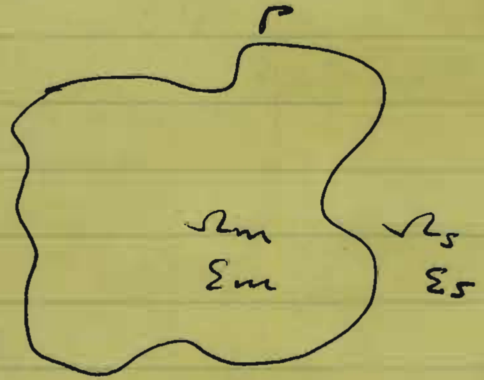
The Poisson-Nernst-Planck Equations (PNP)

- The set up and the PNP equations.
- Reduced PNP systems.
- Application to a special case: a spherical charged molecule in solution, determination of reaction rates

1. Set up. the PNP system



Ω_m .... charged molecular region

Ω_s .... solvent region

Γ ......dielectric boundary or solute-solvent interface

$c_i = c_i(x)$ ..... local concentration at $x \in \Omega_s$ of ions of ith ionic species

[$c_i = c_i(x,t)$, t — time]

$\rho_f = \rho_f(x)$ ..... fixed charge density. Often the charges are from charged molecules

$\rho_i(x) = \sum_{i=1}^{M} q_i c_i(x)$ ..... induced charge density.

$q_i = Z_i e$ ..... Z_i valence. e = elementary charge.

D_i ... diffusion coefficient of the ith ionic species

$\beta^{-1} = k_B T$, k_B = Boltzmann's constant, T = absolute temperature

$$\varepsilon = \begin{cases} \varepsilon_m \varepsilon_0 & \Omega_m \\ \varepsilon_s \varepsilon_0 & \Omega_s \end{cases} \text{ — dielectric coefficient.}$$

Note: we can just consider the ionic solution (e.g. the salted water), and treat ρ_f as fixed surface charges.

The PNP system describes the dynamics of diffusion of ions and small molecules (or in general some ~~chemical~~ charged species) in an electrostatic potential

The PNP system

$$\begin{cases} \dfrac{\partial c_i}{\partial t} = \nabla \cdot D_i\left[\nabla c_i + \beta q_i c_i \nabla \psi\right] \quad = \nabla\cdot\left[D_i e^{-\beta q_i \psi} \nabla\left(c_i e^{\beta q_i \psi}\right)\right] & \text{in } \Omega \\ \nabla \cdot \varepsilon \nabla \psi = -\rho_f - \sum_{i=1}^{M} q_i c_i & [\Omega = \Omega_s \text{ e.g.}] \\ \text{B.C. for } c_i, \psi, \text{ I.C. for } c_i \end{cases}$$

e.g. far from the source of charges

$$c_i = c_i^{\infty} \quad (i=1,\cdots,M)$$

$$\psi = 0$$

Equilibrium $c_i = c_i(x)$ (Without considering the B.C. for a moment.)

$$c_i(x) = c_i^{\infty} e^{-\beta q_i \psi} \quad \text{— Boltzmann's distribution.}$$

Check. $\nabla \cdot D_i\left[\nabla c_i + \beta q_i c_i \nabla \psi\right]$

$$= \nabla \cdot D_i e^{-\beta q_i \psi} \nabla\left(c_i e^{\beta q_i \psi}\right)$$

Since $c_i e^{\beta q_i \psi} = c_i^{\infty} = \text{const.}$ we have

$$\nabla \cdot D_i\left(\nabla c_i + \beta q_i c_i \nabla \psi\right) = 0$$

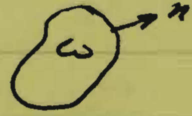
If $c_i(x) = c_i^{\infty} e^{-\beta q_i \psi}$. ~~then the normal flux~~ ~~$\vec{J}_i \cdot \vec{n} = D_i\left(\frac{\partial c_i}{\partial n} + \beta q_i c_i \frac{\partial \psi}{\partial n}\right) = 0$~~. then

$$\nabla \cdot D_i\left(\nabla c_i + \beta q_i c_i \nabla \psi\right) = 0 \quad \text{in } \omega$$

for any region ω

$$\int_{\omega} \nabla\cdot D_i\left(\nabla c_i + \beta q_i c_i \nabla\psi\right) dV = 0$$

$$\Longrightarrow \int_{\partial\omega} D_i\left(\frac{\partial c_i}{\partial n} + \beta q_i c_i \frac{\partial \psi}{\partial n}\right) dS = 0$$



Define $J_i = -D_i\left(\nabla c_i + \beta q_i c_i \nabla\psi\right)$, $i = 1 \cdots M$.
Call it flux (vectors).

The PNP is
$$\begin{cases} \dfrac{\partial c_i}{\partial t} + \nabla\cdot J_i = 0 \\ \nabla\cdot\varepsilon\nabla\psi = -\rho_f - \rho_i \end{cases}$$

If the B.C. is the no-flux bdry condition, ~~then~~ i.e.

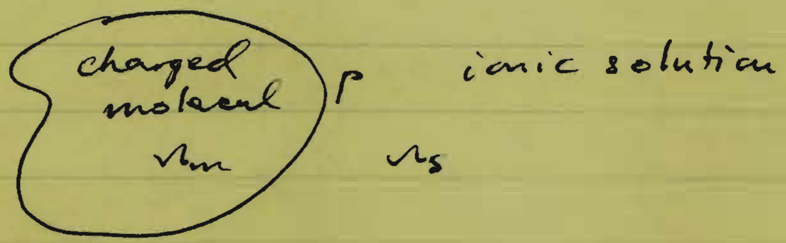
$$J_i \cdot n = 0 \quad \text{on a boundary.}$$

then we have the steady-state solutions

$$c_i(x) = c_i^{\infty} e^{-\beta q_i \psi}, \quad i = 1, 2, \cdots, M.$$

In general, Boltzmann distributions may not give the steady-state solutions.

Application to reaction



$i = 1, \cdots, m$: reaction species.

$i = m+1, \cdots, M$. non-reactive species

$$c_i(x) = c_i^\infty e^{-\beta q_i \psi(x)} \qquad i = m+1, \cdots, M.$$

$$[\quad J_i n = 0 \quad \text{on } \partial\Gamma.]$$

$$J_i(x) = -D_i \left(\nabla c_i + \beta q_i c_i \nabla \psi \right).$$

Linearize $\quad c_i(x) \approx c_i^\infty (1 - \beta q_i \psi(x)) \qquad i = m+1, \cdots, M.$

$1 \le i \le m$: $\quad \boxed{\dfrac{\partial c_i}{\partial t} = \nabla \cdot D_i \left(\nabla c_i + \beta q_i c_i \nabla \psi \right)}$

B.C. $\longrightarrow$ $c_i(x,t) = 0$ for $x \in \Gamma$. $\forall t > 0$, $c_i(\infty) = c_i^\infty$.

I.C. $\quad c_i(x,0)$: given.

$\qquad$ e.g. $c_i(x,0) = c_i^\infty e^{-\beta q \psi(x)}$

Total charge density

$$\begin{aligned}
\rho &= \rho_f + \sum q_i c_i \\
&= \rho_f + \sum_{i=1}^{m} q_i c_i + \sum_{i=m+1}^{M} q_i c_i \\
&= \rho_f + \sum_{i=1}^{m} q_i c_i + \sum_{i=m+1}^{M} q_i c_i^\infty (1 - \beta q_i \psi(x)) \\
&= \rho_f + \sum_{i=1}^{m} q_i c_i + \sum_{i=1}^{M} q_i c_i^\infty - \sum_{i=1}^{m} q_i c_i^\infty \\
&\quad - \left(\sum_{i=m+1}^{M} q_i^2 \beta c_i^\infty \right) \psi(x) \\
&= \rho_f + \sum_{i=1}^{m} q_i (c_i - c_i^\infty) - \varepsilon_s \kappa_p^2 \psi
\end{aligned}$$

where: $\sum_{i=1}^{M} q_i c_i^\infty = 0$ — charge neutrality

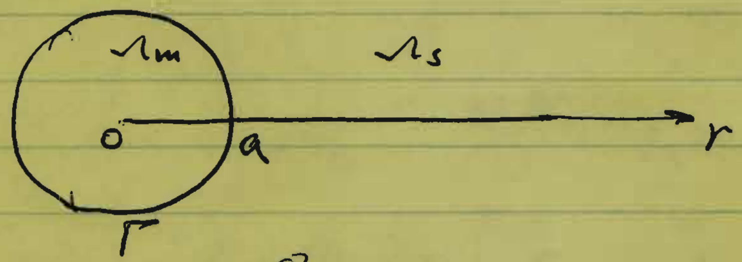
$$\kappa_p^2 = \sum_{i=m+1}^{M} q_i^2 \beta c_i^\infty / \varepsilon_s$$

— (partial) ionic strength.

$$\boxed{\nabla\cdot\varepsilon\nabla\psi = -\rho_f - \sum_{i=1}^{m} q_i (c_i - c_i^\infty) - \varepsilon_s \kappa_p^2 \psi.}$$

$\psi(\infty) = 0$.

A special case



$$\begin{cases} \Delta\psi = -\dfrac{Q}{\varepsilon_m} & \text{if } |x| < a \\ \Delta\psi - \kappa_p^2\psi = -\sum_{i=1}^{m} \dfrac{q_i}{\varepsilon_s}(c_i - c_i^\infty) & |x| > a. \\ [\![\psi]\!] = [\![\varepsilon\nabla\psi\cdot n]\!] = 0 & \text{on } \Gamma \end{cases}$$

$$\nabla\cdot(\nabla c_i + \beta q_i c_i \nabla\psi) = 0 \quad \text{if } |x| > a, \quad i = 1, \cdots, m$$

$c_i = 0$ if $|x| = a$.

$c_i(\infty) = c_i^\infty$.

$$\nabla\cdot\varepsilon\nabla\psi - \chi_{\Omega_s}\varepsilon_s\kappa^2\psi = -\chi_{\Omega_m}Q - \chi_{\Omega_s}\sum_{i=1}^{m} q_i(c_i - c_i^\infty)$$

in $\mathbb{R}^3$.