Nonlinear Effects of Electromigration on Strained Films

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What is Electromigration?

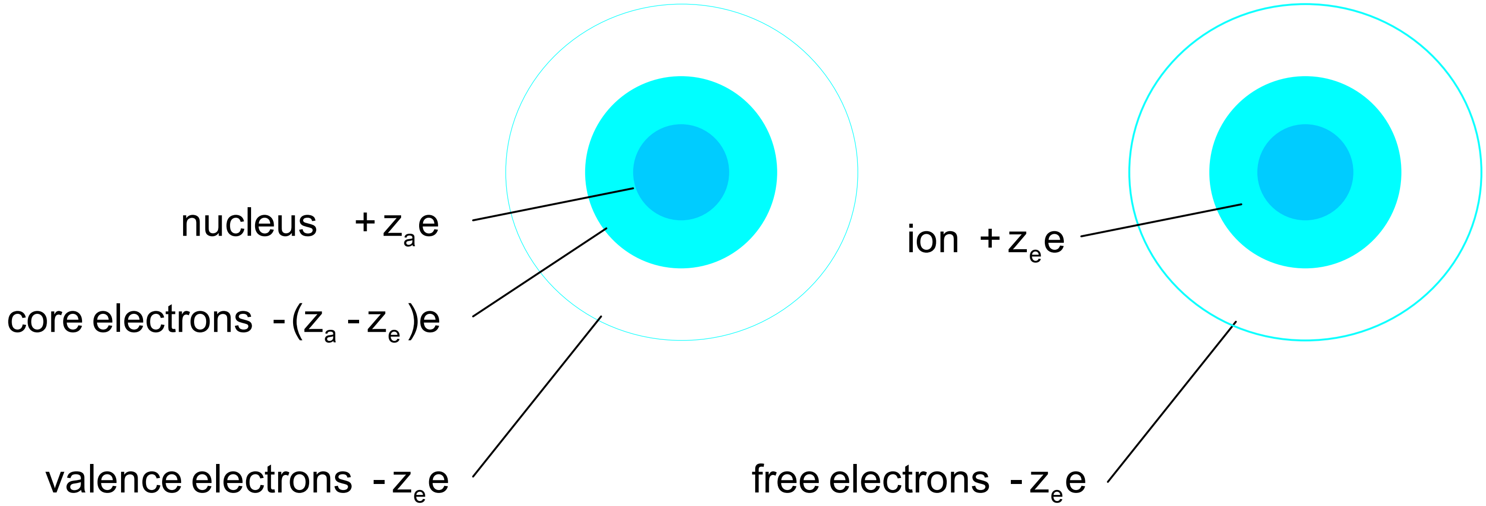
Apply an electrical potential to a coherently strained conducting film	Coherent strain has no effect
Free electrons driven by the electric field form an 'electron wind'	
Electrons in the wind collide with the atoms and cause them to drift	CURRENT STATUS
Atomic movements lead to a non-uniform concentration which gives rise to a chemical potential	
The nonuniform concentration also gives rise to an incompatible eigen-strain field which causes elastic strain	Linear Theory
Elastic strain also contributes to the chemical potential	Linear Theory

An Atom and It's Associated Ion and Free Electrons

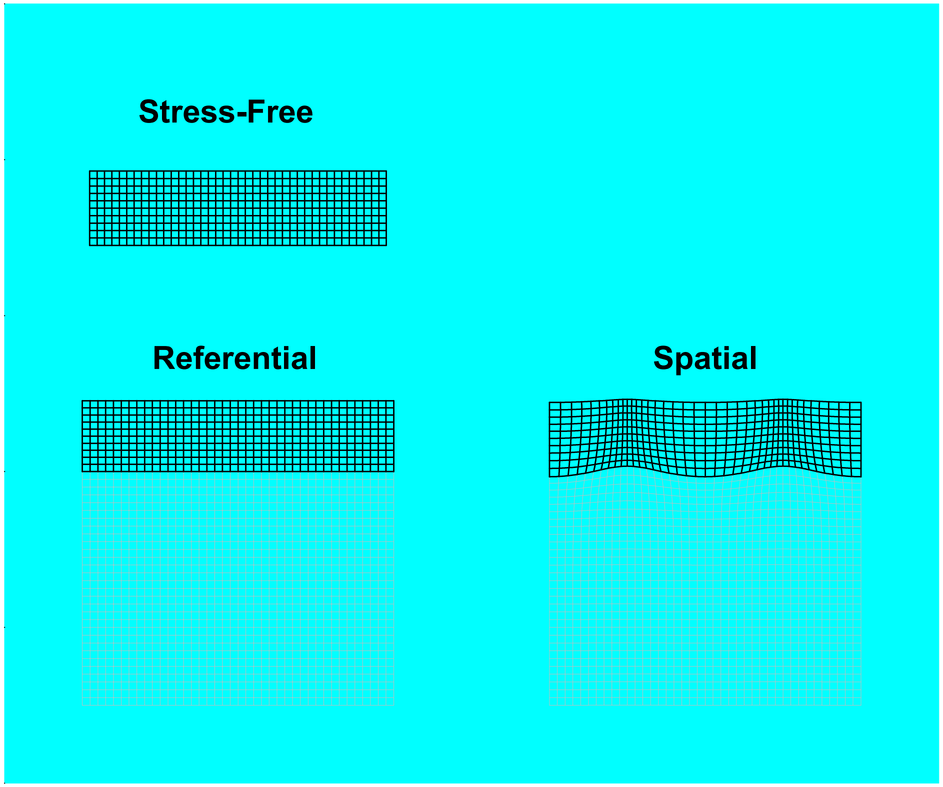
$$z_a = \text{Atomic Number} = \text{Number of Electrons/Atom}$$

$$z_e = \text{Number of Valence Electrons}$$

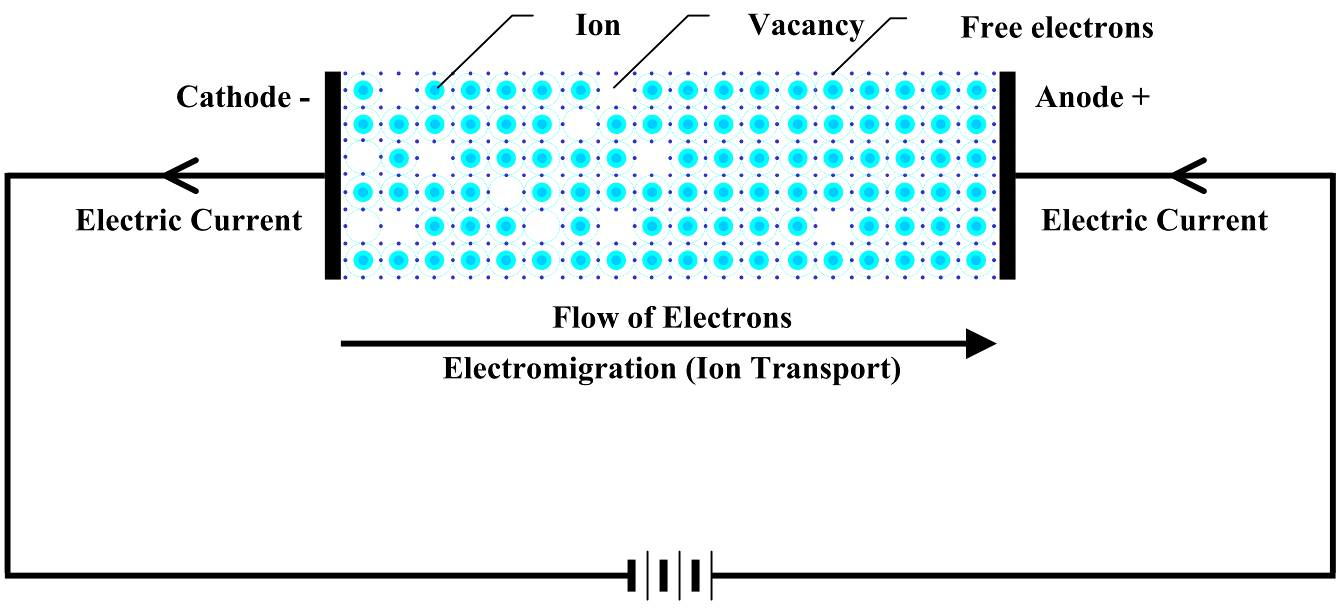
$$e = 1.6 \times 10^{-19} \text{ Coulomb/Electronic Charge}$$



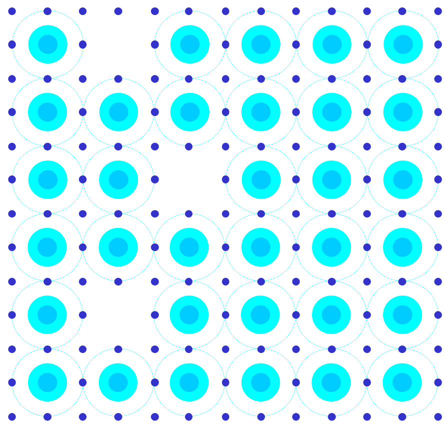
Mismatch Strain In A Film



The Collision of the Moving Ions by the Charge Carriers in the 'Electron Wind'



A Single-Component Solid with Vacancies



Molar Concentrations $[mol/m^3]$:

C_a (atom concentration), C_v (vacancy concentration), C (total concentration)

Mole Fractions: $x_a = C_a/C$, $x_v = C_v/C$

Relationships:

$C_a + C_v = C$ and $x_a + x_v = 1$. Let $x_a = x$ and $x_v = 1 - x$

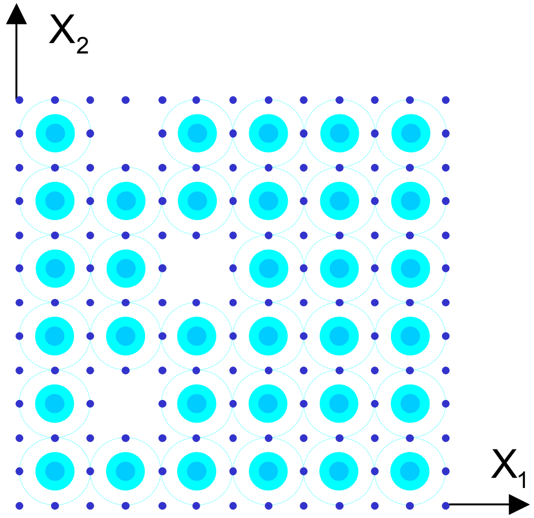
C is the total number of lattice sites per unit volume, but what unit volume?

A Uniform State as a Reference

$\underline{V}(P,T,x) \equiv$ Molar volume [m^3/mol]
at pressure P, temperature T, and mole fraction x.

$\underline{V}(0,T_o,x_o)$ is the molar volume [m^3/mol]
at pressure $P = 0$, temperature T_o, and mole fraction x_o.

Use $\underline{V}(0,T_o,x_o)$ to define a uniform state for a solid body occupying a region V in a reference coordinate system $\mathbf{X}$.



Reference Coordinate System $\mathbf{X}$

What happens when the system becomes nonuniform?

A Nonuniform State

For a nonuniform state,

the temperature $T = T(\mathbf{X}, t) \neq T_o$ and mole fraction $x = x(\mathbf{X}, t) \neq x_o$

The associated molar volume

$\underline{V}(0, T, x)$ is a stress-free transformation from $\underline{V}(0, T_o, x_o)$.

The transformation is termed an

eigentransformation which will be denoted by $\mathbf{F}^*$.

The transformation $\mathbf{F}^*$ converts $d\mathbf{X}$ and dV of the reference

coordinate system to $d\mathbf{X}^{SF}$ and dV^{SF} in a stress-free state.

$$d\mathbf{X}^{SF} = \mathbf{F}^* d\mathbf{X}, \quad dV^{SF} = J^* \, dV, \quad J^* = \det \mathbf{F}^* = \underline{V}(0, T, x)/\underline{V}(0, T_o, x_o)$$

$\mathbf{F}^*$ is, in general, incompatible

and cannot be interpreted as a deformation gradient $\partial\mathbf{X}^{SF}/\partial\mathbf{X}$.

There is an associated elastic transformation $\mathbf{F}^e$.

Eigentransformation, Elastic Transformation and Deformation Gradient

The incompatible eigentransformation $\mathbf{F}^*$ forces the material body to deform :

V in reference coordinate system $\mathbf{X} \rightarrow v$ in spatial coordinate system $\mathbf{x}$

The three sets of transformations are :

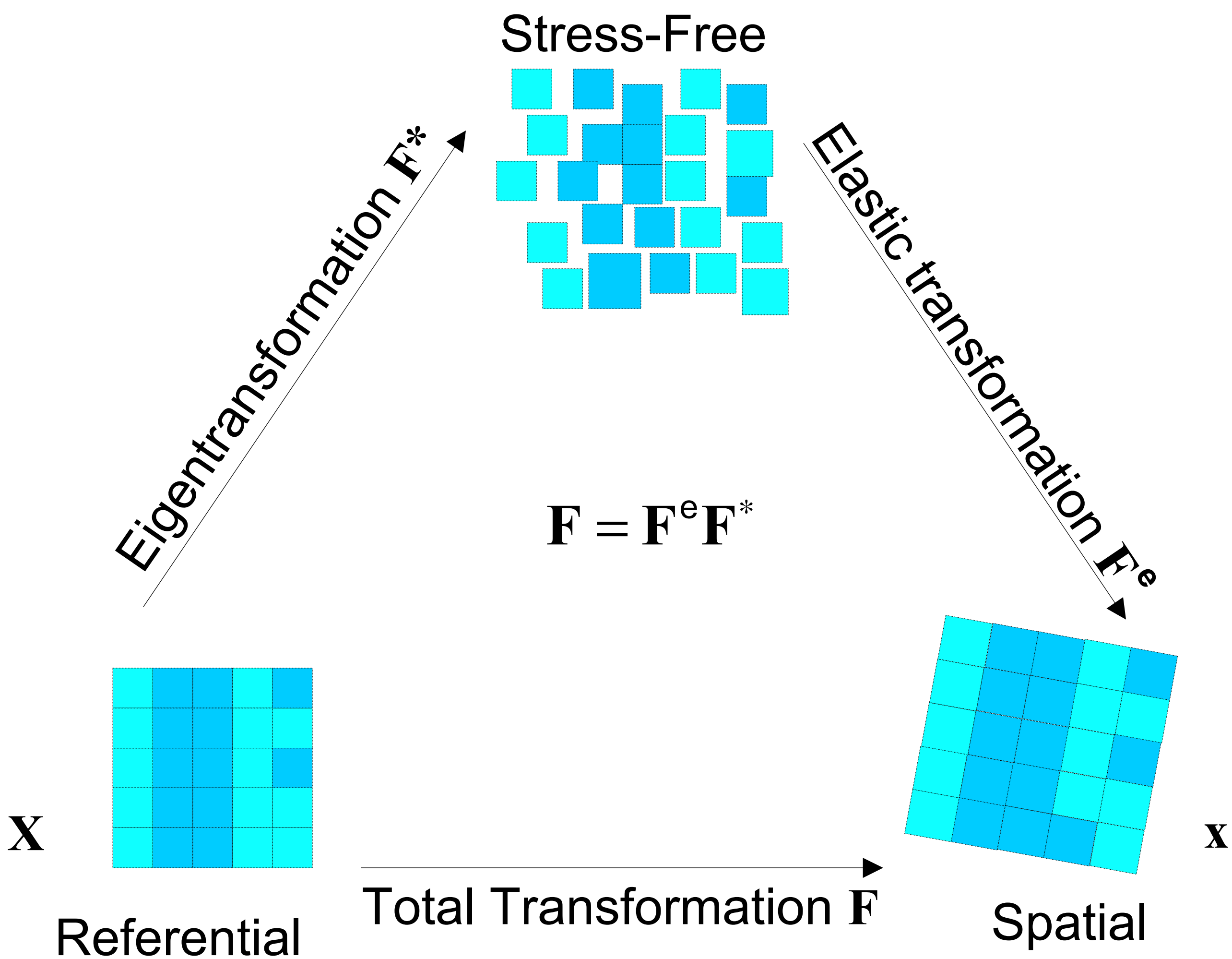
$$d\mathbf{x} = \mathbf{F}\,d\mathbf{X}, \qquad dv = \mathrm{J}\,dV, \qquad \mathrm{J} = \det \mathbf{F}, \qquad \mathbf{F} = \partial\mathbf{x}/\partial\mathbf{X}$$

$$d\mathbf{x} = \mathbf{F}^{\mathrm{e}} d\mathbf{X}^{\mathrm{SF}}, \qquad dv = \mathrm{J}^{\mathrm{e}}\,dV^{\mathrm{SF}}, \qquad \mathrm{J}^{\mathrm{e}} = \det \mathbf{F}^{\mathrm{e}} = \mathrm{J}/\mathrm{J}^*, \qquad \mathbf{F}^{\mathrm{e}} = \mathbf{F}\mathbf{F}^{*-1}$$

$$d\mathbf{X}^{\mathrm{SF}} = \mathbf{F}^* d\mathbf{X}, \qquad dV^{\mathrm{SF}} = \mathrm{J}^*\,dV, \qquad \mathrm{J}^* = \det \mathbf{F}^* = \underline{\mathrm{V}}(0,\mathrm{T},\mathrm{x})/\underline{\mathrm{V}}(0,\mathrm{T}_\mathrm{o},\mathrm{x}_\mathrm{o})$$

Only the total transformation $\mathbf{F}$ is a deformation gradient.

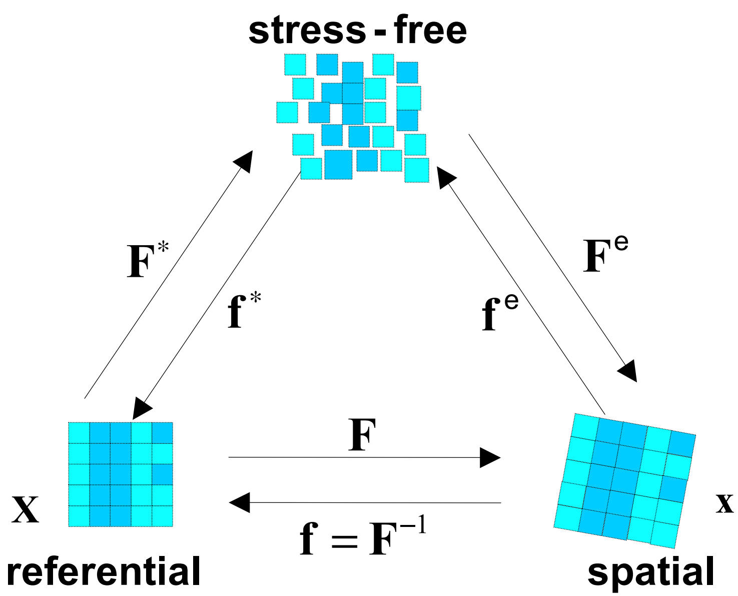
Eigentransformation, Elastic Transformation and Total Transformation



Eigentransformation, Elastic Transformation and Total Transformation

Molar Concentrations in Referential, Stress-Free and Spatial Systems:

$$C = C_a(\mathbf{X},t) + C_v(\mathbf{X},t), \qquad C^{SF} = C_a^{SF}(\mathbf{X},t) + C_a^{SF}(\mathbf{X},t), \qquad c = c_a(\mathbf{x},t) + c_v(\mathbf{x},t)$$



$$J^* = \frac{dV^{SF}}{dV} = \frac{C}{C^{SF}(\mathbf{X},t)} = \frac{C_a(\mathbf{X},t)}{C_a^{SF}(\mathbf{X},t)} = \frac{C_v(\mathbf{X},t)}{C_v^{SF}(\mathbf{X},t)}$$

$$J^e = \frac{dv}{dV^{SF}} = \frac{C^{SF}(\mathbf{X},t)}{c(\mathbf{x},t)} = \frac{C_a^{SF}(\mathbf{X},t)}{c_a(\mathbf{x},t)} = \frac{C_v^{SF}(\mathbf{X},t)}{c_v(\mathbf{x},t)}$$

$$J = \frac{dv}{dV} = \frac{C}{c(\mathbf{x},t)} = \frac{C_a(\mathbf{X},t)}{c_a(\mathbf{x},t)} = \frac{C_v(\mathbf{X},t)}{c_v(\mathbf{x},t)}$$

Maxwell's Equations in Matter

Electric Field $\mathbf{E}$ [V/m]

Polarization $\mathbf{P}$ [C/m^2]

Electric-Flux Density $\mathbf{D}$[C/m^2]

Permittivity $\varepsilon_o = 8.854 \times 10^{-12}$ F/m

Charge Density q_c[C/m^3]

Magnetic Field $\mathbf{H}$[A-turn/m]

Magnetization $\mathbf{M}$[A/m]

Magnetic-Flux Density $\mathbf{B}$[W/m^2]

Permeability $\mu_o = 4\pi \times 10^{-7}$ H/m

Current Density $\mathbf{j}_c$[C/m^{2}s]

Faraday's Law	$\text{curl}\ \mathbf{E}(\mathbf{x},t) = -\partial\mathbf{B}(\mathbf{x},t)/\partial t$
Ampere's Law	$\text{curl}\ \mathbf{H}(\mathbf{x},t) = \mathbf{j}_c(\mathbf{x},t) + \partial\mathbf{D}(\mathbf{x},t)/\partial t$
Gauss's Law	$\text{div}\ \mathbf{D}(\mathbf{x},t) = q_c(\mathbf{x},t)$
Magnetic Flux	$\text{div}\ \mathbf{B}(\mathbf{x},t) = 0$
Charge Conservation	$\text{div}\ \mathbf{j}_c(\mathbf{x},t) = -\partial q_c(\mathbf{x},t)/\partial t$
Magnetic-Flux Density	$\mathbf{B} = \mu_o(\mathbf{H} + \mathbf{M})$
Electric-Flux Density	$\mathbf{D} = \varepsilon_o\mathbf{E} + \mathbf{P}$

For this presentation, only the electric field $\mathbf{E} \neq 0$.

Electromagnetic Force

Molar Charge Density: $\underline{q}_c$ [C/mol]

Drift Velocity of Charge (spatial & referential): $\mathbf{v}_c(\mathbf{x},t)=\mathbf{F}\mathbf{V}_c(\mathbf{X},t)$ [m/s]

Drift Velocity of Element (spatial & referential): $\mathbf{v}_a(\mathbf{x},t)=\mathbf{F}\mathbf{V}_a(\mathbf{X},t)$ [m/s]

Velocity of Charge (spatial & referential): $\dot{\mathbf{x}}+\mathbf{v}_c$ or $\dot{\mathbf{x}}+\mathbf{V}_c$ [m/s]

Velocity of Element (spatial & referential): $\dot{\mathbf{x}}+\mathbf{v}_a$ or $\dot{\mathbf{x}}+\mathbf{V}_a$ [m/s]

Molar EM Force Density: $\underline{\mathbf{f}}^{(em)}(\mathbf{x},t)$ or $\underline{\mathbf{F}}^{(em)}(\mathbf{X},t)$ [C/mol]

Magnetic-Flux Density: $\mathbf{B}=\mu_o(\mathbf{H}+\mathbf{M})$

Electric-Flux Density: $\mathbf{D}=\varepsilon_o\mathbf{E}+\mathbf{P}$

Molar EM Force Density (spatial): $\underline{\mathbf{f}}^{(em)}=\underline{q}_c\mathbf{E}+\underline{q}_c(\dot{\mathbf{x}}+\mathbf{v}_c)\times\mathbf{B}$

Molar EM Force Density (referential): $\underline{\mathbf{F}}^{(em)}=\underline{q}_c\mathbf{E}+\underline{q}_c(\dot{\mathbf{x}}+\mathbf{V}_c)\times\mathbf{B}$

For this paper

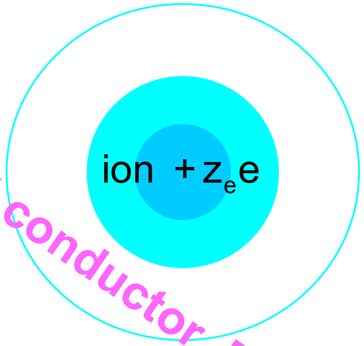
Electromagnetic Force - Metals

z_e = Number of Valence Electrons

Electronic Charge: $e = 1.6 \times 10^{-19}$ Coulomb

Avogadro's Number: $N = 0.6022 \times 10^{24}$

Faraday $\mathscr{F} = Ne = 96352$ C/mol



For perfect conductor, EM force=0

Molar Charge Density: $\underline{q}_c$ for ion $= \underline{q}_+ = \mathscr{F} z_e x_a$

$\underline{q}_c$ for free electrons $= \underline{q}_- = -\mathscr{F} z_e x_a$

$$\underline{\mathbf{f}}^{(em)} = (\underline{q}_+ + \underline{q}_-)\mathbf{E} + [\underline{q}_+(\dot{\mathbf{x}} + \mathbf{v}_+) + \underline{q}_-(\dot{\mathbf{x}} + \mathbf{v}_-)] \times \mathbf{B} = (\underline{q}_+ \mathbf{v}_+ + \underline{q}_- \mathbf{v}_-) \times \mathbf{B}$$

$$\underline{\mathbf{F}}^{(em)} = (\underline{q}_+ \mathbf{V}_+ + \underline{q}_- \mathbf{V}_-) \times \mathbf{B}, \quad \mathbf{V}_+ = \mathbf{V}_a, \quad \mathbf{v}_+ = \mathbf{v}_a$$

$$\mathbf{f}^{(em)}(\mathbf{x}, t) = c\underline{\mathbf{f}}^{(em)} = (\mathscr{F} z_e \mathbf{j}_a + \mathbf{j}_-) \times \mathbf{B}, \quad \mathbf{F}^{(em)}(\mathbf{X}, t) = C\underline{\mathbf{F}}^{(em)} = (\mathscr{F} z_e \mathbf{J}_a + \mathbf{J}_-) \times \mathbf{B}$$

Balance Law - Linear Momentum

$$\mathbf{X} \xrightleftharpoons[\mathbf{f}\ \text{and}\ \mathrm{j}]{\mathbf{F}\ \text{and}\ \mathrm{J}} \mathbf{x}$$

EM Force [N/m^3]	$\mathbf{F}^{(em)} = C\underline{\mathbf{F}}^{(em)} = J\,\mathbf{f}^{(em)}$	$j\mathbf{F}^{(em)} = c\underline{\mathbf{f}}^{(em)} = \mathbf{f}^{(em)}$

EM Force [N/m^3] = 0 for this paper

Mass Density [Kg/m^3]	$\rho_o = J\rho$	$j\rho_o = \rho$
Stress [Pa]	Piola $\mathbf{S} = J\,\boldsymbol{\sigma}\mathbf{f}^T$	$j\mathbf{S}\mathbf{F}^T = \boldsymbol{\sigma}$ Cauchy
Balance Law	$\rho_o\ddot{\mathbf{x}} = \mathrm{Div}\,\mathbf{S} + \mathbf{F}^{(em)}$	$\rho\ddot{\mathbf{x}} = \mathrm{div}\,\boldsymbol{\sigma} + \mathbf{f}^{(em)}$
Moment of Momentum	$\mathbf{S}\mathbf{F}^T = \mathbf{F}\mathbf{S}^T$	$\boldsymbol{\sigma} = \boldsymbol{\sigma}^T$

Balance Law - Heat

$$\mathbf{X} \underset{\mathbf{f}\ \text{and}\ j}{\overset{\mathbf{F}\ \text{and}\ J}{\rightleftarrows}} \mathbf{x}$$

Molar Heat Content [J/mol] $\underline{q}_h$

Heat Content [J/m³] $Q_h(\mathbf{X},t) = C\underline{q}_h = Jq_h$ $\quad jQ_h = c\underline{q}_h = q_h$

Heat Flux [J/m²s] $\mathbf{J}_h(\mathbf{X},t) = J\,\mathbf{f}\mathbf{j}_h$ $\quad j\mathbf{F}\mathbf{J}_h = \mathbf{j}_h(\mathbf{x},t)$

Balance Law $\dot{Q}_h = -\text{Div}\ \mathbf{J}_h$ $\quad c\dot{\underline{q}}_h = -\text{div}\ \mathbf{j}_h$

Balance Law – Free Electrons

$$\mathbf{X} \;\underset{\mathbf{f}\ \text{and}\ j}{\overset{\mathbf{F}\ \text{and}\ J}{\rightleftarrows}}\; \mathbf{x}$$

Molar Charge Density [C/mol] $\underline{q}_- = -\mathscr{F}\, z_e x_a$

Charge Density [C/m^3] $Q_-(\mathbf{X},t) = C\underline{q}_- = J q_-$ $\qquad j Q_- = c\underline{q}_- = q_-$

Current Density [A/m^2] $\mathbf{J}_-(\mathbf{X},t) = J\,\mathbf{f}\mathbf{j}_-$ $\qquad j\,\mathbf{F}\mathbf{J}_- = \mathbf{j}_-(\mathbf{x},t)$

Balance Law $\partial Q_- / \partial t = -\,\mathrm{Div}\,\mathbf{J}_-$ $\qquad c\dot{\underline{q}}_- = -\mathrm{div}\,\mathbf{j}_-$

Electron Density [1/m^3] $Q_e(\mathbf{X},t) = Q_-(\mathbf{X},t)/(\text{-e})$

Electron Flux [1/m^{2}s] $\mathbf{J}_e(\mathbf{X},t) = \mathbf{J}_-(\mathbf{X},t)/(\text{-e})$

Balance Law - Masses

$$\mathbf{X} \quad \underset{\mathbf{f} \text{ and } \mathrm{j}}{\overset{\mathbf{F} \text{ and } \mathrm{J}}{\rightleftarrows}} \quad \mathbf{x}$$

Concentrations [mol/m^3]

Element	$C_a(\mathbf{X},t) = Jc_a$	$jC_a = c_a(\mathbf{x},t)$
Vacancy	$C_v(\mathbf{X},t) = Jc_v$	$jC_v = c_v(\mathbf{x},t)$
Total	$C = Jc(\mathbf{x},t)$	$jC = c(\mathbf{x},t)$
Mass Flux [mol/m^{2}s]	$\mathbf{J}_a(\mathbf{X},t) = C_a\mathbf{V}_a$	$c_a\mathbf{v}_a = \mathbf{j}_a(\mathbf{x},t)$
Vacancy Flux [mol/m^{2}s]	$\mathbf{J}_v(\mathbf{X},t) = J\,\mathbf{f}\mathbf{j}_v$	$j\mathbf{F}\mathbf{J}_v = \mathbf{j}_v(\mathbf{x},t)$
Mole Fractions	$x_a = x\,, \quad x_v = 1 - x$	
Balance Law	$\partial C_a/\partial t = -\,\mathrm{Div}\ \mathbf{J}_a$	$c\dot{x}_a = -\mathrm{div}\ \mathbf{j}_a$
Balance Law	$\partial C_v/\partial t = -\,\mathrm{Div}\ \mathbf{J}_v$	$c\dot{x}_v = -\mathrm{div}\ \mathbf{j}_v$

Balance Law - Energy

Spatial Representation

$$\frac{d}{dt}\int_{v} c\underline{u}\,dv = \int_{\partial v} [\dot{\mathbf{x}}\cdot\mathbf{t}_{\mathbf{n}} - \mathbf{j}_h\cdot\mathbf{n}]\,da + \int_{v}\{\dot{\mathbf{x}}\cdot\mathbf{f}^{(em)} + [\mathscr{F} z_e\,\mathbf{j}_a + \mathbf{j}_-]\cdot[-\mathrm{grad}\,\phi(\mathbf{x},t)]\}\,dv$$

$\underline{u}$: molar internal energy, $\mathbf{t}_{\mathbf{n}} = \boldsymbol{\sigma}\mathbf{n}$: Cauchy traction, $\mathbf{j}_h$: heat flux

$\mathbf{j}_a$: mass flux, $\mathbf{j}_-$: current density, $\mathbf{n}$: exterior normal

$\phi(\mathbf{x},t)$: electrostatic potential and $\mathbf{E} = -\mathrm{grad}\,\phi(\mathbf{x},t)$

$$c\dot{\underline{u}} = c\dot{\underline{q}}_h + \dot{\mathbf{x}}_{,i}\cdot\mathbf{t}_i - [\mathscr{F} z_e\,\mathbf{j}_a + \mathbf{j}_-]\cdot\mathrm{grad}\,\phi(\mathbf{x},t)$$

Referential Representation

EM Force $[N/m^3] = 0$ for this paper

$$\frac{d}{dt}\int_{V} C\underline{U}\,dV = \int_{\partial V} [\dot{\mathbf{x}}\cdot\mathbf{T}_{\mathbf{N}} - \mathbf{J}_h\cdot\mathbf{N}]\,dA + \int_{V}\{\dot{\mathbf{x}}\cdot\mathbf{F}^{(em)} + [\mathscr{F} z_e\,\mathbf{J}_a + \mathbf{J}_-]\cdot[-\mathrm{Grad}\,\Phi(\mathbf{X},t)]\}\,dV$$

$\underline{U}$: molar internal energy, $\mathbf{T}_{\mathbf{N}} = \mathbf{S}\mathbf{N}$: Piola traction, $\mathbf{J}_h$: heat flux

$\mathbf{J}_a$: mass flux, $\mathbf{J}_-$: current density, $\mathbf{N}$: exterior normal

$$\Phi(\mathbf{X},t) = \phi(\mathbf{x}(\mathbf{X},t),t)$$

$$\dot{U} = C\dot{\underline{U}} = \dot{Q}_h + \dot{\mathbf{x}}_{,I}\cdot\mathbf{T}_I - [\mathscr{F} z_e\,\mathbf{J}_a + \mathbf{J}_-]\cdot\mathrm{Grad}\,\Phi(\mathbf{X},t)$$

The Second Law

Spatial Representation: $$\frac{d}{dt}\int_v c\underline{s}\,dv + \int_{\partial v}[\mathbf{j}_h - \bar{\mu}_a\mathbf{j}_a - \bar{\mu}_v\mathbf{j}_v]\cdot\frac{\mathbf{n}}{T}\,da \geq 0$$

$\underline{s}$: molar entropy, $\mathbf{j}_h$: heat flux, $\mathbf{j}_a, \mathbf{j}_v$: molal mass, vacancy flux

$\bar{\mu}_a, \bar{\mu}_v$: (partial molar) chemical potential for element, vacancy

T : temperature, $\mathbf{n}$: exterior normal

$$cT\dot{\underline{s}} - c\dot{\underline{q}}_h - \frac{1}{T}\mathbf{j}_h\cdot \text{grad}\,T + c\bar{\mu}_a\dot{x}_a - T\mathbf{j}_a\cdot\text{grad}\,\frac{\bar{\mu}_a}{T} + c\bar{\mu}_v\dot{x}_v - T\mathbf{j}_v\cdot\text{grad}\,\frac{\bar{\mu}_v}{T} \geq 0$$

Referential Representation: $$\frac{d}{dt}\int_V C\underline{S}\,dV + \int_{\partial V}[\mathbf{J}_h - \bar{\mu}_a\mathbf{J}_a - \bar{\mu}_v\mathbf{J}_v]\cdot\frac{\mathbf{N}}{T}\,dA \geq 0$$

$\underline{S}$: molar entropy, $\mathbf{J}_h$: heat flux, $\mathbf{J}_a, \mathbf{J}_v$: molal mass, vacancy flux

$\bar{\mu}_a, \bar{\mu}_v$: (partial molar) chemical potential for element, vacancy

T : temperature, $\mathbf{N}$: exterior normal

$$T\dot{S} - \dot{Q}_h - \frac{1}{T}\mathbf{J}_h\cdot\text{Grad}\,T + \bar{\mu}_a\dot{C}_a - T\mathbf{J}_a\cdot\text{Grad}\,\frac{\bar{\mu}_a}{T} + \bar{\mu}_v\dot{C}_v - T\mathbf{J}_v\cdot\text{Grad}\,\frac{\bar{\mu}_v}{T} \geq 0$$

The Second Law – Helmholtz Free Energy

Referential Representation

Energy Balance

$$-\dot{U} + \dot{Q}_h + \dot{\mathbf{x}}_{,I} \cdot \mathbf{T}_I - [\mathscr{F} z_e \mathbf{J}_a + \mathbf{J}_-] \cdot \mathrm{Grad}\,\Phi(\mathbf{X}, t) = 0$$

Second Law

$$T\dot{S} - \dot{Q}_h - \frac{1}{T}\mathbf{J}_h \cdot \mathrm{Grad}\,T + \bar{\mu}_a \dot{C}_a - T\mathbf{J}_a \cdot \mathrm{Grad}\,\frac{\bar{\mu}_a}{T} + \bar{\mu}_v \dot{C}_v - T\mathbf{J}_v \cdot \mathrm{Grad}\,\frac{\bar{\mu}_v}{T} \geq 0$$

Combining and in terms of Helmholtz Energy : $A = U - TS$

Dissipation Inequality

$$-[\dot{A} + S\dot{T} - \mathbf{S} \cdot \dot{\mathbf{F}} - \bar{\mu}_a \dot{C}_a - \bar{\mu}_v \dot{C}_v] - \frac{1}{T}[\mathbf{J}_h - \bar{\mu}_a \mathbf{J}_a - \bar{\mu}_v \mathbf{J}_v] \cdot \mathrm{Grad}\,T$$
$$- \mathbf{J}_v \cdot \mathrm{Grad}\,\bar{\mu}_v - \mathbf{J}_a \cdot \mathrm{Grad}\,[\bar{\mu}_a + \mathscr{F} z_e \Phi] - \mathbf{J}_- \cdot \mathrm{Grad}\,\Phi \geq 0$$

The Helmholtz Free Energy

Helmholtz per unit referential volume — Molar Helmholtz — Molar Gibbs — Piola . Deformation Gradient

$$A(\mathbf{F},T,C_a,C_v) = C\underline{A}(\mathbf{F},T,x) = C\underline{G}(\mathbf{S},T,x) + \mathbf{S}\cdot\mathbf{F} \quad \text{and} \quad \mathbf{F} = \mathbf{F}^e\mathbf{F}^*$$

$$\underline{A}(\mathbf{1},T_o,x_o) = 0 \quad \text{as a reference}$$

$$\underline{A}(\mathbf{F}^*,T,x) = \underline{G}^{SF}(T,x) \equiv \underline{G}(\mathbf{S},T,x)\big|_{\mathbf{S}=\mathbf{0}}, \quad \mathbf{F}^* \text{ stress-free eigentransformation}$$

$$\underline{A}(\mathbf{F},T,x) = \underline{A}(\mathbf{F}^e\mathbf{F}^*,T,x) = \underline{A}(\mathbf{F}^*,T,x) + [\underline{A}(\mathbf{F}^e\mathbf{F}^*,T,x) - \underline{A}(\mathbf{F}^*,T,x)]$$

$$\text{Define: } \underline{W}^{SF}(\mathbf{F}^e,T,x) \equiv \underline{A}(\mathbf{F}^e\mathbf{F}^*,T,x) - \underline{A}(\mathbf{F}^*,T,x), \quad \underline{W}^{SF}(\mathbf{1},T,x) = 0$$

CONCLUSION

$$A(\mathbf{F},T,C_a,C_v) = C\underline{A}(\underline{\mathbf{F}}^e\mathbf{F}^*,T,x) = C\,[\underline{A}(\mathbf{F}^*,T,x) + \underline{W}^{SF}(\mathbf{F}^e,T,x)], \text{ or}$$

Stress-free molar Gibbs — Stress-free strain energy

$$A = C\underline{G}(0,T,x) + \frac{C}{C^{SF}}[C^{SF}\underline{W}^{SF}(\mathbf{F}^e,T,x)] = C\underline{G}^{SF}(T,x) + J^*W^{SF}(\mathbf{F}^e,T,x)$$

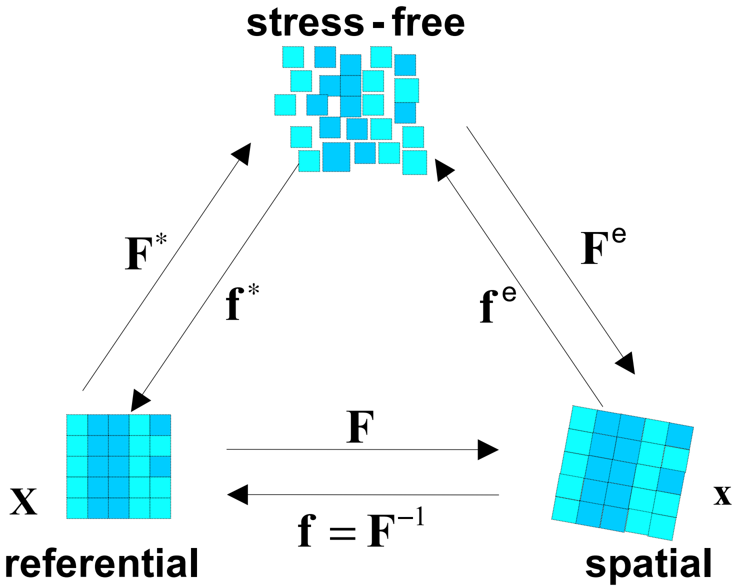
The Helmholtz Free Energy

Helmholtz per unit referential volume — Molar Helmholtz — Molar Gibbs — Piola . Deformation Gradient

$$A(\mathbf{F},T,C_a,C_v) = C\underline{A}(\mathbf{F},T,x) = C\underline{G}(\mathbf{S},T,x) + \mathbf{S}\cdot\mathbf{F} \quad \text{and} \quad \mathbf{F} = \mathbf{F}^e\mathbf{F}^*$$

Stress-free molar Gibbs — Stress-free strain energy density

$$A(\mathbf{F},T,C_a,C_v) = C\underline{G}^{SF}(T,x) + J^* W^{SF}(\mathbf{F}^e,T,x)$$



Piola Stress & Entropy

CLAUSIUS-DUHEM INEQUALITY

$$-[\dot{A} + S\dot{T} - \mathbf{S}\cdot\dot{\mathbf{F}} - \bar{\mu}_a \dot{C}_a - \bar{\mu}_v \dot{C}_v] - \frac{1}{T}[\mathbf{J}_h - \bar{\mu}_a \mathbf{J}_a - \bar{\mu}_v \mathbf{J}_v]\cdot \mathrm{Grad}\,T$$

$$-\mathbf{J}_v \cdot \mathrm{Grad}\,\bar{\mu}_v - \mathbf{J}_a \cdot \mathrm{Grad}\,[\bar{\mu}_a + \mathscr{F} z_e \Phi] - \mathbf{J}_- \cdot \mathrm{Grad}\,\Phi \geq 0$$

HELMHOLTZ ENERGY

Stress-free molar Gibbs: $\underline{G}^{SF}$

strain energy density per unit stress-free volume: W^{SF}

$$A(\mathbf{F}, T, C_a, C_v) = C\underline{G}^{SF}(T, x) + \underbrace{J^* W^{SF}(\mathbf{F}^e, T, x)}_{W}$$

W strain energy density per unit referential volume

Piola Stress: $\mathbf{S} = \frac{\partial A}{\partial \mathbf{F}} = \frac{\partial W}{\partial \mathbf{F}} = J^* \mathbf{S}^e (\mathbf{f}^*)^T$ where $\mathbf{S}^e \equiv \frac{\partial W^{SF}}{\partial \mathbf{F}^e}$, $\mathbf{f}^* = (\mathbf{F}^*)^{-1}$

Entropy: $-S = \frac{\partial A}{\partial T} = C\frac{\partial \underline{G}^{SF}(T, x)}{\partial T} + J^* \frac{\partial W^{SF}(\mathbf{F}^e, T, x)}{\partial T}$

Chemical Potential - Eshelby Stress

CLAUSIUS-DUHEM INEQUALITY

$$-[\dot{A} + S\dot{T} - \mathbf{S}\cdot\dot{\mathbf{F}} - \bar{\mu}_a\dot{C}_a - \bar{\mu}_v\dot{C}_v] - \frac{1}{T}[\mathbf{J}_h - \bar{\mu}_a\mathbf{J}_a - \bar{\mu}_v\mathbf{J}_v]\cdot \text{Grad}\, T$$
$$-\mathbf{J}_v\cdot\text{Grad}\,\bar{\mu}_v - \mathbf{J}_a\cdot\text{Grad}\,[\bar{\mu}_a + \mathscr{F} z_e\Phi] - \mathbf{J}_- \cdot \text{Grad}\,\Phi \geq 0$$

HELMHOLTZ FREE ENERGY

$$A(\mathbf{F}, T, C_a, C_v) = C\underline{G}^{SF}(T, x) + J^* W^{SF}(\mathbf{F}^e, T, x)$$

$$\bar{\mu}_a = \underline{G}^{SF} + (1\text{-}x)\frac{\partial \underline{G}^{SF}}{\partial x} + \frac{J^*}{C}(1\text{-}x)\frac{\partial W^{SF}}{\partial x} + J^*\mathbf{C}^e\cdot\left[\frac{\partial \mathbf{F}^*}{\partial C_a}(\mathbf{f}^*)^T\right] \quad \text{or} \quad \mathbf{C}\cdot\left[\mathbf{f}^*\frac{\partial \mathbf{F}^*}{\partial C_a}\right]$$

$$\bar{\mu}_v = \underline{G}^{SF} - x\frac{\partial \underline{G}^{SF}}{\partial x} - \frac{J^*}{C}x\frac{\partial W^{SF}}{\partial x} + J^*\mathbf{C}^e\cdot\left[\frac{\partial \mathbf{F}^*}{\partial C_v}(\mathbf{f}^*)^T\right] \quad \text{or} \quad \mathbf{C}\cdot\left[\mathbf{f}^*\frac{\partial \mathbf{F}^*}{\partial C_v}\right]$$

where $\mathbf{C}^e = W^{SF}\mathbf{1} - (\mathbf{F}^e)^T\mathbf{S}^e,\ \mathbf{C} = J^*W^{SF}\mathbf{1} - \mathbf{F}^T\mathbf{S}$ are the generalized Eshelby stress

The Rest Of The Dissipation Inequality

$$-\mathbf{J}_h \cdot \frac{1}{T}\,\text{Grad}\,T - \mathbf{J}_a \cdot [\text{Grad}\,(\bar{\mu}_a + \mathscr{F}\, z_e \Phi) - \frac{\bar{\mu}_a}{T}\,\text{Grad}\,T]$$

$$-\mathbf{J}_v \cdot [\text{Grad}\,\bar{\mu}_v - \frac{\bar{\mu}_v}{T}\,\text{Grad}\,T] - \mathbf{J}_- \cdot \text{Grad}\,\Phi \geq 0$$

Using $\mathbf{J}_v + \mathbf{J}_a = 0$ and for isothermal cases

$$-\mathbf{J}_a \cdot \text{Grad}\,[\bar{\mu}_a - \bar{\mu}_v + \mathscr{F}\, z_e \Phi] - \mathbf{J}_- \cdot \text{Grad}\,\Phi \geq 0$$

FOUR PHENOMENOLOGICAL CONSTANTS

$$\mathbf{J}_a = -\frac{DC_a}{RT}\nabla\,[\bar{\mu}_a - \bar{\mu}_v + \mathscr{F}\, z_e \Phi] - \frac{DC_a}{RT}\mathscr{F}\, z_{wd} \nabla\,\Phi$$

$$\mathbf{J}_- = -\frac{1}{\rho}\frac{n_{ch}}{\mathscr{F}\, z_e}\nabla\,[\bar{\mu}_a - \bar{\mu}_v + \mathscr{F}\, z_e \Phi] - \frac{1}{\rho}\nabla\,\Phi$$

Diffusion Coefficient $D[m^2/s]$, Temperature $T[K]$

Molar Botzmann constant $R[J/mol\ K]$, Resistivity ρ

Electromigration

$$\mathbf{J}_a = -\frac{DC_a}{RT}\nabla[\bar{\mu}_a - \bar{\mu}_v + \mathscr{F} z_e \Phi] - \frac{DC_a}{RT}\mathscr{F} z_{wd}\nabla\Phi = -\frac{DC_a}{RT}\nabla[\bar{\mu}_a - \bar{\mu}_v + \mathscr{F} z^*\Phi]$$

chemical potential — **electromigration** — **electron-wind** — $z^* = z_e + z_{wd}$

Diffusion Coefficient $D[m^2/s]$, Temperature $T[K]$

Molar Botzmann constant $R[J/mol\ K]$

In terms of strees - free molar Gibbs Energy $\underline{G}^{SF}(T,x)$, strain energy density $W^{SF}(\mathbf{F}^e,T,x)$ and eigentransformation $\mathbf{F}^*(x)$

$$\bar{\mu}_a - \bar{\mu}_v = \frac{\partial \underline{G}^{SF}}{\partial x} + \frac{J^*}{C}\frac{\partial W^{SF}}{\partial x} + \mathbf{J}^*\mathbf{C}^e \cdot \left[\frac{1}{C}\frac{\partial \mathbf{F}^*}{\partial x}(\mathbf{f}^*)^T\right] \quad \text{or} \quad \mathbf{C}\cdot\left[\mathbf{f}^*\frac{1}{C}\frac{\partial \mathbf{F}^*}{\partial x}\right]$$

where $\mathbf{C}^e = W^{SF}\mathbf{1} - (\mathbf{F}^e)^T\mathbf{S}^e$, $\mathbf{C} = J^* W^{SF}\mathbf{1} - \mathbf{F}^T\mathbf{S}$ are the generalized Eshelby stress

Electromigration (continued)

$$\mathbf{J}_a = -\frac{DC_a}{RT}\nabla[\bar{\mu}_a - \bar{\mu}_v + \mathscr{F} z^* \Phi]$$

Let $\underline{V}^{SF}(T,x)$ be the stress-free molar volume. By definition and for

cubic crystals, $J^*(T,x) = \underline{V}^{SF}(T,x)/\underline{V}^{SF}(T,x_o)$, $\mathbf{F}^* = (J^*)^{1/3}\mathbf{1}$, and

$$\bar{\mu}_a - \bar{\mu}_v = \frac{\partial \underline{G}^{SF}}{\partial x} + \frac{J^*}{C}\frac{\partial W^{SF}}{\partial x} + [\mathbf{C}\cdot\mathbf{1}]\frac{1}{C}\frac{\partial \ln J^*}{\partial x}$$

where $\mathbf{C} = J^* W^{SF}\mathbf{1} - \mathbf{F}^T\mathbf{S} = J^* W^{SF}\mathbf{1} - [\mathbf{1} + \nabla\mathbf{u}]\mathbf{S} = J^* W^{SF}\mathbf{1} - [\mathbf{1} + \nabla\mathbf{u}]\mathbf{S}$