9) Mass Transport in solids

Background: many applications where some mobile species can flow or diffuse through a solid

Examples: (1) Li-ion battery electrodes

(2) Hydrogels

(3) "Poroelasticity" diffusion of fluid through rock
Goal: Develop continuum equations describing diffusion through elastic solid

Review: Classical diffusion equations

* Spatial concentration $c$: (mols per unit spatial vol)

* Flux $i$: $i = n \cdot da$: mols per time crossing $n \cdot da$

* Fick's law: $i = -D \nabla c$

* Mass conservation $\frac{dc}{dt} = - \nabla \cdot i$

* Boundary conditions $i \cdot n = z^\ast \frac{c}{c^\ast}$ on boundary
Goal: extend this to combine with deformation

* Question: how to distinguish diffusion & deformation?

Solution: Raphé-Cahn "network model"

Solid is a network of lattice sites

Diffusion: hops from one lattice site to another

Deformation: motion of the lattice sites

Assumptions: Lattice sites conserved
Distortion of lattice from stress is reversible
Neglect body forces; Quasi-static; const $\Theta$
**Basic Definitions**

Concentrations $C_A$, $C_B$, $C_V$ denote mols per unit vol of A, B, V

Spatial: $c_A$, $c_B$, $c_V$ : mols per unit vol

Lattice site conservation:

$$C_A + C_B + C_V = C_L = \text{constant}$$

Let $m_A$, $m_B$ be molar masses

$$\rho_0 = m_A C_A + m_B C_B$$

$$\rho = m_A c_A + m_B c_B$$

$$C_A = J c_A \quad C_B = J c_B \quad C_V = J c_V$$
Deformation $Y(x)$ describes motion of lattice sites

$$F = \nabla Y, \quad \mathcal{J} = \det(F)$$

Decompose $F$ into a compositional shape change $F^c$ (shape change at zero stress), plus an elastic deformation induced by external stress $F^e$

$$F = F^e \cdot F^c$$

Usually assumed $F^c$ is only a vol change

$$F^c = \left[ \mathcal{J}(C_A, C_B, C_V) \right]^{1/3} I$$

Note adding equal amounts of $A$, $B$, $V$ produces an isotropic vol expansion
\[ \delta L(\lambda C_A, \lambda C_B, \lambda C_V) = \lambda \delta L(C_A, C_B, C_V) \]

**Euler's theorem for homogeneous functions**

\[ \frac{\delta L}{\delta C_A} C_A + \frac{\delta L}{\delta C_B} C_B + \frac{\delta L}{\delta C_V} C_V = \delta L \]

**Mass Transport**

**Spatial flux vectors** \( i_A, i_B, i_V \)

By definition \( \int i \cdot n \, dA = \text{mol/s} \text{ crossing } n \, dA \)

**Referential flux vectors** \( \hat{I}_A, \hat{I}_B, \hat{I}_V \)

satisfy \( \hat{I}_A \cdot n_0 \, dA_0 = \text{mol/s} \text{ crossing } n_0 \, dA_0 \)
Recall that $\text{d}A_n = J F^{-T} n_0 \text{d}A_0$

$$\Rightarrow \begin{aligned} \vec{I} \cdot n_0 \text{d}A_0 &= \vec{I} \cdot (J F^{-T} n_0 \text{d}A_0) \\ &= (J F^{-1} \vec{I}) \cdot n_0 \text{d}A_0 \end{aligned}$$

$$\Rightarrow \vec{I} = J F^{-1} \vec{I}$$

Also introduce "Flux exchange vectors"

$\vec{I}_{AB}$: referential flux from $A/B$ exchange

$\vec{I}_{AV}$: " $A$ / vacancy "

$\vec{I}_{B V}$: " $B$ / vacancy exchange "
\[ I_A = I_{AB} + I_{AV} \quad I_B = -I_{AB} + I_{BV} \]

\[ I_V = -I_{AV} - I_{BV} \]

Hence \[ I_A + I_B + I_V = 0 \] (lattice site conserved)

Conservation Laws

Mass conservation

\[ \frac{\partial C_A}{\partial t} + \nabla \cdot I_A = 0 \]

\[ \frac{\partial C_B}{\partial t} + \nabla \cdot I_B = 0 \]


\[ \frac{d}{dx} \int_{V_0} C_0 \, dv + \int_{A_0} \mathbf{J}_0 \cdot \mathbf{n} \, dA_0 = 0 \]

Apply divergence theorem; localize

**Linear momentum:** Stress acts on lattice

Neglect momentum of fluxes

Quasi-static

\[ \nabla \sigma \approx 0 \]