École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering

sunmil.epfl.ch

SuNMIL
Supramolecular NanoMaterials and Interfaces Laboratory

Charged Solid-Liquid Interfaces
Lesson 6

MSE 304

Francesco Stellacci

桑缪 썬밀 सानमिल ΣouNMιΛ سنمل CaHMΠЛ

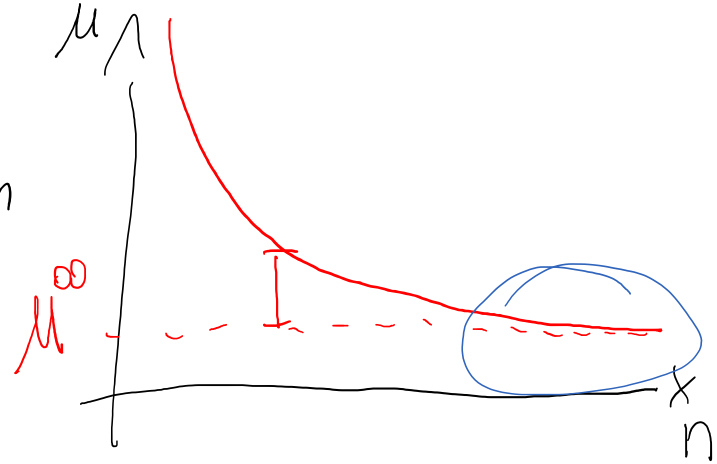
Key Topics in the Previous Class

γ_{12} → interfacial energy

→ phase transition temperature for phases of finite size

→ nucleation and growth

→ melting point depression



SuNMIL EPFL

The Chemical Potential of a Real Material

potential

$$dG = V\,dp - S\,dT + \sum_\alpha \sum_i \mu_i^\alpha \, dn_i^\alpha + \sum_{\alpha\beta} \gamma_{\alpha\beta}\, dA_\alpha + zF\psi\, dn_i$$

charge of the carrier

Faraday constant

equilibrium condition $\mu_i^\alpha = \mu_i^\beta \quad \forall i, \forall \alpha$

$$\mu_i^\alpha = \left(\frac{\delta G}{\delta n_i^\alpha}\right)_{T,P,n_{j\neq i}} = \mu_i^{\infty,\alpha} + \left(\frac{\delta\left[\gamma_{\alpha\beta}\, dA_\alpha\right]}{\delta n_i^\alpha}\right)_{T,P,n_{j\neq i}}$$

$$= \mu_i^{\infty,\alpha} + \mu_i^{s,\alpha} + zF\psi$$

SuNMIL EPFL

Equilibrium for Materials with Charged Interfaces

α = solid phase

$$\mu_i^{\alpha} = \mu_i^{\infty} + \mu_i^{s,\alpha\beta} + zF\varphi_0 = \mu_i^{0,\infty} + \underbrace{RT\ln a_i^{\alpha}}_{=0} + \cancel{\mu_i^{s,\alpha\beta}} + zF\varphi_0$$

very large

≈ ideality

$\rightarrow a_i = 1$

$\rightarrow \approx 0$

β = liquid phase

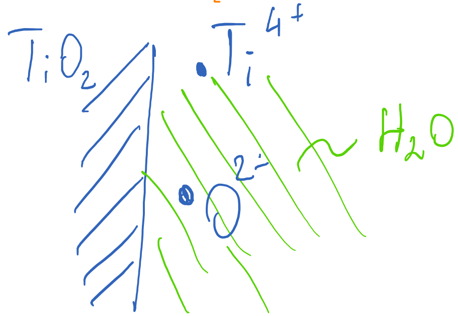
$$\mu_i^{\beta} = \mu_i^{\infty} + zF\varphi_0 = \mu_i^{0,\infty} + RT\ln c_i^{\beta} + \cancel{zF\varphi_0}$$

$\rightarrow \varphi_0 = 0$

$\rightarrow$ neutral

$$\mu_i^{\alpha} = \mu_i^{\beta}$$

$$\mu_{Ti}^{\alpha} = \mu_{Ti}^{\beta}$$



The Point of Zero Charge

$$\mu_i^{0,\alpha} + zF\psi_0 = \mu_i^{0,\beta} + RT \ln C_i^{\beta}$$

$$\Delta\mu^{\alpha\beta} = \mu_i^{0,\beta,\infty} - \mu_i^{0,\alpha,\infty}$$

PZC = point of zero charge

$\psi_0 = 0 \qquad -\Delta\mu^{\alpha\beta} = RT \ln C_i^{PZC}$

$$\psi_0 = \frac{\Delta\mu^{\alpha\beta}}{zF} + \frac{RT}{zF}\ln C_i = \underline{\frac{RT}{zF}\left(\ln C_i - \ln C_i^{PZC}\right)} = \frac{RT}{zF}\ln\frac{C_i}{C_i^{PZC}}$$

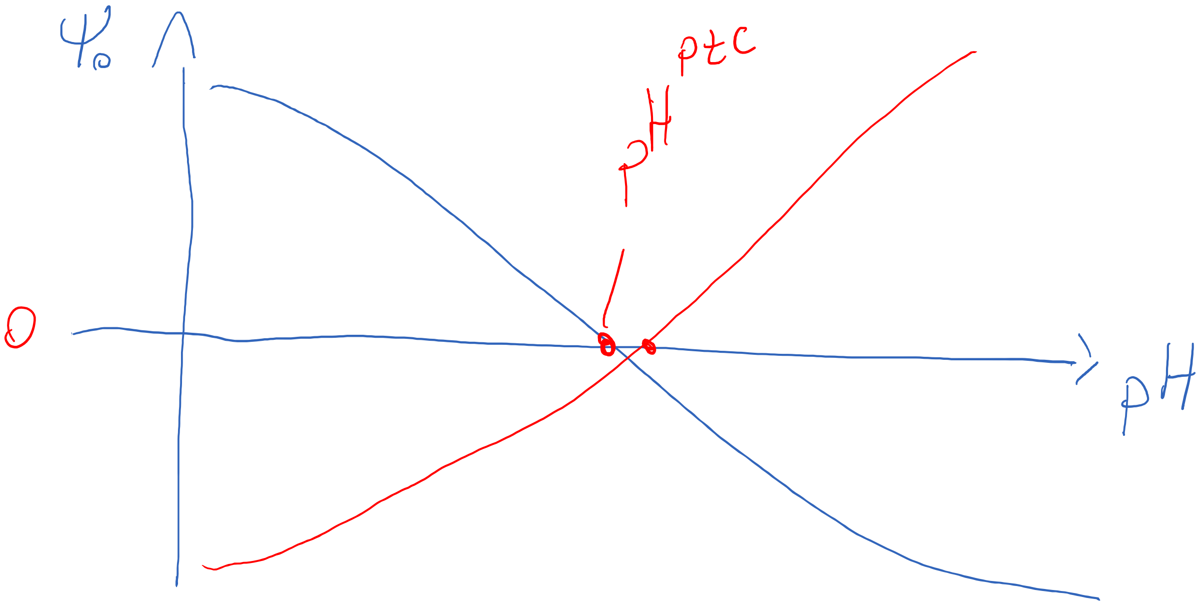
$i = H^+ \qquad \psi_0 = \frac{RT}{zF}\left(\ln [H^+] - \ln [H^+]^{PZC}\right)$

SuNMIL EPFL

Surface Charge at an Interface

$$\psi_0 = -0.059\left(pH - pH^{pzc}\right)$$

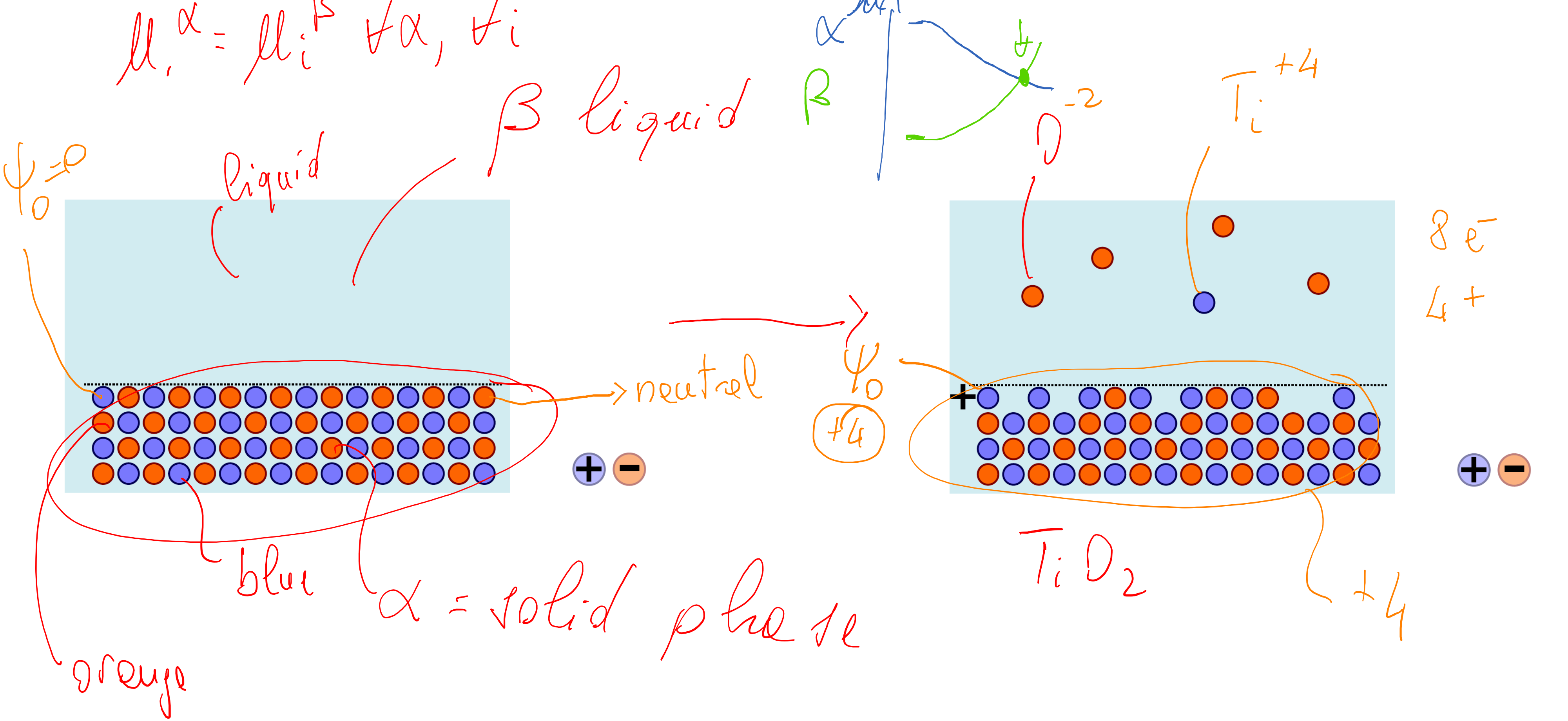
@ Room temperature



Atomistic Origin of the Surface Potential

$H^+ + OH^- \rightleftharpoons H_2O$

$\mu_i^\alpha = \mu_i^\beta \quad \forall \alpha, \forall i$



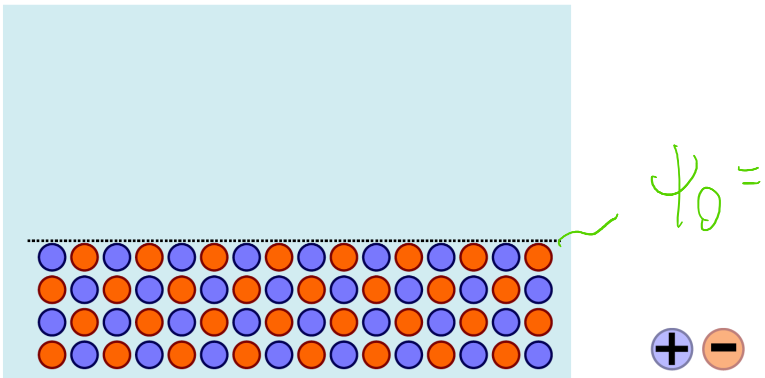
SuNMIL EPFL

Atomistic Origin of the Surface Potential

Na^+

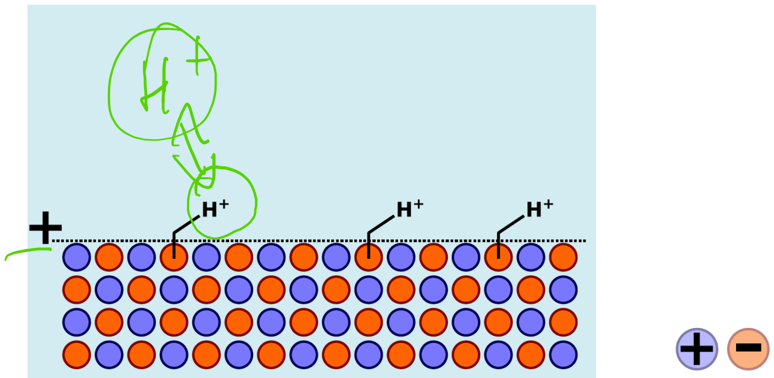
Cl^-

OH^-



$\psi_0 = 0$

ψ_0

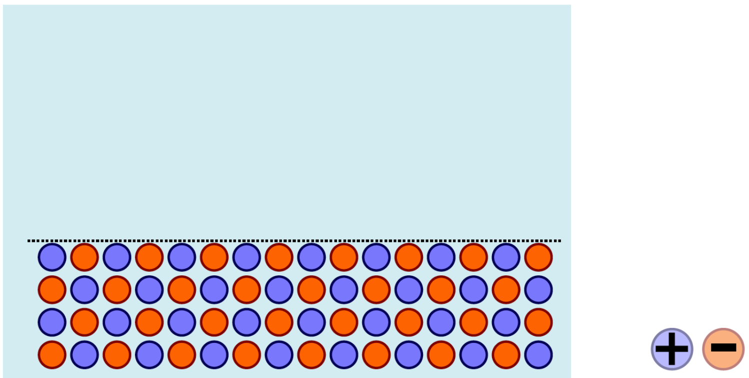


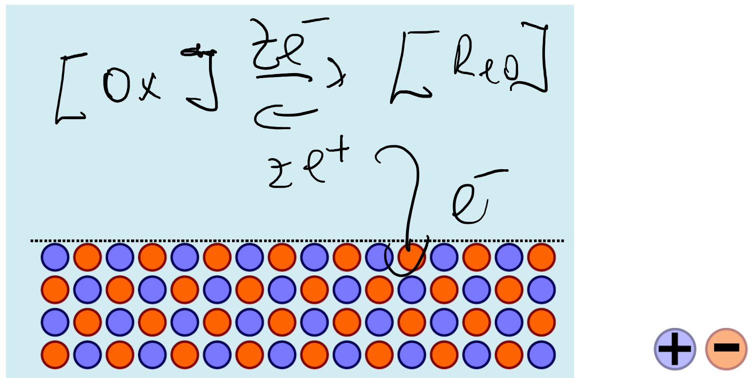
chemically modify the surface

SuNMIL EPFL

Atomistic Origin of the Surface Potential

Redox equilibrium potential



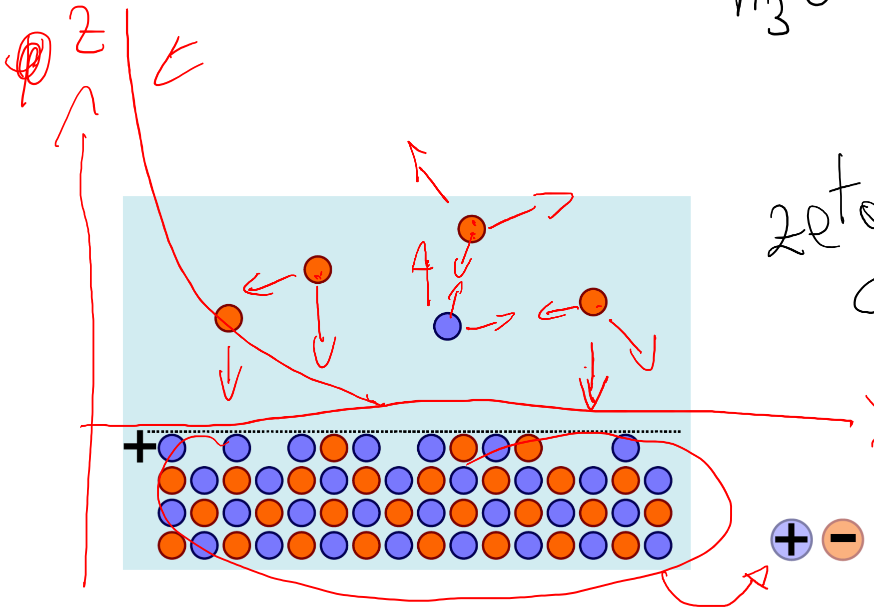


$$\Psi_0 = \Psi_0(\text{crystallography, shape, composition of } \alpha, \beta \text{ phase})$$

The Helmholtz Plane // Stern layer

H_3O^+, OH^-

z

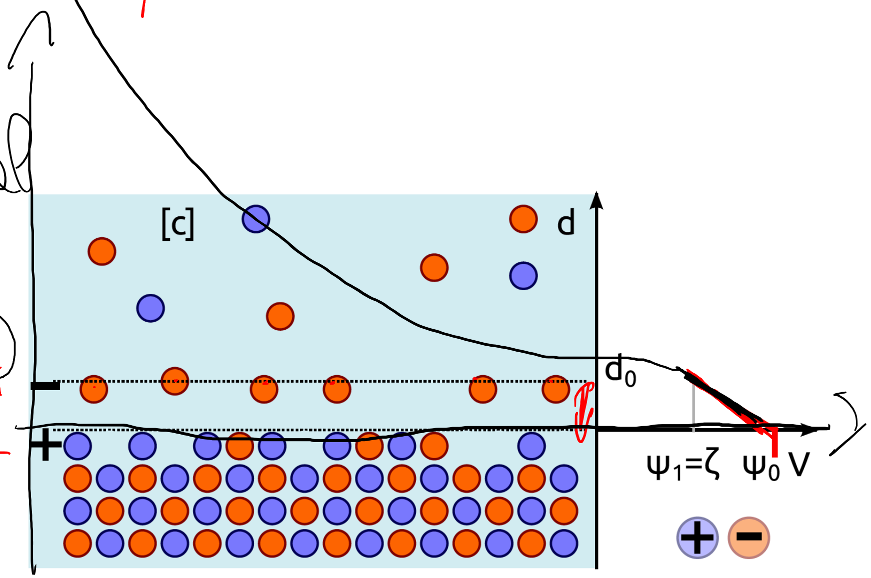


zeta potential

ζ

ψ_1

ψ_0

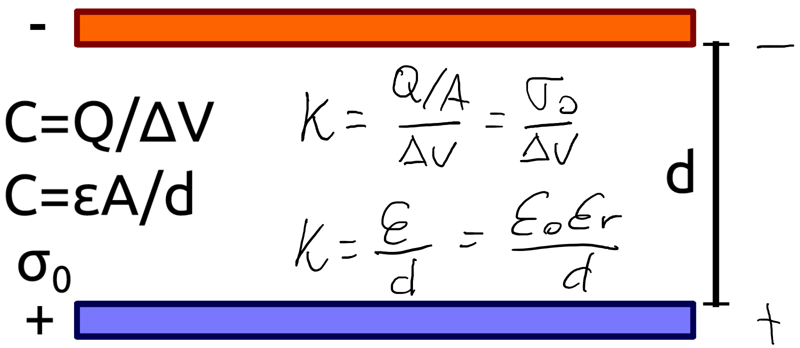


surface potential

The Helmholtz Plane

$$\Delta V = \psi_1 - \psi_0$$

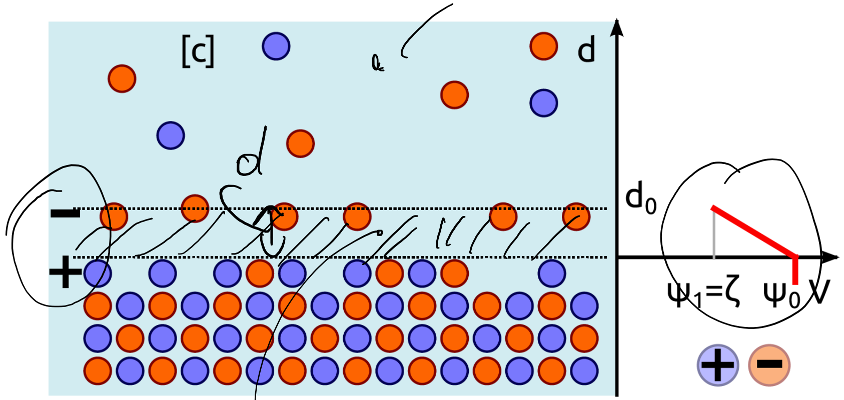
$$K = \frac{C}{A} \qquad \frac{Q}{A} = \sigma_0 \text{ charge density}$$



$$K = \frac{Q/A}{\Delta V} = \frac{\sigma_0}{\Delta V}$$

$$K = \frac{\varepsilon}{d} = \frac{\varepsilon_0 \varepsilon_r}{d}$$

$\varepsilon_r = 3$



$\varepsilon_r = 80$

$$K = \frac{\sigma_0}{\psi_1 - \psi_0} = \frac{\varepsilon_0 \varepsilon_r}{d}$$

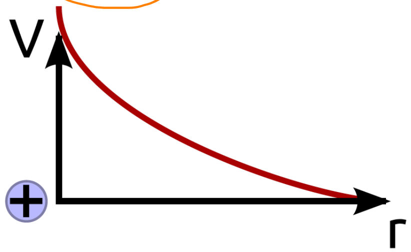
$$\psi_1 = \psi_0 + \frac{\sigma_0 d}{\varepsilon_0 \varepsilon_r}$$

ζ surface potential

$\boxed{\psi_1 \text{ @ PZC ?}}$

The Helmholtz Plane

$$\psi_0(r) = \frac{e}{4\pi\epsilon_0\epsilon_r}\frac{z_+}{r}$$



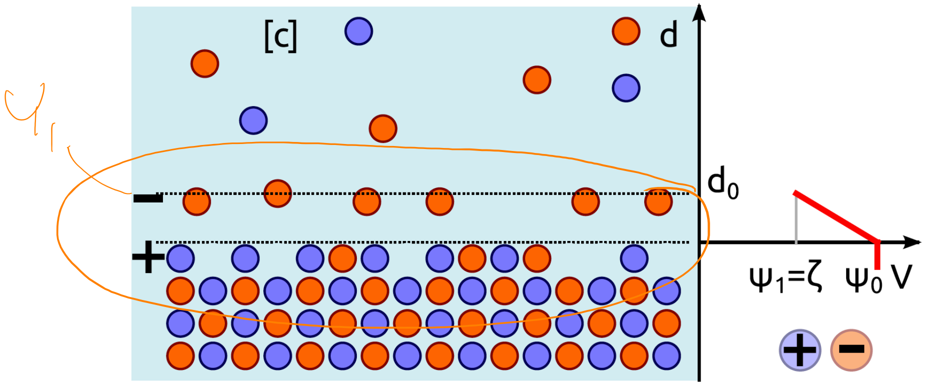
- Electric potential induced by an ion in a dielectric medium

$z_+ e$

electron $z = -1$

H^+ $z = +1$

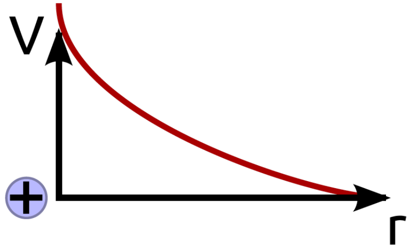
Ca^{2+} $z = +2$

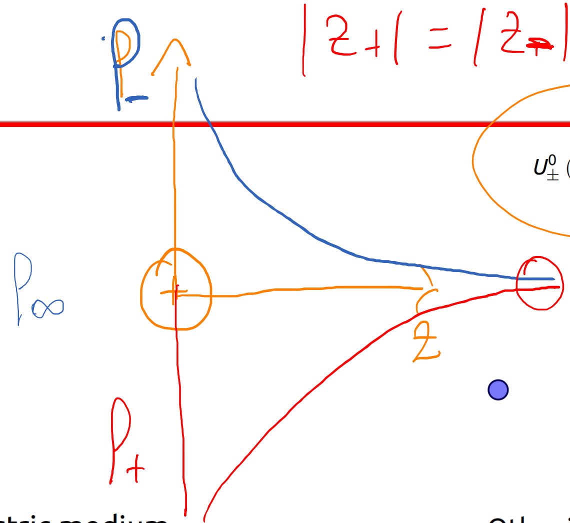


Debye-Hückel Theory

$|z_+| = |z_-|$

$$\psi_0(r) = \frac{e}{4\pi\epsilon_0\epsilon_r}\frac{z_+}{r}$$

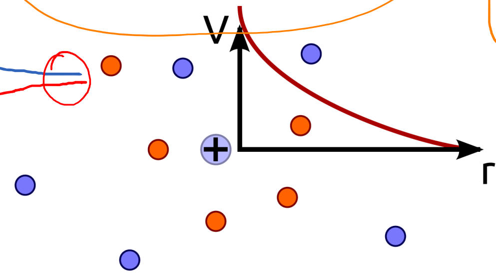




- Electric potential induced by an ion in a dielectric medium

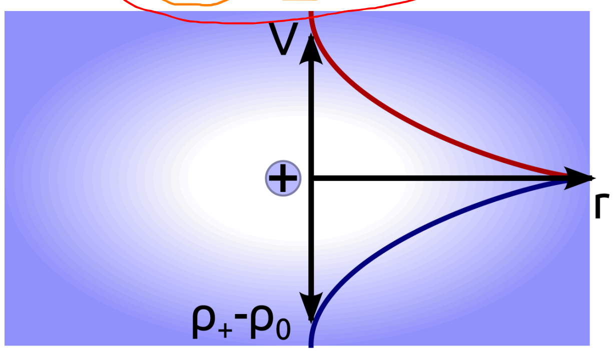
$$U^0_\pm(r) = ez_\pm\psi_0(r) = \frac{e^2}{4\pi\epsilon_0\epsilon_r}\frac{z_\pm z_+}{r}$$

$U = \psi \cdot z_\pm e$



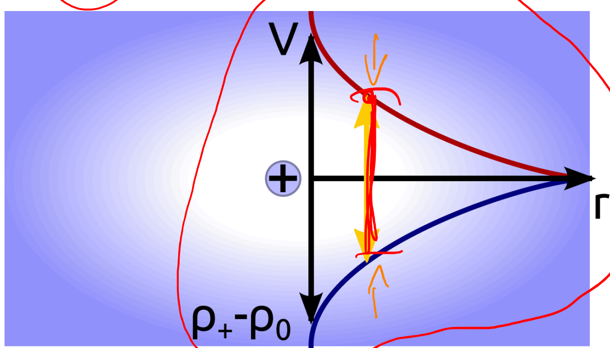
- Other ions interact with this potential

$$\rho_\pm(r) = \exp - \frac{ez_\pm}{k_B T}\psi(r)$$



$$\nabla^2\psi = -\frac{\rho}{\epsilon_0\epsilon_r}$$

$$\nabla^2\psi = -\frac{\rho}{\epsilon_0\epsilon_r} = -\frac{e}{\epsilon_0\epsilon_r}\left[z_+\rho_+ + z_-\rho_-\right]$$



- Mean-field model: ion distribution represented by a Boltzmann density

Debye-Hückel Theory

$$\nabla^2\psi = 2\frac{n^\infty z e}{\varepsilon_1\varepsilon_0}\sinh\left(\frac{ze\psi}{kT}\right)$$

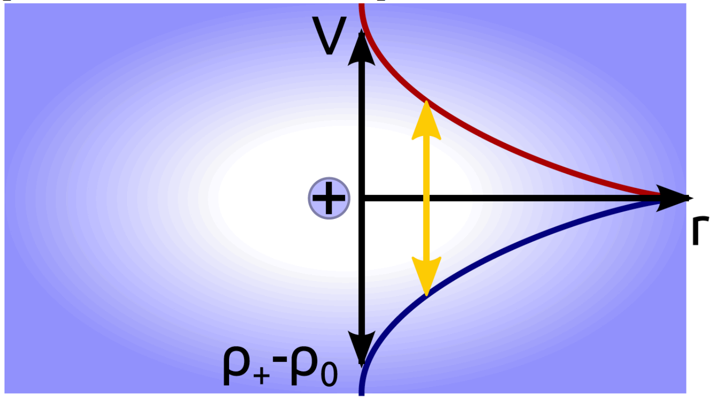
if $|z_+| = |z_-|$

$n^\infty \cdot z$ = ionic strength $\neq \frac{n_+ z + n_- z}{2}$

$$\nabla^2\psi = -\frac{eC}{\epsilon_0\epsilon_r}\left[z_+ n_+ e^{-\frac{ez_+}{k_BT}\psi} + z_- n_- e^{-\frac{ez_-}{k_BT}\psi}\right] \approx \frac{e}{\epsilon_0\epsilon_r}\frac{eC}{k_BT}\left[n_+ z_+^2 + n_- z_-^2\right]\psi = \kappa^2\psi$$

1M

CaO 2M



1.5M

- Can be solved analytically if **linearized**

1M

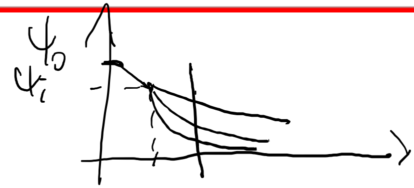
$CaCl_2 \rightarrow Ca^{+2} + 2Cl^{-1}$

$2[Ca^{2+}] = [Cl^{-1}]$

$n_+C = n_-C$

$n^\infty = n_+C = n_-C$

Debye Length



$$\nabla^2\psi = 2\frac{n^\infty ze}{\varepsilon_1\varepsilon_0}\sinh\left(\frac{ze\psi}{kT}\right)$$

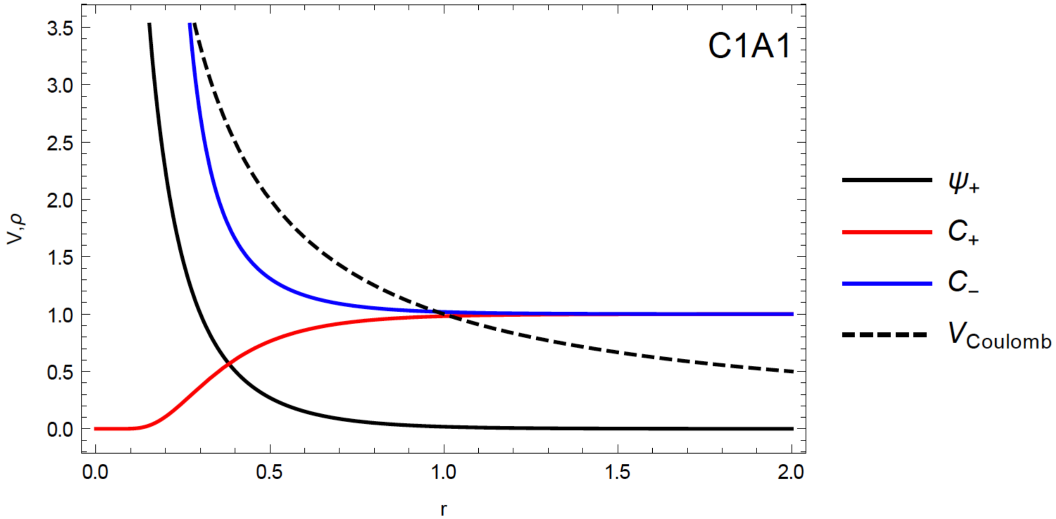
- Solving the Poisson-Boltzmann equation.

$$\boxed{\psi(r) = \frac{ez_+}{4\pi\epsilon_0\epsilon_r}\frac{e^{-\kappa r}}{r},} \quad \boxed{\kappa^2 = \frac{e^2}{\epsilon_0\epsilon_r}\frac{n_+z_+^2 + n_-z_-^2}{k_BT}}$$

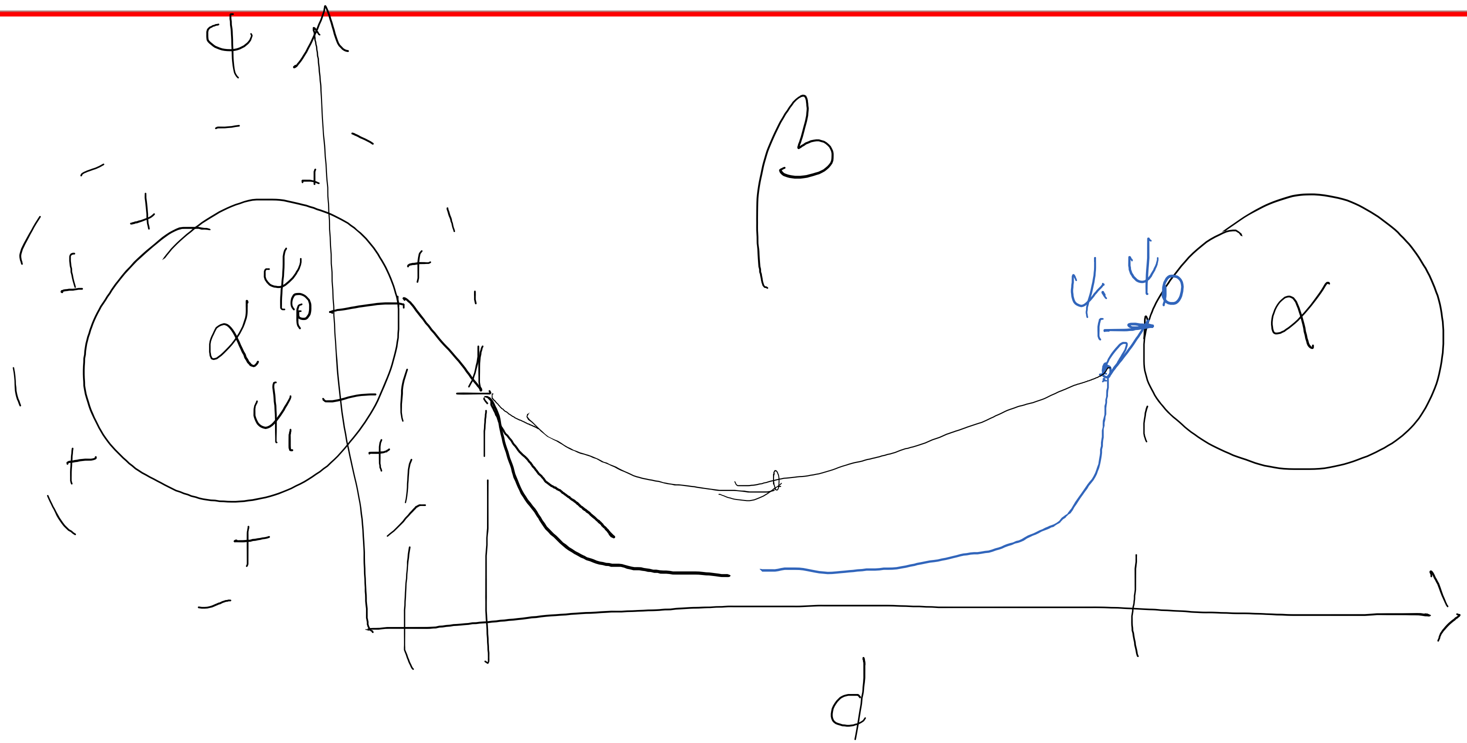
κ^2

$\frac{1}{\kappa} = \lambda_D$ Debye length

$\psi\left(\frac{1}{\kappa}\right) = \frac{1}{e}\psi_1 = \frac{\zeta}{e}$



Colloidal Particles



Colloidal Particles

$$\nabla^2\psi = 2\frac{n^\infty ze}{\varepsilon_1\varepsilon_0}\sinh\left(\frac{ze\psi}{kT}\right)$$

κ

a

TABLE 5.1 Solutions to the Poisson–Boltzmann equation for microparticles and nanoparticles

	Small κa	Large κa
Low potentials	$\psi(r) = \psi_0 \frac{a}{r}\exp[-\kappa(r-a)]$	$\psi(x) = \psi_0 \exp(-\kappa x)$
High potentials	$\nabla^2\psi = \frac{2zn^\infty e}{\varepsilon_r\varepsilon_0}\sinh\left(\frac{e\psi}{kT}\right)$	$\tanh\left(\frac{ze\psi(x)}{4kT}\right) = \tanh\left(\frac{ze\psi_0}{4kT}\right)\exp(-\kappa x)$
	where $\kappa^2 = \frac{2z^2e^2n^\infty}{\varepsilon_r\varepsilon_0 kT}$	

Colloidal Particles

$$\nabla^2\psi = 2\frac{n^\infty ze}{\varepsilon_1\varepsilon_0}\sinh\left(\frac{ze\psi}{kT}\right)$$

TABLE 5.1 Solutions to the Poisson–Boltzmann equation for microparticles and nanoparticles

	Small κa	Large κa
Low potentials	$\psi(r) = \psi_0 \frac{a}{r}\exp[-\kappa(r-a)]$	$\psi(x) = \psi_0 \exp(-\kappa x)$
High potentials	$\nabla^2\psi = \frac{2zn^\infty e}{\varepsilon_r\varepsilon_0}\sinh\left(\frac{e\psi}{kT}\right)$	$\tanh\left(\frac{ze\psi(x)}{4kT}\right) = \tanh\left(\frac{ze\psi_0}{4kT}\right)\exp(-\kappa x)$
	where $\kappa^2 = \frac{2z^2e^2n^\infty}{\varepsilon_r\varepsilon_0 kT}$	

$$V_{rep} = 4\pi\varepsilon_1\varepsilon_0\zeta^2\frac{a^2}{r}\exp\left[-\kappa a\left(\frac{r}{a}-2\right)\right]$$

Unfortunately they attract by van der Waals forces:

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

A is the Hamaker constant.

why is there an attraction potential

Colloidal Particles

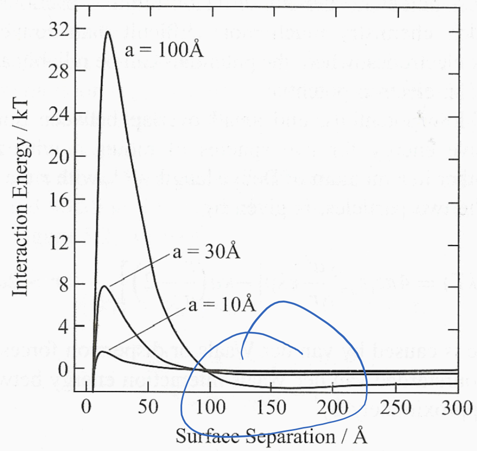
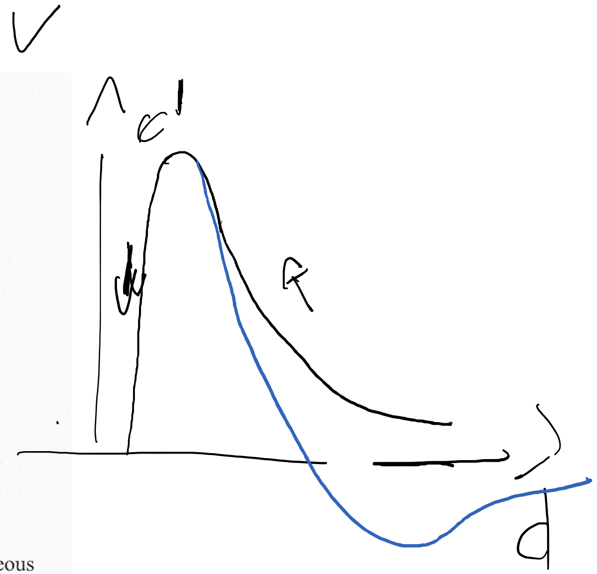


FIGURE 5.4 Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation, for several particle radii. Hamaker constant = 25×10^{-20} J, $I = 1$ mM, $\psi_0 = 0.10$ V, $a = 1.0$ nm, 3.0 nm, and 10.0 nm, Debye length = 10 nm. Note that the secondary minimum is negligible for nanoparticles, but becomes important above 10 nm.



are colloids stable

what is the meaning of this

SuNMIL EPFL

Conclusions

1) surfece @ a solid liqeuid
interfece will get charged
to establish an equilibrium
2) there will be an Helmholtz plane
3) a specific charge distribution
in solution

SuNMIL EPFL