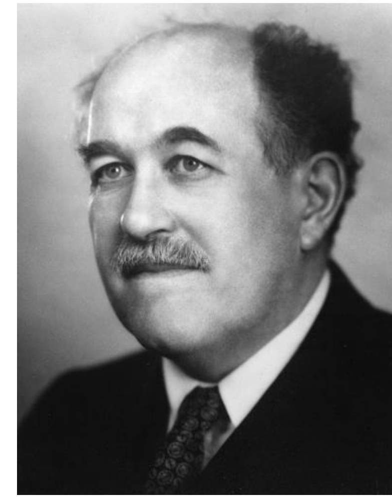
Physical Chemistry of Colloids

Louis Georges Gouy
1854 – 1926
French physicist

images from Wikipedia

David Leonard Chapman
1869 – 1958
British physical chemist

Peter Joseph William Debye
1884 – 1966
Dutch-American physicist
(Nobel Chem. 1936)



Otto Stern
1888 – 1969
German-American physicist
(Nobel Phys. 1943)

Lecture 7, *April 10, 2019*

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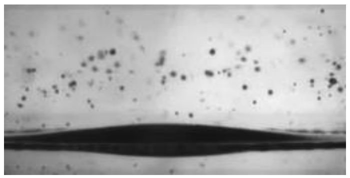
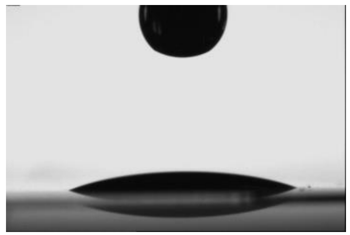
Previously in ColloidsPhysChem…(I)

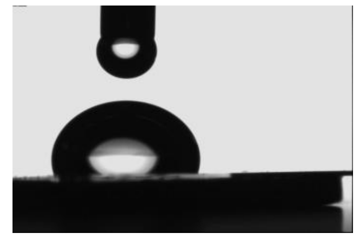
wetting regimes based on the contact angle

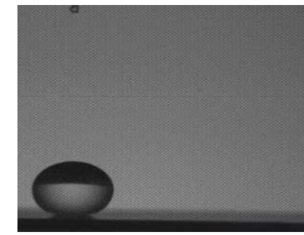
complete wetting	partial wetting	partial non-wetting	non-wetting
$\theta = 0^o$	$0^o < \theta < 90^o$	$90^o < \theta < 180^o$	$\theta = 180^o$



nagelgroup.uchicago.edu







web.mit.edu/nnf/education/wettability/wetting.html

spreading parameter

$$S = E_{dry\ sub} - E_{wet\ sub}$$

$$S = \sigma_{SG} - (\sigma_{SL} + \sigma_{LG})$$

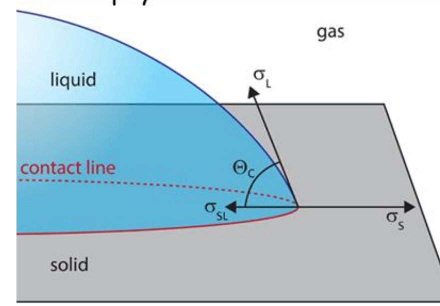
$E_{dry\ sub}$: surface energy (per unit area) of dry substrate

$E_{wet\ sub}$: surface energy (per unit area) of wet substrate

S≥0: complete wetting

- liquid spreads completely to lower its surface energy
- high σ_{SG} (e.g., clean glass, silicon) & low σ_{LG} (e.g. organic solvents) → favorable conditions

dataphysics-instruments.com



S<0: partial wetting

- drop forms a spherical cap with contact angle θ (@ equilibrium)
- *'mostly wetting'* & *'mostly non-wetting'* states

Previously in ColloidsPhysChem…(II)

simple experiments with sessile drops on *real surfaces* give irreproducible θ values

What is the reason for the θ data irreproducibility?

- only uppermost layers of the substrate determine θ; coatings/contaminants important!
- difference between θ when liquid is advanced over (θ_{adv}) or receded from (θ_{rec}) the surface

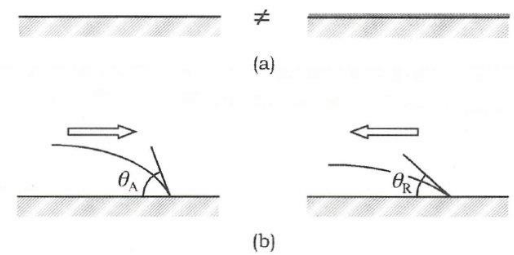


Fig. 4-7: "Irreproducible" contact angles: (a) Surface composition is different between nominally identical bulk solids, (b) Contact angle depends on whether liquid is advancing or receding across solid surface: hysteresis.

contact angle hysteresis

$H = \theta_{adv} - \theta_{rec}$

origin of H

- surface roughness
- chemical heterogeneity

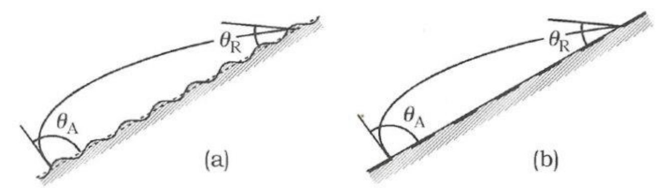


Fig. 4-9: Origins of contact angle hysteresis: (a) Surface roughness, (b) Surface chemical (energetic) heterogeneity.

Wenzel model

for rough surfaces: $A_{true} = rA_{smooth}$

r: rugosity factor (>1)

$$cos\theta_{app} = r\frac{(\sigma_{SG} - \sigma_{SL})}{\sigma_{LG}} = rcos\theta_0$$

- *size scale of roughness small*
- *drop larger than roughness size scale*

θ_0: intrinsic contact angle (Young)

Cassie & Baxter model

for heterogeneous surfaces consisting of two types of patches with θ_1 & θ_2

$$cos\theta_{app} = \varphi_1 cos\theta_1 + \varphi_2 cos\theta_2$$

φ_1, φ_2: area fractions

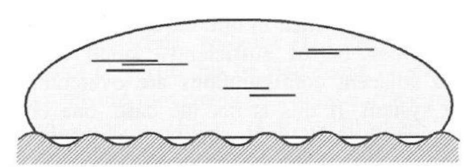


Fig. 4-16: A composite surface with unwetted gas pockets on the rough solid surface.

Previously in ColloidsPhysChem…(III)

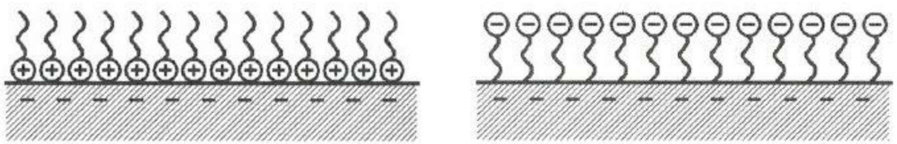
several applications require the change of wettability of solid materials

surface roughening (physical)

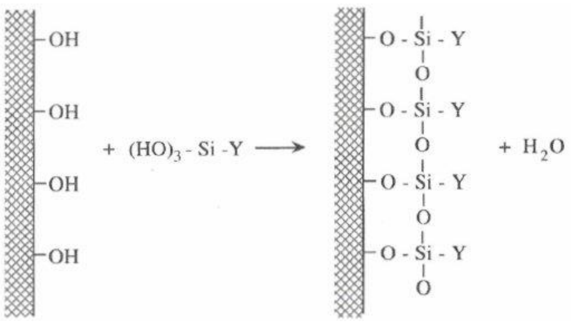
- can be achieved by sanding, plasma or chemical etching
- if $\theta_0 < 90^o$ → wetting promoted
- if $\theta_0 > 90^o$ → wetting hindered

surfactant addition (physical)

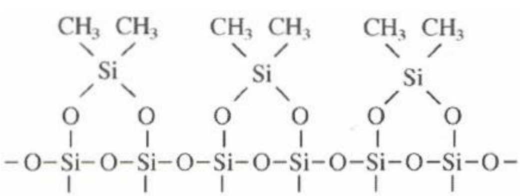
- decreases σ_{LG} → promotes wetting
- might increase/decrease σ_{SL} due to adsorption → promotes/hinders wetting



enrich surface with specific atoms (chemical)

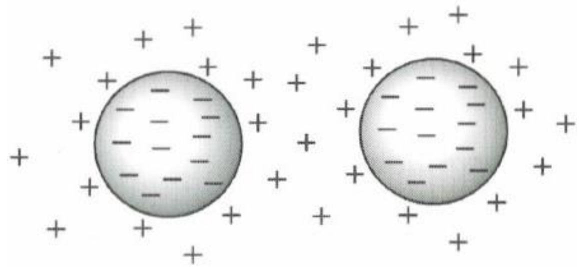


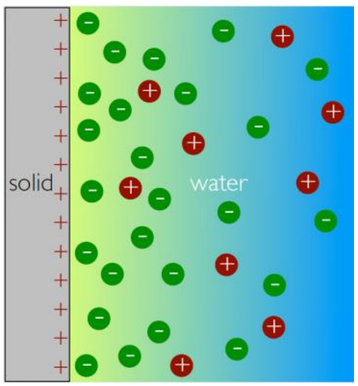
- oxygen enrichment → promotes wetting
- treatment with plasma, corona discharge, flame; produce reactive radicals, limited permanence
- wet chemical treatment (strong bases or acids)
- fluorine enrichment → wetting hindered
- adsorption of polymers containing F
- treatment with silanes Y-Si-$(OR)_3$, Y-Si-Cl_3



Previously in ColloidsPhysChem…(IV)

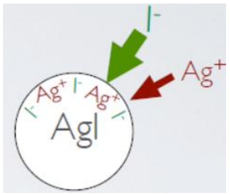
interfaces divide electrically neutral bulk (solvent) phases
→ positive & negative charges separate in direction normal to interface



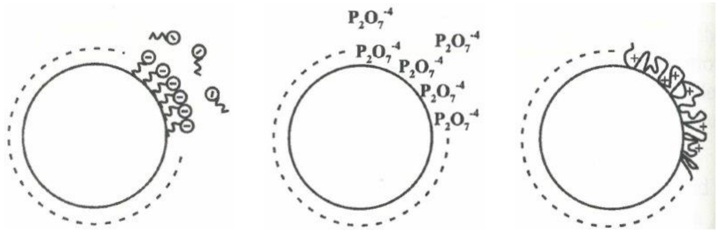


Origins of electric charge @ interfaces

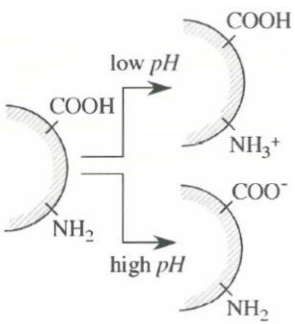
preferential adsorption/desorption of lattice ions
ions of the surface lattice of crystalline particles preferentially adsorb or desorb to the surface



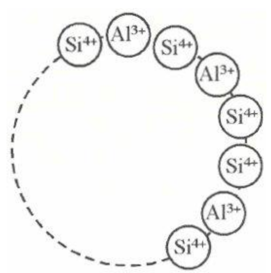
specific adsorption of (foreign) charged species
ions that are present in the system but are not an integral part of the dispersed phase adsorb on surface



ionization of surface functional groups
chemical functional groups of the dispersed phase may lose or gain an H^+ → negative/positive charge



isomorphic substitution
mineral particles exchange one ion type in their lattice with another one of different valence but similar size



Interface charging in non-aqueous systems

electrostatic model of ion dissolution

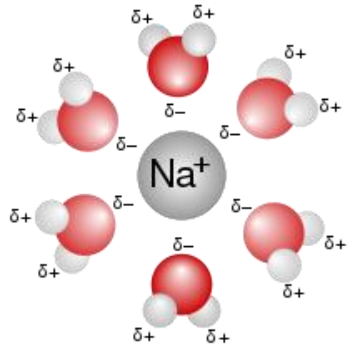
- interaction of ions in a solvent is screened through solvent polarization
- polarization ~ relative dielectric permittivity ε_r (dielectric constant)
- ***water:*** $\varepsilon_r \approx 80$; ***alkane:*** $\varepsilon_r \approx 2$ → water polarized more strongly
- attractive potential Ψ between two charges +q & -q @ distance r

$$\Psi = \frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{q^2}{r}$$

- $\Psi \gg k_B T$ → charges strongly associate, dissolved state unstable
- $\Psi = k_B T$ → Bjerrum length: $\lambda_B = \frac{1}{4\pi\varepsilon_r\varepsilon_0}\frac{q^2}{k_B T}$ *distance between the ions req. for stable dissociation*

aqueous systems

- $\lambda_B \approx 0.7$ nm, about twice the thickness of hydration shell (easy to dissolve salts in water)



wikipedia

non-polar media

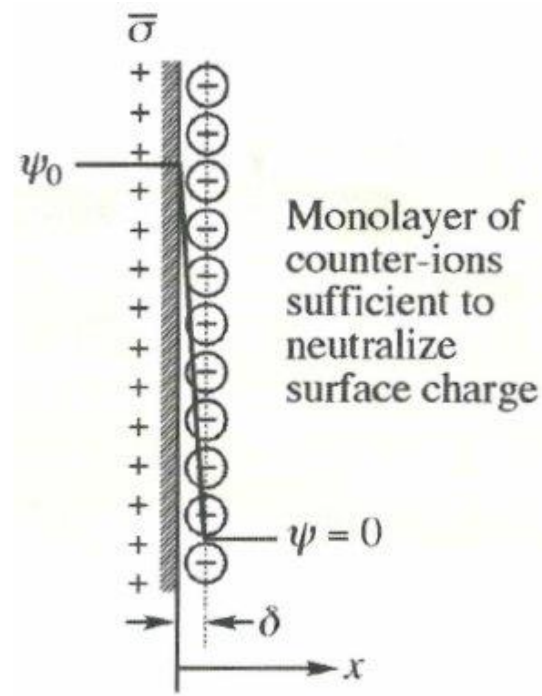
- $\lambda_B \approx 28$ nm
- for stable dissociation → ions must "hide" in a structure providing a shell of substantial thickness, which is very difficult
- ions "caged" inside or adsorbed onto large structures (reverse micelles, polymers, NPs)

Models of the electric double layer

regardless of charging mechanism, a structure is formed such that surface charge is neutralized by a layer of counterions in solution

Helmholtz model

- two adjacent monolayers of opposite charge ("molecular capacitor") @ distance δ
- δ: the hydrated radius of the counterions
- all of the potential drop occurs across δ
- surface charge density: $\bar{\sigma} = \dfrac{\varepsilon\varepsilon_0}{\delta}\psi_0$

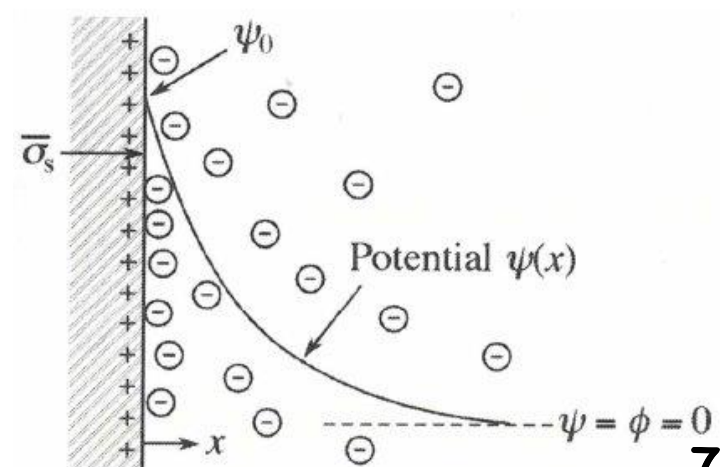


Gouy-Chapman model

- counterion layer should be diffuse because of thermal motion → uniform concentration
- equilibrium: balance between orienting effect of surface electric field & diffusion
  → high [counterion] near surface, ↓ with x

assumptions

- *ions point charges (they have no volume)*
- *no specific adsorption of ions*
- *ε_r of medium constant within the double layer*
- *surface charge uniform over the surface*



Basic electrostatics & the Poisson's equation

Coulomb's law

electrostatic force F between two point charges q_1, q_2:
-proportional to the product of the charges
-inversely proportional to the square of their distance r

$$|\vec{F}| = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}$$

Electric field $\vec{E}$

a vector field that is defined as the electrostatic force F on a hypothetical small charge q at a point due to Coulomb's law, divided by the magnitude of the charge

$$\vec{E} = \frac{\vec{F}}{q} \qquad |\vec{E}| = \frac{q}{4\pi\varepsilon_0 r^2}$$

A collection of N charges q_i located at points $\vec{r_i}$ produces an electric field (superposition principle):

$$\vec{E}(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\sum_{i=1}^{N}\frac{\widehat{R}_i q_i}{|\vec{R_i}|^2}$$

A charge density ρ(r') produces an electric field:

$$\vec{E}(\vec{r}) = \frac{1}{4\pi\varepsilon_0}\iiint \frac{\vec{r}-\vec{r}'}{|\vec{r}-\vec{r}'|^3}\rho(\vec{r}')d^3r'$$

Gauss' law: the total electric flux through any closed surface in an $\vec{E}$ is proportional to total electric charge enclosed within the surface

$$\oint_S \vec{E}\cdot d\vec{A} = \frac{1}{\varepsilon_0}q_{enclosed} = \int_V \frac{\rho}{\varepsilon_0}dV$$

Divergence theorem: $\vec{\nabla}\cdot\vec{E} = \frac{\rho}{\varepsilon_0}$

Poisson's equation: $\nabla^2\psi(r) = -\frac{1}{\varepsilon_0}\rho\,(r)$

Gouy-Chapman model of double layer: potential

consider a collection of ions in space

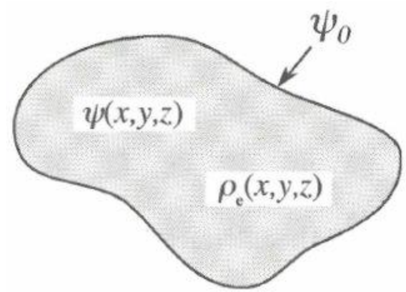


Fig. 6-9: Ionic cloud in space; basis for derivation of Poisson's equation.

we calculate the force F_i on any charge q_i in this region exerted by the other charges q_j using Coulomb's law (vectorial summation)

$$\vec{F_i} = q_i \sum_{j \neq i} \frac{q_j}{4\pi\varepsilon_r\varepsilon_0} \frac{\vec{r_{ij}}}{r_{ij}^3}$$

$\vec{r_{ij}}$: spatial displacement vector from q_i to q_j

ion distribution ρ_e described by "smearing" them over the volume, [=] charge/vol

$$\rho_e(x,y,z) = \sum_i z_i e n_i$$

n_i: number conc. of ion i [=] #/vol

z_i: valence of ion i

Poisson's equation
based on additive contribution of charge to the potential at any location

$$\nabla^2\psi = -\frac{1}{\varepsilon_r\varepsilon_0}\rho_e(x,y,z)$$

in one (x) dimension:

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\varepsilon_r\varepsilon_0}\sum_i z_i e n_i(x)$$

ε_0: vacuum permittivity

ε_r: relative permittivity

both $\psi(x)$ and $n_i(x)$ are dependent variables
→ *we need additional information to solve for any of them*

The Poisson-Boltzmann equation

we must consider the effect of diffusion on the ions

Boltzmann factor
ratio of the probability to find an ion at x
to that of finding it in the bulk liquid (x=∞)

$$\frac{n_i(x)}{n_i(\infty)} = \exp\left(-\frac{w_i}{k_B T}\right)$$

w_i: work required to bring ion i from x=∞ to x=x

$$w_i = z_i e\psi(x)$$

Poisson-Boltzmann equation

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\varepsilon_r\varepsilon_0}\sum_i z_i e n_{i,\infty} exp\left(-\frac{z_i e\psi}{k_B T}\right)$$

simplif. 1: *symmetric z-z electrolyte*

$$\frac{d^2\psi}{dx^2} = -\frac{zen_{i,\infty}}{\varepsilon_r\varepsilon_0}\left[exp\left(\frac{ze\psi}{k_B T}\right) - exp\left(\frac{-ze\psi}{k_B T}\right)\right] = \frac{2zen_{i,\infty}}{\varepsilon_r\varepsilon_0} sinh\left(\frac{ze\psi}{k_B T}\right)$$

simplification 2: $|z\psi_0| \leq \frac{k_B T}{e}$ **Debye-Hückel approximation**

linearized **Poisson-Boltzmann equation**

$$\frac{d^2\psi}{dx^2} = \frac{2z^2e^2n_\infty}{\varepsilon_r\varepsilon_0 k_B T}\psi = \kappa^2\psi$$

unrealistic for most situations; a good qualitative picture of the Gouy-Chapman diffuse double layer

$$\psi(x) = \psi_0 exp(-\kappa x)$$

Coffee break

Time is chasing us…

The Debye screening length (I)

$$\psi(x) = \psi_0 exp(-\kappa x)$$

$$\frac{n_i(x)}{n_i(\infty)} = exp\left(-\frac{w_i}{k_B T}\right)$$

$$w_i = z_i e \psi(x)$$

$$C_i(x) = C_{i,\infty} exp\left[-\frac{z_i e}{k_B T}\psi_0 exp(-\kappa x)\right]$$

- diffuse part of the double layer: enriched in counterions & depleted in co-ions
- sum of the ion concentrations in the double layer larger than their total bulk concentration
  → important for understanding electrostatic repulsion between approaching particles

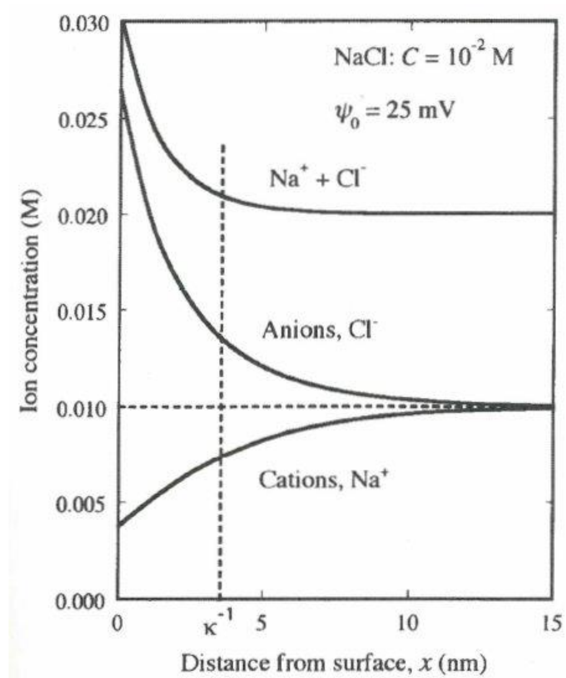


Fig. 6-10: Ion concentration profiles near a charged surface.

C: salt conc. in mol/L

κ^{-1} [=] nm

Debye screening length κ^{-1}
a measure of the thickness of the double layer; κ[=] 1/length

$$\kappa = \sqrt{\frac{2z^2 e^2 n_\infty}{\varepsilon_r \varepsilon_0 k_B T}} = \sqrt{\frac{2000 z^2 e^2 N_{Av}^2 C}{\varepsilon_r \varepsilon_0 RT}}$$

$$\kappa^{-1} = \frac{0.304}{|z|\sqrt{C}}$$

for symmetrical electrolytes

The Debye screening length (II)

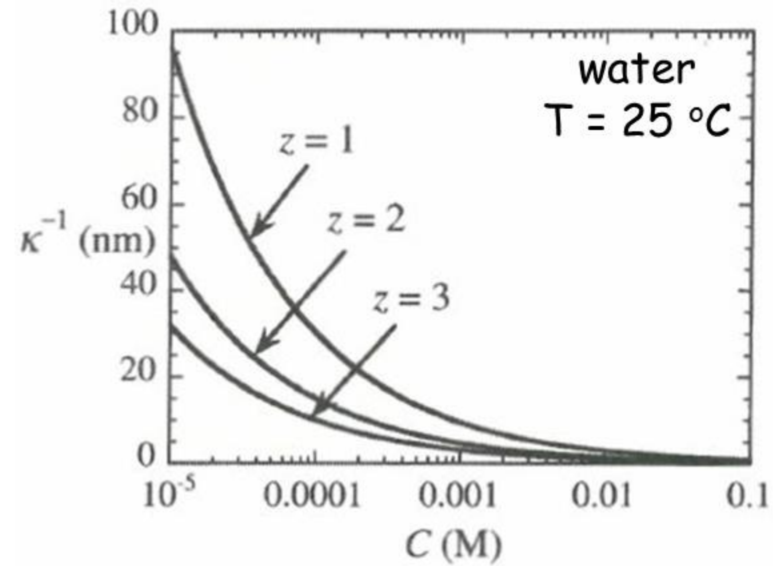
Debye length κ^{-1}

- a property of the electrolyte solution & a measure of its screening power (length scale over which charge carriers screen-out electric fields)

example: NaCl electrolyte solution

- C = 1 M → $\kappa^{-1} \approx$ 0.3 nm
- C = 0.1 M → $\kappa^{-1} \approx$ 1 nm
- C = 0.01 M → $\kappa^{-1} \approx$ 3 nm

- κ^{-1} decreases significantly with ion concentration & valence



For mixed electrolytes:
κ is expressed in terms of the ionic strength I:

$$I = \frac{1}{2}\sum z_i^2 C_i \qquad \kappa = \sqrt{\frac{2000 e^2 N_{Av}^2 I}{\varepsilon_r \varepsilon_0 RT}}$$

For non-aqueous media (@ 25 °C):

$$\kappa^{-1} = \frac{0.0343\sqrt{\varepsilon_r}}{\sqrt{I}} \, [=] \, nm$$

- the lower dielectric constants (ε_r) of organic solvents compared to water (~80) should give thinned double layers, but the much lower ion concentrations yield double layers which are more than one order of magnitude thicker

The Stern model

The Gouy-Chapman model provides a better approximation of reality compared to the Helmholtz model, however its predictions are sometimes unacceptable because:

- assumes that ions are point charges → no physical limits for ions while they approach the surface
- treats all ions (of same valence) as being identical with respect to their adsorption

The Stern model

- modification of Gouy-Chapman model
- double layer consists of an inner & an outer portion
- ***inner portion:*** monolayer of counterions at a distance δ away from the surface; δ = ion radius
- ***Stern plane:*** the plane @ x=δ; all of charge in Stern layer resides here
- assumption: ions can specifically adsorb onto the Stern layer → potential ψ_0-ψ_δ
- ***outer portion:*** this is a Gouy-Chapman diffuse layer, as described before

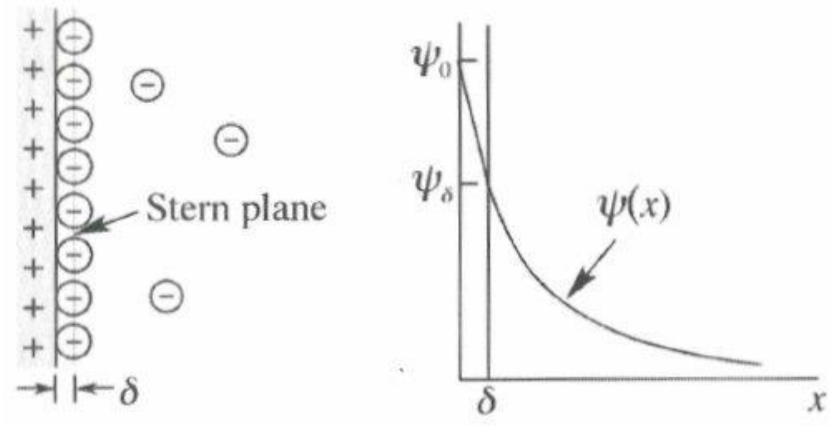


Fig. 6-17: Stern model of the electric double layer.

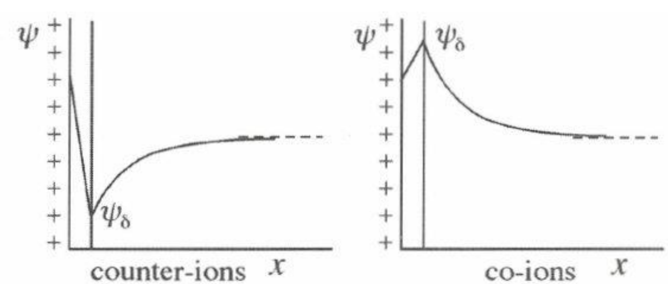


Fig. 6-18: Potential profiles in the case of specific adsorption of counterions (left) and coions (right), in accord with the Stern model.

The zeta potential (I)

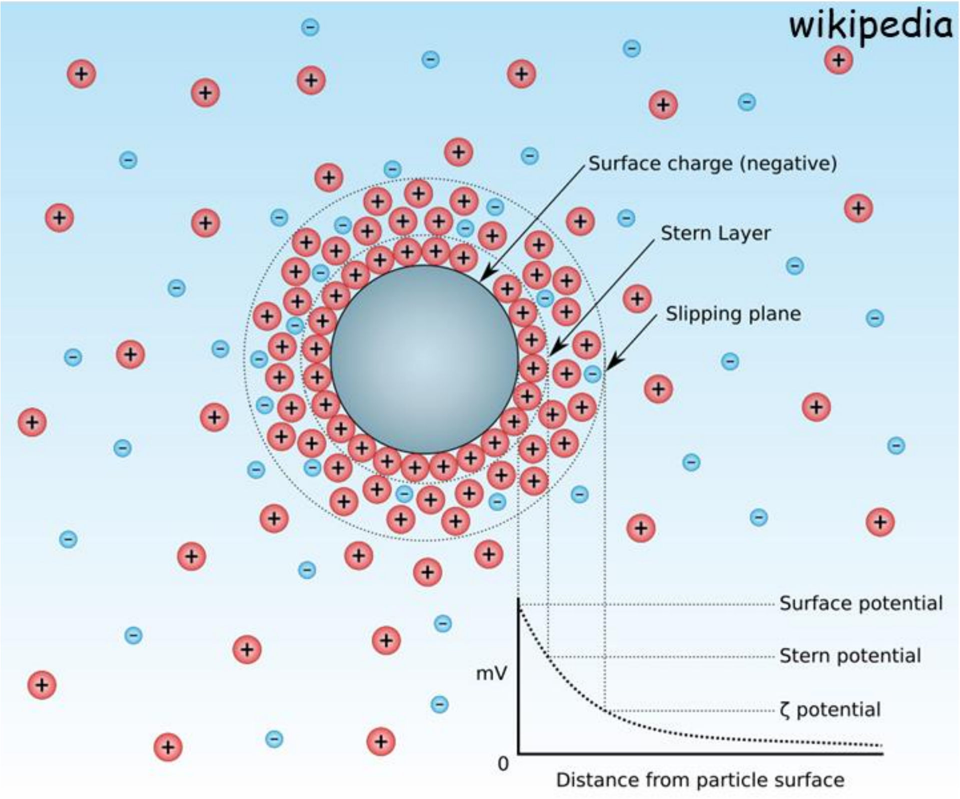
Consider a negatively charged colloid particle dispersed in water

there are three important locations:

- the (physical) particle surface (ψ_0)
- the Stern layer (ψ_δ)
- the slipping plane

The diffuse layer can move under the influence of tangential stress

Slipping plane
conventionally introduced plane that separates mobile fluid from fluid that is attached to the surface



Zeta (ζ) potential
the electric potential corresponding to the slipping plane, [=] V or mV

- not equal to Stern potential or surface potential (different locations)
- practical for determining stability against aggregation

|ζ|	Colloid stability
0 - 5	Rapid coagulation or flocculation
10 - 30	Incipient instability
30 - 40	Moderate stability
40 - 60	Good stability
>60	Excellent stability

The zeta potential (II)

ζ potential of colloidal particles strongly depends on the dispersion pH

Basic continuous phase

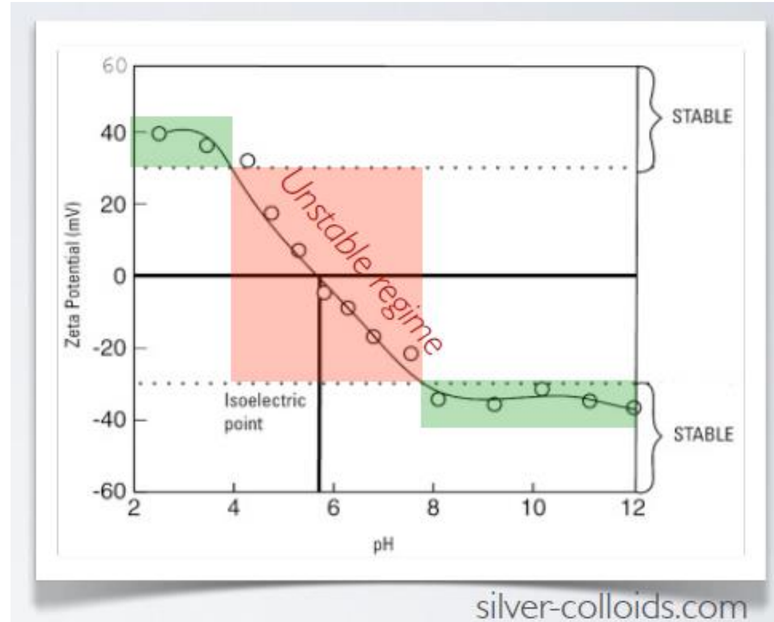
- OH^- ions decrease ζ; particles tend to aqcuire more negative charge

Addition of acid → intermediate pH

- isoelectric point: charge is neutralized
- minimum colloidal stability

Further acid addition→ acidic conditions

- H^+ ions increase ζ, particles positively charged



ζ potential (& stability) can be adjusted by additives (e.g. surfactants)

Addition of cationic surfactant to a dispersion of negatively charged particles

- charge reversal (negative → positive) with increasing surfactant concentration
- dependent on surfactant type

Langmuir **2015**, *31*, 4113

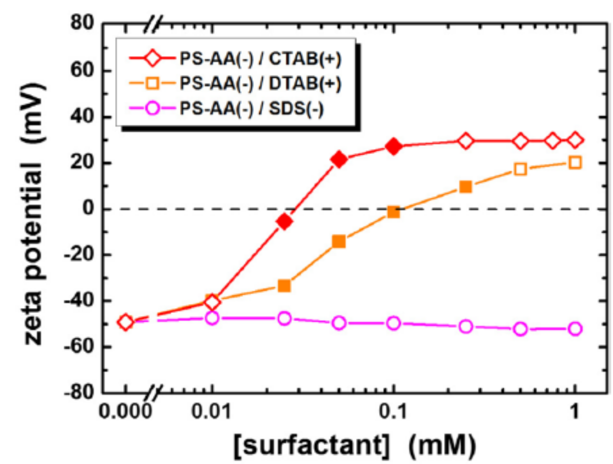


Figure 2. Zeta potential measurements of mixtures of anionic PS particles (PS-AA, 500 nm diameter, 2 mg/mL) with anionic (SDS) or cationic (DTAB, CTAB) surfactants at various concentrations.