

The Pairing of Energy Momentum Tensor and Eigentransformation Rate in a Cylindrically Orthotropic Elastic Circular Tube or Bar

Chien H. Wu¹

ABSTRACT

The pairing of a chemical potential and its associated concentration rate in the thermodynamic identity is well known. The existence of an experimentally determinable molar volume as a function of molar concentrations is also widely used in chemical engineering. What is perhaps less known and infrequently used is the fact that a spatially nonuniform molar volume leads to a field of geometrically incompatible eigenstrain, or eigentransformation in finite deformation. This incompatibility forces the material environment to deform, and the result is a strain energy trapped inside the material body. The change of this energy with respect to the eigentransformation is a generalized configurational stress, which, in the limit as the eigentransformation tends to the identity transformation, tends to the classical energy momentum tensor of Eshelby [1], or the so-called configurational stress. It is shown that the generalized configurational stress is an integral part of the chemical potentials that are responsible for atomic diffusion. This cycle of cause and effect is demonstrated in an axially symmetric setting where the material configuration is taken to be cylindrically orthotropic.

Symmetry can be used in many occasions to bare the simple meaning of a complex mathematical expression hiding under the disguise of tensors and index notation. We used it to elucidate the “missing” term in surface chemical potential in 1996 [2] and are now applying it to identify the chemical potential in the bulk. Both Professor Thomas C. T. Ting and I are civil engineering graduates of Tai-Da, but did not know each other until we joined UIC. It has been a wonderful friendship of many stimulating anisotropic discussions and numerous delicious potluck dinners. Happy birthday, Tom!

Keywords: Energy momentum tensor, configurational stress, chemical potential, and eigentransformation.

INTRODUCTION

The configurational deformation of a single-component solid from a uniform reference state to a nonuniform state is characterized by an *eigentransformation* that may be defined in terms of the underlying crystal structure and the experimentally measured molar volume of the solid. If the uniform reference state is defined in a fixed reference coordinate system \mathbf{X} , then the effect of an eigentransformation, \mathbf{F}^* , is to convert a

¹ Professor of Mechanics and Materials, Department of Civil and Materials Engineering (MC 246), University of Illinois at Chicago, 842 West Taylor Street, Chicago, Illinois 60607-7023, USA, 312-413-2644 (voice), 312-996-2426 (fax), E-mail cwu@uic.edu

differential element $d\mathbf{X}$ into a new differential element $d\mathbf{X}^{\text{SF}} = \mathbf{F}^* d\mathbf{X}$. For convenience, \mathbf{X}^{SF} will be referred to as a *stress-free coordinate system*. An eigentransformation field is, in general, incompatible and, as a result, must be accompanied by an elastic transformation, \mathbf{F}^e , so that the combined effect is an integrable deformation-gradient field, $\mathbf{F} = \mathbf{F}^e \mathbf{F}^*$, and $d\mathbf{x} = \mathbf{F} d\mathbf{X}$ is the differential element in the spatial coordinate system \mathbf{x} . In general, neither $d\mathbf{X}^{\text{SF}} = \mathbf{F}^* d\mathbf{X}$ nor $d\mathbf{X}^{\text{SF}} = \mathbf{F}^* \mathbf{F}^{-1} d\mathbf{x}$ is integrable but $\mathbf{F}^e = \mathbf{F} \mathbf{F}^{*-1}$ ties the stress-free element $d\mathbf{X}^{\text{SF}}$ to the spatial element $d\mathbf{x}$. We exploit this last observation by insisting that the Helmholtz free energy involved in $d\mathbf{X} \rightarrow d\mathbf{x}$ may be obtained in terms of the enthalpy of mixing in $d\mathbf{X} \rightarrow d\mathbf{X}^{\text{SF}}$ and the elastic strain energy in $d\mathbf{X}^{\text{SF}} \rightarrow d\mathbf{x}$. The derivative of this free energy with respect to the eigentransformation is a generalized configurational stress, which, in the limit as the eigentransformation tends to the identity transformation, tends to the classical energy momentum tensor of Eshelby [1]. Moreover, the generalized configurational stress may be directly linked to the chemical potential, a result that was first reported by Wu [3].

The eigentransformation in a single-component solid with vacancies as well as the three-way transformations among the three sets of coordinates are explicitly defined in Section 2 in an axially symmetric setting. The thermodynamics of a single-component solid is presented in Section 3 where the desired Helmholtz free energy is established in terms of the molar Gibbs free energy and the isothermal strain energy per unit stress-free volume. This concept was first conceived in a recent paper by Wu [3]. A number of related results may be found in Sandler [4], and Larche and Cahn [5].

THE EIGENTRANSFORMATION IN A SINGLE-COMPONENT SOLID WITH VACANCIES

Let a single-component solid be defined by a molar concentration [mol/m^3] C_a and a vacancy concentration C_v , so that the total molar concentration C , which is the number of available lattice sites per unit volume, and the associated mole fractions $x_a = C_a / C$ and $x_v = C_v / C$ satisfy

$$C = C_a + C_v, \quad 1 = x_a + x_v. \quad (1)$$

Since the two mole fractions are not independent, we express them in terms of a single mole-fraction value x as follows

$$x_a = x, \quad x_v = 1-x. \quad (2)$$

The use of x as the kernel letter for mole fractions is a historical one and should not cause any confusion with the three components of the spatial coordinate system.

Let $\underline{V}(P, T, x)$ be the molar volume [m^3 / mol] of the solid at pressure P , temperature T , and mole fraction x . It is an important material property that may be experimentally determined. The molar volume $\underline{V}(0, T_0, x_0)$ may be used to define a uniform state for a

solid body occupying a region V in a chosen reference cylindrical coordinate system $\mathbf{X} : (R, \Theta, Z)$. Axial symmetry is implied throughout the paper. When $T = T(R, t)$, and hence $x = x(R, t)$, becomes radially nonuniform, the associated $\underline{V}(0, T, x)$ may be used to compute the associated diagonal eigentransformation \mathbf{F}^* defined in terms of $J^*(R, t) = \underline{V}(0, T(R, t), x(R, t)) / \underline{V}(0, T_0, x_0)$ by

$$\mathbf{F}^* = \begin{bmatrix} F_{\rho R}^* & 0 & 0 \\ 0 & F_{\vartheta\Theta}^* & 0 \\ 0 & 0 & F_{cZ}^* \end{bmatrix} = \begin{bmatrix} \Lambda_R^* & 0 & 0 \\ 0 & \Lambda_\Theta^* & 0 \\ 0 & 0 & \Lambda_Z^* \end{bmatrix} = (J^*)^{1/3} \begin{bmatrix} K_R & 0 & 0 \\ 0 & K_\Theta & 0 \\ 0 & 0 & K_Z \end{bmatrix}, \quad K_R K_\Theta K_Z = 1 \quad (3)$$

where K_R, K_Θ, K_Z are constants that may be related to the underlying cylindrically orthotropic crystal structure (The deformation of cylindrically orthotropic cylinders has been the investigation of a number of Ting's numerous publications on anisotropic elasticity [6,7,8]). For convenience, we let $d\mathbf{X}^{\text{SF}} \equiv (d\rho, \rho d\Theta, d\zeta)$ to represent the result of applying \mathbf{F}^* to $d\mathbf{X} \equiv (dR, R d\Theta, dZ)$ and use

$$d\mathbf{X}^{\text{SF}} = \mathbf{F}^* d\mathbf{X}, \quad dV^{\text{SF}} = J^* dV \quad (4)$$

to stress the existence of a stress-free state. The molar volume $\underline{V}(P, T, x)$ may be written as

$$\underline{V}(P, T, x) = x_a \bar{V}_a(P, T, x) + x_v \bar{V}_v(P, T, x), \quad \bar{V}_i(P, T, x) = \left. \frac{\partial [C \underline{V}(P, T, x)]}{\partial C_i} \right|_{P, T, C_{j \neq i}} \quad (5)$$

where the subscript i is either a or v , and $\bar{V}_a(P, T, x)$ and $\bar{V}_v(P, T, x)$ are the partial molar volumes.

The transformation \mathbf{F}^* is, in general, incompatible in the sense that the first of (4) cannot be integrated to obtain ρ as a single-valued function of R . The solid body, which occupies V in (R, Θ, Z) , is therefore forced to deform into a new configuration that occupies v in a spatial coordinate system (r, θ, z) . The associated transformation is the diagonal deformation gradient \mathbf{F} defined by

$$\mathbf{F} = \begin{bmatrix} F_{rR} & 0 & 0 \\ 0 & F_{\theta\Theta} & 0 \\ 0 & 0 & F_{zZ} \end{bmatrix} = \begin{bmatrix} \Lambda_R & 0 & 0 \\ 0 & \Lambda_\Theta & 0 \\ 0 & 0 & \Lambda_Z \end{bmatrix} = \begin{bmatrix} \partial r / \partial R & 0 & 0 \\ 0 & r/R & 0 \\ 0 & 0 & \partial z / \partial Z \end{bmatrix}, \quad (6)$$

where $z = \Lambda_Z(t)Z$ is presumed. Finally, the combination of \mathbf{F} and \mathbf{F}^* is termed the elastic transformation $\mathbf{F}^e = \mathbf{F}\mathbf{F}^{*-1}$, which has the principal form

$$\mathbf{F}^e = \mathbf{F}\mathbf{F}^{*-1} = \begin{bmatrix} \Lambda_R^e & 0 & 0 \\ 0 & \Lambda_\Theta^e & 0 \\ 0 & 0 & \Lambda_Z^e \end{bmatrix} = \begin{bmatrix} \Lambda_R / \Lambda_R^* & 0 & 0 \\ 0 & \Lambda_\Theta / \Lambda_\Theta^* & 0 \\ 0 & 0 & \Lambda_Z / \Lambda_Z^* \end{bmatrix}, \quad (7)$$

We have, with $d\mathbf{x} \equiv (dr, r d\theta, dz)$,

$$d\mathbf{x} = \mathbf{F}d\mathbf{X}, \quad dv = JdV, \quad J = \det\mathbf{F} \quad (8)$$

$$d\mathbf{x} = \mathbf{F}^e d\mathbf{X}^{\text{SF}}, \quad dv = J^e dV^{\text{SF}}, \quad J^e = \det\mathbf{F}^e = J/J^* \quad (9)$$

which, together with (4), complete the needed three-frame kinematics. Let us now denote the pressure in the spatial coordinate system by $p(\mathbf{r}, t)$, then $\underline{v}(p, T, \mathbf{x})$, which is just $\underline{V}(p(\mathbf{x}, t), T(\mathbf{x}, t), \mathbf{x}(\mathbf{x}, t))$, is the partial molar volume of the mixture associated with (p, T, \mathbf{x}) which happens to be present at (\mathbf{r}, t) . Thus,

$$J = \frac{\underline{v}(p, T, \mathbf{x})}{\underline{V}(0, T_0, \mathbf{x}_0)}, \quad J^e = \frac{\underline{v}(p, T, \mathbf{x})}{\underline{V}(0, T, \mathbf{x})}, \quad (10)$$

which compliments (3). We now identify $C = 1/\underline{V}(0, T_0, \mathbf{x}_0)$, so that C is the constant number of lattice sites per unit volume of the solid in $\mathbf{X} : (\mathbf{R}, \Theta, Z)$. Molar densities may now be defined in terms of unit volumes in $\mathbf{x} : (\mathbf{r}, \theta, z)$ and $\mathbf{X}^{\text{SF}} : (\rho, \vartheta, \zeta)$. The three sets of densities are:

$$C = C_a(\mathbf{R}, t) + C_v(\mathbf{R}, t), \quad C^{\text{SF}} = C_a^{\text{SF}}(\mathbf{R}, t) + C_v^{\text{SF}}(\mathbf{R}, t), \quad c = c_a(\mathbf{r}, t) + c_v(\mathbf{r}, t). \quad (11)$$

There are also the identities:

$$J^* = dV^{\text{SF}}/dV = C/C^{\text{SF}}(\mathbf{R}, t) = C_a(\mathbf{R}, t)/C_a^{\text{SF}}(\mathbf{R}, t) = C_v(\mathbf{R}, t)/C_v^{\text{SF}}(\mathbf{R}, t), \quad (12)$$

$$J = dv/dV = C/c(\mathbf{r}, t) = C_a(\mathbf{R}, t)/c_a(\mathbf{r}, t) = C_v(\mathbf{R}, t)/c_v(\mathbf{r}, t), \quad (13)$$

$$J^e = dv/dV^{\text{SF}} = C^{\text{SF}}(\mathbf{R}, t)/c(\mathbf{r}, t) = C_a^{\text{SF}}(\mathbf{R}, t)/c_a(\mathbf{r}, t) = C_v^{\text{SF}}(\mathbf{R}, t)/c_v(\mathbf{r}, t), \quad (14)$$

$$x_i = c_i/c = C_i/C = C_i^{\text{SF}}/C^{\text{SF}} \quad (i=a \text{ or } v). \quad (15)$$

In terms of the partial molar thermodynamic description of (5), we have

$$\underline{v}(p, T, \mathbf{x}) = x_a \bar{v}_a(p, T, \mathbf{x}) + x_v \bar{v}_v(p, T, \mathbf{x}), \quad \bar{v}_i(p, T, \mathbf{x}) = \left. \frac{\partial c \underline{v}(p, T, \mathbf{x})}{\partial c_i} \right|_{p, T, c_{j \neq i}}, \quad (16)$$

$$\underline{V}(0, T_0, \mathbf{x}_0) = x_a \bar{V}_a(0, T_0, \mathbf{x}_0) + x_v \bar{V}_v(0, T_0, \mathbf{x}_0), \quad \bar{V}_i(0, T_0, \mathbf{x}_0) = \left. \frac{\partial C \underline{V}(0, T_0, \mathbf{x}_0)}{\partial C_i} \right|_{p, T, C_{j \neq i}} \quad (17)$$

where, again, the subscript i is either a or v . It follows from the first of (9) and the above that

$$\bar{v}_a(p, T, \mathbf{x}) = J \bar{V}_a(0, T_0, \mathbf{x}_0), \quad \bar{v}_v(p, T, \mathbf{x}) = J \bar{V}_v(0, T_0, \mathbf{x}_0). \quad (18)$$

We conclude this section by defining the following convenient symbols for a number of inverse quantities:

$$\mathbf{f} \equiv \mathbf{F}^{-1}, \quad j \equiv 1/J; \quad \mathbf{f}^* \equiv \mathbf{F}^{*-1}, \quad j^* \equiv 1/J^*; \quad \mathbf{f}^e \equiv \mathbf{F}^{e-1}, \quad j^e \equiv 1/J^e. \quad (19)$$

THE THERMODYNAMICS OF A SINGLE-COMPONENT SOLID WITH VACANCIES

Mass Balance

The mass balance equations are:

$$c\dot{x}_a = -\frac{1}{r} \frac{\partial}{\partial r} (rj_{ar}), \quad c\dot{x}_v = -\frac{1}{r} \frac{\partial}{\partial r} (rj_{vr}), \quad (20)$$

where j_{ar} and j_{vr} are the radial mass and void diffusion fluxes [mol / m²s] defined with respect to the spatial coordinate system $\mathbf{x} : (r, \theta, z)$ and over dots indicate material time derivatives. It is implicitly assumed that j_{az} and j_{vz} are zero. The result of expressing the above in \mathbf{X} is

$$\dot{C}_a = \frac{\partial C_a}{\partial t} = -\frac{1}{R} \frac{\partial}{\partial R} (RJ_{aR}), \quad \dot{C}_v = \frac{\partial C_v}{\partial t} = -\frac{1}{R} \frac{\partial}{\partial R} (RJ_{vR}), \quad (21)$$

where

$$J_{aR} = \Lambda_Z \Lambda_\Theta j_a, \quad J_{vR} = \Lambda_Z \Lambda_\Theta j_{vr}, \quad J_{aZ} = J_{vZ} = 0 \quad (22)$$

are the components of the diffusion fluxes [mol / m²s] defined with respect to the referential coordinate system $\mathbf{X} : (R, \Theta, Z)$.

Energy Balance

We balance the energy associated with an arbitrary cylindrical volume, $r_1 \leq r \leq r_0$ and $0 \leq z \leq z_0$:

$$\frac{d}{dt} \int_0^{z_0} \int_{r_1}^{r_0} c \underline{U} 2\pi r dr dz = \left[(\dot{r}\sigma_r - j_{qr}) 2\pi r z_0 \right]_{r_1}^{r_0} + \left[\int_{r_1}^{r_0} (\dot{z}\sigma_z - j_{qz}) 2\pi r dr \right]_0^{z_0}, \quad (23)$$

where \underline{U} is the molar internal energy, \dot{r} and \dot{z} are the r- and z- components of the velocity $\dot{\mathbf{x}}$, j_{qr} and j_{qz} are the r- and z- components of the heat flux vector \mathbf{j}_q , and $(\sigma_r, \sigma_\theta, \sigma_z)$ are the principal Cauchy stresses. Converting the right-hand side of the above into a volume integral, we obtain

$$\frac{d}{dt} \int_0^{z_0} \int_{r_1}^{r_0} c \underline{U} 2\pi r dr dz = \int_0^{z_0} \int_{r_1}^{r_0} \left[\frac{\partial}{\partial r} (\dot{r}\sigma_r - rj_{qr}) + \frac{\partial}{\partial z} (\dot{z}\sigma_z - j_{qz}) \right] 2\pi r dr dz. \quad (24)$$

Applying the condition $j_{qz} = 0$, the heat balance equation

$$c\dot{q} = -\text{div} \mathbf{j}_q = -\frac{1}{r} \frac{\partial}{\partial r} (rj_{qr}), \quad (25)$$

and the quasi-static equations of equilibrium

$$\frac{1}{r} \frac{\partial}{\partial r} (r\sigma_r) - \frac{\sigma_\theta}{r} = 0, \quad \frac{\partial}{\partial z} \sigma_z = 0, \quad (26)$$

we obtain from (24) the local form of the energy equation

$$c\dot{U} = c\dot{q} + \frac{\partial \dot{r}}{\partial r} \sigma_r + \frac{\dot{r}}{r} \sigma_\theta + \frac{\partial \dot{z}}{\partial z} \sigma_z \quad (27)$$

The result of converting the above into the \mathbf{X} -representation is

$$\dot{U} = C\dot{U} = \dot{Q} + P_R \dot{\Lambda}_R + P_\Theta \dot{\Lambda}_\Theta + P_Z \dot{\Lambda}_Z \quad (28)$$

where $U = \underline{CU}$ is the internal energy per unit volume in \mathbf{X} , $\dot{Q} = C\dot{q}$, and (P_R, P_Θ, P_Z) are the principal Piola stresses, which are related to the principal Cauchy stresses by

$$\mathbf{P} = \mathbf{J}\mathbf{f}\boldsymbol{\sigma} \quad : \quad P_R = \Lambda_Z \Lambda_\Theta \sigma_r, \quad P_\Theta = \Lambda_Z \Lambda_R \sigma_\theta, \quad P_Z = \Lambda_R \Lambda_\Theta \sigma_z. \quad (29)$$

Entropy Balance and The Second Law

The statement, for $j_{qz} = j_{az} = j_{vz} = 0$, is:

$$\frac{d}{dt} \int_0^{z_0} \int_{r_i}^{r_0} c \underline{S} 2\pi r dr dz + \left[(j_{qr} - \mu_a j_{ar} - \mu_v j_{vr}) \frac{1}{T} 2\pi r z_0 \right]_{r_i}^{r_0} \geq 0, \quad (30)$$

where \underline{S} is the molar entropy and μ_a and μ_v are the chemical potentials. The surface term in the above equation is again converted into a volume integral and the result is

$$\frac{d}{dt} \int_0^{z_0} \int_{r_i}^{r_0} c \underline{S} 2\pi r dr dz + \int_0^{z_0} \int_{r_i}^{r_0} \frac{\partial}{\partial r} \left[(j_{qr} - \mu_a j_{ar} - \mu_v j_{vr}) \frac{r}{T} \right] 2\pi r dr dz \geq 0. \quad (31)$$

The associated local forms are:

$$cT\dot{\underline{S}} - c\dot{q} - \frac{1}{T} j_{qr} \frac{\partial T}{\partial r} + c\mu_a \dot{x}_a - T j_{ar} \frac{\partial}{\partial r} \left(\frac{\mu_a}{T} \right) + c\mu_v \dot{x}_v - T j_{vr} \frac{\partial}{\partial r} \left(\frac{\mu_v}{T} \right) \geq 0, \quad (32)$$

$$T\dot{S} - \dot{Q} - \frac{1}{T} J_{qR} \frac{\partial T}{\partial R} + \mu_a \dot{C}_a - T J_{aR} \frac{\partial}{\partial R} \left(\frac{\mu_a}{T} \right) + \mu_v \dot{C}_v - T J_{vR} \frac{\partial}{\partial R} \left(\frac{\mu_v}{T} \right) \geq 0, \quad (33)$$

where $S = \underline{CS}$ is the entropy per unit volume in \mathbf{X} . Introducing Helmholtz free energy per unit volume in \mathbf{X} by $A = U - TS$ and combining (28) and (33), we obtain the Clausius-Duhem inequality

$$-\left[\dot{A} + S\dot{T} - P_R \dot{\Lambda}_R - P_\Theta \dot{\Lambda}_\Theta - P_Z \dot{\Lambda}_Z - \mu_a \dot{C}_a - \mu_v \dot{C}_v \right] - \frac{1}{T} J_{qr} \frac{\partial T}{\partial R} - T J_{vr} \frac{\partial}{\partial R} \left(\frac{\mu_v}{T} \right) - T J_{ar} \frac{\partial}{\partial R} \left(\frac{\mu_a}{T} \right) \geq 0. \quad (34)$$

It follows that the above constitutive constraint may be met by the use of $A(\Lambda_R, \Lambda_\Theta, \Lambda_Z, T, C_a, C_v) = \underline{CA}(\Lambda_R, \Lambda_\Theta, \Lambda_Z, T, x)$, where \underline{A} is the molar Helmholtz energy, as a potential such that

$$S = -\frac{\partial A}{\partial T}, \quad P_R = \frac{\partial A}{\partial \Lambda_R}, \quad P_\Theta = \frac{\partial A}{\partial \Lambda_\Theta}, \quad P_Z = \frac{\partial A}{\partial \Lambda_Z}, \quad \mu_a = \frac{\partial A}{\partial C_a}, \quad \mu_v = \frac{\partial A}{\partial C_v}, \quad (35)$$

and

$$-\frac{1}{T} J_{qR} \frac{\partial}{\partial R} T - T J_{vR} \frac{\partial}{\partial R} \frac{\mu_v}{T} - T J_{aR} \frac{\partial}{\partial R} \frac{\mu_a}{T} \geq 0. \quad (36)$$

The main purpose of this paper is to link the chemical potentials to an appropriately defined energy-momentum tensor or configurational stress. This is accomplished by the Helmholtz energy introduced in the following section.

THE HELMHOLTZ FREE ENERGY

We begin with the assumption that the stress-free molar Gibbs energy $\underline{G}^{\text{SF}}(T, \mathbf{x}) = \underline{G}(0, T, \mathbf{x})$ and the isothermal strain energy per unit stress-free volume $W^{\text{SF}}(\Lambda_R, \Lambda_\Theta, \Lambda_Z, T, C_a^{\text{SF}}, C_v^{\text{SF}})$ are known, as they are the mixture properties that can be experimentally measured. The desired Helmholtz free energy per unit volume of V in \mathbf{X} is

$$\mathbf{A}(\mathbf{F}, T, C_a, C_v) = C \underline{\mathbf{A}}(\mathbf{F}, T, \mathbf{x}) \quad \text{and} \quad \mathbf{F} = \mathbf{F}^e \mathbf{F}^* \quad (37)$$

where the tensors \mathbf{F}^* , \mathbf{F} , and \mathbf{F}^e are defined by (3), (6), (7). The molar Helmholtz energy $\underline{\mathbf{A}}(\mathbf{F}, T, \mathbf{x}) = \underline{G}(\mathbf{P}, T, \underline{\mathbf{x}}) + \mathbf{P} \cdot \mathbf{F} / C$ has the properties

$$\underline{\mathbf{A}}(\mathbf{I}, T_0, \mathbf{x}_0) = 0, \quad (38)$$

$$\underline{\mathbf{A}}(\mathbf{F}^*, T, \mathbf{x}) = \underline{G}^{\text{SF}}(T, \mathbf{x}) \equiv \underline{G}(\mathbf{P}, T, \mathbf{x}) \Big|_{\mathbf{P}=0}, \quad (39)$$

$$\underline{\mathbf{A}}(\mathbf{F}^e \mathbf{F}^*, T, \mathbf{x}) = \underline{\mathbf{A}}(\mathbf{F}^*, T, \mathbf{x}) + \underline{\mathbf{A}}^{\text{SF}}(\mathbf{F}^e, T, \mathbf{x}), \quad (40)$$

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

The condition (38) sets the uniform state as a reference, (39) follows from the fact that \mathbf{F}^* is the stress-free eigentransformation at temperature T and composition \mathbf{x} , and the definition of $\underline{\mathbf{A}}^{\text{SF}}$ requires that $\underline{\mathbf{A}}^{\text{SF}}(\mathbf{I}, T, \underline{\mathbf{x}}) = 0$. Using the above properties, we obtain from (37)

$$\mathbf{A}(\mathbf{F}, T, C_a, C_v) = C \underline{\mathbf{A}}(\mathbf{F}^e \mathbf{F}^*, T, \mathbf{x}) = C [\underline{\mathbf{A}}(\mathbf{F}^*, T, \mathbf{x}) + \underline{\mathbf{A}}^{\text{SF}}(\mathbf{F}^e, T, \mathbf{x})], \quad \text{or} \quad (41)$$

$$\mathbf{A} = C \underline{G}(0, T, \mathbf{x}) + \frac{C}{C^{\text{SF}}} C^{\text{SF}} \underline{\mathbf{A}}^{\text{SF}}(\mathbf{F}^e, T, \mathbf{x}) = C \underline{G}^{\text{SF}}(T, \mathbf{x}) + J^* W^{\text{SF}}(\mathbf{F}^e, T, C_a^{\text{SF}}, C_v^{\text{SF}}), \quad (42)$$

where (12) has been used and $W^{\text{SF}}(\mathbf{F}^e, T, C_a^{\text{SF}}, C_v^{\text{SF}}) = C^{\text{SF}} \underline{\mathbf{A}}^{\text{SF}}(\mathbf{F}^e, T, \mathbf{x})$ is the strain energy per unit stress-free volume at temperature T and concentrations C_a^{SF} and C_v^{SF} . In the following we shall ignore the dependence of strain energy density on concentrations and write $W^{\text{SF}} = W^{\text{SF}}(\mathbf{F}^e, T)$.

In terms of the principal forms of \mathbf{F}^* , \mathbf{F} , and \mathbf{F}^e , the desired Helmholtz energy is

$$\mathbf{A}(\Lambda_R, \Lambda_\Theta, \Lambda_Z, T, C_a, C_v) = C \underline{G}^{\text{SF}}(T, \mathbf{x}) + W(\Lambda_R, \Lambda_\Theta, \Lambda_Z, T), \quad (43)$$

$$W(\Lambda_R, \Lambda_\Theta, \Lambda_Z, T) = J^* W^{\text{SF}}(\Lambda_R^e, \Lambda_\Theta^e, \Lambda_Z^e, T), \quad (44)$$

where W is the strain energy density per unit volume in \mathbf{X} and the application of (7) is presumed. The principal stresses are now calculated by substituting (43) into (35) and applying (7). We get

$$P_R = \frac{\partial \mathbf{A}}{\partial \Lambda_R} = \frac{\partial W}{\partial \Lambda_R} = \frac{J^*}{\Lambda_R^*} \frac{\partial W^{\text{SF}}}{\partial \Lambda_R^e} = \frac{J^*}{\Lambda_R^*} P_R^e, \quad P_R^e = \frac{\partial W^{\text{SF}}}{\partial \Lambda_R^e}, \quad (45)$$

$$P_\Theta = \frac{\partial \mathbf{A}}{\partial \Lambda_\Theta} = \frac{\partial W}{\partial \Lambda_\Theta} = \frac{J^*}{\Lambda_\Theta^*} \frac{\partial W^{\text{SF}}}{\partial \Lambda_\Theta^e} = \frac{J^*}{\Lambda_\Theta^*} P_\Theta^e, \quad P_\Theta^e = \frac{\partial W^{\text{SF}}}{\partial \Lambda_\Theta^e}, \quad (46)$$

$$P_Z = \frac{\partial A}{\partial \Lambda_Z} = \frac{\partial W}{\partial \Lambda_Z} = \frac{J^*}{\Lambda_Z^*} \frac{\partial W^{\text{SF}}}{\partial \Lambda_Z^e} = \frac{J^*}{\Lambda_Z^*} P_Z^e, \quad P_R^e = \frac{\partial W^{\text{SF}}}{\partial \Lambda_Z^e}. \quad (47)$$

The chemical potentials may also be calculated from (35) and (43). The expression for μ_a is

$$\mu_a = \mu_a^{\text{SF}} + \left[\Sigma_R \left(\frac{1}{\Lambda_R^*} \frac{\partial \Lambda_R^*}{\partial C_a} \right) + \Sigma_\Theta \left(\frac{1}{\Lambda_\Theta^*} \frac{\partial \Lambda_\Theta^*}{\partial C_a} \right) + \Sigma_Z \left(\frac{1}{\Lambda_Z^*} \frac{\partial \Lambda_Z^*}{\partial C_a} \right) \right] \quad (48)$$

where μ_a^{SF} is the partial molar Gibbs stress-free free energy given by

$$\mu_a^{\text{SF}} = \bar{G}_a^{\text{SF}}(T, x) = \frac{\partial}{\partial C_a} \left[\text{CG}^{\text{SF}}(T, x) \right], \quad (49)$$

and $(\Sigma_R, \Sigma_\Theta, \Sigma_Z)$ are the principal configurational stresses defined by

$$\Sigma_R = W - P_R \Lambda_R = J^* \Sigma_R^{\text{SF}}, \quad \Sigma_R^{\text{SF}} = W^{\text{SF}} - P_R^e \Lambda_R^e, \quad (50)$$

$$\Sigma_\Theta = W - P_\Theta \Lambda_\Theta = J^* \Sigma_\Theta^{\text{SF}}, \quad \Sigma_\Theta^{\text{SF}} = W^{\text{SF}} - P_\Theta^e \Lambda_\Theta^e, \quad (51)$$

$$\Sigma_Z = W - P_Z \Lambda_Z = J^* \Sigma_Z^{\text{SF}}, \quad \Sigma_Z^{\text{SF}} = W^{\text{SF}} - P_Z^e \Lambda_Z^e. \quad (52)$$

The chemical potential μ_a finally becomes

$$\mu_a = \mu_a^{\text{SF}} + (\Sigma_R + \Sigma_\Theta + \Sigma_Z) \left(\frac{1}{3J^*} \frac{\partial J^*}{\partial C_a} \right) = \mu_a^{\text{SF}} + (3W - P_R \Lambda_R - P_\Theta \Lambda_\Theta - P_Z \Lambda_Z) \left(\frac{1}{3J^*} \frac{\partial J^*}{\partial C_a} \right). \quad (53)$$

It is noted that the configurational stress, or energy momentum tensor, in tensor notation is $\Sigma = \mathbf{W}\mathbf{I} - \mathbf{P}\mathbf{F}$. The chemical potential μ_v may be obtained from either (48) or (53) by changing all subscripts a to v . The derivation of the configurational stress (energy momentum tensor) via the introduction of an eigentransformation has been reported in Wu [3], Epstein and Maugin [9], Maugin [10]. The linking of the eigentransformation to the underlying molar volume in this connection appears to have been first introduced by Wu [3]. This step, while trivial in many ways in hindsight, is necessary in completing the widely held belief that configurational force is a ‘‘material driving force’’ responsible for configurational evolution [11]. Our approach has also enabled us to arrive at the chemical potential (48) in its most complete and nonlinear form, as opposed to the special nature of several published results Larche and Cahn [5,12,13], Stephenson [14], Bartholomeusz [15].

EIGENTRANSFORMATION AND ELASTIC DEFORMATION

Nonuniform elastic deformations of a solid contribute to the non-uniformity of the associated chemical potentials, which, in turn, cause atoms to diffuse. The resulting nonuniform molar concentrations, however, lead to a state of eigentransformation and the incompatible nature of which forces the solid to deform further. This nonlinear, three-way interplay among deformation, diffusion and Eigentransformation, is briefly summarized in this section. Under isothermal condition and when the fluxes of the element and vacancy are conserved $J_{aR} + J_{vR} = 0$, (36) becomes

$$-J_{aR} \frac{\partial}{\partial R} (\mu_a - \mu_v) \geq 0. \quad (54)$$

The associated flux equation may be written as

$$J_{aR} = -D_a \frac{\partial}{\partial R} (\mu_a - \mu_v) \quad (55)$$

where D_a is a phenomenological coefficient (Groot & Mazur[16], Prigogine [17]). The diffusion associated with (55) describes the atomic motion, but the atomic motion-induced deformation is now absorbed in the chemical potential via (48). Finally, the diffusion equation (21a) and the equation of equilibrium (26a) form the governing equations for the determination of $C_a(R, t)$ and $r(R, t)$.

ACKNOWLEDGEMENT

The research support of the National Science Foundation, CMS-0010077, is gratefully acknowledged.

REFERENCES

1. Eshelby, J. D., "Energy relations and the energy-momentum tensor in continuum mechanics," *Inelastic behavior of Solids*. eds. Kanninen, M. F., Adler, W. F. Rosenfeld, A. R., and Jaffee, R. I., McGraw-Hill, NY, pp. 77-114 (1970).
2. Wu, C. H., "Axial Deformation as The-Simpler-The-Better Vehicle for Revealing the Missing Term in the Chemical Potential on Strained Surfaces," *The Chinese J Mech.*, 12, pp. 59-64 (1996).
3. Wu, C. H., "The role of Eshelby stress in composition-generated and stress-assisted diffusion," *J. Mech. Phys. Solids* **49**, pp. 1771-1794 (2001).
4. Sandler, S. I., *Chemical and Engineering Thermodynamics*, 3rd edition. John Wiley & Sons, Inc., New York (1999).
5. Larche, F., and Cahn, J. W., "A nonlinear theory of thermochemical equilibrium of solids under stress," *Acta metall.* **26**, pp. 53-60 (1978).
6. Ting, T.C.T., "Pressuring, Shearing, Torsion and Extension of a Circular Tube or Bar of Cylindrically anisotropic Material," *Proc. R. Soc. Lond. A* **452**, pp. 2397-2421(1996).
7. Ting, T.C.T., "The Remarkable Nature of Cylindrically Orthotropic Elastic Material Under Plane Strain Deformations," *Q. Jl Mech. Appl. Math.*, 52, pp. 387-404 (1999).
8. Ting, T.C.T., "New Solutions to Pressuring, Shearing, Torsion and Extension of a Cylindrically Anisotropic Elastic Circular Tube or Bar," *Proc. R. Soc. Lond. A* **455**, pp. 3527-3542 (1999).
9. Epstein, M. and Maugin, G. A., "The energy momentum tensor and material uniformity in finite elasticity," *Acta Mechanica* **83**, pp. 127-133 (1990).
10. Maugin, G. A., *Material Inhomogeneities in Elasticity*. Chapman and Hall, London (1993).

11. Gurtin, M. E., *Configurational Forces as Basic Concepts of Continuum Physics*, Applied Math. Sci. 137, Springer (2000).
12. Larche, F., and Cahn, J. W., "Thermochemical equilibrium of multiphase solids under stress," *Acta metall.* **26**, pp. 1579-1589 (1978).
13. Larche, F., and Cahn, J. W., "The Effect of Self-stress on diffusion in solids," *Acta metall.* 30, pp. 1835-1845 (1982).
14. Stephenson, G. B., "Deformation during interdiffusion," *Acta metall.* 36, pp. 2663-2683 (1988).
15. Bartholomeusz, B. J., "The chemical potential at the surface of a non-hydrostatically stressed, defect-free solid," *Phil. Magazine A* 71, pp. 489-495 (1995).
16. De Groot, S. R. & P. Mazur, *Non-equilibrium Thermodynamics*. Dover, New York (1984).
17. Prigogine, I., *Introduction to Thermodynamics of Irreversible Processes*, 3 rd ed. Wiley-Interscience, New York (1967).