The Conjugate Roles of Eshelby Stress and Eigentransformation in Composition-Generated and Stress-Assisted Diffusion

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Outline

Motivation: The self-assembly of an alloy epilayer by diffusion.

Diffusion: Deformation is affected by composition but not vice versa.

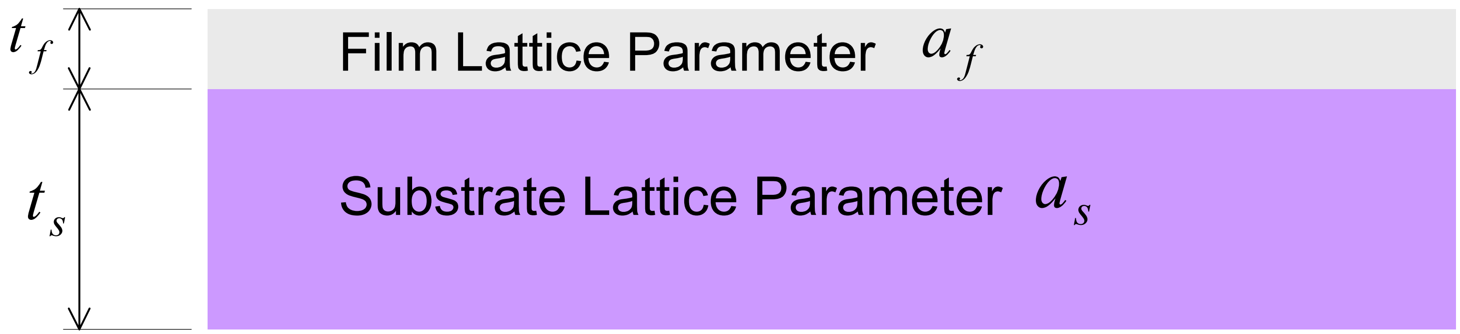
Reason: The chemical potential is only proportional to the trace of the stress.

Assertion: It should be the trace of a properly defined Eshelby stress.

Approach:

- Composition induced eigentransformation.
- Helmholtz free energy in terms of the stress-free strain energy and molar Gibbs free energy of mixing.

Films on Substrates



Lattice Mismatch Parameter $\varepsilon_{\mathrm{m}} = \left(a_s - a_f\right) / a_f, \quad \pm 1 \text{ to } \pm 5\%$

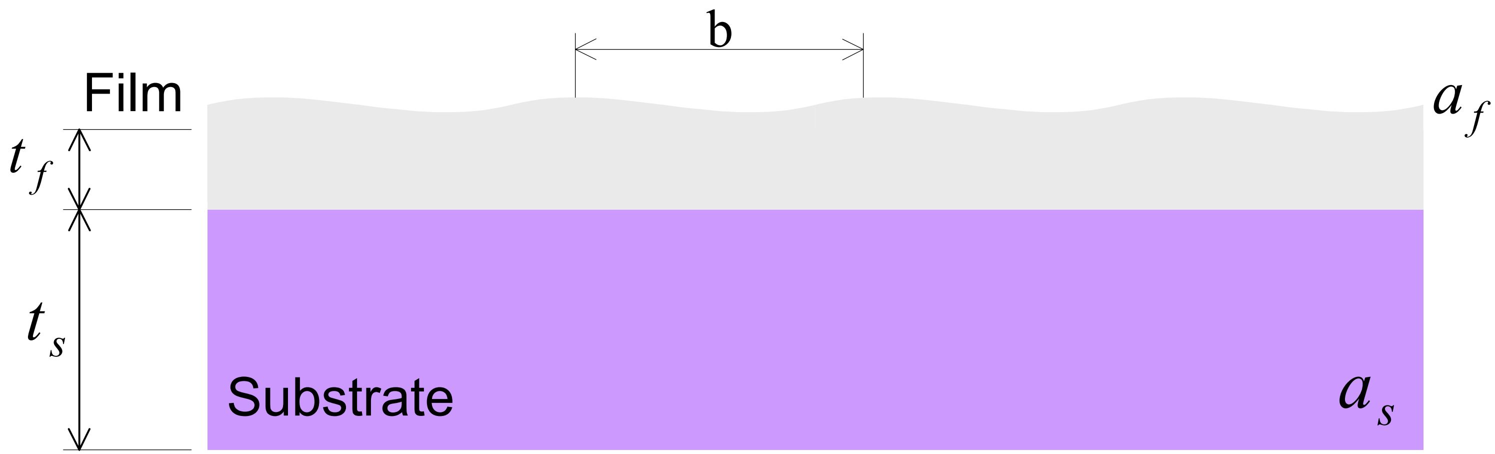
Thin Film on Rigid Substrate $t_f << t_s$

Compliant Substrate $t_f \approx t_s$

Single-Component Crystal on Single-Component Crystal

Alloy on Alloy

Films on Substrates



Lattice Mismatch Parameter $\varepsilon_m = (a_s - a_f)/a_f$, ± 1 to $\pm 5\%$

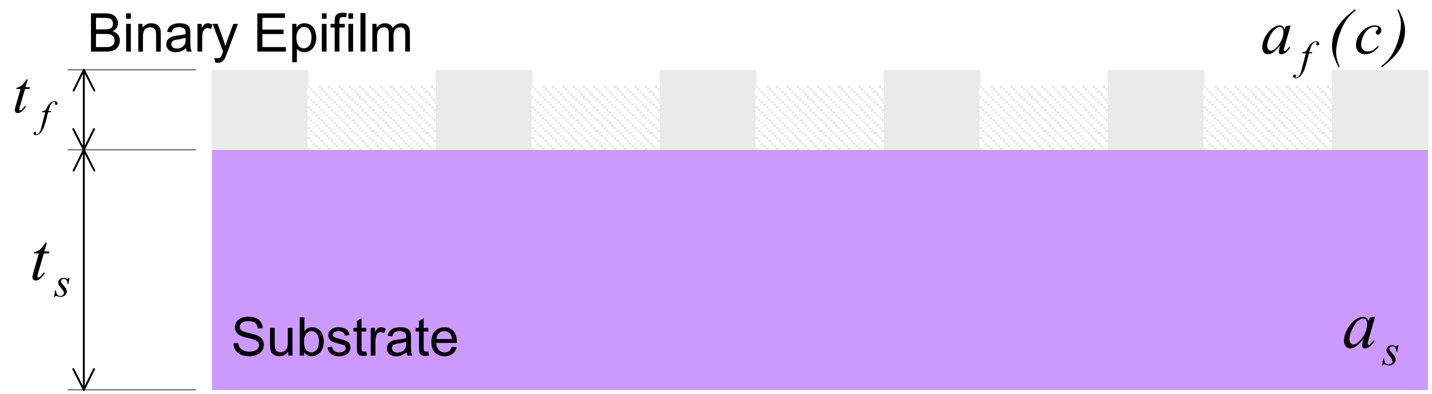
For Stable Uniform Film Thickness

$b \le b_c = (1-\nu^2)\pi\Gamma / E\varepsilon_m^2$ Asaro & Tiller, Grinfeld, Srolovitz

$b \le b_c(1 - 4\varepsilon_m\Sigma/\Gamma)$ Surface Stress Effect (Wu, 1998)

$b \le b_c\{[1+(2+\nu)e_m]/(1+e_m)\}$ Finite Mismatch (Wu, 2000)

Alloy Films / Single-Crystal Substrate



Lattice Mismatch Parameter $\varepsilon_m = \left(a_s - a_f\right)/a_f, \quad \pm 1 \; to \; \pm 5\%$

Binary epifilms may self-organize into two-phase (nano) patterns.

May be used as templates for making functional structures.

Diffusion may have a role in the phenomenon.

According to well-established theory: elastic misfit has no effect.

Will show: misfit may be important.

Deformation vs. Diffusion

Displacement	Configuration (composition)
Deformation Gradient F	Eigentransformation F*
Energy Density W	Energy-Mom. Tensor
Piola Stress $\mathbf{P} = (\partial W / \partial \mathbf{F})^T$	Eshelby Stress
Cauchy Stress $\sigma = \mathbf{FP} / J$	$\Sigma = W\mathbf{I} - \mathbf{PF}$
Low Temperature	High Temperature
Large Scales	Small scales
Equilibrium/Motion(fast)	Equilibrium/ Diffusion(slow)

Deformation by Non-uniform Composition

Eshelby(1957,59), Mura (1982), Larche & Cahn (1982)

Total Strain $\varepsilon_{ij} = (u_{i,j} + u_{j,i})/2$

Eigenstrain $\varepsilon^*_{ij} = (c - c_o)\eta\delta_{ij}, \quad \eta = \partial \ln a(c)/\partial c$

Elastic Strain $e_{ij} = \varepsilon_{ij} - \varepsilon^*_{ij}$

Elastic Stress $\sigma_{ij} = 2\mu e_{ij} + \lambda e_{kk}\delta_{ij}$

Equilibrium $\sigma_{ij,j} = 0$

A Compatibility $\nabla^2\sigma_{kk} = -\frac{2E\eta}{1-\nu}\nabla^2(c - c_0)$

Displacement Eqm. $\mu u_{i,jj} + (\lambda + \mu)u_{j,ji} = 3K\eta(c - c_o)_{,i}$

Diffusion Kinetics

Cahn (1961), Larche & Cahn (1973,1978, 1982)

Gibbs Free Energy	$f(\sigma_{ij}, \theta, c)$
Chemical Potential	$\overline{\mu}(\sigma_{ij}, \theta, c) = \partial f / \partial c$
Flux via Mobility	$\mathbf{J} = -M\,\mathbf{Grad}\,\overline{\mu}$
Mass Conservation	$\partial c / \partial t = -J_{i,i} = M \nabla^2 \overline{\mu}$

The Chemical Potential (Li, Oriani & Darken, 1966; Larche & Cahn)

$$\overline{\mu}(\sigma_{ij}, \theta, c) = \overline{\mu}(0, \theta, c) - \frac{\eta}{\rho}\sigma_{kk} - \frac{1}{2\rho}\frac{\partial S_{ijmn}}{\partial c}\sigma_{ij}\sigma_{mn}$$

$$\frac{\partial c}{\partial t} = M\left[f_{,cc}(0, \theta, c) + \frac{2E\eta^2}{(1-\nu)\rho}\right]\nabla^2 c$$

Diffusion Kinetics

Continued

The Chemical Potential (Li,Oriani & Darken,1966;Larche & Cahn)

$$\bar{\mu}(\sigma_{ij},\theta,c) = \bar{\mu}(0,\theta,c) - \frac{\eta}{\rho}\sigma_{kk} - \frac{1}{2\rho}\frac{\partial S_{ijmn}}{\partial c}\sigma_{ij}\sigma_{mn}$$

Compatibility:

$$\nabla^2\sigma_{kk} = -\frac{2E\eta}{1-\nu}\nabla^2(c - c_o)$$

Diffusion:

$$\frac{\partial c}{\partial t} = M\nabla^2\bar{\mu} = M\left[f_{,cc}(0,\theta,c) + \frac{2E\eta^2}{(1-\nu)\rho}\right]\nabla^2 c$$

Conclusion: Stress is affected by composition but not vice versa.
Stephenson (1988): Coupling via plasticity.

Assertion: The chemical potential must involve the full Eshelby stress.

Chemical Potential

Li, Oriani & Darken (1966) and Larche & Cahn (1978)

$$\bar{\mu}(\sigma_{ij},\theta,c)=\bar{\mu}(0,\theta,c)-\frac{\eta}{\rho}\sigma_{kk}-\frac{1}{2\rho}\frac{\partial S_{ijmn}}{\partial c}\sigma_{ij}\sigma_{mn}$$

Diffusion:

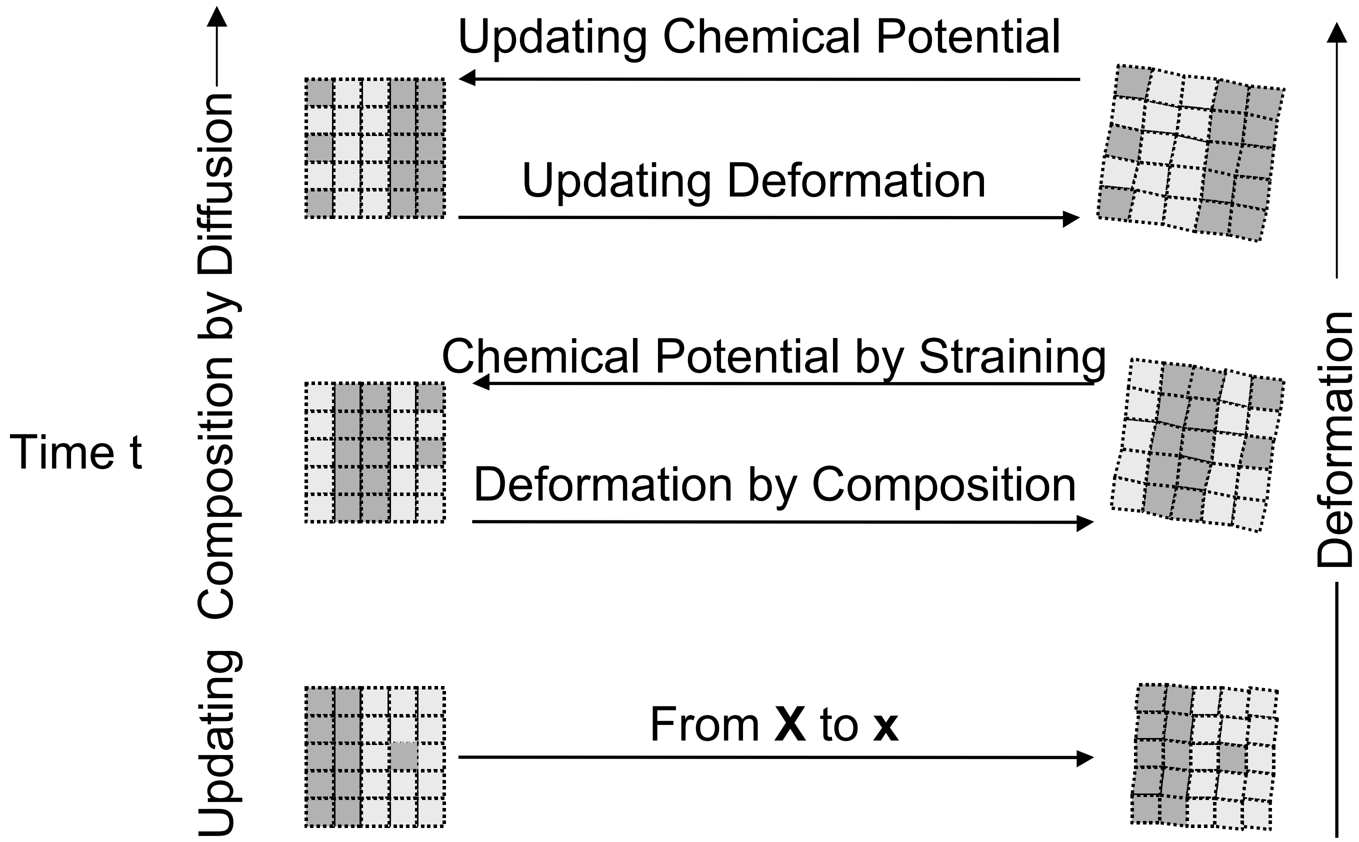
$$\frac{\partial c}{\partial t}=M\nabla^2\bar{\mu}=M\left[f_{,cc}(0,\theta,c)+\frac{2E\eta^2}{(1-\nu)\rho}\right]\nabla^2 c$$

Assertion: $\bar{\mu}(\sigma_{ij},\theta,c)=\bar{\mu}(0,\theta,c)+\frac{\eta}{\rho}\Sigma_{KK}=\bar{\mu}(0,\theta,c)+\frac{\eta}{\rho}(W-\sigma_{kk})$

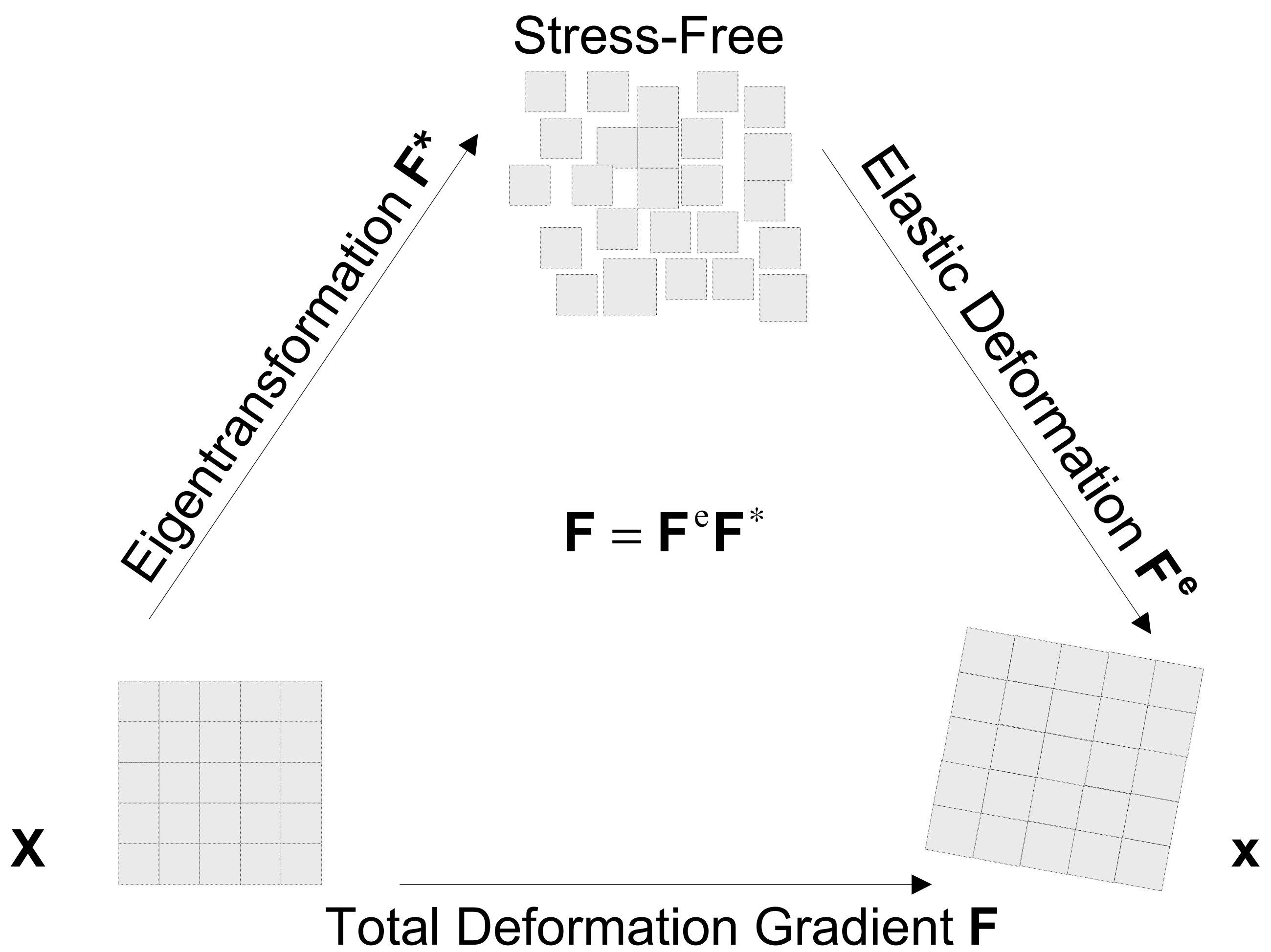
Where: $\Sigma = W\mathbf{I}-\mathbf{PF}$ is the Eshelby Stress

New Diffusion: $\frac{\partial c}{\partial t}=M\nabla^2\bar{\mu}=M\left\{\left[f_{,cc}(0,\theta,c)+\frac{2E\eta^2}{(1-\nu)\rho}\right]\nabla^2 c+\frac{\eta}{\rho}\nabla^2 W\right\}$

Deformation and Diffusion



Eigentransformation



The Three-Reference Kinematics for An n-Component System

Partial Molar Density (Molar Concentration) for Component i

Per Unit Volume in **X**: ρ_i $\qquad \rho = \sum \rho_i$

Per Unit Volume in **x**: ρ_i^D $\qquad \rho^D = \sum \rho_i^D$

Per Unit Volume in Stress-Free Reference: ρ_i^{SF} $\qquad \rho^{SF} = \sum \rho_i^{SF}$

Mole Fraction (Composition) $c_i = \rho_i / \rho = \rho_i^D / \rho^D = \rho_i^{SF} / \rho^{SF}$

Jacobians of Transformation

$$J = dv / dV = \rho / \rho^D = \rho_i / \rho_i^D$$

$$J^e = dv / dV^{SF} = \rho^{SF} / \rho^D = \rho_i^{SF} / \rho_i^D$$

$$J^* = dV^{SF} / dV = \rho / \rho^{SF} = \rho_i / \rho_i^{SF}$$

Thermodynamics-First Law

(In Terms of Quantities Defined on X and for Quasi-static deformation)

Local Form: $$\dot{\varepsilon} = \mathbf{P} \cdot \dot{\mathbf{F}} - \mathrm{Div}\, \mathbf{J}_q + R_q$$

(Internal Energy) = (Piola Stress)(Deformation Gradient Rate)
- (Divergence)(Heat Flux) +(Heat Source)

Mechanical Equilibrium: $$\mathrm{Div}\, \mathbf{P} = -\mathbf{B}$$

(Divergence)(Piola Stress) = - (Body Force)

Thermodynamics-Second Law

(In Terms of Quantities Defined on X and for Quasi-static deformation)

Local Form:

$$\theta\dot{\eta} - \left[R_{\mathbf{q}} - \mathrm{Div}\,\mathbf{J}_{\mathbf{q}}\right] + \theta\mathbf{J}_{\mathbf{q}} \cdot \mathbf{Grad}\left(\frac{1}{\theta}\right) + \sum_{i=1}^{n}\left[\bar{\mu}_i\dot{\rho}_i - \theta\mathbf{J}_i \cdot \mathbf{Grad}\left(\frac{\bar{\mu}_i}{\theta}\right)\right] \geq 0$$

(Temperature)(Entropy Rate) + (Heat Terms)

+ Sum of [(Chemical Potential i)(Rate of Molar Density i)

-(temperature)(Flux i)(Gradient)(Chemical Potential i/Temperature)] > 0

Thermodynamics-Second Law

(Continued 1)

In Terms of Helmholtz Free Energy $\phi = \varepsilon - \theta\eta$

$$-\left[\dot{\phi} + \eta\dot{\theta} - \mathbf{P}\cdot\mathbf{F} - \sum_{i=1}^{n}\bar{\mu}_i\dot{\rho}_i\right] + \theta\mathbf{J}_q\cdot\mathbf{Grad}\left(\frac{1}{\theta}\right) + \sum_{i=1}^{n}\left[\theta\mathbf{J}_i\cdot\mathbf{Grad}\left(-\frac{\bar{\mu}_i}{\theta}\right)\right] \geq 0$$

Helmholtz Energy as the Potential:

$$\eta = -\partial\phi/\partial\theta, \quad \mathbf{P} = (\partial\phi/\partial\mathbf{F})^T, \quad \bar{\mu}_i = \partial\phi/\partial\rho_i$$

What is the right form for the Helmholtz energy?

Thermodynamics-Second Law

(Continued 2)

In Terms of Gibbs Free Energy $\psi = \phi - \mathbf{P} \cdot \mathbf{F}$

The Stress-Free Gibbs Energy is

$$\psi\left(0, \theta, \rho_i^{SF}\right) = J^* \psi^{SF}\left(\theta, \rho_i^{SF}\right) = J^* \rho^{SF} \underline{\mu}^{SF}\left(\theta, c_1, \ldots, c_{n-1}\right) = \rho \underline{\mu}^{SF}$$

where $\underline{\mu}^{SF}$ is the Stress-Free Molar Gibbs Free Energy

Partial Molar Gibbs Energy of Component i

$$\overline{\mu}_i^{SF} = \partial\left[\rho^{SF} \underline{\mu}^{SF}\right] / \partial \rho_i^{SF}$$

$$\overline{\mu}_n^{SF} = \underline{\mu}^{SF} - \sum_{j=1}^{n-1} c_j \frac{\partial \underline{\mu}^{SF}}{\partial c_j} \quad \text{and} \quad \overline{\mu}_i^{SF} = \overline{\mu}_n^{SF} + \frac{\partial \underline{\mu}^{SF}}{\partial c_i} \quad .$$

Thermodynamics-Second Law

(Continued 3)

Molar Density at Zero Stress $\rho^{SF}\left(\theta, c_1, \ldots, c_{n-1}\right)$

Volume per Mole of Mixture $\underline{V}^{SF}\left(\theta, c_1, \ldots, c_{n-1}\right) = \dfrac{1}{\rho^{SF}} = \sum_{i=1}^{n} c_i \overline{V}_i^{SF}$

Partial Molar Volumes $\overline{V}_i^{SF} = \partial\left[\rho / \rho^{SF}\right] / \partial \rho_i$

Jacobian of Eigentransformation $J^* = \det \mathbf{F}^* = \rho / \rho^{SF}$

$$\dot{J}^* = \sum_{i=1}^{n} \overline{V}_i^{SF} \dot{\rho}_i$$

Thermodynamics-Second Law

(Continued 4)

Elastic Free Energy per Mole of Mixture

$$\underline{W}^{SF}\left(\mathbf{F}^{e},\theta,c_1,\cdots,c_{n-1}\right)=\sum_{i=1}^{n}c_i\overline{W}_i^{SF}(\mathbf{F}^{e},\theta,c_1,\cdots,c_{n-1})$$

For Compositions Deviating Slightly From c_{i0}

$$\underline{W}^{SF}(\mathbf{F}^{e},\theta,c_i)=\underline{W}^{SF}(\mathbf{F}^{e},\theta,c_{i0})+\sum_{i=1}^{n}(c_i-c_{i0})\overline{W}_{i0}^{SF}+\cdots$$

Strain energy per unit stress-free volume

$$W^{SF}(\mathbf{F}^{e},\theta,\rho_i^{SF})=\rho^{SF}\underline{W}^{SF}(\mathbf{F}^{e},\theta,c_i)$$

$$=W_0^{SF}(\mathbf{F}^{e})+\rho^{SF}\sum(c_i-c_{i0})\overline{W}_{i0}^{SF}+\cdots$$

Thermodynamics-Second Law

(Continued 5)

Isothermal & Isocomposition Elastic Free Energy

$$W^{SF}\left(\mathbf{F}^{e},\theta,\rho_i^{SF}\right) \text{ per Unit Stress - Free Volume}$$

For Compositions Deviating Slightly From Such a State

$$\phi\left(\mathbf{F},\theta,\rho_i\right) = J^{*}W^{SF}\left(\mathbf{F}^{e},\theta,\rho_i / J^{*}\right) + \rho\underline{\mu}^{SF}\left(\theta,c_1,\cdots,c_{n-1}\right)$$

$$J^{*} = \det\mathbf{F}^{*} = \frac{dV^{SF}}{dV} = \frac{\rho}{\rho^{SF}}, \quad \mathbf{F}^{e} = \mathbf{F}\mathbf{f}^{*}, \quad \mathbf{F}^{*}\mathbf{f}^{*} = \mathbf{I}$$

Thermodynamics-Second Law

(Continued 6)

$$\phi(\mathbf{F},\theta,\rho_i) = J^* W^{SF}\left(\mathbf{F}^e,\theta,\rho_i / J^*\right) + \rho \underline{\mu}^{SF}(\theta, c_1, \cdots c_{n-1})$$

$$\phi(\mathbf{F},\theta,\rho_i) = J^*\left[W_0^{SF}(\mathbf{F}^{\mathbf{e}}) + \rho^{SF}\sum(c_i - c_{i0})\overline{W}_{i0}^{SF} + \cdots\right] + \rho \underline{\mu}^{SF}$$

$$\phi(\mathbf{F},\theta,\rho_i) = W(\mathbf{F},\mathbf{F}^*) + \rho\sum(c_i - c_{i0})\overline{W}_{i0}^{SF} + \rho \underline{\mu}^{SF}$$

The Chemical Potential

$$\overline{\mu}_i = \overline{\mu}_i^{SF} + \overline{W}_{i0}^{SF}(\mathbf{F}^{\mathbf{e}}) + \frac{\partial W}{\partial \mathbf{F}^*} \cdot \frac{\partial \mathbf{F}^*}{\partial \rho_i} = \overline{\mu}_i^{SF} + \overline{W}_{i0}^{SF}(\mathbf{F}^{\mathbf{e}}) + \Sigma \mathbf{f}^* \cdot \frac{\partial \mathbf{F}^*}{\partial \rho_i}$$

Eshelby Stress

$$\Sigma = W\mathbf{I} - \mathbf{PF}, \quad \mathbf{P} = \left(\partial W / \partial \mathbf{F}\right)^T$$

Back To Linear Theory

$$\mathbf{F} = \delta + \nabla\mathbf{u} \Rightarrow \varepsilon = (\nabla\mathbf{u} + \mathbf{u}\nabla)/2, \quad \mathbf{F}^* = \delta + \varepsilon^*\delta \Rightarrow \varepsilon^* = \varepsilon^*\delta$$

$$\mathbf{F}^e = \mathbf{F}(\mathbf{F}^*)^{-1} \approx \delta + \nabla\mathbf{u} - \varepsilon^* - \varepsilon^*\nabla\mathbf{u} \Rightarrow \mathbf{E}(\varepsilon, \varepsilon^*) = \varepsilon - \varepsilon^* - \varepsilon^*\varepsilon$$

$$W\left(\varepsilon, \varepsilon^*\right) = \left(1 + \varepsilon^*_{kk}\right)W_0^{SF}(\mathbf{E})$$

The Chemical Potential

$$\overline{\mu}_i = \overline{\mu}_i^{SF} + \overline{W}_{i0}^{SF} + \frac{\partial W}{\partial \varepsilon^*} \cdot \frac{\partial \varepsilon^*}{\partial \rho_i} = \overline{\mu}_i^{SF} + \overline{W}_{i0}^{SF} + \Sigma \cdot \frac{\partial \varepsilon^*}{\partial \rho_i}$$

Eshelby Stress: $\Sigma = W_0^{SF}(\mathbf{e})\delta - \sigma\varepsilon - \sigma = \partial W / \partial \varepsilon^*$

New Field Equations

Displacement Eqm. $\mu u_{i,jj} + (\lambda + \mu) u_{j,ji} = 3K\eta(c - c_o)_{,i}$

New Diffusion Equation:

$$\frac{\partial c}{\partial t} = (1 - c_0)c_0 M_0 \left\{ \left[f''(c_0) + \frac{2E\eta^2}{(1-\nu)\rho} \right] \nabla^2 c + \frac{\eta}{\rho} \nabla^2 W_0^{SF}(\mathbf{e}) \right\}$$

Interaction Energy:

For: $\mathbf{u},\ \varepsilon,\ \mathbf{e},\ \sigma\ = \mathbf{u} + \mathbf{u}^o,\ \varepsilon + \varepsilon^o,\ \mathbf{e} + \varepsilon^o,\ \sigma + \sigma^o$

$$W_0^{SF}(\varepsilon^o + \mathbf{e}) = W_0^{SF}(\varepsilon^o) + W_0^{SF}(\mathbf{e}) + W_{Inter}$$

$$W_{Inter} = (\sigma^o \cdot \mathbf{e} + \sigma \cdot \varepsilon^o)/2 = \sigma^o \cdot \mathbf{e} = \sigma \cdot \varepsilon^o$$

Cahn's Spinodal Decomposition (1961)

An Infinite Isotropic Binary Solid

Given: $c - c_o = A\cos\beta x_1, \quad \varepsilon^*_{ij} = (c - c_o)\eta\delta_{ij} = \delta_{ij}\eta A\cos\beta x_1$

Uniform Stress (Not considered by Cahn):

$$\sigma^o_{11} = \sigma^o_{22} = E\varepsilon_m/(1-\nu), \quad \sigma^o_{33} = 0$$

$$\varepsilon^o_{11} = \varepsilon^o_{22} = \varepsilon_m, \quad \varepsilon^o_{33} = -2\nu\varepsilon_m/(1-\nu)$$

Solution: $\varepsilon_{11} = \frac{1+\nu}{1-\nu}\eta A\cos\beta x_1, \quad \text{Other} \quad \varepsilon_{ij} = 0$

$$e_{11} = \frac{2\nu}{1-\nu}\eta A\cos\beta x_1, \quad e_{22} = e_{33} = -\eta A\cos\beta x_1$$

$$\sigma_{11} = 0, \quad \sigma_{22} = \sigma_{33} = -\frac{E}{1-\nu}\eta A\cos\beta x_1$$

Cahn's Spinodal Decomposition (1961)

An Infinite Isotropic Binary Solid(continued 1)

Interaction Energy: $W_0^{SF}(\varepsilon^o + \mathbf{e}) = W_0^{SF}(\varepsilon^o) + W_0^{SF}(\mathbf{e}) + W_{Inter}$

$$W_{Inter} = \sigma \cdot \varepsilon^o = \sigma^o \cdot \mathbf{e} = -\frac{2\eta E}{(1-\nu)} \frac{(1-3\nu)}{2(1-\nu)} \varepsilon_m A(t) \cos\beta x_1$$

Regular Solution:

$$\underline{\mu}^{SF} = f(c) = \Omega c(1-c) + RT\left[c \ln c + (1-c)\ln(1-c)\right]$$

New Diffusion Equation:

$$\frac{\partial c}{\partial t} = (1-c_0)c_0 M_0 \left\{ \left[f''(c_0) + \frac{2E\eta^2}{(1-\nu)\rho} \right] \nabla^2 c + \frac{\eta}{\rho} \nabla^2 W_{Inter} \right\}$$

Cahn's Spinodal Decomposition (1961)

An Infinite Isotropic Binary Solid(continued 2)

Stability Against Fluctuation:

$$\frac{dA}{dt} = (1-c_0)c_0 M_0 \beta^2 \left\{ -2\Omega + \frac{RT}{(1-c_0)c_0} + \frac{2\eta^2 E}{(1-\nu)\rho} m_{Glas} \left[1 + \frac{(1-3\nu)}{2(1-\nu)} \varepsilon_m \right] \right\} A(t)$$

A Parameter of Glas(1987):

M_{Glas} was determined as a function of (film thickness)$\cdot\beta$

$M_{Glas} = 1$ for infinitly thick film (Cahn's pro blem)

$M_{Glas} < 1$ for typical (film thickness)$\cdot\beta$ values

Cahn's Spinodal Decomposition (1961)

An Infinite Isotropic Binary Solid (continued 3)

Critical Temperature (just regular solution) :

$$T_0 = \frac{c_0(1-c_0)2\Omega}{R}, \quad T_{0MAX} = \frac{\Omega}{2R} \quad \text{for } c_0 = 1/2$$

Critical Temperature (Cahn): **Critical Temperature (Glas):**

$$T_{Cahn} \equiv \left[1 - \frac{\eta^2 E}{\Omega(1-\nu)}\right] T_0 \qquad T_{Glas} \equiv \left[1 - \frac{\eta^2 E}{\Omega(1-\nu)} m(t_f)\right] T_0$$

Critical Temperature as a function of misfit:

$$T_C(\varepsilon_m) = \frac{c_0(1-c_0)2\Omega}{R}\left\{1 - \frac{\eta^2 E}{(1-\nu)\rho\Omega} m_{Glas}\left[1 + \frac{(1-3\nu)}{2(1-\nu)}\varepsilon_m\right]\right\}$$

Estimates of Critical Temperature

Alloy	η	Ω (kcal/mol)	$E/(1-\nu)\rho$ (kcal/mol)	T_0 K	T_{Cahn} K	T_{Glas} K	$T_C(\varepsilon_m)$ for $\nu = 0$ K, ε_m = -0.05	ε_m = 0.05
$GaAs_yP_{1-y}$	0.036	0.92	836	230	-50	100	103	97
$In_xGa_{1-x}P$	0.074	3.60	778	910	-160	400	409	382
$In_xGa_{1-x}As$	0.069	2.90	726	730	-140	320	328	306
$InAs_yP_{1-y}$	0.032	0.59	668	150	-20	70	72	69
$GaAs_ySb_{1-y}$	0.075	3.39	778	850	-250	330	348	318
$InAs_ySb_{1-y}$	0.067	2.30	633	580	-140	260	266	255
$In_xGa_{1-x}Sb$	0.061	1.90	685	480	-170	180	187	172