# Electrokinetic Phenomena in Micro- and Nanochannels

## I. Electrostatic Potential in Micro and Nanochannels

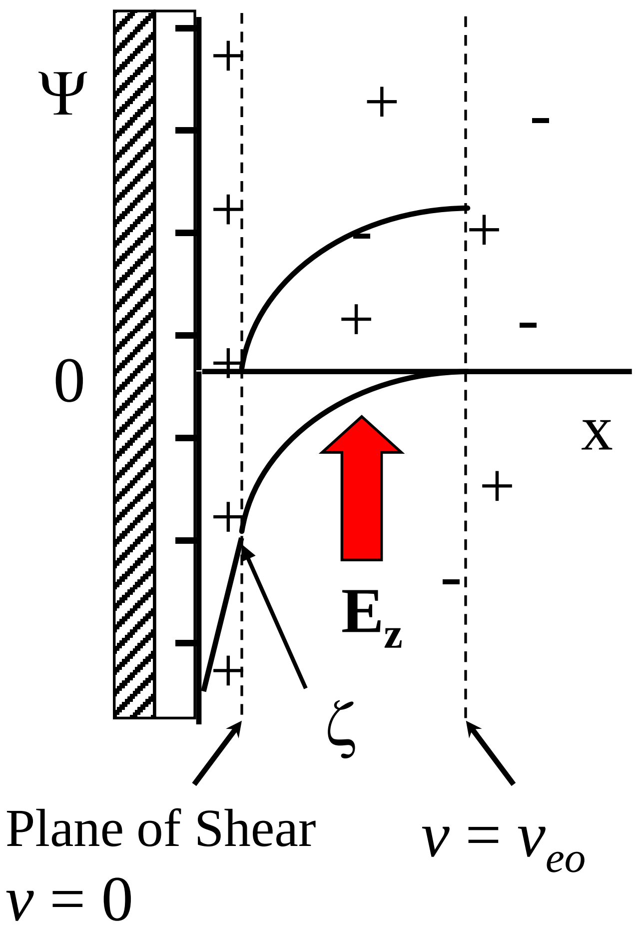
*CBE/NE/BME 525*

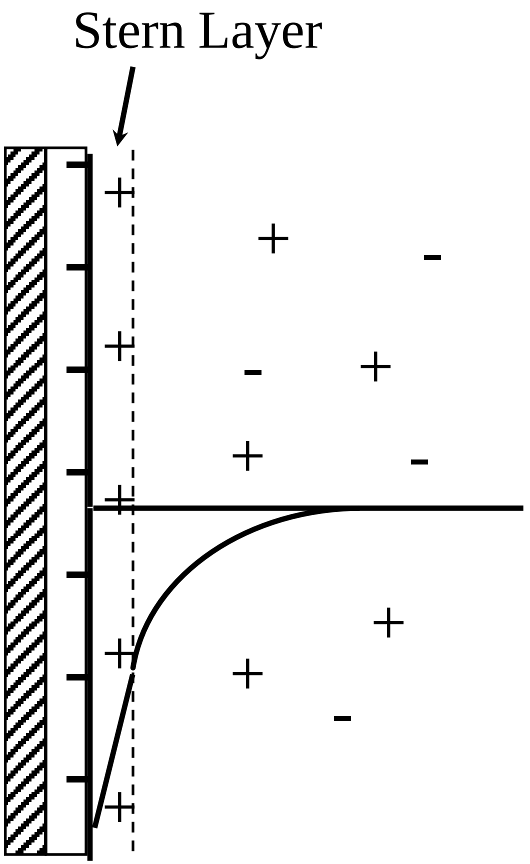
**D. N. Petsev**

# Outline

1. Concept of Electric Double Layer.  Stern layer
2. Poisson and Poisson-Boltzman Equations.
3. Approximated and exact solutions for some typical cases.
4. Surface Charge and Stern Theory

# Solid Liquid Interface and Characteristic Lengths



# Poisson and Poisson-Boltzmann Equations

Poisson

$$\nabla \bullet \varepsilon \nabla \Psi = -\frac{\rho_e}{\varepsilon_0}$$

$$\nabla^2 \Psi = -\frac{\rho_e}{\varepsilon \varepsilon_0}, \quad \varepsilon = \text{const}$$

$\Psi$ – electrostatic potential

$\rho_e$ – charge density

$\varepsilon$– relative dielectric permittivity (78.25)

$\varepsilon_0$ – dielectric constant in vacuum

($8.854 \times 10^{-12}$ F $m^{-1}$)

Poisson-Boltzmann

(Nonlinear)

$$\rho_e = e \sum_i z_i n_i, \quad e = 1.60217646 \times 10^{-19} \text{ Coulombs}$$

$$n_i = n_i^0 \exp\left( -\frac{z_i e \Psi}{kT} \right)$$

$$\nabla^2 \Psi = -\frac{e}{\varepsilon \varepsilon_0} \sum_i z_i n_i^0 \exp\left( -\frac{z_i e \Psi}{kT} \right)$$

For $\rho_e = 0$, Laplace Equation $\nabla^2 \Psi = 0$

# Poisson-Boltzmann Equation: Special Cases

Low potential

(Linear)

$$\frac{z_i e\Psi}{kT} \ll 1, \quad \frac{kT}{e} = 25.9 \text{ mV at } T = 298^{\circ} K$$

$$\nabla^2 \Psi = \kappa^2 \Psi, \quad \kappa = \left( \frac{e^2 \sum_i z_i^2 n_i^0}{\varepsilon \varepsilon_0 kT} \right)^{\frac{1}{2}} \leftarrow \quad \text{Inverse Debye length}$$

Binary symmetric electrolyte

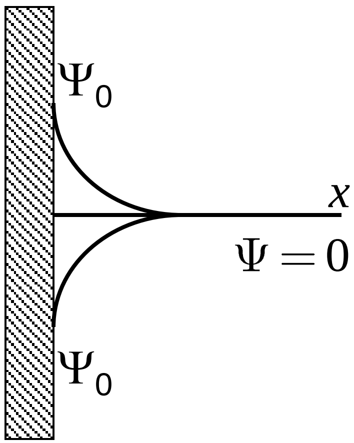
(Nonlinear)

$$\nabla^2 \left( \frac{ze\Psi}{kT} \right) = \kappa^2 \sinh\left( \frac{ze\Psi}{kT} \right), \quad z_1 = z_2 = z$$

$$\nabla^2 \tilde{\Psi} = \kappa^2 \sinh \ \tilde{\Psi} \ , \quad \tilde{\Psi} = \frac{ze\Psi}{kT}$$

# Poisson-Boltzmann Equation: Approximate Solutions

## Low Surface Potential, Single Double Layer



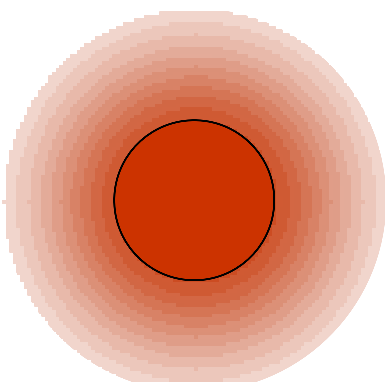

Flat Double Layer

Gouy & Chapman, Debye & Huckel

$$\nabla^2 \Psi = \frac{d^2\Psi}{dx^2} = \kappa^2 \Psi$$

$\Psi = \Psi_0$ at the surface, $\Psi = 0$ at infinity

$$\boxed{\Psi = \Psi_0 \exp\ -\kappa x}$$



Spherical Double Layer

$$\nabla^2 \Psi = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\Psi}{dr} \right) = \kappa^2 \Psi$$

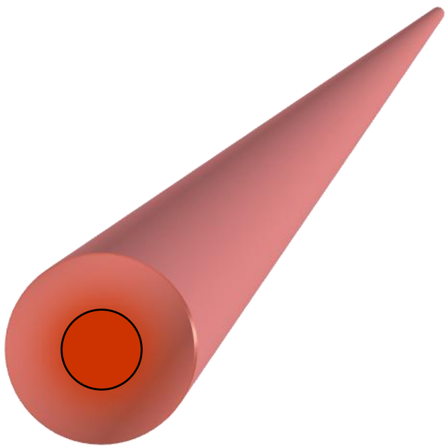
$\Psi = \Psi_0$ at the surface ($r = R$), $\Psi = 0$ at infinity

$$\boxed{\Psi = \Psi_0 \frac{\exp\left[-\kappa\ \ r - R\ \right]}{r}}$$

# Poisson-Boltzmann Equation: Approximate Solutions

## Low Surface Potential, Single Double Layer

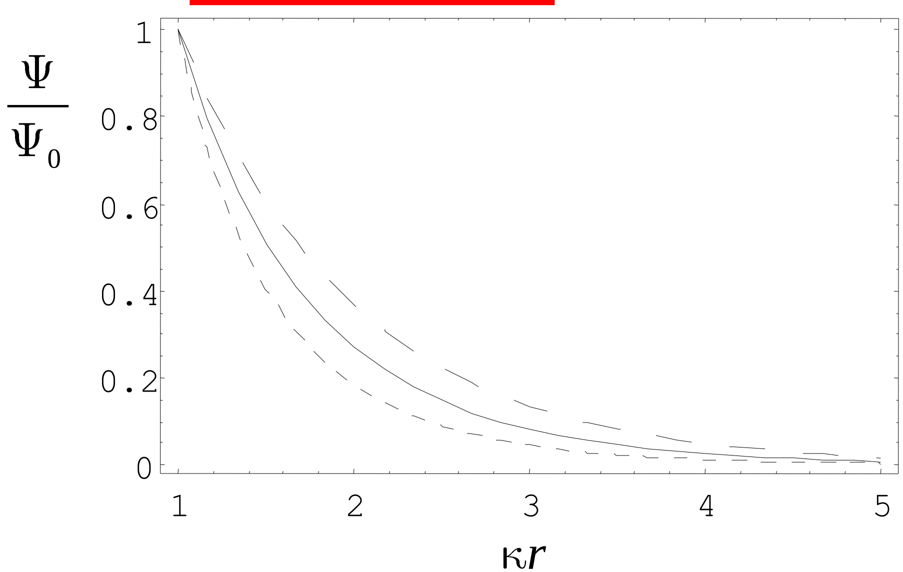
Potential around and outside an infinitely long cylinder



$$\nabla^2\Psi = \frac{1}{r}\frac{d}{dr}\left(r\frac{d\Psi}{dr}\right) = \kappa^2\Psi$$

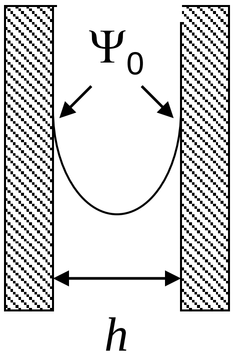
$\Psi = \Psi_0$ at the surface ($r = R$), $\Psi = 0$ at infinity

$$\boxed{\Psi = \Psi_0 \frac{K_0(\kappa r)}{K_0(\kappa R)}}$$



# Poisson-Boltzmann Equation: Approximate Solution. Low Surface Potential, Potential Distribution in a Plane-Parallel Slit or Cylindrical Capillary

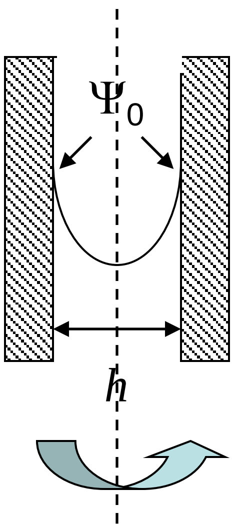
J. Th. G. Overbeek; Rice & Whitehead




$$\nabla^2\Psi = \frac{d^2\Psi}{dx^2} = \kappa^2\Psi$$

$$\Psi = \Psi_0 \text{ at the surface, } \frac{d\Psi}{dx} = 0 \text{ in the center}$$

$$\boxed{\Psi = \Psi_0 \frac{\cosh\left[\kappa\ \ h/2 - x\ \right]}{\cosh\ \ \kappa h/2}}$$



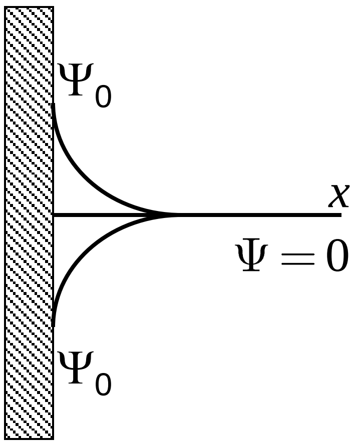

$$\nabla^2\Psi = \frac{1}{r}\frac{d}{dr}\left(r\frac{d\Psi}{dr}\right) = \kappa^2\Psi$$

$$\Psi = \Psi_0 \text{ at the surface } (r = R),\ \frac{d\Psi}{dr} = 0 \text{ in the center}$$

$$\boxed{\Psi = \Psi_0 \frac{\mathrm{I}_0\ \ \kappa r}{\mathrm{I}_0\ \ \kappa R}}$$

# Poisson-Boltzmann Equation: Exact Solution for Single Double Layer, Arbitrary Surface Potential

Flat Double Layer, Symmetric Electrolyte




$$\nabla^2\left(\frac{ze\Psi}{kT}\right) = \frac{d^2}{dx^2}\left(\frac{ze\Psi}{kT}\right) = \kappa^2 \sinh\left(\frac{ze\Psi}{kT}\right), \quad z_1 = z_2 = z$$

$$\nabla^2\tilde{\Psi} = \frac{d^2\tilde{\Psi}}{dx^2} = \kappa^2 \sinh\ \tilde{\Psi}\ , \quad \tilde{\Psi} = \frac{ze\Psi}{kT}$$

$$\Psi = \Psi_0 \text{ at the surface, } \Psi = 0, \frac{d\Psi}{dx} = 0 \text{ at infinity}$$

Solution

# Poisson-Boltzmann Equation: Exact Solution for Single Double Layer, Arbitrary Surface Potential.

## Solution

$$2\frac{d\tilde{\Psi}}{dx}\frac{d^2\tilde{\Psi}}{dx^2} = \kappa^2 \sinh \tilde{\Psi} \; 2\frac{d\tilde{\Psi}}{dx} \quad \Rightarrow \quad \frac{d}{dx}\left(\frac{d\tilde{\Psi}}{dx}\right)^2 = 2\kappa^2 \sinh \tilde{\Psi} \; \frac{d\tilde{\Psi}}{dx}$$

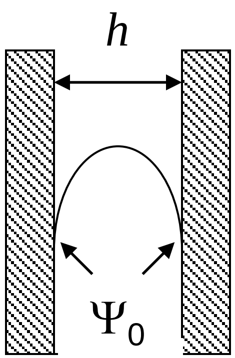
$$\int_{\frac{d\tilde{\Psi}}{dx}}^{0} d\left(\frac{d\tilde{\Psi}}{dx}\right)^2 = 2\kappa^2 \int_{\tilde{\Psi}}^{0} \sinh \tilde{\Psi} \; d\tilde{\Psi} \quad \Rightarrow \quad \left(\frac{d\tilde{\Psi}}{dx}\right)^2 = 2\kappa^2 \left[\cosh \tilde{\Psi} - 1\right] \qquad \text{1st Integration}$$

$$\frac{d\tilde{\Psi}}{dx} = \kappa \sqrt{2\left[\cosh \tilde{\Psi} - 1\right]} \quad \Rightarrow \quad \int_{\tilde{\Psi}_0}^{\tilde{\Psi}} \frac{d\tilde{\Psi}}{\sqrt{2\left[\cosh \tilde{\Psi} - 1\right]}} = \kappa \int_0^x dx \qquad \text{2nd Integration}$$

$$\boxed{\tilde{\Psi} \;\; x = 4\,\mathrm{artanh}\left[\tanh\left(\frac{\tilde{\Psi}_0}{4}\right)\exp \; -\kappa x\right] = 2\ln\left[\frac{1+\tanh \frac{\tilde{\Psi}_0}{4} \; \exp \; -\kappa x}{1-\tanh \frac{\tilde{\Psi}_0}{4} \; \exp \; -\kappa x}\right]}$$

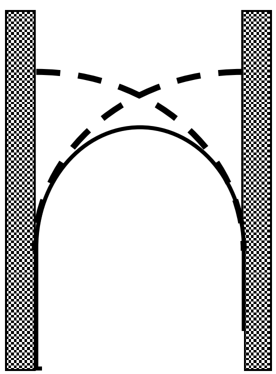
# Poisson-Boltzmann Equation: Weak Double Layer Overlap Approximation. Potential Distribution in a Slit

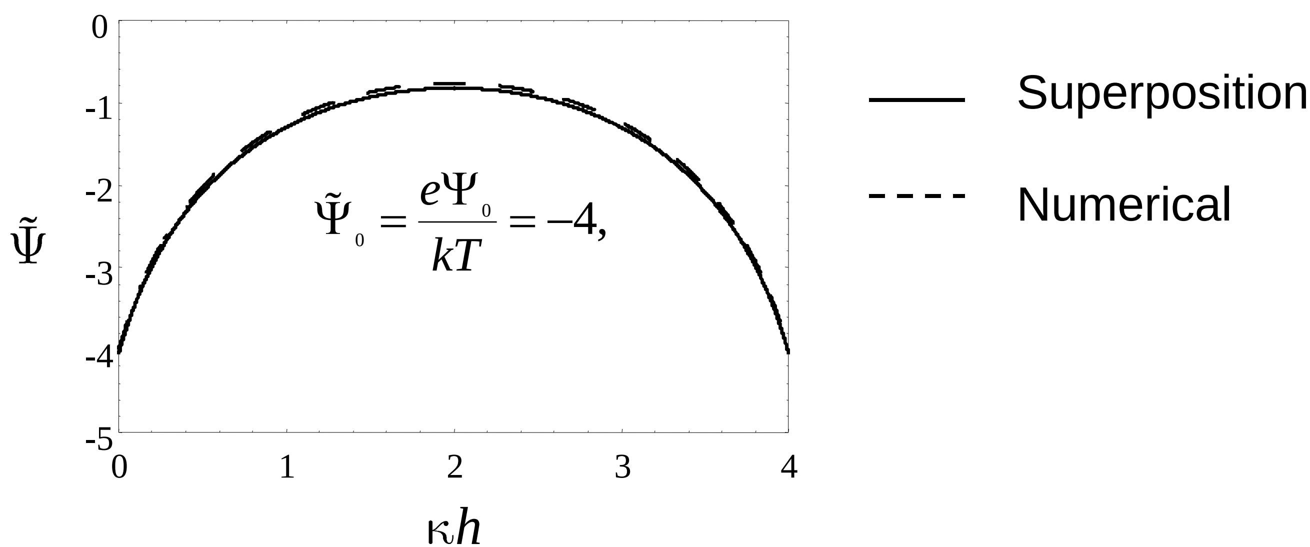
Derjaguin & Landau; Verwey & Overbeek



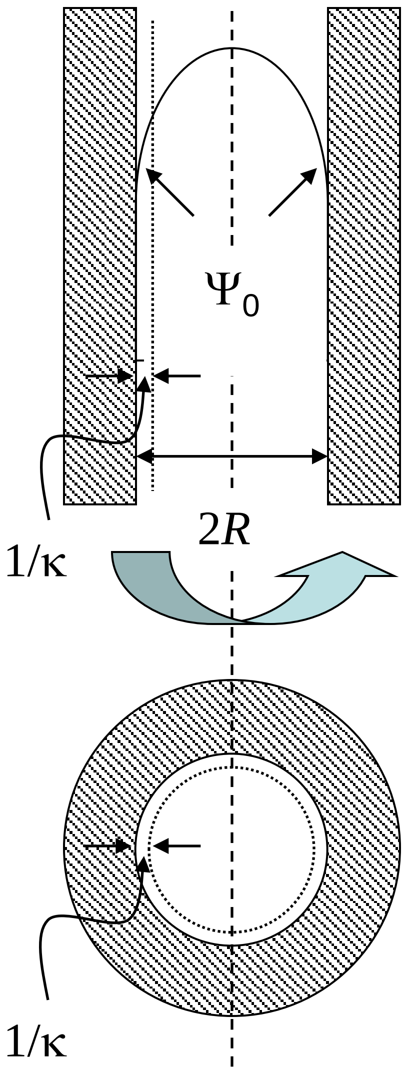

Weak Double Layer Approximation $\kappa h \geq 4$

$$\tilde{\Psi}(x) = \tilde{\Psi}_{\text{single}}(x) + \tilde{\Psi}_{\text{single}}(h-x)$$





# Poisson-Boltzmann Equation: Weak Double Layer Overlap Approximation. Potential Distribution in a Cylindrical Capillary

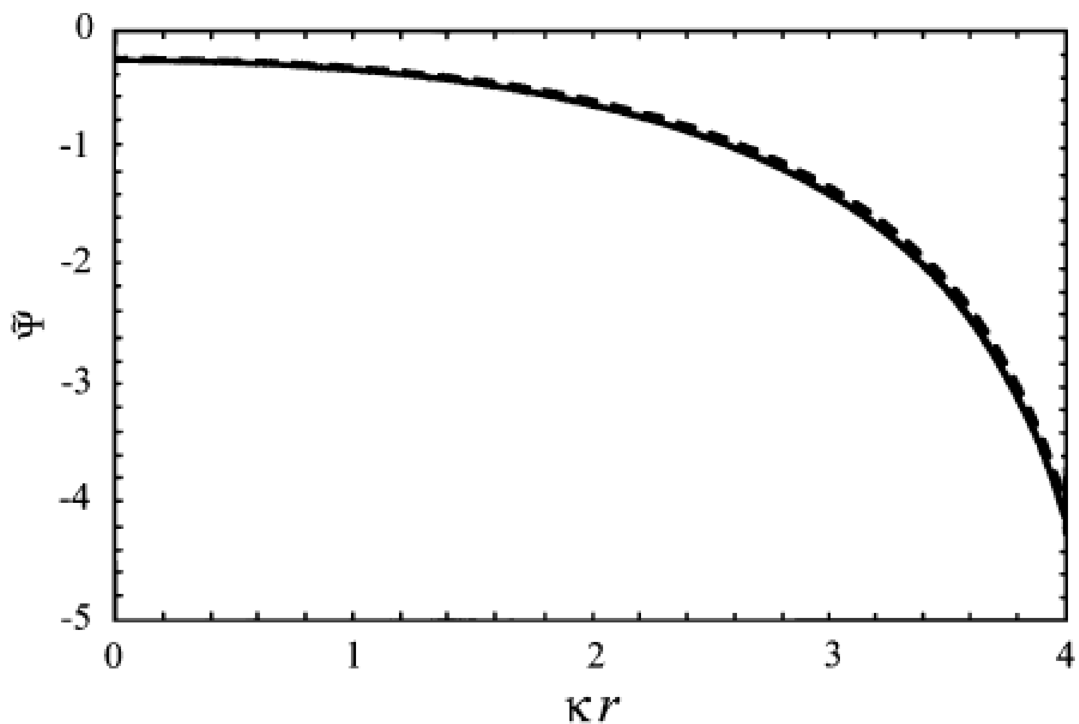



D. N. Petsev & G. P. Lopez

$$\tilde{\Psi}(r) = \tilde{\Psi}^0(r) + \frac{1}{\kappa R}\tilde{\Psi}^1(r)$$

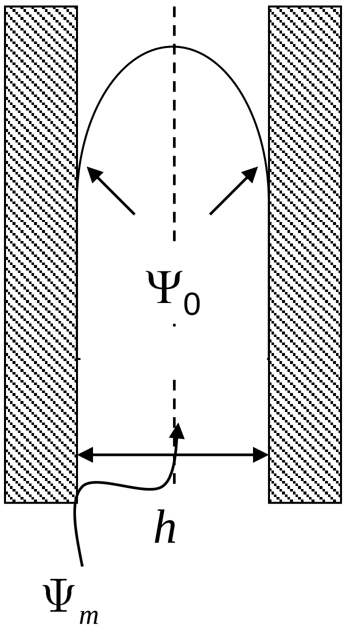
—— Superposition

- - - - Numerical



# Poisson-Boltzmann Equation: Exact Solution for a Plane-Parallel Slit

I. Langmuir




$$2\frac{d\tilde{\Psi}}{dx}\frac{d^2\tilde{\Psi}}{dx^2} = \kappa^2 \sinh(\tilde{\Psi})\, 2\frac{d\tilde{\Psi}}{dx} \quad \Rightarrow \quad \frac{d}{dx}\left(\frac{d\tilde{\Psi}}{dx}\right)^2 = 2\kappa^2 \sinh(\tilde{\Psi})\frac{d\tilde{\Psi}}{dx}$$

$$\int_{\frac{d\tilde{\Psi}}{dx}}^{0} d\left(\frac{d\tilde{\Psi}}{dx}\right)^2 = 2\kappa^2 \int_{\tilde{\Psi}}^{0} \sinh(\tilde{\Psi})\, d\tilde{\Psi} \quad \Rightarrow \quad \text{1st Integration}$$

$$\frac{d\tilde{\Psi}}{dx} = \kappa\sqrt{2\left[\cosh(\tilde{\Psi}) - \cosh(\tilde{\Psi}_m)\right]}$$

$$\int_{\tilde{\Psi}}^{\tilde{\Psi}_m} \frac{d\tilde{\Psi}}{\sqrt{2\left[\cosh(\tilde{\Psi}) - \cosh(\tilde{\Psi}_m)\right]}} = -\kappa\int_0^x dx \qquad \text{2nd Integration}$$

$$\kappa x = 2k^{\frac{1}{2}}\left[K(k) - F(\phi,k)\right], \quad F(\phi,k) = \int_0^{\phi}\frac{d\theta}{\left(1-k^2\sin^2\theta\right)^{\frac{1}{2}}}, \quad K(k) = F\left(\frac{\pi}{2},k\right)$$

$$k = \exp(-\tilde{\Psi}_{\mathrm{m}}), \quad \phi(x) = \arcsin\left(k^{-\frac{1}{2}}\exp\left[-\tilde{\Psi}(x)\right]\right)$$

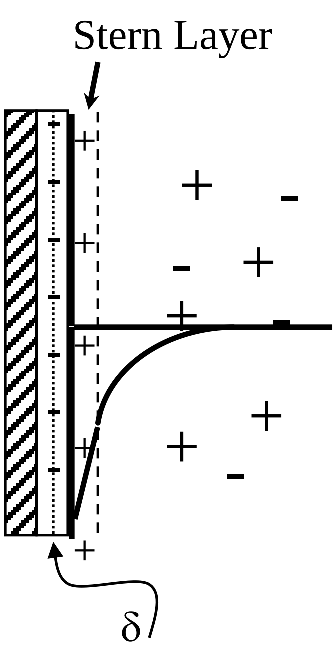
# Surface Charge Density. Stern Theory. Charge Regulation

Charge-Potential Relationship $\sigma = -\varepsilon\varepsilon_0 \nabla\Psi$

At the wall

$$\sigma = -\varepsilon\varepsilon_0 \left(\frac{d\Psi}{dx}\right)_{\text{wall}} \quad \text{for flat surface}$$

$$\sigma = -\varepsilon\varepsilon_0 \left(\frac{d\Psi}{dr}\right)_{\text{wall}} \quad \text{for cylindrical capillary}$$




Stern Adsorption Isotherm

$$\Gamma_i = \frac{v_0 n_i \exp\left[-\dfrac{\varphi_i - z_i e\Psi_\delta}{kT}\right]}{1 + v_0 n_i \exp\left[-\dfrac{\varphi_i - z_i e\Psi_\delta}{kT}\right]}$$

$\Gamma_i$ – adsorption of species $i$

$v_0$ – molecular volume of the solvent

$n_i$ – number of ions “$i$” per unit volume

$\varphi_i$ – specific (nonelectrostatic) energy of interaction

$\Psi_\delta$ -- electrostatic potenjtial at the adsorption plane

$z_i$ – charge number of ionic species $i$

# Summary

1. The potential in the electric double layer is a key quantity to the properties of narrow channels (slits and capillaries).
2. The Poisson-Boltzmann equation describes the potential distribution. The level of complexity of the solution depends on the surface potential and the geometry of the system.
3. Knowledge of the electrostatic potential allows to determine the surface charge at the channel wall.
4. The boundary conditions that specify potential and/or charge at the channel walls are well defined mathematically but have significant physical shortcoming.  The best and most physical condition is “charge regulation”.