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The role of Eshelby stress in composition-generated and stress-assisted diffusion

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Abstract

The chemical potential used in interdiffusion analysis was derived by Li et al. in 1966 and by Larche and Cahn in 1982. It contains the trace of the stress tensor as the essential elasticity contribution to the configurational force conjugate to the material composition. As a result, the underlying diffusion equation is totally independent of any accompanying elastic field. In particular, when an alloy epilayer is annealed, the theory implies that the rather large lattice mismatch has no effect on the ensuing diffusion process. However, it is perhaps intuitively clear by now — almost 50 years since Eshelby published his first paper on energy momentum tensor in 1951 — that the trace of the (canonical) Eshelby stress tensor should be the total elasticity contribution to the desired configurational force. This conjecture is formally established in this paper for an n -component substitutional solid. Since the elastic energy is now a part of the chemical potential, the interplay between a composition-generated deformation and another elastic field may become important via the interaction energy. As an example, the effect of this interaction is calculated for the spinodal decomposition of a binary alloy solid/epilayer. The modification of the critical temperature is such that it is now a function of mismatch. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

If an inhomogeneous single-phase alloy is annealed, matter will flow in a manner that will decrease the concentration gradients. If the specimen is annealed long enough, it will become homogeneous and the net flow of matter will cease. This description is

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called Fick's first law:

$$\mathbf{J}_i = -D_i \mathbf{Grad} \rho_i, \quad (1.1)$$

where \mathbf{J}_i , ρ_i and D_i are, respectively, the flux vector, the partial molar density (molar concentration) and the diffusion coefficient associated with component i . The condition of conservation of mass is

$$\partial \rho_i / \partial t = -\text{Div} \mathbf{J}_i, \quad (1.2)$$

which is also called Fick's second law of diffusion. Fick's first law of diffusion is sometimes referred to as a local law in that it relates the local flux to the local concentration gradient.

The local law may be amended to include local gradients of other field variables through the introduction of a chemical potential $\bar{\mu}_i$ such that

$$\mathbf{J}_i = -M_i \rho_i \mathbf{Grad} \bar{\mu}_i, \quad (1.3)$$

where M_i is the molar mobility of component i . For example, in a multicomponent solid under stress, $\bar{\mu}_i$ may be explicitly expressed in terms of the local stress (Larche and Cahn, 1973, 1978a, b, 1982, 1985, 1992). Since the local stress depends on the solution of a boundary-value problem, the amended Fick's first law now becomes what is called by Larche and Cahn (1982, 1985, 1992) a nonlocal law. Their emphasis, however, has been on the effect of self-stress, i.e. the stress induced by a non-uniform composition. The combined action of such a state of self-stress together with either an applied stress or another form of internal stress is routinely not considered, apparently for the reason that, in the well-accepted field equations, the elastic field does not appear in the diffusion equation. One of the major conclusions of this paper is that, depending on situation, the effect of a combined action may become important. This conclusion is actually the consequence of another fundamental result that the chemical potential of Eq. (1.3) is proportional to the trace of the (canonical) Eshelby stress tensor Σ defined by

$$\Sigma = W\mathbf{I} - \mathbf{P}\mathbf{F}, \quad \mathbf{P} = (\partial W / \partial \mathbf{F})^T, \quad (1.4)$$

where the Piola stress \mathbf{P} is given as the derivative of the strain energy density W with respect to the deformation gradient \mathbf{F} . Since \mathbf{F} may be written in terms of the displacement gradient $\nabla \mathbf{u}$, the trace of the Eshelby stress is

$$\Sigma_{II} = 3W - P_{II} u_{i,I} - P_{II} \delta_{II}. \quad (1.5)$$

The linear-theory counterpart of the above is

$$\Sigma_{II} = W - \sigma_{II}, \quad (1.6)$$

where σ is the Cauchy stress tensor, and the case of the subscripts is immaterial. We shall return to see that the commonly used chemical potential is only proportional to the trace of the Cauchy stress.

To fix ideas, let us consider the linear deformation of a binary solid of composition (mole fraction of component 1) c defined by $c = c_1 = \rho_1 / \rho$. If $c = c_0$ is the (uniform)

average composition, then the eigenstrain (stress-free composition strain) ϵ^* associated with a non-uniform composition $c - c_0$ is

$$\epsilon_{ij}^* = (c - c_0)\eta\delta_{ij}, \tag{1.7}$$

where δ_{ij} is the Kronecker delta and η the linear expansion per unit composition change. In other words, if $a(c)$ is the lattice constant of the binary solid, then

$$\eta = \frac{d}{dc} \ln a(c). \tag{1.8}$$

We have adopted the term eigenstrain and the notation of Mura (1982) for the availability of the many useful solutions that may be found in his book.

Let \mathbf{u} , $\boldsymbol{\epsilon}$, \mathbf{e} and $\boldsymbol{\sigma}$ be, respectively, the displacement, total strain, elastic strain and stress induced by $\boldsymbol{\epsilon}^*$ in a body \mathcal{B} . Then

$$\epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) = \epsilon_{ij}^* + e_{ij}, \tag{1.9}$$

$$\sigma_{ij} = 2\mu e_{ij} + \lambda\delta_{ij}e_{kk}, \tag{1.10}$$

$$\sigma_{ij,j} = 0, \tag{1.11}$$

where μ and λ are Lamé constants. There are also the displacement equilibrium equations,

$$\mu u_{i,jj} + (\lambda + \mu)u_{j,ji} = 3\kappa\eta(c - c_0)_{,i} \tag{1.12}$$

and one form of a compatibility condition

$$\nabla^2 \sigma_{kk} = -\frac{2E\eta}{1-\nu} \nabla^2 (c - c_0), \tag{1.13}$$

where κ , E and ν are, respectively, the bulk modulus, Young’s modulus and Poisson’s ratio. The above equations may in principle be solved in terms of $\boldsymbol{\epsilon}^*$.

For a binary solid the result of substituting Eq. (1.3) into Eq. (1.2) is

$$\partial\rho_i/\partial t = \text{Div}[M_i\rho_i \mathbf{Grad} \bar{\mu}_i], \quad (i = 1 \text{ and } 2). \tag{1.14}$$

Differentiating $c = \rho_1/\rho$ and applying the above, we get

$$\partial c/\partial t = c_0(1 - c_0)[M_{10}\nabla^2 \bar{\mu}_1 - M_{20}\nabla^2 \bar{\mu}_2], \tag{1.15}$$

where a subscript zero on a quantity indicates evaluation of the quantity at $c = c_0$, the average composition. In terms of the molar Gibbs free energy $\underline{\mu}(\sigma, \theta, c)$, the chemical potentials are

$$\bar{\mu}_1 = \partial(\rho\underline{\mu})/\partial\rho_1 = \underline{\mu} + (1 - c)\partial\underline{\mu}/\partial c, \tag{1.16}$$

$$\bar{\mu}_2 = \partial(\rho\underline{\mu})/\partial\rho_2 = \underline{\mu} - c\partial\underline{\mu}/\partial c. \tag{1.17}$$

Thus, for the case $M_{10} = M_{20} = M_0$, (1.15) becomes

$$\partial c/\partial t = c_0(1 - c_0)M_0\nabla^2 \bar{\mu}, \tag{1.18}$$

where

$$\bar{\mu} = \bar{\mu}_1 - \bar{\mu}_2 = \partial\underline{\mu}/\partial c. \tag{1.19}$$

For isothermal conditions, the potential $\bar{\mu}$ obtained by Larche and Cahn (1982) is

$$\bar{\mu}(\boldsymbol{\sigma}, \theta, c) = \frac{\partial \underline{\mu}(0, \theta, c)}{\partial c} - \frac{1}{2\rho} \frac{\partial S_{ijmn}}{\partial c} \sigma_{ij} \sigma_{mn} - \frac{\eta}{\rho} \sigma_{kk}, \quad (1.20)$$

where \mathbf{S} is the compliance tensor. This result is in agreement with the expression obtained by Li et al. (1966). Substituting the above into Eq. (1.18), neglecting the variation of compliance with respect to composition, and making use of Eq. (1.13), we arrive at the equation

$$\frac{\partial c}{\partial t} = c_0(1 - c_0)M_0 \left[f''(c_0)\nabla^2 c - \frac{\eta}{\rho} \nabla^2 \sigma_{kk} \right] \quad (1.21)$$

or

$$\frac{\partial c}{\partial t} = c_0(1 - c_0)M_0 \left[f''(c_0) + \frac{2E\eta^2}{(1 - \nu)\rho} \right] \nabla^2 c, \quad (1.22)$$

where f is $\underline{\mu}(0, \theta, c)$, the stress-free molar free energy, and $\bar{\mu}(0, \theta, c) = \partial f / \partial c$. The solution to Eqs. (1.22), (1.12) and certain prescribed initial and boundary conditions describes the interaction between self-stress and interdiffusion. For each solution an apparent diffusion coefficient may be deduced from Eq. (1.18). Some of the apparent diffusion coefficients are of a local character in that the local flux is only related to the local concentration gradient. In general, though, the flux is a functional of the composition field. This is the so-called nonlocal law studied by Larche and Cahn (1982, 1992).

The governing equations (1.12) and (1.22) indicate a one-way coupling between the composition c and the elastic field \mathbf{u} in that the latter is totally absent in Eq. (1.22). Thus, unless the two fields are coupled through boundary conditions, the behavior of the composition field is totally independent of any applied elastic field. The stability investigations of Cahn (1961, 1962) are basically of this nature, although the effect of a gradient energy is not the central issue of the present study. It should be noted that one could introduce plastic deformation to enforce a coupling between deformation and interdiffusion (Stephenson, 1988). The two-dimensional counterpart of Cahn's 1961 study was completed in (Glas, 1987) whereby Cahn's theory of spinodal decomposition was extended to epitaxial layers. Such layers are invariably strained by a lattice mismatch parameter ε_m , which routinely falls between $\pm 5\%$ (Freund, 2000). The theory behind Eqs. (1.12) and (1.22), however, suggests that ε_m plays no role in interdiffusion. On the other hand, if the full Eshelby stress (cf. Eq. (1.6)) is the source of the chemical potential, the effect of ε_m should produce the desired coupling via the energy density W . This is the motivation behind our investigation.

The bulk of this paper is devoted to the derivation of our conjecture that the trace of the (canonical) nonlinear Eshelby stress tensor is the total elasticity contribution to the configurational force conjugate to the nonuniform composition. The formulation begins with a natural state in which all the thermodynamic quantities are either uniform or zero. As soon as the composition becomes nonuniform, every continuum element takes up its own metric and the associated per-unit-reference-volume variables are redefined to account for the element's own stress-free state. This is where the complication comes in and the remedy is to introduce a three-frame kinematics involving

a reference coordinate system, a stress-free system, and a spatial coordinate system. In this setup, the (total) deformation is taken as the product of an elastic transformation and an *eigentransformation*, which is coined after the word eigenstrain that was introduced by Mura in 1982 for nonelastic strains. The elastic stress is identified as the (total) stress. What is left is then re-grouped in the Clausius–Duhem inequality and the pairing of Eshelby stress and eigentransformation is formally established there. In this paper, the eigentransformation is taken as a nonuniform stress-free strain generated by nonuniform composition. The final product is a chemical potential consisting of a stress-free component plus an Eshelby-stress contribution. Thus, the role of Eshelby stress in configurational evolution is once again demonstrated.

The needed three-frame kinematics is introduced in Section 2, and the thermodynamics of an n -component system is summarized in Section 3. The structure of the Helmholtz free energy is prescribed in Section 4 and represents the main contribution of this paper. While the three-frame kinematics has been freely used by many (Lee, 1969; Cohen and Epstein, 1984; Epstein and Maugin, 1990; Maugin, 1993), the actual connection between the physical composition and the Eshelby stress that is established here appears to be new. The nonlinear result of Section 4 is reformulated in the context of elasticity in Section 5. Finally, the spinodal decomposition of an alloy solid/epifilm is treated in Section 6, and the results are compared with those of Cahn (1961) and Glas (1987).

2. Notation and kinematics

2.1. Deformation gradient, eigentransformation and elastic deformation

Let (z_1, z_2, z_3) denote the rectangular coordinates of a point in a Cartesian frame of unit vectors $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$, so that the position vector of the point is $\mathbf{z} = z_i \mathbf{e}_i$ where, and throughout this paper, summation on repeated indices is presumed. We use $\mathbf{z} = \mathbf{X} = X_K \mathbf{e}_K$ to denote a point in a continuum material body \mathcal{B} in some reference configuration. The collection of all such points forms the reference coordinate system embedded in \mathcal{B} . The deformation of this embedded coordinate system may be defined by the path line

$$\mathbf{z} = \check{\xi}(\mathbf{X}, \tau) \quad (\tau_0 \leq \tau \leq t), \quad (2.1)$$

which traces the particle \mathbf{X} as time τ varies from τ_0 to t such that

$$\check{\xi}(\mathbf{X}, \tau_0) = \mathbf{X}, \quad \check{\xi}(\mathbf{X}, t) = \mathbf{x}. \quad (2.2)$$

We shall call $\mathbf{x} = x_i \mathbf{e}_i$ the place of the particle \mathbf{X} . It is noted that the use of lower and upper case indices, and later on Greek indices, is introduced to facilitate interpretation.

A most often used reference configuration for crystalline solids may be obtained by embedding the reference coordinate system \mathbf{X} in a material body when it is stress free and also has a uniform temperature and uniform composition. This initial state will be called the *natural state* and will be specified once and for all. The maintenance of a uniform composition is not always possible and, as a result, interdiffusion and composition-generated deformation may take place. This coupled process of diffusion

and deformation may also interact with additional deformations brought about by other sources.

Before proceeding we first define notation for products of vectors and higher order quantities. Products such as $\mathbf{A} = \mathbf{BC}$ are $A_{ij} = B_{ik}C_{kj}$, or $A_i = B_{ik}C_k$, or $A_j = B_kC_{kj}$, depending on whether \mathbf{B} and \mathbf{C} are first- or second-order quantities. Inner products are denoted by \cdot and signify contraction over all indices; thus, $\mathbf{A} \cdot \mathbf{B} = A_iB_i$ or $A_{ik}B_{ki}$.

The transformation $\mathbf{X} \rightarrow \mathbf{x}$ is assumed to be continuous with a well-defined deformation gradient \mathbf{F} and inverse \mathbf{f} ,

$$\mathbf{F} = \mathbf{Grad} \mathbf{x}(\mathbf{X}), \quad \mathbf{f} = \mathbf{grad} \mathbf{X}(\mathbf{x}) \quad (2.3)$$

or, in component form,

$$F_{kK} = \partial x_k / \partial X_K, \quad f_{Kk} = \partial X_K / \partial x_k. \quad (2.4)$$

The Jacobian of the transformation and its inverse are defined as

$$J = dv/dV = \det \mathbf{F}, \quad j = dV/dv = \det \mathbf{f}, \quad jJ = 1. \quad (2.5)$$

We record for future purposes the Euler–Piola–Jacobi identities

$$\operatorname{div} \mathbf{a} = j \operatorname{Div}(\mathbf{J}\mathbf{fa}), \quad \operatorname{Div} \mathbf{A} = J \operatorname{div}(j\mathbf{FA}) \quad (2.6)$$

and the formulas

$$\partial J / \partial \mathbf{F} = \mathbf{J}\mathbf{f}^T \quad \text{i.e.} \quad \partial J / \partial F_{kK} = \text{Cofactor of } F_{kK} = Jf_{Kk}, \quad (2.7)$$

$$\partial f_{Mm} / \partial F_{nN} = -f_{Mn}f_{Nm}. \quad (2.8)$$

It is now assumed that the (total) deformation gradient \mathbf{F} is not totally the consequence of stressing. The portion of \mathbf{F} that is not the result of stressing is termed an eigentransformation, which reduces to Mura's eigenstrain (1982) upon linearization. Following Mura's use of $\boldsymbol{\varepsilon}^*$ for eigenstrain, we shall denote by \mathbf{F}^* the eigentransformation. The deformation gradient \mathbf{F} is then written as the product of an elastic transformation, \mathbf{F}^c , and \mathbf{F}^* , i.e.

$$\mathbf{F} = \mathbf{F}^c \mathbf{F}^* \quad (2.9)$$

which was first used by Lee (1969) in decomposing an elastic–plastic deformation. Cohen and Epstein (1984), Epstein and Maugin (1990), and Maugin (1993) have also used the decomposition in studying material uniformity and inhomogeneity. Our main objective here is to establish the conjugate roles of \mathbf{F}^* and Eshelby stress in the Clausius–Duhem inequality whereby the necessary diffusion kinetics may be deduced in a consistent manner.

We assume that $\mathbf{F}^*(\mathbf{X}, t)$ is merely a property of the material at coordinate \mathbf{X} and time t . It converts a linear reference-coordinate-system segment $d\mathbf{X}$ into a *stress-free segment* $d\mathbf{X}^{\text{SF}}$ defined by

$$d\mathbf{X}^{\text{SF}} \equiv \mathbf{F}^*(\mathbf{X}, t) d\mathbf{X}. \quad (2.10)$$

It is emphasized that while \mathbf{F} is the deformation gradient given by Eq. (2.3), neither \mathbf{F}^* nor \mathbf{F}^c is necessarily a gradient. The transformations \mathbf{F}^* and \mathbf{F}^c are assumed to

be invertible with inverses \mathbf{f}^* and \mathbf{f}^e , respectively. Introducing the *stress-free volume element* dV^{SF} and following Eq. (2.3), we have

$$J^* = dV^{\text{SF}}/dV = \det \mathbf{F}^*, \quad j^* = dV/dV^{\text{SF}} = \det \mathbf{f}^*, \quad j^* J^* = 1, \quad (2.11)$$

$$J^e = dv/dV^{\text{SF}} = \det \mathbf{F}^e, \quad j^e = dV^{\text{SF}}/dv = \det \mathbf{f}^e, \quad j^e J^e = 1. \quad (2.12)$$

Finally, the component forms of Eq. (2.9) and its inverse are

$$F_{iJ} = F_{i\alpha}^e F_{\alpha J}^*, \quad f_{Ji} = f_{J\alpha}^* f_{\alpha i}^e, \quad (2.13)$$

where the simultaneous use of Greek and lower and upper case indices should help the interpretation of the three sets of quantities.

Any quantity that is a function of position can be expressed as a function of either \mathbf{X} or \mathbf{x} , since one determines the other. For simplicity and unless otherwise noted, no notational distinction is made between the function of \mathbf{X} and that of \mathbf{x} for a particular quantity. Gradients and divergences taken with respect to the reference and spatial coordinates have been implicitly introduced in Eqs. (2.3) and (2.6). The notation for time derivatives of any quantity a are

$$\hat{\partial}a/\hat{\partial}t \equiv \partial a/\partial t|_{\mathbf{x} \text{ Constant}}, \quad \dot{a} \equiv Da/Dt = \partial a/\partial t|_{\mathbf{X} \text{ Constant}}. \quad (2.14)$$

2.2. An n -component system

A system with n chemical components is considered. We assume that these components are uncharged, and electric field effects are not explicitly considered. For partial molar density of component i , we use the following notation: $\rho_i(\mathbf{X}, t)$ denotes the density per unit reference-coordinate-system volume; $\rho_i^{\text{D}}(\mathbf{x}, t)$ denotes the density per unit spatial-coordinate-system volume; $\rho_i^{\text{SF}}(\mathbf{X}, t)$ is the corresponding density per unit stress-free volume. The total reference-coordinate-system density $\rho(\mathbf{X}, t)$, total spatial-coordinate-system density $\rho^{\text{D}}(\mathbf{x}, t)$, and total stress-free density $\rho^{\text{SF}}(\mathbf{X}, t)$ are just the sums of the corresponding partial densities. We shall restrict ourselves to substitutional solid solutions so that $\rho(\mathbf{X}, t) = \rho$, the constant number of substitutional sites that is fixed by the choice of the reference coordinate system \mathbf{X} at the outset. Thus,

$$\rho = \sum_{i=1}^n \rho_i(\mathbf{X}, t), \quad \rho^{\text{SF}}(\mathbf{X}, t) = \sum_{i=1}^n \rho_i^{\text{SF}}(\mathbf{X}, t), \quad \rho^{\text{D}}(\mathbf{x}, t) = \sum_{i=1}^n \rho_i^{\text{D}}(\mathbf{x}, t). \quad (2.15)$$

The conservation of mass must hold for each of the three transformations linking the reference-coordinate-system volume element dV , the spatial-coordinate-system volume element dv , and the stress-free volume element dV^{SF} , i.e.

$$J^* = \frac{dV^{\text{SF}}}{dV} = \frac{\rho}{\rho^{\text{SF}}(\mathbf{X}, t)} = \frac{\rho_i(\mathbf{X}, t)}{\rho_i^{\text{SF}}(\mathbf{X}, t)}, \quad (2.16)$$

$$J = \frac{dv}{dV} = \frac{\rho}{\rho^{\text{D}}(\mathbf{x}, t)} = \frac{\rho_i(\mathbf{X}, t)}{\rho_i^{\text{D}}(\mathbf{x}, t)}, \quad (2.17)$$

$$J^e = \frac{dv}{dV^{\text{SF}}} = \frac{\rho^{\text{SF}}(\mathbf{X}, t)}{\rho^{\text{D}}(\mathbf{x}, t)} = \frac{\rho_i^{\text{SF}}(\mathbf{X}, t)}{\rho_i^{\text{D}}(\mathbf{x}, t)}, \quad (2.18)$$

where $i = 1$ to n . It follows from the above that the composition variable c_i satisfies

$$c_i = \frac{\rho_i^D}{\rho^D} = \frac{\rho_i}{\rho} = \frac{\rho_i^{SF}}{\rho^{SF}} \quad (i = 1 \text{ to } n) \tag{2.19}$$

and

$$\sum_{i=1}^n c_i = 1. \tag{2.20}$$

We shall henceforth consider the composition variables as functions of \mathbf{X} and t .

Since a deformation gradient exists only between \mathbf{x} and \mathbf{X} , we concentrate on the interpretation of Eq. (2.17). The integral form of Eq. (2.17) is

$$\begin{aligned} \frac{D}{Dt} \int_v \rho_i^D dv &= \frac{D}{Dt} \int_V \rho_i dV = \int_V \dot{\rho}_i dV, \\ \frac{D}{Dt} \int_v \rho^D dv &= \frac{D}{Dt} \int_V \rho dV = \int_V \dot{\rho} dV = 0. \end{aligned} \tag{2.21}$$

Now let $f(\mathbf{x}, t)$ be any per-mole field quantity in a material volume $v(t)$, we have

$$\frac{D}{Dt} \int_v \rho^D f dv = \frac{D}{Dt} \int_V \rho f dV = \int_V \dot{F} dV, \tag{2.22}$$

where F is the per-unit-reference-coordinate-system-volume value of that quantity. The above integral identities will be used to express all the local-form equations in terms of quantities defined with respect to \mathbf{X} .

3. Thermodynamics of an n -component system

3.1. Balance of masses

We balance the mass for component i associated with an arbitrary volume $v(t)$:

$$\frac{D}{Dt} \int_v \rho_i^D dv = - \int_{\partial v} \mathbf{j}_i \cdot \mathbf{n} da, \tag{3.1}$$

where \mathbf{j}_i is the mass diffusion flux and \mathbf{n} the outward normal to ∂v . All quantities are defined with respect to the spatial coordinate system \mathbf{x} . The conversion to reference-coordinate-system \mathbf{X} is now performed. We have, with the help of Eq. (2.6),

$$\int_{\partial v} \mathbf{j}_i \cdot \mathbf{n} da = \int_v \text{div } \mathbf{j}_i dv = \int_V \text{Div } \mathbf{J}_i dV = \int_{\partial V} \mathbf{J}_i \cdot \mathbf{N} dA, \tag{3.2}$$

where

$$\mathbf{J}_i = J \mathbf{j}_i \tag{3.3}$$

is the mass flux in \mathbf{X} and \mathbf{N} the outward normal to ∂V . Using Eqs. (2.15) and (3.2), we obtain from Eq. (3.1) its equivalent local form

$$\frac{D\rho_i}{Dt} = \frac{\partial \rho_i}{\partial t} = -\text{Div } \mathbf{J}_i \quad (i = 1 \text{ to } n). \tag{3.4}$$

It follows from the first of Eq. (2.15) and the above that

$$\frac{\partial \rho}{\partial t} = 0 = \sum_{i=1}^n -\text{Div } \mathbf{J}_i, \tag{3.5}$$

which indicates that only $n - 1$ of the n equations given by Eq. (3.4) are independent. The procedure leading from Eq. (3.1) to Eq. (3.5) will be followed in the following deductions.

3.2. The first law

We balance the energy associated with an arbitrary volume $v(t)$:

$$\frac{D}{Dt} \int_v \rho^D e \, dv = \int_v [\mathbf{v} \cdot \mathbf{b} \rho^D + \rho^D r_{(q)}] \, dv + \int_{\partial v} [\mathbf{v} \cdot (\mathbf{n} \boldsymbol{\sigma}) - \mathbf{j}_{(q)} \cdot \mathbf{n}] \, da, \tag{3.6}$$

where e is the specific internal energy per mole of mixture, $\mathbf{v} = \dot{\mathbf{x}}$ is the velocity, \mathbf{b} is the specific body force vector per mole, $r_{(q)}$ is the source heat per mole, $\mathbf{j}_{(q)}$ is the heat flux vector, and $\boldsymbol{\sigma}$ is the Cauchy stress tensor. The result of converting the above into the \mathbf{X} -representation is

$$\int_V \dot{\varepsilon} \, dV = \int_V [\mathbf{v} \cdot (\text{Div } \mathbf{P} + \mathbf{B}) + \mathbf{P} \cdot \dot{\mathbf{F}} - \text{Div } \mathbf{J}_{(q)} + R_{(q)}] \, dV, \tag{3.7}$$

where $\varepsilon = \rho e$, $\mathbf{B} = \rho \mathbf{b}$, $\mathbf{J}_{(q)} = J \mathbf{j}_{(q)}$, $R_{(q)} = \rho r_{(q)}$, and \mathbf{P} is the Piola stress tensor given by

$$\mathbf{P} = J \mathbf{f} \boldsymbol{\sigma}, \text{ i.e., } P_{Ij} = J f_{Ii} \sigma_{ij}. \tag{3.8}$$

The local form of Eq. (3.7) is

$$\dot{\varepsilon} = \mathbf{P} \cdot \dot{\mathbf{F}} - \text{Div } \mathbf{J}_{(q)} + R_{(q)}, \tag{3.9}$$

where \mathbf{P} satisfies the equilibrium equation

$$\text{Div } \mathbf{P} = -\mathbf{B}. \tag{3.10}$$

3.3. The second law

The second law states

$$\frac{D}{Dt} \int_v \rho^D \zeta \, dv \geq \int_v \frac{\rho^D r_{(q)}}{\theta} \, dv + \int_{\partial v} \left[-\frac{\mathbf{j}_{(q)} \cdot \mathbf{n}}{\theta} + \sum_{i=1}^n \frac{\bar{\mu}_i \mathbf{j}_i \cdot \mathbf{n}}{\theta} \right] \, da, \tag{3.11}$$

where ζ is the specific entropy per mole of mixture, θ the absolute temperature, and $\bar{\mu}_i$ the chemical potential for component i . The local form of the above in \mathbf{X} is

$$\theta \dot{\eta} - [R_{(q)} - \text{Div } \mathbf{J}_{(q)}] + \theta \mathbf{J}_{(q)} \cdot \mathbf{Grad} \left(\frac{1}{\theta} \right) + \sum_{i=1}^n \left[\bar{\mu}_i \dot{\rho}_i - \theta \mathbf{J}_{(i)} \cdot \mathbf{Grad} \left(\frac{\bar{\mu}_i}{\theta} \right) \right] \geq 0, \tag{3.12}$$

where $\eta = \rho\zeta$ is the entropy per unit reference-coordinate-system volume and $\dot{\rho}_i$ is defined by Eq. (3.4). Introducing Helmholtz free energy per unit reference-coordinate-system volume, $\phi = \varepsilon - \theta\eta$, and combining Eqs. (3.9) and (3.12), we obtain the Clausius–Duhem inequality

$$-\left[\dot{\phi} + \eta\dot{\theta} - \mathbf{P} \cdot \dot{\mathbf{F}} - \sum_{i=1}^n \bar{\mu}_i \dot{\rho}_i\right] + \theta \mathbf{J}_{(q)} \cdot \mathbf{Grad}\left(\frac{1}{\theta}\right) + \sum_{i=1}^n \theta \mathbf{J}_i \cdot \mathbf{Grad}\left(-\frac{\bar{\mu}_i}{\theta}\right) \geq 0. \tag{3.13}$$

It follows that the above constitutive constraint may be met by the use of $\phi(\mathbf{F}, \theta, \rho_i)$ as a potential such that

$$\eta = -\partial\phi/\partial\theta, \tag{3.14}$$

$$\varepsilon = \phi - \theta(\partial\phi/\partial\theta), \tag{3.15}$$

$$\mathbf{P} = (\partial\phi/\partial\mathbf{F})^T, \tag{3.16}$$

$$\bar{\mu}_i = \partial\phi/\partial\rho_i \tag{3.17}$$

and

$$\theta \mathbf{J}_{(q)} \cdot \mathbf{Grad}\left(\frac{1}{\theta}\right) \geq 0, \tag{3.18}$$

$$\sum_{i=1}^n \theta \mathbf{J}_i \cdot \mathbf{Grad}\left(-\frac{\bar{\mu}_i}{\theta}\right) \geq 0, \tag{3.19}$$

where the dissipation inequality of Eq. (3.13) is more restrictively required to satisfy Eqs. (3.18) and (3.19). For isothermal conditions, requirement (3.19) is satisfied by the diffusion flux

$$\mathbf{J}_i = -M_i \rho_i \mathbf{Grad} \bar{\mu}_i \quad (\text{no sum and } i = 1 \text{ to } n), \tag{3.20}$$

where M_i is the molar mobility of component i , relative to the tracer diffusivity D_i^* by

$$M_i = \frac{D_i^*}{R\theta} \quad (i = 1 \text{ to } n), \tag{3.21}$$

in which R is the molar Boltzmann constant. The diffusion equation for each density (3.4), becomes

$$\frac{\partial\rho_i}{\partial t} = \text{Div}(M_i \rho_i \mathbf{Grad} \bar{\mu}_i) \quad (i = 1 \text{ to } n). \tag{3.22}$$

Finally, to express diffusion in terms of the composition variables, we differentiate the second of Eq. (2.19) and then apply Eq. (3.22) to obtain

$$\frac{Dc_i}{Dt} = \text{Div}(M_i c_i \mathbf{Grad} \bar{\mu}_i) - c_i \sum_{j=1}^n \text{Div}(M_j c_j \mathbf{Grad} \bar{\mu}_j) \quad (i = 1 \text{ to } n - 1). \tag{3.23}$$

The equations of this section are developed relative to a reference coordinate system \mathbf{X} , but the explicit nature of the material state in this reference configuration has so far not been specified. Its specification, together with a constructive constitutive development, will be given in the following section.

4. Natural state and states of nonuniform composition

4.1. Natural state and the related thermodynamic quantities

Suppose that a body is in its undeformed and stress-free state (the external forces being absent), and has the constant temperature θ . It is also in a state of uniform composition defined by $\rho_i(\mathbf{X}, 0) = \rho_{i0}$ and $c_i(\mathbf{X}, 0) = c_{i0}$ where

$$\rho = \sum_{i=1}^n \rho_{i0} = \sum_{i=1}^n \rho_i(\mathbf{X}, t), \quad 1 = \sum_{i=1}^n c_{i0} = \sum_{i=1}^n c_i(\mathbf{X}, t). \tag{4.1}$$

Such a stress-free, isothermal and isocomposition state is called a *natural state*. The thermodynamic conditions summarized in Section 3 require the consideration of states of nonuniform composition. In particular, a volume element of the mixture of partial molar densities $\rho_i(\mathbf{X}, t)$ will undergo a change in size and be subjected to the action of stress. This composition-generated deformation will manifest in the form of a time-dependent metric in the analysis to follow.

Let $\underline{V}^{\text{SF}}(\theta, c_1, \dots, c_{n-1})$ be the volume per mole of the mixture at zero stress and constant temperature θ . It is a fundamental mixture property that may be experimentally generated (Sandler, 1999). By definition, $\underline{V}^{\text{SF}}$ is just the inverse of $\rho^{\text{SF}}(\mathbf{X}, t)$ of Eq. (2.15). We have

$$\frac{1}{\rho^{\text{SF}}} = \underline{V}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) = \sum_{i=1}^n c_i \bar{V}_i^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) = \frac{1}{\rho} \sum_{i=1}^n \rho_i \bar{V}_i^{\text{SF}}, \tag{4.2}$$

where the partial molar volumes \bar{V}_i^{SF} are given by

$$\bar{V}_i^{\text{SF}} = \frac{\partial}{\partial \rho_i}(\rho \underline{V}^{\text{SF}}) = \frac{\partial}{\partial \rho_i} \left(\frac{\rho}{\rho^{\text{SF}}} \right). \tag{4.3}$$

They may be explicitly expressed in terms $\underline{V}^{\text{SF}}$ as follows:

$$\bar{V}_n^{\text{SF}} = \underline{V}^{\text{SF}} - \sum_{k=1}^{n-1} c_k \frac{\partial \underline{V}^{\text{SF}}}{\partial c_k}, \tag{4.4}$$

$$\bar{V}_i^{\text{SF}} = \bar{V}_n^{\text{SF}} + \frac{\partial \underline{V}^{\text{SF}}}{\partial c_i} \quad (i = 1 \text{ to } n - 1). \tag{4.5}$$

Setting $c_i = c_{i0}$ in $\underline{V}^{\text{SF}}(\theta, c_1, \dots, c_{n-1})$, we obtain

$$\underline{V}_0^{\text{SF}} = \underline{V}^{\text{SF}}(\theta, c_{10}, \dots, c_{(n-1)0}), \tag{4.6}$$

which is the volume per mole of the mixture in the natural state. Thus,

$$\underline{V}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) = \underline{V}_0^{\text{SF}} + \sum_{i=1}^{n-1} (\bar{V}_{i0}^{\text{SF}} - \bar{V}_{n0}^{\text{SF}})(c_i - c_{i0}) + \dots, \tag{4.7}$$

where a subscript zero on a quantity indicates evaluation of the quantity at c_{i0} , and the variation of \bar{V}_i^{SF} with respect to c_j has been ignored. The volumetric strain affected by a change in composition is therefore given by

$$\frac{\underline{V}^{\text{SF}} - \underline{V}_0^{\text{SF}}}{\underline{V}_0^{\text{SF}}} = \sum_{i=1}^{n-1} 3\eta_i(c_i - c_{i0}), \quad (4.8)$$

where the linear expansion coefficients η_i are

$$\eta_i = \frac{1}{3} \frac{\partial}{\partial c_i} \ln \underline{V}^{\text{SF}}|_{c_i=c_{i0}} = \frac{\bar{V}_{i0}^{\text{SF}} - \bar{V}_{n0}^{\text{SF}}}{3\underline{V}^{\text{SF}}}. \quad (4.9)$$

The Jacobian J^* is, by Eqs. (2.11), (2.16) and (4.2),

$$J^* = \det \mathbf{F}^* = \frac{\rho}{\rho^{\text{SF}}} = \sum_{i=1}^n \bar{V}_i^{\text{SF}} \rho_i. \quad (4.10)$$

It follows from applying Eq. (4.3) to the above that

$$\dot{j}^* = \sum_{i=1}^n \bar{V}_i^{\text{SF}} \dot{\rho}_i. \quad (4.11)$$

For isotropic materials, the eigentransformation \mathbf{F}^* brought about by $c_i - c_{i0}$ may be defined by

$$\mathbf{F}^* = (J^*)^{1/3} \delta^* \quad \text{or} \quad F_{\beta l}^* = (J^*)^{1/3} \delta_{\beta l}^*, \quad (4.12)$$

where $\delta_{\beta l}^*$ is the Kronecker delta. Differentiating the above and applying (4.11), we conclude that

$$\dot{\mathbf{F}}^* = \mathbf{F}^* \sum_{i=1}^n \frac{\bar{V}_i^{\text{SF}}}{3J^*} \dot{\rho}_i \quad \text{and} \quad \frac{\partial \mathbf{F}^*}{\partial \rho_i} = \frac{\bar{V}_i^{\text{SF}}}{3J^*} \mathbf{F}^*. \quad (4.13)$$

Let $\psi(\mathbf{P}, \theta, \rho_i)$ be the Gibbs free energy per unit reference-coordinate-system volume defined by

$$\psi = \varepsilon - \theta\eta - \mathbf{P} \cdot \mathbf{F} = \phi - \mathbf{P} \cdot \mathbf{F}. \quad (4.14)$$

The isothermal, stress-free Gibbs energy is

$$\psi(0, \theta, \rho_i) = J^* \psi^{\text{SF}}(\rho_i^{\text{SF}}) = J^* \rho^{\text{SF}} \underline{\mu}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) = \rho \underline{\mu}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}), \quad (4.15)$$

where ψ^{SF} is the stress-free Gibbs free energy per unit stress-free volume and $\underline{\mu}^{\text{SF}}$ the stress-free molar Gibbs free energy, a function of composition and temperature that may be experimentally determined. The first equality of Eq. (4.15) follows from the fact that a unit reference-coordinate-system volume of mixture of density ρ_i will expand into J^* units of stress-free-system volume of partial molar densities ρ_i^{SF} . The

partial molar Gibbs free energies $\bar{\mu}_i^{\text{SF}}$ are defined by

$$\underline{\mu}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) = \sum_{i=1}^n c_i \bar{\mu}_i^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) = \frac{1}{\rho} \sum_{i=1}^n \rho_i \bar{\mu}_i^{\text{SF}}, \tag{4.16}$$

$$\bar{\mu}_i^{\text{SF}} = \frac{\partial}{\partial \rho_i}(\rho \underline{\mu}^{\text{SF}}) = \frac{\partial \psi^{\text{SF}}(\mathbf{0}, \theta, \rho_i)}{\partial \rho_i}. \tag{4.17}$$

The explicit formulas are

$$\bar{\mu}_n^{\text{SF}} = \underline{\mu}^{\text{SF}} - \sum_{j=1}^{n-1} c_j \frac{\partial \underline{\mu}^{\text{SF}}}{\partial c_j}, \tag{4.18}$$

$$\bar{\mu}_i^{\text{SF}} = \bar{\mu}_n^{\text{SF}} + \frac{\partial \underline{\mu}^{\text{SF}}}{\partial c_i} \quad (i = 1 \text{ to } n - 1). \tag{4.19}$$

Consider now the isothermal and isocomposition elastic deformation \mathbf{F}^e that is defined relative to a stress-free state. The associated Helmholtz free energy is simply the strain energy density per unit stress-free volume $W^{\text{SF}}(\mathbf{F}^e, \theta, \rho_i^{\text{SF}})$. It may be expressed in terms of the molar strain energy density $\bar{W}^{\text{SF}}(\mathbf{F}^e, \theta, c_1, \dots, c_{n-1})$ by

$$W^{\text{SF}}(\mathbf{F}^e, \theta, \rho_i^{\text{SF}}) = \rho^{\text{SF}} \bar{W}^{\text{SF}}(\mathbf{F}^e, \theta, c_1, \dots, c_{n-1}), \tag{4.20}$$

$$\bar{W}^{\text{SF}}(\mathbf{F}^e, \theta, c_1, \dots, c_{n-1}) = \sum_{i=1}^n c_i \bar{W}_i^{\text{SF}}(\mathbf{F}^e, \theta, c_1, \dots, c_{n-1}), \tag{4.21}$$

where the partial molar strain energy densities \bar{W}_i^{SF} may be obtained by substituting W for μ in Eqs. (4.17), (4.18) and (4.19). Expanding Eq. (4.21) about $c_i = c_{i0}$ and ignoring the dependence of \bar{W}_i^{SF} on c_i , we also have

$$\bar{W}^{\text{SF}}(\mathbf{F}^e, \theta, c_1, \dots, c_{n-1}) = \bar{W}^{\text{SF}}(\mathbf{F}^e, \theta, c_{10}, \dots, c_{(n-1)0}) + \sum_{i=1}^n (c_i - c_{i0}) \bar{W}_{i0}^{\text{SF}} + \dots, \tag{4.22}$$

where $\bar{W}_{i0}^{\text{SF}} = \bar{W}_i^{\text{SF}}(\mathbf{F}^e, \theta, c_{10}, \dots, c_{(n-1)0})$. Substituting the above into Eq. (4.20), we obtain the expansion for the strain energy density per unit stress-free volume of mixture of partial molar densities ρ_i^{SF} :

$$W^{\text{SF}}(\mathbf{F}^e, \theta, \rho_i^{\text{SF}}) = W_0^{\text{SF}}(\mathbf{F}^e) + \rho^{\text{SF}} \sum_{i=1}^n (c_i - c_{i0}) \bar{W}_{i0}^{\text{SF}} + \dots \tag{4.23}$$

where

$$W_0^{\text{SF}}(\mathbf{F}^e) = \rho^{\text{SF}} \bar{W}^{\text{SF}}(\mathbf{F}^e, \theta, c_{10}, \dots, c_{(n-1)0}) \tag{4.24}$$

is the strain energy density per unit stress-free volume. The strain energy density function is assumed to satisfy the conditions

$$W^{\text{SF}}(\mathbf{0}, \theta, \rho_i^{\text{SF}}) = \partial W^{\text{SF}}(\mathbf{0}, \theta, \rho_i^{\text{SF}}) / \partial \mathbf{F}^e = 0. \tag{4.25}$$

Table 1
Reference, stress-free, and spatial states

	Reference	Stress-free	Spatial
Linear element	$d\mathbf{X}$	$d\mathbf{X}^{\text{SF}} \equiv \mathbf{F}^* d\mathbf{X}$	$d\mathbf{x} \equiv \mathbf{F} d\mathbf{X} = \mathbf{F}^e d\mathbf{X}^{\text{SF}}$
Volume element	dV	$dV^{\text{SF}} = J^* dV$	$dv = J dV$
Partial molar density	ρ_i	$\rho_i^{\text{SF}} = \rho_i/J^*$	$\rho_i^{\text{D}} = \rho_i/J$
Moles of component i	$\rho_i dV$	$\rho_i^{\text{SF}} dV^{\text{SF}} = \rho_i dV$	$\rho_i^{\text{D}} dv = \rho_i^{\text{SF}} dV^{\text{SF}} = \rho_i dV$

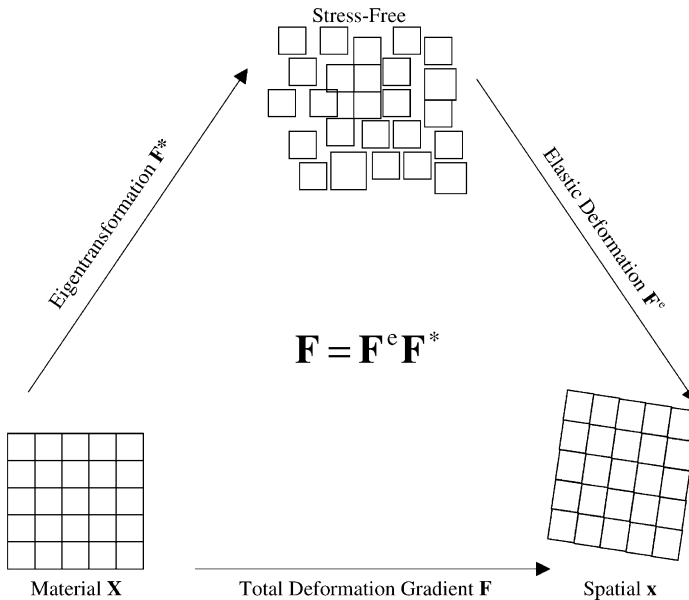


Fig. 1. The total deformation gradient is the product of an elastic deformation and an eigentransformation. Neither one of the latter two is a gradient.

4.2. States of nonuniform composition

The evolution of a nonequilibrium thermodynamic state is governed by the system of diffusion equation (3.23), which is built on the as yet undefined Helmholtz free energy $\phi(\mathbf{F}, \theta, \rho_i)$. We shall now express this function in terms of the molar Gibbs energy μ^{SF} and the molar strain energy density \mathcal{W}^{SF} . It is instructive to recall that for a given \mathbf{X} and t there are the reference, stress-free, and spatial states, whose properties are summarized in Table 1. This three-frame kinematics is also schematically illustrated in Fig. 1.

The function $\phi(\mathbf{F}(\mathbf{X}, t), \theta(t), \rho_i(\mathbf{X}, t))$ is an implicit and yet precise statement about how the three states are related. Let us examine the volume element dV . It has $\rho_i dV$ moles of element i ($i = 1$ to n). The moles of elements are mixed in the stress-free

state, and the required energy is

$$\phi dV = \rho \underline{\mu}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) dV. \tag{4.26}$$

However, unless $c_i = c_{i0}$, there is a volumetric eigentransformation associated with the mixing. Due to the nonuniform nature of the eigentransformation, an elastic transformation \mathbf{F}^c is induced and the associated energy is

$$\phi dV = J^* W^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*), \theta, \rho_i/J^*) dV, \quad \mathbf{F}^c(\mathbf{F}, \mathbf{F}^*) \equiv \mathbf{F}^{\mathbf{F}^*}, \tag{4.27}$$

where \mathbf{f}^* is the inverse of \mathbf{F}^* . The complete Helmholtz free energy now becomes

$$\phi(\mathbf{F}, \theta, \rho_i) = J^* W^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*), \theta, \rho_i/J^*) + \rho \underline{\mu}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}), \tag{4.28}$$

which will be used to deduce the needed chemical potential.

Substituting Eq. (4.28) into Eq. (3.16), we obtain

$$\mathbf{P} = J^* \mathbf{f}^* \mathbf{P}^c \quad \text{or} \quad P_{li} = J^* \mathbf{f}^*_{lx} \mathbf{P}^c_{xi} \tag{4.29}$$

where

$$\mathbf{P}^c = (\partial W^{\text{SF}} / \partial \mathbf{F}^c)^T. \tag{4.30}$$

Since

$$\mathbf{P} = (\partial \phi / \partial \mathbf{F})^T = \left\{ \frac{\partial}{\partial \mathbf{F}} [J^* W^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*), \theta, \rho_i/J^*)] \right\}^T, \tag{4.31}$$

we simply write

$$\mathbf{P} = (\partial W / \partial \mathbf{F})^T, \tag{4.32}$$

where, by Eqs. (4.23) and (4.24),

$$W(\mathbf{F}, \mathbf{F}^*) \equiv J^* W^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*), \theta, \rho_i/J^*) = J^* W_0^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*)). \tag{4.33}$$

In terms of ϕ of Eq. (4.28) and W^{SF} of Eq. (4.23), the chemical potential (3.17) becomes

$$\bar{\mu}_i - \bar{\mu}_i^{\text{SF}} = \frac{\partial}{\partial \rho_i} [J^* W_0^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*))] + \bar{W}_{i0}^{\text{SF}}(\mathbf{F}^c) \quad (i = 1 \text{ to } n). \tag{4.34}$$

Carrying out the differentiation and applying Eqs. (2.7) and (2.8) to J^* and \mathbf{F}^* , we get

$$\bar{\mu}_i - \bar{\mu}_i^{\text{SF}} - \bar{W}_{i0}^{\text{SF}}(\mathbf{F}^c) = \left\{ \frac{\partial}{\partial \mathbf{F}^*} [J^* W_0^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*))] \right\} \cdot \frac{\partial \mathbf{F}^*}{\partial \rho_i}, \tag{4.35}$$

$$\bar{\mu}_i - \bar{\mu}_i^{\text{SF}} - \bar{W}_{i0}^{\text{SF}}(\mathbf{F}^c) = \{ J^* \mathbf{f}^* [W_0^{\text{SF}}(\mathbf{F}^c(\mathbf{F}, \mathbf{F}^*)) - \mathbf{P}^c \mathbf{F}^*] \} \cdot \frac{\partial \mathbf{F}^*}{\partial \rho_i}, \tag{4.36}$$

$$\bar{\mu}_i - \bar{\mu}_i^{\text{SF}} - \bar{W}_{i0}^{\text{SF}}(\mathbf{F}^c) = (J^* \mathbf{f}^* \Sigma^c) \cdot \frac{\partial \mathbf{F}^*}{\partial \rho_i} = (\Sigma \mathbf{f}^*) \cdot \frac{\partial \mathbf{F}^*}{\partial \rho_i}, \tag{4.37}$$

where

$$\Sigma^e: \Sigma_{\alpha\beta}^e = W_0^{\text{SF}}(\mathbf{F}^e(\mathbf{F}, \mathbf{F}^*))\delta_{\alpha\beta} - P_{\alpha i}^e F_{i\beta}^e, \tag{4.38}$$

$$\Sigma: \Sigma_{IJ} = W(\mathbf{F}, \mathbf{F}^*)\delta_{IJ} - P_{Im} F_{mJ}, \tag{4.39}$$

and $\delta_{\alpha\beta}$ and δ_{IJ} are Kronecker deltas. The various transformations and identities associated with Eqs. (4.35)–(4.39) may be found in Cohen and Epstein (1984), Epstein and Maugin (1990), and Maugin (1993). Substituting the second of Eq. (4.13) into Eq. (4.37), we conclude that

$$\bar{\mu}_i - \bar{\mu}_i^{\text{SF}} - \bar{W}_{i0}^{\text{SF}}(\mathbf{F}^e) = (\boldsymbol{\Sigma}\mathbf{f}^*) \cdot \frac{\partial \mathbf{F}^*}{\partial \rho_i} = \boldsymbol{\Sigma} \cdot \mathbf{f}^* \frac{\partial \mathbf{F}^*}{\partial \rho_i} = \frac{\Sigma_{KK} \bar{V}_i^{\text{SF}}}{3J^*} = \frac{\bar{V}_i^{\text{SF}}}{3V^{\text{SF}}} \frac{\Sigma_{KK}}{\rho}. \tag{4.40}$$

The final form of the chemical potential is

$$\bar{\mu}_i(\mathbf{F}, \theta, \rho_i) = \bar{\mu}_i^{\text{SF}} + \bar{W}_{i0}^{\text{SF}}(\mathbf{F}^e) + \frac{\bar{V}_i^{\text{SF}}}{3V^{\text{SF}}} \frac{\Sigma_{KK}}{\rho}, \tag{4.41}$$

where the first term is the result of mixing the elements at zero stress, and the rest account for the elastic energy built-up due to nonuniform composition. The second term, defined by Eq. (4.23), reflects the dependence of elasticity on composition, a variation that is usually ignored. Finally, the last term is the full contribution of the Eshelby stress. It is this term that distinguishes our result from all known results on chemical potential derived for nonuniform composition. In fact, Eqs. (4.32), (4.33) and (4.39) indicate that as $c_i \rightarrow c_{i0}$, Σ_{KK} tends to the trace of the Eshelby stress obtained for the same body under the same loads but in its natural state.

The desired system of diffusion equations obtained by substituting the above into Eq. (3.23) is highly nonlinear. We linearize Eq. (3.23) with respect to c_{i0} and the result is

$$\frac{\partial c_i}{\partial t} = c_{i0}(1 - c_{i0})[M_{i0}\nabla^2 \bar{\mu}_i - M_{n0}\nabla^2 \bar{\mu}_n] - c_{i0} \sum_{j \neq i}^{n-1} c_{j0}[M_{j0}\nabla^2 \bar{\mu}_j - M_{n0}\nabla^2 \bar{\mu}_n]. \tag{4.42}$$

For a binary system with $c_1 = c$, $c_{10} = c_0$ and $\underline{\mu}^{\text{SF}} = f(c)$, we have from Eqs. (4.18) and (4.19)

$$\bar{\mu}_1^{\text{SF}} = f(c) + (1 - c)f'(c), \quad \bar{\mu}_2^{\text{SF}} = f(c) - cf'(c). \tag{4.43}$$

Substituting Eq. (4.40) into Eqs. (4.41), applying Eq. (4.42) and ignoring $\bar{W}_{i0}^{\text{SF}}(\mathbf{F}^e)$, we finally obtain

$$\begin{aligned} \frac{\partial c}{\partial t} &= (1 - c_0)c_0 f''(c_0)[M_{10}(1 - c_0) + M_{20}c_0]\nabla^2 c \\ &\quad + (1 - c_0)c_0[M_{10}\bar{V}_{10}^{\text{SF}} - M_{20}\bar{V}_{20}^{\text{SF}}] \frac{1}{3\rho V^{\text{SF}}} \nabla^2 \Sigma_{KK}, \end{aligned} \tag{4.44}$$

For the special case $M_{10} = M_{20} = M_0$, the last equation becomes

$$\frac{\partial c}{\partial t} = (1 - c_0)c_0 M_0 \left[f''(c_0)\nabla^2 c + \frac{\eta}{\rho} \nabla^2 \Sigma_{KK} \right], \tag{4.45}$$

in which $\eta = \eta_1 = (\bar{V}_{10}^{\text{SF}} - \bar{V}_{20}^{\text{SF}})/3\bar{V}^{\text{SF}}$, by Eq. (4.9). The last equation is to be compared with Eq. (1.21) and represents the first immediate consequence of Eq. (4.40). Since the energy is a part of Σ_{KK} , the interaction energy between a composition-generated deformation and, say, an elastic field produced by a lattice mismatch may now exercise a control on the ensuing diffusion.

We have successfully employed the geometric nonlinearity of the three-frame kinematics to retain the full contribution of the Eshelby stress, but the result should hold even for linear elasticity. This special deduction is next presented.

5. Linearly elasticity

The (canonical nonlinear) Eshelby stress is defined by Eq. (1.4) (Eshelby, 1970; Chadwick, 1975). In terms of the displacement gradient $u_{i,l}$ and in component form

$$\Sigma_{IJ} = W\delta_{IJ} - P_{Ii}u_{i,J} - P_{Ii}\delta_{iJ}, \quad (5.1)$$

which is symmetric, and \mathbf{P} and $\nabla\mathbf{u}$ are two-point tensors. The infinitesimal strain tensor, which is not a strain measure, is used in linear elasticity to define the metric. It is actually an awkward setup for configurational studies for the reason that configurational evolutions are more conveniently described in a Lagrangian formulation, whereas linear strain makes no distinction between Lagrangian and Eulerian coordinates. For a uniform body without eigenstrain, the components of the (canonical linear) Eshelby stress is

$$\Sigma_{ij} = W\delta_{ij} - \sigma_{ik}u_{k,j} - \sigma_{ij}, \quad (5.2)$$

which is not symmetric although $\boldsymbol{\sigma}$, which replaces the \mathbf{P} in (5.1), is now the symmetric stress tensor derived from Hooke's law. Neither Eq. (5.1) nor Eq. (5.2) was based on some preconceived notion of *configurational strain*, but whenever there is a change in geometric shape that change invariably turns out to be conjugate to a *generalized traction or force* calculated from $\boldsymbol{\Sigma}$. The translation, rotation, and expansion of voids (Budiansky and Rice, 1973), the motion of phase boundaries (Eshelby, 1951, 1970), the crack driving force (Rice, 1968), and the surface chemical potential (Wu, 1996; Freund, 1998; Norris, 1998; Bartholomeusz, 1995) are but a few of the more familiar examples. Modern electronic and photonic devices are solid structures of small feature sizes. Such structures evolve over time and many of the driving forces have origin in Eshelby stress (Suo, 2000; Suo and Wang, 1994; Sun et al., 1994).

Let $\nabla\mathbf{u}$ denote the displacement gradient, so that the infinitesimal strain $\boldsymbol{\varepsilon}$ is related to the deformation gradient \mathbf{F} by the definition

$$\mathbf{F} = \boldsymbol{\delta} + \nabla\mathbf{u} \Rightarrow \boldsymbol{\varepsilon} \equiv (\nabla\mathbf{u} + (\nabla\mathbf{u})^T)/2. \quad (5.3)$$

Since $\boldsymbol{\varepsilon}$ makes no distinction between Lagrangian and Eulerian coordinates, we shall use lower case subscripts for all quantities to follow. The eigentransformation \mathbf{F}^* and the associated (linear) eigenstrain $\boldsymbol{\varepsilon}^*$ are assumed to be isotropic so that they may be defined by a single scalar function ε^* as follows:

$$\mathbf{F}^* = \boldsymbol{\delta} + \varepsilon^*\boldsymbol{\delta} \Rightarrow \boldsymbol{\varepsilon}^* \equiv (\varepsilon^*\boldsymbol{\delta} + \varepsilon^*\boldsymbol{\delta}^T)/2 = \varepsilon^*\boldsymbol{\delta}. \quad (5.4)$$

We also have

$$\frac{\partial \varepsilon^*}{\partial \rho_i} = \frac{\bar{V}_i^{\text{SF}}}{3} = \frac{\bar{V}_i^{\text{SF}}}{3 \bar{V}^{\text{SF}}} \frac{\rho}{\rho^{\text{SF}}} \frac{1}{\rho} = \frac{\bar{V}_i^{\text{SF}}}{3 \bar{V}^{\text{SF}}} (1 + \varepsilon_{kk}^*) \frac{1}{\rho} \approx \frac{\bar{V}_i^{\text{SF}}}{3 \bar{V}^{\text{SF}}} \frac{1}{\rho}, \tag{5.5}$$

which follows from Eq. (4.13). The elastic transformation is now computed from Eq. (2.9)

$$\mathbf{F}^c = \mathbf{F}(\mathbf{F}^*)^{-1} = (\boldsymbol{\delta} + \nabla \mathbf{u}) \boldsymbol{\delta} / (1 + \varepsilon^*) \approx \boldsymbol{\delta} + \nabla \mathbf{u} - \boldsymbol{\varepsilon}^* - \boldsymbol{\varepsilon}^* \nabla \mathbf{u} + \dots \tag{5.6}$$

It is now convenient to define an elastic strain \mathbf{E} by the expression

$$\mathbf{E}(\boldsymbol{\varepsilon}, \boldsymbol{\varepsilon}^*) \equiv \frac{1}{2} [(\nabla \mathbf{u} - \boldsymbol{\varepsilon}^* - \boldsymbol{\varepsilon}^* \nabla \mathbf{u}) + (\nabla \mathbf{u} - \boldsymbol{\varepsilon}^* - \boldsymbol{\varepsilon}^* \nabla \mathbf{u})^T] = \mathbf{e} - \boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon}, \quad \mathbf{e} = \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^*, \tag{5.7}$$

where \mathbf{e} is commonly referred to as the elastic strain (Mura, 1982). What is the point of including the nonlinear term $\boldsymbol{\varepsilon}^* \boldsymbol{\varepsilon}$ in a presumably linear strain expression? There is of course no need to include such a term if mechanical equilibrium is of our only concern. To investigate the configurational equilibrium or evolution associated with the configurational variable $\boldsymbol{\varepsilon}^*$, functional derivatives of the total energy must be taken with respect to $\boldsymbol{\varepsilon}^*$. It is therefore very important to keep all terms that are linear in $\boldsymbol{\varepsilon}^*$ in all expressions before the required differentiation has been completed. After that simply replace \mathbf{E} with \mathbf{e} to complete a consistent linear theory.

Consider now the strain energy density per unit stress-free volume W^{SF} defined by Eq. (4.20). For linear elasticity, we write

$$W^{\text{SF}}(\mathbf{E}, \theta, \rho_i^{\text{SF}}) = \mu(c_i) E_{kj} E_{kj} + \frac{\lambda(c_i)}{2} E_{kk} E_{jj}, \tag{5.8}$$

where the Lamé constants $\mu(c_i)$ and $\lambda(c_i)$ are assumed to be functions of c_i ($i = 1$ to $n - 1$). The molar strain energy density \bar{W}^{SF} is thus given by

$$\bar{W}^{\text{SF}}(\mathbf{E}, \theta, c_i, \dots, c_{n-1}) = \frac{1}{\rho^{\text{SF}}} \left[\mu(c_i) E_{kj} E_{kj} + \frac{\lambda(c_i)}{2} E_{kk} E_{jj} \right], \tag{5.9}$$

and the associated partial molar densities \bar{W}_i^{SF} may be calculated:

$$\bar{W}_n^{\text{SF}} = \frac{1}{\rho^{\text{SF}}} \left\{ \left[\mu(c_i) E_{kj} E_{kj} + \frac{\lambda(c_i)}{2} E_{kk} E_{jj} \right] - \sum_{i=1}^{n-1} c_i \left[\frac{\partial \mu}{\partial c_i} E_{kj} E_{kj} + \frac{1}{2} \frac{\partial \lambda}{\partial c_i} E_{kk} E_{jj} \right] \right\}, \tag{5.10}$$

$$\bar{W}_i^{\text{SF}} = \bar{W}_n^{\text{SF}} + \frac{1}{\rho^{\text{SF}}} \left[\frac{\partial \mu}{\partial c_i} E_{kj} E_{kj} + \frac{1}{2} \frac{\partial \lambda}{\partial c_i} E_{kk} E_{jj} \right]. \tag{5.11}$$

The expansion of Eq. (5.8), in the form of Eq. (4.23), is

$$W^{\text{SF}}(\mathbf{E}, \theta, \rho_i^{\text{SF}}) = W_0^{\text{SF}}(\mathbf{E}) + \rho^{\text{SF}} \sum_{i=1}^n (c_i - c_{i0}) \bar{W}_{i0}^{\text{SF}}, \tag{5.12}$$

where

$$W_0^{\text{SF}}(\mathbf{E}) = \mu E_{kj} E_{kj} + \frac{\lambda}{2} E_{kk} E_{jj} \tag{5.13}$$

is the strain energy density per unit stress-free volume and $\mu = \mu(c_{i0})$ and $\lambda = \lambda(c_{i0})$. The Helmholtz free energy per unit reference-coordinate-system volume may be obtained from Eqs. (4.28) and (5.12). It is

$$\phi(\varepsilon, \theta, \rho_i) = \rho \underline{\mu}^{\text{SF}}(\theta, c_1, \dots, c_{n-1}) + \rho \sum_{i=1}^n (c_i - c_{i0}) \bar{W}_{i0}^{\text{SF}} + W(\varepsilon, \varepsilon^*), \tag{5.14}$$

where

$$W(\varepsilon, \varepsilon^*) = (1 + \varepsilon_{kk}^*) W_0^{\text{SF}}(\mathbf{E}) \tag{5.15}$$

and $(1 + \varepsilon_{kk}^*)$ is J^* . Once again, there is the temptation to leave out ε_{kk}^* from the above equation, as the strain energy density is supposed to be only quadratic in strain. But the energy momentum tensor is by definition an energy already, and the associated “work” term must be of third order.

The linear-elasticity version of (4.35) is

$$\bar{\mu}_i = \bar{\mu}_i^{\text{SF}} + \bar{W}_{i0}^{\text{SF}} + \frac{\partial W(\varepsilon, \varepsilon^*)}{\partial \varepsilon^*} \frac{\partial \varepsilon^*}{\partial \rho_i}, \tag{5.16}$$

where, after the completion of the differentiation with respect to ε^* ,

$$\frac{\partial W(\varepsilon, \varepsilon^*)}{\partial \varepsilon^*} = \left[W_0^{\text{SF}}(\mathbf{E}) \delta - (1 + \varepsilon_{kk}^*) \frac{\partial W_0^{\text{SF}}}{\partial \mathbf{E}} \frac{\partial \mathbf{E}}{\partial \varepsilon^*} \right]_{\mathbf{E}=\mathbf{e} \text{ and } 1+\varepsilon_{kk}^*=1} = \Sigma \tag{5.17}$$

and

$$\Sigma = W_0^{\text{SF}}(\mathbf{e}) \delta - \sigma \varepsilon - \sigma, \quad \sigma = 2\mu \mathbf{e} + \lambda e_{kk} \delta. \tag{5.18}$$

Substituting the above into Eq. (5.16) and applying Eq. (5.5), we finally obtain the complete chemical potential appropriate for linear elasticity, i.e.

$$\bar{\mu}_i(\varepsilon, \theta, \rho_i) = \bar{\mu}_i^{\text{SF}}(c_1, \dots, c_{n-1}) + \bar{W}_{i0}^{\text{SF}}(\mathbf{e}) + \frac{\bar{V}_i^{\text{SF}}}{3V^{\text{SF}}} \frac{\Sigma_{kk}}{\rho}. \tag{5.19}$$

For a binary system with $c_1 = c = 1 - c_2$, $c_{10} = c_0 = 1 - c_{20}$, $\underline{\mu}^{\text{SF}} = f(c)$ and Lamé Constants $\lambda(c)$ and $\mu(c)$, we have

$$\rho(\bar{\mu}_1 - \bar{\mu}_2) = \rho f'(c) + \frac{\rho}{\rho^{\text{SF}}} \left[\mu'(c) e_{kj} e_{kj} + \frac{\lambda'(c)}{2} e_{kk} e_{jj} \right] + \frac{\bar{V}_1^{\text{SF}} - \bar{V}_2^{\text{SF}}}{3V^{\text{SF}}} \Sigma_{kk} \tag{5.20}$$

or

$$\bar{\mu} = \frac{1}{\rho} \frac{\partial \phi}{\partial c} = \bar{\mu}_1 - \bar{\mu}_2 = f'(c) + \frac{1}{2\rho} [2\mu'(c) e_{kj} e_{kj} + \lambda'(c) e_{kk} e_{jj}] + \frac{\eta}{\rho} [W_0^{\text{SF}}(\mathbf{e}) - \sigma_{kk}]. \tag{5.21}$$

It can be straightforwardly shown from the following:

$$W_c \equiv \frac{1}{2} [2\mu(c) e'_{ij} e'_{ij} + \kappa(c) e_{ii} e_{jj}], \quad e'_{ij} \equiv e_{ij} - \frac{1}{3} e_{kk} \delta_{ij}, \tag{5.22}$$

$$W_\sigma \equiv \frac{1}{2} \left[\frac{1}{2\mu(c)} \sigma'_{ij} \sigma'_{ij} + \frac{1}{\kappa(c)} \sigma \sigma \right], \quad \sigma'_{ij} \equiv \sigma_{ij} - \sigma \delta_{ij}, \quad \sigma \equiv \frac{\sigma_{kk}}{3} \tag{5.23}$$

that

$$\frac{\partial W_\sigma}{\partial c} = -\frac{1}{2} \left[\frac{2\mu'(c)}{(2\mu)^2} \sigma'_{ij} \sigma'_{ij} + \frac{\kappa'(c)}{(\kappa)^2} \sigma \sigma \right] = -\frac{1}{2} [2\mu'(c) e'_{ij} e'_{ij} + \kappa'(c) e_{ii} e_{jj}] = -\frac{\partial W_e}{\partial c}. \tag{5.24}$$

Thus, if the energy term is dropped from Eq. (5.21), we recover the chemical potential of Larche and Cahn (1982) and Li et al. (1966) in the form of Eq. (1.20). Such an action is justifiable if the total strain ε is solely due to the eigenstrain ε^* , so that the energy term becomes second order relative to σ_{kk} . On the other hand, if ε is actually $\varepsilon + \varepsilon^\circ$ where ε° is produced by other sources, in the notation of Mura (1982), then the contribution of the interaction energy could become significant. In any case, the complete form of the diffusion equation (4.45) now becomes

$$\frac{\partial c}{\partial t} = (1 - c_0) c_0 M_0 \left\{ \left[f''(c_0) + \frac{2E\eta^2}{(1 - \nu)\rho} \right] \nabla^2 c + \frac{\eta}{\rho} \nabla^2 W_0^{\text{SF}}(\mathbf{e}) \right\}, \tag{5.25}$$

which is to be coupled with Eq. (1.12), i.e.

$$\mu u_{i,jj} + (\lambda + \mu) u_{j,ji} = 3\kappa\eta(c - c_0)_{,i} = 3\kappa\eta c_{,i}. \tag{5.26}$$

It is noted that if $\boldsymbol{\sigma}$ is actually $\boldsymbol{\sigma} + \boldsymbol{\sigma}^\circ$, then $\nabla^2 \sigma_{kk}^\circ = 0$ by Eq. (1.13) and \mathbf{u} and $\boldsymbol{\varepsilon}$ are, respectively, $\mathbf{u} + \mathbf{u}^\circ$ and $\boldsymbol{\varepsilon} + \boldsymbol{\varepsilon}^\circ$. The strain energy density associated with this general case is

$$W_0^{\text{SF}}(\boldsymbol{\varepsilon}^\circ + \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^*) = \frac{1}{2} (\boldsymbol{\sigma}^\circ \cdot \boldsymbol{\varepsilon}^\circ + \boldsymbol{\sigma}^\circ \cdot \mathbf{e} + \boldsymbol{\sigma} \cdot \boldsymbol{\varepsilon}^\circ + \boldsymbol{\sigma} \cdot \mathbf{e}) = W_0^{\text{SF}}(\boldsymbol{\varepsilon}^\circ) + W_{\text{Int}} + W_0^{\text{SF}}(\mathbf{e}), \tag{5.27}$$

where W_{Int} is the interaction energy given by

$$W_{\text{Int}} = \frac{1}{2} (\boldsymbol{\sigma}^\circ \cdot \mathbf{e} + \boldsymbol{\sigma} \cdot \boldsymbol{\varepsilon}^\circ) = \boldsymbol{\sigma}^\circ \cdot \mathbf{e} = \boldsymbol{\sigma} \cdot \boldsymbol{\varepsilon}^\circ. \tag{5.28}$$

The roles of the three energy components defined by Eq. (5.27) may now be examined via Eq. (5.25). The component $W_0^{\text{SF}}(\mathbf{e})$ is nonlinear in $c - c_0$, and may be ignored in that Eq. (5.25) is already a linearized version of Eq. (3.23). The component $W_0^{\text{SF}}(\boldsymbol{\varepsilon}^\circ)$ is a source term in the full diffusion equation, and may play a role in nucleation. Finally, the interaction energy is linear in $c - c_0$, and, hence, the elastic field has a direct influence on the diffusion coefficient. The spinodal decomposition is worked out in the next section as an example.

6. Spinodal decomposition as an example

Let us now consider the implications of a uniform elastic field on the thermodynamical stability of a binary alloy $A_c B_{1-c}$. We assume that the stress-free molar Gibbs energy $\mu^{\text{SF}} = f(c)$ is described by a regular solution:

$$\mu^{\text{SF}} = f(c) = \Omega c(1 - c) + RT[c \ln c + (1 - c) \ln(1 - c)], \tag{6.1}$$

where Ω is the interaction parameter, R is the gas constant, and T the absolute temperature. We shall be concerned with testing the stability of an initially homogeneous

solution of infinite extent and of composition c_0 to infinitesimal composition fluctuations given by

$$c - c_0 = A(t) \cos \beta x_1. \tag{6.2}$$

Moreover, the infinite solid is biaxially stressed by

$$\sigma_{11}^\circ = \sigma_{22}^\circ = E\varepsilon_m / (1 - \nu), \quad \sigma_{33}^\circ = 0, \tag{6.3}$$

so that

$$\varepsilon_{11}^\circ = \varepsilon_{22}^\circ = \varepsilon_m, \quad \varepsilon_{33}^\circ = -2\nu\varepsilon_m / (1 - \nu), \tag{6.4}$$

where ε_m is a pre-specified biaxial strain. The eigenstrain induced by Eq. (6.2) is

$$\varepsilon_{ij}^* = (c - c_0)\eta\delta_{ij} = \delta_{ij}\eta A(t) \cos \beta x_1. \tag{6.5}$$

It also follows from Eq. (5.26) and (6.2) that

$$u_1 = A(t) \frac{\eta}{\beta} \frac{3\kappa}{\lambda + 2\mu} \sin \beta x_1, \quad u_2 = u_3 = 0, \tag{6.6}$$

so that

$$\varepsilon_{11} = A(t)\eta \frac{3\kappa}{\lambda + 2\mu} \cos \beta x_1 \quad \text{other } \varepsilon_{ij} = 0. \tag{6.7}$$

The elastic strain is just

$$e_{11} = \frac{2\nu}{1 - \nu} \eta A(t) \cos \beta x_1, \quad e_{22} = e_{33} = -\eta A(t) \cos \beta x_1 \tag{6.8}$$

and the associated stress is

$$\sigma_{11} = 0, \quad \sigma_{22} = \sigma_{33} = -\frac{E}{1 - \nu} \eta A(t) \cos \beta x_1. \tag{6.9}$$

The interaction energy for the given situation becomes

$$W_{\text{Int}} = \sigma \cdot \varepsilon^\circ = \sigma^\circ \cdot \mathbf{e} = -\frac{2\eta E}{(1 - \nu)} \frac{(1 - 3\nu)}{2(1 - \nu)} \varepsilon_m A(t) \cos \beta x_1. \tag{6.10}$$

Applying Eqs. (6.2), (5.27), (5.28) and (6.10) to Eq. (5.25), we obtain

$$\begin{aligned} \frac{dA}{dt} = (1 - c_0)c_0M_0\beta^2 \left\{ -2\Omega + \frac{RT}{(1 - c_0)c_0} \right. \\ \left. + \frac{2E\eta^2}{(1 - \nu)\rho} m_{\text{Glas}} \left[1 + \frac{(1 - 3\nu)}{2(1 - \nu)} \varepsilon_m \right] \right\} A(t), \end{aligned} \tag{6.11}$$

where m_{Glas} is a parameter introduced by Glas (1987) to adapt the stability analysis for an infinite solid for that of an epilayer. The case of an infinite solid corresponds to $m_{\text{Glas}} = 1$, and m_{Glas} is considerably less than one for typical (thickness) $\cdot \beta$ values. The critical temperature T_C , above which the uniform configuration defined by the constant composition c_0 is stable, is therefore given by

$$T_C(\varepsilon_m) = \frac{c_0(1 - c_0)2\Omega}{R} \left\{ 1 - \frac{E\eta^2}{(1 - \nu)\rho\Omega} m_{\text{Glas}} \left[1 + \frac{(1 - 3\nu)}{2(1 - \nu)} \varepsilon_m \right] \right\}. \tag{6.12}$$

It is noted that

$$\begin{aligned}
 T_{\text{Cahn}} &= T_0 \left[1 - \frac{E\eta^2}{(1-\nu)\rho\Omega} \right] < T_{\text{Glas}} = T_0 \left[1 - \frac{E\eta^2}{(1-\nu)\rho\Omega} m_{\text{Glas}} \right] < T_0 \\
 &= \frac{c_0(1-c_0)2\Omega}{R}, \tag{6.13}
 \end{aligned}$$

where $T_0 = \Omega/2R$ is a maximum for $c_0 = 1/2$. We note that $T_C(\varepsilon_m)$ falls on either side of T_{Glas} , depending on the sign of ε_m . The above simplified result provides an indication on how the mismatch strain can be coupled with the composition variable to affect diffusion during annealing. The precise effect of the added terms in the chemical potential on film stability and self-organization can only be determined from more refined numerical calculations and simulations. There is the need to include the gradient energy (Cahn, 1961), and the full nonlinear form of μ^{SF} must be retained. On this subject, Suo and Lu (2001) have recently introduced a composition-dependent surface stress to couple the surface diffusion with the substrate deformation. The interaction energy (5.28), gives another form of that coupling.

7. Summary and conclusions

The total deformation is taken as the product of an elastic transformation and an eigentransformation, which is known to be conjugate to the Eshelby stress in the Clausius–Duhem inequality. The identification of the eigentransformation with the composition-generated deformation, however, enables us to prove that the trace of the (canonical) Eshelby stress tensor, instead of just the trace of the stress tensor, is the chemical potential associated with interdiffusion. This result, while intuitively obvious, appears to be new. Since the strain energy is now a part of the chemical potential, the physical implication of an interaction-energy may be fully exploited. It is anticipated that an extensive numerical analysis of the refined diffusion equation could yield useful information about the phenomenon of self-organizing nanophases in epilayers.

Why was the result concerning the Eshelby stress not picked up in previous analyses? The answer lies in the intricate implications of the three-frame kinematics depicted in Fig. 1. It may also be found in the implicit deduction of Section 5. The strain energy density function W^{SF} is defined per unit stress-free volume but the actual analysis is performed in the reference coordinate system where the appropriate density becomes $W = J^* W^{\text{SF}}$. Moreover, the strain needed in defining W^{SF} is a function of the total strain and eigenstrain. It follows from Eqs. (5.7), (5.8) and (5.15) that

$$W(\varepsilon_{ij}, \varepsilon_{ij}^*) = (1 + \varepsilon_{kk}^*) \left[\mu E_{kj} E_{kj} + \frac{\lambda}{2} E_{kk} E_{jj} \right], \tag{7.1}$$

where

$$E_{ij} = \varepsilon_{ij} - \varepsilon_{ij}^* - \varepsilon_{ik}^* \varepsilon_{kj}. \tag{7.2}$$

Thus, for small eigenstrains, the energy density becomes

$$W(\varepsilon_{ij}, \varepsilon_{ij}^*) \rightarrow W^*(\varepsilon_{ij}, \varepsilon_{ij}^*) = \left[\mu(\varepsilon_{kj} - \varepsilon_{kj}^*)(\varepsilon_{kj} - \varepsilon_{kj}^*) + \frac{\lambda}{2}(\varepsilon_{kk} - \varepsilon_{kk}^*)(\varepsilon_{jj} - \varepsilon_{jj}^*) \right]. \quad (7.3)$$

The derivative of $W(\varepsilon_{ij}, \varepsilon_{ij}^*)$ with respect to ε_{ij}^* is the Eshelby stress (5.17), while that of $W^*(\varepsilon_{ij}, \varepsilon_{ij}^*)$ is simply $-\sigma_{ij}$. This appears to be the source of the discrepancy between our result and that of the previous analyses.

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