$\boxed{\text{TODAY}}$: Ⅰ Charge Relaxation; Diffusion, & the $\boxed{\text{Electrical Double Layer}}$ @ "Bio-Interfaces" (cell, molecular; Electrode - Electrolyte) 10/20

Ⅱ $\boxed{\text{Donnan Equilibrium}}$: Partitioning of Charged Solutes into Charged Tissue / Gels / Membranes

- Nano-scale vs. Tissue scale

Ⅲ Ionization / Titration of biomolecules, cells, tissues.

Last time Ⓒ ⇄ Ⓔ ElectroChem Coupling.

(1) $\underline{N_i} = -D\nabla C_i + \frac{z_i}{|z_i|} \mu_i C_i \underline{E}$

(2) $\frac{\partial C_i}{\partial t} = -\nabla \cdot \underline{N} + R_i$

B.C.'s on C_i or ∇C_i

(3) $\nabla \cdot \varepsilon \underline{E} = \rho_e = \sum_i z_i F c_i$

(4) $\underline{E} = -\nabla \Phi$

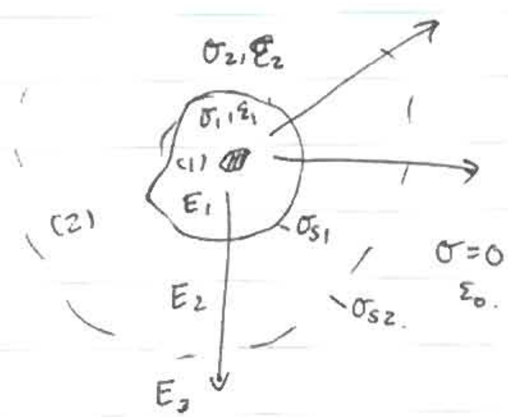
(5) $\nabla \cdot \underline{J} = -\frac{\partial \rho_e}{\partial t}$

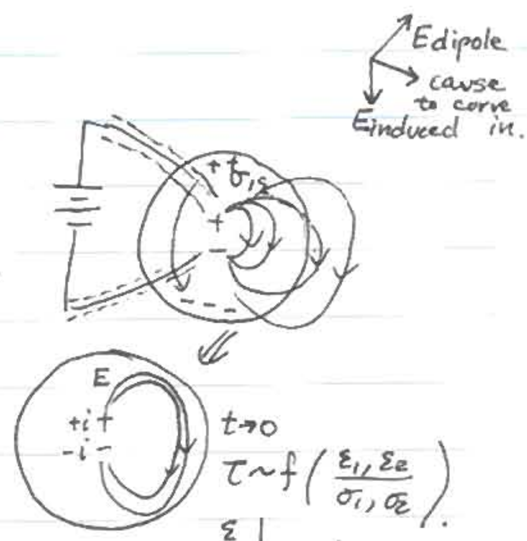
(6) $\underline{J} = \sigma \underline{E} + (\ \ ) \nabla C_i$

$\underline{n} \cdot (\varepsilon_1 E_1 - \varepsilon_2 E_2) = \sigma_s$

$\Phi_1 = \Phi_2$

$\underline{n} \cdot (\sigma_1 E_1 - \sigma_2 E_2) = -\frac{\partial \sigma_s}{\partial t}$





$\tau \sim f\left(\frac{\varepsilon_1, \varepsilon_2}{\sigma_1, \sigma_2}\right)$.

$\frac{\varepsilon}{\sigma}\Big|_{us} \sim 1\,\text{ns}.$

- @ steady state, only charge @ outer surface
- only E_3, no E_1, E_2 @ steady state. when source is turned off.

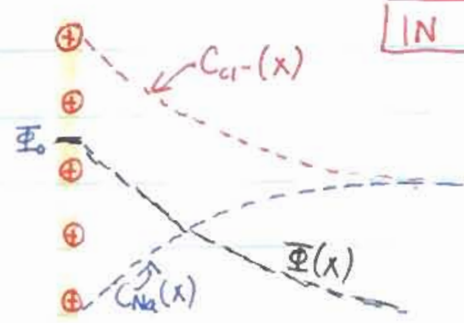
Last Time: Elec. Double Layer @ "Bio-Interfaces"

IN EQUIL

$COOH \rightleftharpoons COO^- + H^+$ (pK ~ 3.5 ~ 4)

$NH_3^+ \rightleftharpoons NH_2 + H^+$ (pK ~ 10 ~ 12)

$SO_3H \rightleftharpoons SO_3^- + H^+$ (pK ~ 1.5)



Given: ① $x = 0,\ \Phi = \Phi_0$

② $x \to \infty,\ \Phi \to 0$

③ $C_+ = C_- = C_0$ bath

Find: $\bar{C}_\pm(x),\ \Phi(x)$

④ $C_i(x) = C_{i0}\, e^{-zF\Phi(x)/RT}$

Boltzmann Distribution.

$$\nabla^2 \Phi(x) = \frac{1}{\varepsilon} \sum_i z_i F c_i(x)$$

Poisson-Boltzmann

for small enough $\frac{|zF\Phi|}{RT} \ll 1$

$$\boxed{\frac{d^2\Phi}{dx^2} = \kappa^2 \Phi(x)}$$ Linearlized P-B Eq.

$$\left.\frac{1}{\kappa} = \sqrt{\frac{\varepsilon RT}{2z^2F^2C_0}}\ \right\}\text{ Debye Length}$$

z : z electrolyte.

$\frac{1}{\kappa} \sim 1\text{nm}$ for 0.1 M NaCl

$\boxed{\text{In Equil: } N_i = 0}$; $\frac{\partial C_i}{\partial t} = 0$ for ① & ②.

$$\frac{z_i}{|z_i|} \mu_i \phi_i \int_{-\infty}^{x} \frac{d\Phi}{dx} = -\frac{D_i}{\frac{|z_i|}{|z_i|}\mu_i} \frac{1}{C_i} \int_{\infty}^{x} \frac{dC_i}{dx}$$

$\frac{RT}{|z_i|F}$ × $\frac{RT}{|z_i|F}$

$$\Phi(x) - \cancel{\Phi(\infty)}^{\,0} = -z_i \frac{RT}{F} \ln\left(\frac{C_i(x)}{C_0}\right)$$

$$= -\frac{RT}{z_iF} \ln\left(\frac{C_i(x)}{C_0}\right)$$

$$\boxed{C_i(x) = C_0\, e^{-z_iF\Phi(x)/RT}}$$

Charge Relax, Diffusion, & the Double Layer

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon RT}{2(zF)(zF)C_0}} = \sqrt{\frac{\varepsilon D_i}{2zF\mu_i C_0}} \approx \sqrt{\frac{\varepsilon}{\sigma} D_i}$$

$L^{char} \gg \frac{1}{\kappa}$, system is macro-neutral

$L^{ch} \sim \frac{1}{\kappa}$, system is large net charge

$$\frac{\left(\frac{1}{\kappa}\right)^2}{D_i} \sim \left(\frac{\varepsilon}{\sigma}\right)$$ $\tau_{ch.rel}$ (1ns).

when $\tau_{ch\,rel} \sim \tau_{diff}$, this is only "time" balance between migration + diffusion → occurs on length scale of $1/\kappa$. NANO Cont. w/ lots of charge.