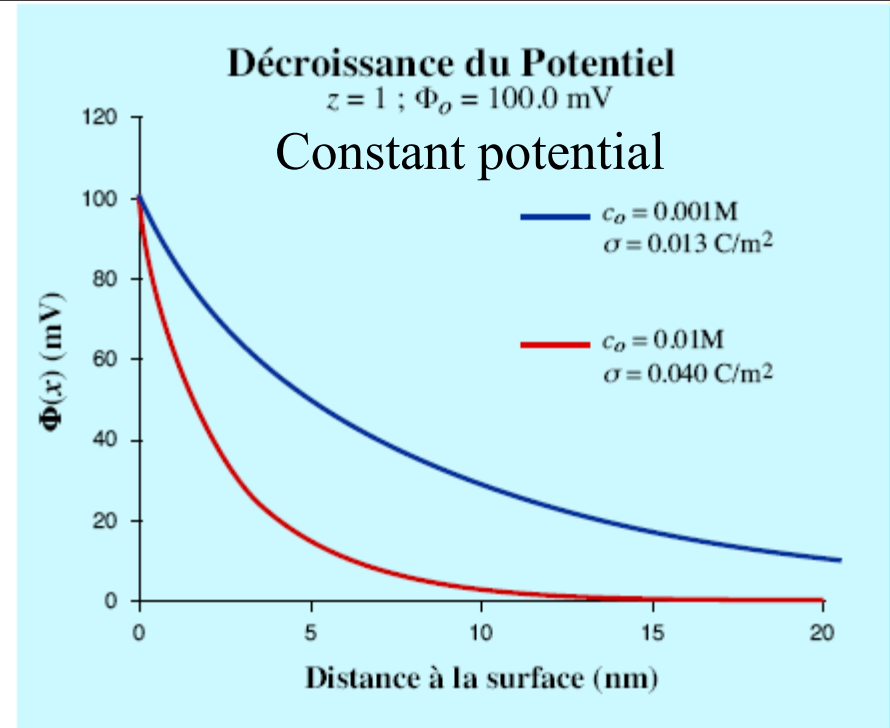
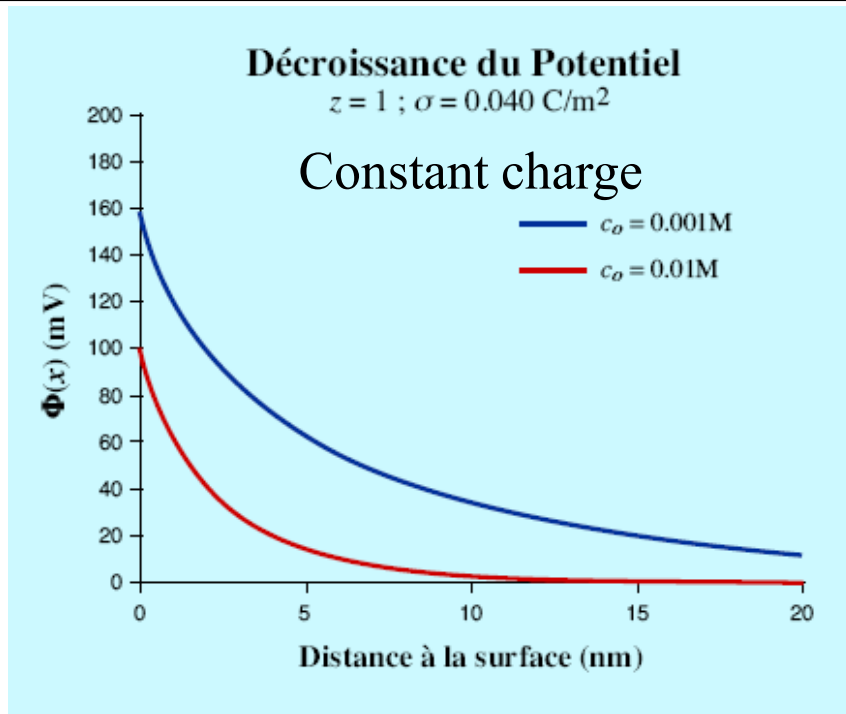


*R. J. Flatt, P. Bowen, Cement and Concrete Research 33 (2003) 781-791

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



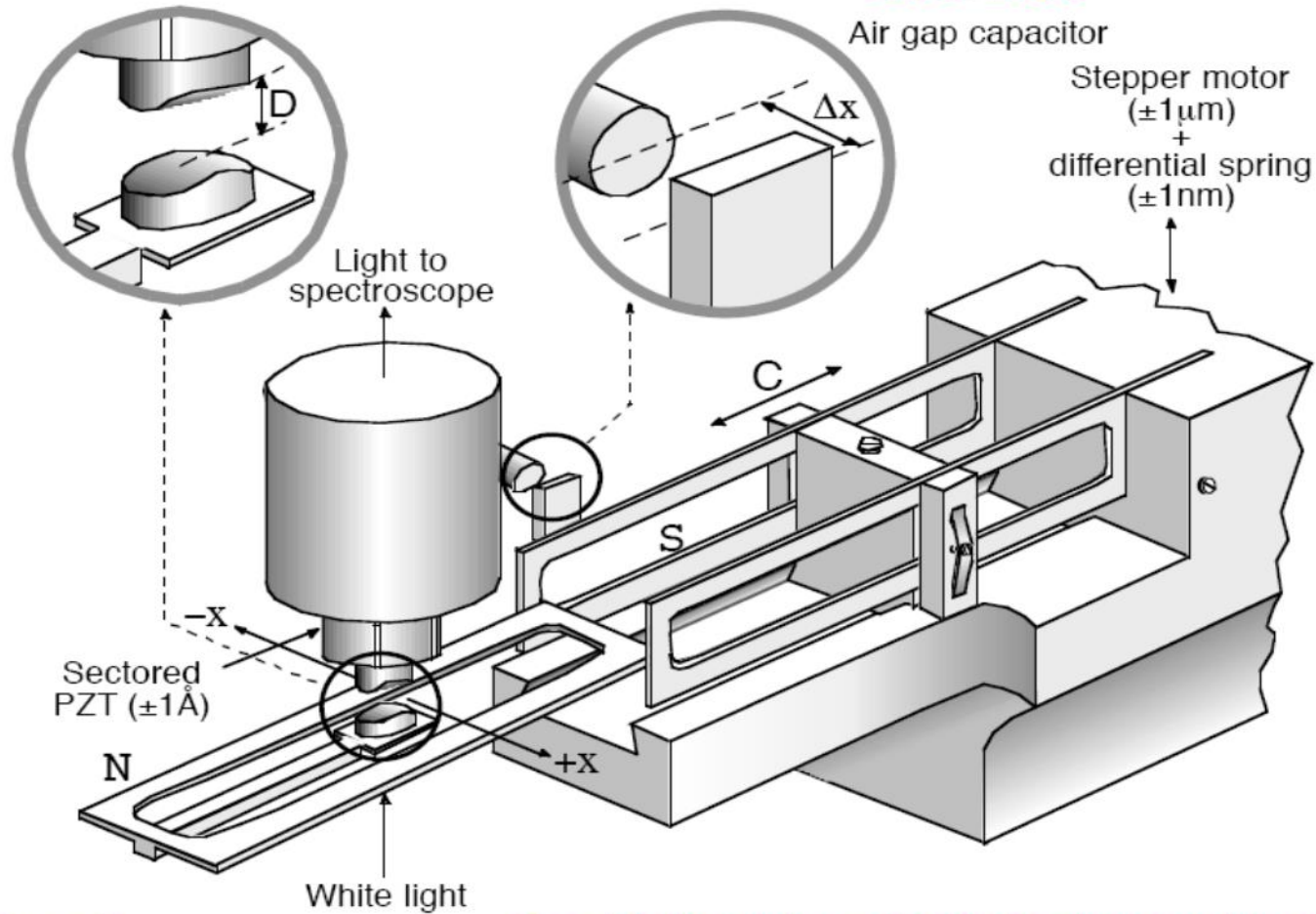
- Recent work at Geneva University – suggests charge regulation model needed for accurate DLVO predictions (depends on adsorption equilibria of pdi's)
- F. Javier Montes Ruiz-Cabello, Plinio Maroni, and Michal Borkovec. J.CHEM.PHYS. 138, 234705 (2013)

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

Atomic Force Apparatus

D & ΔD to $\pm 1-2 \text{ \AA}$

Δx to $\pm 2 \text{ \AA}$

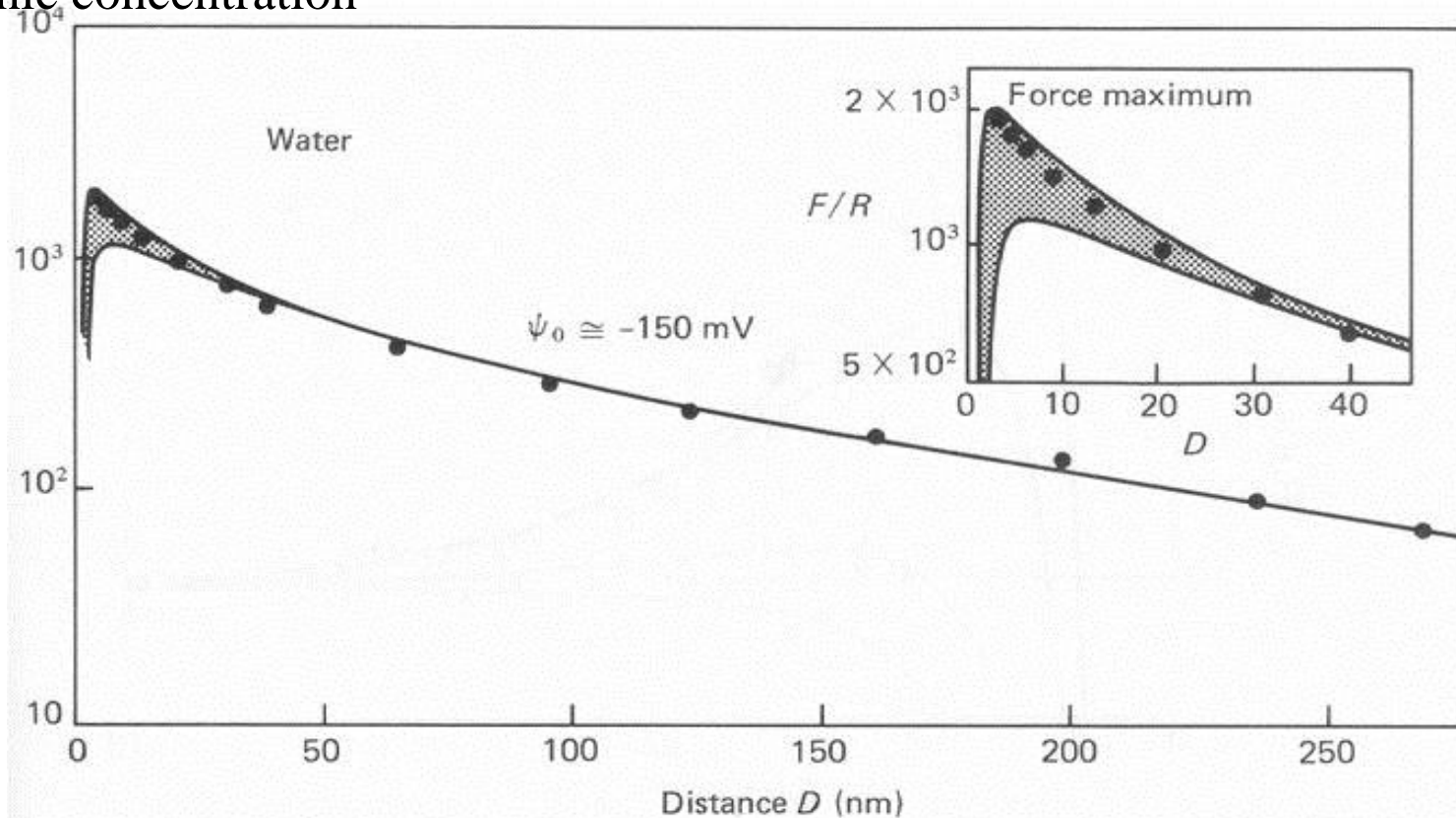


J. Phys. Chem. B
105, 8125 (2001)

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 charge density and ionic concentration



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

Ionic concentration and surface potential (1)

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

$$\left(\frac{d\Phi}{dz}\right)^2 = \frac{2kT}{\epsilon_0\epsilon_r} \sum_i c_{i0}^* \left[\exp\left(\frac{-z_i e\Phi}{kT}\right) - 1 \right] \quad \text{Eq. 3.8.10}$$

- ◆ with boundary condition of 3.8.7
 - surface behaves like capacitor
- $$\left.\frac{d\Phi}{dz}\right|_{z=0} = \frac{-\sigma}{\epsilon_0\epsilon_r} \quad \text{Eq. 3.8.7}$$

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

$$\sum_i c_i^*(0) = \frac{\sigma^2}{2kT\epsilon_0\epsilon_r} + \sum_i c_{i0}^* = \frac{\sigma^2}{2kT\epsilon_0\epsilon_r} + \frac{\Pi_{osm}}{kT}$$

Ionic concentration and surface potential (2)

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

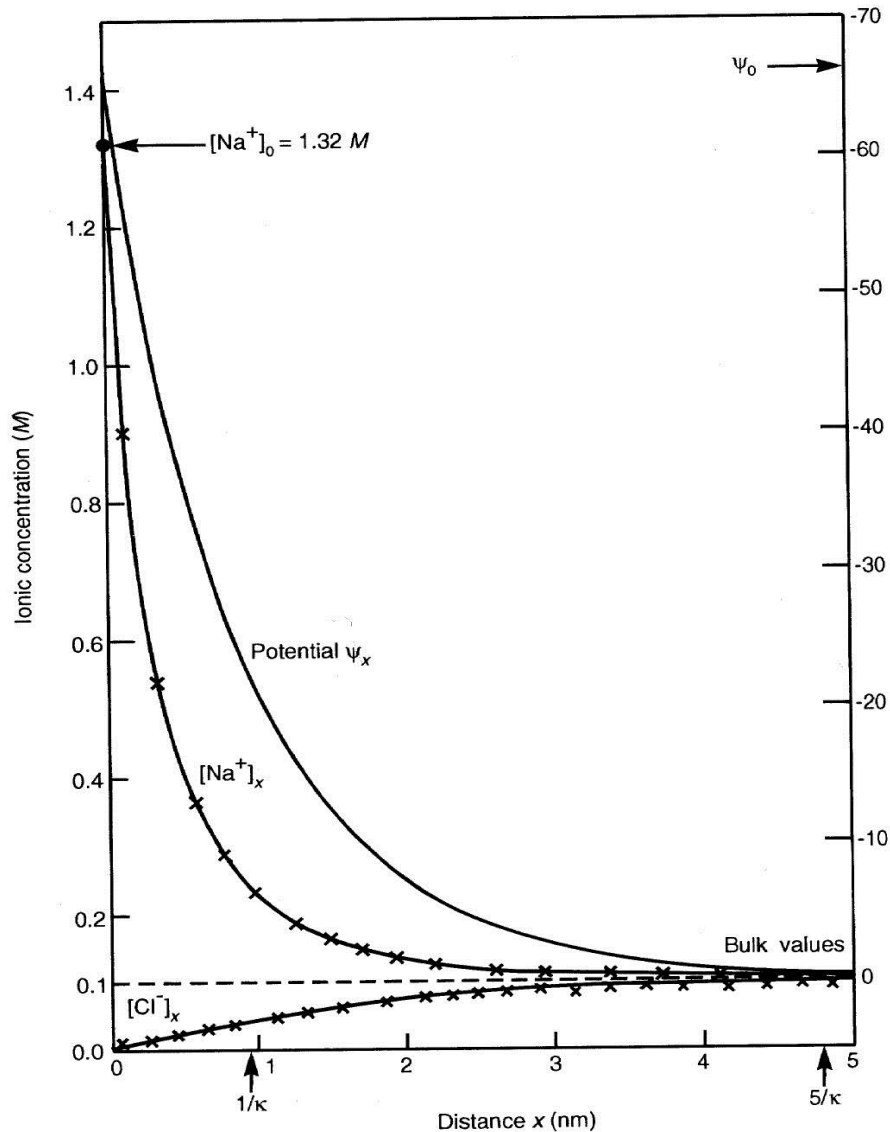
From Thermodynamics course - definition of osmotic pressure in an ideal solution

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

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

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 -from Israelachvili*
 - $\sigma = 0.0621$ C/m² ($1e/2.6\text{nm}^2$)
 - $\Phi_0 = -66.2$ mV (from Graham eq.)
 - x Monte Carlo simulation
- ◆ Counterion distribution (conc) very near surface (84% within 3Å) - independent of ionic concentration (for fixed σ and high $\sigma > 0.05$ C/m²)
- ◆ 0.1 and 0.0001 M give very similar results
- ◆ According to this Gouy – Chapman double layer approach

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

Ionic concentration and surface potential

- ◆ Concentration of counter ions at surface $\sim 1-3\text{M}$! such high concentrations raise questions about assumptions for PB eq.
- ◆ Limitations of **mean field theory** on close approach 2-5 nm (Stern layer)
 - Ion-correlation effects due to highly polarisable layers – **attractive**
 - Finite ion size – excluded volume effect – **repulsive**
 - Image forces – "reflected" charge by surface gives "image in surface" - **repulsive**
 - Surface charges discrete – not averaged as above – **attractive**
 - Solvation forces - displacement/ordering of solvent – **attractive, repulsive, oscillatory**
- ◆ Molecular modelling and numerical simulations (Monte Carlo) – show limitations – examples later

Dependance on valence, z

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

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

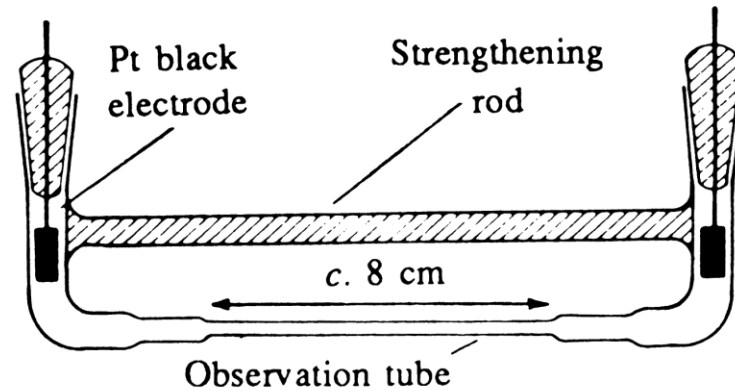
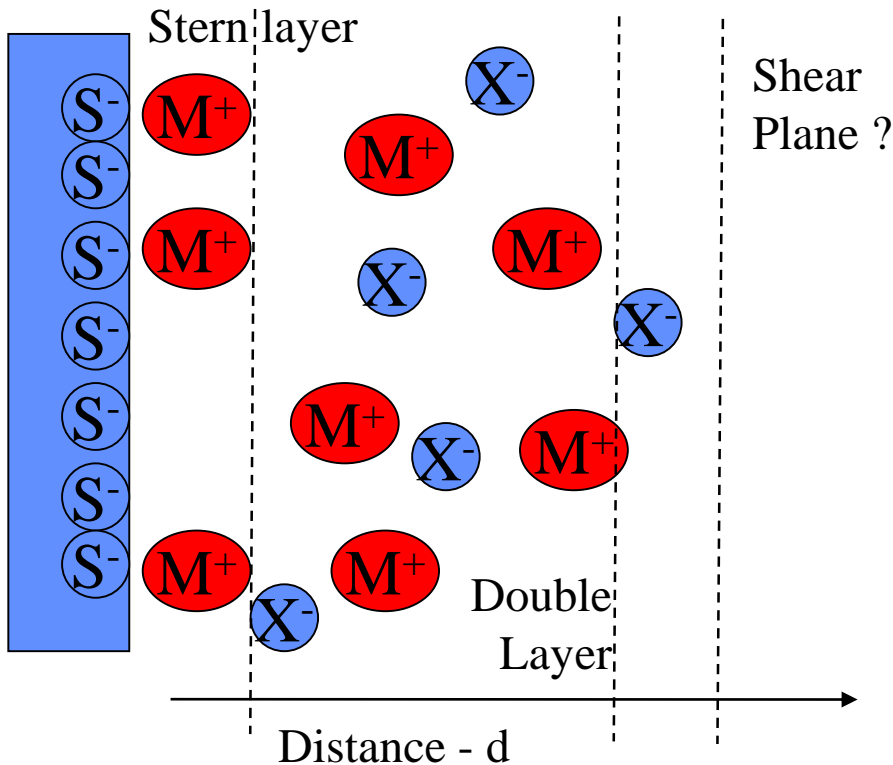
- ◆ when $e\Phi \geq kT$ valence effect z becomes more pronounced
- ◆ Clays or resins used in ion exchangers to soften water by removing divalent ions
 - surfaces preloaded with Na^+ exchange for divalent ions eg Ca^{2+}
- ◆ Ca^{2+} surface concentration enhanced by 50 times for surface potentials of 100 mV (low electrolyte concentrations) because of electrostatic interaction

- ◆ Consequences of electrical double layer or near surface ion distribution
 - Particle size measurement of Silica and iron oxides

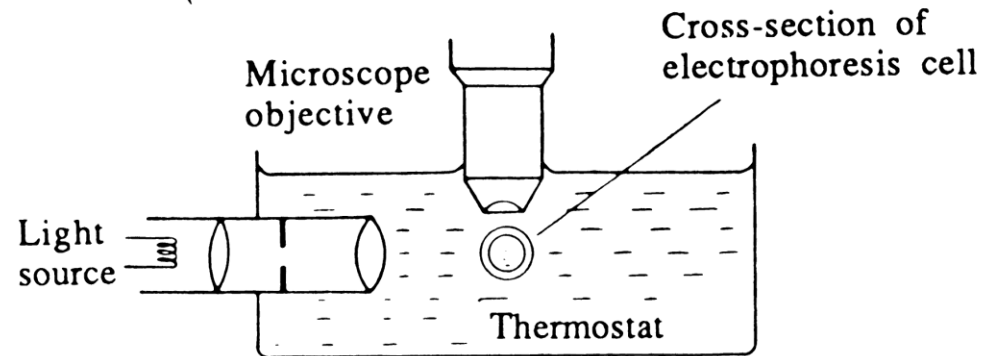
Zeta potential measurement

- ◆ Classically – electrophoresis – measures mobility of a charged particle in an electric field
- ◆ The zeta potential can be related to the mobility – traditionally in capillaries – dilute suspensions $\ll 1\% \text{ wt}$ – must not sediment

Shear plane – and zeta potential »poorly defined«



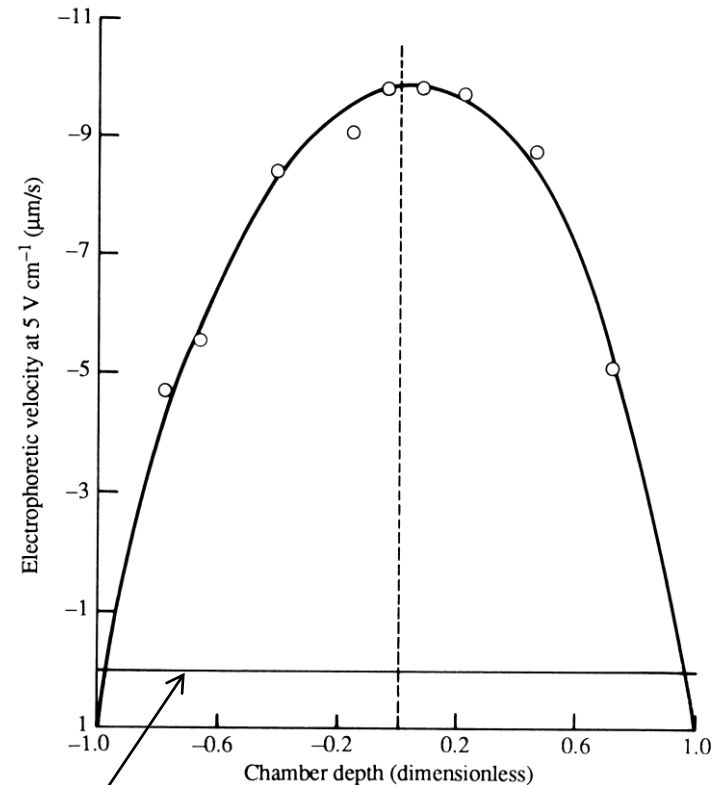
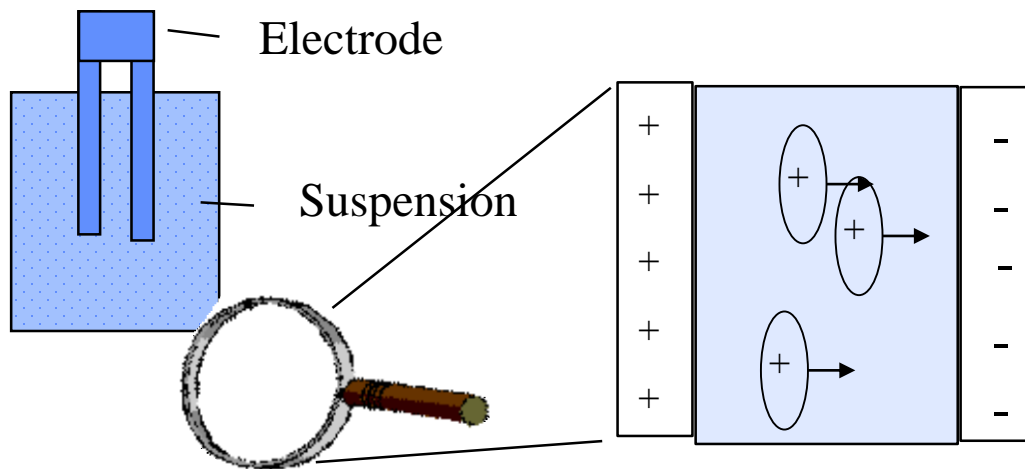
(Internal diameter: c. 2 mm)
(Wall thickness: c. 0.05 mm)



Electrophoresis - approach

- ◆ Currently use laser Doppler shift to measure velocity of particle – difficult to find stationary layer – big errors
- ◆ Capillary still used but made very quickly at centre of capillary – no effect of electro osmosis as in past – much more reliable
- ◆ Second alternative Brookhaven ZetaPALS electrode directly into suspension- easy quick and good for multiple users – noisy results

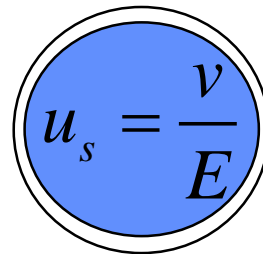
Electro-osmosis, ions move towards opposite electrodes cause flow in cell – charged walls modify velocity – at certain distance (stationary plane) fluid has zero velocity – measure.....



Zeta potential calculation – Thin double layer

- **Thin** double layer – large κa ($1/\kappa$ – double layer thickness – Debye length)
- Smoluchowski approximation – thickness of double layer negligible wrt to particle

$$u_s = \frac{\epsilon \zeta}{\mu}$$



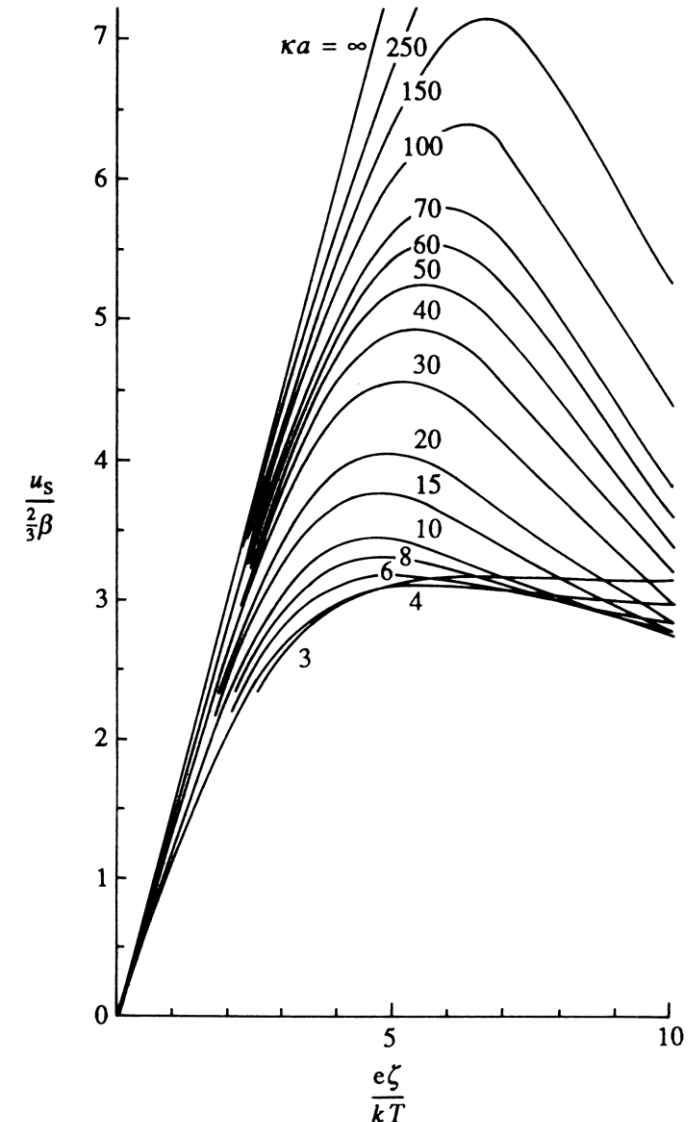
$$u_s = \frac{v}{E}$$

u_s – mobility, ζ – zeta potential,

μ – viscosity ϵ – permittivity

v is the drift velocity induced by the electric field E

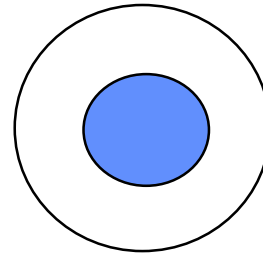
- O'Brien, R.W. White, L.R. "Electrophoretic Mobility of a Spherical Colloidal Particle" J. Chem. Soc. Faraday Trans. 2. 74 1607, 1978.
- Plot of dimensionless mobility vs. Dimensionless zeta potential ($1 = 25$ mV) shows limits – mobility does not give unique zeta even show maxima here ($\kappa a > 3$) for zeta potentials >25 mV – careful with zeta – can simply quote mobility



Zeta potential calculation – Thick Double Layer

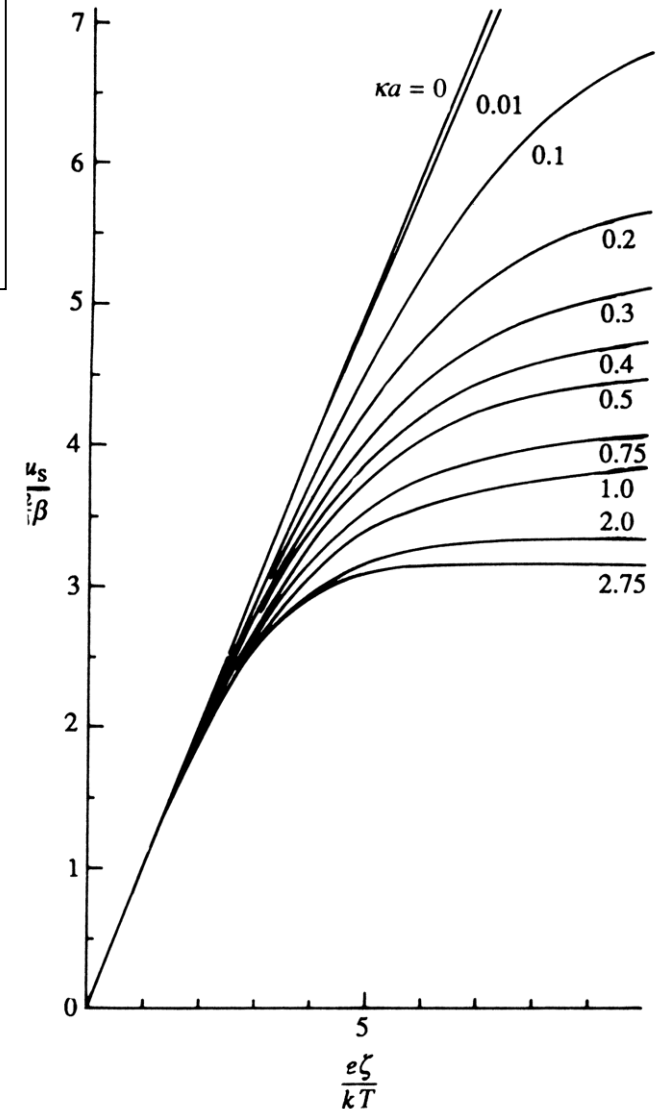
- **Thick** double layer – small κa ($1/\kappa$ – double layer thickness – Debye length)
- Hückel approximation – treat particle as point charge but big enough to use Stoke's Law

$$u_s = \frac{2\varepsilon\zeta}{3\mu}$$



- ◆ u_s – mobility, ζ – zeta potential,
- ◆ μ – viscosity ε – permittivity

- O'Brien and White – took into account distortion of double layer and relaxation time
- Plot of dimensionless mobility vs. Dimensionless zeta potential ($2 = 50$ mV) - shows limits – mobility does not give unique zeta ($\kappa a < 3$) at high surface charge density

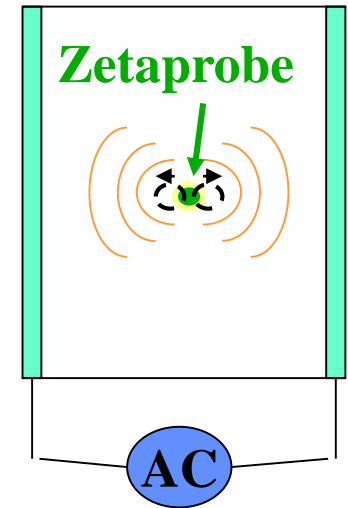


Mesures électroacoustiques

Colloidal Dynamics Model Acoustosizer™

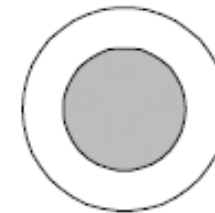
- Particle range 20 nm – 10 μm
- Conc. suspension 1wt % to 30%wt
- Automatic titration
- Size from electroacoustics and
- Acoustic attenuation
- Limited to log-normal distributions

Cell

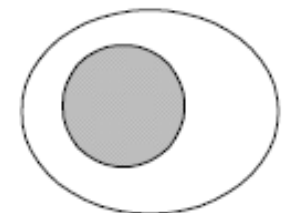


- High frequency electric field is applied (MHz)
- Particle oscillation
If particle density \neq medium density
- Produces a sound wave of same frequency
- Measuring its amplitude and phase on a range of frequencies
- Calculation of particle mobility and zeta potential with O'Brien theory
- J.Coll.Inter.Sci., 173 406-418 (1995).

Electric field



Particle surrounded by equilibrium double layer

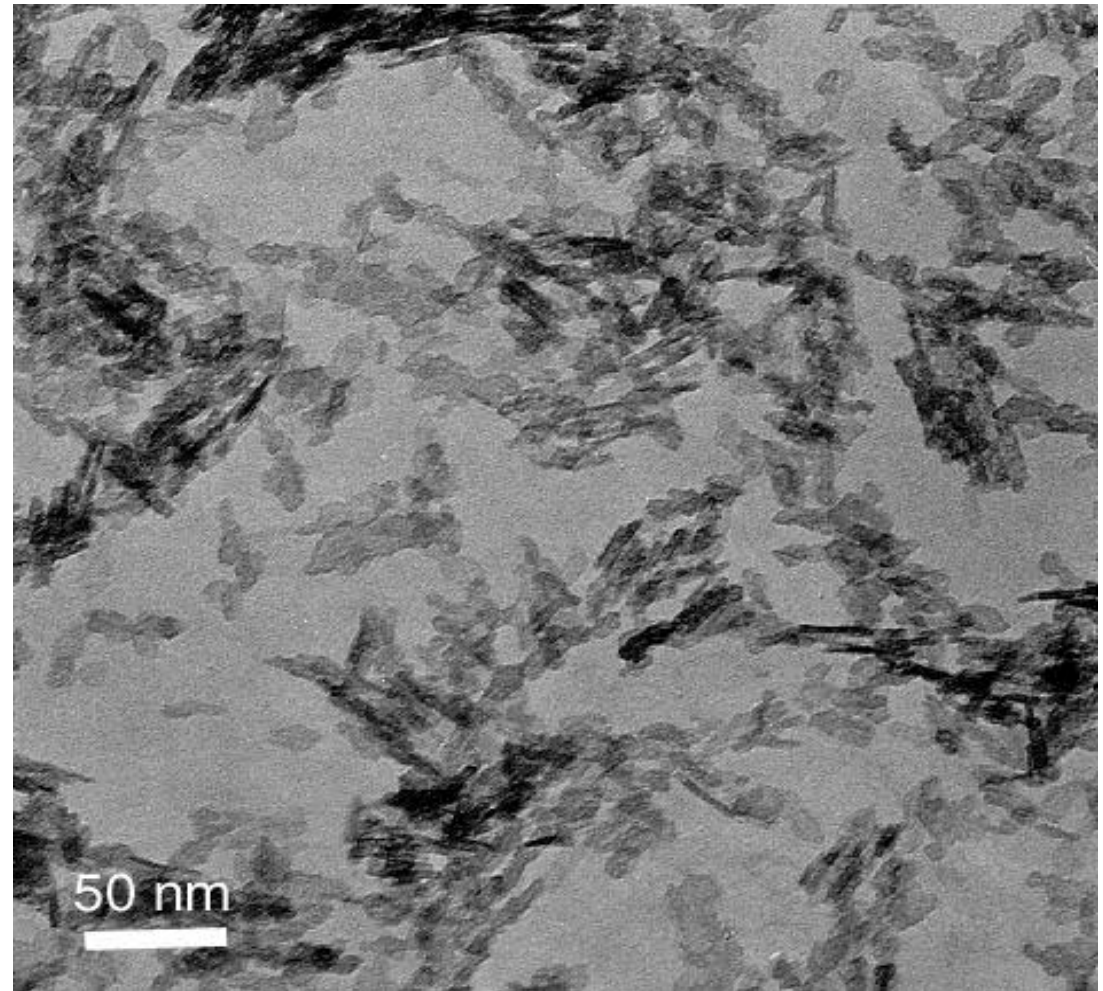
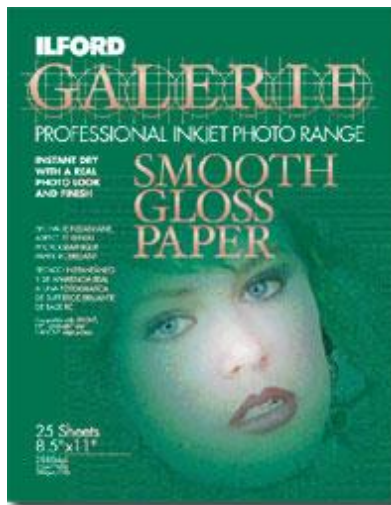


Distorted double layer

Figure 3: Distortion of double layer by applied electric field

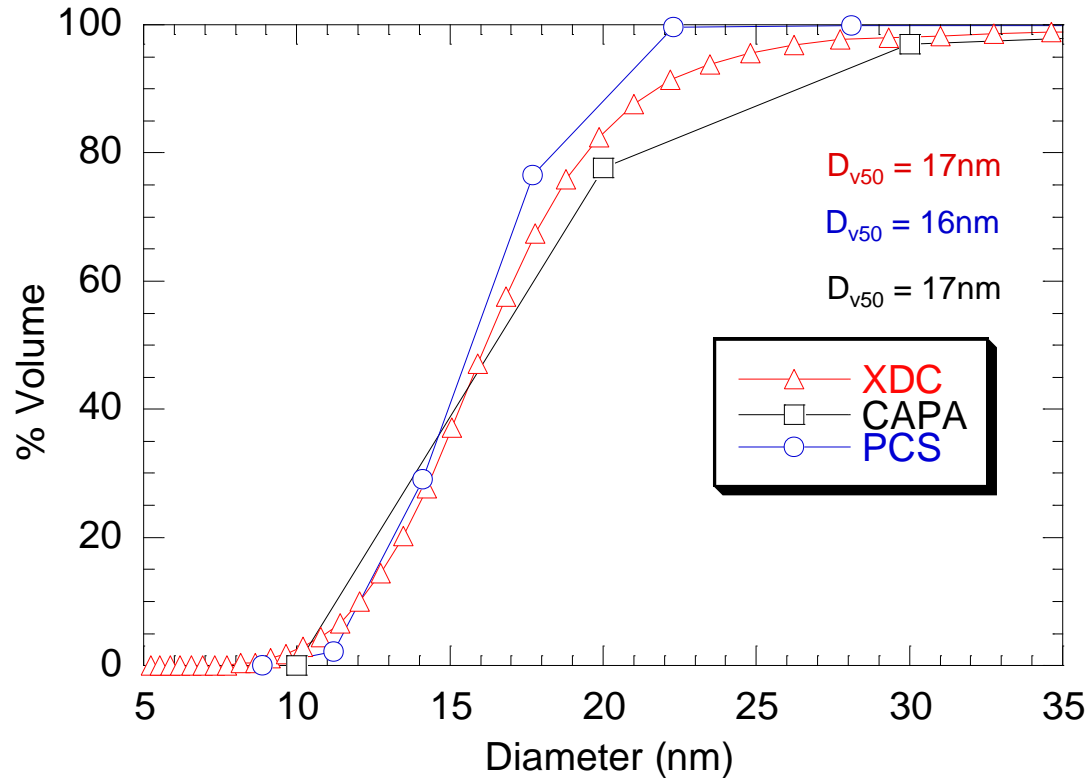
Sol-Gel – AlOOH precipitation – Boehmite

- ◆ Aluminium iso-propoxide - AlOOH
- ◆ Drying by atomisation– **re-dispersible** at 20 nm
- ◆ $d_{\text{BET}} = 9.3 \text{ nm}$ $F_{\text{ag}} = 1.7$
- ◆ Porous layer applications
- ◆ Inkjet paper (ILFORD)



PSD measurement - Boehmite - Horiba - XDC – PCS*

3 different instruments- particle size distribution (PSD) – very good results
Boehmite 1 - Condea - (AlOOH) 213 m²/g $d_{\text{BET}} = 9.4 \text{ nm}$



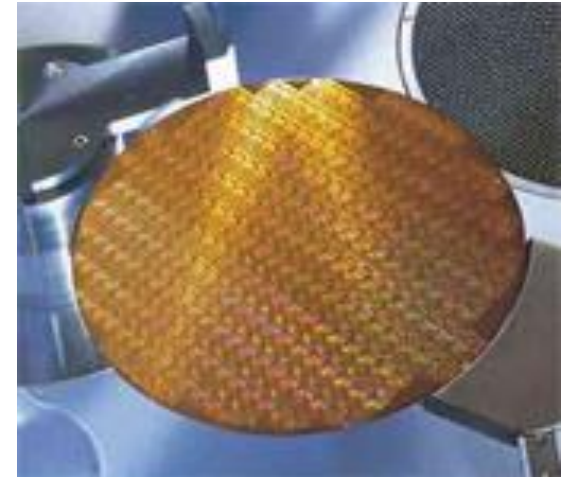
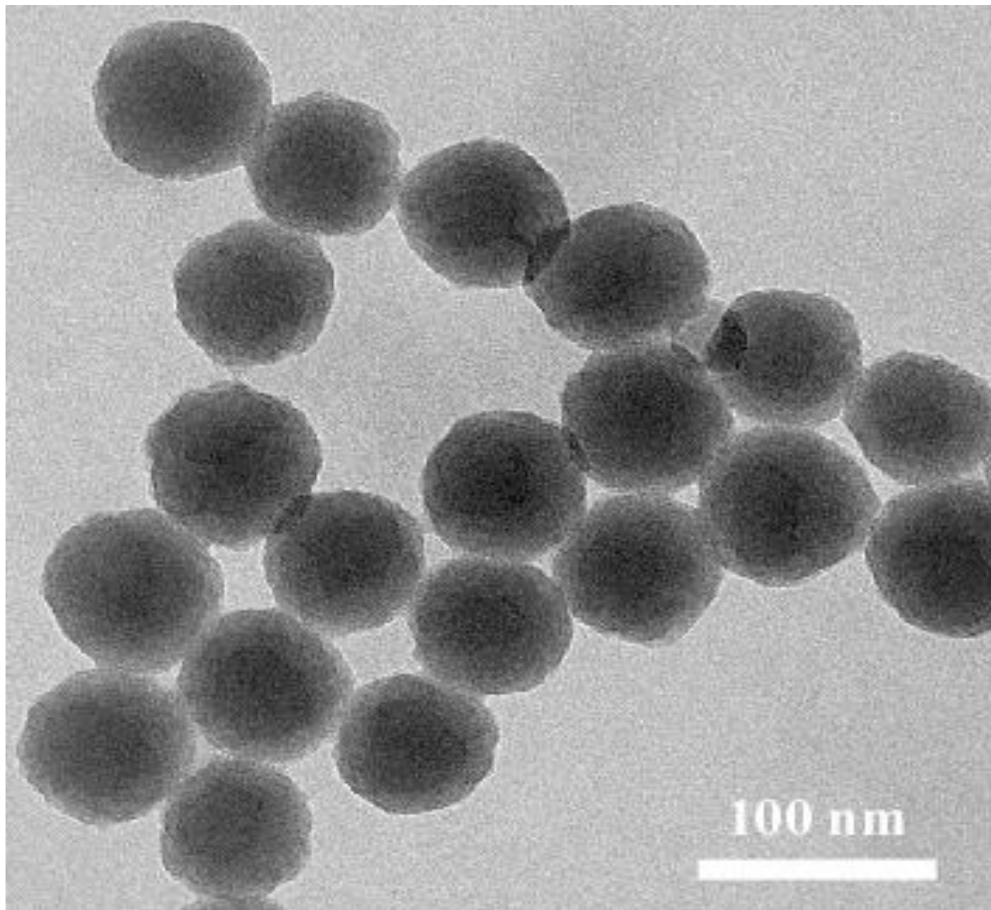
Distribution **narrow** ($\sigma_{v50}/d_{v50} = 2.2$)

- ◆ Median diameters **very similar**
- ◆ **Resolution** with XDC best
- ◆ XDC 2hrs
- ◆ PCS 10 -20mins
 - ◆ (single angle, CONTIN)
- ◆ Horiba 2 days!
- ◆ Image analysis to confirm – XDC best – difficult because of particle shape and size
- ◆ Non-sphericallooked for model particles

Horiba – CAPA – centrifuge – light absorption detector
XDC – centrifuge – x-ray absorption detector
PCS – dynamic light scattering

Spherical Silica - Real size ??-1

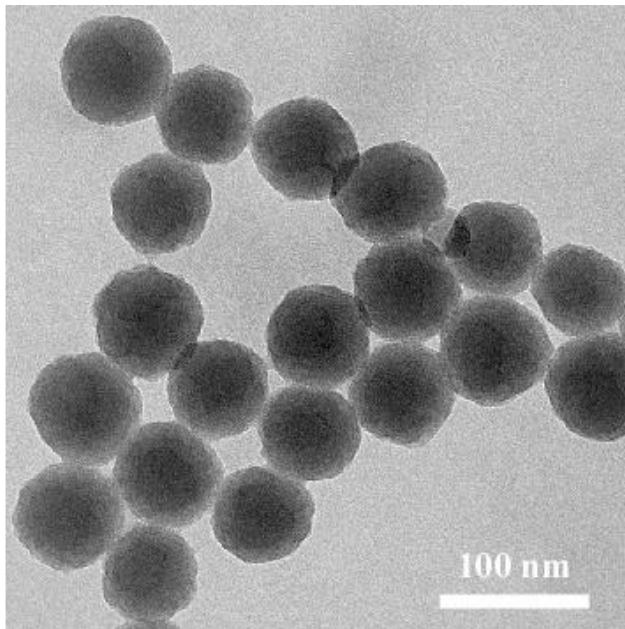
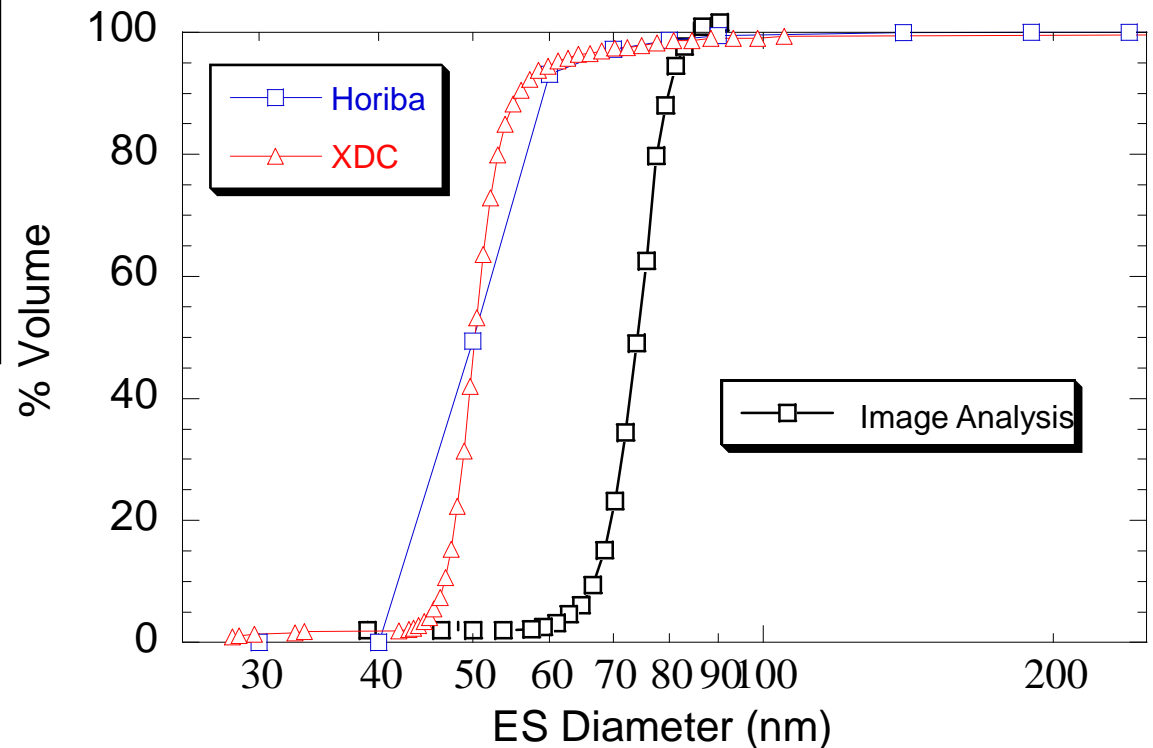
- ◆ Klebosol – A-Z chemicals – Klebosol used for chemical mechanical polishing of silicon wafers



<http://www.grace.com/EngineeredMaterials/ProductsAndApplications/Electronics/WaferPolishing.aspx>

Spherical Silica - Real size ??-2

- ◆ AlOOH very good agreement between XDC, Horiba
- ◆ Use spherical particles to illustrate accuracy
- ◆ Counted 1000 particles – image analysis program

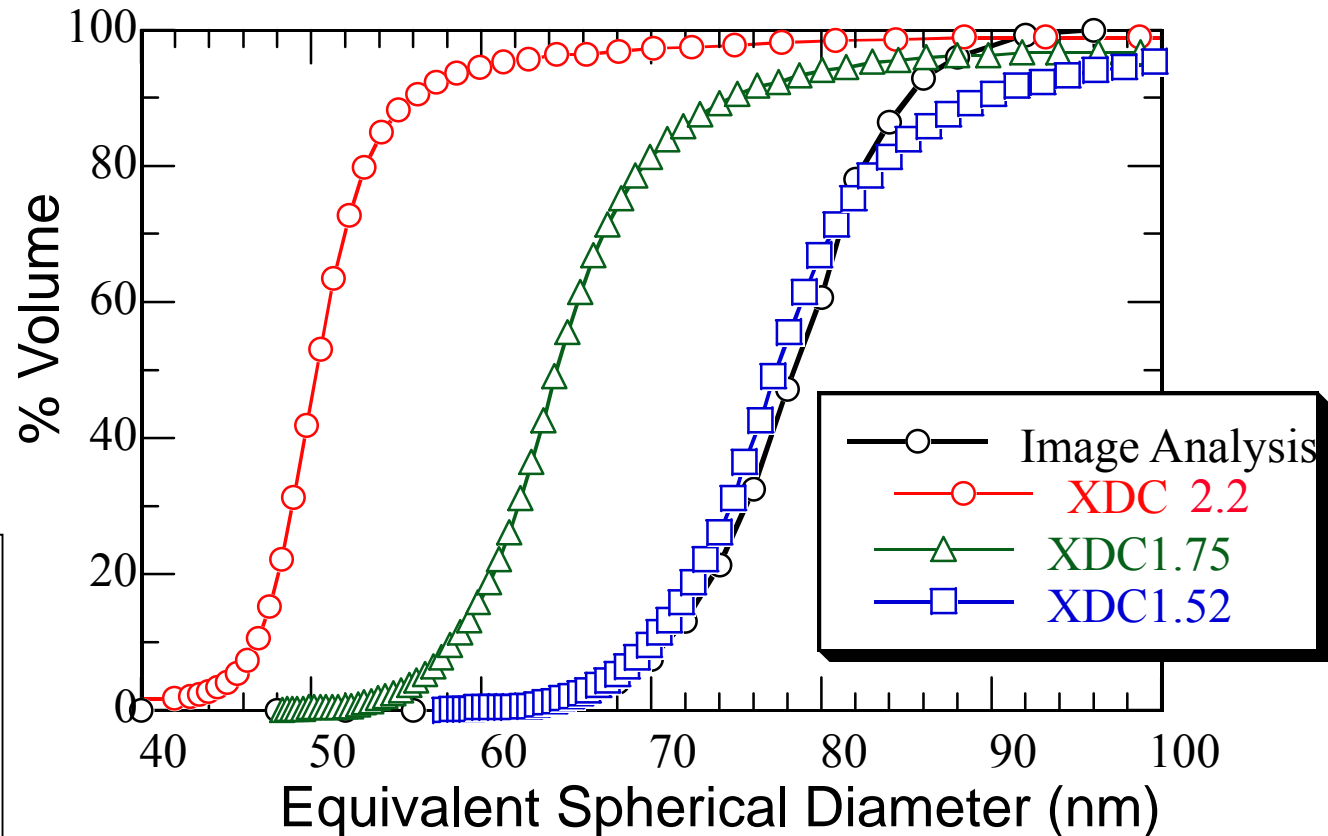


- ◆ Klebosol – A-Z chemicals
- ◆ Sold initially as 50 nm particles - $d_{\text{BET}} = 50\text{nm}$
- ◆ Porosity?

Spherical Silica - Real size ??-3

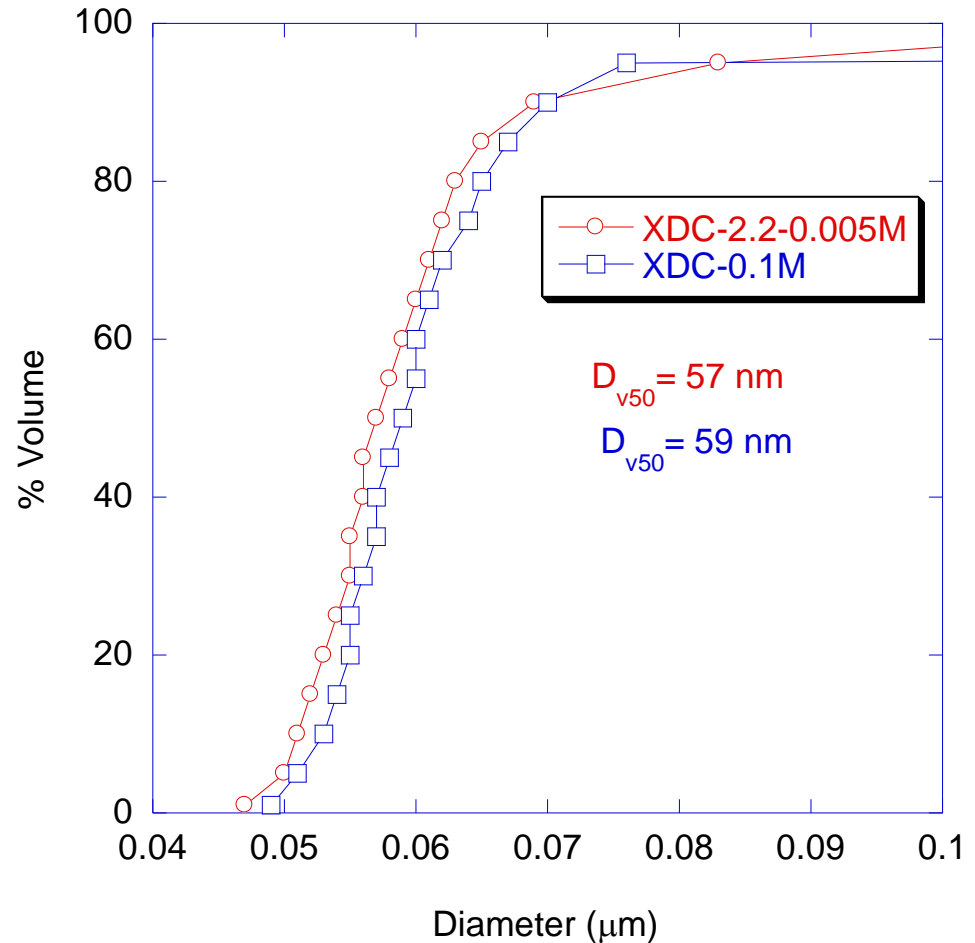
- ◆ Golden Rule No. 3: even if different methods give same result not necessarily "absolute"
- ◆ Only parameter – hydrodynamic density

- ◆ Take into account porosity - NAD – 1.75 g/cm^3
- ◆ Sold as acid dispersion - measured in - 0.005M HCl
 - double layer 5 nm
 - 1.52 g/cm^3



Spherical Silica - Real size ??-4

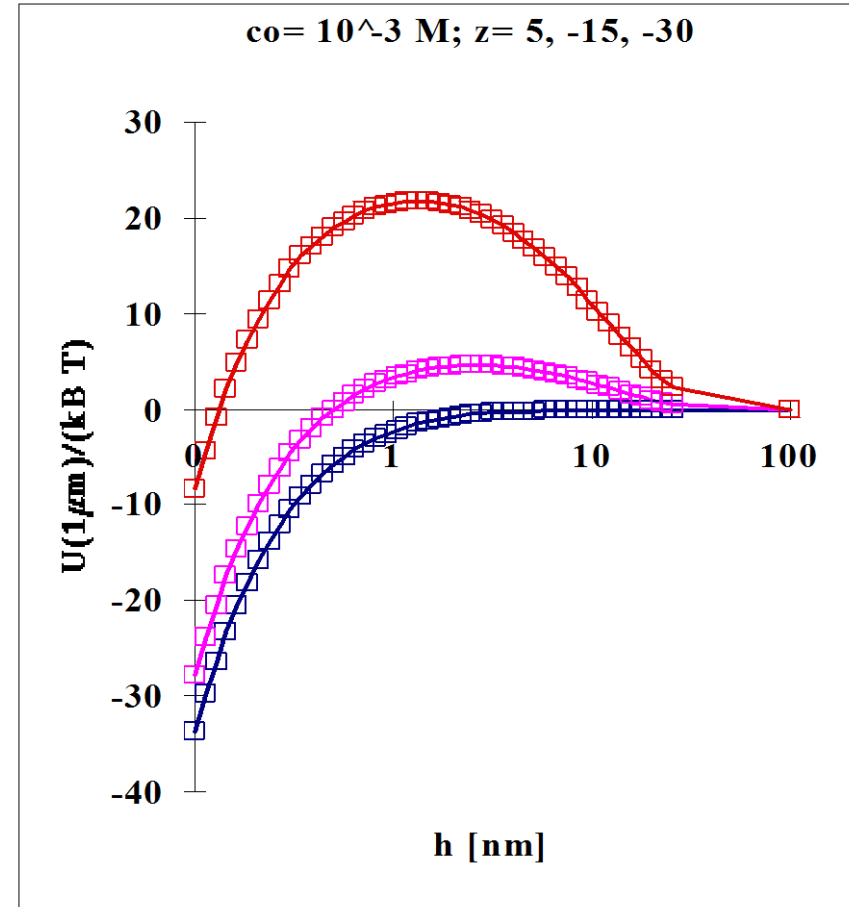
- ◆ Using density 2.2 g/cm^3
- ◆ Added salt KNO_3 0.1M
- ◆ double layer $< 1 \text{ nm}$
- ◆ No significant difference
- ◆ « anomalous » stability of silica sols – even at iep?
- ◆ Often attributed to hydration layer - thickness?



Spherical Silica - Real size ??*

- ◆ Interparticle energy calculations suggest steric layer - thickness of around 1 nm enough to stabilise
- ◆ Dense silica particles normally synthesised at basic pH
- ◆ End point for Klebosol acidic pH near 2 – where porous polymeric gels form
- ◆ Perhaps a « fuzzy » hydrated layer – porous gel giving « steric stability »?

- ◆ Have studied smaller sizes (35/50 nm and 12/18nm) and batch to batch variation
- ◆ Density/porosity reasonably consistent – but have to characterise each batch
- ◆ Tried to modify « fuzzy layer » by ageing in acid or base but no effect 2-28 days pH 2-10
- ◆ Conclusion poorly ordered « fuzzy » gel layer effects hydrodynamic density



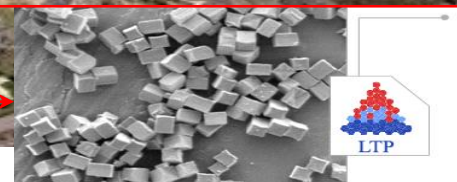
*More complete study on silica particles:
M. Kobayashi, F. Juillerat, P. Galetto, P. Bowen, M. Borkovec, Langmuir 21, 5761 (2005).

7. Example

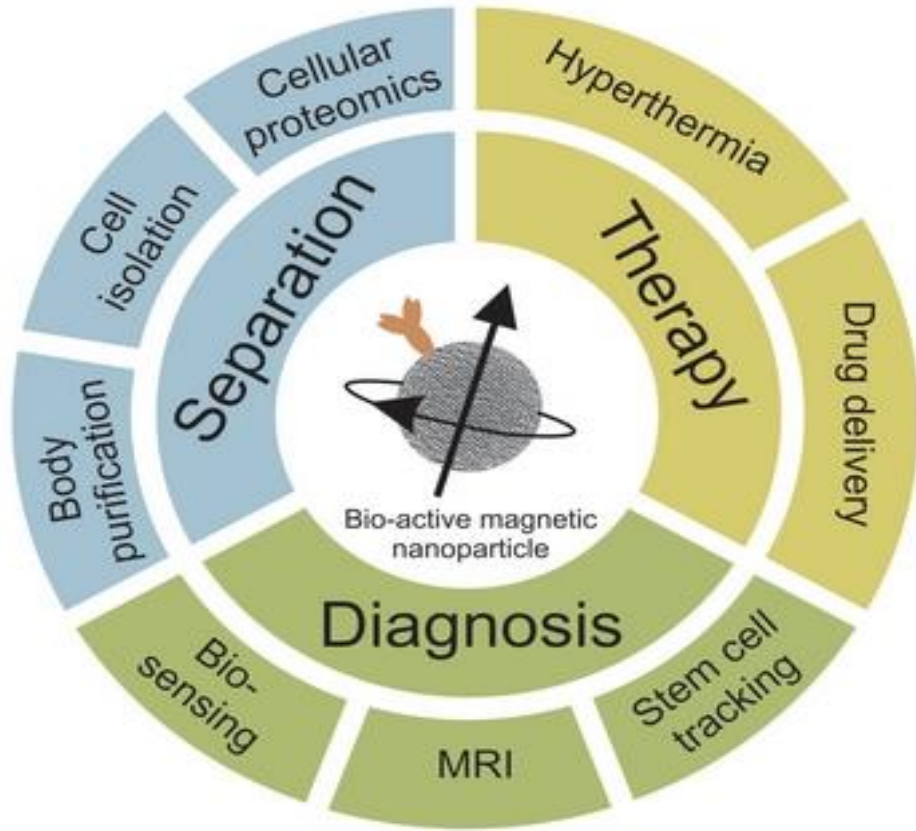
Nanoparticles for Diagnostic and Therapeutic Applications

Heinrich Hofmann

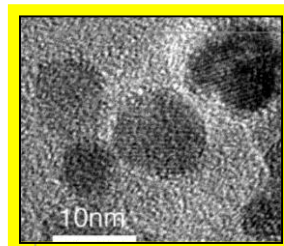
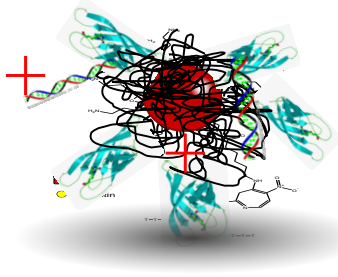
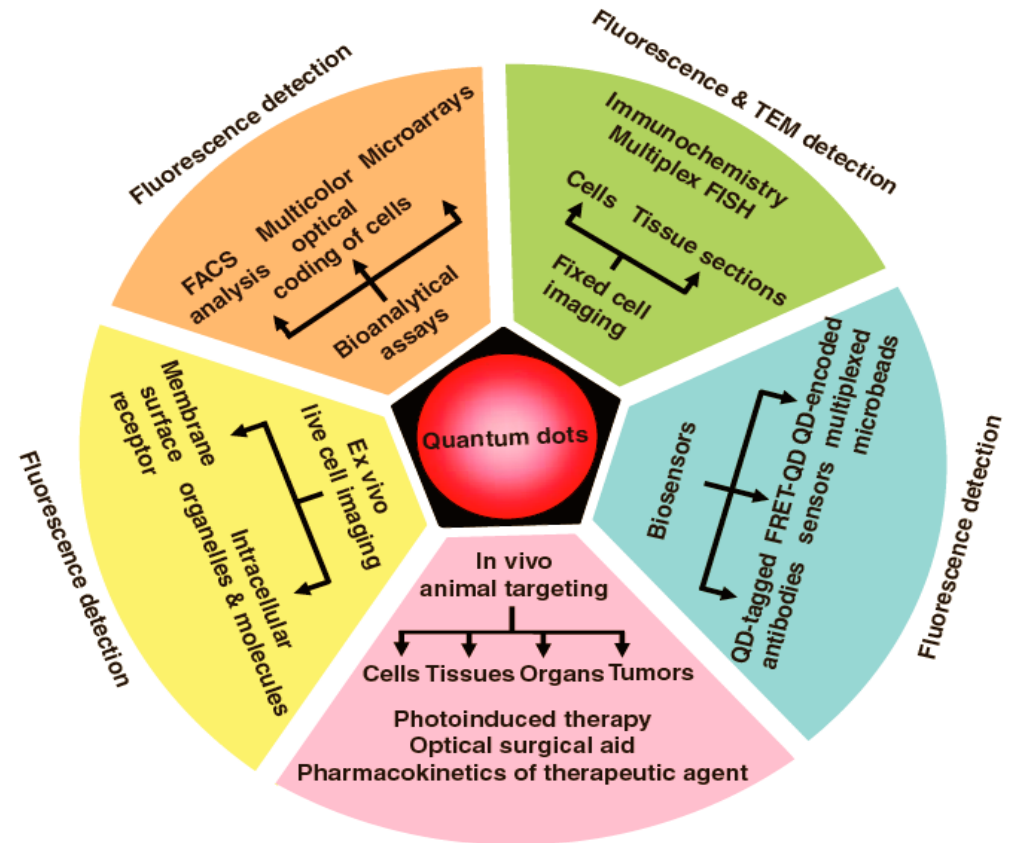
Ecole Polytechnique Fédérale Lausanne,
EPFL Powder Technology Laboratory



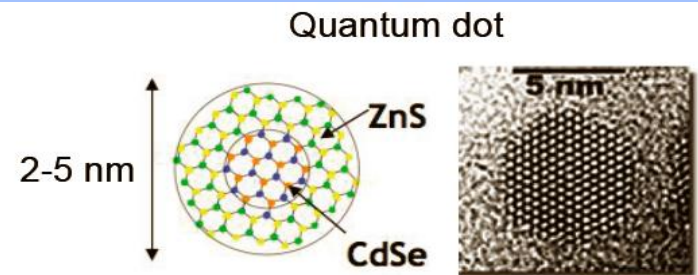
Superparamagnetic Iron Oxide Nanoparticle



Quantum Dots

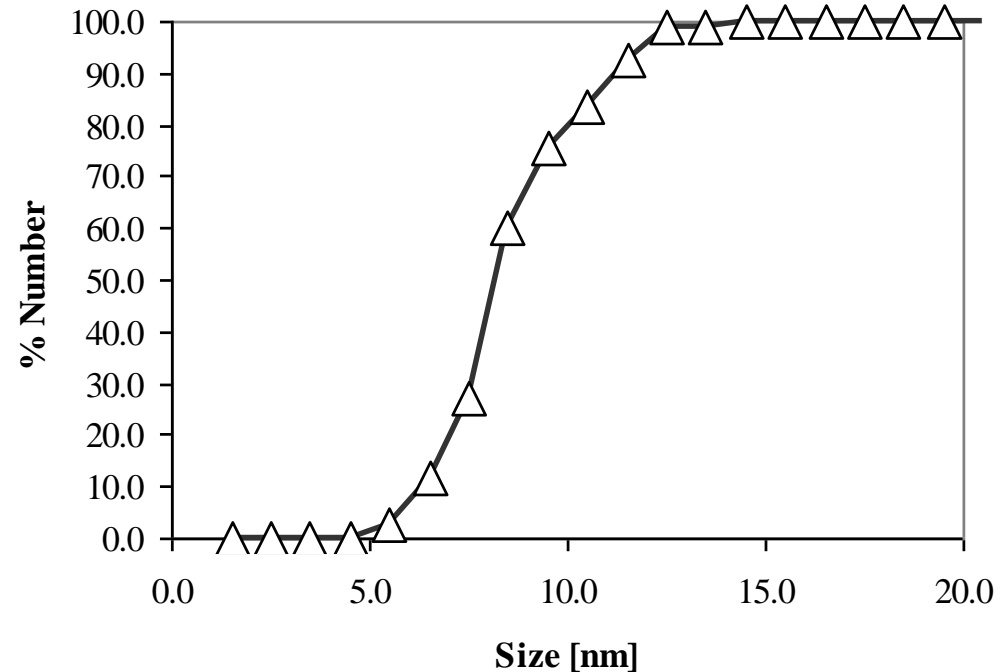
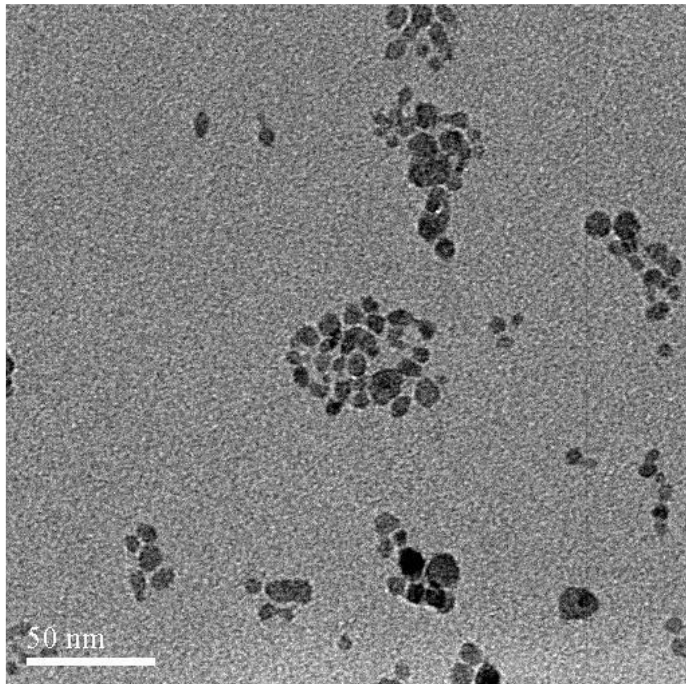


Fi



Iron Oxides – approaching 10 nm

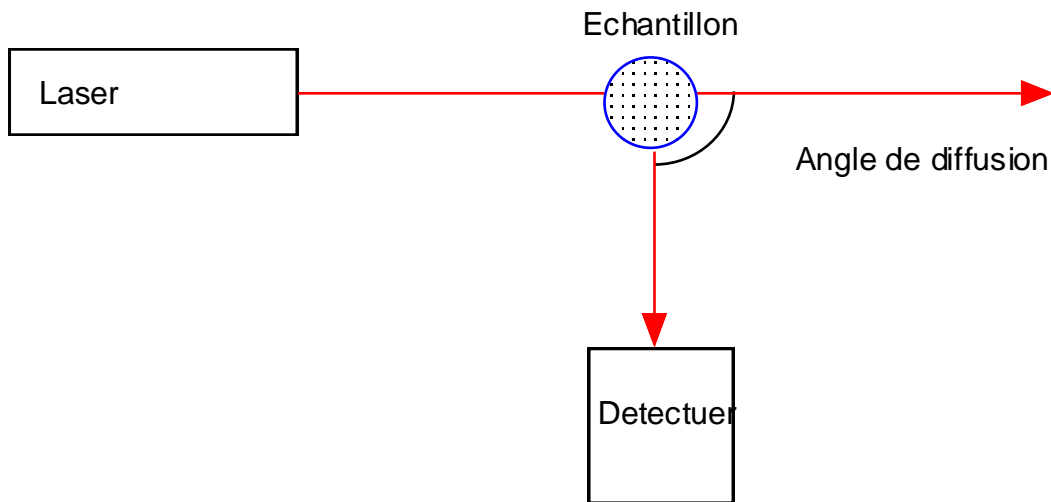
- ◆ Iron oxides synthesised by precipitation for biomedical applications – superparamagnetic
- ◆ Properties strongly linked to size – narrow distribution key for certain applications
- ◆ TEM – counted 100 particles
- ◆ Photon Correlation Spectroscopy (PCS), XRD line broadening, TEM



Mathieu Chastellain, EPFL Thesis No. 3045, - synthesis high salt concentrations

Photon Correlation Spectroscopy - PCS

- ◆ Dynamic light scattering (DLS) method or
- ◆ Photon correlation spectroscopy (PCS) or
- ◆ Quasielastic light scattering (QELS) (as it was first termed)



- ◆ Dependence of the scattered intensity
- ◆ - Proportional R^6
- ◆ - Particle only twice the size
- ◆ will give 64 times the intensity.

- ◆ Rayleigh limit $R \ll \lambda$

$$I = \frac{I_0 16\pi^4 R^6 (n^2 - 1)(n^2 + 2))^2}{r^2 \lambda^4}$$

- ◆ I_0 is the incident intensity,
- ◆ $n = n_1/n_0$ relative refractive index for
 - particle of refractive index n_1
 - suspending medium n_0 ,
- ◆ R is particle radius,
- ◆ λ the wavelength of light in the medium
- ◆ r the distance between the scattering particle and the detector.

Iron Oxides –10 nm comparison of PSD methods

- ◆ XRD line broadening, TEM, PCS
- ◆ PCS after optimisation
 - all liquids filtered at 20nm
 - Data collection optimised (baselines)
 - Data analysis – CONTIN
- ◆ XRD, TEM volume and number
9-10 nm
- ◆ PCS 13-14nm

Method	distribution type	Average diameter [nm] $\pm \sigma$
XRD	volume	10 \pm 1
TEM	number	9 \pm 2
TEM	volume	9 \pm 2
PCS	number	13 \pm 10

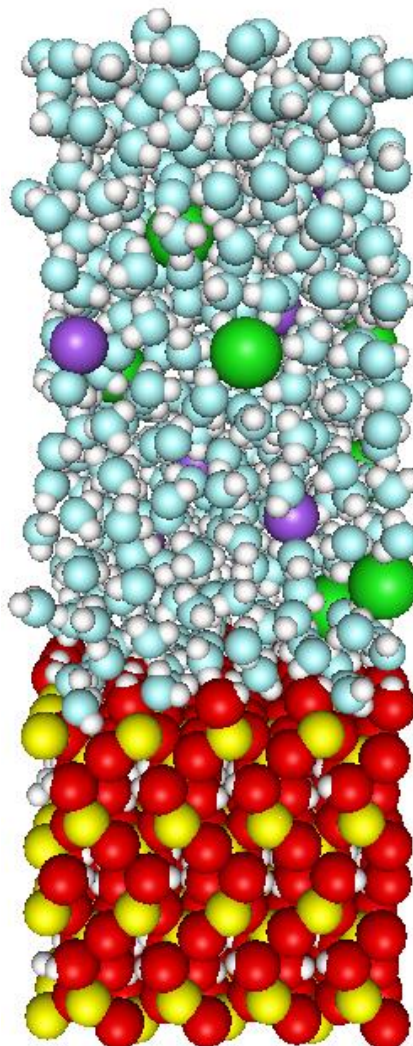
- ◆ « Hydrodynamic » surface layer seen by other researchers (Jolivet)
- ◆ Here – 2nm « layer » thickness
- ◆ Parker (Bath, UK) – molecular modelling in conc. salt (0.5 M)
- ◆ 1 nm structured water but 2.5 nm structured ions

Goethite Surface in Contact with Electrolyte Solution

Prof. Steve Parker
Dr. S. Kerisit

- **Atomistic modelling**
- **Combination of**
- **energy minimisation and**
- **molecular dynamics**

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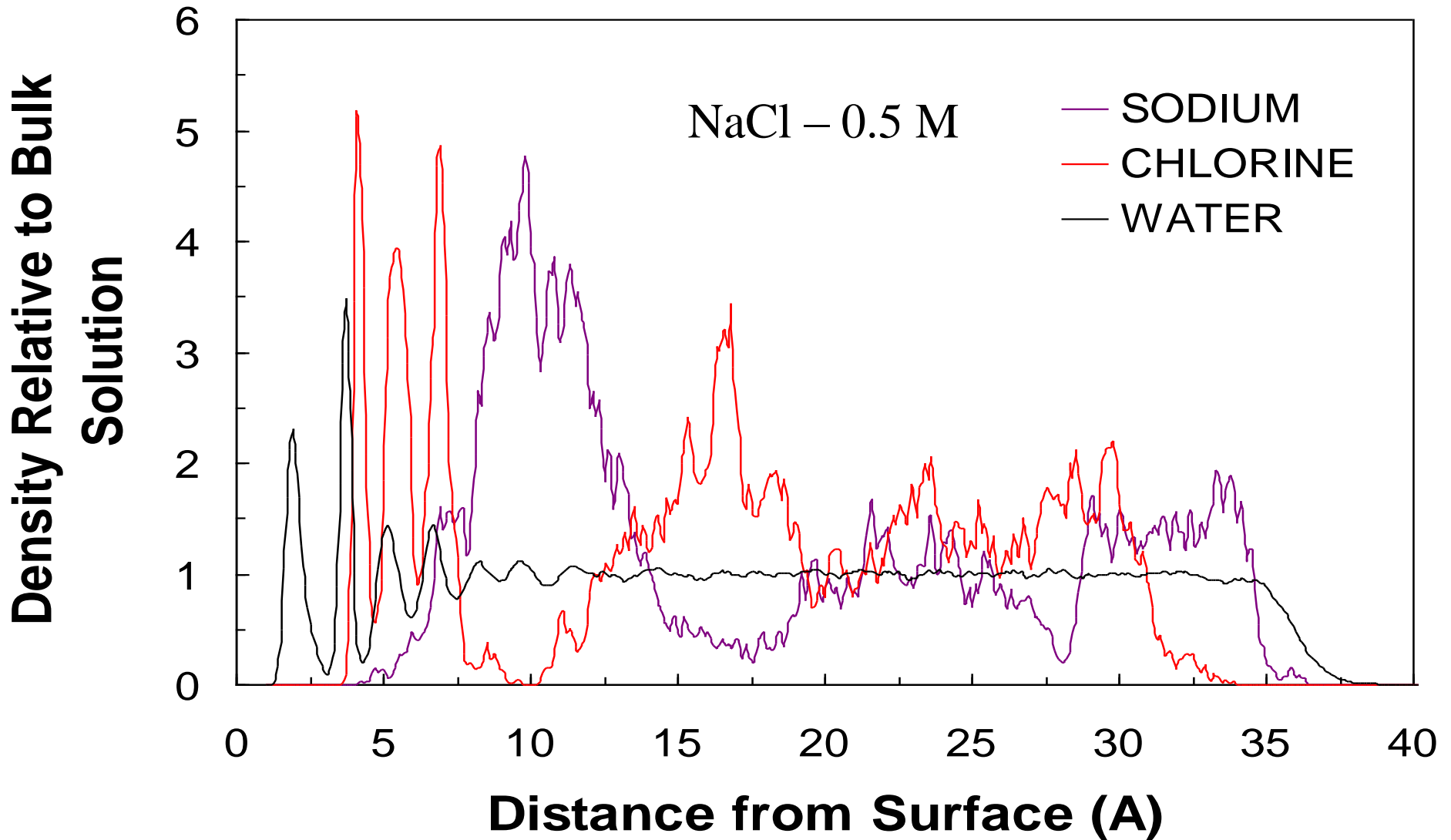


NaCl – 0.5 M

Kerisit S, Cooke DJ,
Marmier A, Parker SC ,
CHEMICAL
COMMUNICATIONS (24):
3027-3029 (2005)

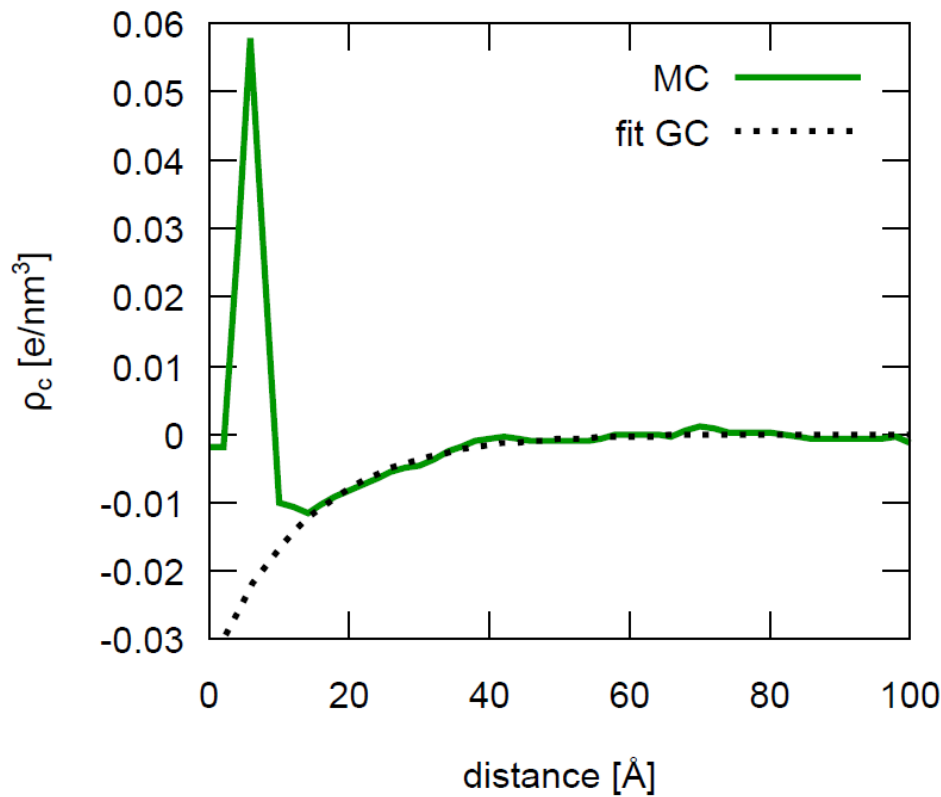
Na – purple
Cl - green
Fe - yellow
H -white
O - red/blue

Goethite Surface in Contact with Electrolyte Solution

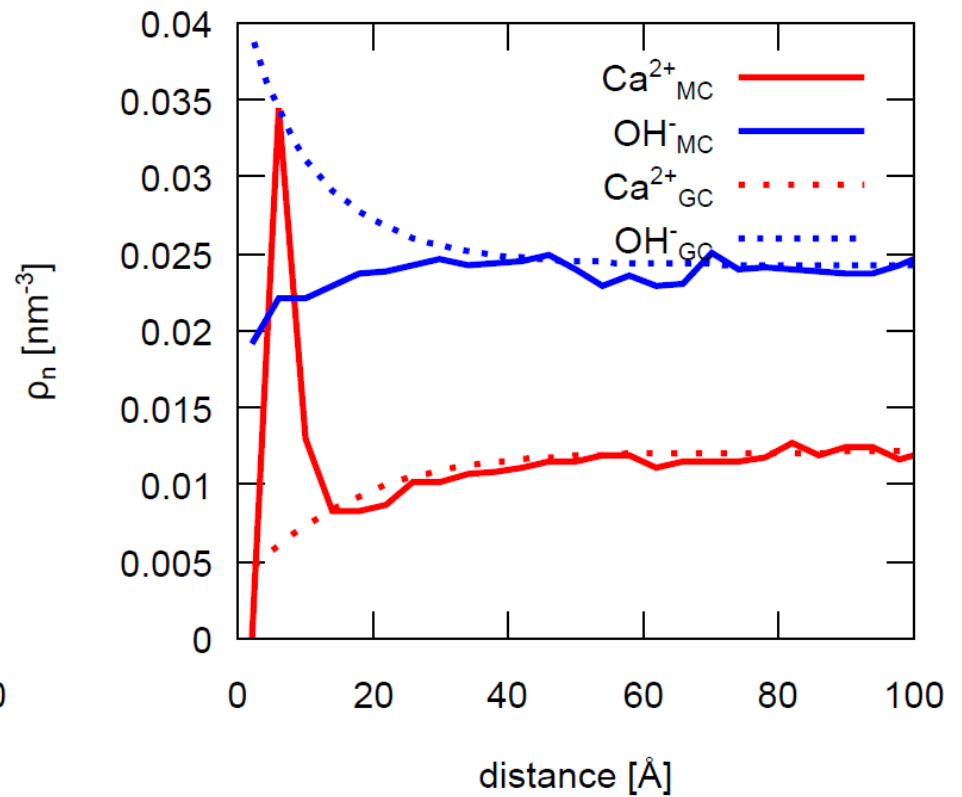


Oscillating concentration profiles – not what expected from mean Field Approach - slide 40

Ionic distribution at Ca(OH)₂-water interface*



(a) Charge distribution



(b) ionic distribution

- ◆ perpendicular to the [00.1] portlandite-water interface according to Monte Carlo (MC) simulations, and the Gouy-Chapman (GC) theory using the Debye-Hückel approximation, fitted to the Monte Carlo charge density.

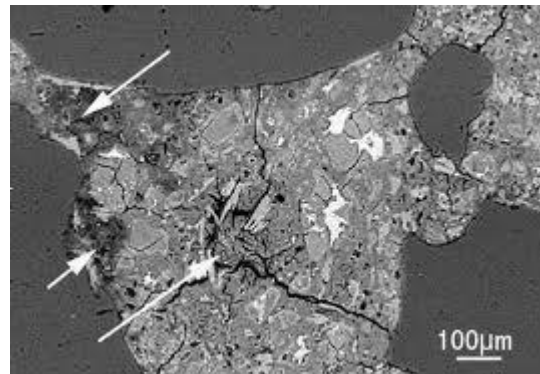
*S. Galmarini – EPFL Thesis No. 5754 (2013) Chp.8

Next Week – Particle –Particle Interactions 2

- ◆ Interparticle forces – continued – limitations of Mean Field Approaches
- ◆ Repulsive forces – electrostatic
 - Poisson-Boltzmann Equation – limitations - atomistic approach
 - Forces between charged surfaces
 - Close approach – limit of mean field approach
 - Ion correlation forces and others.....
- ◆ What is the coherent force in concrete and cement?
 - CSH - Calcium Silicate Hydrates
- ◆ Capillary forces – colloidal crystals from nanosized particles
- ◆ Electrophoretic deposition...



P. Bowen, EPFL.



09/10/2018

