

APPLICATIONS OF THE THERMODYNAMICS OF ELASTIC, CRYSTALLINE
MATERIALS

A Dissertation

by

XIUHUA SI

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2005

Major Subject: Aerospace Engineering

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ABSTRACT

Applications of the Thermodynamics of Elastic, Crystalline Materials. (August 2005)

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The thermodynamic behaviors of multicomponent, elastic, crystalline solids under stress and electro-magnetic fields are developed, including the extension of Euler's equation, Gibbs equation, Gibbs-Duhem equation, the conditions to be expected at equilibrium, and an extension of the Gibbs phase rule. The predictions of this new phase rule are compared with experimental observations.

The stress deformation behaviors of the single martensitic crystal with and without magnetic fields were studied with the stress deformation equation derived by Slattery and Si (2005). One coherent interfacial condition between two martensitic variants was developed and used as one boundary condition of the problem. The dynamic magnetic actuation process of the single crystal actuator was analyzed. The extension velocity and the actuation time of the single crystal actuator are predicted. The relationship between the external stress and the extension velocity and the actuation time with the presence of a large external magnetic field was studied.

The extended Gibbs-Duhem equation and Slattery-Lagoudas stress-deformation expression for crystalline solids was used. Interfacial constraints on the elastic portion of stress for crystalline-crystalline interfaces and crystalline-fluids or crystalline-amorphous solids interfaces were derived and tested by the oxidation on the exterior of a circular cylinder, one-sided and two-sided oxidation of a plate. An experiment for measuring solid-solid interface surface energies was designed and the silicon-silicon

dioxide surface energy was estimated.

A new generalized Clausius-Clapeyron equation has been derived for elastic crystalline solids as well as fluids and amorphous solids. Special cases are pertinent to coherent interfaces as well as the latent heat of transformation.

To my parents, my husband, and my son

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CHAPTER I

INTRODUCTION

The literature review about the thermodynamics for multicomponent, elastic, crystalline materials has been done by Slattery and Lagoudas (2005). I will not repeat what they did. Additionally, I will add the reviews for the related research with the presence of electric-magnetic fields, the equilibrium thermodynamics for austenite-martensite transitions, and the interfacial constraints for crystalline-crystalline solids in the following sections.

A. Magnetic field controlled actuation of single crystal shape memory alloy

Shape memory effects are due to a diffusionless structural transformation from a high temperature phase (austenite) to a low temperature low symmetry phase (martensite). If the martensitic transformation is induced by temperature in the absence of biasing stress or fields, all of the invariants are equally likely to form. When a biased field or stress is applied to the mixture of variants, certain variants will be favored and appear in larger amounts than other variants.

Ferromagnetic shape memory effect is due to a magnetic field induced redistribution of twin variants in a martensitic phase.

In ferromagnetic crystalline materials, magnetization vectors lie along the easy axes (certain crystallographic axes along which crystal is easy to be magnetized), or called c axes in a tetragonal crystal. When an external magnetic field is applied, the magnetization tends to turn from the easy axes to the direction of the external field, or reorient the easy axes to the direction of the external field. The second case may

This dissertation follows the style and format of *Mechanics of Materials*.

need lower energy through the twin boundary motion, it means the external field reorient the tetragonal cells. An increasing magnetic field will thus cause a growth of variants with easy axes along with the external field through the move of the twin boundaries. The reorientation of the c axis will cause a giant strain.

Magnetic control of the shape memory effect should be possible in several ferromagnetic materials. Ni_2MnGa are the mostly studied alloys to possess shape memory effects which can be excited through magnetic fields. In recent years, most research has been devoted to the Ni_2MnGa system to date, which has shown a 6 percentage strain in a field of 300 kA/m (O’Handley et al. 2000; Tickle and James 1999; Henry et al. 2002; Enkovaara et al. 2002; Murray et al. 2000b; Jin et al. 2003).

Magnetic controlled actuation is rapid and precise. It is attracting more and more attentions from industry. With the appearance of commercial devices based on Ni-Mn-Ga, the focus on applications has increased. Understanding the dynamics of the field-induced twin boundary motion and the speed of the actuation are necessary for the design of actuators.

Several models have been developed and applied to explain quantitatively the static results of some experiments (Vasilev et al. 1999). However, no theoretical study has been done to investigate the dynamic process of the magnetic induced actuation of the shape memory alloys.

In chapter IV, we will study the dynamic actuation process of a cubic or tetragonal martensitic variant under stress with switching on a strong static external magnetic field. We assume the stress deformation behavior (Slattery and Si, 2005) can be applied to a dynamic system. This is supported by (Tian et al., 2005), who use it to correctly predict wave propagation in cubic crystals. The applied magnetic field is sufficiently large that variant B in the figure on page 48 is aligned with its easy axis in the z_1 direction. This appears to conform to the experiments of Murray et al.

(2001). In considering the dynamic transformation from A to B, we will assume that the magnetization of variant A was unaffected by the application of the external magnetic field. The interfaces between two martensitic variants are coherent.

In section 4.1, we will study the static properties of the two martensitic variants. In section 4.2, we will study the dynamic actuation process through the jump mass, momentum balances, and the coherent interfacial condition.

B. Equilibrium thermodynamics of martensitic transformation

The equilibrium thermodynamic theory has been applied to martensitic transformation for many years. This transformation can be considered as a recoverable, but never reversible, because of a hysteresis is present. However, reversible thermodynamic is still used if an equilibrium temperature T_0 is defined. This T_0 is usually approximated to be half way between M_s (martensitic start temperature) and A_f (austenite finish temperature) for thermally induced martensitic transformation. Analogously, in stress-induced transformation, the equilibrium stress \mathbf{T} is also assumed to lie half way between the T_s (the transformation stress) and T_i (retransformation stress)(Yawny et al., 1995).

A lot of attempts have been done for the thermodynamic description of the martensitic transformation (Ortin and Planes, 1988, 1990, 1991, Wollants et al. 1979, 1983, 1991, Otsuka et al. 1976). Deng and Ansell (1991) have pointed out that the "null entropy production" made by Ortin and Planes (1988, 1990, 1991) is not consistent with the second law of thermodynamics. Later, Torra and Tachoire (1992) have also shown that the assumption of Ortin and Planes (1988) are unjustified. More recently, (Wollants et al., 1993) also remarked that the "null entropy production" is "contradiction in terminis".

The equilibrium values of stress \mathbf{T} and temperature T or thermodynamics pressure P and temperature T are described by the Clausius-Clapeyron equation. The Clausius-Clapeyron relationship of stress and temperature has attracted a lot of attentions from the experimentalists (Kato et al. 2002, Liu et al. 2004, Chernenko et al. 2003, 2004, Karaca et al. 2004). They have found that the critical stress for martensitic transformation has a linear relationship with the martensitic start temperature or austenite finish temperature.

Several Clausius-Clapeyron-like equations have been derived (Otsuka et al. 1976; Wollants et al. 1979; 1983; 1991; Kato and Pak 1984; 1985). Otsuka et al. (1976, eq. 4.1) begin with an assumed form for the Clausius-Clapeyron equation in terms of the critical stress for inducing a martensitic transformation, the associated strain, temperature and heat of transformation. Wollants (1979; 1983; 1991) begin their discussions assuming an equation of state for the Gibbs free energy of a macroscopic phase that has undergone a one-dimensional strain. Kato and Pak use a non-standard definition of Gibbs free energy (1984, eq. 26; 1985, eq. 6). They study a system with only one phase rather than two phases in equilibrium (Kato and Pak, 1984, eq. 36). The Clausius-Clapeyron equation refers to two phases in equilibrium.

In Chapter V, we derive a generalized Clausius-Clapeyron equation for multicomponent fluids, amorphous solids, and crystalline solids at equilibrium state. At the same time, we also derive the Clausius-Clapeyron equation for fluids and amorphous solids and Clausius-Clapeyron equation for crystalline solids with uniform compositions respectively.

Martensitic transformation usually is considered as a "diffusionless process", the composition in each phase is the same. A martensitic transformation is studied through the Clausius-Clapeyron equation for crystalline solids.

C. Interfacial constraints

When there are phase change or chemical reactions, the interfacial conditions on the interfaces of two different phases are crucial conditions to study the properties of the the two phases and their relationship. Fluid-fluid interfaces and fluid-amorphous solids interfaces have been studied a lot in the classic thermodynamics (Denbigh, 1963) through the studying of the phase change. And also, they are quite simpler compare with the crystalline-crystalline solids interface because the elastic portion of stress in fluids and amorphous solids does not exist. The interfacial constraints of the crystalline-crystalline interfaces have attracted a lot of attentions recently.

Recently, people defined two different forms of solid state phase interface, coherent interface and incoherent interface.

Johnson and Muller (1991) found that the equilibrium characteristics of elastically stressed two-phase coherent solids are fundamentally different from those of the incoherent system. The difference is thought to be the result of the long-range elastic interaction between phases which renders the state of deformation.

The characteristics of the coherent equilibrium have been studied intensively in the recent decades.

Larche and Cahn (1973; 1978) defined that coherency of the solids is subjected to what is called as the network constraints, which requires that only one reference configuration exist to which each of the phases in the system may be referred; the displacement from a single crystal state to the current state is continuous across all interfaces. Larche and Cahn (1978)proposed that “. . . if the interface is coherent, the two phases, as far as lattices are concerned, appear as a single phase.” Apparently, they are considering the two different phases as one single phase, in other words, they are using the unique reference configuration for two different phase.

Johnson and Voorhees (1999) investigated the interfacial stress of the binary alloys. In the α - β phase transformation, he calculated the stress with a strain based on a unique reference configuration for the two different phases.

Bhattacharya (2003) and Bhattacharya et al. (1994) described the coherent interface as the crystalline-crystalline interface where the tangential vectors on the interface are continuous. They also consider the adjoining phases have the same reference configurations.

The choice of reference configuration is very important because the computation of the displacements, strains, and stresses are directly related to it. Oh et al. (2005) have a clear description about the reference configuration. They pointed out that stress is a functional of the history of the deformation gradient for simple materials; for a single phase, if different reference configurations are used, the functional has the same form, but there is a $\nabla\lambda$ to connect the new reference configuration and the old one, where λ is the map of the old reference configuration onto the new reference configuration (Truesdell, 1977). But for different phases, there is no map which can bridge the two different reference configurations. For example, metal and oxide have to have different reference configurations. This one confirms the point of views of Rajagopal and Srinivasa (1998). All these descriptions mean that for a interface between two different phases, we have to use two different reference configurations rather than an unique one.

In chapter V, we will examine a two-phase system at quasi-static or static state. An interfacial condition for the two different phases will be derived, which let us be able to see stress relationship based on different reference configurations for two different phases in the crystalline-crystalline solids interfaces. With the derived interfacial stress constraints, the stress and strain distributions of the oxidation of a beam, oxidation of a cylinder, and oxidation of a plate will be studied. An exper-

iment of measuring the solid-solid surface energies will be proposed. At the same time, a generalized Clausius-Clapeyron equation will be derived and compared with the experimental data of austenite-martensite transition.

CHAPTER II

THERMODYNAMICS OF MULTICOMPONENT, ELASTIC, CRYSTALLINE
SOLIDS: EFFECTS OF ELECTRIC AND MAGNETIC FIELDS

A. Introduction

Slattery and Lagoudas (2005) have presented a review of the literature as well as a development of the thermodynamics of elastic crystalline solids emphasizing the consequences of equilibrium. Perhaps their most important results were a new description of stress-deformation behavior for these crystals as well as an extension of the Gibbs phase rule.

In what follows, we wish to extend their work to include the effects of electric and magnetic fields.

B. Problem statement

Our objective in what follows is to develop the thermodynamics of elastic, crystalline solids, including the effects of electric and magnetic fields.

With this point of view, we will assume that for a solid the specific Helmholtz free energy

$$\hat{A} = \hat{A}(T, \rho, \omega_{(1)}, \dots, \omega_{(N-1)}, \mathbf{E}_{(1)}, \mathbf{E}_{(2)}, \mathbf{E}_{(3)}, \mathbf{e}_{(1)}, \mathbf{e}_{(2)}, \mathbf{e}_{(3)}, \mathbf{M}, \mathbf{P}) \quad (2.1)$$

Here T is the temperature, ρ the total mass density, $\omega_{(A)}$ is the mass fraction of species A , $\mathbf{E}_{(i)}$ ($i = 1, \dots, 3$) the lattice vectors in the reference or natural configuration of the solid (a stress-free, electric field-free, and magnetic field-free state),

$$\mathbf{e}_{(i)} \equiv \mathbf{F}\mathbf{E}_{(i)} \quad (2.2)$$

the deformed lattice vectors,

$$\mathbf{F} \equiv \text{grad } \mathbf{z} \quad (2.3)$$

the deformation gradient (the gradient operation grad is to be performed in the reference configuration), \mathbf{M} the magnetization of the material, and \mathbf{P} the electric polarization. In the reference state, $\mathbf{M} = \mathbf{M}_{(0)}$ and $\mathbf{P} = \mathbf{P}_{(0)}$.

From the implications of the principle of frame indifference (Truesdell and Noll, 1965, p. 44), \hat{A} is an isotropic scalar function of the vectors $\mathbf{e}_{(i)}$, \mathbf{P} and \mathbf{M} (Truesdell and Noll, 1965, p. 29). The most general form of such a function is one in which all possible scalar products of the various lattice vectors appear. Slattery and Lagoudas (2005) argued that, in the absence of electric and magnetic fields, the scalar product $\mathbf{E}_{(m)} \cdot \mathbf{e}_{(n)}$ should not appear, since it would lead to a non-symmetric stress tensor. In view of this reasoning, we will write

$$\begin{aligned} \hat{A} = \hat{A} & \left(T, \rho, \omega_{(1)}, \dots, \omega_{(N-1)}, \mathbf{e}_{(1)} \cdot \mathbf{e}_{(1)}, \mathbf{e}_{(1)} \cdot \mathbf{e}_{(2)}, \dots, \mathbf{e}_{(3)} \cdot \mathbf{e}_{(3)}, \mathbf{E}_{(1)} \cdot \mathbf{E}_{(1)}, \right. \\ & \mathbf{E}_{(1)} \cdot \mathbf{E}_{(2)}, \dots, \mathbf{E}_{(3)} \cdot \mathbf{E}_{(3)}, \mathbf{M} \cdot \mathbf{E}_{(1)}, \dots, \mathbf{M} \cdot \mathbf{E}_{(3)}, \mathbf{e}_{(1)} \cdot \mathbf{M}, \dots, \mathbf{e}_{(3)} \cdot \mathbf{M}, \\ & \left. \mathbf{P} \cdot \mathbf{E}_{(1)}, \dots, \mathbf{P} \cdot \mathbf{E}_{(3)}, \mathbf{e}_{(1)} \cdot \mathbf{P}, \dots, \mathbf{e}_{(3)} \cdot \mathbf{P}, \mathbf{M} \cdot \mathbf{M}, \mathbf{P} \cdot \mathbf{P}, \mathbf{M} \cdot \mathbf{P} \right) \end{aligned} \quad (2.4)$$

In applying this equation of state, it is important to recognize that two materials which differ only by a rotation, a translation, or a reflection are identical.

For present purposes, we will find it more convenient to abbreviate the representation of the scalar products appearing in (2.4). For example

$$\begin{aligned} I_{(mn)}^{(1)} & \equiv \mathbf{e}_{(m)} \cdot \mathbf{e}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\ & = \mathbf{F} \mathbf{E}_{(m)} \cdot \mathbf{F} \mathbf{E}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\ & = \mathbf{E}_{(m)} \cdot \mathbf{F}^T \mathbf{F} \mathbf{E}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\ & = \mathbf{E}_{(m)} \cdot (\mathbf{C} - \mathbf{I}) \mathbf{E}_{(n)} \quad m = 1, \dots, 3 \text{ and } n = 1, \dots, m \end{aligned} \quad (2.5)$$

where

$$\mathbf{C} \equiv \mathbf{F}^T \mathbf{F} \quad (2.6)$$

is the right Cauchy-Green strain tensor in phase j and $I_{(mn)}$ can be interpreted as the components of $\mathbf{C} - \mathbf{I}$ with respect to a set of basis vectors formed by the lattice vectors $\mathbf{E}_{(m)}$ ($m = 1, \dots, 3$). In view of (2.5) and (3.9),

$$\begin{aligned} \rho &= \frac{\rho_0}{\sqrt{\det \mathbf{C}}} \\ &= \rho_0 - \frac{\rho_0}{2} (I_{(11)} + I_{(22)} + I_{(33)}) + \dots \end{aligned} \quad (2.7)$$

In other words, ρ , $I_{(11)}$, $I_{(22)}$, and $I_{(33)}$ are not independent. Similarly, we will introduce

$$I_{(m)}^{(2)} \equiv \mathbf{e}_{(m)} \cdot \mathbf{M} - \mathbf{E}_{(m)} \cdot \mathbf{M} \quad (2.8)$$

$$I_{(m)}^{(3)} \equiv \mathbf{e}_{(m)} \cdot \mathbf{P} - \mathbf{E}_{(m)} \cdot \mathbf{P} \quad (2.9)$$

$$I^{(4)} \equiv \mathbf{M} \cdot \mathbf{M} - \mathbf{M}_{(0)} \cdot \mathbf{M}_{(0)} \quad (2.10)$$

$$I^{(5)} \equiv \mathbf{P} \cdot \mathbf{P} - \mathbf{P}_{(0)} \cdot \mathbf{P}_{(0)} \quad (2.11)$$

$$I^{(6)} \equiv \mathbf{M} \cdot \mathbf{P} - \mathbf{M}_{(0)} \cdot \mathbf{P}_{(0)} \quad (2.12)$$

This permits us to write (2.4) as^a

$$\begin{aligned} \hat{A} = \hat{A} \left(T, \rho, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}^{(1)}, \dots, I_{(32)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I_{(1)}^{(3)}, \dots, I_{(3)}^{(3)}, \right. \\ \left. I^{(4)}, I^{(5)}, I^{(6)} \right) \end{aligned} \quad (2.14)$$

^aAs an alternative to (2.4), one can consider

$$\begin{aligned} \hat{A} = \hat{A} \left(T, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}^{(1)}, \dots, I_{(33)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I_{(1)}^{(3)}, \dots, I_{(3)}^{(3)}, \right. \\ \left. I^{(4)}, I^{(5)}, I^{(6)} \right) \end{aligned} \quad (2.13)$$

$$\hat{A} = \hat{A} \left(T, \hat{V}, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}^{(1)}, \dots, I_{(32)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I_{(1)}^{(3)}, \dots, I_{(3)}^{(3)}, I^{(4)}, I^{(5)}, I^{(6)} \right) \quad (2.15)$$

$$\check{A} = \check{A} \left(T, \rho_{(1)}, \dots, \rho_{(N)}, I_{(11)}^{(1)}, \dots, I_{(32)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I_{(1)}^{(3)}, \dots, I_{(3)}^{(3)}, I^{(4)}, I^{(5)}, I^{(6)} \right) \quad (2.16)$$

in which \hat{V} is the volume per unit mass and $\rho_{(A)}$ is the mass density of species A .

It should always be kept in mind that the functional forms of (2.14) through (2.16) are different for each phase.

C. Euler, Gibbs, and Gibbs-Duhem equations

From the differential entropy inequality (Slattery, 1999, p. 438), we conclude

$$\hat{S} = - \left(\frac{\partial \hat{A}}{\partial T} \right)_{\rho, \omega_{(B)} (B=1, \dots, N-1), I_{(mn)}^{(1)}, \dots} \quad (2.17)$$

Extending the standard definition for the *thermodynamic pressure*

$$P \equiv - \left(\frac{\partial \hat{A}}{\partial \hat{V}} \right)_{T, \omega_{(B)} (B \neq N), I_{(mn)}^{(1)} (mn \neq 33), \dots} \quad (2.18)$$

and the *chemical potential for species A on a mass basis*, we have

$$\mu_{(A)} \equiv \left(\frac{\partial \check{A}}{\partial \rho_{(A)}} \right)_{T, \rho_{(B)} (B \neq A), I_{(mn)}^{(1)} (mn \neq 33), \dots} \quad (2.19)$$

We will also require

$$\mu_{(I^{(1)}, mn)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(mn)}^{(1)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(rs)}^{(1)} (rs \neq mn), I_{(m)}^{(2)}, I_{(m)}^{(3)}, \dots} \quad (2.20)$$

and

$$\mu_{(I^{(2)}, m)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(m)}^{(2)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(mn)}^{(1)}, I_{(r)}^{(2)} (r \neq m), I_{(m)}^{(3)}, \dots} \quad (2.21)$$

$$\mu_{(I^{(3)},m)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(m)}^{(3)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(rs)}, I_{(m)}^{(2)}, I_{(r)}^{(3)} (r \neq m), \dots} \quad (2.22)$$

$$\mu_{(I^{(4)})} \equiv \left(\frac{\partial \hat{A}}{\partial I^{(4)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), \dots, I_{(r)}^{(3)}, I^{(5)}, \dots} \quad (2.23)$$

$$\mu_{(I^{(5)})} \equiv \left(\frac{\partial \hat{A}}{\partial I^{(5)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), \dots, I^{(4)}, I^{(6)}} \quad (2.24)$$

$$\mu_{(I^{(6)})} \equiv \left(\frac{\partial \hat{A}}{\partial I^{(6)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), \dots, I^{(5)}} \quad (2.25)$$

With these expressions, the differentials of (2.15) and (2.16) may consequently be expressed as

$$\begin{aligned} d\hat{A} = & -P d\hat{V} - \hat{S} dT + \sum_{B=1}^{N-1} \left(\frac{\partial \hat{A}}{\partial \omega_{(B)}} \right)_{T, \hat{V}, \omega_{(C)} (C \neq B, N), I_{(i)}^{(1)}} d\omega_{(B)} \\ & + \sum_{m=1}^3 \left[\left(\sum_{n=1}^2 \mu_{(I^{(1)},mn)} dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2)},m)} dI_{(m)}^{(2)} + \mu_{(I^{(3)},m)} dI_{(m)}^{(3)} \right] \\ & + \mu_{(I^{(4)})} dI^{(4)} + \mu_{(I^{(5)})} dI^{(5)} + \mu_{(I^{(6)})} d(I^{(6)}) \end{aligned} \quad (2.26)$$

$$\begin{aligned} d\check{A} = & -\frac{\hat{S}}{\hat{V}} dT + \sum_{B=1}^N \mu_{(B)} d\rho_{(B)} \\ & + \frac{1}{\hat{V}} \left\{ \sum_{m=1}^3 \left[\left(\sum_{n=1}^2 \mu_{(I^{(1)},mn)} dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2)},m)} dI_{(m)}^{(2)} + \mu_{(I^{(3)},m)} dI_{(m)}^{(3)} \right] \right. \\ & \left. + \mu_{(I^{(4)})} dI^{(4)} + \mu_{(I^{(5)})} dI^{(5)} + \mu_{(I^{(6)})} d(I^{(6)}) \right\} \end{aligned} \quad (2.27)$$

Equation (2.27) may be rearranged to read

$$\begin{aligned}
d\left(\frac{\hat{A}}{\hat{V}}\right) &= -\frac{\hat{S}}{\hat{V}}dT + \sum_{B=1}^N \mu_{(B)}d\left(\frac{\omega_{(B)}}{\hat{V}}\right) \\
&\quad + \frac{1}{\hat{V}} \left\{ \sum_{m=1}^3 \left[\left(\sum_{n=1}^2 \mu_{(I^{(1),mn})}dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2),m})}dI_{(m)}^{(2)} + \mu_{(I^{(3),m})}dI_{(m)}^{(3)} \right] \right. \\
&\quad \left. + \mu_{(I^{(4)})}dI^{(4)} + \mu_{(I^{(5)})}dI^{(5)} + \mu_{(I^{(6)})}d(I^{(6)}) \right\} \\
d\hat{A} &= \left(\frac{\hat{A}}{\hat{V}} - \sum_{B=1}^N \mu_{(B)}\rho_{(B)} \right) d\hat{V} - \hat{S}dT + \sum_{B=1}^{N-1} (\mu_{(B)} - \mu_{(N)}) d\omega_{(B)} \\
&\quad + \sum_{m=1}^3 \left[\left(\sum_{n=1}^2 \mu_{(I^{(1),mn})}dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2),m})}dI_{(m)}^{(2)} + \mu_{(I^{(3),m})}dI_{(m)}^{(3)} \right] \\
&\quad + \mu_{(I^{(4)})}dI^{(4)} + \mu_{(I^{(5)})}dI^{(5)} + \mu_{(I^{(6)})}d(I^{(6)})
\end{aligned} \tag{2.28}$$

Comparison of the coefficients in (2.26) and (2.28) gives

$$\left(\frac{\partial \hat{A}}{\partial \omega_{(B)}} \right)_{T, \rho, \omega_{(C)} (C \neq B, N), I_{(mn)}, \dots} = \mu_{(B)} - \mu_{(N)} \tag{2.29}$$

as well as Euler's equation

$$\hat{A} = -P\hat{V} + \sum_{B=1}^N \mu_{(B)}\omega_{(B)} \tag{2.30}$$

Equations (2.26) and (2.29) yield the *modified Gibbs equation*

$$\begin{aligned}
d\hat{A} &= -P d\hat{V} - \hat{S}dT + \sum_{B=1}^{N-1} (\mu_{(B)} - \mu_{(N)}) d\omega_{(B)} \\
&\quad + \sum_{m=1}^3 \left[\left(\sum_{n=1}^2 \mu_{(I^{(1),mn})}dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2),m})}dI_{(m)}^{(2)} + \mu_{(I^{(3),m})}dI_{(m)}^{(3)} \right] \\
&\quad + \mu_{(I^{(4)})}dI^{(4)} + \mu_{(I^{(5)})}dI^{(5)} + \mu_{(I^{(6)})}d(I^{(6)})
\end{aligned} \tag{2.31}$$

The *modified Gibbs-Duhem equation* follow immediately by subtracting (2.31)

from the differential of (2.30):

$$\begin{aligned} \hat{S} dT - \hat{V} dP + \sum_{B=1}^N \omega_{(B)} d\mu_{(B)} - \sum_{m=1}^3 \left[\left(\sum_{n=1}^2 \mu_{(I^{(1),mn})} dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2),m})} dI_{(m)}^{(2)} \right. \\ \left. + \mu_{(I^{(3),m})} dI_{(m)}^{(3)} \right] - (\mu_{(I^{(4)})} dI^{(4)} + \mu_{(I^{(5)})} dI^{(5)} + \mu_{(I^{(6)})} dI^{(6)}) = 0 \quad (2.32) \end{aligned}$$

We would like to emphasize that the modified Euler's equation, the modified Gibbs equation, and the modified Gibbs-Duhem equation all apply to dynamic processes, so long as the underlying statements about behavior are applicable to the materials being considered.

D. Equilibrium: constraints on isolated systems

We define *equilibrium* to be achieved by an isolated body, when the entropy inequality becomes an equality. In the following sections, we wish to develop necessary and sufficient criteria for the achievement of equilibrium in a multiphase, multicomponent body that at some time $t = 0$ becomes isolated. We will assume that, the once the body is isolated, it is capable of undergoing a number of simultaneous chemical reactions and that it is totally enclosed by an impermeable, stationary boundary at which the energy flux and charge flux (current) are both zero. Each species is acted upon by what may be a different external or mutual force, although these forces are assumed to be independent of time once the body is isolated. We restrict the analysis somewhat by requiring each of these external or mutual forces to be representable by a potential. These boundary conditions on the system and constraints on the external forces are consistent with commonly observed experiments, in particular the experiments discussed in Sec. F.

In this paper, we will not discuss intrinsically stable equilibrium and metastable equilibrium. These questions have been discussed elsewhere for a simpler case Slattery

(1990).

Let us begin by examining the constraints imposed upon an isolated, multiphase, multicomponent body by the mass balances for the individual species, by the momentum balance, by the energy balance, and by the entropy inequality. For simplicity, we will neglect all interfacial effects other than surface (heterogeneous) reactions; the more general case can be constructed by extending the discussion of Slattery (1990).

1. Species mass balance

The mass balance for each species requires that the time rate of change of the mass of each component A be equal to the rate at which the mass of that component is produced by chemical reactions (Slattery, 1990, p. 679):

$$\frac{d}{dt} \int_R \rho \omega_{(A)} dV = \int_R \sum_{j=1}^J r_{(A,j)} dV + \int_{\Sigma} \sum_{k=1}^K r_{(A,k)}^{(\sigma)} dA \quad (2.33)$$

Here R denotes the region occupied by the body, Σ represents its internal phase interface, $r_{(A,j)}$ is the rate per unit volume at which mass of species A is produced by homogeneous chemical reaction j ($= 1, 2, \dots, J$); $r_{(A,k)}^{(\sigma)}$ is the rate per unit area at which mass of species A is produced by heterogeneous chemical reaction k ($= 1, 2, \dots, K$). After an application of the transport theorem (Slattery, 1999, p. 433) as well as Green's transformation recognizing that all velocities are zero on the boundary

of the system, we have

$$\begin{aligned}
& \int_R \left\{ \rho \frac{d_{(v)}\omega_{(A)}}{dt} + \operatorname{div} [\rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v})] - \sum_{j=1}^J r_{(A,j)} \right\} dV \\
& \quad + \int_{\Sigma} \left(- \sum_{k=1}^K r_{(A,k)}^{(\sigma)} + [\rho\omega_{(A)} (\mathbf{v}_{(A)} - \mathbf{u}) \cdot \boldsymbol{\xi}] \right) dA \\
& = \int_R \left\{ \rho \frac{d_{(v)}\omega_{(A)}}{dt} - \sum_{j=1}^J r_{(A,j)} \right\} dV + \int_{\Sigma} \left(- \sum_{k=1}^K r_{(A,k)}^{(\sigma)} + [\rho\omega_{(A)} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi}] \right) dA \\
& = 0 \tag{2.34}
\end{aligned}$$

Let us introduce the j th homogeneous reaction coordinate $\psi_{(j)}$ by defining for all $A = 1, \dots, N$:

$$\frac{\partial\psi_{(j)}}{\partial t} \equiv \frac{r_{(A,j)}}{M_{(A)}\nu_{(A,j)}} \tag{2.35}$$

The right side of this equation represents a normalized rate of production of moles of species A by the homogeneous chemical reaction j ; $M_{(A)}$ is the molecular weight of species A and $\nu_{(A,j)}$ is the stoichiometric coefficient for species A in chemical reaction j . The stoichiometric coefficient is taken to be a negative number for a reactant, positive for a product. Overall mass conservation requires that for each homogeneous reaction

$$\sum_{A=1}^N r_{(A,j)} = \frac{\partial\psi_{(j)}}{\partial t} \sum_{A=1}^N M_{(A)}\nu_{(A,j)} = 0 \tag{2.36}$$

Our assumption is that

$$\frac{\partial\psi_{(j)}}{\partial t} \neq 0 \tag{2.37}$$

which implies ($j = 1, 2, \dots, J$)

$$\sum_{A=1}^N M_{(A)}\nu_{(A,j)} = 0 \tag{2.38}$$

In much the same manner, we can introduce the k th heterogeneous reaction

coordinate $\psi_{(k)}^{(\sigma)}$ by defining for all $A = 1, 2, \dots, N$ (Slattery, 1999, p. 830)

$$\frac{\partial \psi_{(k)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \psi_{(k)}^{(\sigma)} \cdot \mathbf{u} \equiv \frac{r_{(A,k)}^{(\sigma)}}{M_{(A)} \nu_{(A,k)}^{(\sigma)}} \quad (2.39)$$

Here $\psi_{(k)}^{(\sigma)}$ is a function of time t and two surface coordinates on the moving and deforming interface (Slattery, 1999, p. 1065); $\nabla_{(\sigma)}$ denotes the surface gradient operation (Slattery, 1999, p. 1075); \mathbf{u} is the time rate of position following a surface point (Slattery, 1999, p. 24). On the right side of this equation, we have a normalized rate of production of moles of species A by the heterogeneous chemical reaction k at a point fixed on the surface in such a way that its only motion is normal to the interface; $\nu_{(A,k)}^{(\sigma)}$ is the stoichiometric coefficient for species A in the heterogeneous reaction k . Overall mass conservation requires that for each heterogeneous reaction

$$\sum_{A=1}^N r_{(A,k)}^{(\sigma)} = \left(\frac{\partial \psi_{(k)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \psi_{(k)}^{(\sigma)} \cdot \mathbf{u} \right) \sum_{A=1}^N M_{(A)} \nu_{(A,k)}^{(\sigma)} = 0 \quad (2.40)$$

Again our assumption is that

$$\frac{\partial \psi_{(k)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \psi_{(k)}^{(\sigma)} \cdot \mathbf{u} \neq \mathbf{0} \quad (2.41)$$

which means that $k = 1, 2, \dots, K$)

$$\sum_{A=1}^N M_{(A)} \nu_{(A,k)}^{(\sigma)} = 0 \quad (2.42)$$

In view of (2.35) and (2.39), we may express (2.34) as

$$\begin{aligned}
Z_{(A)} &\equiv \int_R \left[\rho \frac{d_{(v)}\omega_{(A)}}{dt} - \frac{\partial}{\partial t} \left(\sum_{j=1}^J M_{(A)} \nu_{(A,j)} \psi_{(j)} \right) \right] dV \\
&\quad + \int_{\Sigma} \left\{ -\frac{\partial}{\partial t} \sum_{j=1}^J M_{(A)} \nu_{(A,j)}^{(\sigma)} \psi_{(j)}^{(\sigma)} + \nabla_{(\sigma)} \left(\sum_{j=1}^J M_{(A)} \nu_{(A,j)}^{(\sigma)} \psi_{(j)}^{(\sigma)} \right) \cdot \mathbf{u} \right. \\
&\quad \left. + [\rho \omega_{(A)} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi}] \right\} dA \\
&= 0
\end{aligned} \tag{2.43}$$

2. Momentum balance

The momentum balance requires (Slattery, 1990, p. 709):

$$\frac{d}{dt} \int_R \rho \mathbf{v} dV = \int_S \mathbf{T} \mathbf{n} dA + \int_R \rho \mathbf{f} dV \tag{2.44}$$

(Because there is no mass transfer at the boundary, we do not distinguish between the region occupied by a body of species A and the region occupied by the multicomponent body, the material particles of which move with the mass-averaged velocity \mathbf{v} .) Applications of the transport theorem (Slattery, 1999, p. 433) and of Green's theorem yields

$$\begin{aligned}
\mathbf{Z}_m &\equiv \int_R \left[\rho \frac{d_{(v)}\mathbf{v}}{dt} - \operatorname{div} \mathbf{T} - \rho \mathbf{f} \right] dV + \int_{\Sigma} [\rho \mathbf{v} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} - \mathbf{T} \boldsymbol{\xi}] dA \\
&= 0
\end{aligned} \tag{2.45}$$

3. Moment-of-momentum balance

In order to allow for a non-symmetric stress tensor, we must consider the moment-of-momentum balance:

$$\frac{d}{dt} \int_R \rho (\mathbf{p} \times \mathbf{v}) dV = \int_S \mathbf{p} \times \mathbf{T} \mathbf{n} dA + \int_R (\mathbf{L} + \rho \mathbf{p} \times \mathbf{f}) dV \tag{2.46}$$

where \mathbf{p} is the position vector and \mathbf{L} is a source of moment-of-momentum per unit volume. This reduces to (Slattery, 1999, p. 36)

$$\begin{aligned} \mathbf{Z}_{mom} \equiv & \int_R \left[\mathbf{p} \times \left(\rho \frac{d_{(v)}\mathbf{v}}{dt} - \text{div } \mathbf{T} - \rho \mathbf{f} \right) - e_{ijk} T_{kj} e_i - \mathbf{L} \right] dV \\ & + \int_{\Sigma} \left[\mathbf{p} \times (\rho \mathbf{v} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} - \mathbf{T} \boldsymbol{\xi}) \right] dA \end{aligned} \quad (2.47)$$

If $\mathbf{L} = \mathbf{0}$ as is commonly assumed in the absence of magnetic and electric fields, \mathbf{T} is symmetric. One objective in what follows will be to determine \mathbf{L} at equilibrium.

4. Energy balance

For this isolated body totally enclosed by an adiabatic boundary, the energy balance (Slattery, 1990, p. 716) states that

$$\begin{aligned} & \frac{d}{dt} \int_R \rho \left(\hat{U} + \frac{1}{2} v^2 \right) dV \\ & = \int_S \mathbf{v} \cdot \mathbf{T} \mathbf{n} dA + \int_R \sum_{A=1}^N \rho_{(A)} (\mathbf{v}_{(A)} \cdot \mathbf{f}_{(A)}) dV \\ & = \int_S \mathbf{v} \cdot \mathbf{T} \mathbf{n} dA + \int_R \left[\sum_{A=1}^N \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}_{(A)} - \rho \mathbf{v} \cdot \mathbf{f} \right] dV \end{aligned} \quad (2.48)$$

We also neglect the possibility of mutual radiant energy transmission.

The first term on the right of (2.48) can be rearranged using Green's transformation as

$$\int_S \mathbf{v} \cdot \mathbf{T} \mathbf{n} dA = \int_R \left\{ \mathbf{v} \cdot \text{div } \mathbf{T} + \text{tr} [\mathbf{T} (\nabla \mathbf{v})^T] \right\} dV + \int_{\Sigma} [\mathbf{v} \cdot \mathbf{T} \boldsymbol{\xi}] dA \quad (2.49)$$

The body force $\mathbf{f}_{(A)}$ is a sum of two contributions, an external (or mutual) body force $\mathbf{f}_{(A)}^{ext}$ that can be represented in terms of a potential and an electro-magnetic body

force \mathbf{f}^{mag} that is the same for all species:

$$\begin{aligned}\mathbf{f}_{(A)} &= \mathbf{f}_{(A)}^{ext} + \mathbf{f}^{mag} \\ &= -\nabla\phi_{(A)}^{ext} + \mathbf{f}^{mag}\end{aligned}\quad (2.50)$$

If we assume that this potential is only a function of position and not a function of time, we may write

$$\begin{aligned}\rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}_{(A)}^{ext} &= -\operatorname{div}[\rho_{(A)}\phi_{(A)}(\mathbf{v}_{(A)} - \mathbf{v})] + \phi_{(A)}\operatorname{div}[\rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v})] \\ &= -\operatorname{div}[\rho_{(A)}\phi_{(A)}(\mathbf{v}_{(A)} - \mathbf{v})] \\ &\quad + \phi_{(A)}\left[-\rho\frac{d_{(v)}\omega_{(A)}}{dt} + \sum_{j=1}^J r_{(A,j)}\right]\end{aligned}\quad (2.51)$$

From (2.35) we see that

$$\sum_{j=1}^J r_{(A,j)} = \sum_{j=1}^J \frac{\partial}{\partial t}(M_{(A)}\nu_{(A,j)}\psi_{(j)})\quad (2.52)$$

This allows us to express (2.51) as

$$\begin{aligned}\rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}_{(A)}^{ext} &= -\operatorname{div}[\rho_{(A)}\phi_{(A)}(\mathbf{v}_{(A)} - \mathbf{v})] \\ &\quad + \sum_{j=1}^J \frac{\partial}{\partial t}(\phi_{(A)}M_{(A)}\nu_{(A,j)}\psi_{(j)}) - \rho\phi_{(A)}\frac{d_{(v)}\omega_{(A)}}{dt}\end{aligned}\quad (2.53)$$

This together with Green's transformation permit us to arrange the second term on the right of (2.48) as

$$\begin{aligned}&\int_R \sum_{A=1}^N \rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}_{(A)} dV \\ &= \int_R \sum_{A=1}^N \left[\sum_{j=1}^J \frac{\partial}{\partial t}(\phi_{(A)}M_{(A)}\nu_{(A,j)}\psi_{(j)}) - \rho\phi_{(A)}\frac{d_{(v)}\omega_{(A)}}{dt} + \rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}_{(A)}^{mag} \right] dV \\ &\quad + \int_{\Sigma} \sum_{A=1}^N \phi_{(A)}[\rho_{(A)}(\mathbf{v}_{(A)} - \mathbf{v}) \cdot \boldsymbol{\xi}] dA\end{aligned}\quad (2.54)$$

An application of the transport theorem (Slattery, 1999, p. 433) allows us to express the left side of (2.48) as

$$\begin{aligned} & \frac{d}{dt} \int_R \rho \left(\hat{U} + \frac{1}{2} v^2 \right) dV \\ &= \int_R \rho \frac{d_{(v)}}{dt} \left(\hat{U} + \frac{1}{2} v^2 \right) dV + \int_{\Sigma} \left[\rho \left(\hat{U} + \frac{1}{2} v^2 \right) (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} \right] dA \end{aligned} \quad (2.55)$$

In view of (2.49), (2.54), and (2.55), equation (2.48) takes the form

$$\begin{aligned} & \int_R \left\{ \rho \frac{d_{(v)}}{dt} \left(\hat{U} + \frac{1}{2} v^2 \right) + \sum_{A=1}^N \left[\left(\frac{\partial}{\partial t} \sum_{j=1}^J -\phi_{(A)} M_{(A)} \nu_{(A,j)} \psi_{(j)} - \rho \phi_{(A)} \frac{d_{(v)} \omega_{(A)}}{dt} \right) \right. \right. \\ & \quad \left. \left. + (\rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}^{mag}) \right] - \mathbf{v} \cdot (\operatorname{div} \mathbf{T} + \rho \mathbf{f}) - \operatorname{tr} [\mathbf{T} (\nabla \mathbf{v})^{\mathbf{T}}] \right\} dV \\ & + \int_{\Sigma} \left[\rho \left(\hat{U} + \frac{1}{2} v^2 \right) (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} \right] dA \\ &= \int_{\Sigma} \left\{ \sum_{A=1}^N \phi_{(A)} \left[\rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \boldsymbol{\xi} \right] + [\mathbf{v} \cdot \mathbf{T} \boldsymbol{\xi}] \right\} dA \end{aligned} \quad (2.56)$$

This can be expressed more conveniently for our purposes as

$$\begin{aligned} Z_e &\equiv \int_R \left\{ \rho \frac{d_{(v)} \hat{E}}{dt} - \sum_{A=1}^N \left[\left(\frac{\partial}{\partial t} \sum_{j=1}^J (\phi_{(A)} M_{(A)} \nu_{(A,j)} \psi_{(j)}) - \rho \phi_{(A)} \frac{d_{(v)} \omega_{(A)}}{dt} \right) \right. \right. \\ & \quad \left. \left. + (\rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}^{mag}) \right] - \mathbf{v} \cdot (\operatorname{div} \mathbf{T} + \mathbf{f}) - \operatorname{tr} [\mathbf{T} (\nabla \mathbf{v})^{\mathbf{T}}] \right\} dV \\ & + \int_{\Sigma} \left\{ [\rho \hat{E} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} - \sum_{A=1}^N \phi_{(A)} \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \boldsymbol{\xi} - \mathbf{v} \cdot \mathbf{T} \boldsymbol{\xi}] \right\} dA \\ &= 0 \end{aligned} \quad (2.57)$$

Here we have introduced the total energy per unit mass associated with each phase

$$\hat{E} \equiv \hat{U} + \frac{1}{2} v^2 \quad (2.58)$$

Neglecting the inertia term, because it is small.

$$\hat{E} = \hat{U} \quad (2.59)$$

5. Conservation of magnetic flux

Conservation of magnetic flux requires for a body (bounded by a closed surface S) (Hutter and vandeVen, 1978, p. 12).

$$\frac{d}{dt} \int_S \mathbf{B} \cdot \mathbf{n} \, dA = 0 \quad (2.60)$$

or

$$\begin{aligned} \int_S \mathbf{B} \cdot \mathbf{n} \, dA &= \text{a constant} \\ &= C \end{aligned} \quad (2.61)$$

Traditionally, we write

$$\int_S \mathbf{B} \cdot \mathbf{n} \, dA = 0 \quad (2.62)$$

(perhaps recognizing by analogy with the conservation of electric charge below that there is no "free magnetic charge" associated with the body). By the divergence theorem,

$$Z_{mag} \equiv \int_R \operatorname{div} \mathbf{B} \, dV + \int_{\Sigma} [\mathbf{B} \cdot \boldsymbol{\xi}] \, dA = 0 \quad (2.63)$$

6. Conservation of charge

Let Q be the charge density. For an isolated body, conservation of charge requires (Hutter and vandeVen, 1978, p. 12)

$$\frac{d}{dt} \int_R \rho Q \, dV = 0 \quad (2.64)$$

or

$$\begin{aligned} \int_R \rho Q \, dV &= C \\ &= \text{a constant} \end{aligned} \quad (2.65)$$

By analogy with the magnetic flux density \mathbf{B} above, we will introduce the dielectric displacement \mathbf{D} :

$$\int_S \mathbf{D} \cdot \mathbf{n} dA = C \quad (2.66)$$

For an isolated body with no free charge,

$$\int_S \mathbf{D} \cdot \mathbf{n} dA = 0 \quad (2.67)$$

Applying the divergence theorem, we find

$$Z_c \equiv \int_R \operatorname{div} \mathbf{D} dV + \int_\Sigma [\mathbf{D} \cdot \boldsymbol{\xi}] dA = 0 \quad (2.68)$$

7. Entropy inequality

For the isolated body under consideration here, the entropy inequality (Truesdell and Toupin 1960, p. 644; Truesdell 1969, p. 35; Slattery 1990, p. 838) says that the time rate of change of the body's entropy must be greater than or equal to zero:

$$\frac{d}{dt} \int_R \rho \hat{S} dV \geq 0 \quad (2.69)$$

Equilibrium is achieved, when this inequality becomes an equality. As equilibrium is approached, (2.69) tells us that the entropy of this isolated body is maximized and

$$\frac{d^2}{dt^2} \int_R \rho \hat{S} dV \leq 0 \quad (2.70)$$

The implications of (2.70) and therefore the requirements for a stable equilibrium have been explored elsewhere [Slattery (1972, 1981, 1990), Edelen 1975]. To the lowest order of perturbations to the system, no new results are developed here, and for this reason they will not be repeated. Applying the transport theorem (Slattery,

1999, p. 433), we find that this may also be written as

$$\int_R \rho \frac{d_{(v)} \hat{S}}{dt} dV + \int_{\Sigma} [\rho \hat{S} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi}] dA \geq 0 \quad (2.71)$$

From (2.69), we define *equilibrium* to be attained, when

$$\int_R \rho \hat{S} dV$$

is maximized, the left side of (2.69) is minimized, and the inequalities in (2.69) and (2.71) become equalities.

E. Implications of equilibrium

Referring to the beginning of the prior section, we continue to restrict our attention to a multiphase, multicomponent body capable of undergoing a number of simultaneous chemical reactions and totally enclosed by an impermeable, adiabatic boundary. As explained above, if equilibrium is to be achieved, the left side of (2.69) must approach zero within the constraints imposed by conservation of mass for each species, by the momentum balance, by the moment of momentum balance, by the energy balance, by the conservation of magnetic flux, and by the conservation of electric charge as developed in the prior section. Since $Z_{(A)}$, \mathbf{Z}_m , \mathbf{Z}_{mom} , Z_e , Z_{mag} , and Z_c are all zero by (2.43), (2.45), (2.47), (2.57), (2.63), and (2.68), there is no loss in generality in writing (2.71) as (Slattery 1981, p. 490; Slattery 1990, p. 839)

$$\begin{aligned} \int_R \rho \frac{d_{(v)} \hat{S}}{dt} dV + \int_{\Sigma} [\rho \hat{S} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi}] dA + \sum_{A=1}^N \lambda_{(A)} Z_{(A)} \\ + \boldsymbol{\lambda}_m \cdot \mathbf{Z}_m + \boldsymbol{\lambda}_{mom} \cdot \mathbf{Z}_{mom} + \lambda_e Z_e + \lambda_{mag} Z_{mag} + \lambda_c Z_c \geq 0 \end{aligned} \quad (2.72)$$

where $\lambda_{(A)}$, λ_e , λ_{mag} , and λ_c are constants or Lagrangian multipliers; $\boldsymbol{\lambda}_m$ and

$\boldsymbol{\lambda}_{mom}$ are constant spatial vectors, the components of which are Lagrangian multipliers. In examining this result, we will require several relationships. From (2.26) and the definition of \hat{A} (Slattery, 1999, p. 446), we have

$$\begin{aligned}
\frac{d_{(v)}\hat{S}}{dt} &= \frac{1}{T} \frac{d_{(v)}U}{dt} + \frac{P}{T} \frac{d_{(v)}\hat{V}}{dt} - \frac{1}{T} \left[\sum_{A=1}^{N-1} (\mu_{(A)} - \mu_{(N)}) \frac{d_{(v)}\omega_{(A)}}{dt} + \mu_{(I^{(4)})} \frac{d_{(v)}I^{(4)}}{dt} \right. \\
&\quad \left. + \mu_{(I^{(5)})} \frac{d_{(v)}I^{(5)}}{dt} + \mu_{(I^{(6)})} \frac{d_{(v)}I^{(6)}}{dt} \right] \\
&\quad - \frac{1}{T} \sum_{m=1}^3 \left[\sum_{n=1}^2 \left(\mu_{(I^{(mn)})} \frac{d_{(v)}I_{(mn)}}{dt} \right) + \mu_{(I^{(2),m})} \frac{d_{(v)}I_{(m)}^{(2)}}{dt} + \mu_{(I^{(3),m})} \frac{d_{(v)}I_{(m)}^{(3)}}{dt} \right] \\
&= \frac{1}{T} \frac{d_{(v)}U}{dt} + \frac{P}{T\rho} \operatorname{div} \mathbf{v} - \frac{1}{T} \left[\sum_{A=1}^{N-1} (\mu_{(A)} - \mu_{(N)}) \frac{d_{(v)}\omega_{(A)}}{dt} + \mu_{(I^{(4)})} \frac{d_{(v)}I^{(4)}}{dt} \right. \\
&\quad \left. + \mu_{(I^{(5)})} \frac{d_{(v)}I^{(5)}}{dt} + \mu_{(I^{(6)})} \frac{d_{(v)}I^{(6)}}{dt} \right] \\
&\quad - \frac{1}{T} \sum_{m=1}^3 \left[\sum_{n=1}^2 \left(\mu_{(I^{(1),mn})} \frac{d_{(v)}I_{(mn)}^{(1)}}{dt} \right) + \mu_{(I^{(2),m})} \frac{d_{(v)}I_{(m)}^{(2)}}{dt} + \mu_{(I^{(3),m})} \frac{d_{(v)}I_{(m)}^{(3)}}{dt} \right]
\end{aligned} \tag{2.73}$$

where we have used the overall differential mass balance (Slattery, 1999, p. 432)

$$\rho \frac{d_{(v)}\hat{V}}{dt} = \operatorname{div} \mathbf{v} \tag{2.74}$$

in this last line. We will also require from (2.30), we see that

$$\hat{S} = \frac{1}{T} \left(\hat{U} + \frac{P}{\rho} - \sum_{A=1}^N \mu_{(A)} \omega_{(A)} \right) \tag{2.75}$$

as well as from (2.5)

$$\begin{aligned}
\frac{d_{(v)}I_{(mn)}^{(1)}}{dt} &= \nabla \mathbf{v} \mathbf{e}_{(m)} \cdot \mathbf{e}_{(n)} + \mathbf{e}_{(m)} \cdot \nabla \mathbf{v} \mathbf{e}_{(n)} \\
&= \operatorname{tr} [(\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) \nabla \mathbf{v}] \\
&= \operatorname{tr} [(\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) (\nabla \mathbf{v})^T]
\end{aligned} \tag{2.76}$$

and from (2.8) through (2.12)

$$\begin{aligned}
\frac{d_{(v)}I_{(m)}^{(2)}}{dt} &= \nabla \mathbf{v} \mathbf{e}_{(m)} \cdot \mathbf{M} + (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \cdot \frac{d_{(v)}\mathbf{M}}{dt} \\
&= \text{tr} \left[(\mathbf{e}_{(m)} \otimes \mathbf{M}) \nabla \mathbf{v} + (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)}\mathbf{M}}{dt} \right] \\
&= \text{tr} \left[(\mathbf{M} \otimes \mathbf{e}_{(m)}) (\nabla \mathbf{v})^T + (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)}\mathbf{M}}{dt} \right] \tag{2.77}
\end{aligned}$$

$$\begin{aligned}
\frac{d_{(v)}I_{(m)}^{(3)}}{dt} &= \nabla \mathbf{v} \mathbf{e}_{(m)} \cdot \mathbf{P} + (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \cdot \frac{d_{(v)}\mathbf{P}}{dt} \\
&= \text{tr} \left[(\mathbf{e}_{(m)} \otimes \mathbf{P}) \nabla \mathbf{v} + (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)}\mathbf{P}}{dt} \right] \\
&= \text{tr} \left[(\mathbf{P} \otimes \mathbf{e}_{(m)}) (\nabla \mathbf{v})^T + (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)}\mathbf{P}}{dt} \right] \tag{2.78}
\end{aligned}$$

$$\begin{aligned}
\frac{d_{(v)}I^{(4)}}{dt} &= 2 \frac{d_{(v)}\mathbf{M}}{dt} \cdot \mathbf{M} \\
&= 2 \text{tr} \left(\frac{d_{(v)}\mathbf{M}}{dt} \otimes \mathbf{M} \right) \tag{2.79}
\end{aligned}$$

$$\begin{aligned}
\frac{d_{(v)}I^{(5)}}{dt} &= 2 \frac{d_{(v)}\mathbf{P}}{dt} \cdot \mathbf{P} \\
&= 2 \text{tr} \left(\frac{d_{(v)}\mathbf{P}}{dt} \otimes \mathbf{P} \right) \tag{2.80}
\end{aligned}$$

$$\begin{aligned}
\frac{d_{(v)}I^{(6)}}{dt} &= \frac{d_{(v)}\mathbf{M}}{dt} \cdot \mathbf{P} + \mathbf{M} \cdot \frac{d_{(v)}\mathbf{P}}{dt} \\
&= \text{tr} \left(\frac{d_{(v)}\mathbf{M}}{dt} \otimes \mathbf{P} + \mathbf{M} \otimes \frac{d_{(v)}\mathbf{P}}{dt} \right) \tag{2.81}
\end{aligned}$$

After rearranging (2.72) by means of (2.73), (2.75), and (2.76) through (2.81), we

have

$$\begin{aligned}
& \int_R \left\{ \rho \left(\frac{1}{T} + \lambda_e \right) \frac{d_{(v)} \hat{U}}{dt} + \sum_{A=1}^N \left[\rho \left(-\frac{\mu_{(A)}}{T} + \lambda_e \phi_{(A)} + \lambda_{(A)} \right) \frac{d_{(v)} \omega_{(A)}}{dt} \right. \right. \\
& \quad + \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}^{mag} \left. \right] + (\lambda_e \mathbf{v} + \boldsymbol{\lambda}_m) \cdot \left(\rho \frac{d_{(v)} \mathbf{v}}{dt} - \operatorname{div} \mathbf{T} - \rho \mathbf{f} \right) \\
& \quad - \sum_{A=1}^N \sum_{j=1}^J (\lambda_e \phi_{(A)} M_{(A)} \nu_{(A,j)} + \lambda_{(A)} M_{(A)} \nu_{(A,j)}) \frac{\partial \psi_{(j)}}{\partial t} + \frac{1}{T} \operatorname{tr} \{ [-T \lambda_e \mathbf{T} + P \mathbf{I} \\
& \quad - \rho \sum_{m=1}^3 \left\{ \sum_{n=1}^2 \mu_{(I^{(1),mn})} (\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) + \mu_{(I^{(2),m})} \mathbf{M} \otimes \mathbf{e}_{(m)} \right. \\
& \quad \left. + \mu_{(I^{(3),m})} \mathbf{P} \otimes \mathbf{e}_{(m)} \right\} (\nabla \mathbf{v})^T - \rho \left[\sum_{m=1}^3 \mu_{(I^{(2),m})} (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)} \mathbf{M}}{dt} \right. \\
& \quad \left. + \mu_{(I^{(3),m})} (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)} \mathbf{P}}{dt} \right] - 2 \mu_{(I^{(4)})} \left(\frac{d_{(v)} \mathbf{M}}{dt} \otimes \mathbf{M} \right) \\
& \quad \left. - 2 \mu_{(I^{(5)})} \left(\frac{d_{(v)} \mathbf{P}}{dt} \otimes \mathbf{P} \right) - \mu_{(I^{(6)})} \left(\frac{d_{(v)} \mathbf{M}}{dt} \otimes \mathbf{P} + \mathbf{M} \otimes \frac{d_{(v)} \mathbf{P}}{dt} \right) \right\} + \lambda_c \operatorname{div} \mathbf{D} \\
& \quad + \lambda_{mag} \operatorname{div} \mathbf{B} + \boldsymbol{\lambda}_{mom} \cdot \left(\mathbf{p} \times \left(\rho \frac{d_{(v)} \mathbf{v}}{dt} - \operatorname{div} \mathbf{T} - \rho \mathbf{f} \right) - e_{ijk} T_{kj} e_i - \mathbf{L} \right) \left. \right\} dV \\
& + \int_{\Sigma} \left\{ \left[\rho \left[\left(\frac{1}{T} + \lambda_e \right) \hat{U} + \frac{P}{T \rho} + \sum_{A=1}^N \left(-\frac{1}{T} \mu_{(A)} \omega_{(A)} + \lambda_e \omega_{(A)} \phi_{(A)} + \lambda_{(A)} \omega_{(A)} \right) \right. \right. \right. \\
& \quad \left. \left. - \frac{\lambda_e}{2} v^2 \right] (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} - \sum_{A=1}^N \lambda_e \phi_{(A)} \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{u}) \cdot \boldsymbol{\xi} \right. \\
& \quad \left. + (\lambda_e \mathbf{v} + \boldsymbol{\lambda}_m) \cdot [\rho \mathbf{v} (\mathbf{v} - \mathbf{u}) - \mathbf{T}] \boldsymbol{\xi} \right. \\
& \quad \left. + \lambda_{mom} (\mathbf{p} \times (\mathbf{v} (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} - \mathbf{T} \boldsymbol{\xi})) + [\lambda_c \mathbf{D} + \lambda_{mag} \mathbf{B}] \cdot \boldsymbol{\xi} \right] \\
& \quad \left. - \sum_{j=1}^J \sum_{A=1}^N \lambda_{(A)} M_{(A)} \nu_{(A,j)}^{(\sigma)} \left(\frac{\partial \psi_{(j)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \psi_{(j)}^{(\sigma)} \cdot \mathbf{u} \right) \right\} dA \geq 0 \quad (2.82)
\end{aligned}$$

or

$$\begin{aligned}
& \int_R \left\{ \rho \left(\frac{1}{T} + \lambda_e \right) \frac{d_{(v)} \hat{U}}{dt} + \sum_{A=1}^N \left[\rho \left(-\frac{\mu_{(A)}}{T} + \lambda_e \phi_{(A)} + \lambda_{(A)} \right) \frac{d_{(v)} \omega_{(A)}}{dt} \right. \right. \\
& \quad \left. \left. - \rho \mathbf{v} \cdot \mathbf{f}^{\text{mag}} \right] - \sum_{A=1}^N \sum_{j=1}^J \left(\lambda_e \phi_{(A)} M_{(A)} \nu_{(A,j)} + \lambda_{(A)} M_{(A)} \nu_{(A,j)} \right) \frac{\partial \psi_{(j)}}{\partial t} \right. \\
& \quad + \frac{1}{T} \text{tr} \left\{ \left[-T \lambda_e \mathbf{T} + P \mathbf{I} - \rho \sum_{m=1}^3 \left\{ \sum_{n=1}^2 \mu_{(I^{(1),mn})} (\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) \right. \right. \right. \\
& \quad \left. \left. + \mu_{(I^{(2),m})} \mathbf{M} \otimes \mathbf{e}_{(m)} + \mu_{(I^{(3),m})} \mathbf{P} \otimes \mathbf{e}_{(m)} \right\} \right] (\nabla \mathbf{v})^T \\
& \quad \left. - \rho \left[\sum_{m=1}^3 \mu_{(I^{(2),m})} (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)} \mathbf{M}}{dt} + \mu_{(I^{(3),m})} (\mathbf{e}_{(m)} - \mathbf{E}_{(m)}) \otimes \frac{d_{(v)} \mathbf{P}}{dt} \right] \right. \\
& \quad \left. - 2 \mu_{(I^{(4)})} \left(\frac{d_{(v)} \mathbf{M}}{dt} \otimes \mathbf{M} \right) - 2 \mu_{(I^{(5)})} \left(\frac{d_{(v)} \mathbf{P}}{dt} \otimes \mathbf{P} \right) \right. \\
& \quad \left. - \mu_{(I^{(6)})} \left(\frac{d_{(v)} \mathbf{M}}{dt} \otimes \mathbf{P} + \mathbf{M} \otimes \frac{d_{(v)} \mathbf{P}}{dt} \right) \right\} - \boldsymbol{\lambda}_{\text{mom}} \cdot (e_{ijk} T_{kj} e_i + \mathbf{L}) \left. \right\} dV \\
& + \int_{\Sigma} \left\{ \left[\rho \left[\left(\frac{1}{T} + \lambda_e \right) \hat{U} + \frac{P}{T \rho} + \sum_{A=1}^N \left(-\frac{1}{T} \mu_{(A)} \omega_{(A)} + \lambda_e \omega_{(A)} \phi_{(A)} + \lambda_{(A)} \omega_{(A)} \right) \right] \right. \right. \\
& \quad \left. \left. \times (\mathbf{v} - \mathbf{u}) \cdot \boldsymbol{\xi} \right] \right. \\
& \quad \left. - \sum_{j=1}^J \sum_{A=1}^N \left(\lambda_{(A)} M_{(A)} \nu_{(A,j)}^{(\sigma)} + \lambda_e \phi_{(A)} M_{(A)} \nu_{(A,k)}^{(\sigma)} \right) \left(\frac{\partial \psi_{(j)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \psi_{(j)}^{(\sigma)} \cdot \mathbf{u} \right) \right\} dA \geq 0
\end{aligned} \tag{2.83}$$

In arriving at this result, we have neglected kinetic energy with respect to internal energy, and we have recognized the differential momentum balance, the Maxwell equations, the jump mass balance for species A (Slattery, 1999, p. 427), the jump momentum balance, the jump moment-of-momentum balance, the jump conditions for conservation of magnetic flux and electric charges, the definition of the total mass density, the definition of the mass-averaged velocity, and (2.40).

A sufficient conditions that (2.83) be satisfied for *equilibrium* is that the system be static.

Necessary and sufficient conditions for (2.83) to be satisfied in the presence of small perturbations to the system are

$$\begin{aligned} T &= -\frac{1}{\lambda_e} \\ &= \text{a constant} \end{aligned} \quad (2.84)$$

$$\begin{aligned} \mu_{(A)} + \phi_{(A)} &= T\lambda_{(A)} \\ &= \text{a constant for each species } A = 1, 2, \dots, N \end{aligned} \quad (2.85)$$

$$\begin{aligned} \sum_{A=1}^N \left(-\frac{1}{T} \phi_{(A)} M_{(A)} \nu_{(A,j)} + \lambda_{(A)} M_{(A)} \nu_{(A,j)} \right) &= \sum_{A=1}^N \frac{\mu_{(A)} M_{(A)} \nu_{(A,j)}}{T} \\ &= 0 \end{aligned} \quad (2.86)$$

$$\begin{aligned} \sum_{A=1}^N \left(-\frac{1}{T} \phi_{(A)} M_{(A)} \nu_{(A,j)}^{(\sigma)} + \lambda_{(A)} M_{(A)} \nu_{(A,j)}^{(\sigma)} \right) &= \sum_{A=1}^N \frac{\mu_{(A)} M_{(A)} \nu_{(A,k)}^{(\sigma)}}{T} \\ &= 0 \end{aligned} \quad (2.87)$$

$$\begin{aligned} \mathbf{T} = -P\mathbf{I} + \rho \sum_{\mathbf{m}=1}^{\mathbf{3}} \left[\sum_{\mathbf{n}=1}^{\mathbf{2}} \mu_{(I^{(1)}, \mathbf{mn})} (\mathbf{e}_{(\mathbf{m})} \otimes \mathbf{e}_{(\mathbf{n})} + \mathbf{e}_{(\mathbf{n})} \otimes \mathbf{e}_{(\mathbf{m})}) \right. \\ \left. + \mu_{(I^{(2)}, m)} \mathbf{M} \otimes \mathbf{e}_{(m)} + \mu_{(I^{(3)}, m)} \mathbf{P} \otimes \mathbf{e}_{(m)} \right] \end{aligned} \quad (2.88)$$

$$\frac{d_{(v)} \mathbf{M}}{dt} = \frac{d_{(v)} \mathbf{P}}{dt} = 0 \quad (2.89)$$

$$\begin{aligned} \mathbf{L} &= -e_{ijk} T_{kj} e_i \\ &= -\boldsymbol{\epsilon} : \mathbf{T} \end{aligned} \quad (2.90)$$

as well as

$$\text{at } \Sigma : P \text{ is continuous} \quad (2.91)$$

It is important to recognize that (2.88) is the description of stress-deformation behavior at equilibrium.

To summarize, for the isolated body described at the beginning of the previ-

ous section, the necessary and sufficient conditions that (2.83) be satisfied and that equilibrium be achieved (under non-trivial conditions) are (2.84) through (2.91).

F. Phase rule

The phase rule was developed by Gibbs (Gibbs 1928, p. 354; Denbigh 1963, p. 180) for multiphase, multicomponent systems at equilibrium with the restriction that in each phase

$$\hat{A} = \hat{A}(T, \rho, \omega_{(1)}, \omega_{(2)}, \dots, \omega_{(N-1)}) \quad (2.92)$$

For such a system, the phase rule states that the maximum number p of phases that can be observed is

$$p \leq N + 2 \quad (2.93)$$

or the number of degrees of freedom one has in observing p phases is

$$f = N + 2 - p \quad (2.94)$$

The phase rule has been extended by Slattery and Lagoudas (2005) to systems that include crystalline solids. They found by analogy with (2.93) and (2.94)

$$p \leq N + 2 + p^{(c)}M - 3Q_c - Q_i \quad (2.95)$$

$$\begin{aligned} f &= N + 2 - p + p^{(c)}M - 3Q_c - Q_i \\ &\geq 0 \end{aligned} \quad (2.96)$$

Here M is the number of independent variants defined by (2.5), restricted by (2.7); Q_c denotes the number of coherent, solid-solid phase interfaces; Q_i denote the number of incoherent, solid-solid phase interfaces.

1. With no homogeneous or heterogeneous chemical reactions

In the case where there are no homogeneous or heterogeneous chemical reactions, we see from (2.14) that the state of each solid crystalline phase is determined by $N + M + 1$ independent variables: T , ρ , $\omega_{(1)}$, \dots , $\omega_{(N-1)}$, and M invariants

$$M \equiv M_1 + M_2 + M_3 + M_4 \quad (2.97)$$

Here $M_1 \leq 5$ denotes the non-zero invariants formed from the deformed lattice vectors, defined by (2.5) and restricted by (2.7); M_2 the non-zero invariants formed from the magnetization and the deformed lattice vectors, defined by (2.8) and (2.10); M_3 the non-zero invariants formed from the polarization and the deformed lattice vectors, defined by (2.9) and (2.11); M_4 the scalar product of the magnetization and the polarization, defined by (2.12). The state of each gas, liquid, or amorphous solid phase is fixed by $N + 1$ variables: T , ρ , $\omega_{(1)}$, \dots , $\omega_{(N-1)}$. If p is the number of phases and $p^{(c)}$ is the number of crystalline solid phases, the system is determined by

$$p(N + 1) + p^{(c)}M$$

variables.

Let us consider a system consisting of p distinct phases and therefore $p-1$ distinct internal phase interfaces. Focusing on these internal phase interfaces, we find that

- From (2.84), there are $p - 1$ independent equations relating T in each phase.
- From (2.85), there are $N(p - 1)$ independent equations relating $\mu_{(A)} + \phi_{(A)}$ in each phase.
- From (2.91), there are $p - 1$ independent equations relating P (thermodynamic pressure) in each phase.

- Let Q_c denoted the number of coherent, solid-solid phase interfaces, where the adjoining solid phases are deformed. From jump condition of stress at equilibrium, there are $3Q_c$ independent components of the jump momentum balance, Q_c jump magnetic flux balances, and Q_c jump charge balances.
- Let Q_i denoted the number of incoherent, solid-solid phase interfaces, where the adjoining solid phases are deformed. The incoherent solid-solid phase interface is one at which the tangential components of stress on the interface are zero; Commonly. such an interface will be the result of fracture. There are Q_i jump momentum balances (the normal component), Q_c jump magnetic flux balances, and Q_c jump charge balances.

To summarize, we have $p(N+1)+p^{(c)}M$ variables related by $(p-1)(N+2)+aQ_c+bQ_i$ equations. Here

$$\begin{aligned}
a &= 3 \text{ if there are no magnetic or electric fields} \\
&= 4 \text{ if there is either a magnetic field or an electric field, but not both} \\
&= 5 \text{ if there are both a magnetic field and an electric field} \\
b &= 1 \text{ if there are no magnetic or electric fields} \\
&= 2 \text{ if there is either a magnetic field or an electric field, but not both} \\
&= 3 \text{ if there are both a magnetic field and an electric field}
\end{aligned} \tag{2.98}$$

We know that

$$p(N+1)+p^{(c)}M \geq (p-1)(N+2)+aQ_c+bQ_i \tag{2.99}$$

we get:

$$p \leq N+2+p^{(c)}M-aQ_c-bQ_i \tag{2.100}$$

This tells us the maximum number of phases that might be observed in a given

equilibrium experiment. Equation (2.99) also can be expressed in terms of the number of degrees of freedom f (or the number of independent variables) one has in observing a fixed number of phases:

$$\begin{aligned} f &= N + 2 - p + p^{(c)}M - aQ_c - bQ_i \\ &\geq 0 \end{aligned} \tag{2.101}$$

If a system is subjected to c constraints, (2.101) should be replaced by

$$f = N + 2 - p + p^{(c)}M - aQ_c - bQ_i - c \tag{2.102}$$

Note that (2.99) and (2.101) reduce to the Gibbs phase rule (2.93) and (2.94), when there are no crystalline phases. They also reduce to the extended phase rule of Slattery and Lagoudas (2005) given by (2.95) and (2.96), when there are no magnetic or electric fields.

Let us apply (2.102) to some observations that have been reported in the literature.

- a. Example 1: Observation in the absence of electric and magnetic fields (Tickle and James, 1999)

Tickle and James (1999) began their studies with a rectangular ($Ni_{51.3}Mn_{24.0}Ga_{24.7}$) austenite bar with $\langle 100 \rangle$ edges (long edge as the axial direction, short edge as the transverse direction), first cooling it below -14 celisius degree to produce a polycrystalline martensite. Following cooling, an axial compressive stress σ was applied to produce a single, tetragonal, axial martensite variant in the absence of magnetic or electric fields.

It is immediately clear that the original Gibbs phase rule (2.94) is not applicable, since it assumes that stress is attributable only to thermodynamic pressure.

Our objective is to determine whether their observation of one variant (or in the case, one phase) is consistent with (2.96) and (2.102).

Since the tangential components of stress exerted on the faces of the sample are all zero, from (2.88) one solution would have two of the deformed lattice vectors $\mathbf{e}_{(i)}$ be everywhere tangent to these faces. In order to account for the normal stresses, the third lattice vector would be normal to the face, which is consistent with their tetragonal crystal structure. In this case, only two of the invariants (2.5) restricted by (2.7) are different from zero or $M = 2$. The initial careful orientation of the parent austenite phase may have been unnecessary.

There are six independent variables: temperature, density, two mass fractions, and two invariants. It is common to replace density by pressure, employing the definition of thermodynamic pressure (2.18).

Here $N = 3$, $P = P^{(c)} = 1$, $M = 2$, $Q_i = Q_c = 0$, and $c = 4$ (temperature, pressure, and two mass fractions). The phase rule (2.102) predicts $f = 2$: the two invariants, which are determined by the normal stresses applied on the boundary.

b. Example 2: Observation with a transverse magnetic field Tickle and James (1999)

Subsequent to the observations described above, Tickle and James (1999) applied a constant transverse magnetic field to the single martensite phase, producing another martensitic variant having a different orientation.

In this case, $M = 4$: $M_1 = 2$ (see Example 1), $M_2 = 2$, and $M_3 = M_4 = 0$. Following the same reasoning, we find $f = 4$: the four invariants, determined by the applied stresses, the magnitude and orientation of the magnetic field.

c. Example 3: Experiment of Murray et al. (2001)

In an experiment similar to that described in Example 2 above (same species but different composition), Murray et al. (2001) observed two variants in equilibrium. As indicated in Example 2, our phase rule predicts that they should have observed only one phase, which is consistent with their observation of two variants of the same phase.

2. With r independent reactions

Let us now assume that the system is capable of undergoing r independent chemical reactions, either homogeneous or heterogeneous. This means that we have an additional r equations describing chemical reaction equilibrium, either (2.86) for homogeneous reactions or (2.87) for heterogeneous reactions.

Following the same reasoning as above, (2.102) should be replaced by

$$f = N + 2 - p + p^{(c)}M - aQ_c - bQ_i - r - c \quad (2.103)$$

Unfortunately, there do not appear to be any experiments with which we can compare these predictions.

G. Summary of new results

Four principal results have been developed here.

1. To our knowledge, this is the first time that the Gibbs phase rule has been extended to crystalline elastic solids exposed to electro-magnetic fields. The result is consistent with three illustrative examples.
2. While the form of Euler's equation (2.30) remains unchanged, the extensions

of the Gibbs equation (2.31) and of the Gibbs-Duhem equation (2.32) to these systems appears to be new.

3. A new expression for stress-deformation behavior, including the effects of magnetization and polarization, has been derived at equilibrium.
4. A new expression for the moment-of-momentum per unit volume at equilibrium has been derived. This is important, since the stress tensor is not necessarily symmetric.

CHAPTER III

STRESS-DEFORMATION BEHAVIOR AT EQUILIBRIUM IN THE LIMIT OF
INFINITESIMAL DEFORMATIONS

Since it is common to consider infinitesimal deformations, let us consider how equation 48 in chapter II reduces in this limit:

$$\begin{aligned}
\mathbf{T} &= -P\mathbf{I} + \rho \sum_{m=1}^3 \left[\sum_{n=1}^2 \mu_{(I,mn)} (\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) \right. \\
&\quad \left. + \mu_{(I^{(2)},m)} \mathbf{M} \otimes \mathbf{e}_{(m)} + \mu_{(I^{(3)},m)} \mathbf{P} \otimes \mathbf{e}_{(m)} \right] \\
&= -P\mathbf{I} + \rho \sum_{m=1}^3 \left[\sum_{n=1}^2 \mu_{(I,mn)} (\mathbf{FE}_{(m)} \otimes \mathbf{FE}_{(n)} + \mathbf{FE}_{(n)} \otimes \mathbf{FE}_{(m)}) \right. \\
&\quad \left. + \mu_{(I^{(2)},m)} \mathbf{M} \otimes \mathbf{FE}_{(m)} + \mu_{(I^{(3)},m)} \mathbf{P} \otimes \mathbf{FE}_{(m)} \right] \quad (3.1)
\end{aligned}$$

Define

$$\begin{aligned}
\mathbf{u} &\equiv \mathbf{z} - \mathbf{z}_{\kappa} \\
&= \hat{\boldsymbol{\chi}}_{\kappa} - \mathbf{z}_{\kappa} \quad (3.2)
\end{aligned}$$

to be the displacement vector, and \mathbf{z}_{κ} is the position vector of a material particle in the natural configuration. It follows that the *displacement gradient*

$$\begin{aligned}
\mathbf{H} &\equiv \text{grad } \mathbf{u} \\
&\equiv \frac{\partial (z_i - z_{\kappa,i})}{\partial z_{\kappa,j}} \mathbf{e}_i \mathbf{e}_j \\
&= \frac{\partial z_i}{\partial z_{\kappa,j}} \mathbf{e}_i \mathbf{e}_j - \delta_{ij} \mathbf{e}_i \mathbf{e}_j \\
&= \mathbf{F} - \mathbf{I} \quad (3.3)
\end{aligned}$$

Let ϵ be a very small dimensionless variable characterizing an infinitesimal deformation process. We will seek a solution of the form

$$\mathbf{u} = \mathbf{u}_{(0)} + \epsilon \mathbf{u}_{(1)} + \epsilon^2 \mathbf{u}_{(2)} + \dots \quad (3.4)$$

Let us recognize that in the absence of an infinitesimal deformation or as $\epsilon \rightarrow 0$

$$\mathbf{u}_{(0)} = \mathbf{0} \quad (3.5)$$

This means that

$$\mathbf{H} = \epsilon \mathbf{H}_{(1)} + \epsilon^2 \mathbf{H}_{(2)} + \dots \quad (3.6)$$

$$\mathbf{H}_{(1)} = \text{grad } \mathbf{u}_{(1)} \quad (3.7)$$

$$\begin{aligned} \mathbf{C} &= (\mathbf{I} + \epsilon \mathbf{H}_{(1)} + \dots)^T (\mathbf{I} + \epsilon \mathbf{H}_{(1)} + \dots) \\ &= \mathbf{I} + \epsilon (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T) + O(\epsilon^2) \end{aligned} \quad (3.8)$$

From (2.6) and (3.8) (the derivative of a determinant is discussed by Slattery (1999, p. 679)),

$$\begin{aligned} \rho &= \frac{\rho_0}{\det \mathbf{F}} \\ &= \frac{\rho_0}{\sqrt{\det \mathbf{C}}} \\ &= \frac{\rho_0}{\sqrt{\det [\mathbf{I} + \epsilon (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T)]} + \dots} \\ &= \frac{\rho_0}{\det \mathbf{I}} - \epsilon \frac{\rho_0}{2(\det \mathbf{I})^2} \text{tr} (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T) + \dots \\ &= \rho_0 - \epsilon \frac{\rho_0}{2} \text{tr} (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T) + \dots \\ &= \rho_0 - \frac{\rho_0}{2} \text{tr} (\mathbf{C} - \mathbf{I}) + \dots \end{aligned} \quad (3.9)$$

Since, in the limit of small deformations, the strain

$$\begin{aligned}
\mathbf{e} &\equiv \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^T] \\
&\doteq \frac{1}{2} [\text{grad } \mathbf{u} + (\text{grad } \mathbf{u})^T] \\
&\doteq \epsilon \frac{1}{2} (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T)
\end{aligned} \tag{3.10}$$

which allows us to also express (3.9) as

$$\rho = \rho_0 (1 - \text{tr } \mathbf{e}) + \dots \tag{3.11}$$

Equations (3.3) and (3.6) also permit us to rewrite (3.1) to the first order in ϵ as (for the moment not addressing the order of $\mu_{(I,mn)}$)

$$\begin{aligned}
\mathbf{T} &= -P\mathbf{I} + \rho \left\{ \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I^{(1)},mn)} (\mathbf{I} + \epsilon \mathbf{H}_{(1)}) (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) (\mathbf{I} + \epsilon \mathbf{H}_{(1)})^T \right. \\
&\quad \left. + [\mu_{(I^{(2)},m)} \mathbf{M} \otimes [(\mathbf{I} + \epsilon \mathbf{H}_{(1)}) \mathbf{E}_{(m)}] + \mu_{(I^{(3)},m)} \mathbf{P} \otimes [(\mathbf{I} + \epsilon \mathbf{H}_{(1)}) \mathbf{E}_{(m)}]] \right\} \\
&= -P\mathbf{I} + \rho \left[\sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I^{(1)},mn)} (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) \right. \\
&\quad \left. + \mu_{(I^{(2)},m)} \mathbf{M} \otimes \mathbf{E}_{(m)} + \mu_{(I^{(3)},m)} \mathbf{P} \otimes \mathbf{E}_{(m)} \right] \\
&\quad + \rho \epsilon \left\{ \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I^{(1)},mn)} \left\{ \mathbf{H}_{(1)} (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) \right. \right. \\
&\quad \left. \left. + [\mathbf{H}_{(1)} (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)})]^T \right\} \right. \\
&\quad \left. + [\mu_{(I^{(2)},m)} \mathbf{M} \otimes \mathbf{H}_{(1)} \mathbf{E}_{(m)} + \mu_{(I^{(3)},m)} \mathbf{P} \otimes \mathbf{H}_{(1)} \mathbf{E}_{(m)}] \right\}
\end{aligned} \tag{3.12}$$

If the natural configuration is a stress-free configuration (an isotropic stress attributable to thermodynamic pressure),

$$0 = \rho_0 \left[\sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I^{(1),mn})_0} (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) + \mu_{(I^{(2),m})_0} \mathbf{M}_{(0)} \otimes \mathbf{E}_{(m)} + \mu_{(I^{(3),m})_0} \mathbf{P}_{(0)} \otimes \mathbf{E}_{(m)} \right] \quad (3.13)$$

where the $\mu_{(I^{(1),mn})_0}$, $\mu_{(I^{(2),m})_0}$, and $\mu_{(I^{(3),m})_0}$ are evaluated in the natural configuration. As a special case, let us assume that \hat{A} , as described by (2.14), can be represented as a quadratic function of $I_{(11)}^{(1)} \dots I_{(33)}^{(1)} \dots I^{(6)}$ (Truesdell and Noll, 1965, pp. 311-312):

$$\begin{aligned} \hat{A} = & c_{(0)} + \sum_{i=1}^3 \sum_{j=1}^2 c_{(ij)} I_{(ij)}^{(1)} + \frac{1}{2} \sum_{i=1}^3 \sum_{j=1}^2 \sum_{m=1}^3 \sum_{n=1}^2 c_{(ijmn)} I_{(ij)}^{(1)} I_{(mn)}^{(1)} + \sum_{i=1}^3 d_{(i)} I_{(i)}^{(2)} \\ & + \sum_{(i=1)}^{(3)} \sum_{(j=1)}^{(2)} \sum_{(m=1)}^{(3)} d_{(ijm)} I_{(ij)}^{(1)} I_{(m)}^{(2)} + \frac{1}{2} \sum_{(i=1)}^{(3)} \sum_{(j=1)}^{(2)} d_{(ij)} I_{(i)}^{(2)} I_{(j)}^{(2)} + \sum_{(i=1)}^{(3)} f_{(i)} I_{(i)}^{(3)} \\ & + \sum_{(i=1)}^{(3)} \sum_{(j=1)}^{(2)} \sum_{(m=1)}^{(3)} f_{(ijm)} I_{(ij)}^{(1)} I_{(m)}^{(3)} + \sum_{(i=1)}^{(3)} \sum_{(j=1)}^{(2)} g_{(ij)} I_{(i)}^{(2)} I_{(j)}^{(3)} \\ & + \frac{1}{2} \sum_{(i=1)}^{(3)} \sum_{(j=1)}^{(2)} f_{(ij)} I_{(i)}^{(3)} I_{(j)}^{(3)} + \sum_{(i=1)}^{(3)} \sum_{(j=1)}^{(2)} G_{(ij)} I_{(ij)}^{(1)} I^{(4)} + \sum_{(i=1)}^{(3)} G_{(i)} I_{(i)}^{(2)} I^{(4)} + \dots \end{aligned} \quad (3.14)$$

It should be understood here that $c_{(0)}$, $c_{(ij)}$, $c_{(ijmn)}$, $d_{(i)}$, $d_{(ij)}$, $d_{(ijm)}$, $f_{(i)}$, $f_{(ij)}$, $f_{(ijm)}$, and $g_{(ij)}$ are functions of T , ρ , and $\omega_{(A)}$ ($A = 1, \dots, N-1$) with the additional restrictions

$$c_{(ij)} = c_{(ji)} \quad (3.15)$$

and

$$\begin{aligned} c_{(ijmn)} &= c_{(mni j)} \\ c_{(ijmn)} &= c_{(ijnm)} \\ c_{(ijmn)} &= c_{(jimn)} \end{aligned} \quad (3.16)$$

$$d_{(ij)} = d_{(ji)} \quad (3.17)$$

$$d_{(ijm)} = d_{(jim)} \quad (3.18)$$

$$f_{(ij)} = f_{(ji)} \quad (3.19)$$

$$f_{(ijm)} = f_{(jim)} \quad (3.20)$$

$$g_{(ij)} = g_{(ji)} \quad (3.21)$$

$$G_{(ij)} = G_{(ji)} \quad (3.22)$$

For this special case, from (2.32)

$$\mu_{(I^{(1)}, mn)} = c_{(mn)} + \sum_{i=1}^3 \sum_{j=1}^2 c_{(ijmn)} I_{(ij)}^{(1)} + \sum_{i=1}^3 d_{(mni)} I_{(i)}^{(2)} + h_{(mn)} I^{(4)} + \dots \quad (3.23)$$

and from (3.13)

$$\mu_{(I^{(1)}, mn)0} = c_{(mn)} + h_{(mn)} I^{(4)} + \dots = 0 \quad (3.24)$$

Similarly:

$$\mu_{(I^{(2)}, m)} = d_{(i)} + \sum_{i=1}^3 \sum_{j=1}^2 d_{(ijm)} I_{(ij)}^{(1)} + \sum_{i=1}^3 d_{(im)} I_{(i)}^{(2)} + \sum_{i=1}^3 f_{(im)} I_{(i)}^{(3)} + h_{(m)} I^{(4)} + \dots \quad (3.25)$$

$$\mu_{(I^{(2)}, m)0} = d_{(i)} + h_{(m)} I^{(4)} + \dots = 0 \quad (3.26)$$

$$\mu_{(I^{(3)}, m)} = f_{(i)} + \sum_{i=1}^3 \sum_{j=1}^2 f_{(ijm)} I_{(ij)}^{(1)} + \sum_{i=1}^3 f_{(im)} I_{(i)}^{(2)} + \sum_{i=1}^3 g_{(im)} I_{(i)}^{(3)} + G_{(m)} I^{(4)} + \dots \quad (3.27)$$

$$\mu_{(I^{(3)}, m)0} = f_{(i)} + G_{(m)} I^{(4)} + \dots = 0 \quad (3.28)$$

From (2.5), (2.8), (2.9), (3.3), (3.6), (3.8), and (3.10), we see that

$$\begin{aligned}
I_{(ij)}^{(1)} &= \mathbf{E}_{(i)} \cdot (\mathbf{C} - \mathbf{I}) \mathbf{E}_{(j)} \\
&= 2\mathbf{E}_{(i)} \cdot \mathbf{e}\mathbf{E}_{(j)} \\
&= \epsilon \mathbf{E}_{(i)} \cdot (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T) \mathbf{E}_{(j)}
\end{aligned} \tag{3.29}$$

$$\begin{aligned}
I_{(i)}^{(2)} &= \mathbf{M} \cdot \mathbf{e}_{(i)} - \mathbf{M} \cdot \mathbf{E}_{(i)} \\
&= \mathbf{M} \cdot \mathbf{F}\mathbf{E}_{(i)} - \mathbf{M} \cdot \mathbf{E}_{(i)} \\
&= \mathbf{M} \cdot \epsilon \mathbf{H}_{(1)} \mathbf{E}_{(i)}
\end{aligned} \tag{3.30}$$

$$\begin{aligned}
I_{(i)}^{(3)} &= \mathbf{P} \cdot \mathbf{e}_{(i)} - \mathbf{P} \cdot \mathbf{E}_{(i)} \\
&= \mathbf{P} \cdot \mathbf{F}\mathbf{E}_{(i)} - \mathbf{P} \cdot \mathbf{E}_{(i)} \\
&= \mathbf{P} \cdot \epsilon \mathbf{H}_{(1)} \mathbf{E}_{(i)}
\end{aligned} \tag{3.31}$$

and

$$P = P_0 + \epsilon P_1 \tag{3.32}$$

then, the stress equation (3.12) can be expressed as:

$$\begin{aligned}
\mathbf{T} &= -P_0 \mathbf{I} - \epsilon P_1 \mathbf{I} \\
&+ \epsilon \rho \left[\sum_{m=1}^3 \sum_{n=1}^2 \sum_{i=1}^3 \sum_{j=1}^2 (c_{(ijmn)} \mathbf{E}_{(i)} \cdot (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T) \mathbf{E}_{(j)} + d_{(imn)} \mathbf{M} \cdot \mathbf{H}_{(1)} \mathbf{E}_{(i)} \right. \\
&\quad \left. + f_{(imn)} \mathbf{P} \cdot \mathbf{H}_{(1)} \mathbf{E}_{(i)}) (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) \right. \\
&\quad + (d_{(mij)} \mathbf{E}_{(i)} \cdot (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T) \mathbf{E}_{(j)} + d_{(im)} \mathbf{M} \cdot \mathbf{H}_{(1)} \mathbf{E}_{(i)} \\
&\quad + f_{(im)} \mathbf{P} \cdot \mathbf{H}_{(1)} \mathbf{E}_{(i)}) \mathbf{M} \otimes \mathbf{E}_{(m)} + (f_{(mij)} \mathbf{E}_{(i)} \cdot (\mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T) \mathbf{E}_{(j)} \\
&\quad \left. + f_{(im)} \mathbf{M} \cdot \mathbf{H}_{(1)} \mathbf{E}_{(i)} + g_{(im)} \mathbf{P} \cdot \mathbf{H}_{(1)} \mathbf{E}_{(i)}) \mathbf{P} \otimes \mathbf{E}_{(m)} \right]
\end{aligned} \tag{3.33}$$

CHAPTER IV

SINGLE CRYSTAL ACTUATOR

A. Introduction

Actuators made from materials which can develop large strokes under precise and rapid control can replace hydraulic, pneumatic, and electromagnetic drives in many applications. An ideal actuator material for engineering applications could develop rapid strokes with large displacement and high forces under precise control. Besides, it should also be economical enough to be in mass products.

Since the initial discovery of a giant magnetic field-induced strain by Ullakko (1996), Ferromagnetic shape memory alloys have attracted considerable attentions. Magnetic control of shape memory materials have been suggested for a principle of a new class of actuator materials due to a rearrangement of the martensite structure induced by a magnetic field (Murray et al. 2000a, 2001; Ullakko 1996).

Shape memory alloys have two stable phases, the lower temperature phase is martensitic with a tetragonal unit cell. A complete characterization of the actuator behavior of bulk $Ni - Mn - Ga$ specimens activated under the influence of magnetic inputs has yet to be fully realized (Couch and Chopra, 2003). Twin boundaries in martensitic $Ni - Mn - Ga$ can move when suitable magnetic fields are applied, some twin variants grow and some shrink to accommodate the shape change, this process produces the magnetic field actuation (Murray et al. 2001; Sozinov et al. 2001).

Magnetic field-induced strains of 6 percent and 10 percent in ferromagnetic Ni-Mn-Ga martensites have been reported at room temperature (Murray et al. 2000a; Sozinov et al. 2002). Ni-Mn-Ga ferromagnetic shape memory alloys have become a new class of actuator materials that deform under a magnetic field in the ferromag-

netic martensite phase.

Several important steps have been made during the last few years to understand the magneto-mechanical phenomena observed in ferromagnetic shape memory alloys (Likhachev and Ullakko 2000; 2001; 2002). In particular, several models have been developed and applied to explain quantitatively the static results of some experiments (Vasilev et al. 1999). However, no theoretical study has been done to investigate the dynamic process of the magnetic induced actuation of the shape memory alloys. With the appearance of commercial devices based on $Ni - Mn - Ga$, the focus on applications has increased. Understanding the dynamics of the field-induced twin boundary motion and the speed of the actuation are necessary for the design of actuators.

In the following sections, based upon the stress-deformation behavior of single crystal with the presence of magnetic field (Slattery and Si, 2005), we will study the dynamic process of the magnetic field induced actuation of a single crystal.

B. Basic theory

Chapter II have discussed the thermodynamic behavior of multicomponent, crystalline, elastic solids in the presence of magnetic and electric fields. In the absence of electric fields but in the presence of a magnetic field and after an application of the principle of frame indifference, their principal assumption reduces for each phase j to

$$\hat{A} = \hat{A} \left(T, \rho, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}^{(1)}, \dots, I_{(32)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I^{(3)} \right) \quad (4.1)$$

Here \hat{A} is the Helmholtz free energy per unit mass in phase j , T the temperature, ρ the density, and $\omega_{(A)}$ the mass fraction of species A . We define

$$\begin{aligned}
I_{(mn)}^{(1)} &\equiv \mathbf{e}_{(m)} \cdot \mathbf{e}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\
&= \mathbf{F}\mathbf{E}_{(m)} \cdot \mathbf{F}\mathbf{E}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\
&= \mathbf{E}_{(m)} \cdot \mathbf{F}^T \mathbf{F}\mathbf{E}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\
&= \mathbf{E}_{(m)} \cdot (\mathbf{C} - \mathbf{I})\mathbf{E}_{(n)}
\end{aligned} \tag{4.2}$$

$$I_{(m)}^{(2)} \equiv \mathbf{e}_{(m)} \cdot \mathbf{M} - \mathbf{E}_{(m)} \cdot \mathbf{M} \tag{4.3}$$

$$I^{(3)} \equiv \mathbf{M} \cdot \mathbf{M} - \mathbf{M}_0 \cdot \mathbf{M}_0 \tag{4.4}$$

with the understanding that

$$\mathbf{e}_{(i)} \equiv \mathbf{F}\mathbf{E}_{(i)} \tag{4.5}$$

are the current (deformed) lattice vectors in phase j , $\mathbf{E}_{(i)}$ are the lattice vectors for phase j in the natural (reference) configuration,

$$\mathbf{F} \equiv \text{grad } \mathbf{z} \tag{4.6}$$

is the deformation gradient, \mathbf{z} the current position of a material particle, \mathbf{H} the magnetic field, and grad denotes a gradient operation in the reference configuration.

Here

$$\mathbf{C} \equiv \mathbf{F}^T \mathbf{F} \tag{4.7}$$

is the right Cauchy-Green strain tensor in phase j . It will be important to note that, in the limit of small deformation (Slattery and Si, 2005, eq. 7),

$$\begin{aligned}
\rho &= \frac{\rho_0}{\sqrt{\det \mathbf{C}}} \\
&= \rho_0 - \frac{\rho_0}{2} \left(I_{(11)}^{(1)} + I_{(22)}^{(1)} + I_{(33)}^{(1)} \right) + \dots
\end{aligned} \tag{4.8}$$

In other words, ρ , $I_{(11)}^{(1)}$, $I_{(22)}^{(1)}$, and $I_{(33)}^{(1)}$ are not independent. One of their conclusions is that at equilibrium

$$\mathbf{T} = -P\mathbf{I} + \rho \sum_{m=1}^3 \left[\sum_{n=1}^2 \mu_{(I^{(1)},mn)} (\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) + \mu_{(I^{(2)},m)} \mathbf{M} \otimes \mathbf{e}_{(m)} \right] \quad (4.9)$$

Here they have introduced

$$\mu_{(I^{(1)},mn)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(mn)}^{(1)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(rs)}^{(1)} (rs \neq mn), I_{(m)}^{(2)}, I^{(3)} \dots} \quad (4.10)$$

$$\mu_{(I^{(2)},m)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(m)}^{(2)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(mn)}, I_{(r)}^{(2)} (r \neq m), \dots} \quad (4.11)$$

and

$$\mu_{(I^{(3)})} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(m)}^{(3)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(mn)}, I_{(r)}^{(2)} (r \neq m), \dots} \quad (4.12)$$

as well as the thermodynamic pressure P . If they choose the independent variables of the Holmholtz free energy per unit mass as all the invariants, temperature, and mass fraction,

$$\hat{A} = \hat{A} \left(T, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}^{(1)}, \dots, I_{(33)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I^{(3)} \right) \quad (4.13)$$

They will get a different Euler's equation, which is only related to species' mass fractions. And the term where the thermodynamic pressure and density are involved in the modified Gibbs equation and modified Gibbs-Duhem equation will be dropped out too. Therefore, the conclusions of the equilibrium will be different. Especially, a different constitutive equation of stress-deformation will be concluded:

$$\mathbf{T} = \rho \sum_{\mathbf{m}=1}^3 \left[\sum_{\mathbf{n}=1}^3 \mu_{(\mathbf{I}^{(1)},\mathbf{mn})} (\mathbf{e}_{(\mathbf{m})} \otimes \mathbf{e}_{(\mathbf{n})} + \mathbf{e}_{(\mathbf{n})} \otimes \mathbf{e}_{(\mathbf{m})}) + \mu_{(\mathbf{I}^{(2)},\mathbf{m})} \mathbf{M} \otimes \mathbf{e}_{(\mathbf{m})} \right] \quad (4.14)$$

Our objective in what follows is to analyze the single crystals' stress-deformation behavior and the dynamic transformation process of different variants in the experiments in the context of this theory. And also to show how this theory can be used to direct the designment of a single crystal actuator.

C. Problem statement

We will consider here the rectangular bar shown in Fig. 1 that is initially composed of a single martensitic variant A . It is subjected to a compressive axial stress σ , but the other four faces of the bar are open to atmospheric pressure. It will be convenient to work in terms of stresses beyond atmospheric pressure. The mechanical boundary conditions for the rectangular bar are the following:

$$\begin{aligned} \text{at } z_2 = L : \quad t_1 = T_{12}^{(A)} = 0 \\ t_2 = T_{22}^{(A)} = -\sigma \\ t_3 = T_{32}^{(A)} = 0 \end{aligned} \tag{4.15}$$

$$\begin{aligned} \text{at } z_2 = 0 : \quad t_1 = 0 \\ t_3 = 0 \\ u_2^{(A)} = 0 \\ v_2^{(A)} = 0 \end{aligned} \tag{4.16}$$

$$\text{at } z_1 = 0 \text{ and } W : \quad \mathbf{t} = 0 \tag{4.17}$$

$$\text{at } z_3 = 0 \text{ and } D : \quad \mathbf{t} = 0 \tag{4.18}$$

Here \mathbf{t} is the traction vector applied on the sample, and t_i is the components of the traction vector. $v_2^{(A)}$ is the second component of velocity of variant A . $u_2^{(A)}$ is the second component of the displacement of variant A . $T_{ij}^{(A)}$ denotes a component of

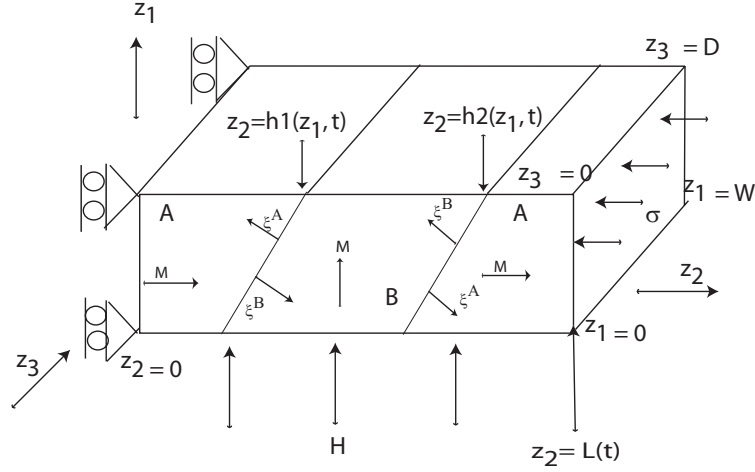


Fig. 1. A single crystal A is compressed and subjected to a constant magnetic field \mathbf{H} , creating a second variant B . The plane interface between variants A and B moves in the z_2 direction.

the stress $\mathbf{T}^{(A)}$ in variant A . At $t = 0$, a transverse magnetic field is switched on, and variant B is nucleated internally, and two interfaces begin sweeping across the sample.

In the analysis that follows, we will make several assumptions.

1. The crystals are either cubic or tetragonal. The analysis is easily extended to orthorhombic crystals.
2. We will assume that (4.14), which was derived for a system at equilibrium (Slattery and Lagoudas, 2005), can be applied to a dynamic system. This is supported by (Tian et al., 2005), who use it to correctly predict wave propagation in cubic crystals. In order to make the argument simpler and clearer, we will ignore the effects of atmospheric pressure.
3. The crystals A and B shown in Fig. 1 are variants of the same phase as in the experiments of Murray et al. (2001). See the discussion of these experiments

given by Slattery and Si (2005).

4. The applied magnetic field is independent of time and position.
5. Variant A is aligned with its easy axis (the short lattice vector seen as $\mathbf{E}_{(2)}$) aligned in the z_2 direction as seen in the reference configuration. The applied magnetic field is sufficiently large that variant B in Fig. 1 is aligned with its easy axis in the z_1 direction. This appears to conform to the experiments of Murray et al. (2001). The only non-zero components of the lattice vectors in the reference configurations for variant A and B are:

$$E_{(1)1}^{(A)} = a \quad (4.19)$$

$$E_{(2)2}^{(A)} = b \quad (4.20)$$

$$E_{(3)3}^{(A)} = a \quad (4.21)$$

$$E_{(1)2}^{(B)} = a \quad (4.22)$$

$$E_{(2)1}^{(B)} = b \quad (4.23)$$

$$E_{(3)3}^{(B)} = -a \quad (4.24)$$

6. We will assume that the system undergoes a plane strain with no dependence upon the z_3 direction.
7. In considering the dynamic transformation from A to B, we will assume that the magnetization of variant A was unaffected by the application of the external magnetic field.
8. The interfaces between two martensitic variants are coherent. By coherent, here we will mean that adjoining deformed lattice vectors have the same length.

9. The magnetic body force (Pao, 1978, p. 264)

$$\mathbf{f} = \mathbf{f}(\nabla\mathbf{B}) \quad (4.25)$$

where \mathbf{B} is the magnetic induction, which is proportional to the magnetic field \mathbf{H} . Since \mathbf{B} is a constant, $\nabla\mathbf{B} = \mathbf{0}$, and there is no body force attributable to the magnetic field.

10. Any effects of gravity will be neglected.

The final objective of the analysis which follows is to determine how the length L of the sample changes with time.

D. Solution

Let us seek a solution of plane strain for each variant ($C = A, B$) of the form

$$\begin{aligned} v_2^{(C)} &= v_2^{(C)}(z_2, t) \\ v_1^{(C)} &= v_3^{(C)} = 0 \end{aligned} \quad (4.26)$$

Here, $v_i^{(C)}$ are components of the velocity of variant C . We will also say that, because one end of the variant is fixed,

$$\text{for } 0 < z_2 < h_1 : v_2^{(A)} = 0 \quad (4.27)$$

Equation (4.26) suggests that we also assume that the velocities $\mathbf{u}_{(i)}$ of interface i in Fig. 1 has only one non-zero component:

$$\begin{aligned} u_{(i)2} &= u_{(i)2}(z_2, t) \\ u_{(i)1} &= u_{(i)3} = 0 \end{aligned} \quad (4.28)$$

The differential mass balances (Slattery, 1999, p. 21) for variants A and B

$$\frac{d_{(m)}\rho}{dt} + \rho \operatorname{div} \mathbf{v} = \mathbf{0} \quad (4.29)$$

Let us introduce some dimensionless variables,

$$\begin{aligned} t^* &\equiv \frac{t}{t_0} \\ \rho^* &\equiv \frac{\rho}{\rho_0} \\ v^* &\equiv \frac{v}{v_0} \end{aligned} \quad (4.30)$$

where ρ_0 is the density in the reference configuration and v_0 is a characteristic velocity that will be defined later, and t_0 is the time required for the lattice vectors to be rotated at the interface, which is very small. In terms of these variables, (4.30) becomes

$$\frac{d_{(m)}\rho^*}{dt^*} + \frac{t_0 v_0}{L_0} \rho^* \operatorname{div} \mathbf{v}^* = 0 \quad (4.31)$$

if

$$v_0 \equiv \sqrt{\frac{\sigma}{\rho_0}} \quad (4.32)$$

Even t_0 is small, but L_0 is small and v_0 is very large, therefore

$$\frac{t_0 v_0}{L_0} \gg 1 \quad (4.33)$$

eq.(4.29) reduces to

$$\begin{aligned} \frac{\partial v_2^{(A)}}{\partial z_2} &= 0 \\ \frac{\partial v_2^{(B)}}{\partial z_2} &= 0 \end{aligned} \quad (4.34)$$

Our conclusion is that

$$\begin{aligned} v_2^{(A)} &= v_2^{(A)}(t) \\ v_2^{(B)} &= v_2^{(B)}(t) \end{aligned} \quad (4.35)$$

In view of (4.26) through (4.28), the jump mass balances for the two interfaces shown in Fig. 1 require (Slattery, 1999, p. 25)

$$\text{at } z_2 = h_1 : \quad \rho^{(A)} u_{(1)2} + \rho^{(B)} (v_2^{(B)} - u_{(1)2}) = 0 \quad (4.36)$$

$$\text{at } z_2 = h_2 : \quad -\rho^{(A)} (v_2^{(A)} - u_{(2)2}) + \rho^{(B)} (v_2^{(B)} - u_{(2)2}) = 0 \quad (4.37)$$

where, $\boldsymbol{\xi}^{(B)}$ is the unit normal to the interfaces pointing into variant B.

In view of assumptions 9 and 10, the differential momentum balance (Slattery, 1999, p. 34) reduces to

$$\rho \frac{d_{(m)} \mathbf{v}}{dt} = \text{div} \mathbf{T} \quad (4.38)$$

Let us introduce two more dimensionless variables

$$\begin{aligned} z_i^* &\equiv \frac{z_i}{L_0} \\ \mathbf{T}^* &\equiv \frac{\mathbf{T}}{\sigma} \end{aligned} \quad (4.39)$$

where L_0 is the length of the sample in the reference configuration. In terms of these variables defined in (4.39) and (4.30), (4.38) becomes

$$\rho^* \frac{d_{(m)} v^*}{dt^*} = \frac{\sigma}{\rho_0 v_0^2} \frac{t_0 v_0}{L_0} \text{div} T^* \quad (4.40)$$

From (4.32), we know

$$\frac{\sigma}{\rho_0 v_0^2} = 1 \quad (4.41)$$

from (4.33), we know that

$$\frac{\sigma}{\rho_0 v_0^2} \frac{t_0 v_0}{L_0} \gg 1 \quad (4.42)$$

and (4.38) reduces to

$$\operatorname{div} \mathbf{T} = \mathbf{0} \quad (4.43)$$

for both variants A and B. With the boundary conditions listed by equation (4.15) and (4.16), recognizing that the other four faces of the bar are exposed to atmospheric pressure, which we are ignoring (assumption 6), we find for variant C (C = A,B)

$$\begin{aligned} T_{22}^{(C)} &= \text{constant} \\ T_{11}^{(C)} &= T_{33}^{(C)} = 0 \end{aligned} \quad (4.44)$$

All other components of stress in both variants are zero.

The jump momentum balance requires (Slattery, 1999, p. 34) at $z_2 = h_1$:

$$T_{22}^{(A)} - T_{22}^{(B)} + \rho^{(B)} v_2^{(B)} \left(v_2^{(B)} - u_{(1)2} \right) = 0 \quad (4.45)$$

Similarly at $z_2 = h_2$:

$$T_{22}^{(A)} - T_{22}^{(B)} - \rho^{(A)} v_2^{(A)} \left(v_2^{(A)} - u_{(2)2} \right) + \rho^{(B)} v_2^{(B)} \left(v_2^{(B)} - u_{(2)2} \right) = 0 \quad (4.46)$$

From the extended Gibbs phase rule derived by Slattery and Si (2005), we know the variants A and B belong to the same phase (see their example 3). Therefore, they have the same reference configuration, although the reference configurations are rotated with respect to one another.

According to assumption 8, for the coherent interface adjoining deformed lattice vectors in variants A and B must have the same length:

$$\begin{aligned} \mathbf{e}_{(1)}^{(A)} &= \mathbf{e}_{(2)}^{(B)} \\ \mathbf{F}^{(A)} \mathbf{E}_{(1)}^{(A)} &= \mathbf{F}^{(B)} \mathbf{E}_{(2)}^{(B)} \end{aligned} \quad (4.47)$$

and

$$\begin{aligned} \mathbf{e}_{(3)}^{(A)} &= -\mathbf{e}_{(3)}^{(B)} \\ \mathbf{F}^{(A)} \mathbf{E}_{(3)}^{(A)} &= -\mathbf{F}^{(B)} \mathbf{E}_{(3)}^{(B)} \end{aligned} \quad (4.48)$$

where the deformation gradient \mathbf{F} can be expressed as

$$\begin{aligned} \mathbf{F} &= \text{grad } \mathbf{u} + \mathbf{I} \\ &\doteq \nabla \mathbf{u} + \mathbf{I} \end{aligned} \quad (4.49)$$

In view of (4.14) and (4.44), we see that all of the deformed lattice vectors in the tetragonal variants A and B are either perpendicular or parallel to the boundaries of the specimen. Substitute (4.5) and (4.49) into (4.47) and recognizing (4.19) through (4.24), we have for both coherent interfaces

$$e_{11}^{(A)} = \frac{b}{a} \left(1 + e_{11}^{(B)} \right) - 1 \quad (4.50)$$

Slattery and Si (2005, eq. 136) have derived an expression for stress-deformation behavior appropriate to small deformations of elastic, crystalline materials in the presence of both electric and magnetic fields. In addition to using density and five invariants $I_{(mn)}^{(1)}$ among their independent variables in describing the specific Helmholtz free energy \hat{A} , they also assumed that the reference configuration was stress-free.

Here we wish to assume that there is no electric field, that the stress distribution $\mathbf{T}_{(0)}$ in the reference configuration is non-zero, and that the independent variables for \hat{A} include all six $I_{(mn)}^{(1)}$ but not density. With these relatively simple changes, their

result for small deformations (Slattery and Si, 2005, p. 136) becomes

$$\begin{aligned}
\mathbf{T} &= \mathbf{T}_{(0)} + \epsilon \mathbf{T}^1 \\
&= \rho_{(0)} \left\{ \sum_{m=1}^3 \sum_{n=1}^3 c_{(mn)} (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) + d_{(m)} \mathbf{M} \otimes \mathbf{E}_{(m)} \right\} \\
&\quad + \epsilon \rho_{(0)} \left\{ \sum_{m=1}^3 \sum_{n=1}^3 c_{(mn)} + \left[\sum_{i=1}^3 \sum_{j=1}^3 c_{(ijmn)} \mathbf{E}_{(i)} \cdot (\mathbf{e} \mathbf{E}_{(j)}) \right. \right. \\
&\quad \left. \left. + d_{(imn)} \mathbf{M} \cdot [(\nabla \mathbf{u}_{(1)}) \mathbf{E}_{(i)}] + \mathbf{c}_{(mn)} (\nabla \mathbf{u}_{(1)}) \right] (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) \right. \\
&\quad \left. + \left[\sum_{i=1}^3 \sum_{j=1}^3 d_{(ijm)} \mathbf{E}_{(i)} \cdot (\mathbf{e} \mathbf{E}_{(j)}) + d_{(im)} \mathbf{M} \cdot [(\nabla \mathbf{u}_{(1)}) \mathbf{E}_{(i)}] \right] \mathbf{M} \otimes \mathbf{E}_{(m)} \right. \\
&\quad \left. + c_{(mn)} (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) (\nabla \mathbf{u}_{(1)})^T + \mathbf{d}_{(m)} \mathbf{M} \otimes [(\nabla \mathbf{u}_{(1)}) \mathbf{E}_{(m)}] \right\} \\
&\quad - \rho_{(0)} \operatorname{tr} \mathbf{e} \left[\sum_{m=1}^3 \sum_{n=1}^3 c_{(mn)} (\mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)}) + d_{(m)} \mathbf{M} \otimes \mathbf{E}_{(m)} \right]
\end{aligned} \tag{4.51}$$

Here ϵ is an unspecified perturbation parameter characterizing the small deformation from the reference configuration, in which the stress $\mathbf{T}_{(0)} \neq \mathbf{0}$. It is important to note that the coefficients used here are functions of only temperature, whereas the coefficients in Slattery and Si (2005, eq. 136) were functions of both temperature and density. In (4.51), the dependence upon density drops out, because we are using all six invariants $I_{(mn)}^{(1)}$ rather than only five.

The important thing we need to remember is that we are studying a plane strain, and there is no dependence upon z_3 .

Assumption 5, (4.19) through (4.21), and (4.51), tells us that the (22) component of the stress in the reference state is:

$$T_{(0)22} = \rho_{(0)} (2 c_{(22)} b^2 + d_{(2)} b M) \tag{4.52}$$

Equation (4.26) and assumption 6 imply that the only non-zero components of

strain are e_{11} and e_{22} . From 6, (4.44) and (4.19) through (4.24), equation (4.51) requires

$$0 = \rho_{(0)} \left[(4a^2b^2c_{(2211)} + 2a^2bMd_{(211)}) e_{22}^{(A)} + 4a^2b^2c_{(1111)}e_{11}^{(A)} \right] \quad (4.53)$$

$$T_{22}^{(A)} - T_{(0)22} = \rho_{(0)} \left[(2b^2c_{(22)} + 4b^4c_{(2222)} + 4b^3Md_{(222)} + M^2b^2d_{(22)}) e_{22}^{(A)} \right. \\ \left. + (4a^2b^2c_{(2211)} + 2a^2bMd_{(211)}) e_{11}^{(A)} \right] \quad (4.54)$$

$$0 = \rho_{(0)} \left[(2b^2c_{(22)} + 4b^4c_{(2222)} + 4b^3Md_{(222)} + M^2b^2d_{(22)}) e_{11}^{(B)} \right. \\ \left. + (4a^2b^2c_{(2211)} + 2a^2bMd_{(211)} - T_0) e_{22}^{(B)} \right] \quad (4.55)$$

$$T_{22}^{(B)} - T_{(0)22} = \rho_{(0)} \left[(4a^2b^2c_{(1122)} + 2a^2bMd_{(211)}) e_{11}^{(B)} \right. \\ \left. + 4a^2b^2c_{(1111)}e_{22}^{(B)} \right] \quad (4.56)$$

E. Analysis of the experiments of Tickle (2000)

Tickle (2000) did a series of experiments to study the relationship between stress and apparent strain with and without a magnetic field. A single austenitic Ni_2MnGa crystal was cooled to -17 celsius degree, which is much lower than the martensite finish temperature (about -13 celsius degree). An axial load was applied to bias the sample into a single axial variant A, whose easy axis, corresponding to the short lattice vector of the tetragonal crystal, is parallel to the compression axis. We will choose the initial configuration of variant A under the smallest compression stress used as the reference configuration, and we will refer to its length as $L_{(0)}$.

A large transverse magnetic field (12 kOe) was then applied to variant A, and a second variant B was nucleated with its short lattice vector or easy axis parallel to the magnetic field. In Fig. 1, we show two interfaces bounding variant B that quickly sweep across the specimen to form a single crystal of variant B. Tickle (2000)

measured for different compressive stresses the length $L^{(A)}$ of variant A before the magnetic field was applied and the length $L^{(B)}$ of variant B after the transformation was concluded.

In reporting his observations, Tickle (2000) speaks in terms of an apparent strain for variant C (C = A, B)

$$\varepsilon^{(C)} \equiv \frac{L^{(C)} - L^{(R)}}{L^{(R)}} \quad (4.57)$$

Here $L^{(C)}$ is the current length of the specimen, and $L^{(R)}$ is the length of the original austenite specimen.

Tickle (2000) reported two static experiments with a single crystal of martensite under compression: with and without a constant magnetic field. In addition to investigating these experiments, we will also examine the dynamic process that occurs in going from the first to the second when the magnetic field is switched on.

Our objective here is to use the two static experiments of Tickle (2000) to determine the parameters in our theory and to use our theory to predict the time required for the complete transformation of A to B in the dynamic portion of his experiments. This is the lag time that a single crystal actuator would exhibit in operation.

1. Static observations of Tickle (2000)

Let us begin by examining the static experiments.

a. Strain in terms of apparent strain

Let us begin by showing that $e_{22}^{(C)}$, where C = A, B. In the initial configuration of variant A, there is no external magnetic field. As shown in Fig. 2, the magnetization of variant A is parallel to the axial direction, but magnetization in different domain has opposite direction. Since the stress is uniform inside variant A, (4.53) and (4.54)

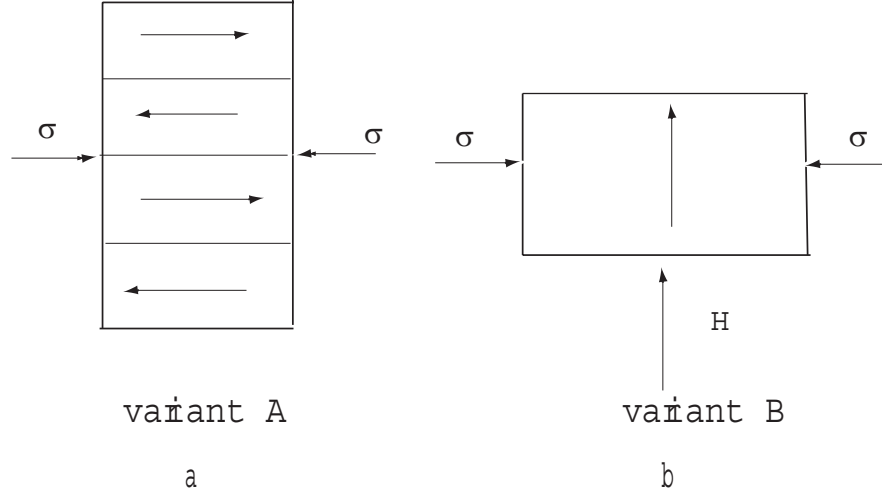


Fig. 2. a: Variant A is compressed by a uniaxial stress; light lines are magnetic domain walls; arrows indicate the magnetization direction of the domains. b: Variant B is exposed to an external magnetic field and an uniaxial stress; the magnetization in variant B is uniform.

suggest that

$$\begin{aligned} d_{(ijk)} &= 0 \\ d_{(m)} &= 0 \end{aligned} \quad (4.58)$$

Substitute (4.58) into (4.53), we find

$$e_{11}^{(A)} = -\frac{b^2 c_{(2211)}}{a^2 c_{(1111)}} e_{22}^{(A)} \quad (4.59)$$

let

$$K^{(A)} \equiv -\frac{b^2 c_{(2211)}}{a^2 c_{(1111)}} \quad (4.60)$$

From (4.60), (4.59) is changed to

$$e_{11}^{(A)} = K^{(A)} e_{22}^{(A)} \quad (4.61)$$

From (4.53), (4.54) and (4.59), We see that T_{22} and e_{22} have a linear relationship:

$$T_{22}^{(A)} - T_{(0)22} = C^{(A)} e_{22}^{(A)} \quad (4.62)$$

where,

$$\begin{aligned} C^{(A)} &\equiv \frac{b^2 \rho(0)}{a^2 c_{(1111)}} [a^2 c_{(1111)} (4b^2 c_{(2222)} - 2c_{(22)} + M^2 d_{(22)}) \\ &\quad + b^2 c_{(2211)} (2c_{(22)} - 4a^2 c_{(2211)})] \\ &= \text{a constant} \end{aligned} \quad (4.63)$$

Similarly, from (4.55), we find

$$e_{11}^{(B)} = \frac{2c_{(22)} - 4a^2 c_{(1122)}}{4b^2 c_{(2222)} + M^2 d_{(22)}} e_{22}^{(B)} \quad (4.64)$$

let

$$K^{(B)} \equiv \frac{2c_{(22)} - 4a^2 c_{(1122)}}{4b^2 c_{(2222)} + M^2 d_{(22)}} \quad (4.65)$$

From (4.65), (4.64) is changed to

$$e_{11}^{(B)} = K^{(B)} e_{22}^{(B)} \quad (4.66)$$

Substituting (4.64) into (4.56), we have

$$T_{22}^{(B)} - T_{(0)22} = C^{(B)} e_{22}^{(B)} \quad (4.67)$$

in which

$$\begin{aligned} C^{(B)} &\equiv \frac{4a^2 \rho(0)}{4b^2 c_{(2222)} + M^2 d_{(22)}} [a^2 c_{(1111)} (4b^2 c_{(2222)} + M^2 d_{(22)}) \\ &\quad + b^2 c_{(2211)} (2c_{(22)} - 4a^2 c_{(2211)})] \\ &= \text{a constant} \end{aligned} \quad (4.68)$$

In Tickle (2000)'s experiments,

$$\begin{aligned} T_{22}^{(C)} &= -\sigma \\ T_{(0)22} &= -\sigma_{(0)} \end{aligned} \tag{4.69}$$

We can summarize (4.62) and (4.67) as

$$\begin{aligned} e_{22}^{(C)} &= \frac{\sigma_{(0)} - \sigma}{C^{(C)}} \\ &= \text{a constant} \end{aligned} \tag{4.70}$$

From (4.70) and the definition of strain

$$e_{22}^{(C)} \int_0^{L^{(C)}} dz_2 = \int_0^{L^{(C)} - L_{(0)}} du_2 \tag{4.71}$$

or

$$e_{22}^{(C)} = \frac{L^{(C)} - L_{(0)}}{L^{(C)}} \tag{4.72}$$

Tickle (2000) did not identify $L_{(0)}$ in his experiments, but he did give the initial apparent strain ε_0

$$\varepsilon_{(0)} \equiv \frac{L_{(0)} - L^{(R)}}{L^{(R)}} \tag{4.73}$$

which means that

$$L_0 = L^{(R)} + \varepsilon_{(0)} L^{(R)} \tag{4.74}$$

From (4.57),

$$L^{(C)} = L^{(R)} + \varepsilon^{(C)} L^{(R)} \tag{4.75}$$

Substitute equations (4.74) and (4.75) into equation (4.72), we conclude

$$e_{22}^{(C)} = \frac{\varepsilon^{(C)} - \varepsilon_{(0)}}{1 + \varepsilon^{(C)}} \tag{4.76}$$

b. Determining $C^{(A)}$ and $C^{(B)}$

Here we will determine $C^{(A)}$ and $C^{(B)}$ for the static observations of Tickle (2000).

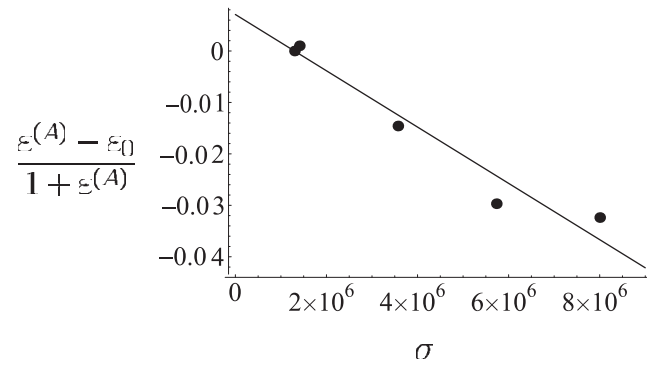


Fig. 3. The experimental data from Tickle (2000) are used to fit a straight line. The slope of the straight line is used to evaluate the coefficient in Equation (4.77) for a single variant A.

From (4.70) and (4.76), we have ($C = A, B$)

$$\frac{\varepsilon^{(C)} - \varepsilon_{(0)}}{1 + \varepsilon^{(C)}} = \frac{\sigma_{(0)} - \sigma}{C^{(C)}} \quad (4.77)$$

Tickle (2000) reported apparent strain $\varepsilon^{(A)}$ as functions of the uniaxial stress σ .

We choose the reference state as variant A under the smallest stress:

$$\begin{aligned} \sigma_{(0)} &= 1.297 \text{ MPa} \\ \varepsilon_{(0)} &= -0.0115 \end{aligned} \quad (4.78)$$

The least-square fits of (4.77) to the data for variants A and B are shown in Figs. 3 and 4 with the results

$$C^{(A)} = 1.82125 \times 10^8 \text{ Pa} \quad (4.79)$$

$$C^{(B)} = 2.02981 \times 10^8 \text{ Pa} \quad (4.80)$$

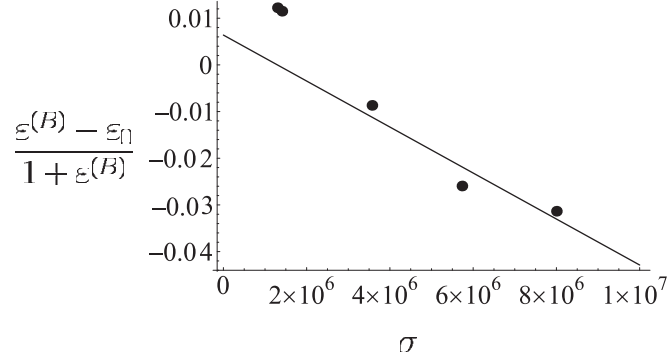


Fig. 4. The experimental data from Tickle (2000) are used to fit a straight line. The slope of the straight line is used to evaluate the coefficient in Equation (4.77) for a single variant B.

c. Determining $K^{(A)}$ and $K^{(B)}$

Let us introduce some variables to substitute those variables in (4.60), (4.65), (4.63) and (4.68)

$$A_1 \equiv -b^2 c_{(2211)} \quad (4.81)$$

$$A_2 \equiv a^2 c_{(1111)} \quad (4.82)$$

$$B_1 \equiv b^2 C_{(2211)} (2 c_{(22)} - 4 a^2 c_{(2211)}) \quad (4.83)$$

$$B_2 \equiv 4 b^2 c_{(2222)} + M^2 d_{(22)} \quad (4.84)$$

Substitute (4.81) and (4.82) into (4.60), we find

$$K^{(A)} = \frac{A_1}{A_2} \quad (4.85)$$

Substitute (4.81) and (4.84) into (4.65), we find

$$K^{(B)} = -\frac{B_1}{A_1 B_2} \quad (4.86)$$

Substitute (4.82), (4.83), and (4.84) into (4.63) and (4.68), we find

$$C^{(A)} = b^2 \rho_0 \left[\frac{A_2 (B_2 - 2c_{(22)}) + B_1}{A_2} \right] \quad (4.87)$$

$$C^{(B)} = 4a^2 \rho_0 \left[\frac{A_2 B_2 + B_1}{B_2} \right] \quad (4.88)$$

B_1 can be expressed by A_1 as

$$B_1 = \frac{-A_1 (2b^2 c_{(22)} + 4a^2 A_1)}{b^2} \quad (4.89)$$

If we substitute (4.61), (4.66), (4.70), (4.81), (4.82), and (4.84) into the coherent interfacial condition (4.50), we have

$$b - a = (\sigma - \sigma_0) \left[\frac{a A_1}{A_2 C^{(A)}} + \frac{b B_1}{A_1 B_2 C^{(B)}} \right] \quad (4.90)$$

From (4.52), (4.58), and (4.69), we find

$$c_{(22)} = -\frac{\sigma_0}{2b^2 \rho_0} \quad (4.91)$$

Tickle (2000) gave us the parameters of the reference configuration:

$$\begin{aligned} a &= 2.95 \text{ \AA} \\ b &= 2.77 \text{ \AA} \\ \rho_{(0)} &= 8020 \text{ kg/m}^3 \end{aligned} \quad (4.92)$$

Now, with the conditions in (4.91) and (4.92), we solve the four equations (4.87) through (4.89) and (4.90) for the four unknowns A_1 , A_2 , B_1 , and B_2 .

Substitute the results into equations (4.85) and (4.86), $K^{(A)}$ and $K^{(B)}$ are calculated,

$$\begin{aligned} K^{(A)} &= -0.0093 \\ K^{(B)} &= -54.83 \end{aligned} \quad (4.93)$$

Substitute (4.93) into (4.61) and (4.66), we find

$$\begin{aligned} e_{11}^{(A)} &= -0.0093 e_{22}^{(A)} \\ e_{11}^{(B)} &= -54.83 e_{22}^{(B)} \end{aligned} \quad (4.94)$$

2. Dynamic transformation from variant A to variant B

The solution to the dynamic problem shown in Fig. 1 has been developed in Sec. D, except for the constants of integration. In each variant C, the only non-zero component of stress $T_{22}^{(C)}$.

Starting from the right in Fig. 1 and using boundary condition (4.15), we have $T_{22}^{(A)} = \sigma$. From (4.62), (4.69), (4.78), and (4.79), we have $e_{(22)}^{(A)}$. Given (4.94), we can compute $e_{(11)}^{(A)}$.

the coherent condition for both interfaces (4.50) let us get $e_{(11)}^{(B)}$ from $e_{(11)}^{(A)}$. similarly, from (4.94), we get $e_{(22)}^{(B)}$. We knew $C^{(B)}$ from (4.80). Then, from (4.67), we got $T_{(22)}^{(B)}$.

With a similar process, we calculated the stress and strain of the left side variant A.

At this point, we get the stress and strain of all the variants. In order to get the extension velocity, we need to solve the four equations, the jump mass balances (4.36) and (4.37), the jump momentum balances (4.45) and (4.46) with four unknowns, $u_{(1)2}$, $u_{(2)2}$, $v_{(2)}^{(A)}$, and $v_{(2)}^{(B)}$, the second component of the velocities of the two interfaces and the second component of the velocities of variant B and the right side variant A.

The relationship between the extension velocity, $v_{(2)}^{(A)}$ and the magnitude of the uniaxial load σ is described in Fig. 5 and the relationship of the extension time and the magnitude of the uniaxial stress σ is showed in Fig. 6. From Fig. 5, we find that the extension velocities are large, which makes the transformation between two

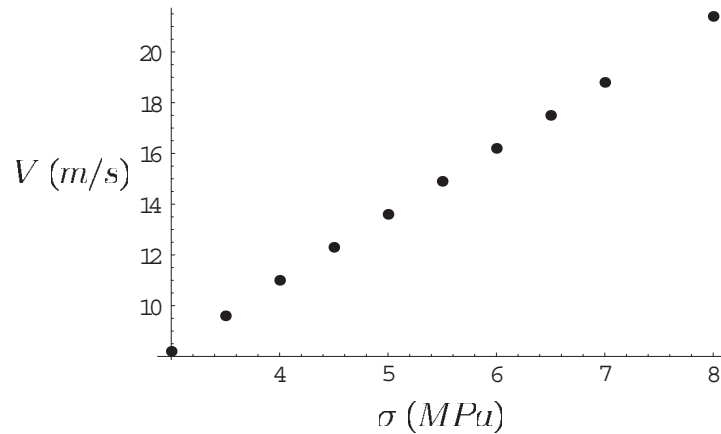


Fig. 5. Extension velocity changes with the magnitude of the uniaxial load; V is the extension velocity, σ is the magnitude of the uniaxial stress

variants instantaneously, that is the actuation process is very fast. Fig. 6 shows that the time needed for the actuation is very short, which means the pulsed magnetic field with certain frequency is applicable for the magnetic actuation. Experimentally, pulsed magnetic fields are easier to get and to operate practically than static constant magnetic fields. The prediction of the actuation time is very important for the design of a magnetic single crystal actuator with a pulsed magnetic field. For example, if the uniaxial stress is 5 MPa, from Fig. 6, we know the actuation time is 40 μ s, which requires the frequency of the pulsed magnetic field can not extend than 2500 Hz.

We haven't found any experimental or theoretical report about the quantity of the actuator's extension velocity, and the quantity of the actuation time under the same condition. But most of the experimentalists did describe that the actuation process is transient (Murray et al. 2001; O'Handley et al. 2000).

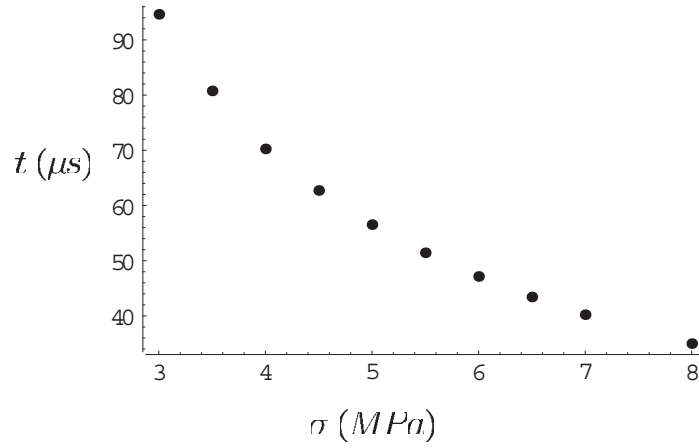


Fig. 6. Actuation time changes with the magnitude of the uniaxial load; t is the actuation time, σ is the magnitude of the uniaxial stress

F. Discussion and summary

The stress deformation behavior for multicomponent, elastic, crystalline solids with the presence of magnetic fields derived by Slattery and Si (2005) was tested with Tickle (2000)'s static experimental data, and fits the data very well.

The Slattery-Si stress deformation behavior was derived for the equilibrium state, it can be applicable in a quasi-equilibrium dynamic process through the assumption of local equilibrium.

A new coherent interfacial condition, matching the lattice vectors of the two variants, between two martensitic variants was developed and used in studying the dynamic process of the martensitic variants transition. This coherent condition is applicable to fairly simple case like this. For polycrystalline materials, the relationship between the lattice vectors will be too complicated to study. A different coherent condition will be used. Si and Slattery (2005) derived a coherent condition which can be applicable in the complex polycrystalline coherent interfaces.

This is the first theoretical study of the dynamic process of the magnetic field

induced martensitic variant transition. The extension velocity and the actuation time of the single crystal actuator were calculated.

CHAPTER V

INTERFACE CONSTRAINTS, OXIDATION, AND A GENERALIZED
CLAUSIUS-CLAPEYRON EQUATION

A. Introduction

This paper derives a new constraint on stress at interfaces with crystalline solids as well as an extension of the Clausius-Clapeyron equation for systems with crystalline solids. The derivations are based upon results derived by Slattery and Lagoudas (2005).

1. Boundary conditions at interfaces with solids

Perhaps the most common conditions imposed at interfaces are the jump mass, momentum, and energy balances (Slattery, 1990, 1999).

It is also common in solving problems, either dynamic or static, to assume local equilibrium at the interface. This means that thermodynamic pressure, temperature, and all of the chemical potentials are continuous across the interface.

Another common condition at solid-solid interfaces is to say that the normal component of displacement is continuous (Larche and Cahn, 1973, 1978) . This of course assumes that both phases have the same reference configuration. While this is often true, it is not true for phases that are formed either by phase transitions (austenite-martensite transformations) or by chemical reactions (oxidation) (Rajagopal and Srinivasa, 1998; Oh et al., 2005; Slattery and Lagoudas, 2005). If continuity of displacement can not be used, one normally finds that one boundary condition is missing in solving a problem involving an interface with a crystalline solid.

The Hadamard condition (Bhattacharya, 2003, p. 28) is a constraint on strain in the plane tangent to an interface. It is appropriate for a coherent interface between phases having the same reference configuration. A coherent interface is one in which material points in adjoining phases stay together in all configurations, reference or current. It for example is appropriate for a martensite-martensite transformation. It would not be appropriate for an interface formed by an oxidation, because the metal and the oxide would have different reference configurations.

In Sec. C we derive a new constraint to be applied at interfaces with crystalline solids. This is based upon upon the extended Gibbs-Duhem equation derived by (Slattery and Lagoudas, 2005, eq. 24).

2. Clausius-Clapeyron equation

For fluids, amorphous solids, and crystalline solids in the absence of residual elastic stresses, the Clausius-Clapeyron equation describes how thermodynamic pressure changes as a function of temperature for two phases in equilibrium (Denbigh, 1963, p. 197). Up to this point, there has been no general agreement on its derivation for crystalline solids with stress.

Otsuka et al. (1976, eq. 4.1) begin with an assumed form for the Clausius-Clapeyron equation in terms of the critical stress for inducing a martensitic transformation, the associated strain, temperature and heat of transformation.

Wollants (1979; 1983; 1991) begin their discussions assuming an equation of state for the Gibbs free energy of a macroscopic phase that has undergone a one-dimensional strain.

Kato and Pak use a non-standard definition of Gibbs free energy (1984, eq. 26; 1985, eq. 6). They study a system with only one phase rather than two phases in equilibrium (Kato and Pak, 1984, eq. 36). The Clausius-Clapeyron equation refers

to two phases in equilibrium.

In Sec. D, we will present a new derivation of the Clausius-Clapeyron equation which is also based upon the extended Gibbs-Duhem equation derived by (Slattery and Lagoudas, 2005, eq. 24).

3. Summary of results from Slattery and Lagoudas (2005)

Slattery and Lagoudas (2005) have discussed the thermodynamic behavior of multi-component, crystalline, elastic solids. Their principal assumption for each phase j is

$$\hat{A} = \hat{A}(T, \rho, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}, \dots, I_{(32)}) \quad (5.1)$$

For phase j , \hat{A} is the Helmholtz free energy per unit mass in phase j , T the temperature, ρ the density, and $\omega_{(A)}$ the mass fraction of species A . They defined

$$I_{(mn)} \equiv \mathbf{e}_{(m)} \cdot \mathbf{e}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \quad (5.2)$$

with the understanding that

$$\mathbf{e}_{(i)} \equiv \mathbf{F}\mathbf{E}_{(i)} \quad (5.3)$$

are the current (deformed) lattice vectors in phase j , $\mathbf{E}_{(i)}$ are the lattice vectors for phase j in the natural (reference) configuration,

$$\mathbf{F} \equiv \text{grad } \mathbf{z} \quad (5.4)$$

is the deformation gradient, \mathbf{z} the current position of a material particle, and grad denotes a gradient operation in the reference configuration.

Two of their results that we shall require here are an extended Gibbs-Duhem

equation (Slattery and Lagoudas, 2005, eq. 24)

$$\hat{S} dT - \hat{V} dP + \sum_{i=1}^N \omega_{(i)} d\mu_{(i)} - \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I,mn)} dI_{(mn)} = 0 \quad (5.5)$$

which was derived for non-equilibrium conditions, and a new expression for stress-deformation behavior (Slattery and Lagoudas, 2005, eq. 55)

$$\mathbf{T} = -P\mathbf{I} + \rho \sum_{m=1}^3 \left[\sum_{n=1}^2 \mu_{(I,mn)} (\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) \right] \quad (5.6)$$

which was derived under equilibrium conditions. Here \mathbf{T} is the stress tensor, P the thermodynamic pressure and

$$\mu_{(I,mn)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(mn)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(rs)} (rs \neq mn), \dots} \quad (5.7)$$

B. Dynamic interfaces

An (phase) interface between two solid phases can be formed only by a phase change or by a chemical reaction, such as oxidation. It can not be formed by bringing two solid phases together, since there will always be a (discontinuous) thin film of air between them. There of course is no such problem in forming fluid-fluid or fluid-solid interfaces.

The discussion that immediately follows is based upon the extended Gibbs-Duhem equation (5.5), which was derived for non-equilibrium or dynamic conditions. We will make only two assumptions:

1. The crystalline solid undergoes only infinitesimally small deformations.
2. At each point on a dynamic phase interface, there is local equilibrium:

$$\mu_{(i)}^{(A)} = \mu_{(i)}^{(B)} \equiv \mu_{(i)}, \quad T^{(A)} = T^{(B)} \equiv T, \quad P^{(A)} = P^{(B)} \equiv P \quad (5.8)$$

or

$$d\mu_{(i)}^{(A)} = d\mu_{(i)}^{(B)} = d\mu_{(i)}, \quad dT^{(A)} = dT^{(B)} = dT, \quad dP^{(A)} = dP^{(B)} = dP \quad (5.9)$$

From (5.2), we have

$$\begin{aligned} dI_{(mn)} &= d(\mathbf{e}_{(m)} \cdot \mathbf{e}_{(n)}) \\ &= \frac{1}{2} d [\text{tr}(\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)})] \end{aligned} \quad (5.10)$$

and

$$\begin{aligned} \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I,mn)} dI_{(mn)} &= \\ \frac{1}{2} \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I,mn)} d [\text{tr}(\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)})] \end{aligned} \quad (5.11)$$

From (5.6), we see that

$$\begin{aligned} d[\text{tr}(\mathbf{T} + \mathbf{PI})] &= \rho \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I,mn)} d [\text{tr}(\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)})] \\ &\quad + \rho \sum_{m=1}^3 \sum_{n=1}^2 \text{tr}(\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) d\mu_{(I,mn)} \end{aligned} \quad (5.12)$$

We conclude from (5.11) that

$$\begin{aligned} \rho \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I,mn)} dI_{(mn)} &= \frac{1}{2} d[\text{tr}(\mathbf{T} + \mathbf{PI})] \\ &\quad - \frac{\rho}{2} \sum_{m=1}^3 \sum_{n=1}^2 \text{tr}(\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) d\mu_{(I,mn)} \end{aligned} \quad (5.13)$$

Let ϵ be a dimensionless parameter characterizing an infinitesimal deformation from the reference configuration. To the zeroth order we know

$$I_{(mn)}^{(0)} = 0 \quad (5.14)$$

and (Slattery and Lagoudas, 2005, eq. A.18)

$$\mu_{(I,mn)}^{(0)} = 0 \quad (5.15)$$

This means that, to the second order in ϵ , (5.13) reduces to

$$\begin{aligned} \rho_0 \sum_{m=1}^3 \sum_{n=1}^2 \mu_{(I,mn)} dI_{(mn)} &= \frac{1}{2} d [\text{tr} (\mathbf{T} + \mathbf{PI})] \\ &\quad - \frac{\rho_0}{2} \sum_{m=1}^3 \sum_{n=1}^2 \text{tr} (\mathbf{e}_{(\mathbf{m})} \otimes \mathbf{e}_{(\mathbf{n})} + \mathbf{e}_{(\mathbf{n})} \otimes \mathbf{e}_{(\mathbf{m})}) d\mu_{(I,mn)} \end{aligned} \quad (5.16)$$

where ρ_0 is the density at the zeroth order or the density in the reference configuration.

With (5.9) and (5.16), the extended Gibbs-Duhem equation (5.5) requires

$$\begin{aligned} \hat{V}^{(A)} dP - \hat{S}^{(A)} dT - \sum_{i=1}^N \omega_{(i)}^{(A)} \mu_{(i)} + \frac{1}{2} d \left[\text{tr} \left(\frac{\mathbf{T}^{(A)} + \mathbf{PI}}{\rho_0^{(A)}} \right) \right] \\ - \frac{1}{2} \sum_{m=1}^3 \sum_{n=1}^2 \left(\mathbf{e}_{(\mathbf{m})}^{(\mathbf{A})} \otimes \mathbf{e}_{(\mathbf{n})}^{(\mathbf{A})} + \mathbf{e}_{(\mathbf{n})}^{(\mathbf{A})} \otimes \mathbf{e}_{(\mathbf{m})}^{(\mathbf{A})} \right) d\mu_{(I^{(A)},mn)} = \\ \hat{V}^{(B)} dP - \hat{S}^{(B)} dT - \sum_{i=1}^N \omega_{(i)}^{(B)} \mu_{(i)} + \frac{1}{2} d \left[\text{tr} \left(\frac{\mathbf{T}^{(B)} + \mathbf{PI}}{\rho_0^{(B)}} \right) \right] \\ - \frac{1}{2} \sum_{m=1}^3 \sum_{n=1}^2 \left(\mathbf{e}_{(\mathbf{m})}^{(\mathbf{B})} \otimes \mathbf{e}_{(\mathbf{n})}^{(\mathbf{B})} + \mathbf{e}_{(\mathbf{n})}^{(\mathbf{B})} \otimes \mathbf{e}_{(\mathbf{m})}^{(\mathbf{B})} \right) d\mu_{(I^{(B)},mn)} \end{aligned} \quad (5.17)$$

or

$$\begin{aligned} \left(\hat{V}^{(A)} - \hat{V}^{(B)} \right) dP - \left(\hat{S}^{(A)} - \hat{S}^{(B)} \right) dT - \sum_{i=1}^N \left(\omega_{(i)}^{(A)} - \omega_{(i)}^{(B)} \right) d\mu_{(i)} \\ + \frac{1}{2} d \left[\text{tr} \left(\frac{\mathbf{T}^{(B)} + \mathbf{PI}}{\rho_0^{(B)}} \right) - \text{tr} \left(\frac{\mathbf{T}^{(A)} + \mathbf{PI}}{\rho_0^{(A)}} \right) \right] \\ - \frac{1}{2} \sum_{m=1}^3 \sum_{n=1}^2 \left(\mathbf{e}_{(\mathbf{m})}^{(\mathbf{A})} \otimes \mathbf{e}_{(\mathbf{n})}^{(\mathbf{A})} + \mathbf{e}_{(\mathbf{n})}^{(\mathbf{A})} \otimes \mathbf{e}_{(\mathbf{m})}^{(\mathbf{A})} \right) d\mu_{(I^{(A)},mn)} \\ + \frac{1}{2} \sum_{m=1}^3 \sum_{n=1}^2 \left(\mathbf{e}_{(\mathbf{m})}^{(\mathbf{B})} \otimes \mathbf{e}_{(\mathbf{n})}^{(\mathbf{B})} + \mathbf{e}_{(\mathbf{n})}^{(\mathbf{B})} \otimes \mathbf{e}_{(\mathbf{m})}^{(\mathbf{B})} \right) d\mu_{(I^{(B)},mn)} = 0 \end{aligned} \quad (5.18)$$

Since

$$\hat{S}^{(A)} - \hat{S}^{(B)} = \frac{\Delta \hat{H}}{T}, \quad \Delta \hat{V} \equiv \hat{V}^{(A)} - \hat{V}^{(B)} \quad (5.19)$$

(5.18) reduces to

$$\begin{aligned} \Delta \hat{V} dP - \frac{\Delta \hat{H}}{T} dT - \sum_{i=1}^N \left(\omega_{(i)}^{(A)} - \omega_{(i)}^{(B)} \right) d\mu_{(i)} \\ + d \left[\text{tr} \left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{2\rho_0^{(B)}} \right) - \text{tr} \left(\frac{\mathbf{T}^{(A)} + P\mathbf{I}}{2\rho_0^{(A)}} \right) \right] \\ - \frac{1}{2} \sum_{m=1}^3 \sum_{n=1}^2 \left(\mathbf{e}_{(\mathbf{m})}^{(\mathbf{A})} \otimes \mathbf{e}_{(\mathbf{n})}^{(\mathbf{A})} + \mathbf{e}_{(\mathbf{n})}^{(\mathbf{A})} \otimes \mathbf{e}_{(\mathbf{m})}^{(\mathbf{A})} \right) d\mu_{(I^{(A)}, mn)} \\ + \frac{1}{2} \sum_{m=1}^3 \sum_{n=1}^2 \left(\mathbf{e}_{(\mathbf{m})}^{(\mathbf{B})} \otimes \mathbf{e}_{(\mathbf{n})}^{(\mathbf{B})} + \mathbf{e}_{(\mathbf{n})}^{(\mathbf{B})} \otimes \mathbf{e}_{(\mathbf{m})}^{(\mathbf{B})} \right) d\mu_{(I^{(B)}, mn)} = 0 \end{aligned} \quad (5.20)$$

Note that (5.20) describes how changes in P , T , $\mu_{(i)}$, \dots at an interface are related to one another.

The extended Gibbs-Duhem equation (5.5) was derived by Slattery and Lagoudas (2005) for a dynamic system. Although Slattery and Lagoudas (2005) derived (5.6) for a system at equilibrium, it has been demonstrated to correctly predict wave propagation in cubic crystals (Tian et al., 2005), which is a nonequilibrium problem. This suggests that it may be appropriate to use (5.20) to describe dynamic systems as well.

C. Static interfaces with crystalline solids

In this section, we will make two further assumptions:

1. At least one of the phases adjoining the interface is a crystalline solid.
2. The system is either static or quasi-static.

In a quasi-static or static system where T , P , the chemical potentials $\mu_{(i)}$, and $\mu_{(I,mn)}$ can be considered to be nearly independent of time, (5.20) requires

$$\frac{d}{dt} \left[\text{tr} \left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{\rho_0^{(B)}} \right) - \text{tr} \left(\frac{\mathbf{T}^{(A)} + P\mathbf{I}}{\rho_0^{(A)}} \right) \right] = 0 \quad (5.21)$$

or

$$\text{tr} \left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{\rho_0^{(B)}} \right) - \text{tr} \left(\frac{\mathbf{T}^{(A)} + P\mathbf{I}}{\rho_0^{(A)}} \right) = \text{a constant} \quad (5.22)$$

To emphasize the point, this is a condition to be satisfied at an interface between two crystalline solids.

For a crystalline solid-fluids(or amorphous solids) interface, (5.22) becomes

$$\text{tr} \left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{\rho_0^{(B)}} \right) = \text{a constant} \quad (5.23)$$

where the constants are to be determined in each application.

Perhaps the most difficult cases are those involving polycrystalline solids. The interface is a discontinuous surface, each segment of which is seen in a two-phase crystal. We recommend applying either (5.22) or (5.23) to each of these interface segments, and therefore to the entire interface.

But working with polycrystalline materials one anisotropic crystal at a time is generally avoided. Commonly, a polycrystalline solid is replaced by a single-phase isotropic solid. In what follows, we will assume that the stress-deformation behavior of this isotropic solid can be described by the generalized Hooke's law in which stress is a linear function of strain.

In summary, while (5.22) or (5.23) have been derived for interfaces adjoining a crystalline solid whose stress-deformation behavior is described by (5.6), we will assume, in agreement with common practice, that the stress-deformation behavior of the isotropic crystalline solid can be described by the generalized Hooke's law.

Note that, because two solid crystalline phases adjoining an interface will have different reference configurations (Slattery and Lagoudas, 2005; Oh et al., 2005), one can not use continuity of displacement. Equation (5.22) or (5.23) must be used instead.

Note that in deriving (5.22) and (5.23) we assumed that the stress-deformation behavior can be described by (5.6). We have also argued above that it can be applied at every point on an interface formed by polycrystalline solids. But, at a larger scale, polycrystalline solids are typically viewed as isotropic, and their stress-deformation behavior is expressed by the generalized Hooke's law. That will be the view taken here in considering polycrystalline solids.

Hooke's law is commonly expressed in terms of the elastic portion of the stress

$$\sigma \equiv \mathbf{T} + P\mathbf{I} \quad (5.24)$$

The inertial and body forces having been neglected, the differential momentum balance (Slattery, 1999, p. 52) is reduced to

$$\operatorname{div} \sigma = 0 \quad (5.25)$$

In what follows, we will consider several examples.

1. Bending of plate as the result of oxidation

We will describe several cases.

a. Oxidation on one side of a plate

Here we wish to determine the stress and displacement distributions in a two-dimensional (thin) plate as it is oxidized from one side. Because the density of the oxide is smaller than that of the metal, the oxide expands more than the metal, an unbalanced stress

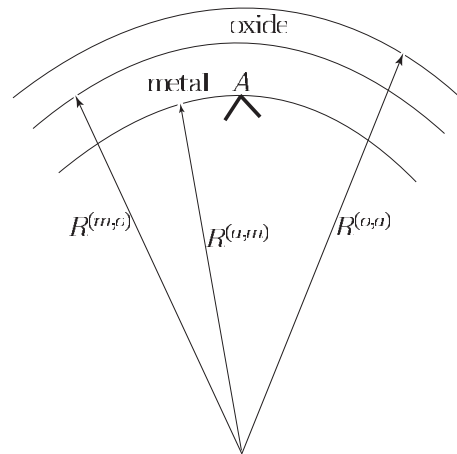


Fig. 7. Oxidation on one side of a plate; point A is the point where the pivot is placed.

distribution is developed, and the plate bends to form a concave, unoxidized metal surface.

A strip or beam of silicon is initially flat or bounded by parallel planes. After oxidation, it is bent as shown in Figure 7, where it is shown balanced on a pivot at its center. In what follows we will seek a solution in which the components of stress are independent of θ . We will further recognize that, because the system is assumed to be at equilibrium, P is uniform throughout the system (Slattery and Lagoudas, 2005)

A general solution Let us make no assumption about stress-deformation behavior. Let us make four assumptions.

1. We will seek a plane stress solution.
2. The system is axisymmetric in cylindrical coordinates. All quantities are independent of θ .
3. Because the system is assumed to be at equilibrium, P is uniform throughout the system (Slattery and Lagoudas, 2005).

4. The plate has a finite length, and, referring to Fig. 7

$$\text{at } \theta = \pm\theta_1 : \sigma_{\theta\theta} = \sigma_{r\theta} = 0 \quad (5.26)$$

With the assumption of plane stress, the non-zero components of the differential momentum balance can be expressed as (Slattery, 1999),

$$\frac{1}{r} \frac{\partial}{\partial r} (r\sigma_{rr}) - \frac{\sigma_{\theta\theta}}{r} = 0 \quad (5.27)$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} (r^2\sigma_{\theta r}) = 0 \quad (5.28)$$

In view of (5.26), we conclude that

$$\sigma_{\theta\theta} = \sigma_{\theta r} = 0 \quad (5.29)$$

and

$$\sigma_{rr} = \frac{c}{r} \quad (5.30)$$

Here, c is a unknown constant for each phase.

The jump momentum balance (Slattery, 1990, p. 252) at the air-metal interface is

$$\text{at } r = R^{(a,m)} : \frac{\gamma^{(a,m)}}{R^{(a,m)}} = \sigma_{rr}^{(m)} \quad (5.31)$$

where $\gamma^{(a,m)}$ is the surface energy of the air-metal interface and $R^{(a,m)}$ the radius of the air-metal interface. At the metal-oxide interface, the jump momentum balance requires

$$\text{at } r = R^{(m,o)} : \frac{\gamma^{(m,o)}}{R^{(m,o)}} = \sigma_{rr}^{(o)} - \sigma_{rr}^{(m)} \quad (5.32)$$

in which $\gamma^{(m,o)}$ is the surface energy of the metal-oxide interface and $R^{(m,o)}$ the radius of the metal-oxide interface. The jump momentum balance on the oxide-air interface

requires

$$\text{at } r = R^{(o,a)} : \frac{\gamma^{(o,a)}}{R^{(o,a)}} = -\sigma_{rr}^{(o)} \quad (5.33)$$

Here, $\gamma^{(o,a)}$ is the surface energy of the air-oxide interface and $R^{(o,a)}$ the radius of the oxide-air interface.

Let's consider two cases.

- If we neglect surface energies in (5.31) through (5.33), we find in (5.30)

$$c = 0 \quad \text{for both phases} \quad (5.34)$$

and the stress distributions in both the oxide and the metal are zero.

- If the surface energies are all nonzero, (5.31) through (5.33) suggest that there is no solution, since (5.32) would require an unlikely relation among the three surface energies. This means that something in the problem formulation is physically unrealistic. We believe that (5.26) does not describe reality, since it assumes that there is no curvature at the ends of the beam

Polycrystalline phases Here we will retain only the first four assumptions above. We will assume that both phases are polycrystalline, and, following the discussion above, we will represent the stress-deformation behavior of each phase by the linearized Hooke's law. The beam will be considered sufficiently long that end effects can be neglected.

Under these conditions, the elastic portion of the stress tensor can be written in terms of the Airy stress function φ as

$$\sigma = \nabla^2 \varphi \mathbf{I} - \nabla \nabla \varphi \quad (5.35)$$

which is a solution of the biharmonic equation

$$\nabla^4 \varphi = 0 \quad (5.36)$$

For an axisymmetric system, solution is (Little, 1999, p. 156)

$$\varphi = A \ln r + Br^2 \ln r + Cr^2 + D \quad (5.37)$$

The corresponding components of stress in the metal and oxide are

$$\sigma_{rr}^{(m)} = \frac{c_1}{r^2} + 2c_2 \ln r + c_2 + 2c_3 \quad (5.38)$$

$$\sigma_{\theta\theta}^{(m)} = -\frac{c_1}{r^2} + 2c_2 \ln r + 3c_2 + 2c_3 \quad (5.39)$$

$$\sigma_{rr}^{(o)} = \frac{c_4}{r^2} + 2c_5 \ln r + c_5 + 2c_6 \quad (5.40)$$

$$\sigma_{\theta\theta}^{(o)} = -\frac{c_4}{r^2} + 2c_5 \ln r + 3c_5 + 2c_6 \quad (5.41)$$

The jump momentum balances (5.31) through (5.33) continue to apply.

From (5.22) and (5.23) at the three interfaces, we have

$$\text{at } r = R^{(a,m)} : \frac{\sigma_{rr}^{(m)} + \sigma_{\theta\theta}^{(m)}}{\rho_0^{(m)}} = C^{(a,m)} \quad (5.42)$$

$$\text{at } r = R^{(m,o)} : \frac{\sigma_{rr}^{(o)} + \sigma_{\theta\theta}^{(o)}}{\rho_0^{(o)}} - \frac{\sigma_{rr}^{(m)} + \sigma_{\theta\theta}^{(m)}}{\rho_0^{(m)}} = C^{(m,o)} \quad (5.43)$$

$$\text{at } r = R^{(o,a)} : \frac{\sigma_{rr}^{(o)} + \sigma_{\theta\theta}^{(o)}}{\rho_0^{(o)}} = C^{(o,a)} \quad (5.44)$$

Here, $C^{(a,m)}$, $C^{(m,o)}$, and $C^{(o,a)}$ are the constants defined by (5.22) and (5.23) for the air-metal, metal-oxide, and oxide-air interface.

We have six equations (5.31) through (5.33) and (5.42) through (5.44) in 9 unknowns. We will seek a solution in which

$$C^{(a,m)} = C^{(m,o)} = C^{(o,a)} = 0 \quad (5.45)$$

If surface energies are zero, we conclude that

$$\sigma_{rr} = \sigma_{\theta\theta} = 0 \quad (5.46)$$

There is no stress in the metal-oxide plate.

Let us assume that the surface energies for all three interfaces are non-zero. Recognizing (5.45), we can solve the six equations (5.31) through (5.33) and (5.42) through (5.44) for the six unknowns c_1 through c_6 using Mathematica (2003).

The reference configuration for the metal is that portion of the initial metal beam remaining after oxidation. The corresponding r -component of displacement at the metal-air interface is available from Little (1999, p. 159) in terms of two additional parameters. One is eliminated, when we recognize that the r -component of displacement must be a symmetric function of θ . The other constant is determined by saying that the displacement is zero at $\theta = 0$, since it is supported on a pivot.

b. Oxidation on two sides of a plate with different thickness

In addition to the first three assumptions stated above, we will also assume

- (4'.) We will assume that the pivot shields the beam from oxidation at the point ($r = R^{(o,m)}$, $\theta = 0$). In other words, we assume that the displacement of this point from the reference configuration of the metal is zero.
- (5.) We will continue to assume that both the metal and oxide phases are polycrystalline and that their behavior can be represented by Hooke's law.
- (6.) We will assume that the radii of curvature of the four interfaces in Fig. 7 are very large compared with the thickness of the metal beam.
- (7.) We will assume that the x_1 , the thickness of the thinner oxide in Fig. 7, is very

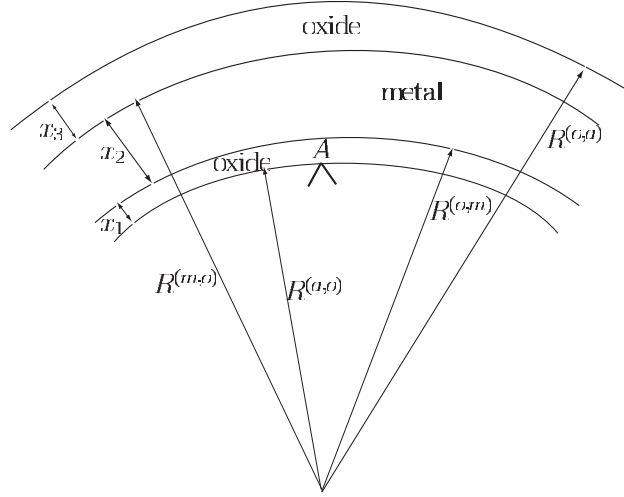


Fig. 8. Oxidation on two sides of a plate with different thickness, x_1 , x_2 , and x_3 are the thickness of the second layer of the oxide, the thickness of the metal, and the thickness of the first layer of oxide; point A is the point where the pivot is placed.

small compared with the thickness of the metal beam.

Extending the solution described above, we find that the components of stress in the metal and oxide are

$$\sigma_{rr}^{(m)} = \frac{c_1}{r^2} - 2c_2 \ln \frac{1}{r} + c_2 + 2c_3 \quad (5.47)$$

$$\sigma_{\theta\theta}^{(m)} = -\frac{c_1}{r^2} - 2c_2 \ln \frac{1}{r} + 3c_2 + 2c_3 \quad (5.48)$$

$$\sigma_{rr}^{(o)1} = \frac{c_4}{r^2} - 2c_5 \ln \frac{1}{r} + c_5 + 2c_6 \quad (5.49)$$

$$\sigma_{\theta\theta}^{(o)1} = -\frac{c_4}{r^2} - 2c_5 \ln \frac{1}{r} + 3c_5 + 2c_6 \quad (5.50)$$

$$\sigma_{rr}^{(o)2} = \frac{c_7}{r^2} - 2c_8 \ln \frac{1}{r} + c_8 + 2c_9 \quad (5.51)$$

$$\sigma_{\theta\theta}^{(o)2} = -\frac{c_7}{r^2} - 2c_8 \ln \frac{1}{r} + 3c_8 + 2c_9 \quad (5.52)$$

Referring to Figure 8, we can write jump momentum balances as

$$\text{at } r = R^{(a,o)} : \frac{\gamma^{(a,o)}}{R^{(a,o)}} = \sigma_{rr}^{(o1)} \quad (5.53)$$

$$\text{at } r = R^{(o,m)} : \frac{\gamma^{(o,m)}}{R^{(o,m)}} = \sigma_{rr}^{(m)} - \sigma_{rr}^{(o1)} \quad (5.54)$$

$$\text{at } r = R^{(m,o)} : \frac{\gamma^{(m,o)}}{R^{(m,o)}} = \sigma_{rr}^{(o2)} - \sigma_{rr}^{(m)} \quad (5.55)$$

$$\text{at } r = R^{(o,a)} : -\sigma_{rr}^{(o2)} = \frac{\gamma^{(a,o)}}{R^{(o,a)}} \quad (5.56)$$

From (5.22) and (5.23) at the four interfaces, we have

$$\text{at } r = R^{(a,o)} : \frac{\sigma_{rr}^{(o1)} + \sigma_{\theta\theta}^{(o1)}}{\rho_0^{(o)}} = C^{(a,o)} \quad (5.57)$$

$$\text{at } r = R^{(o,m)} : \frac{T_{rr}^{(m)} + T_{\theta\theta}^{(m)}}{\rho_0^{(m)}} - \frac{\sigma_{rr}^{(o1)} + \sigma_{\theta\theta}^{(o1)}}{\rho_0^{(o1)}} = C^{(o,m)} \quad (5.58)$$

$$\text{at } r = R^{(m,o)} : \frac{\sigma_{rr}^{(o2)} + \sigma_{\theta\theta}^{(o2)}}{\rho_0^{(o)}} - \frac{\sigma_{rr}^{(m)} + \sigma_{\theta\theta}^{(m)}}{\rho_0^{(m)}} = C^{(m,o)} \quad (5.59)$$

$$\text{at } r = R^{(o,a)} : \frac{\sigma_{rr}^{(o2)} + \sigma_{\theta\theta}^{(o2)}}{\rho_0^{(o)}} = C^{(o,a)} \quad (5.60)$$

The eight equations (5.53) through (5.60) are in terms of 13 unknowns: c_1 through c_9 and the four constants in (5.57) through (5.60). The problem is ill posed; there is no axisymmetric solution for this problem.

However there is an axisymmetric solution in the limit where the radii of curvature are very large compared with the thickness of the metal beam. In that limit,

$$c_1 = c_4 = c_7 = 0 \quad (5.61)$$

From (5.61) and (5.47) through (5.60), we find that we have eight equations in 10 unknowns.

If the surface energies are all zero, (5.53) through (5.56) require that

$$\sigma_{rr} = \sigma_{\theta\theta} = 0 \quad (5.62)$$

There are two obvious solutions to this problem assuming that the surface energies are not all zero.

Solution one

One solution assumes

$$C^{(a,o)} = C^{(o,a)} = 0 \quad (5.63)$$

This together with (5.61) mean that the eight equations (5.47) through (5.60) now involve only eight unknowns, assuming that the radii of curvature of the four interfaces are known. We have solved this problem symbolically using Mathematica (Mathematica, 2003).

At this point, we have solved for stress as a function of the radii of curvature and the surface energies. Our objective is to find a relation between $R^{(o,m)}$ and the surface energies. In order to do that, we must first determine the the r -component of displacement of that interface.

As Slattery and Lagoudas (2005) and Oh et al. (2005) have discussed, the metal and the oxide phases will have different reference configurations. In this case, the reference configuration for the metal is that portion of the initial metal beam remaining after oxidation. Since we know only the reference configuration of the metal, we will discuss only the r -component of the displacement of the metal (Little, 1999, p. 159):

$$u_r^{(m)} = \frac{1}{E^{(m)}} \left\{ 2c_3 (1 - \nu^{(m)}) R^{(o,m)} + F \sin \theta + G \cos \theta \right. \\ \left. + c_2 \left[(1 - \nu^{(m)}) (2R^{(o,m)} \ln R^{(o,m)} r - R^{(o,m)}) - 2\nu^{(m)} R^{(o,m)} \right] \right\} \quad (5.64)$$

where, $E^{(m)}$ and $\nu^{(m)}$ are the Young's modulus and the Poisson's ratio of the metal.

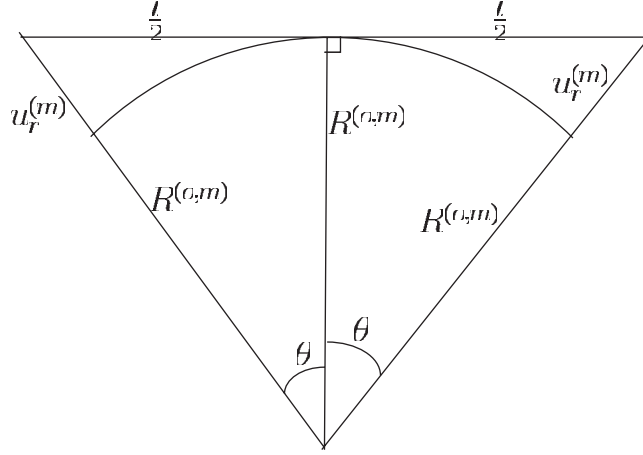


Fig. 9. The relationship of the r -component of displacement u_r , the radius of curvature R , and the length of the beam l .

Since $u_r^{(m)}$ is symmetric with respect to $\theta = 0$, we conclude that

$$F = 0 \quad (5.65)$$

Assumption 4' requires that

$$\text{at } \theta = 0, \quad u_r^{(m)} = 0 \quad (5.66)$$

and

$$\begin{aligned} G = & -2c_3 (1 - \nu^{(m)}) R^{(o,m)} \\ & - c_2 [(1 - \nu^{(m)}) (2R^{(o,m)} \ln R^{(o,m)} - R^{(o,m)}) - 2\nu^{(m)} R^{(o,m)}] \end{aligned} \quad (5.67)$$

From Fig. 9, we see

$$\cos \theta = \frac{R^{(o,m)}}{R^{(o,m)} - u_r^{(m)}} \quad (5.68)$$

Substitute (5.65), (5.67), and (5.68) into (5.64), we have

$$\begin{aligned} u_r^{(m)} = & \frac{1}{E^{(m)}} \left\{ 2c_3 (1 - \nu^{(m)}) R^{(o,m)} + \frac{G R^{(o,m)}}{R^{(o,m)} - u_r^{(m)}} \right. \\ & \left. + c_2 [(1 - \nu^{(m)}) (2R^{(o,m)} \ln R^{(o,m)} - R^{(o,m)}) - 2\nu^{(m)} R^{(o,m)}] \right\} \end{aligned} \quad (5.69)$$

This equation can be solved for $u_r^{(m)}$.

From Fig. 9, we find that:

$$\frac{l^2}{4} + R^{2(o,m)} = (R^{(o,m)} - u_r^{(m)})^2 \quad (5.70)$$

The length of the beam is

$$l = 2R^{(o,m)} \theta \quad (5.71)$$

In practice, θ in Fig. 9 is very small. We will take only the first two terms of the Taylor expansion of it,

$$\cos \theta = 1 - \frac{\theta^2}{2} \quad (5.72)$$

From (5.68) and (5.72), we find that

$$\theta^2 = \frac{2u_r^{(m)}}{R^{(o,m)} - u_r^{(m)}} \quad (5.73)$$

From (5.70), (5.71), and (5.73), we find

$$3R^{(o,m)} - u_r^{(m)} = 0 \quad (5.74)$$

From (5.69) and (5.74), we can determine $R^{(o,m)}$. Because

$$R^{(a,o)} = R^{(o,m)} - x_1 \quad (5.75)$$

we also have $R^{(a,o)}$.

Solution two

As an alternative to $C^{(a,o)} = C^{(o,a)} = 0$ in solution one, the second solution assumes

$$C^{(m,o)} = C^{(o,m)} = 0 \quad (5.76)$$

An experiment for measuring the surface energies

EerNisse (1979) studied oxidation of (100) *Si* wafers. The cleaned wafers were oxidized on both sides until the SiO_2 was 4000 \AA thick. The oxide on one side was removed, leaving a two-layer beam of total thickness $1.5 \times 10^{-2} \text{ cm}$. New SiO_2 grows on the back surface at $900 \text{ }^\circ\text{C}$ degree. In a subsequent operation at $900 \text{ }^\circ\text{C}$, the curvature of the beam was measured in the oven as a thin layer of SiO_2 was formed on the bare side.

In his experiments, $R^{(o,m)}$ is a weak function of x_1 (EerNisse, 1979, fig. 2), and

$$R^{(o,m)} \approx R^{(a,m)} = 5.03 \text{ m} \quad (5.77)$$

where $R^{(a,m)}$ is the radius of curvature at the air-Si interface at the beginning of the experiment.

From (5.69) and (5.74), we used Mathematica (2003) symbolically determine

$$\frac{d(1/R^{(o,m)})}{dx_1}$$

in the limit as $x_1/x_2 \rightarrow 0$ as a function of the material properties, including $\gamma^{(o,a)}$ and $\gamma^{(o,m)}$. For the experimental observations of EerNisse (1979, figure 2)

$$\frac{d(1/R^{(o,m)})}{dx_1} = 5.8 \times 10^5 \text{ m}^{-2} \quad (5.78)$$

Girifalco and Good (1957) and Adamson (1976) proposed that $\gamma^{(a,o)}$ can be estimated as

$$\gamma^{(a,o)} = \gamma^{(m,o)} + \gamma^{(a,m)} - 2(\gamma^{(a,m)}\gamma^{(m,o)})^{1/2} \quad (5.79)$$

The surface energy of the air-silicon interface at 300 K is 1.4 N/m (Israelachvili, 2000, p. 205). We will assume that the surface energy is proportional to the Hamaker constant (Israelachvili, 2000, p. 202) and that the Hamaker constant is proportional

Table I. Mechanical properties of silicon and silicon dioxide (Nikanorov et al., 1972)

$E^{(m)}(Pa)$	$\nu^{(m)}$	$\rho^{(m)}(kg/m^3)$	$\rho^{(o)}(kg/m^3)$
119.7	0.265	2330	2198

to the absolute temperature (Israelachvili, 2000, p. 181). This suggests that at 1173 K,

$$\gamma^{(a,m)} = \frac{1173}{300} \times 1.4 = 5.5 \text{ N/m}$$

Using (5.79), we can eliminate $\gamma^{(a,o)}$ in terms of $\gamma^{(m,o)}$:

$$\gamma^{(a,o)} = \gamma^{(m,o)} + 5.5 - 2(5.5\gamma^{(m,o)})^{1/2} \quad (5.80)$$

Some mechanical properties of silicon and silicon dioxide at 1173 K listed in Table I, where $E^{(m)}$ is the Young's Modulus of silicon, $\nu^{(m)}$ the Poisson's ratio of silicon, $\rho^{(m)}$ the density of the silicon, and $\rho^{(o)}$ the density of silicon dioxide.

Using the symbolic expression for

$$\frac{d(1/R^{(o,m)})}{dx_1}$$

from Mathematica (2003) and the experimental value of this slope from (5.78), we find

$$\gamma^{(m,o)} = 106.8 \text{ N/m} \quad (5.81)$$

and from (5.80), we find

$$\gamma^{(a,o)} = 62.9 \text{ N/m} \quad (5.82)$$

Solution two give us a physically unrealistic (negative) number.

Unfortunately, there are no previous estimates with which to compare these results.

c. Oxidation equally on two sides of a plate

When a two-dimensional plate is oxidized on both sides, it will not bend. Our objective here is to determine the stress distributions in the three phases.

In this case, the Airy stress function is (Little, 1999, p. 108)

$$\varphi = A_1 + B_1x + C_1x^2 + D_1x^3 + B_2y + C_2y^2 + D_2y^3 + E_1xy + E_2x^2y + E_3xy^2 \quad (5.83)$$

and the corresponding components of stress in the metal and oxide are

$$\sigma_{xx}^{(m)} = c_1 + c_2y \quad (5.84)$$

$$\sigma_{yy}^{(m)} = c_3 + c_4y \quad (5.85)$$

$$\sigma_{xx}^{(o)} = c_5 + c_6y \quad (5.86)$$

$$\sigma_{yy}^{(o)} = c_7 + c_8y \quad (5.87)$$

The plate is symmetric with $y = 0$ plane.

The jump momentum balances (Slattery, 1990, p. 252) require at the air-oxide interfaces

$$\text{at } y = \pm l^{(o,a)} : \sigma_{yy}^{(o)} = 0 \quad (5.88)$$

and at the oxide-metal interfaces

$$\text{at } y = \pm l^{(m,o)} : 0 = \sigma_{yy}^{(o)} - \sigma_{yy}^{(m)} \quad (5.89)$$

From (5.22) and (5.23), the coherent conditions on the air-oxide, oxide-metal interfaces are described as

$$\text{at } y = \pm l^{(o,a)} : \frac{\sigma_{xx}^{(o)} + \sigma_{yy}^{(o)}}{\rho_0^{(o)}} = C^{(a,o)} \quad (5.90)$$

$$\text{at } y = \pm l^{(m,o)} : \frac{\sigma_{xx}^{(o)} + \sigma_{yy}^{(o)}}{\rho_0^{(o)}} - \frac{\sigma_{xx}^{(m)} + \sigma_{yy}^{(m)}}{\rho_0^{(m)}} = C^{(m,o)} \quad (5.91)$$

Here, $C^{(a,o)}$ and $C^{(m,o)}$ are the constants defined by (5.22) and (5.23) for the air-oxide and metal-oxide interface.

Up to this point, we have eight equations (5.88) through (5.91) in ten unknowns c_1 through c_8 , $C^{(a,o)}$ and $C^{(m,o)}$. One solution to this problem is:

$$C^{(a,o)} = C^{(m,o)} = c_1 = c_2 = \dots = c_8 = 0 \quad (5.92)$$

It means there is no stress in this two-sided oxidation plate. Equation (5.88) and (5.89) suggest that it is physically correct.

d. Oxidation on the exterior of a circular cylinder

Oh et al. (2005) have analyzed oxidation on the exterior surface of a metal cylinder, assuming that the oxide and the metal are in a state of plane stress. They found

$$\sigma_{rr}^{(m)} = \sigma_{\theta\theta}^{(m)} = C_1 \quad (5.93)$$

$$\sigma_{rr}^{(o)} = \frac{C_2}{r^2} + C_3 \quad (5.94)$$

$$\sigma_{\theta\theta}^{(o)} = -\frac{C_2}{r^2} + C_3 \quad (5.95)$$

At each point on the metal-oxide interface, the jump momentum balance (Slatery, 1990, p. 252) tells us

$$\text{at } r = R^{(m,o)} : \frac{\gamma^{(m,o)}}{R^{(m,o)}} = \sigma_{rr}^{(o)} - \sigma_{rr}^{(m)} \quad (5.96)$$

Here, $\gamma^{(m,o)}$ is the surface energy of the metal-oxide interface; $R^{(m,o)}$ is the radius of this interface. The jump momentum balance at the oxide-air interface requires

$$\text{at } r = R^{(o,a)} : -\sigma_{rr}^{(o)} = \frac{\gamma^{(o,a)}}{R^{(o,a)}} \quad (5.97)$$

where, $\gamma^{(o,a)}$ and $R^{(o,a)}$ are the surface energy and radius of the oxide-air interface. For simplicity, we are neglecting the effect of atmospheric pressure.

Equations (5.96) and (5.97) must be solved consistent with (5.22) and (5.23) in the form

$$\text{at } r = R^{(m,o)} : \text{tr} \left(\frac{\sigma^{(m)}}{\rho_0^{(m)}} \right) - \text{tr} \left(\frac{\sigma^{(o)}}{\rho_0^{(o)}} \right) = C^{(m,o)} \quad (5.98)$$

$$\text{at } r = R^{(o,a)} : \text{tr} \left(\frac{\sigma^{(o)}}{\rho_0^{(o)}} \right) = C^{(o,a)} \quad (5.99)$$

Here, $C^{(m,o)}$ and $C^{(o,a)}$ are the constants defined by (5.22) and (5.23) for the metal-oxide and oxide-air interface.

This leaves us with four equations (5.96) through (5.99) in five unknowns C_1 through C_3 , $C^{(m,o)}$ and $C^{(o,a)}$. There are several solutions.

Surface energies are neglected Oh et al. (2005) assumed that $\gamma^{(m,o)} = \gamma^{(o,a)} = 0$. Either $C^{(m,o)} = 0$ or $C^{(o,a)} = 0$, since there are only four equations in five unknowns. We conclude that the only solution is

$$C_1 = C_2 = C_3 = 0 \quad (5.100)$$

in which case there is no stress in the oxide-metal cylinder.

In addition to neglecting the surface energies, Oh et al. (2005) did not use the compatibility conditions defined by (5.22) and (5.23), and they found that the stresses were non-zero. Unfortunately, there are no experimental data that would allow us to distinguish between these solutions, but we do know that the surface energies should be non-zero.

Surface energies are not neglected Since there are four equations to be solved in five unknowns, there are two possible solutions.

The first solution corresponds to $C^{(m,o)} = 0$, in which case we find

$$\begin{aligned}
C^{(o,a)} &= -\frac{2\gamma^{(m,o)}R^{(m,o)} + 2\gamma^{(o,a)}R^{(o,a)}}{\rho^{(m)}R^{(m,o)2} - \rho^{(o)}R^{(m,o)2} + \rho^{(o)}R^{(o,a)2}} \\
\sigma_{\theta\theta}^{(o)} &= \frac{\gamma^{(o,a)}\rho^{(m)} - 2\gamma^{(m,o)}\rho^{(o)} - 2\gamma^{(o,a)}\rho^{(o)}}{\rho^{(o)}R^{(o,a)}} \\
\sigma_{rr}^{(o)} &= -\frac{\gamma^{(o,a)}}{R^{(o,a)}} \\
\sigma_{rr}^{(m)} = \sigma_{\theta\theta}^{(m)} &= -\frac{\gamma^{(m,o)} + \gamma^{(o,a)}}{R^{(o,a)}}
\end{aligned} \tag{5.101}$$

We reject this solutions, since intuitively we expect $\sigma_{\theta\theta}^{(o)}$ and $\sigma_{\theta\theta}^{(m)}$ to have opposite signs.

The second solution corresponds to $C^{(o,a)} = 0$, and

$$\begin{aligned}
C^{(m,o)} &= -\frac{2\gamma^{(m,o)}R^{(m,o)} + 2\gamma^{(o,a)}R^{(o,a)}}{\rho^{(m)}R^{(m,o)2}} \\
\sigma_{\theta\theta}^{(o)} &= \frac{2\gamma^{(m,o)}}{R^{(o,a)}} \\
\sigma_{rr}^{(o)} &= -\frac{\gamma^{(o,a)}}{R^{(o,a)}} \\
\sigma_{rr}^{(m)} = \sigma_{\theta\theta}^{(m)} &= -\frac{\gamma^{(m,o)} + \gamma^{(o,a)}}{R^{(o,a)}}
\end{aligned} \tag{5.102}$$

The signs of these stresses are in agreement with our intuition as well as with the signs of the stresses determined by Oh et al. (2005).

D. The generalized Clausius-Clapeyron equation

Here we wish to extend the Clausius-Clapeyron equation derived for fluid and amorphous solid systems (Denbigh, 1963, p. 197) to systems involving crystalline solids. In particular, we wish to examine a sequence of system formed as temperature changes, in which all interfaces are governed by (5.20). In addition to the assumptions made in deriving that equation, we will assume each system is at equilibrium. It is important to recognize that, for a system at equilibrium, P , T , and chemical potential $\mu_{(A)}$ are

uniform throughout the system.

At equilibrium, the derivative of (5.20) with respect to time is reduced to,

$$\Delta\hat{V}\frac{dP}{dt} - \frac{\Delta\hat{H}}{T}\frac{dT}{dt} + \frac{d}{dt}\left[\text{tr}\left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{2\rho_0^{(B)}}\right) - \text{tr}\left(\frac{\mathbf{T}^{(A)} + P\mathbf{I}}{2\rho_0^{(A)}}\right)\right] = 0 \quad (5.103)$$

For a fluid or an amorphous solid system, the elastic component of stress is zero at equilibrium, if

$$\frac{\Delta\hat{H}}{T\Delta\hat{V}} = \text{a constant} \quad (5.104)$$

Equation (5.103) reduces to

$$\frac{d}{dt}\left[P - \left(\frac{\Delta\hat{H}}{T\Delta\hat{V}}\right)T\right] = 0 \quad (5.105)$$

or

$$P - \left(\frac{\Delta\hat{H}}{T\Delta\hat{V}}\right)T = \text{a constant} \quad (5.106)$$

If we only consider a limited range of temperature that in which the constant in (5.106) will not change with temperature. We can get a common form of the Clausius-Clapeyron equation (Denbigh, 1963, p. 197)

$$\frac{dP}{dT} = \frac{\Delta\hat{H}}{T\Delta\hat{V}} \quad (5.107)$$

where $\Delta\hat{H}$ is the latent heat of transformation.

For a crystalline system at a constant thermodynamic pressure, if

$$\frac{\Delta\hat{H}}{T} = \text{a constant} \quad (5.108)$$

Equation (5.103) is reduced to

$$\frac{d}{dt}\left\{\left[\text{tr}\left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{2\rho_0^{(B)}}\right) - \text{tr}\left(\frac{\mathbf{T}^{(A)} + P\mathbf{I}}{2\rho_0^{(A)}}\right)\right] - \left(\frac{\Delta\hat{H}}{T}\right)T\right\} = 0 \quad (5.109)$$

or

$$\left[\text{tr} \left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{2\rho_0^{(B)}} \right) - \text{tr} \left(\frac{\mathbf{T}^{(A)} + P\mathbf{I}}{2\rho_0^{(A)}} \right) \right] - \left(\frac{\Delta\hat{H}}{T} \right) T = \text{a constant} \quad (5.110)$$

If we also only consider a limited range of temperature in which the constant in (5.110) will not change with temperature, we conclude that

$$\frac{d}{dT} \left[\text{tr} \left(\frac{\mathbf{T}^{(B)} + P\mathbf{I}}{2\rho_0^{(B)}} \right) - \text{tr} \left(\frac{\mathbf{T}^{(A)} + P\mathbf{I}}{2\rho_0^{(A)}} \right) \right] = \frac{\Delta\hat{H}}{T} \quad (5.111)$$

1. Experiments of Sehitoglu et al. (2001)

Beginning with a 51.5at%Ni – Ti austenite single crystal, Sehitoglu et al. (2001) lowered the temperature and applied an uniaxial stress to create a sequence of equilibrium, two-phase mixtures of martensite and austenite at atmospheric pressure. The equilibrium temperature T for austenite and martensite phase transformation was approximated as (Funakubo 1984; Tong and Wayman 1974),

$$T = \frac{M_s + A_f}{2} \quad (5.112)$$

where M_s is the martensite start temperature and A_f is the austenite finish temperature.

Referring to Fig. 10, we see that one solution of the differential momentum balance

$$\text{div}\mathbf{T} = \mathbf{0} \quad (5.113)$$

and the jump momentum balances at the austenite-martensite interface requires that

$$\mathbf{T}^{(A)}\xi^{(A)} + \mathbf{T}^{(B)}\xi^{(B)} = \mathbf{0} \quad (5.114)$$

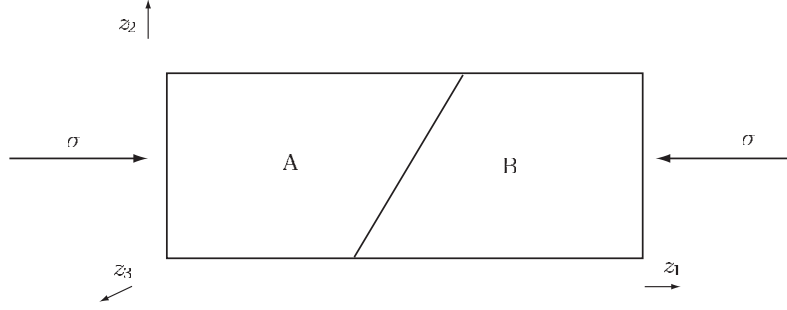


Fig. 10. The schematic description of the equilibrium state of austenite-martensite phase transition under uniaxial stress σ at certain temperature. The crystal is three-dimensional, exposed to the atmosphere on four sides. Phase A is austenite and B is martensite. The shape of the interface does not have to be the same shape as the figure, it is not specified in our analysis.

together with the appropriate boundary conditions is

$$\begin{aligned}
 T_{11}^{(A)} &= \sigma \\
 T_{22}^{(A)} &= T_{33}^{(A)} = 0 \\
 T_{ij,i \neq j}^{(A)} &= 0
 \end{aligned} \tag{5.115}$$

and

$$\begin{aligned}
 T_{11}^{(B)} &= \sigma \\
 T_{22}^{(B)} &= T_{33}^{(B)} = 0 \\
 T_{ij,i \neq j}^{(B)} &= 0
 \end{aligned} \tag{5.116}$$

This means that

$$\text{tr}(\mathbf{T}^{(A)}) = \text{tr}(\mathbf{T}^{(B)}) = \sigma \tag{5.117}$$

and (5.111) reduces to

$$\frac{d\sigma}{dT} = \frac{2\rho_0^{(A)}\rho_0^{(B)}\Delta H}{\left(\rho_0^{(B)} - \rho_0^{(A)}\right)T} \tag{5.118}$$

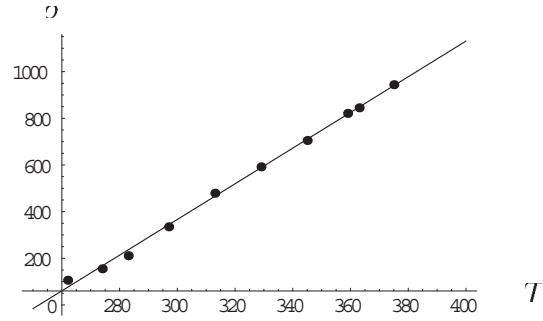


Fig. 11. σ , defined by (5.117), as a function of temperature T under a uniaxial stress in the [100] direction. The straight line is (5.118), which assumes that the latent heat ΔH is a linear function of T .

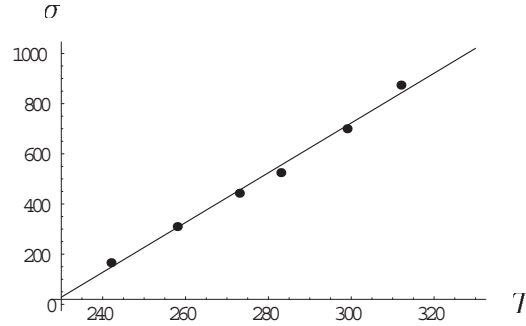


Fig. 12. σ , defined by (5.117), as a function of temperature T under a uniaxial stress in the [122] direction. The straight line is (5.118), which assumes that the latent heat ΔH is a linear function of T .

Equations (5.118) is compared with the experimental data of Sehitoglu et al. (2001) in Figs. 11 and 12. Our conclusion is that ΔH is slightly dependent upon the orientation of the crystal with respect to the axis of compression or extension.

For crystalline materials with the same density in the reference state, for example, the martensite-martensite transformation, (5.111) is changed to

$$\frac{d}{dT} [\text{tr}(\mathbf{T}^{(B)} - \mathbf{T}^{(A)})] = \frac{2\rho_0\Delta\hat{H}}{T} \quad (5.119)$$

At the equilibrium condition,

$$\text{tr}(\mathbf{T}^{(B)} - \mathbf{T}^{(A)}) = 0 \quad (5.120)$$

Substitute (5.120) into (5.119), we get

$$\frac{2\rho_0\Delta\hat{H}}{T} = 0 \quad (5.121)$$

We find

$$\Delta\hat{H} = 0$$

It means that the latent heat is zero when there is no phase change. It is physically true.

E. Discussion

Equations (5.22) and (5.23) represent new constraints on the stress at an interface where at least one of the adjoining phase is a crystalline solid. The constants introduced in (5.22) and (5.23) are unknown, and they must be determined as part of the solution of a problem. Four examples in the context of oxidation are give, but unfortunately there are no experimental data available with which to check the results.

In analyzing these oxidation problems, we have demonstrated that all residual stresses are zero, unless we recognize that the surface energies at the interfaces are non-zero.

To our knowledge, there have been no experiments previously proposed to measure the surface energy of an interface between two crystalline solids. We have proposed that the bending of a beam with unequal oxide thicknesses can be used as such an experiment, and we have demonstrated the analysis with the data of EerNisse

(1979) for the silicon-silicon dioxide system.

Again starting with (5.20), a Clausius-Clapeyron equation (5.107) for fluids and amorphous solids, a well-known form of the Clausius-Clapeyron equation (Denbigh, 1963), has been derived for two phases in equilibrium.

In discussing crystalline solids, we assume that the stress-deformation behavior (5.6) derived by Slattery and Lagoudas (2005) applies.

For the special case where both phases are crystalline solids at a uniform pressure, (5.103) reduces to (5.111), which is reduced to either (5.118) under a uniaxial stress. In comparison with the experimental data available, it implies that, for the system studied, the latent heat of transformation $\Delta\hat{H}$ is slightly dependent upon the orientation of the crystal with respect to the axis of compression or extension.

CHAPTER VI

SUMMARY

In this dissertation, we studied the thermodynamics of the multicomponent, elastic, crystalline materials with the presence of the electric-magnetic fields and its applications. The following results are derived:

1. The equilibrium condition of the multicomponent, elastic, crystalline solids under stress and electric and magnetic fields are investigated. A new constitutive equation of stress deformation behavior of a single crystal with the existence of electromagnetic fields under stress are derived.
2. An extended Gibbs equation. Gibbs-Duhem equation, and an extended Gibbs phase rule are derived, which can help predict the phase transition of the crystalline solids under stress and electromagnetic fields.
3. The mechanism of the magnetic single crystal actuator was studied. The dynamic actuation process was modeled. The relationship of actuation time and stress are studied.
4. An interfacial condition for interfaces with crystalline solids are derived for a static or quasi-static system. The stress-strain distribution of the oxidation of a beam, the exterior of a cylinder are studied. It showed that the surface energies play important roles in the distribution of the residual stress of the oxidation. The oxidation on two sides of a plate with different thickness was proposed as an experiment of measuring the surface energies of the crystalline-crystalline solid interfaces.
5. A generalized Clausius-Clapeyron equation was derived for an equilibrium crystalline-

crystalline solids system. It showed that the trace of the elastic portion of stress of the two different phases and the temperature have a linear relationship, which agrees with the experimental data.

NOTATION

Roman Symbols

\hat{A}	Helmholtz free energy per unit mass
\check{A}	Helmholtz free energy per unit volume
\mathbf{B}	magnetic flux
\mathbf{C}	relative right Cauchy-Green strain tensor defined by (2.6)
$C^{(o,a)}$	the constant in the coherent condition of the oxide-air interface
$C^{(m,o)}$	the constant in the coherent condition of the metal-oxide interface
$C^{(a,m)}$	the constant in the coherent condition of the air-metal interface
\mathbf{e}	strain tensor defined in Appendix A
$\mathbf{e}_{(i)}^{(j)}$	deformed lattice vectors for phase j defined by (2.2)
\hat{E}	sum of internal energy and kinetic energy per unit mass as defined in equation (2.58)
$\mathbf{E}_{(i)}^{(j)}$	unit lattice vectors in natural (equilibrium) configuration for phase j
$\mathbf{E}_{(i)}^{(0)}$	lattice vectors in natural (equilibrium) configuration for the parent phase 0 (as seen in the current frame of reference)
E	Young's modulus
f	degrees of freedom
$\mathbf{f}_{(A)}$	body force per unit mass acting on species A
	body force per unit mass
\mathbf{F}	deformation gradient
\mathbf{H}	displacement gradient defined in Appendix A
\mathbf{I}	identity tensor

$I_{(mn)}^{(1)}$	scalar invariants defined by (2.5)
$I_{(mn)}^{(2)}$	scalar invariants defined by (2.8)
$I_{(mn)}^{(3)}$	scalar invariants defined by (2.9)
$I^{(4)}$	scalar invariants defined by (2.10)
$I^{(5)}$	scalar invariants defined by (2.11)
$I^{(6)}$	scalar invariants defined by (2.12)
J	number of homogeneous chemical reactions
K	number of heterogeneous chemical reactions
M	number of non-zero invariants described by (2.97)
\mathbf{M}	Magnetization of the materials
$M_{(A)}$	molecular weight of species A
N	number of species
p	number of phases
$p^{(c)}$	number of crystalline phases
P	thermodynamic pressure defined by (2.18)
\mathbf{P}	electric polarization
Q	number of internal, coherent, solid-solid phase interfaces at which elastic components of stress exist. In the absence of deformation, $Q = 0$.
$r_{(A,j)}$	rate of production of species A by homogeneous reaction j
$r_{(A,k)}^\sigma$	rate of production of species A by heterogeneous reaction k

R	region occupied by body (Because there is no mass transfer at the boundary, we do not distinguish between the region occupied by a body of species A and the region occupied by the multicomponent body, the material particles of which move with the mass-averaged velocity \mathbf{v} .)
$R^{(o,a)}$	the radius of the oxide-air interface
$R^{(m,o)}$	the radius of the metal-oxide interface
$R^{(a,m)}$	the radius of the air-metal interface
S	bounding surface of body
\hat{S}	entropy per unit mass
t	time
T	temperature
\mathbf{T}	stress tensor
\mathbf{u}	time rate of change of position following a surface point (Slattery, 1999, p. 24); used as displacement in Appendix A
\hat{U}	internal energy per unit mass
\mathbf{v}	mass average velocity
$\mathbf{v}_{(A)}$	velocity of species A
\hat{V}	volume per unit mass
\mathbf{z}	position vector
\mathbf{z}_κ	position of material particle in reference configuration
$Z_{(A)}$	defined by (2.43)
Z_c	defined by (2.68)
Z_{mag}	defined by (2.63)
Z_{mom}	defined by (2.47)

Z_e	defined by (2.57)
\mathbf{Z}_m	defined by (2.45)
ϵ	dimensionless parameters representing the disturbance from equilibrium
$\lambda_{(A)}$	Lagrangian multiplier
$\lambda_{(c)}$	Lagrangian multiplier
$\lambda_{(e)}$	Lagrangian multiplier
$\lambda_{(mag)}$	Lagrangian multiplier
$\lambda_{\mathbf{m}}$	Lagrangian multiplier
$\mu_{(A)}$	chemical potential for species A defined by (2.19)
$\mu_{(I^{(1)},mn)}$	defined by (2.20)
$\mu_{(I^{(2)},mn)}$	defined by (2.21)
$\mu_{(I^{(3)},mn)}$	defined by (2.22)
$\mu_{(I^{(4)})}$	defined by (2.23)
$\mu_{(I^{(5)})}$	defined by (2.24)
$\mu_{(I^{(6)})}$	defined by (2.25)
$\nu_{(A,j)}$	stoichiometric coefficient for species A in homogeneous reaction j . The stoichiometric coefficient is taken to be a negative number for a reactant, positive for a product.
$\nu_{(A,k)}^{(\sigma)}$	stoichiometric coefficient for species A in heterogeneous reaction k . The stoichiometric coefficient is taken to be a negative number for a reactant, positive for a product.
ξ	unit normal to phase interface
Σ	phase interface
ρ	overall mass density

$\rho_{(A)}$	mass density of species A
ϕ_A	potential energy of species A introduced in (2.50)
$\psi_{(j)}$	reaction coordinate of homogeneous reaction j introduced in (2.35)
$\psi_{(j)}^{(\sigma)}$	reaction coordinate of heterogeneous reaction j introduced in (2.39)
$\omega_{(A)}$	mass fraction of species A or $\rho_{(A)}/\rho$
$\gamma^{(o,a)}$	surface energy of the oxide-air interface
$\gamma^{(m,o)}$	surface energy of the metal-oxide interface
$\gamma^{(a,m)}$	surface energy of the air-metal interface
σ	the magnitude of the uniaxial stress applied on the sample
σ	the stress includes atmospheric pressure defined by (5.24)
θ	the angle of the beam
ν	Poisson's ratio
φ	Airy stress function
$[a\xi]$	$= a^{(1)}\xi^{(1)} + a^{(2)}\xi^{(2)}$ at an interface separating phases 1 and 2. Here $a^{(i)}$ is the value of the quantity a in phase i adjacent to the interface Σ ; $\xi^{(i)}$ is the unit normal to the interface pointing into phase i .
dA	indicates that an area integration should be performed
dV	indicates that a volume integration should be performed. The integrand will be discontinuous generally at phase interfaces.
$\frac{d_{(v)}}{dt}$	derivative following a particle that moves with the mass-averaged velocity \mathbf{v}
grad	gradient with respect to reference configuration
$\nabla_{(\sigma)}$	denotes the surface gradient operation (Slattery, 1999, p. 1075)

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APPENDIX A

Slattery and Si (2005) set Holmholtz free energy as a function of temperature, density, species' mass fractions, crystals' reference lattice vector, deformed lattice vector, magnetization, and electric polarization. In order to satisfy the implications of the principle of frame indifference (Truesdell and Noll, 1965, p. 44), they defined a series of invariants: $I_{(mn)}^{(1)}$, $I_{(m)}^{(2)}$, $I_{(m)}^{(3)}$, $I^{(4)}$, $I^{(5)}$, and $I^{(6)}$. They then define A as a function of T , ρ , ω , and invariants.

$$\begin{aligned}
I_{(mn)}^{(1)} &\equiv \mathbf{e}_{(m)} \cdot \mathbf{e}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\
&= \mathbf{F}\mathbf{E}_{(m)} \cdot \mathbf{F}\mathbf{E}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\
&= \mathbf{E}_{(m)} \cdot \mathbf{F}^T \mathbf{F}\mathbf{E}_{(n)} - \mathbf{E}_{(m)} \cdot \mathbf{E}_{(n)} \\
&= \mathbf{E}_{(m)} \cdot (\mathbf{C} - \mathbf{I})\mathbf{E}_{(n)} \quad m = 1, \dots, 3 \text{ and } n = 1, \dots, m
\end{aligned} \tag{A.1}$$

$$I_{(m)}^{(2)} \equiv \mathbf{e}_{(m)} \cdot \mathbf{M} - \mathbf{E}_{(m)} \cdot \mathbf{M} \tag{A.2}$$

$$I_{(m)}^{(3)} \equiv \mathbf{e}_{(m)} \cdot \mathbf{P} - \mathbf{E}_{(m)} \cdot \mathbf{P} \tag{A.3}$$

$$I^{(4)} \equiv \mathbf{M} \cdot \mathbf{M} - \mathbf{M}_{(0)} \cdot \mathbf{M}_{(0)} \tag{A.4}$$

$$I^{(5)} \equiv \mathbf{P} \cdot \mathbf{P} - \mathbf{P}_{(0)} \cdot \mathbf{P}_{(0)} \tag{A.5}$$

$$I^{(6)} \equiv \mathbf{M} \cdot \mathbf{P} - \mathbf{M}_{(0)} \cdot \mathbf{P}_{(0)} \tag{A.6}$$

Slattery and Lagoudas (2005) have already found that density is a function of the invariants. In other words, ρ , $I_{(11)}$, $I_{(22)}$, and $I_{(33)}$ are not independent.

$$\begin{aligned}
\rho &= \frac{\rho_0}{\sqrt{\det \mathbf{C}}} \\
&= \rho_0 - \frac{\rho_0}{2} \left(I_{(11)}^{(1)} + I_{(22)}^{(1)} + I_{(33)}^{(1)} \right) + \dots
\end{aligned} \tag{A.7}$$

This permits us to write the Holmholtz free energy as:

$$\hat{A} = \hat{A} \left(T, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}^{(1)}, \dots, I_{(33)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I_{(1)}^{(3)}, \dots, I_{(3)}^{(3)}, I^{(4)}, I^{(5)}, I^{(6)} \right) \quad (\text{A.8})$$

$$\check{A} = \check{A} \left(T, \omega_{(1)}, \dots, \omega_{(N-1)}, I_{(11)}^{(1)}, \dots, I_{(33)}^{(1)}, I_{(1)}^{(2)}, \dots, I_{(3)}^{(2)}, I_{(1)}^{(3)}, \dots, I_{(3)}^{(3)}, I^{(4)}, I^{(5)}, I^{(6)} \right) \quad (\text{A.9})$$

in which $\omega_{(A)}$ is the mass fraction of species A . From the differential entropy inequality (Slattery, 1999, p. 438), we conclude

$$\hat{S} = - \left(\frac{\partial \hat{A}}{\partial T} \right)_{\rho, \omega_{(B)} (B=1, \dots, N-1), I_{(mn)}^{(1)}, \dots} \quad (\text{A.10})$$

We also require

$$\mu_{(I^{(1)}, mn)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(mn)}^{(1)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(rs)}^{(1)} (rs \neq mn), I_{(m)}^{(2)}, I_{(m)}^{(3)}, \dots} \quad (\text{A.11})$$

and

$$\mu_{(I^{(2)}, m)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(m)}^{(2)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(mn)}^{(1)}, I_{(r)}^{(2)} (r \neq m), I_{(m)}^{(3)}, \dots} \quad (\text{A.12})$$

$$\mu_{(I^{(3)}, m)} \equiv \left(\frac{\partial \hat{A}}{\partial I_{(m)}^{(3)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), I_{(rs)}^{(1)}, I_{(m)}^{(2)}, I_{(r)}^{(3)} (r \neq m), \dots} \quad (\text{A.13})$$

$$\mu_{(I^{(4)})} \equiv \left(\frac{\partial \hat{A}}{\partial I^{(4)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), \dots, I_{(r)}^{(3)}, I^{(5)}, \dots} \quad (\text{A.14})$$

$$\mu_{(I^{(5)})} \equiv \left(\frac{\partial \hat{A}}{\partial I^{(5)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), \dots, I^{(4)}, I^{(6)}} \quad (\text{A.15})$$

$$\mu_{(I^{(6)})} \equiv \left(\frac{\partial \hat{A}}{\partial I^{(6)}} \right)_{T, \rho, \omega_{(B)} (B \neq N), \dots, I^{(5)}} \quad (\text{A.16})$$

With these expressions, the differentials of (A.8) and (A.9) may consequently be expressed as

$$\begin{aligned}
d\hat{A} = & -\hat{S} dT + \sum_{B=1}^{N-1} \left(\frac{\partial \hat{A}}{\partial \omega_{(B)}} \right)_{T, \hat{V}, \omega_{(C)} (C \neq B, N), I_{(i)}^{(1)}} d\omega_{(B)} \\
& + \sum_{m=1}^3 \left[\left(\sum_{n=1}^3 \mu_{(I^{(1)}, mn)} dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2)}, m)} dI_{(m)}^{(2)} + \mu_{(I^{(3)}, m)} dI_{(m)}^{(3)} \right] \\
& + \mu_{(I^{(4)})} dI^{(4)} + \mu_{(I^{(5)})} dI^{(5)} + \mu_{(I^{(6)})} dI^{(6)}
\end{aligned} \tag{A.17}$$

$$\begin{aligned}
d\check{A} = & -\frac{\hat{S}}{\hat{V}} dT + \sum_{B=1}^N \mu_{(B)} d\rho_{(B)} \\
& + \frac{1}{\hat{V}} \left\{ \sum_{m=1}^3 \left[\left(\sum_{n=1}^3 \mu_{(I^{(1)}, mn)} dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2)}, m)} dI_{(m)}^{(2)} + \mu_{(I^{(3)}, m)} dI_{(m)}^{(3)} \right] \right. \\
& \left. + \mu_{(I^{(4)})} dI^{(4)} + \mu_{(I^{(5)})} dI^{(5)} + \mu_{(I^{(6)})} dI^{(6)} \right\}
\end{aligned} \tag{A.18}$$

Comparison of the coefficients in (A.17) and (A.18) gives

$$\left(\frac{\partial \hat{A}}{\partial \omega_{(B)}} \right)_{T, \rho, \omega_{(C)} (C \neq B, N), I_{(mn)}, \dots} = \mu_{(B)} - \mu_{(N)} \tag{A.19}$$

as well as

$$\hat{A} = \sum_{B=1}^N \mu_{(B)} \omega_{(B)} \tag{A.20}$$

Equations (A.19) and (A.20) yield the *modified Gibbs equation*

$$\begin{aligned}
d\hat{A} = & -\hat{S} dT + \sum_{B=1}^{N-1} (\mu_{(B)} - \mu_{(N)}) d\omega_{(B)} \\
& + \sum_{m=1}^3 \left[\left(\sum_{n=1}^2 \mu_{(I^{(1)}, mn)} dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2)}, m)} dI_{(m)}^{(2)} + \mu_{(I^{(3)}, m)} dI_{(m)}^{(3)} \right] \\
& + \mu_{(I^{(4)})} dI^{(4)} + \mu_{(I^{(5)})} dI^{(5)} + \mu_{(I^{(6)})} dI^{(6)}
\end{aligned} \tag{A.21}$$

The *modified Gibbs-Duhem equation* :

$$\hat{S} dT + \sum_{B=1}^N \omega_{(B)} d\mu_{(B)} - \sum_{m=1}^3 \left[\left(\sum_{n=1}^3 \mu_{(I^{(1)},mn)} dI_{(mn)}^{(1)} \right) + \mu_{(I^{(2)},m)} dI_{(m)}^{(2)} + \mu_{(I^{(3)},m)} dI_{(m)}^{(3)} \right] - (\mu_{(I^{(4)})} dI^{(4)} + \mu_{(I^{(5)})} dI^{(5)} + \mu_{(I^{(6)})} dI^{(6)}) = 0 \quad (\text{A.22})$$

We would like to emphasize that the modified Euler's equation, the modified Gibbs equation, and the modified Gibbs-Duhem equation all apply to dynamic processes, so long as the underlying statements about behavior are applicable to the materials being considered. from the definition of A and (A.20), we get:

$$\hat{S} = \frac{1}{T} \left(\hat{U} - \sum_{B=1}^N \mu_{(B)} \omega_{(B)} \right) \quad (\text{A.23})$$

Referring to Slattery and Si (2005), we continue to restrict our attention to a multiphase, multicomponent body capable of undergoing a number of simultaneous chemical reactions and totally enclosed by an impermeable, adiabatic boundary. If equilibrium is to be achieved, the entropy inequality must be minimized and approach zero within the constraints imposed by conservation of mass for each species, by the momentum balance, by the energy balance, by the conservation of the magnetic flux, and by the conservation of charge as developed (Slattery and Si, 2005). we get a conclusion about the stress-deformation behavior of this body as:

$$\mathbf{T} = \rho \sum_{\mathbf{m}=1}^3 \left[\sum_{\mathbf{n}=1}^3 \mu_{(I^{(1)},\mathbf{mn})} (\mathbf{e}_{(\mathbf{m})} \otimes \mathbf{e}_{(\mathbf{n})} + \mathbf{e}_{(\mathbf{n})} \otimes \mathbf{e}_{(\mathbf{m})}) + \mu_{(I^{(2)},\mathbf{m})} \mathbf{M} \otimes \mathbf{e}_{(\mathbf{m})} \right] \quad (\text{A.24})$$

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