Chemical Subsystem

Governing Equations:

(1) Conservation Law (R_v=Rate of Formation) $\frac{\partial C}{\partial t} = -\nabla \cdot N_i + R_v$

(2) Nernst-Planck Flux Equation (Fick's diffusion + convection + migration)

$$N_i = -D\nabla C_i + \underline{v}C_i + \frac{z_i}{|z_i|} u_i C_i \underline{E}$$

Boundary conditions come from

1. flux matching $0 = \underline{n}_1 \cdot (\underline{N}_1 - \underline{N}_2) + R_S$
2. concentration matching $c(x_+) = K \cdot c(x_-)$
3. symmetry $\underline{N}_i = 0$

Solution Methods

Scale first to get more easily solved equations, and more general solutions. You should already have the solutions to most scaled equations you might encounter in your notes, homework solutions, and textbook examples…

Linear ODE's

1. Direct Integration
2. Tables
3. Green's Functions

Linear PDE's

1. Linear Operator Theory

   Sturm-Liouville Operators $L = \frac{1}{w(x)}\left[\frac{\partial}{\partial x}\left(p(x)\frac{\partial}{\partial x}\right) + q(x)\right]$

2. Separation of Variables

   Assume $\phi(x, y) = X(x)Y(y)$

3. Finite Fourier Transform (Chapter 4 Deen, tables)

Dimensionless Groups (Generate by scaling governing equations)

(1) Dahmkohler (reaction/diffusion) $Da = \begin{cases} kL^2/D & \text{hom}og.rxn \\ kL/D & heterog.rxn \end{cases}$

(2) Peclet

(3) Reynolds (inertial/viscous) $\mathrm{Re} = \frac{\rho UL}{\mu}$

2nd Order Chemistry

$A + B \Leftrightarrow C$

$R_{vA} = R_{vB} = -k_{on}AB + k_{off}C$

$R_{vC} = k_{on}AB - k_{off}C$

Rapid Equilibrium

$$K_d = \frac{k_{off}}{k_{on}} = \frac{AB}{C}$$

$$\frac{\partial A}{\partial t} = \frac{\partial B}{\partial t} = \frac{\partial C}{\partial t} = 0$$

$$C_T^A = A + C$$

$$C = \frac{C_T^A B}{K_d + B}$$

Mechanical Subsystem

Governing Equations

(1) Conservation of Mass $\quad \frac{\partial \rho}{\partial t} + \nabla \cdot \rho \underline{v} = 0$

Incompressible Fluid $\quad \nabla \cdot \underline{v} = 0$

(2) Conservation of Momentum $\quad \rho \frac{D\underline{v}}{Dt} = \underline{F}$

(3) Navier-Stokes $\quad \rho \frac{D\underline{v}}{Dt} = -\nabla P + \rho_e \underline{E} + \mu \nabla^2 \underline{v} + F_{other}$

Poiseulle Pipe Flow

$$v_z(r) = -\frac{R^2}{4\mu}\frac{\partial p}{\partial z}\left[1 - \left(\frac{r}{R}\right)^2\right]$$

$$U = -\frac{R^2}{8\mu}\frac{\partial p}{\partial z}$$

Stress

Stress and stress tensor (units F/A) $\quad \underline{\tau}_{ij} = \underline{n}_{ij} \cdot \underline{\underline{T}}$

$$\underline{F} = \nabla \cdot \underline{\underline{T}}$$

Viscous stress $\quad \dot{e}_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right)$

Generalized Hooke's Law $\quad T_{ij}^v = 2\mu \dot{e}_{ij} + \left(\lambda - \frac{2}{3}\mu\right)\delta_{ij}\dot{e}_{kk}$

Electrical Subsystem

Electroquasistatic approximation: Assumes that magnetic field (B) is negligibly small, so the change with time is also negligible. This is applicable when L (the characteristic length) is much smaller than the wavelength.

Governing Equations:

(1) Gauss's Law $\nabla \cdot \varepsilon \underline{E} = \rho$

(2) Faraday's Law $\nabla \times E = 0 \Rightarrow \underline{E} = -\nabla \Phi$

(3) Conservation of Charge $\dfrac{\partial \rho}{\partial t} = -\nabla \cdot \underline{J}$

(4) Current Constitutive Law $\underline{J} = \sum_i z_i F \underline{N_i} = \sigma \underline{E} + ()\nabla c_i + ()\underline{v}_{fluid}$

Boundary Conditions:

(1) $\underline{n} \cdot (\varepsilon_1 \underline{E}_1 - \varepsilon_2 \underline{E}_2) = \sigma_s$

(2) $\underline{n} \cdot (\sigma_1 \underline{E}_1 - \sigma_2 \underline{E}_2) = -\dfrac{\partial \rho}{\partial t} = 0(steady - state)$

(3) $\underline{n} \times (\underline{E}_1 - \underline{E}_2) = 0 \Rightarrow \Phi_1 = \Phi_2$

Modification to Species Flux:

$\underline{N}_i = -D_i \nabla c_i + \left(\dfrac{z_i}{|z_i|} u_i c_i \right) \underline{E}$ where u is the mobility of species I

Charge relaxation:

$\tau = \dfrac{\varepsilon}{\sigma}$ In most bio-systems, relaxation time is on the order of nanoseconds.

Diffusion and migration occur through very different mechanisms, leading to very different relaxation profiles.

Conductivity of a solution can be described by: $\sigma = \sum_i u_i c_i$

Electrical Double Layer:

Boltzmann distribution $c_i(x) = c_0 e^{-z_i F \Phi / RT}$

→ equilibrium distribution of ions, obtained from setting flux = 0 and using the **Einstein Relation** $\dfrac{RT}{z_i F} = \dfrac{D_i}{u_i}$

Debye length: $\dfrac{1}{\kappa} = \sqrt{\dfrac{\varepsilon RT}{2 c_0 z^2 F^2}}$ as solved in HW 3, Problem 4.

The debye length has several interpretations: a.) length over which the potential of a charged surface decays, b.) length scale over which diffusion and charge relaxation time scales are on the same order, c.) length scale over which diffusion and migration compete.

In bio-systems, this is generally on the order of nanometers.

For $L_{characteristic} >> \frac{1}{\kappa}$, **electroneutrality** applies:

$$\rho_e = \rho_m + \sum_i z_i F c_i = 0$$

This simplifies Gauss's Law. This, combined with Faraday's Law gives **Laplace's Equation**: $\nabla^2 \Phi = 0$

Donnan Potential:

Often used as a boundary condition. This equation describes the equilibrium concentration gradient and potential due to a charged material immersed in an ionic solution.

$$\Delta\Phi_D = -\frac{1}{z_i}\frac{RT}{F}\ln\left(\frac{\overline{c_i}}{c_i}\right)$$

Examples:

- Non-equilibrium/non-steady transport of ions across neutral material
- Donnan equilibrium problems of 2 classes: a.) given fixed charge of material, concentration in bath, find internal concentrations and potential, b.) given bath concentration and constitutive equation describing fixed charge of material, find self-consistent material charge, internal ion concentration, and potential.
- IGF Diffusion/Reaction through tissue
- Tendon swelling experiment
- Electrodiffusion through the glycocalyx
- Minority carrier phenomenon – majority carriers shield the fixed charges. Minority carriers travel through the material as if charges aren't present.(See example 2.6.4 in AJG manuscript)

Electrokinetic Phenomena – Electrical and Mechanical coupling

Navier-Stokes with electrical forces:

$$\rho \frac{D\underline{v}}{Dt} = -\nabla P + \rho_e \underline{E} + \mu \nabla^2 \underline{v} + F_{other}$$

Assumptions/Boundary Conditions:

(1) Frequently used, $|E_r| >> E_{0z}$. This allows decouple of fields in two directions when solving equations
(2) Potential at "wall" (really the slip boundary) is ζ (zeta potential).
(3) Models for the Debye layer (see AJG p.357):
   a. Diffuse Double layer $\Phi(x) = \Phi_{wall} e^{-\kappa x}$
   b. Guoy-Chapmann $\Phi(x) = \zeta e^{-\kappa(x-\delta)}$
   c. Helmholtz $\left.\frac{\partial \Phi}{\partial x}\right|_{x=\delta} = \frac{\zeta}{1/\kappa}$ linear potential profile

$\rho_e = -\sigma_d \delta_f \left(x - 1/\kappa\right)$ impulse model for charge

$\sigma_d = \frac{\varepsilon}{1/\kappa}\zeta$

(4) No-slip boundary at $x = \delta$
(5) Symmetry

Electrokinetic Phenomena:

Solved for the pipe problem:

$$v_z(r) = \frac{-\varepsilon}{\mu}(\zeta - \Phi(r))E_{0z} - \frac{(R-\delta)^2 - r^2}{4\mu}\left(\frac{\Delta P}{L}\right)$$

$$i = \int_0^{R-\delta} 2\pi r \rho_e(r) v_z(r) dr + \int_0^{R-\delta} 2\pi r \sigma(r) E_{0z} dr$$

$$Q = \int_0^{R-\delta} 2\pi r v_z(r) dr$$

Using Helmholtz model, and assuming $R >> 1/\kappa$ we get:

$$\begin{bmatrix} Q_p \\ i_p \end{bmatrix} = \begin{bmatrix} -\frac{\pi R^4}{8\mu L} & \frac{\pi R^2 \varepsilon \zeta}{\mu L} \\ \frac{\pi R^2 \varepsilon \zeta}{\mu L} & -\left(\frac{\pi R^2 \sigma}{L} + \frac{2\pi R \varepsilon^2 \zeta^2}{\mu (1/\kappa) L}\right) \end{bmatrix} \cdot \begin{bmatrix} \Delta P \\ \Delta V \end{bmatrix}$$

Special Cases:

- Darcy's Law $\left.U_z\right|_{\Delta V=0} = -k_{11}\nabla P$
- Streaming Current $\left.J_z\right|_{\Delta V=0} = L_{21}\Delta P$
- Electroosmotic Flow $\left.U_z\right|_{\Delta P=0} = L_{12}\Delta V$

- Streaming Potential $\left.\Delta V\right|_{J=0} = -\frac{L_{21}}{L_{22}}\Delta P$
- Filtration $\left.U_z\right|_{J=0} = \left(L_{11} - \frac{L_{12}L_{21}}{L_{22}}\right)\Delta P$

<u>Electrophoresis (see ALG section 6.4):</u>

Electrophoretic mobility = $\frac{U}{E_{0z}} = \frac{\frac{\varepsilon\zeta}{\mu}}{1 + \frac{\varepsilon\zeta\sigma_m}{\mu\sigma R} + \frac{|\sigma_m|u}{\sigma R}}$

- First correction term: $\frac{\varepsilon\zeta\sigma_m}{\mu\sigma R} \approx \frac{\tau_{relax}}{\tau_{convection}}$ considers relative importance of counter-ion flow
- Second correction term: $\frac{|\sigma_m|u}{\sigma R}$ where u is the mobility of counter-ion describes effects of surface current
- For $R >> 1/\kappa$, $\sigma_m = \frac{\varepsilon\zeta}{1/\kappa}$

<u>Problems/Examples/Applications:</u>

- Comparison of macroscale and microscale model
- Continuous flow PCR on a chip
- Capillary electrophoresis