

Modeling the electrical double layer ~ requirement of total electrical neutrality

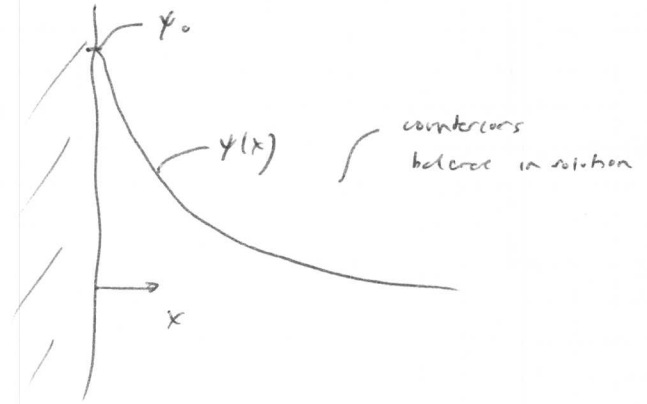
assume a planar, isolated, constant potential surface

variation in potential from a surface: poisson eqn.

$$\nabla^2 \psi = -\rho^+ / \epsilon$$

↑ charge density [ $C/m^3$ ]  
 $\rho^+(x, y, z)$

$$\epsilon = \epsilon_r \epsilon_0$$



in 1D,  $\frac{d^2 \psi}{dx^2} = -\rho^+(x) / \epsilon \sim \text{constant}$

BCs:  $\psi(0) = \psi_0, \quad \psi(\infty) = 0$

now we need to relate  $\rho$  to  $\psi$

consider the ions obey a Boltzmann distribution

$$\frac{n_i}{n_{i,\infty}} = \exp\left\{-z_i e \psi / k_B T\right\} \quad \text{= probability of finding an ion at a potential } \psi$$

↑ # ions/m<sup>3</sup>      ↑ at ∞

$$\rho^+ = z_i e n_i = (\text{charge})(\text{volume})(\#/\text{m}^3)$$

if we have multiple ions in solution, then

$$\rho^+ = \sum z_i e n_i = \sum z_i e n_{i,\infty} \exp\left\{-z_i e \psi / k_B T\right\}$$

↳ poisson-boltzmann equation can now be written (P/B<sup>n</sup> eqn)

$$\text{P/B eqn} \Rightarrow \frac{d^2\psi}{dx^2} = -\frac{e}{\epsilon} \sum_i z_i n_{i,\infty} \exp\left\{-z_i e\psi / k_b T\right\}$$

implies superposition of charges

no general solution: need to make assumptions.

$$\text{first, assume } z_i e\psi < k_b T = \frac{k_b T}{e} \approx 298 \text{ K} = 25.7 \text{ mV}$$

rule of comparing potentials

given this assumption, we can expand the exponential term (power series)

keep first-order terms

$$\rho^+ = \sum_i z_i e n_{i,\infty} (1 - (z_i e\psi / k_b T))$$

$\rho^- = 0$  because of electroneutrality

$$\Rightarrow \rho^+ = -\sum_i z_i^2 e^2 \psi n_{i,\infty} / k_b T$$

now the linearized P/B eqn is

$$\frac{d^2\psi}{dx^2} = \left( \left( \frac{e^2}{\epsilon k_b T} \right) \sum_i z_i^2 n_{i,\infty} \right) \psi$$

$$\text{define } k^2 = \left( \frac{e^2}{\epsilon k_b T} \right) \sum_i z_i^2 n_{i,\infty}$$

$$\text{then } \frac{d^2\psi}{dx^2} = k^2 \psi \Rightarrow \psi = \psi_0 e^{-kx} \quad \text{or} \quad \psi = \psi_0 e^{-x/k^{-1}}$$

$k^{-1}$  = double layer thickness

"Debye length"

example, 0.1 M solution of 1:1 electrolyte, e.g. KOH, NaCl

$$\Rightarrow \kappa^{-1} = 3.04 \text{ nm}$$

$M = \text{molarity}$

useful conversion:  $n_i = 1000 M_i N_A$

$$\left(\frac{\text{ions}}{\text{m}^3}\right) = \left(\frac{\text{L}}{\text{m}^3}\right) \left(\frac{\text{mol}}{\text{L}}\right) \left(\frac{\text{ions}}{\text{mol}}\right)$$

$$\kappa \approx \left[ \left( \frac{1000 e^2 N_A}{\epsilon_0 \epsilon_r k_B T} \right) \sum z_i^2 M_i \right]^{1/2}$$

$\swarrow$  molarity of  $i$

gouy-chapman solution: if we don't make the D-H approximation

$$\Phi = \Phi_0 e^{-\kappa x}$$

$$\Phi_0 = \Phi(\psi_0)$$

$$\Phi = \frac{(\Delta - 1)}{(\Delta + 1)}, \quad \Delta = \exp\left(\frac{ze\psi}{2k_B T}\right)$$

for a symmetrical 1:1 electrolyte.

if we expand with  $(ze\psi) \ll k_B T \Rightarrow$  D-H approx  $\Rightarrow$  previous solution

2 more cases:

(i) large  $x$ , where  $\psi \ll \psi_0$

$$\frac{ze\psi}{4k_B T} = \Phi_0 \exp(-\kappa x) \Rightarrow \psi = \frac{4k_B T}{ze} \Phi_0 \exp(-\kappa x)$$

large  $\psi_0$ , so  $\bar{p}_0 \approx 1$

$$\Rightarrow \psi = \frac{\psi_0 k_B T}{ze} \exp(-kx)$$

in a typical dispersion,  $ze\psi \approx 1$

consider overlapping double layers: electrostatics = repulsive force.

$$F_x + F_{el} = 0.$$

$$F_x = -\frac{dp}{dx}$$

$$F_{el} = -p + \frac{d\psi}{dx}$$

$$\Sigma F = 0 : \frac{dp}{dx} + p + \frac{d\psi}{dx} = 0$$

$$\frac{dp}{dx} + \epsilon \left( \frac{d\psi}{dx} \right) \left( \frac{d^2\psi}{dx^2} \right) = 0$$

$$= \frac{1}{2} \frac{d}{dx} \left( \frac{d\psi}{dx} \right)^2$$

$$\Rightarrow \frac{d}{dx} \left( p - \frac{\epsilon}{2} \left( \frac{d\psi}{dx} \right)^2 \right) = 0$$

$$\text{so, } p - \frac{\epsilon}{2} \left( \frac{d\psi}{dx} \right)^2 = \text{constant.}$$

pressure

electric field contribution  
"Maxwell pressure"

