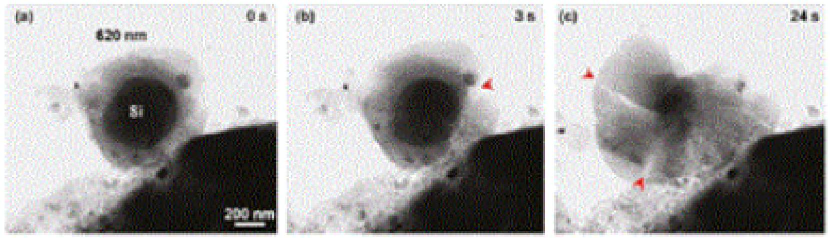
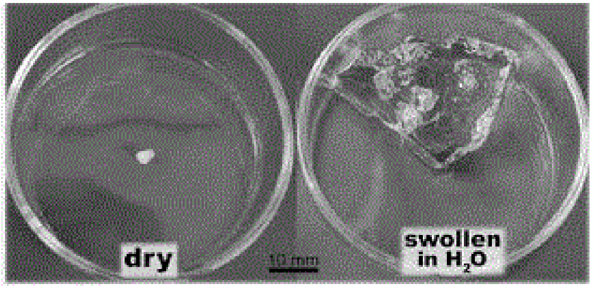
9) Mass Transport in solids

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

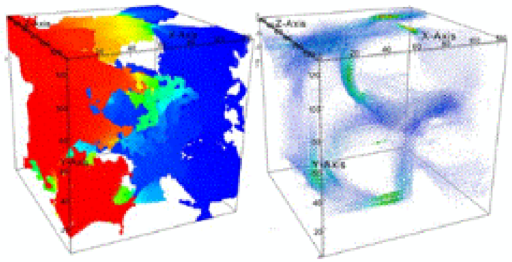
Examples: (1) Li-ion battery electrodes



(2) Hydrogels



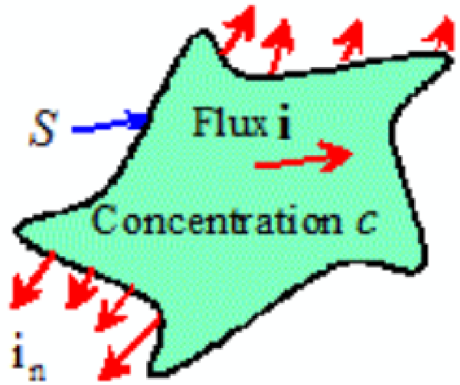
(3) "Poroelasticity" diffusion of fluid through rock



Petrophysical simulation for NMR.
Pore-scale Darcy flow in a sandstone

Goal: Develop continuum equations describing diffusion through elastic solid

Review : Classical diffusion equations



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

* Flux $\underline{i}$; $\underline{i}\cdot\underline{n}\,dA$: mols per time crossing $\underline{n}\,dA$

* Ficks law: $\underline{i} = -D\,\nabla_y c$

* Mass conservation $\frac{\partial c}{\partial t} = -\nabla_y\cdot\underline{i}$

* Boundary conditions $\underline{i}\cdot\underline{n} = i_n^*$ on boundaries or $c = c^*$

Goal: extend this to combine with deformation

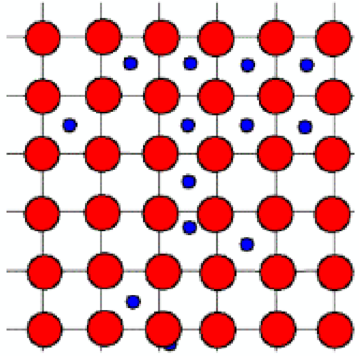
* Question: how to distinguish diffusion & deformation?

+ Solution: Larché - Cahn "network model"

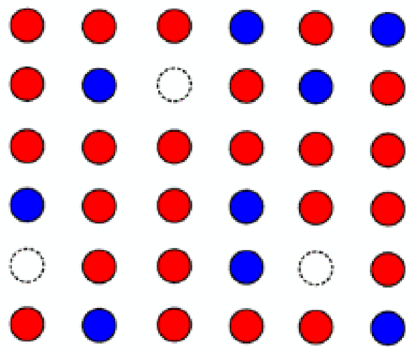
Solid is a network of lattice sites

Diffusion: hops from one lattice site to another

Deformation: motion of the lattice sites



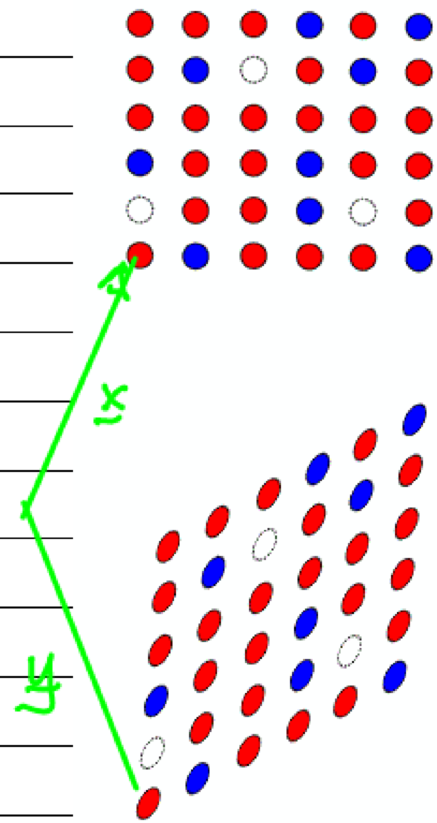
Interstitial



Substitutional

Assumptions: Lattice sites conserved
Distortion of lattice from stress is reversible
Neglect body forces; Quasi-static; const Θ

Basic Definitions



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

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

Lattice site conservation :

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

Let m_A, m_B be molar masses

$$\rho_0 = m_A C_A + m_B C_B \qquad \rho = m_A c_A + m_B c_B$$

$$C_A = J c_A \qquad C_B = J c_B \qquad C_V = J c_V$$

Deformation $\underline{y}(\underline{x})$ describes motion of lattice sites

$F = \nabla \underline{y}$ $\quad J = \det(F)$

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

$$F = F^e F^c$$

Usually assumed F^c is only a vol change

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

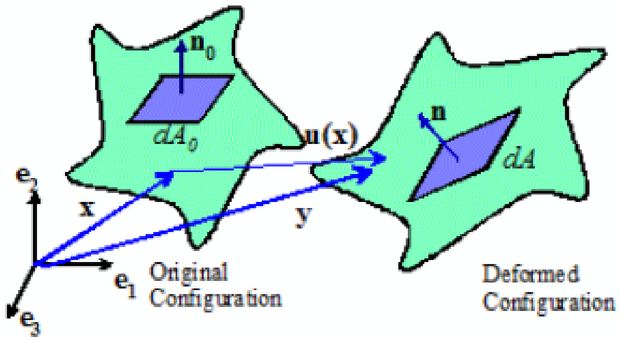
Note adding equal amounts of A, B, V produces an isotropic Vol expansion

$$\Omega(\lambda C_A, \lambda C_B, \lambda C_V) = \lambda \Omega(C_A, C_B, C_V)$$

Eulers theorem for homogeneous functions

$$\frac{\partial \Omega}{\partial C_A} C_A + \frac{\partial \Omega}{\partial C_B} C_B + \frac{\partial \Omega}{\partial C_V} C_V = \Omega$$

Mass Transport



Spatial flux vectors i_A, i_B, i_V

By definition $\underset{\sim}{i} \cdot \underset{\sim}{n}\, dA$ = mols/sec crossing $\underset{\sim}{n}\, dA$

Referential flux vectors $\underset{\sim}{I}_A$, $\underset{\sim}{I}_B$, $\underset{\sim}{I}_V$

satisfy $\underset{\sim}{I}_A \cdot \underset{\sim}{n}_0\, dA_0$ = mols/sec crossing $\underset{\sim}{n}_0\, dA_0$

Recall that $dA\,\underset{\sim}{n} = J F^{-T} \underset{\sim}{n}_0\, dA_0$

$$\Rightarrow \underset{\sim}{I} \cdot \underset{\sim}{n}_0\, dA_0 = \underset{\sim}{i} \cdot \left(J F^{-T} \underset{\sim}{n}_0\, dA_0 \right)$$

$$= \left(J F^{-1} \underset{\sim}{i} \right) \cdot \underset{\sim}{n}_0\, dA_0$$

$$\Rightarrow \underset{\sim}{I} = J F^{-1} \underset{\sim}{i}$$

Also introduce "Flux exchange vectors"

I_{AB} : referential flux $\left.\begin{array}{l}\text{of } A\\ \text{of } A\end{array}\right\}$ from A/B exchange

I_{AV} : " " " A / vacancy "

I_{BV} : " " of B " B / vacancy exchange

$$I_A = I_{AB} + I_{AV} \qquad I_B = -I_{AB} + I_{BV}$$

$$I_V = -I_{AV} - I_{BV}$$

Hence $I_A + I_B + I_V = 0$ (lattice sites conserved)

Conservation Laws

Mass conservation $\qquad \dfrac{\partial C_A}{\partial t} + \nabla \cdot \underline{I}_A = 0$

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

Derivation $\frac{d}{dt}\int_{V_0} C_A \, dV_0 + \int_{A_0} \mathbf{I}_A \cdot \mathbf{n}_0 \, dA_0 = 0$

Apply divergence theorem; localize

Linear momentum: Stress acts on lattice
Neglect momentum of fluxes
Quasi-static

$\nabla_y \sigma \approx 0$