Review: Mass Transport

Larche-Cahn Network Model:

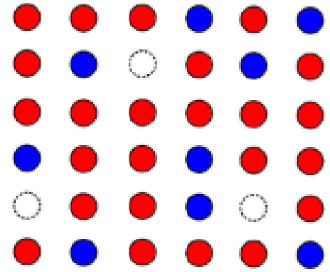
Referential concentrations C_A, C_B, C_V

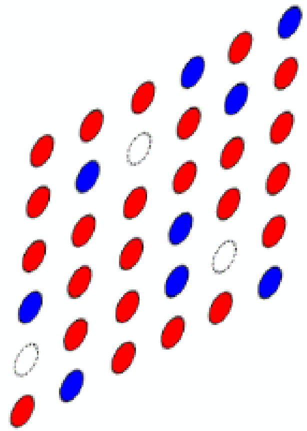
Spatial concentrations $c_A, c_B, c_V \qquad c = JC$

Network Constraint $C_A + C_B + C_V = C_L = const$

Molar masses m_A, m_B

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





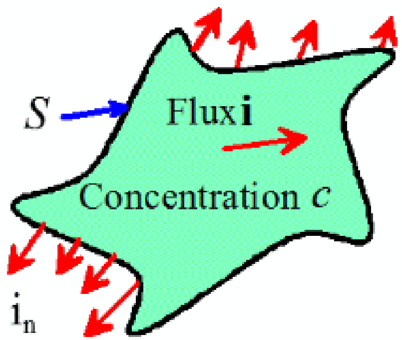
Deformation: $\mathbf{F} = \nabla \mathbf{y} \qquad J = \det \mathbf{F}$

Decomposition $\mathbf{F} = \mathbf{F}^e \mathbf{F}^c$

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

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

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



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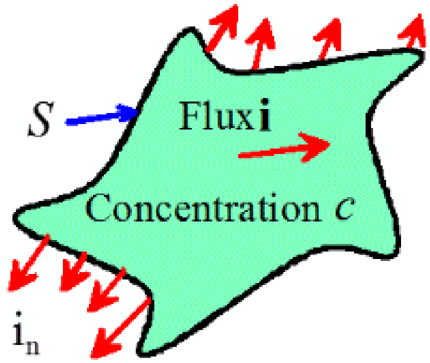


Transport:

Spatial fluxes $\mathbf{i}_A, \mathbf{i}_B, \mathbf{i}_V$

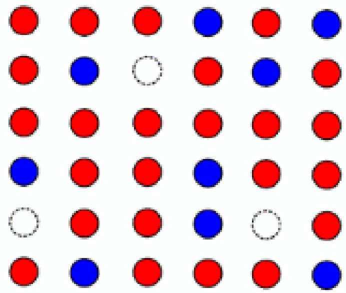
Referential fluxes $\mathbf{I}_A, \mathbf{I}_B, \mathbf{I}_V$

$$\mathbf{I} = J\mathbf{F}^{-1}\mathbf{i}$$

Flux of A from A/B exchange $\mathbf{I}_{AB}$

Flux of A from A/V exchange $\mathbf{I}_{AV}$

Flux of B from B/V exchange $\mathbf{I}_{BV}$



$$\mathbf{I}_A = \mathbf{I}_{AB} + \mathbf{I}_{AV} \qquad \mathbf{I}_B = -\mathbf{I}_{AB} + \mathbf{I}_{BV} \qquad \mathbf{I}_V = -\mathbf{I}_{AV} - \mathbf{I}_{BV}$$

Conservation Laws:

Mass $\dfrac{\partial C_A}{\partial t} + \nabla \cdot \mathbf{I}_A = 0 \qquad \dfrac{\partial C_B}{\partial t} + \nabla \cdot \mathbf{I}_B = 0$

Linear Momentum $\nabla \cdot \boldsymbol{\sigma} = 0$

Velocity Gradient $L = \nabla_y V = \dot{F} F^{-1}$

$$L = (\dot{F}^e F^c + F^e \dot{F}^c) F^{c-1} F^{e-1}$$

$$= \underbrace{\dot{F}^e F^{e-1}}_{\text{Elastic velocity gradient } L^e} + \underbrace{F^e \dot{F}^c F^{c-1} F^{e-1}}_{\text{Compositional } L^c}$$

Recall $F^c = \Omega^{1/3} I$

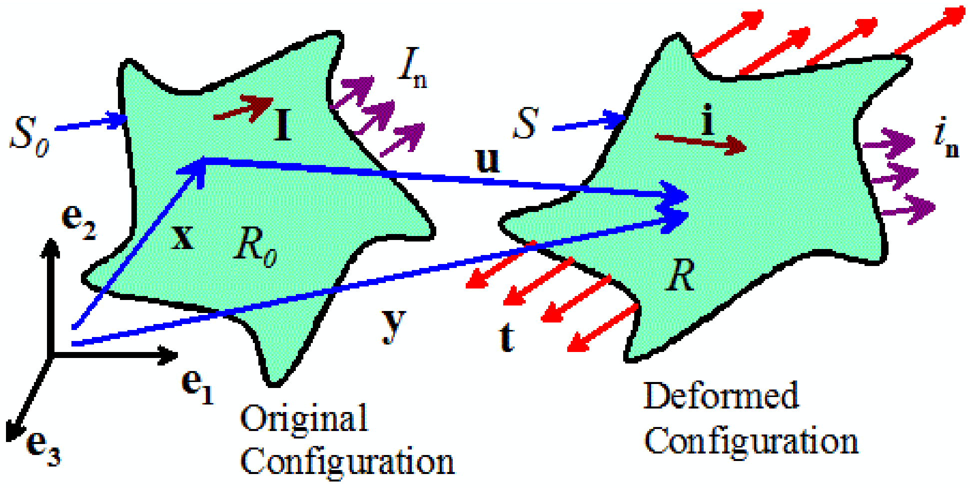
$$\dot{F}^c F^{c-1} = \frac{1}{3}\left(\underbrace{\frac{1}{\Omega}\frac{\partial \Omega}{\partial C_A}}_{\alpha_A} \dot{C}_A + \underbrace{\frac{1}{\Omega}\frac{\partial \Omega}{\partial C_B}}_{\alpha_B} \dot{C}_B + \underbrace{\frac{1}{\Omega}\frac{\partial \Omega}{\partial C_V}}_{\alpha_V} \dot{C}_V \right) I$$

$$\alpha_A C_A + \alpha_B C_B + \alpha_V C_V = 1$$

$$\dot{C}_A + \dot{C}_B + \dot{C}_V = 0$$

$$\dot{F}^c F^{c-1} = \frac{1}{3}\left((\alpha_A - \alpha_V) \dot{C}_A + (\alpha_B - \alpha_V) \dot{C}_B \right) I$$

Thermodynamics



Let ε = specific internal energy
s = " entropy
ψ = " Helmholtz free energy

Quasi-static Iso-thermal processes

First Law:

μ_A - energy per mol of A

$$\frac{d}{dt}\int_{V_0} \rho_0 \varepsilon \, dV_0 = \int_{S} \underline{t} \cdot \underline{v} \, dA - \int_{S_0} (I_n^A \mu_A + I_n^B \mu_B) \, dA_0 - \int_S \underline{q} \cdot \underline{n} \, dA$$

μ - Chemical potential

Second Law

$$\frac{d}{dt}\int_{V_0} \rho_0 s \, dV_0 - \int_{S} \frac{\underline{q}\cdot\underline{n}}{\theta} \, dA \geq 0$$

(1) Eliminate $\underline{q}$

(2) PVW :
$$\int_{V_0} J\sigma : L \, dV_0 = \int_{V_0} S^T : \dot{F} \, dV_0 = \int_S \underline{t}\cdot\underline{v} \, dA$$

Hence

$$\int_{V_0}\left(\frac{d}{dt}\underbrace{\left(\rho_0(\varepsilon - \theta s)\right)}_{\rho_0\psi} - S^T : \dot{F}\right) dV_0 + \int_{S_0}\left(I_n^A \mu_A + I_n^B \mu_B\right) dA_0 \geq 0$$

(Dissipation Inequality DI)

We know that $\psi = \psi(F, C_A, C_B)$

$$\Rightarrow \frac{d \rho_0 \psi}{\partial t} = \frac{\partial \rho_0 \psi}{\partial F} : \dot{F} + \frac{\partial \rho_0 \psi}{\partial C_A} \dot{C}_A + \frac{\partial \rho_0 \psi}{\partial C_B} \dot{C}_B$$

Note C_A, C_B have to satisfy mass conservation $\dot{C}_A, \dot{C}_B$ are not arbitrary

Enforce mass conservation with Lagrange multiplier λ_A, λ_B

$$DI \quad \int \left(\frac{\partial \rho_0 \psi}{\partial t} - S^T : \dot{F} \right) dV_0 + \int_{S_0} (\;)\, dA$$

$$- \int_{V_0} \left(\frac{\partial C_A}{\partial t} + \nabla \cdot \underline{I}_A \right) \lambda_A \, dV_0$$

$$- \int_{V_0} \left(\frac{\partial C_B}{\partial t} + \nabla \cdot I_B \right) \lambda_B \, dV_0 \geq 0$$

Now note $\int_{V_0} (\nabla \cdot \underline{I}) \lambda \, dV_0 = \int_{V_0} \left(\nabla \cdot (\lambda \underline{I}) - \underline{I} \cdot \nabla \lambda \right) dV_0$

$$= \int_{S_0} I_n \lambda \, dA - \int_{V_0} \underline{I} \cdot \nabla \lambda \, dV_0$$

D.I is now:

$$\int_V \left(\frac{\partial \rho_0 \Psi}{\partial F} - S^I \right) : \dot{F} \, dV_0 + \int_V \left(\frac{\partial \rho_0 \Psi}{\partial c_A} \bigg|_F - \lambda_A \right) \dot{c}_A \, dV_0$$

$$+ \int_{V_0} \left(\frac{\partial \rho_0 \Psi}{\partial c_B} \bigg|_F - \lambda_B \right) \dot{c}_B \, dV_0$$

$$+ \int_{V_0} \underline{I}_A \cdot \nabla \lambda_A \, dV_0 + \int \underline{I}_B \cdot \nabla \lambda_B \, dV_0$$

$$+ \int_{S_0} \left[(\mu_A - \lambda_A) I_{nA} + (\mu_B - \lambda_B) I_{nB} \right] dA_0 \geq 0$$

This must hold for all admissible variations in C_A, C_B, I_A, I_B, I_{nA}, I_{nB}

→ guides structure of constitutive equations.