MSE 495 – Advanced Ceramics Technology

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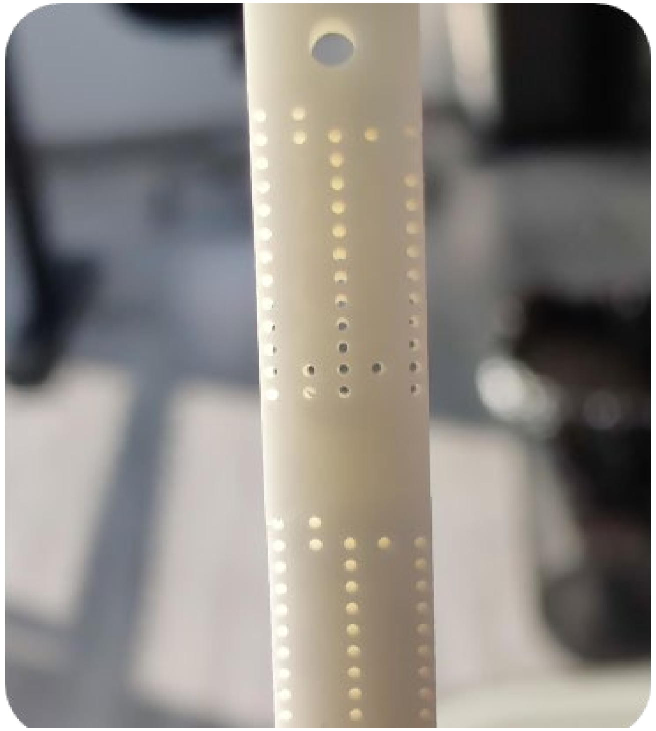
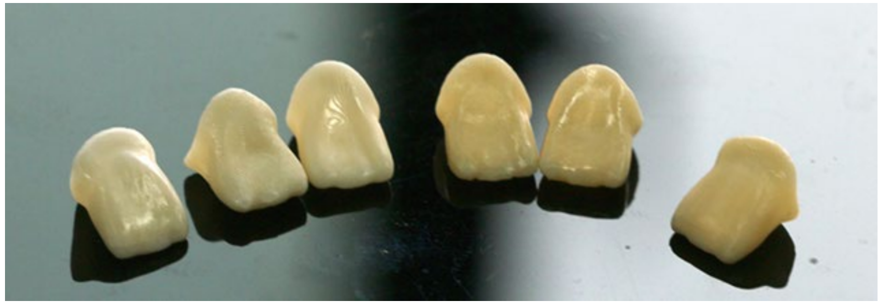
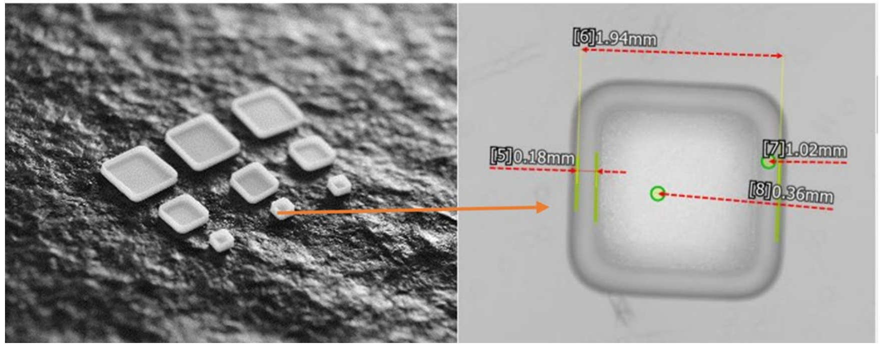
Week 4 – Colloidal stability

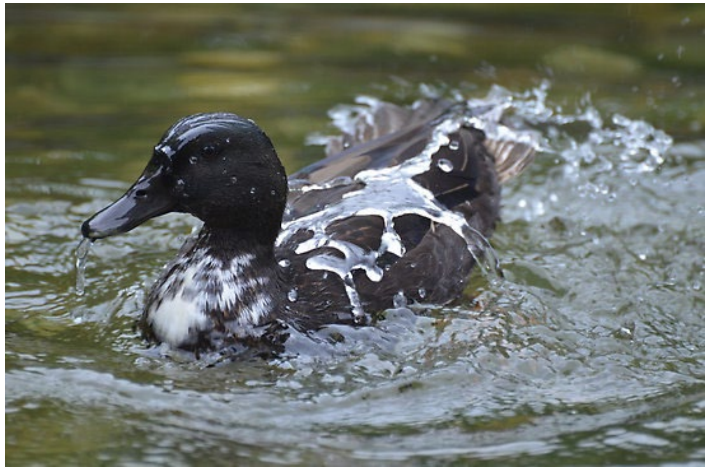






Surface Tension / Interfacial Energy

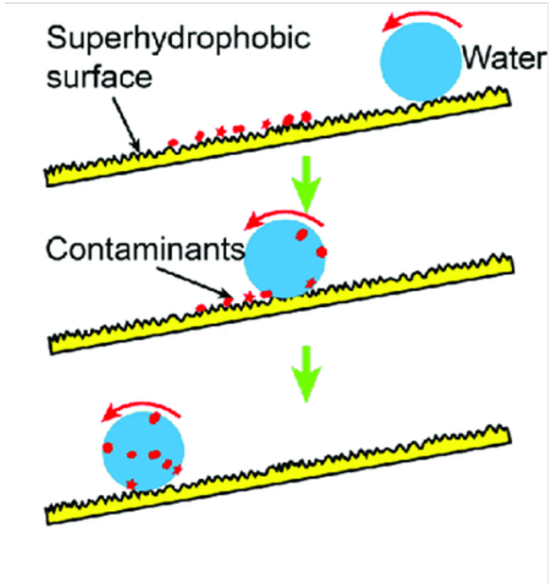
Metallic paper clip.
Density ~ 8 g / cm^3 >> water but does not sink ...



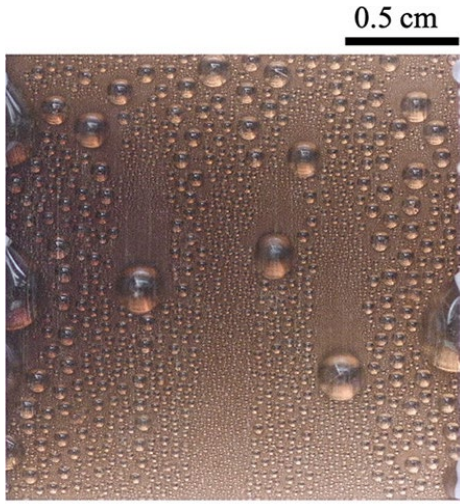
Water on a duck's back...

Superhydrophobic Surfaces: Applications

- **Self cleaning**



- **Efficient condensation heat transfer**



Tripathy A. et al., *Roll-to-Roll Manufacturing of Robust Superhydrophobic Coating on Metallic Engineering Materials, ACS nano, 2021*

- **Anti-icing**

https://www.aviationsafetymagazine.com/features/top-three-aircraft-icing-myths-busted/

- **Protection against corrosion**

Wetting – Contact angle – Young's Law

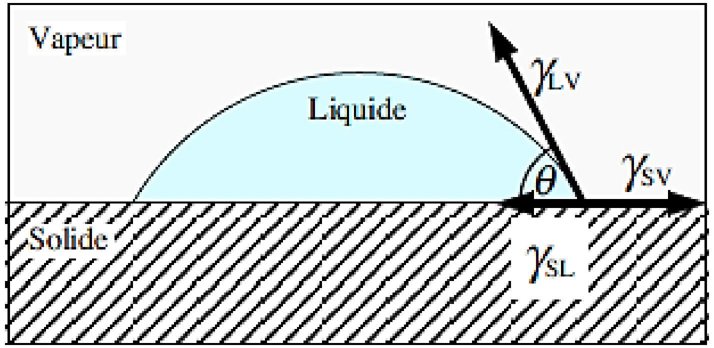
- Wetting

Young's Law (theorem)

- When the spreading of the liquid on the solid is not perfect, the liquid condenses in the form of droplets. If the droplets are small enough to neglect the influence of gravity, they take the form of a spherical cap.
- The balance of forces at the solid-liquid-vapor junction gives:

$$\left.\begin{array}{c} \gamma_{SV}-\gamma_{SL}-\gamma_{LV}\cos\theta=0 \\ \Downarrow \\ \cos\theta=\dfrac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}} \end{array}\right\}$$

ϑ is the *wetting angle* or *contact angle* of a liquid on solid.



Cohesion and Adhesion

Wetting

- Spreading coefficient S_{SL}

It is the decrease in surface energy $-\Delta G_{SL}$ obtained when the solid is completely covered with liquid:

$$\Delta G_{SL} = (\gamma_{LV} + \gamma_{SL}) - \gamma_{SV}$$

- where γ_{SV}, γ_{SL} and γ_{LV} are respectively the interfacial energies of the solid/vapor, solid / liquid and liquid / vapor, interfaces.

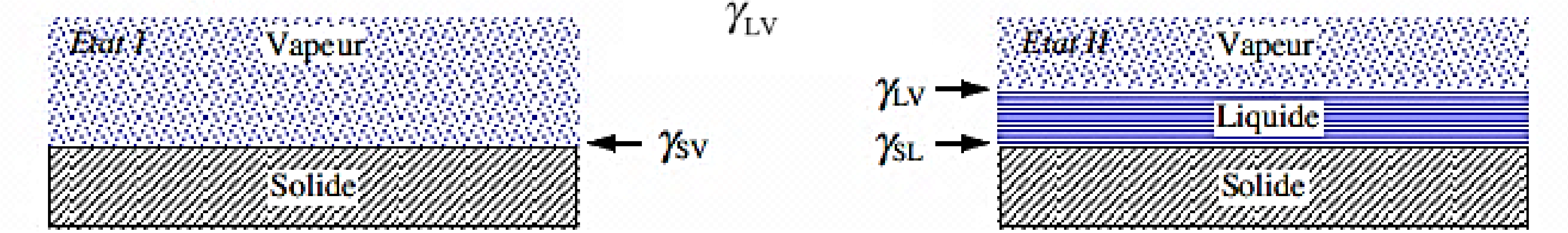
(Energy per unit of area)

$$S_{SL} = -\Delta G_{SL} = (\gamma_{SV} - \gamma_{SL}) - \gamma_{LV}$$

(Dupré equation)

The liquid spreads *spontaneously* on the solid if $S_{SL} \geq 0$, i.e. when:

$$\frac{(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} \geq 1$$

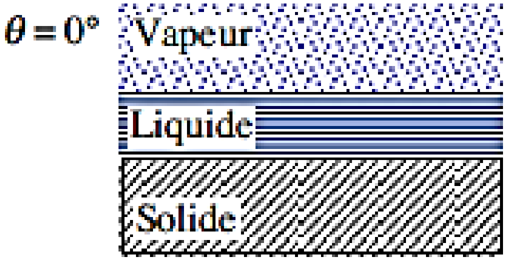


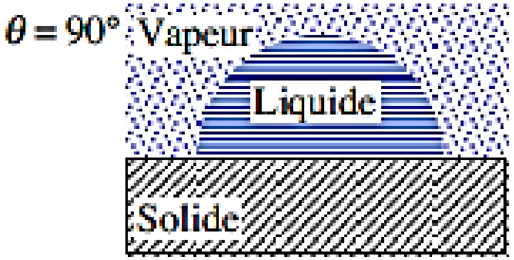
Wetting – Contact Angles

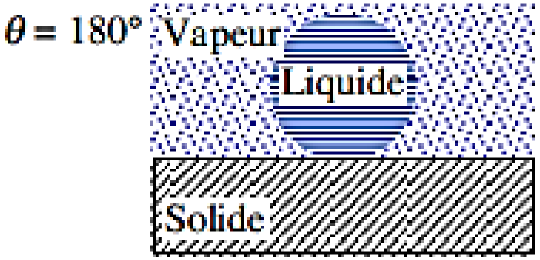
- <u>Wetting</u>
- Characteristic contact angles

θ	$\cos\theta$	γ_{SL}	S_{SL}
0°	1	$\gamma_{SV} - \gamma_{LV}$	0
90°	0	γ_{SV}	$-\gamma_{LV}$
180°	–1	$\gamma_{SV} + \gamma_{LV}$	$-2\gamma_{LV}$

  - ***θ* = 0 °** → wetting *perfect*, the solid is perfectly **lyophilic**
  - ***θ* = 90 °** → wetting *average*
  - ***θ* = 180 °** → *no* wetting, the solid is perfectly **lyophobic**





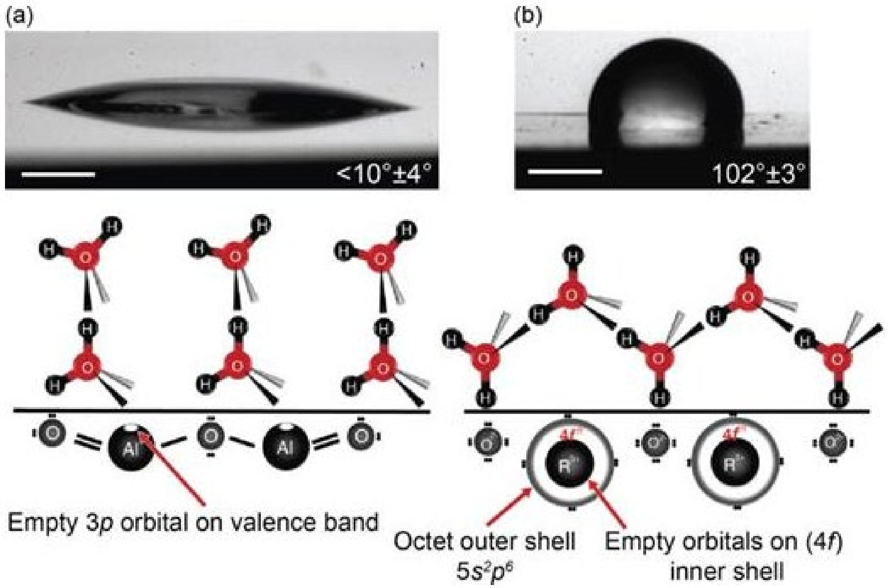


Why is CeO_2 hydrophobic? Possible Explanations

The unique electronic structure of the rare-earth metal atom inhibits hydrogen bonding with interfacial water molecules resulting in a hydrophobic hydration structure where the surface oxygen atoms are the only hydrogen bonding sites.

Aluminum oxide

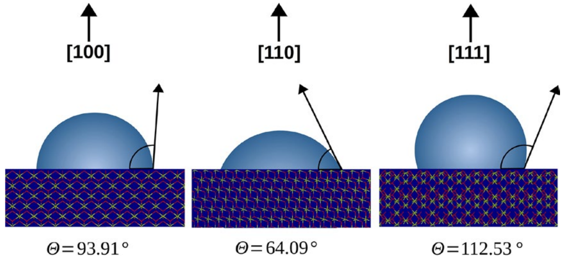
Rare earth oxides

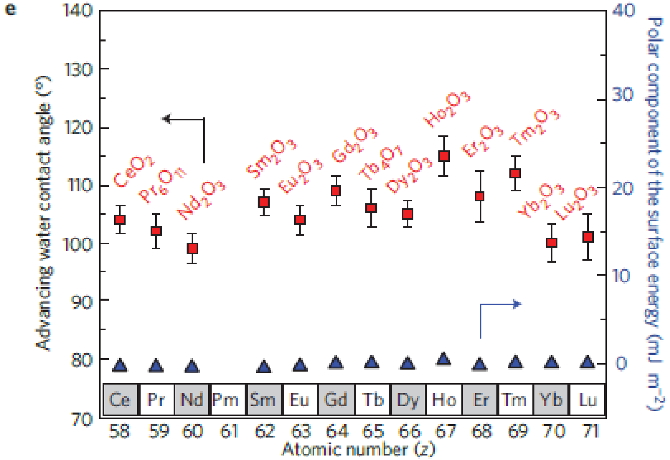


→ Rare-earth oxides are intrinsically hydrophobic

→ Hydrophobicity governed by O/Ce ratio at the surface

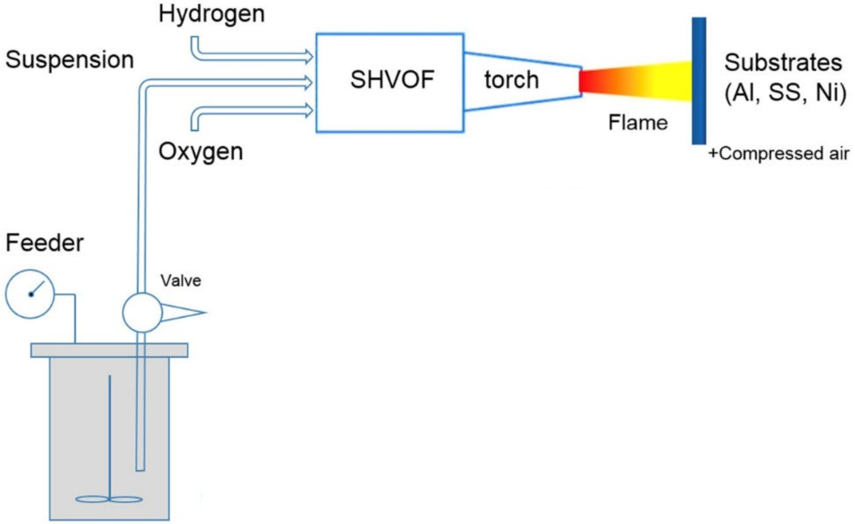
“Khan S. et al., *Role of surface oxygen-to-metal ratio on the wettability of rare-earth oxides*, Applied Physics Letters, 2015

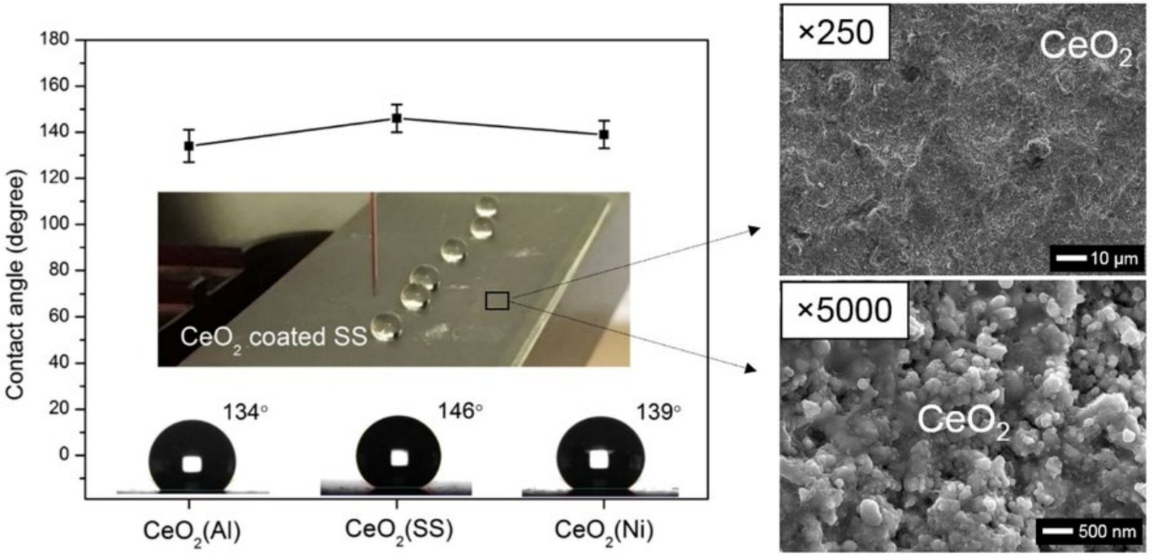




Examples of Hydrophobic/Superhydrophobic CeO_2 Surfaces

- CeO_2 coating applied on different metals using the technique of suspension high velocity oxy-fuel (SHVOF) thermal spraying
- Hierarchically-structured surface (at micro- and nanoscale)
- Surface is superhydrophobic without additional treatments

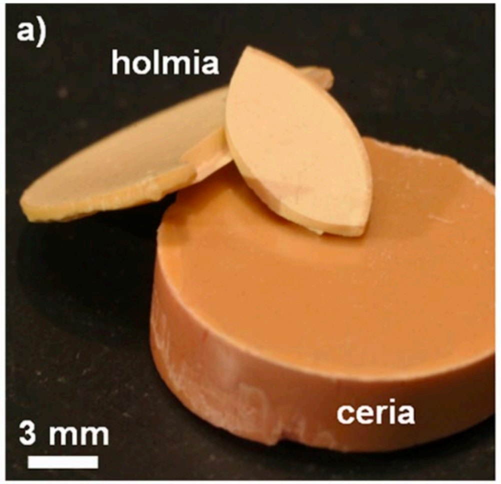


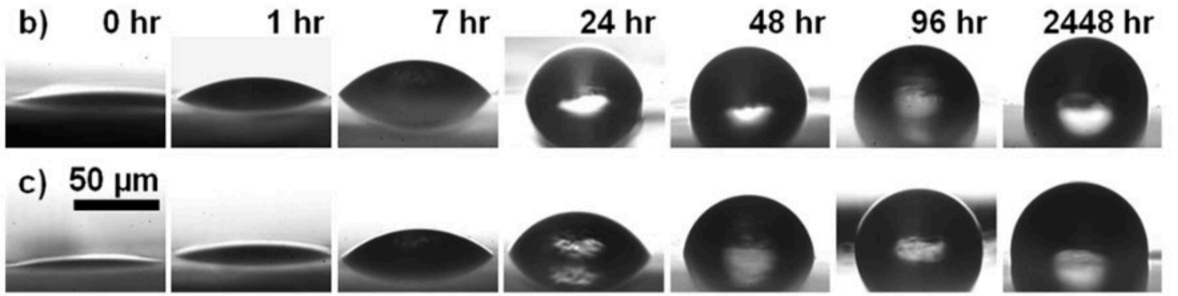


Bai M. et al., Robust *Hydrophobic Surfaces from Suspension HVOF Thermal Sprayed Rare-Earth Oxide Ceramics Coatings*, Scientific reports, 2018

Examples of Hydrophobic/Superhydrophobic CeO_2 Surfaces

- Ceria and holmia pellets prepared by dry pressing and sintering
- At t=0 surfaces cleaned via argon ion bombardment
- Both surfaces initially hydrophilic
- Gradual transition to hydrophobicity via hydrophobic volatile organic compounds absorption



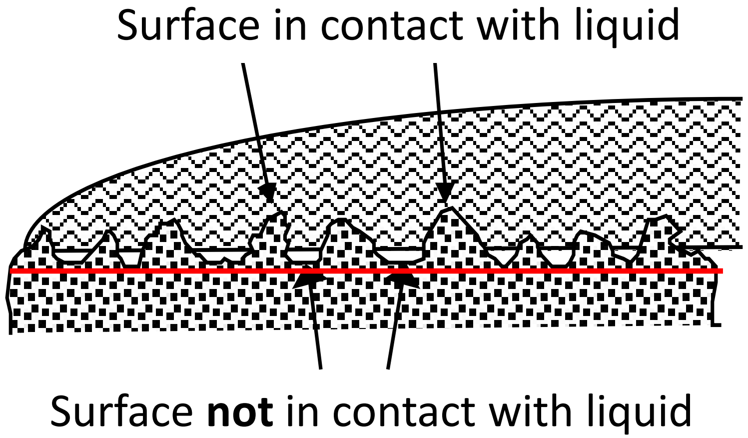


Preston Daniel J. et al., Effect of hydrocarbon adsorption on the wettability of rare earth oxide ceramics, Applied Physics Letters, 2014

Wetting – Surface Roughness

- Wetting
  - Effect of roughness on contact angle

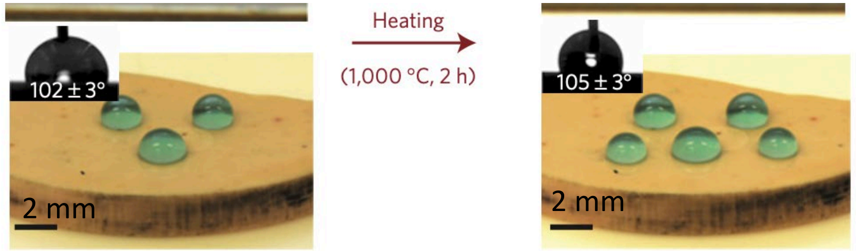
θ	$\cos\theta$	$\cos\theta_R$	θ_R
$< 90°$	> 0	$> \cos\theta$	$< \theta$
$= 90°$	$= 0$	$= \cos\theta$	$= \theta$
$> 90°$	< 0	$< \cos\theta$	$> \theta$



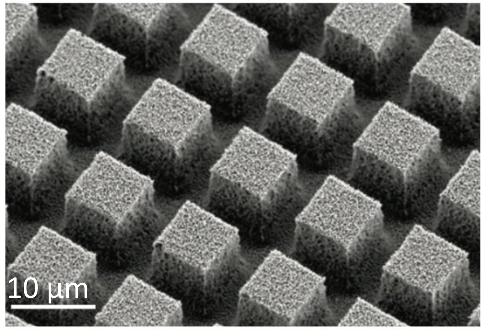
- **$\theta < 90$ °** → Roughness *increases* wetting and makes the solid **more lyophilic**
- **$\theta = 90$ °** → *No effect of* roughness on the wetting
- **$\theta > 90$ °** → Roughness *decreases* wetting and makes the solid **more lyophobic**

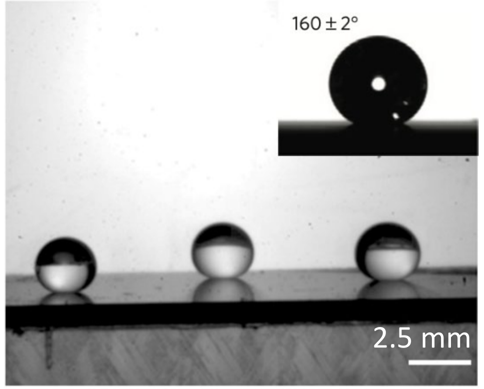
Examples of Hydrophobic/Superhydrophobic CeO_2 Surfaces

- CeO_2 pellets prepared by dry pressing of powder and sintering in dry air environment
- Surface is hydrophobic without additional treatment
- Hydrophobicity is robust and maintained even after exposure to 1000 °C for 2 h



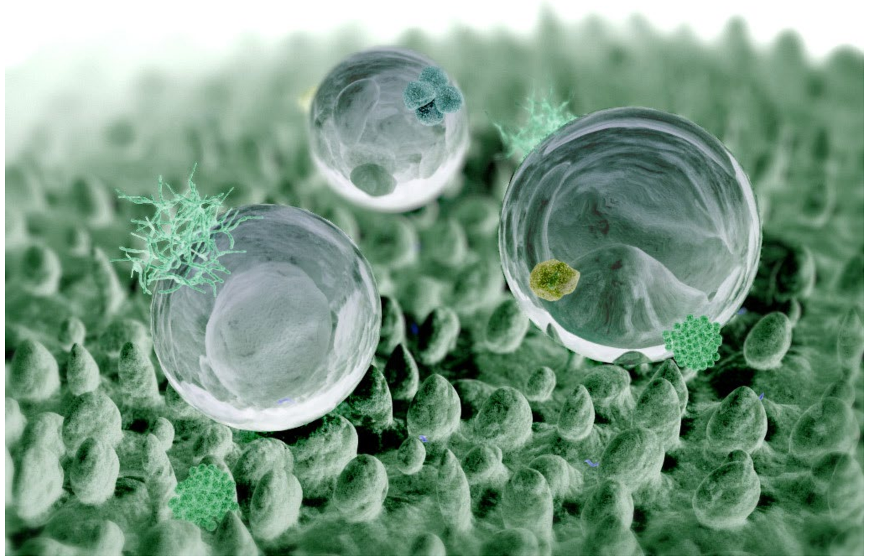
- ~ 200 nm CeO_2 sputtered on hierarchically structured surface (silicon micropillars covered with nanograss)
- Surface becomes superhydrophobic

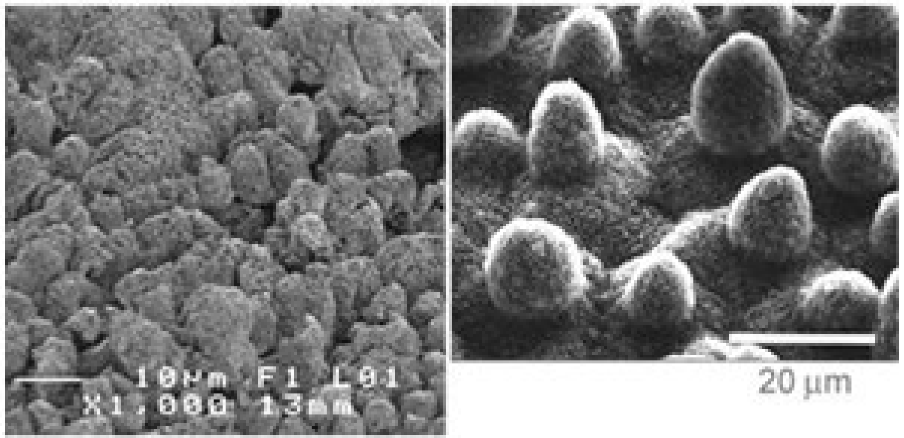




Azimi G. et al., *Hydrophobicity of rare-earth oxide ceramics*", Nature Materials, 2013

Lotus leaf effect





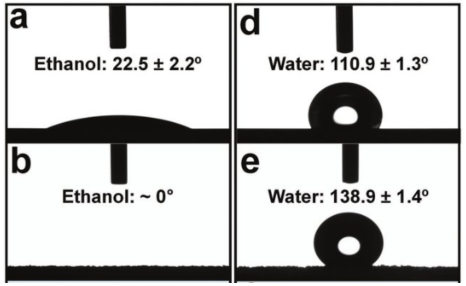
Left: SEM image of surface produced within the project.
Right: SEM image of the surface of a Lotus leaf.
(D. Chakarov, P. Holgerson)

Textile applications…

One technique to render a surface of aluminum superhydrophobic is by immersing it in a solution of sodium hydroxide for several hours, then applying a layer of perfluorononan with a thickness of 2 nanometers. This operation increases the contact angle from 67 ° to 168 °.
The lotus effect, M Reyssat, D Quéré, Pour la science, September 2006, p 34-40

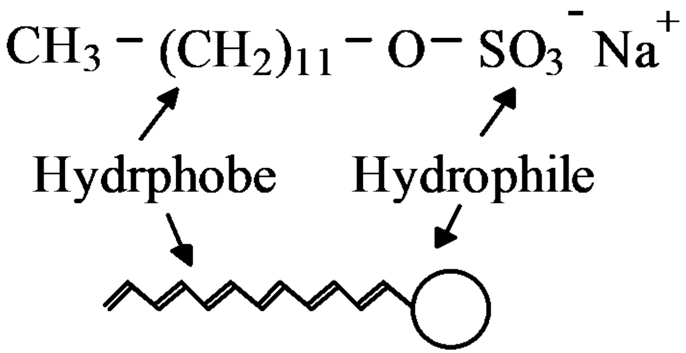
Contact angle - Surfactants

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$



Contact angle on PDMS
and roughness effect

- Mixing with ethanol, γ_{LV} = 23 mN / m; water γ_{LV} 73 mN / m
- To reduce γ_{SL} a surfactant is adsorbed at the solid-liquid interface.
- Surfactant = surface active agent
- An ionic surfactant - hydrophilic head - hydrophobic tail e.g.
- Sodium Dodecyl Sulfonate (SDS) or
- Soap - sodium stearate $C_{17}H_{35}COONa$,



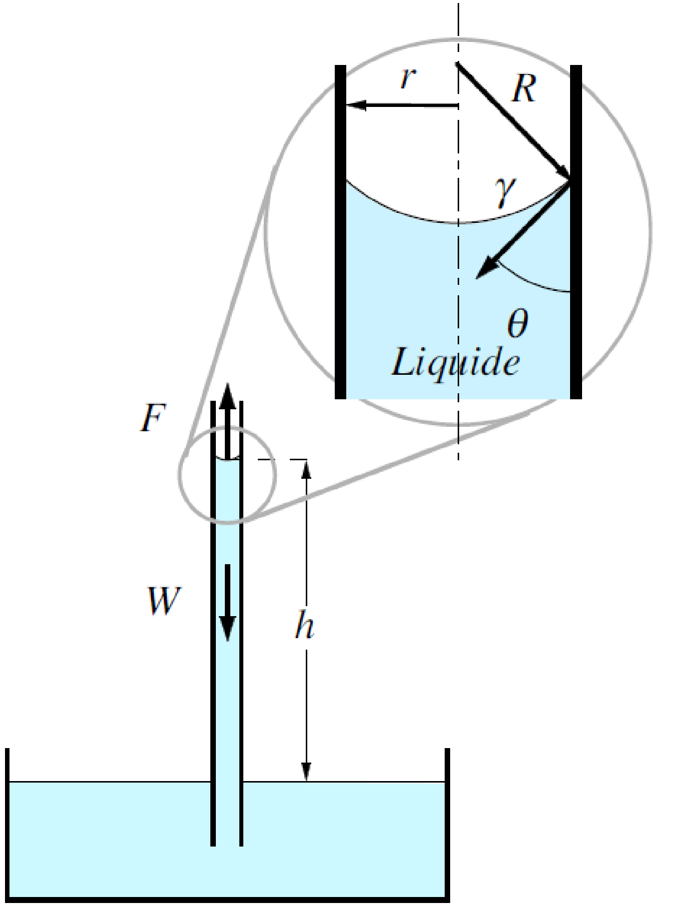
$$CH_3 - (CH_2)_{11} - O - SO_3^- \, Na^+$$

Surface tension measurement

- Capillary rise
  - Balance of forces at meniscus

The balance between the capillary rise force and the weight of the liquid column (mgh): gives,

$$\left.\begin{aligned} W &= \pi r^2 h g \Delta\rho \\ F &= 2\pi r \gamma \cos\theta \end{aligned}\right\} \rightarrow F = W \Rightarrow \gamma = \frac{rhg\Delta\rho}{2\cos\theta}$$



With:

$\Delta\rho = \rho_L - \rho_V \cong \rho_L$: density difference between liquid and vapor (1 and 0.0012 g / cm^3)

g : gravitational force

h : height of capillary rise

r : Inner radius of capillary tube

θ : Contact angle of the liquid in the capillary with the solid surface

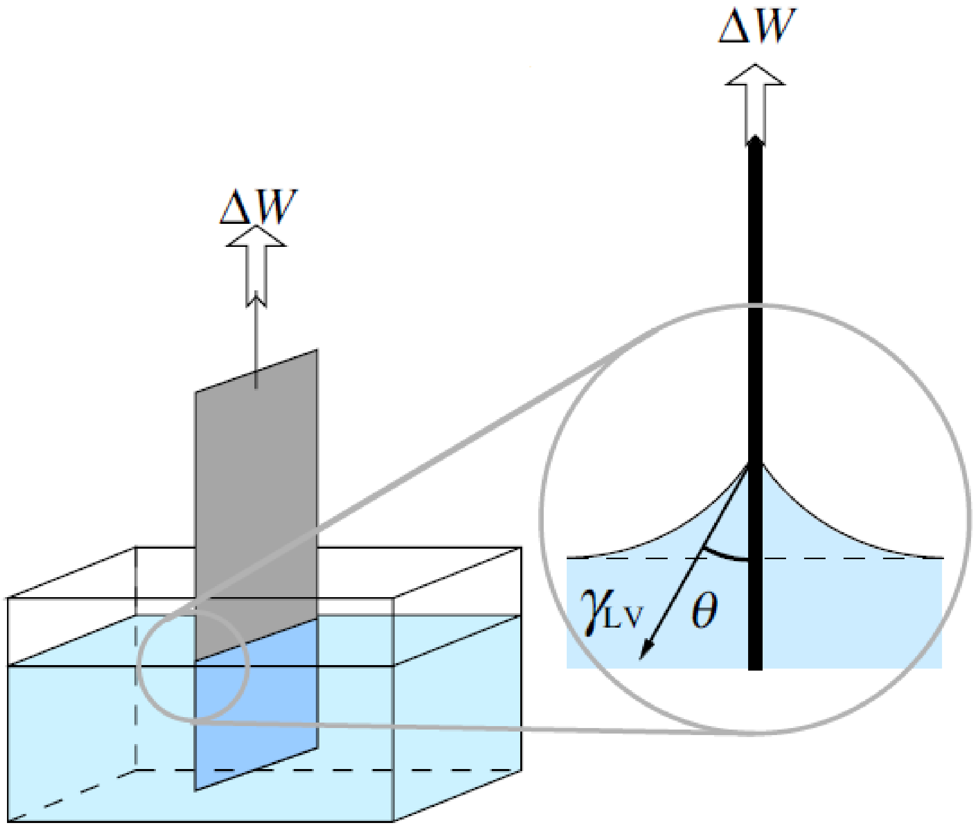
Surface tension measurement

- *Wilhelmy* Balance
  - Balance of forces

Increased apparent weight ΔW of a plate immersed in a liquid:

$$\Delta W = 2L\gamma_{LV}\cos\theta \Rightarrow \gamma_{LV} = \frac{\Delta W}{2L\cos\theta}$$

ΔW : Additional weight of the meniscus
L: Plate width (negligible thickness)
θ : Angle of wetting of the liquid on the plate



Advantage:
Possibility of continuous measurement, by modifying certain characteristics liquid (temperature, composition, etc.)

Colloidal Stability - Interparticle Forces

- Attractive

Van der Waals forces V_A

- Repulsive

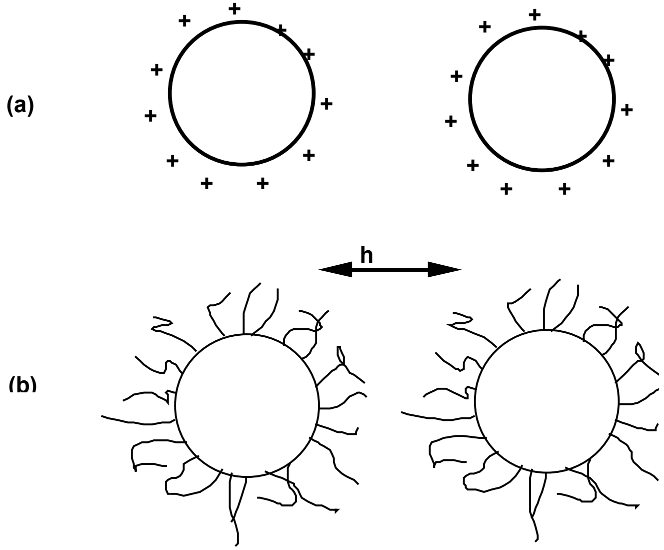
(a) electrostatic, V_E

charged surfaces

(b) steric repulsion, V_S

polymer adsorption

soluble polymers -



W. B. Russel, D. A. Saville, W. R. Schowalter - Colloidal Dispersions-Cambridge University Press (1990)

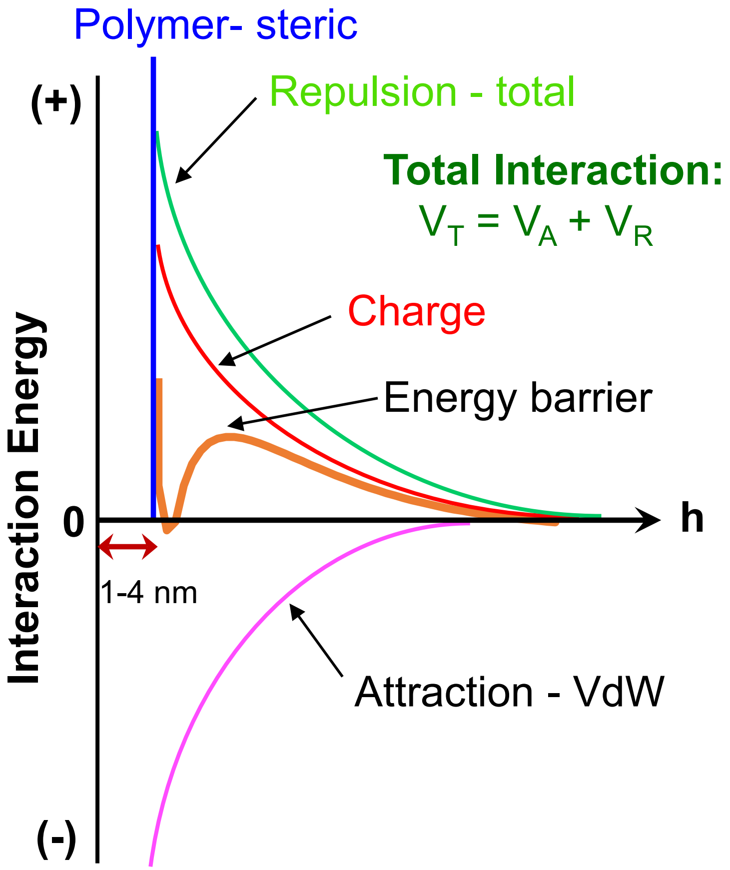
R.G. Horn, J. Am. Ceram. Soc., 73(5) 1117-35 (1990).

Overall Interaction Energy

- Total Interaction (Potential) Energy $V(h)_T$:
- DLVO theory
- Derjaguin/Landau and Vervey/Overbeck
  = algebraic sum….

$$V(h)_T = V(h)_A + \underbrace{V(h)_E \; (+ \, V(h)_S)}_{V(h)_R}$$

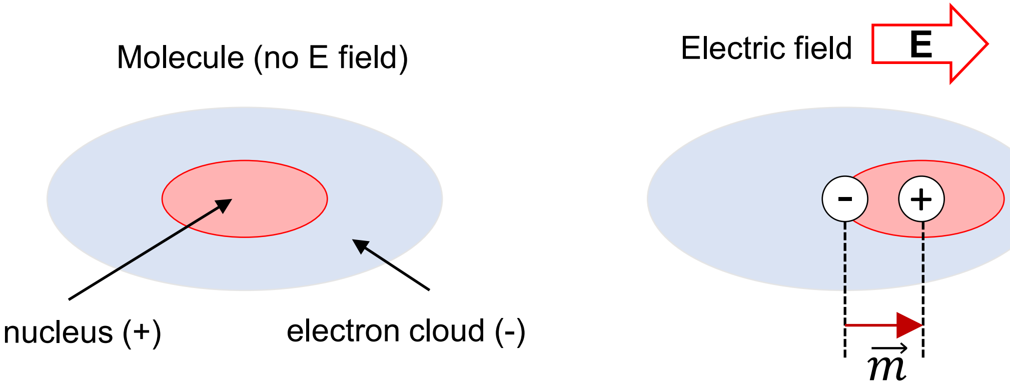
- Influences:
  - Rheology (flow of suspension)
  - Particle packing
  - Green body density/ sedimentation
- Which in turn influences:
  - Sintering
  - Microstructure and
  - Properties



Attractive Forces - Intermolecular Forces

- Van der Waals
  - Always attractive between particles of the same nature
  - Interaction between dipoles* (induced e.g. CH_4) or permanent (e.g. H_2O - hydrogen bond)

  3 types:
  - Dipole - Dipole - interaction between permanent dipoles (Keesom forces)
  - Dipole - Induced Dipoles – induced from permanent dipoles (Debye forces)
  - Induced Dipole - Induced Dipole - instantaneous dipoles from electron cloud fluctuations (London or dispersion forces)
- Material property - depends on dielectric and geometric properties of the system



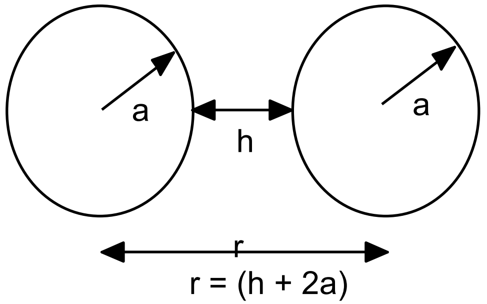
Useful videos
*https://youtu.be/S8QsLUO_tgQ | https://youtu.be/nvJv6mCmk68 | https://youtu.be/ODnqtf3aAvw

Hamaker approach

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

- Attractive Interaction Potential V_A
- Hamaker Constant A, form factor H !!!
- Dispersion forces (instantaneous dipoles - induced dipoles)
- Permanent Dipoles and Induced by permanent diploes
- A - depends on dielectric properties (~ polarizability)
  - particles and the continuous medium separating them,
  - over the entire spectral range of electromagnetic waves.
- For identical particles - size and chemistry in vacuum

} Van der Waals



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

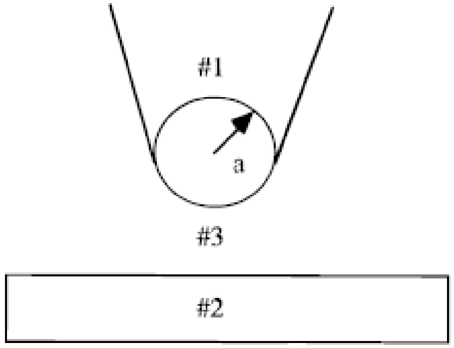
N - number of molecules per unit volume of the material,

α is the polarizability of these molecules (dielectric constant), ξ_n is the electromagnetic frequency

Al_2O_3 in water is A ≈36.7 x 10^{-21} J, under vacuum A ≈ 152 x 10^{-21} J,
SiO_2 (silica) in water is A ≈ 4.6 x 10^{-21} J, under vacuum A ≈ 65 x 10^{-21} J

Van der Waals Forces - Measurement by AFM

- Measurement of interparticle forces between the same material or different materials
- A. Meurk, P. F. Luckham and L. Bergstrom, *Langmuir* **1997,** *13,* 3896-99



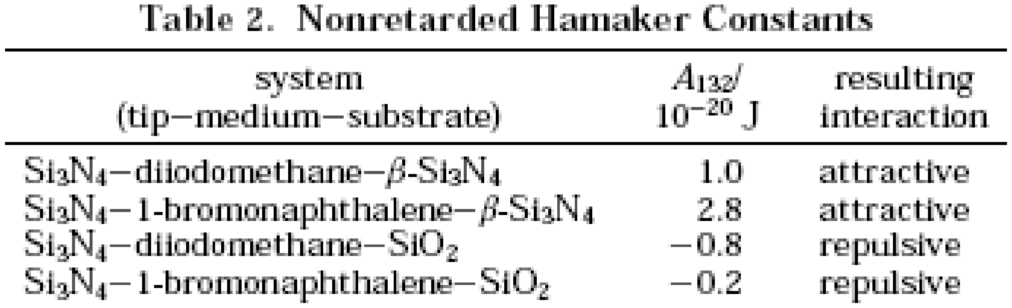
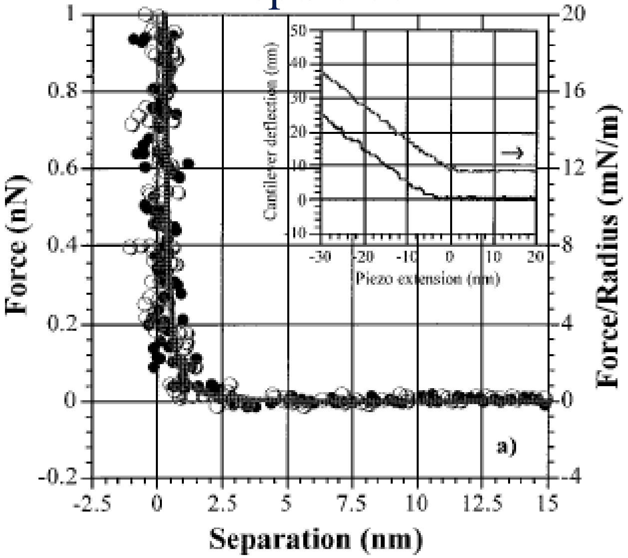


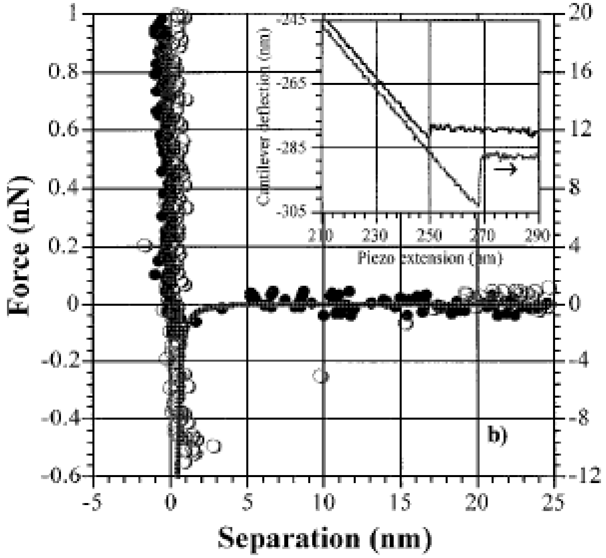
Table 2. Nonretarded Hamaker Constants

system (tip−medium−substrate)	A_{132}/ 10^{-20} J	resulting interaction
Si_3N_4−diiodomethane−β-Si_3N_4	1.0	attractive
Si_3N_4−1-bromonaphthalene−β-Si_3N_4	2.8	attractive
Si_3N_4−diiodomethane−SiO_2	−0.8	repulsive
Si_3N_4−1-bromonaphthalene−SiO_2	−0.2	repulsive

(a) Si_3N_4-diiodomethane-SiO_2 Repulsive



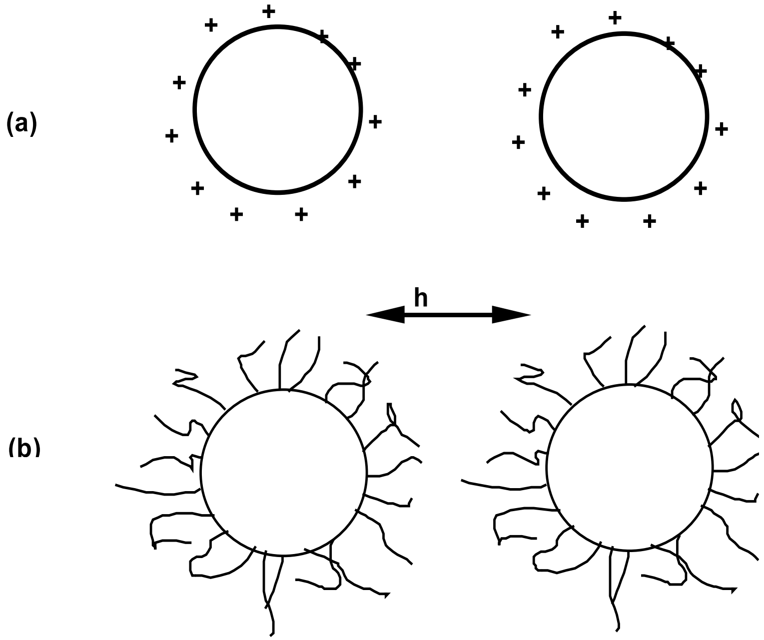
(b) Si_3N_4- diiodomethane-Si_3N_4. Attractive



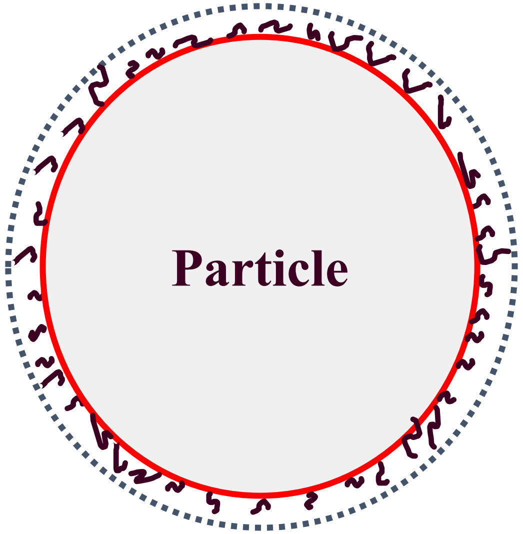
filled circles denote approach, open circles denote retraction,

Repulsive forces

- Electrostatic
  - dissociation of species at the surface
  - adsorption of charged species
  - dissociated ions, molecules or polymers
- Steric
  - molecules - often adsorbed polymers



(distance h between particles)

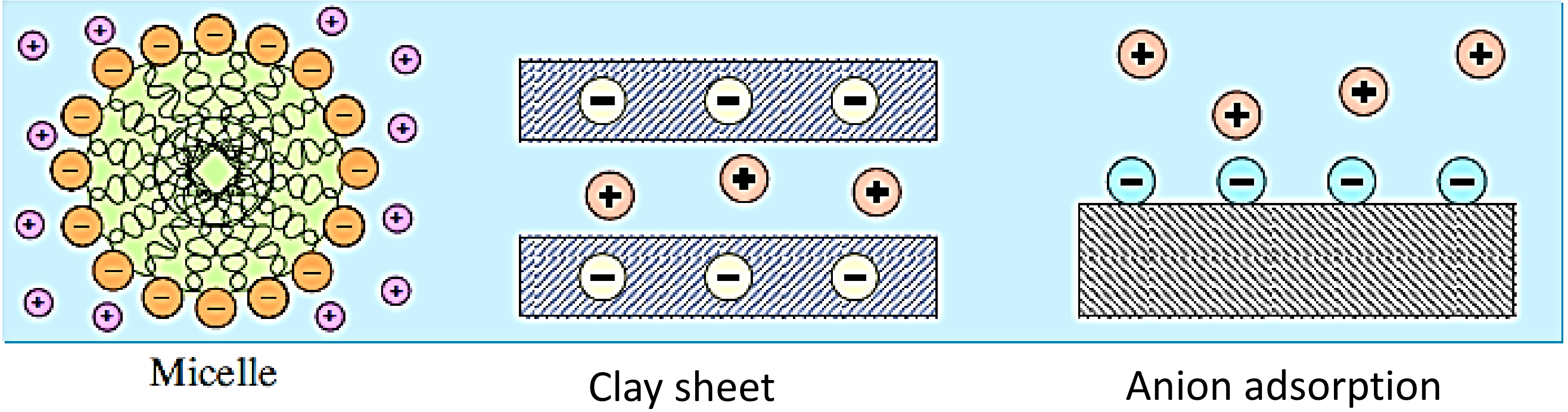


Formation of Charged Interfaces

- <u>Ion adsorption at interfaces</u>
  - 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

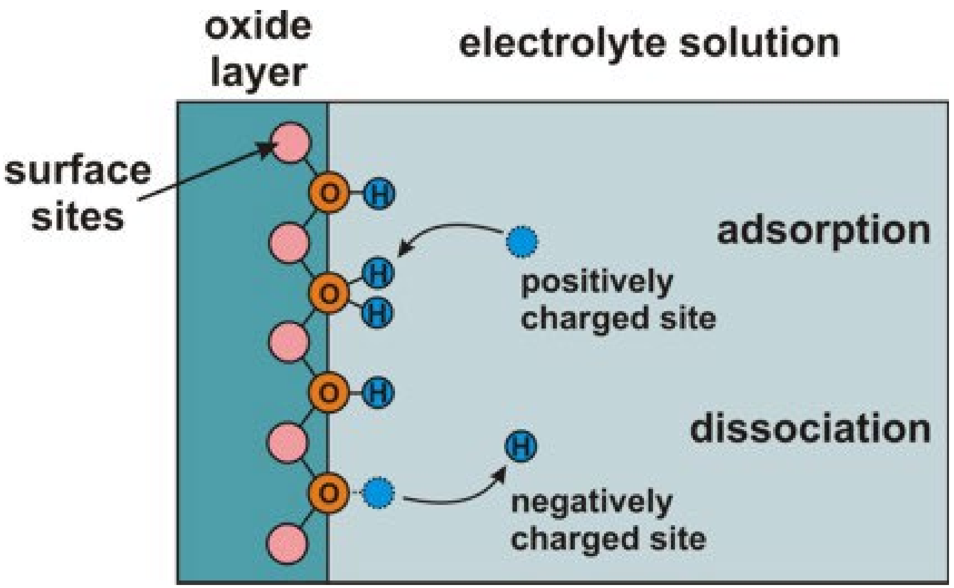
    $–OH, –COOH, –NH_2, –SO_4H, –PO_4H_2...$
  - Adsorption of charged species in solution (*Hofmeister* series):

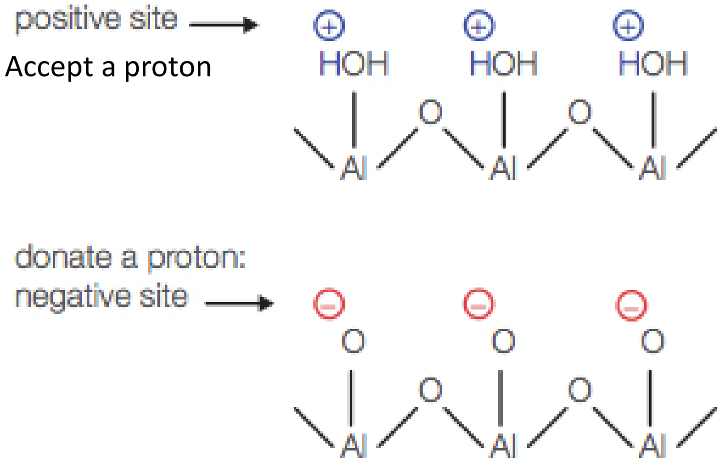
    $I^- > ClO_4^-, NO_3^- > Br^- > Cl^- > OH^- > F^-, SO_4^{2-}$



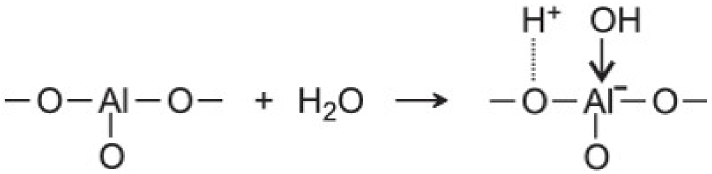
Surface charging – examples

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





Accept a proton



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

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

Brønsted acid: releases a H$^+$ (donor)

Lewis base: donates a pair of electron

Brønsted base: captures a H$^+$(acceptor)

Surface charging - Ion adsorption at interfaces

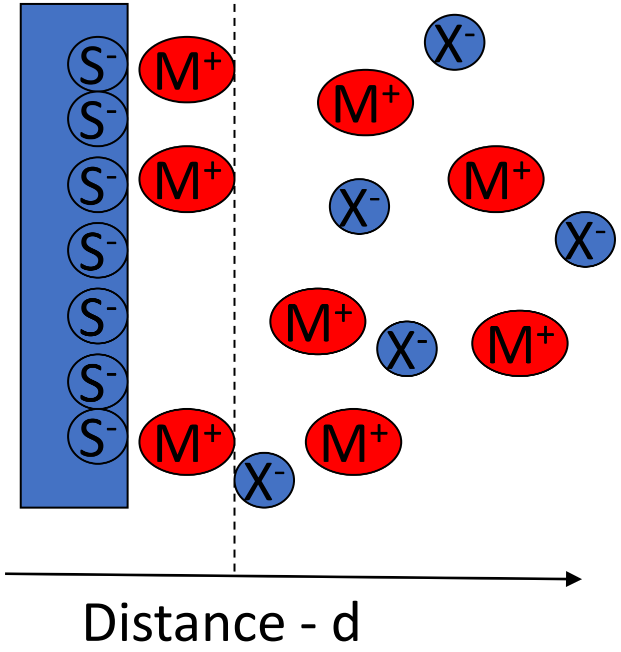
- "**potential determining ions** – pdi "- determines the potential of the surface
  - e.g. Ca^{2+}… preferentially adsorbs on cement surface - surface charge changes from negative to positive
  - NaCl… indifferent electrolyte … no specific adsorption…does not influence potential
  - HCl… H^+ Cl^- - **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

$$\text{-SiOH} \leftrightarrow \text{-SiO}^- + H^+$$

- 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

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)

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

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

Boltzmann distribution

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

c^*_{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·g·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^*_{io}, concentration at Φ=0 i.e. in bulk solution far from interface ***(no. of molecules per m³)***

◆ 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/m³)

Poisson Boltzmann (PB) Equation – charged surface

♦ Ion distribution in an electrolyte outside a charged surface

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

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

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

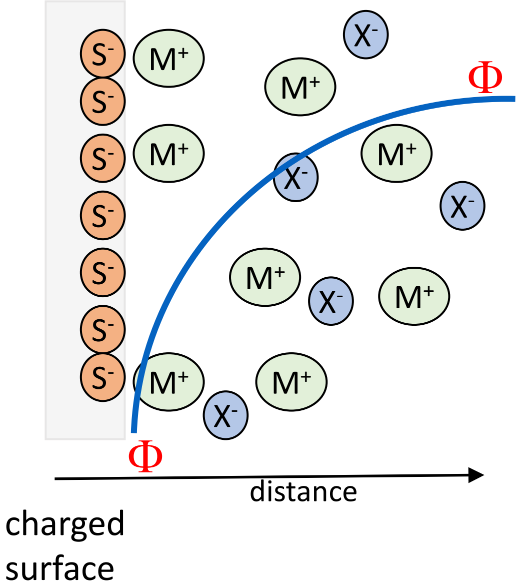
- To solve PB: need geometry – infinite plane ⇨ *d/dz*
- Model of *Gouy (1910) - Chapman (1913) – diffuse layer of counterions outside the charged surface*
  - *spatial distribution of* ions for an *infinite plane* evenly charged.
  - the *Poisson –Boltzmann* equation simplifies to linear form

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

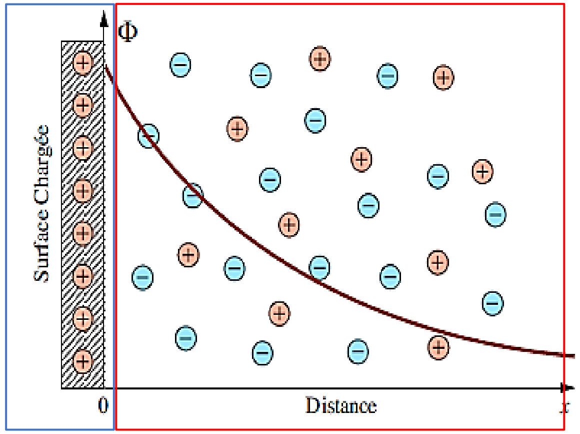
- Boundary conditions:
  - Electroneutrality $d\Phi/dz = 0$ far from surface and
  - c^*_{io}, represents bulk electrolyte concentration (no. ions/m^3)
  - at surface behaves like capacitor $d\Phi/dz = -\sigma/\varepsilon_0\varepsilon_r$
  - no charged species below surface i.e. $z <= 0$, $d\Phi/dz =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

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

◆ Square root of L.H.S. gives ± negative or positive surfaces

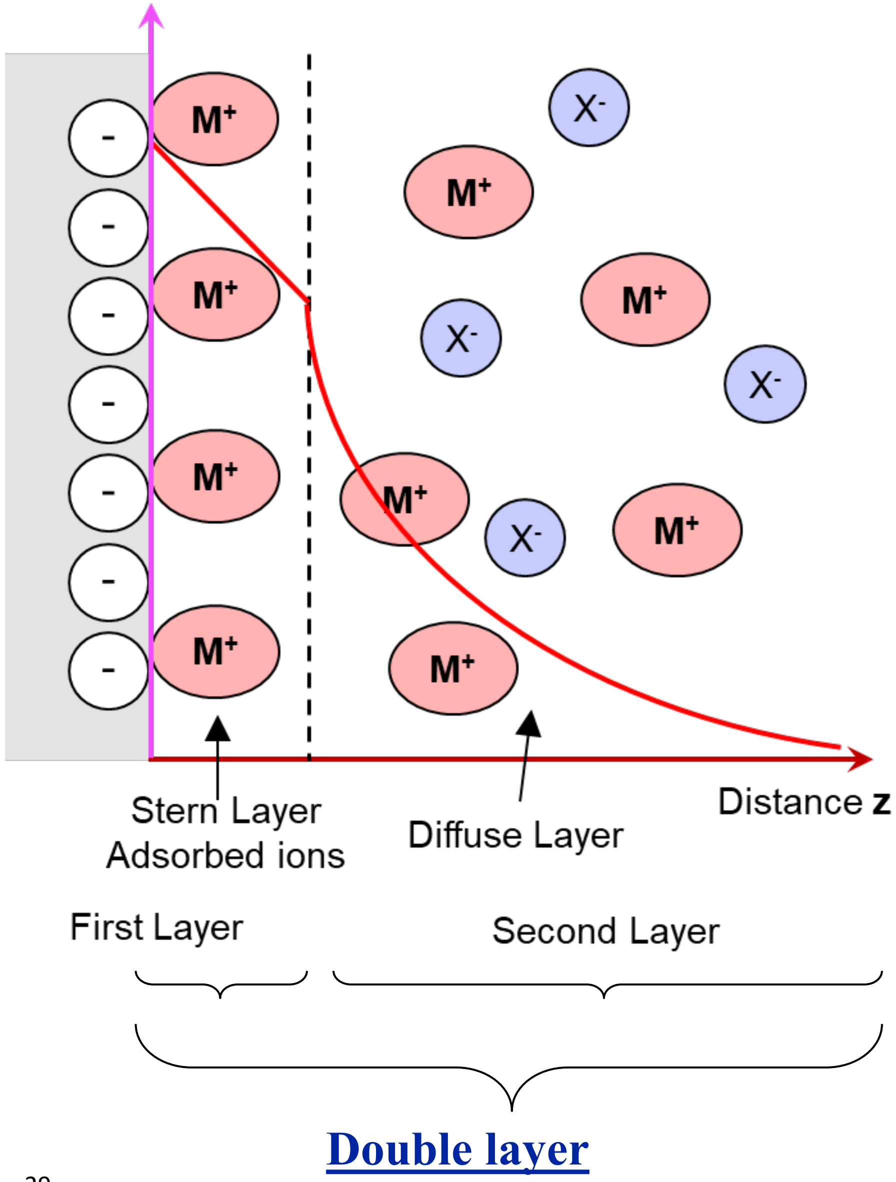


Diffuse layer of counterions



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

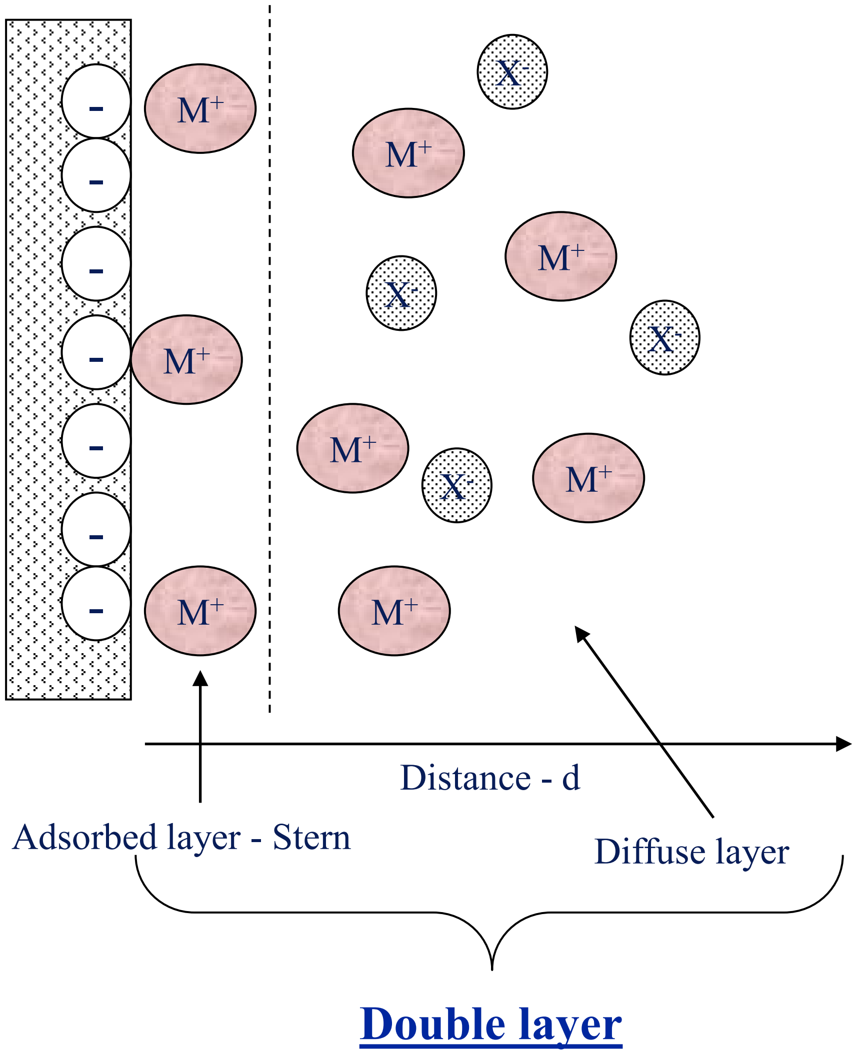
Double layer - Gouy and Chapman – Stern model



- Model of Gouy-Chapman - Treats ions as point charges
- Hydrated ions can adsorb (Helmholtz*). Water can also adsorb via 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 – behaves as capacitor: linear decrease
- Exponential-like decrease of potential in diffuse layer

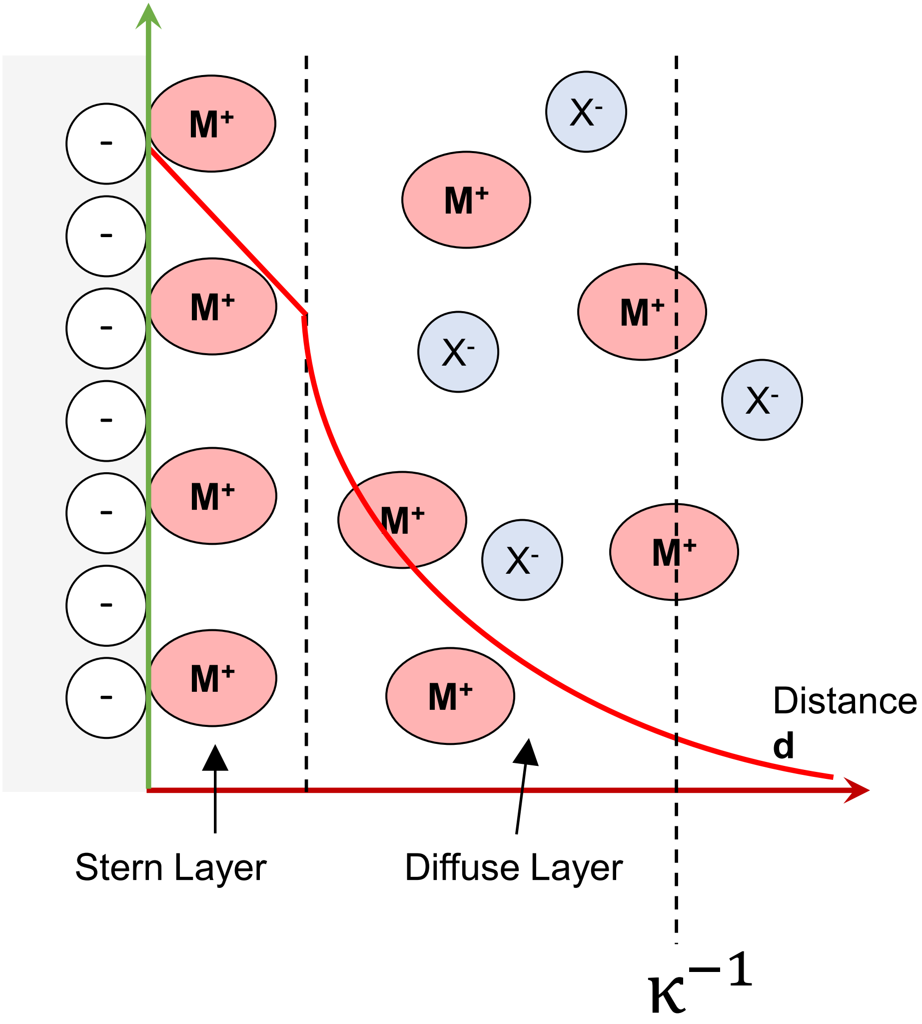
*https://en.wikipedia.org/wiki/Double_layer_(surface_science)

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

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

Boundary conditions for integration

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

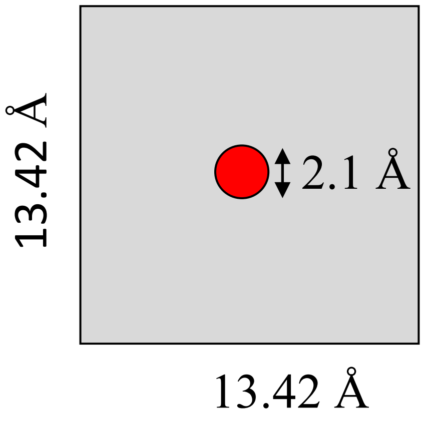
$$\left.\frac{d\Phi}{dz}\right|_{z=0} = \frac{-\sigma}{\varepsilon_0\varepsilon_r}$$

- Gouy – Chapman Theory
  - Surface charge density, σ (C/m^2), as fn of surface potential, Φ (V)

$$\sigma = \left(8kTc_{i0}^{*}\varepsilon_0\varepsilon_r\right)^{1/2}\sinh\left(\frac{z_i e\Phi_0}{2kT}\right)$$

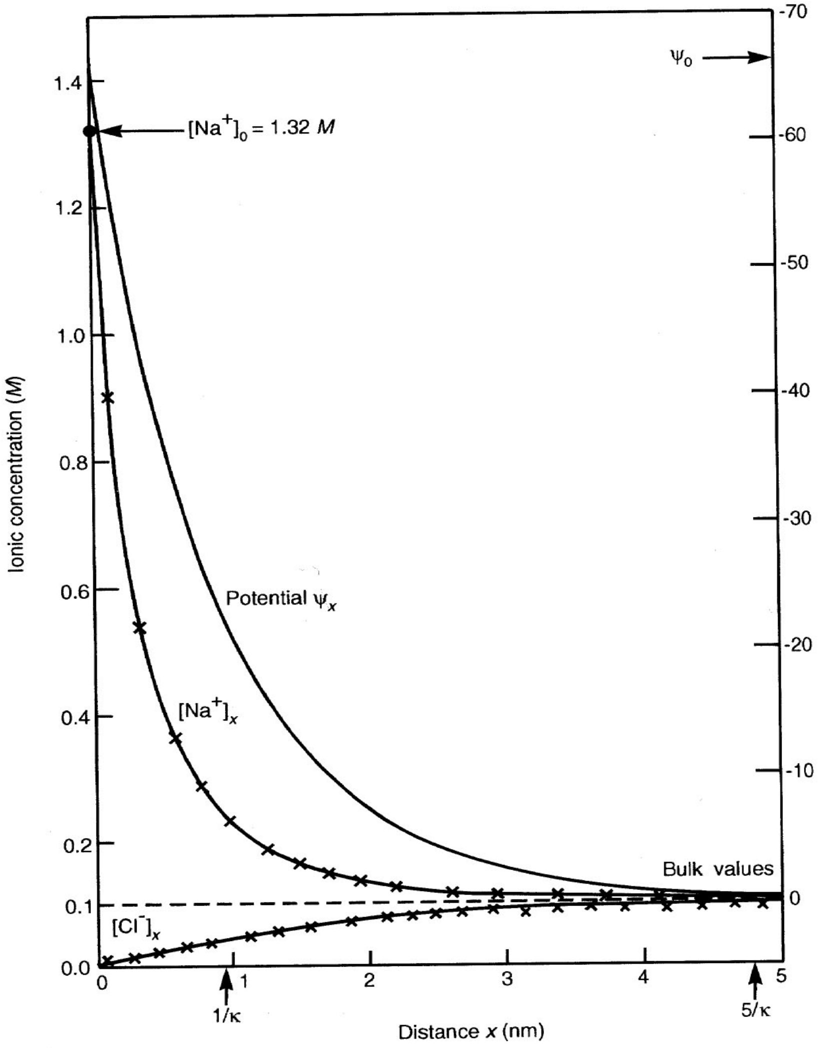
- Example
  - Φ_0 = -75 mV, c = 0.15M, NaCl, 25°C
  - σ = 0.09 C/m^2 means 1 unit charge per 180Å^2
  - Na$^+$ ~ 1 Å (radius) (+ solvation 2.1 Å)

(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.

Ionic concentration and surface potential



- Example – NaCl (0.1 M) - from Israelachvili*
  - σ = 0.0621 C/m^2 (1e/2.6nm^2)
  - Φ_0= -66.2 mV (from Graham)
  - x in figure: 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 linearized Poisson- Boltzmann approach
- Molecular modelling and numerical simulations (Monte Carlo) – show limitations**

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

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

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**)

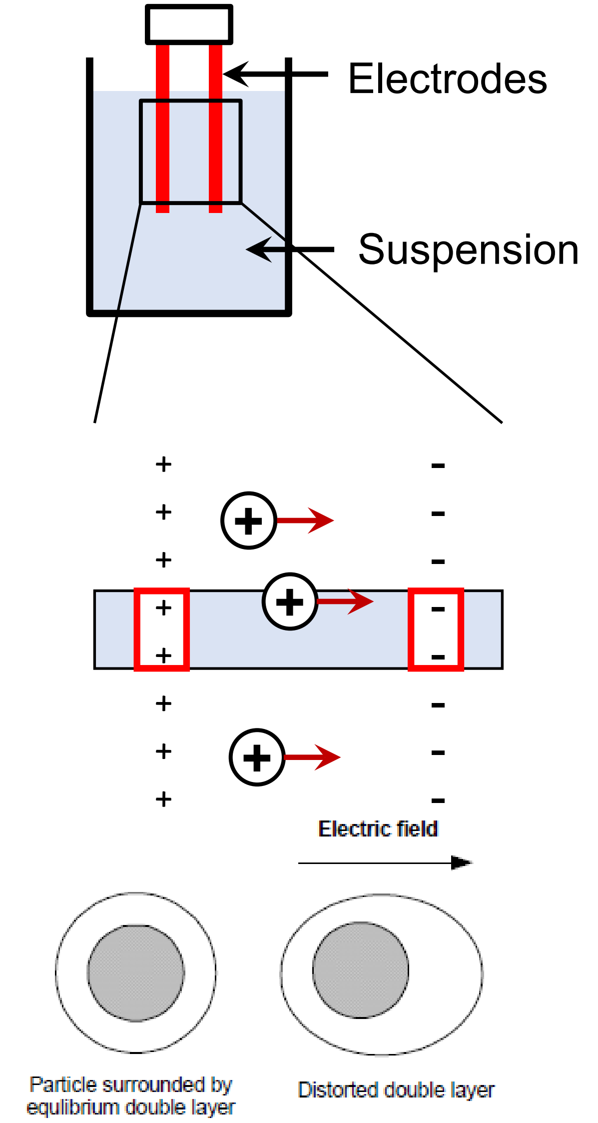


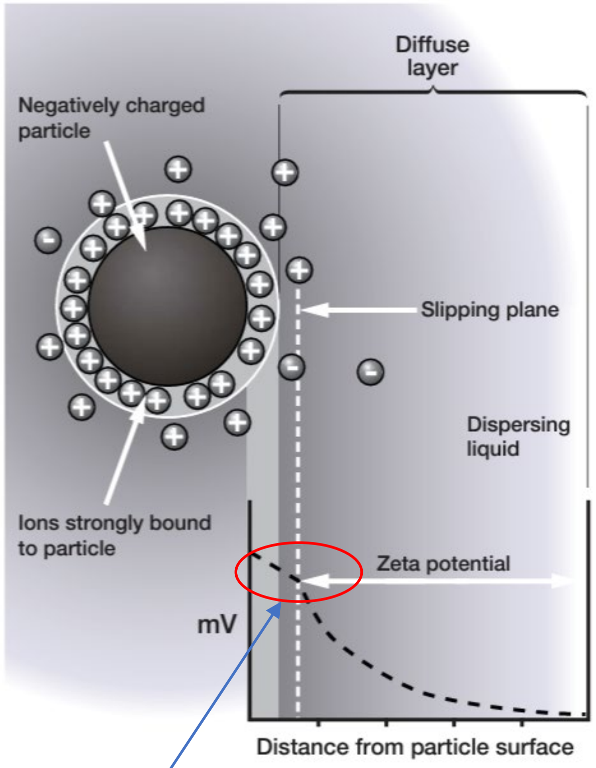
Figure 3: Distortion of double layer by applied electric field

40 nm Al_2O_3 particle speed ≈ 2 m/s

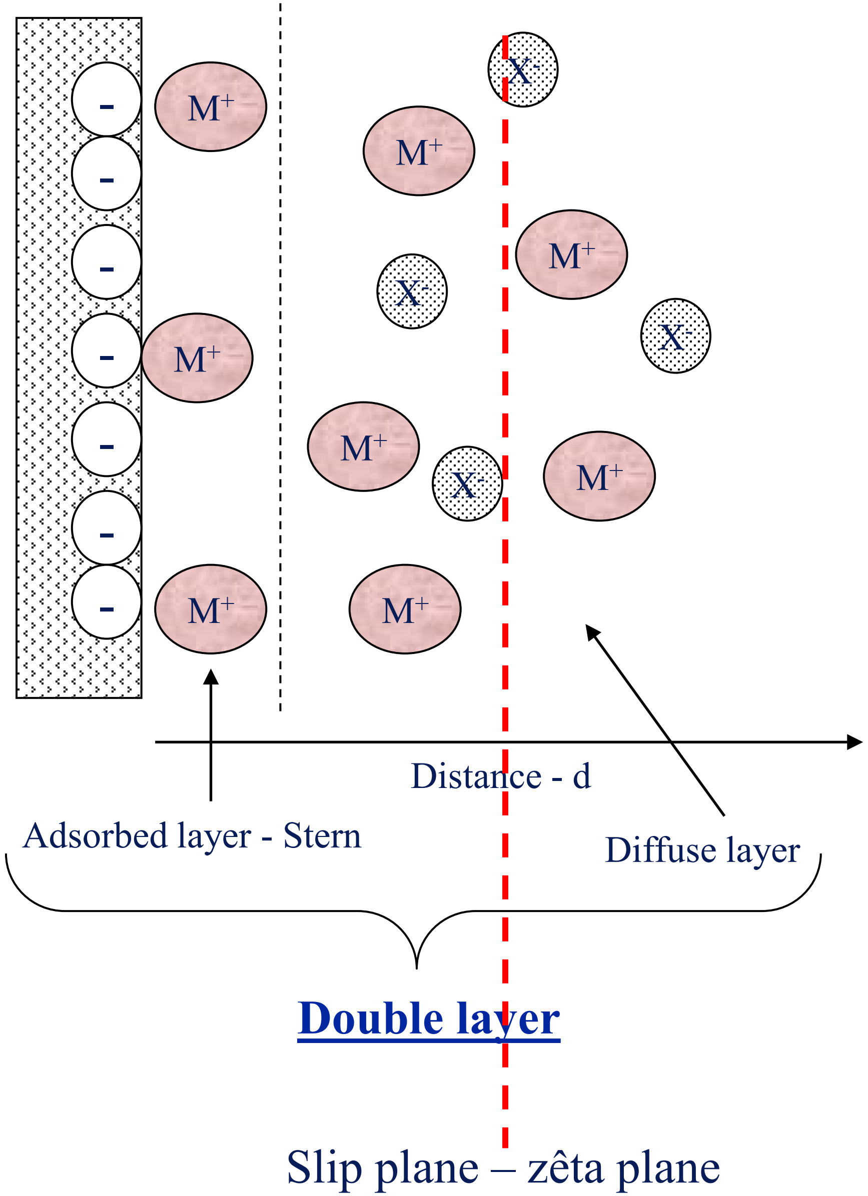
* O'Brien, R.W. White, L.R. -J. Chem. Soc. Faraday Trans. 2, 74 1607 (1978)

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

Double layer - Gouy and Chapman – Stern model



Not fully correct…

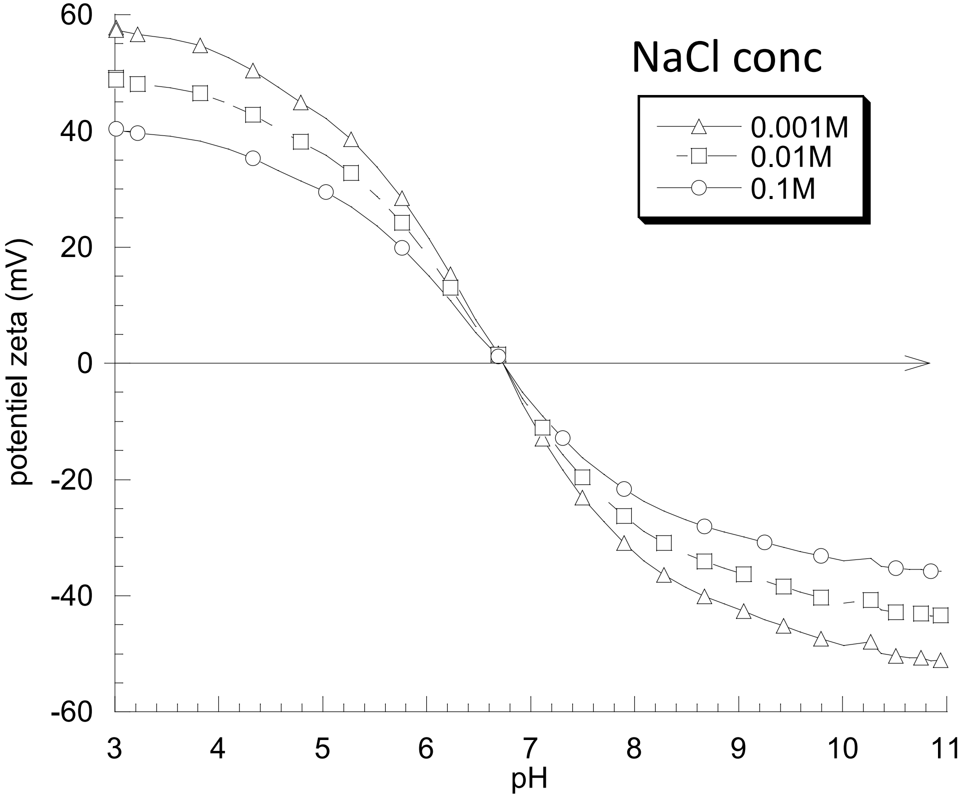


Double layer

Slip plane – zêta plane

Surface potential measurement – zeta potential

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



Examples of iep

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

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* :
- $$F = -\left(\frac{\partial G}{\partial h}\right)_T = -\left(\frac{\partial H}{\partial h}\right)_T + T\left(\frac{\partial S}{\partial h}\right)$$
- 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:
- $$\frac{F}{Area} = -\frac{1}{Area}\left(\frac{\partial G}{\partial h}\right)_T = -\left(\frac{\partial G}{\partial V}\right)_T = -\frac{1}{V_{solute}}\left(\frac{\partial G}{\partial n_{solute}}\right)_T = \Pi_{osm}$$
- “Area” is the surface of the particle.

Interactions between colloidal particles

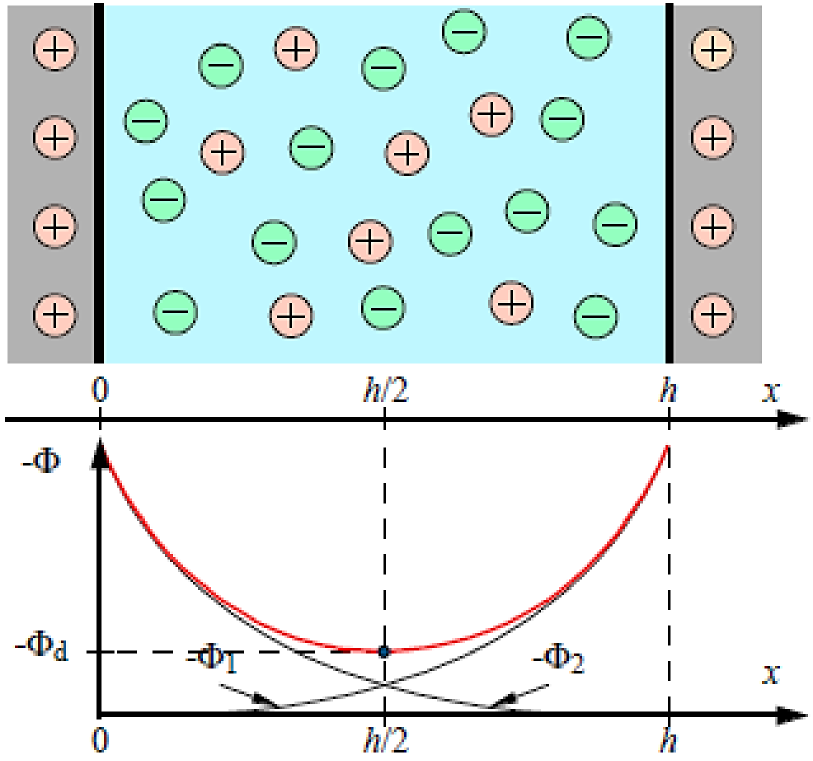
- The attractive / repulsive interactions between particles of a colloidal suspension in an electrolyte result from an *osmotic pressure difference* between the solution located *between* particles and *bulk* of the solution.
- A direct effect of the formation of the double layer at a charged surface.

Interaction Between Charged Surfaces

- 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:
- $\frac{d\Phi}{dx}|_{h/2} = 0; \Phi(h/2) = \Phi_d$
- The ionic distribution between each charged surface

  and the mid-plane (h/2) is identical giving :
- $\frac{F}{Area} = \Pi_{osm} = kT \sum_i c_i(h/2)$
- This equation also applies to *swelling of charged layered crystals such as clays* (e.g. montmorillonites, a 2:1 clay).



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:

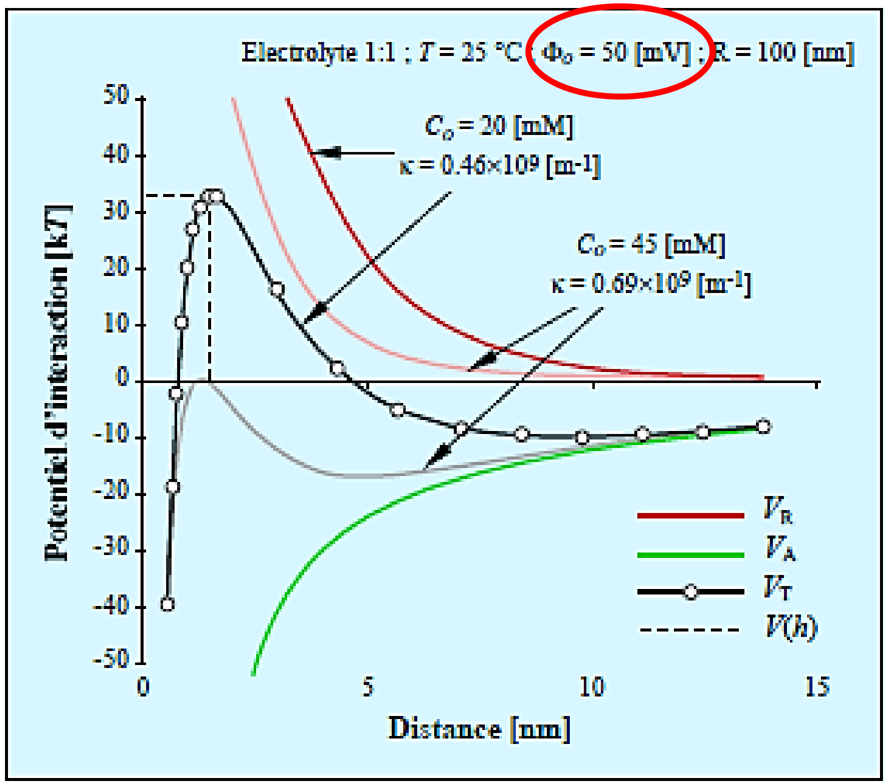
$$F = -\frac{dV}{dh} = -\frac{dV_R}{dh} - \frac{dV_A}{dh}$$

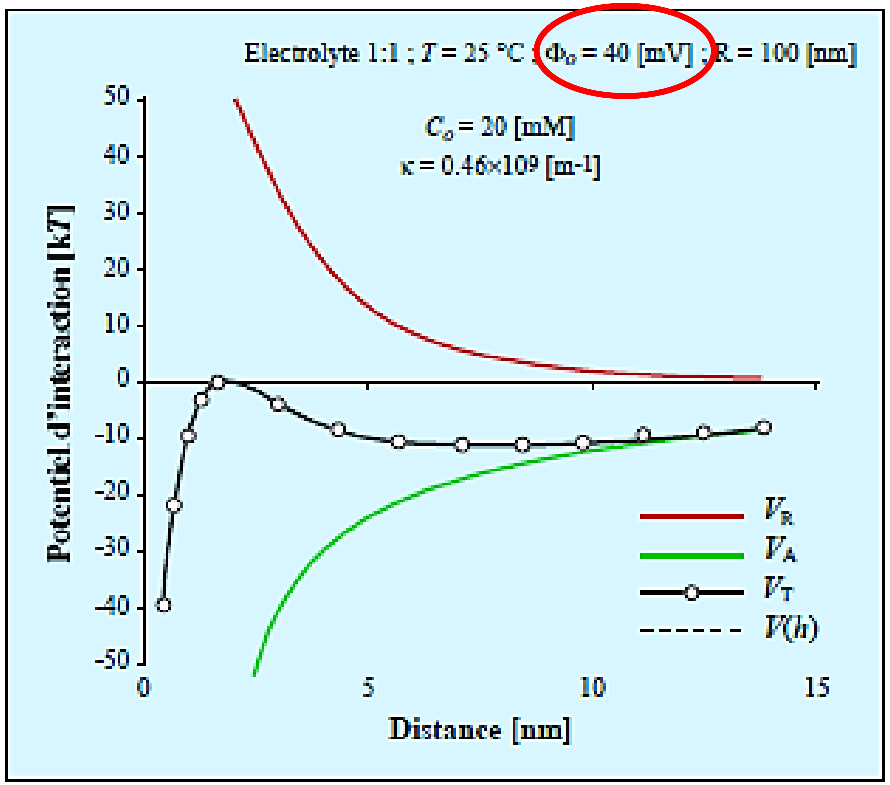
- Theory developed by *B. Derjaguin* & *L. Landau*, and *E. Verwey* & *T. Overbeek*. 2 independent groups at the same time…. 1940's

Colloidal Stability - DLVO Theory

- Interaction between two identical **spheres 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**: the barrier decreases from 33 kT to 0 as potential decreases from 50 to 40 mV.



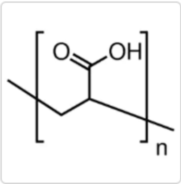


TYPES OF POLYMERS

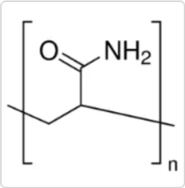
Poly-electrolytes

The chain carries *ionizable* functional groups.

Examples: Poly (sodium acrylate) (PAA-Na): **[–CH (COONa) –CH$_2$-]$_n$**

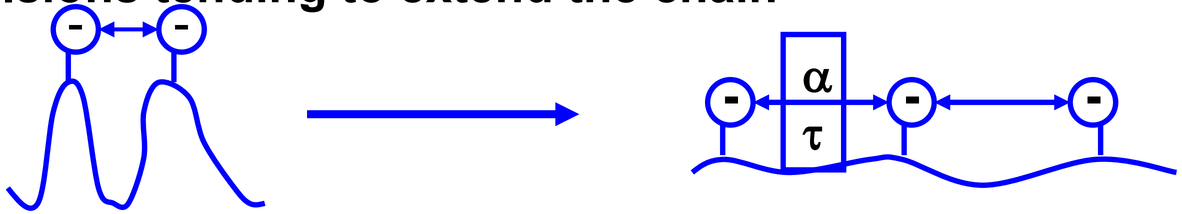


Poly (acrylamide): **[–CH (CONH$_2$) –CH$_2$-]**



✓ **POLYELECTROLYTES: if the monomers carry a charge**

✓ **Intramolecular repulsions tending to extend the chain**

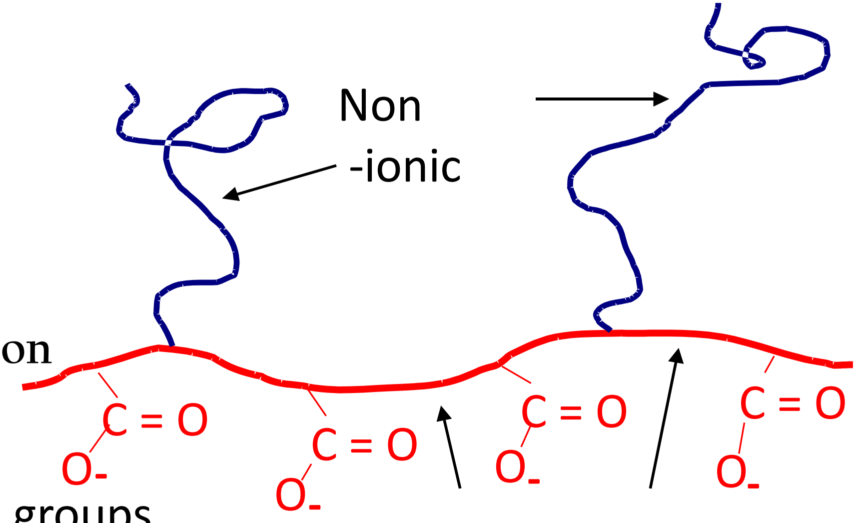


✓**POLYELECTROLYTES - branched**

✓ **:**the monomers carry a charge

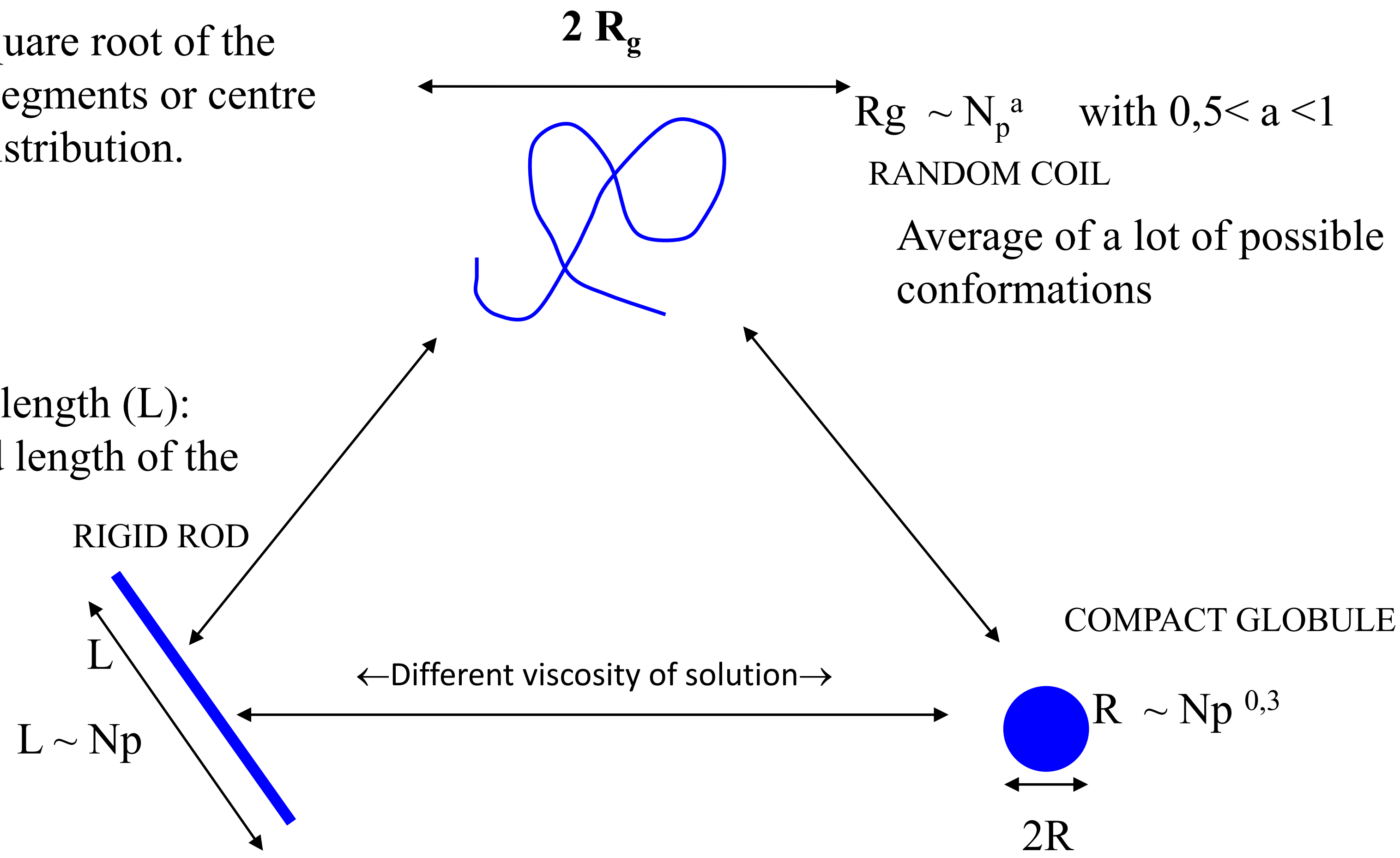
✓- Typical of polycarboxylate –

Superplacticizers used in cement dispersion



Anionic groups

CONFORMATION OF POLYMERS



Radius of gyration : square root of the average length of the segments or centre of gravity the whole distribution.

2 R_g

$Rg \sim N_p^a$ with $0,5 < a < 1$

RANDOM COIL

Average of a lot of possible conformations

Stretched length (L): developed length of the chain

RIGID ROD

L

$L \sim Np$

←Different viscosity of solution→

COMPACT GLOBULE

$R \sim Np^{0,3}$

2R

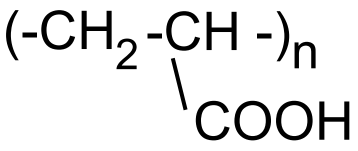
The solvent /monomer interactions play an important role in the solvent's quality for large N_p:

In poor solvent: $R_g \approx N^{0,3} \approx M^{0,3}$ In good solvent: $R_g \approx N^{0,6} \approx M^{0,6}$

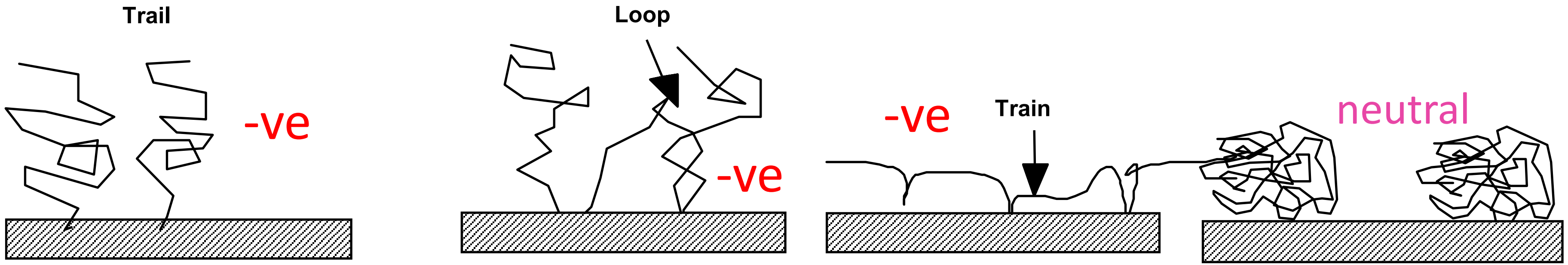
Polymer conformation - Polyacrylic Acid on Alumina

- **Example: polymer conformation**
- Adsorption of polyacrylic acid on alumina (Al_2O_3)
- Isoelectric point - Al_2O_3, pH = 9,
- PAA fully dissociated for pH> 6
- Adsorbed layer thickness can be measured by Atomic Force Microscopy – AFM*
- Or from atomistic modelling$
- Steric and electrostatic contributions from carboxylate groups – electro-steric stabilization

PAA



$(\text{-}CH_2\text{-}\underset{\diagdown COOH}{CH}\text{ -})_n$



PAA - pH > 11

brush

Trail

-ve

Slightly -ve

PAA - pH = 8

mushroom

Loop

-ve

Slightly +ve

PAA - pH = 6

pancake

-ve

Train

+ve

PAA - pH = 2

blob

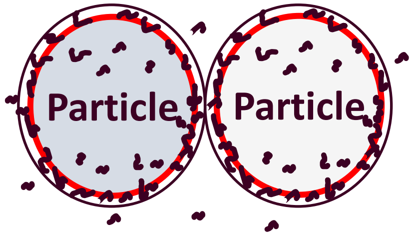
neutral

+ve

- *M. Palacios, P. Bowen , M. Kappl, HJ. Butt, M. Stuer, C. Pecharromán, U. Aschauer, F. Puertas “Repulsion Forces of Superplasticizers on Alkali Activated Slag Pastes” Materiales de Construcción, 489-513, 62 (308), 2012
- $U. Aschauer et al ”,J.Coll.Inter.Sci. 346 (2010) 226–231

Adsorbed layer – steric repulsion

- Repulsion is felt when the polymer layers overlap
- The more these layers are extended the sooner the repulsion is felt and therefore the effect of the attractive van der Waals forces will be limited.



Theoretical approach

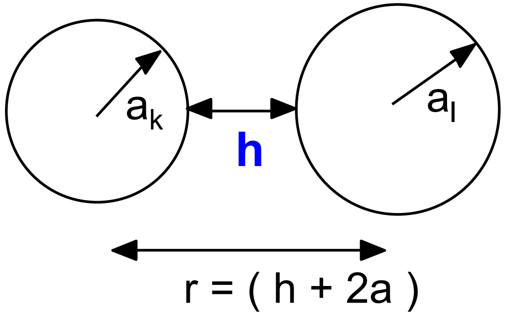
- Both enthalpy and entropy contribute to the force of repulsion.

Enthalpic

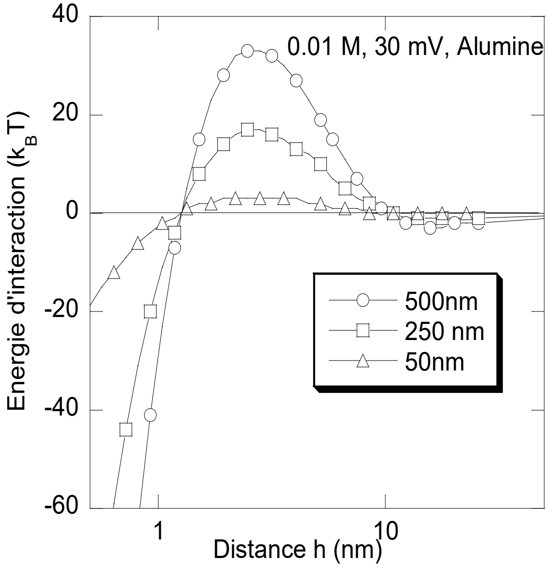
- an interpenetration of the polymers reduces the contact between the solvent and the polymeric chains (due to polymer-polymer contact).
- this changes the mixing enthalpy of the system giving our input enthalpy. (concentration gradient between bulk and interparticle space – osmotic pressure pushes particles apart)

Entropic

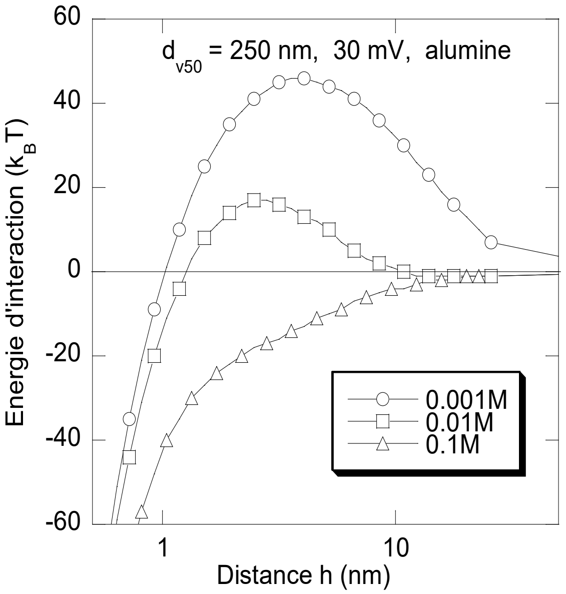
- as the adsorbed layer approach, each polymer can no longer adopt as many configurations as before – loss of disorder higher free energy – repulsion to avoid this – giving a repulsive entropic contribution.



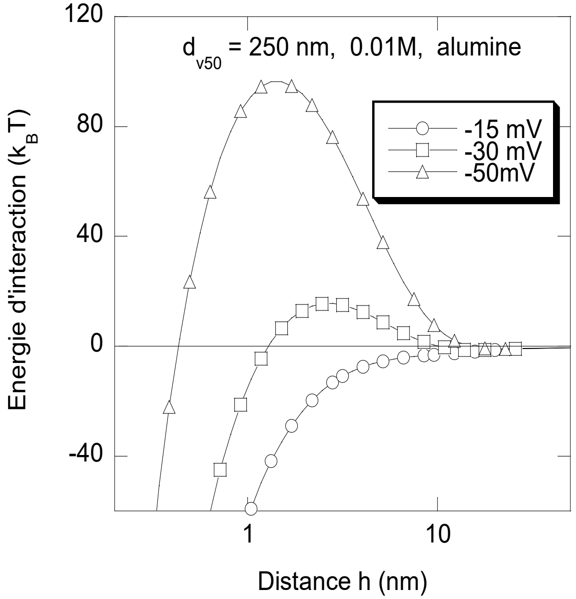
Interparticle potentials – summary - calculations – α Al_2O_3



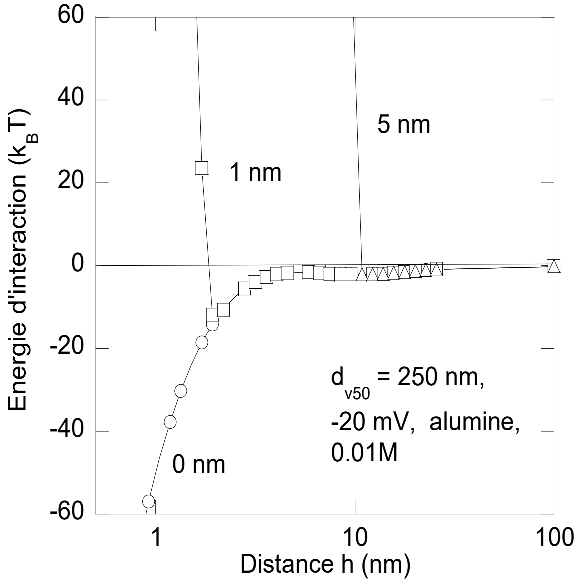
size



Ion conc



charge



Adsorbed layer

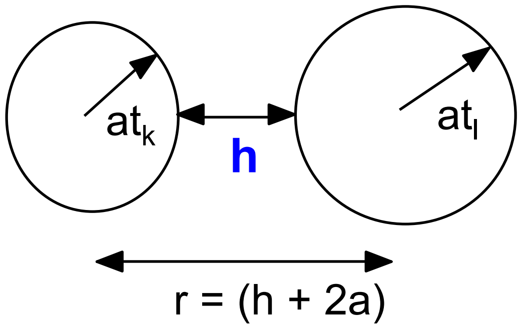
Interparticle Forces - Hamaker*

- **Attractive** - Van der gold dispersion Waals forces - A (h) - Hamaker constant (dielectric properties)

$$F_{(a_k,a_l,h)} \cong -A_{(h)} \frac{\bar{a}}{12h^2}$$

Harmonic average radius

$$\bar{a} = \frac{2a_k a_l}{a_k + a_l}$$



- **Repulsive**

Electrostatic, ion adsorption, dissociation, polyelectrolyte

$$F_{ES} = -2\pi\varepsilon\varepsilon_0 \bar{a} \psi^2 \frac{\kappa e^{-\kappa(h-2L)}}{\left(1+e^{-\kappa(h-2L)}\right)}$$

ψ Electrostatic potential (from zeta potential)

$1/\kappa$– Electrical double layer thickness

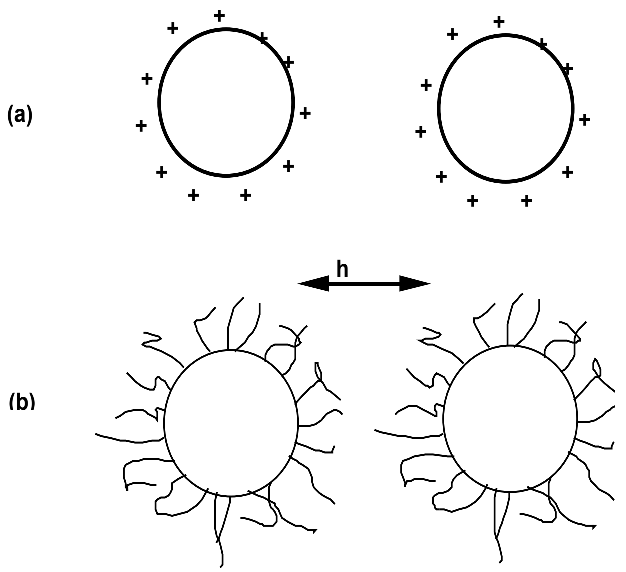
L - load /zeta plane

Steric -polymer adsorption - layer thickness

$$F_{ster}(a_k, a_l) = 2\pi\bar{a}\frac{3}{5}\frac{k_B T}{s^2}\left[\left(\frac{2L_{ads}}{h}\right)^{5/3} - 1\right]$$

L_{ads} - Adsorbed layer thickness, s - Spacing of adsorbed molecules

In mushroom configuration - important geometry



(distance h between particles)

* U. Aschauer,et al J. Dispersion Science Technology, 32 (4), 470-479 (2011).