Thermodynamics of Multicomponent, Elastic, Crystalline Solids

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Abstract

The thermodynamic behavior of multicomponent, elastic, crystalline solids is developed, including Euler’s equation, the Gibbs equation, the Gibbs-Duhem equation, the conditions to be expected at equilibrium, and an extension of the Gibbs phase rule. The predictions of the phase rule are compared with experimental observations as well as the predictions of the original Gibbs phase rule.

1 Introduction

A simple material is one such that, for a fixed material particle and a fixed reference configuration, the stress tensor is a functional (function of a function) of the past history of the deformation gradient

\[ \mathbf{F} \equiv \text{grad} z \]

(1)
as well as temperature and composition (Truesdell and Noll 1965, p. 60), where the gradient operation \text{grad} is to be performed in the reference configuration. A simple material is called elastic, if stress depends only on the current value of \( \mathbf{F} \) (Truesdell and Noll 1965, p. 119).

Non-simple materials fall into three categories: (i) those exhibiting an explicit dependence upon higher-order gradients, (ii) a dependence upon more than one material particle (a non-local theory), or (iii) a dependence upon more than one reference configuration. Rajagopal and Srinivasa (1998) discuss the deformation of inelastic materials in this latter context.

A solid has some natural (preferred, stress-free or undistorted) configuration, deformations from which are always experimentally detectable. Consequently, all nonorthogonal transformations from a natural or preferred configuration for a solid can be detected by experiment (Noll 1958; Truesdell and Noll 1965, p. 81; Truesdell 1966, p. 61). For a non-oriented or isotropic solid, all orthogonal transformations of the natural or preferred configuration are undetectable experimentally. For an oriented or anisotropic solid, some orthogonal transformations are undetectable experimentally (Truesdell and Noll 1965, p. 82). A simple elastic solid is a simple elastic material with the properties of a solid.

A crystalline solid is an anisotropic solid, in which the molecules are arranged in a periodic structure or lattice. The orientation of the lattice, described for each unit of the lattice by a set of three lattice vectors, is defined, once a reference configuration has been chosen. Ericksen (1992) gives an excellent summary of the various closely related concepts: Bravais lattice, point group, symmetry class, symmetry types, lattice group, and change of symmetry. If one chooses not to work in terms of the lattice vectors, one must enforce the the implications of the isotropy group (Truesdell and Noll 1965, p. 310).

Alloys are typically polycrystalline solids formed of many single crystals or grains. Each crystal is a solid solution of two or more species. Steel is an example of a polycrystalline solid formed from iron and carbon as well as one or more species added to give it special properties as well as other unintended species that enter during the steel-making process. The lattice structures and the compositions of the individual phases

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can be varied and difficult to characterize. Simpler alloys such as the NiTi alloys have been the subject of intensive study during the last two or more decades, because of their interesting properties, such as shape memory, which is apparently the result of their phase behavior as temperature changes.

Crystalline solids undergoing martensitic phase transformations appear in at least two forms or phases: austenite and martensite. The austenitic form is stable at high temperatures; the martensitic form is stable (or metastable) at low temperatures. As martensite is deformed, it may be transformed into several different variant forms. Sometimes two variant forms appear together as twins (Ericksen 1992).

A variant form may or may not represent a distinct phase, a phase being a body with a distinct description of material behavior. One of the clearest arguments that martensitic variants are different phases was given by Marcinkowski et al. (1968, p. 956). They observed, for the equi-atomic Ni-Ti alloy, the transformation of the austenitic form into two martensitic variants. They argued on the basis of their observed diffraction patterns that the two martensites can not be simple twins, differing only by a simple rotation.

Phase transformations in crystalline solids and in low molecular weight amorphous materials can be viewed as representing two extremes of the same phenomenon. In both cases there is mass transfer across a moving phase interface. In both cases, the transformation proceeds by nucleation and growth. In the case of low molecular weight gases, liquids, and solids, phase transformations are relatively slow, and the various species transfer across the phase interface at different rates, creating gradients in the mass fractions in the adjoining phases. In martensitic transformations, the processes are very rapid, and mass fractions of the various species are nearly unchanged as the phase interface moves over the solid.

The Gibbs phase rule (Denbigh 1963, p. 183) predicts the number of degrees of freedom one has to observe a given number of phases in an system at equilibrium. It was developed for systems in which the Helmholtz free energy is not a function of the deformation gradient, and for this reason it is not applicable to elastic solids. Denbigh (1963, p. 183) in a footnote observes that Gibbs very well may have been aware of this limitation.

Laue 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 motivated by this proposal, Johnson (1987) presented a variation of the Gibbs phase rule intended for single-phase systems with coherent phases. As demonstrated below in Example 2, his proposal fails to describe experimental observations.

Prior discussions of elastic, crystalline solids have involved several assumptions.

Usually they have employed the Born rule (Ericksen 1984; Ericksen 1992; Zanzotto 1992; James and Hane 2000), which can be stated like this. If the $\mathbf{E}_i (i = 1, 2, 3)$ denote the three unit lattice vectors describing the orientation of a lattice unit in the reference configuration of the material, a deformation gradient $\mathbf{F}$ applied to the material transforms them into three deformed lattice vectors $\mathbf{F}\mathbf{E}_i$. There appears to be general agreement that the Born rule is valid for simpler (fewer components) crystals, but it may not be appropriate for more complex structures (Ericksen 1992; Zanzotto 1992). It is unlikely that the Born rule can be used to describe the deformation that takes place during phase transitions.

In a recent review of martensitic transformations and shape-memory materials, James and Hane (2000) state that the Helmholtz free energy per unit mass has two fundamental invariance properties, one of which is the principle of frame indifference [see their equation 4; see also Truesdell and Noll (1965, p. 44)].

The other fundamental invariance property described by James and Hane (2000, equation 3) is material symmetry. For simple materials, once the symmetry group (isotropy or peer group) with respect to the reference configuration (Truesdell and Noll 1965, p. 310) is known, Noll’s rule allows one to calculate the symmetry group with respect to any other configuration (Rajagopal and Srinivasa 1998; Truesdell 1977, p. 194). However, it is important to recognize that simple materials have only one independent reference configuration (Rajagopal and Srinivasa 1998; Truesdell 1977, p. 162). For a material undergoing a phase transformation, Rajagopal and Srinivasa (1998) argue that the material as a whole is not simple, since the elastic behavior of each phase must be described in terms of its own reference configuration.

The coherent interface condition (Hadamard condition or compatibility condition) (Gurtin 1993) requires that the deformation of tangential vectors be continuous across an interface. Its development requires that adjoining phases have the same reference configuration. Continuing with the view that polycrystalline materials are not simple materials, we conclude that adjoining phases can not have the same reference configuration. The coherent interface condition does not apply to polycrystalline materials.

Similarly, Grinfeld (1991, p. 79) defines a coherent phase interface as being one at which the components of displacement are continuous. This implies that adjoining phases have the same reference configuration,
which as indicated above can not be true for polycrystalline materials.

Finally, prior discussions make the plausible assumption that martensitic variants are solid solutions having the same composition. This results from recognizing that, as discussed above, martensitic transformations occur very rapidly, with little time for diffusion. For this reason, the transformations are described as "diffusionless". However, several investigators have clearly observed that the compositions of two coherent phases can be different, particularly in the immediate neighborhood of a phase interface (Marcinkowski et al. 1968; Huh et al. 1990; Huh et al. 1993; Miyazaki et al. 1994; Na et al. 1999).

In what follows, we begin with a discussion of nonequilibrium thermodynamics in Secs. 2 and 3. Beginning in Sec. 4, we confine our attention to a discussion of the conditions to be expected at a stable equilibrium.

Edelen (1975, 1993) gave a similar discussion of equilibrium with a more general set of boundary conditions: the boundary conditions that we adopt (an isolated system) are sufficient to discuss commonly observed experiments. He assumed \( A \) was an explicit function of \( F \) rather than a function of the deformed lattice vectors as we have done in (6). For this reason, his analysis requires an additional step in which the implications of the isotropy group are observed (Truesdell and Noll 1965, p. 310); the requirements of the isotropy group are automatically accounted for in our analysis through the use of the crystallographic or lattice vectors. More importantly, he did not include a development of the phase rule (see Sec. 6). (There are some additional relatively minor differences between his work and what follows. He did not work in terms of thermodynamic pressure; he did not include heterogeneous chemical reactions; he used a non-standard definition for chemical potential, a derivative with respect to mass fraction rather than mass density; he used a non-standard characterization of homogeneous chemical reactions.)

Some of the results that we are about to derive are similar to those presented by Gibbs (1928), although in a different context. Gibbs (1928) confined his attention to gases, liquids, and rigid solids, accounting for no dependence upon the deformation gradient. In his analysis stress was described only in terms of the thermodynamic pressure.

2 Problem statement

Our particular interest in what follows is a multicomponent single crystal undergoing a phase transformation. This single crystal could be a single grain in a polycrystalline solids, for example a NiTi alloy. We wish to develop for a single crystal the implications of the equation of state, of the criteria for equilibrium, and of the phase rule. In concluding, we will also consider stress-deformation behavior for these materials.

A few definitions will be helpful. For the solid phases, we must be concerned about two issues: the elastic deformation of each phase and the microstructural changes occurring during phase transitions.

Following Rajagopal and Srinivasa (1998), we will assign to each phase \( j \) a natural (preferred, stress-free, or undistorted) configuration \( \kappa^{(j)} \). We suggest that the natural configuration be chosen in a convenient manner consistent with these thoughts:

- The natural configuration should be a stress-free configuration, in the sense that any stresses beyond those attributable to thermodynamic pressure are zero.

- The natural configuration of phase \( j \) should have the same mass as the current configuration of the phase, and as a result it evolves with time during a phase transformation. If no phase transformation occurs, the natural configuration may be the initial configuration.

- This means that the boundary or a portion of the boundary of the natural configuration moves as the phase transition progresses.

- While the boundary of the natural configuration may move, the immediate neighborhood of a material particle in the natural configuration remains unchanged. In particular, the lattice vectors at a point in the natural configuration are independent of time.

In this natural configuration, the lattice vectors are \( \mathbf{E}^{(j)}_{(i)} \). Under the local deformation gradient \( \mathbf{F}^{(j)} \) in phase \( j \), the \( \mathbf{E}^{(j)}_{(i)} \) become the deformed lattice vectors

\[
\mathbf{e}^{(j)}_{(i)} = \mathbf{F}^{(j)} \mathbf{E}^{(j)}_{(i)}
\]  

(2)
In discussing solid-solid phase transitions, we will choose one phase to be a parent phase, say phase 0. This might be the first solid phase to appear. For purposes of discussion, we will assume that this is the austenitic phase. As this parent phase evolves into other phases, the \( \mathbf{E}^{(0)} \) (as seen in the current frame of reference) are transformed (rotated, elongated, deformed relative to one another) into the reference lattice vectors for the various phases \( j \) in their natural configurations:

\[
\mathbf{E}^{(j)}_{(i)} = \mathbf{H}^{(j)} \mathbf{E}^{(0)}_{(i)}
\]  

(3)

Rarely if ever is \( \mathbf{H}^{(j)} \) an orthogonal transformation, but it will be independent of time, since it relates lattice vectors in the natural configurations of the phases, all seen in the same current frame of reference. Note that \( \mathbf{H}^{(0)} = \mathbf{I} \).

With this point of view, we will make the following assumptions.

1. The system, depending upon conditions, may exist in one or more phases: gas, liquid, solid. Phases occupy non-overlapping regions of space, in contrast with some treatments of mixture theory (Bowen 1967).

2. The system consists of \( N \) species. A multicomponent body is represented by superimposing \( N \) bodies, one for each species. This means that at each point in space all species are represented, in the sense that at each point in space the mass densities of all species are defined.

3. For the gas and liquid phases, we will assume that the Helmholtz free energy per unit mass \( \hat{A} \) is a function of the temperature \( T \), the overall mass density \( \rho \), and the \( N - 1 \) independent species mass fractions \( \omega_{(A)} \) \( (A = 1, \ldots, N - 1) \):

\[
\hat{A} = \hat{A} \left( T, \rho, \omega_{(1)}, \ldots, \omega_{(N-1)} \right)
\]

(4)

Here \( \rho \) is the total mass density, \( \omega_{(A)} = \rho_{(A)}/\rho \) the mass fraction of species \( A \), and \( \rho_{(A)} \) the mass density of species \( A \).

4. For each solid phase \( j \), let us initially assume that

\[
\hat{A}^{(j)} = \hat{A}^{(j)} \left( T, \rho, \omega_{(1)}, \ldots, \omega_{(N-1)}, \mathbf{E}^{(0)}_{(1)}, \mathbf{E}^{(0)}_{(2)}, \mathbf{E}^{(0)}_{(3)}, \mathbf{E}^{(j)}_{(1)}, \mathbf{E}^{(j)}_{(2)}, \mathbf{E}^{(j)}_{(3)}, \mathbf{e}^{(j)}_{(1)}, \mathbf{e}^{(j)}_{(2)}, \mathbf{e}^{(j)}_{(3)} \right)
\]

(5)

It is understood that all of these lattice vectors are viewed in the same, current frame of reference. We will reexamine (5) shortly.

5. Since (4) is a special case, we will use (5) to describe the behavior of all phases: gas, liquid, solid. The functional forms will be different in each phase, with discontinuities occurring at the phase interfaces.

Let us begin by looking at the implications of the principle of frame indifference (Truesdell and Noll 1965, p. 44). Since \( \mathbf{E}^{(0)}_{(1)}, \mathbf{E}^{(j)}_{(1)}, \) and \( \mathbf{e}^{(j)}_{(1)} \) are frame-indifferent vectors and \( \hat{A} \) is a frame-indifferent scalar (as well as \( T \) and the various mass fractions \( \omega_{(A)} \)), equation (5) describes an isotropic scalar function of the vectors \( \mathbf{e}^{(j)}_{(1)} \) and \( \mathbf{E}^{(0)}_{(1)} \) (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 (Truesdell and Noll 1965, p. 29). We will eliminate scalar products of the form \( \mathbf{E}^{(0)}_{(m)} \cdot \mathbf{E}^{(0)}_{(n)} \) and \( \mathbf{E}^{(j)}_{(m)} \cdot \mathbf{e}^{(j)}_{(n)} \), since these would lead in the discussion to follow to a non-symmetric stress tensor at equilibrium (see Section 6). Scalar products of the form \( \mathbf{E}^{(j)}_{(m)} \cdot \mathbf{E}^{(j)}_{(n)} \) may be retained in the background contributing to the behavior of phase \( j \). In view of this reasoning, we will write

\[
\hat{A}^{(j)} = \hat{A}^{(j)} \left( T, \rho, \omega_{(1)}, \ldots, \omega_{(N-1)}, \mathbf{e}^{(j)}_{(1)}, \mathbf{e}^{(j)}_{(1)} \cdot \mathbf{e}^{(j)}_{(2)}, \mathbf{e}^{(j)}_{(1)} \cdot \mathbf{e}^{(j)}_{(3)}, \ldots, \mathbf{e}^{(j)}_{(3)} \cdot \mathbf{e}^{(j)}_{(3)} \right)
\]

(6)

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 represent the six scalar products appearing in (6) as
\[ I_{(mn)}^{(j)} = e_{(m)}^{(j)} \cdot e_{(n)}^{(j)} - E_{(m)}^{(j)} \cdot E_{(n)}^{(j)} \]
\[ = F_{(m)}^{(j)} F_{(n)}^{(j)} - E_{(m)}^{(j)} \cdot E_{(n)}^{(j)} \]
\[ = E_{(m)}^{(j)} \cdot F_{(j)}^{(j)T} F_{(n)}^{(j)} - E_{(m)}^{(j)} \cdot E_{(n)}^{(j)} \]
\[ = E_{(m)}^{(j)} \cdot (C_{(j)}^{(j)} - I) E_{(n)}^{(j)} \quad m = 1, \ldots, 3 \text{ and } n = 1, \ldots, m \]

(7)

where
\[ C_{(j)}^{(j)} = F_{(j)}^{(j)T} F_{(j)} \]

(8)
is the right Cauchy-Green strain tensor in phase \(j\) and \(I_{(mn)}^{(j)}\) can be interpreted as the components of \(C_{(j)}^{(j)} - I\) with respect to a set of basis vectors formed by the lattice vectors \(E_{(m)}^{(j)}\) \((m = 1, \ldots, 3)\). In view of (7) and (74),
\[ \rho = \frac{\rho_0}{\sqrt{\det C}} \]
\[ = \rho_0 - \frac{\rho_0}{2} \left( I_{(11)}^{(j)} + I_{(22)}^{(j)} + I_{(33)}^{(j)} \right) + \ldots \]

(9)
In other words, \(\rho\), \(I_{(11)}^{(j)}\), \(I_{(22)}^{(j)}\), and \(I_{(33)}^{(j)}\) are not independent.

In view of (7) and (9), we can write (6) as
\[ \tilde{A}_{(ij)} = \tilde{A}_{(ij)} \left( T, \rho, \omega_{(1)}, \ldots, \omega_{(N-1)}, I_{(11)}^{(j)}, I_{(22)}^{(j)}, I_{(33)}^{(j)} \right) \]

(11)
\[ \tilde{A}_{(ij)} = \tilde{A}_{(ij)} \left( T, \tilde{\nu}, \omega_{(1)}, \ldots, \omega_{(N-1)}, I_{(11)}^{(j)}, I_{(22)}^{(j)}, I_{(33)}^{(j)} \right) \]

(12)
\[ \tilde{A}_{(ij)} = \tilde{A}_{(ij)} \left( T, \rho_{(1)}, \ldots, \rho_{(N)}, I_{(11)}^{(j)}, I_{(22)}^{(j)}, I_{(33)}^{(j)} \right) \]

(13)

Here \(\tilde{\nu}\) is the volume per unit mass and \(\rho_{(A)}\) is the mass density of species \(A\).

In order to simplify the notation in what follows, we will drop the superscripts denoting the phases, unless confusion would otherwise result. However, it should always be kept in mind that functional form of (11) through (13) is different for each phase.

3 Euler, Gibbs, and Gibbs-Duhem equations

From the differential entropy inequality (Slattery 1999, p. 438), we conclude
\[ \dot{S} = - \left( \frac{\partial \tilde{A}}{\partial T} \right)_{\rho, \omega_{(B)} \neq \omega_{(N)}, I_{(mn)}} \]

(14)
Extending the standard definition for the thermodynamic pressure
\[ P = - \left( \frac{\partial \tilde{A}}{\partial \tilde{\nu}} \right)_{T, \omega_{(B)} \neq \omega_{(N)}, I_{(mn)} \neq I_{(33)}} \]

(15)

As an alternative to (11), one can consider
\[ \tilde{A}_{(ij)} = \tilde{A}_{(ij)} \left( T, \omega_{(1)}, \ldots, \omega_{(N-1)}, I_{(11)}^{(j)}, I_{(22)}^{(j)}, I_{(33)}^{(j)}, I_{(12)}^{(j)}, I_{(13)}^{(j)}, I_{(23)}^{(j)} \right) \]

(10)
This has the advantage of being consistent with those of Green and Adkins (1960, chapter 1) (see also Truesdell and Noll 1965, pp. 311–312), who further discussed the particular functional dependence upon the six \(E_{(m)}^{(j)} \cdot C_{(j)}^{(j)} E_{(n)}^{(j)}\) to be expected for various crystal classes. However, (10) is inconsistent with a discussion of amorphous materials, the introduction of thermodynamic pressure as a derivative with respect to \(\tilde{\nu} = 1/\rho\), and the standard development of the Gibbs phase rule (Denbigh 1963, p. 183).
and the chemical potential for species \( A \) on a mass basis, we have

\[
\mu(A) \equiv \left( \frac{\partial A}{\partial \rho(A)} \right)_{T, \rho, \omega(B), \omega(C), I} \quad (16)
\]

We will also require

\[
\mu(I, mn) \equiv \left( \frac{\partial A}{\partial I(mn)} \right)_{T, \rho, \omega(B), \omega(C), I, \omega(C), I} \quad (17)
\]

With these expressions, the differentials of (12) and (13) may consequently be expressed as

\[
dA = -P dV - S dT + \sum_{B=1}^{N-1} \left( \frac{\partial A}{\partial \omega(B)} \right)_{T, \rho(B), \omega(C), I} d\omega(B) + \sum_{m=1}^{3} \sum_{n=1}^{2} \mu(I, mn) dI(mn) \quad (18)
\]

\[
dA = -\frac{S}{V} dT + \sum_{B=1}^{N} \mu(B) d\rho(B) + \frac{1}{V} \sum_{m=1}^{3} \sum_{n=1}^{2} \mu(I, mn) dI(mn) \quad (19)
\]

Equation (19) may be rearranged to read

\[
d\left( \frac{A}{V} \right) = -\frac{S}{V} dT + \sum_{B=1}^{N} \mu(B) d\omega(B) + \frac{1}{V} \sum_{m=1}^{3} \sum_{n=1}^{2} \mu(I, mn) dI(mn)
\]

\[
d\left( \frac{A}{V} \right) = \left( \frac{\mu(B)}{V} - \sum_{B=1}^{N} \mu(B) \rho(B) \right) dV - S dT + \sum_{m=1}^{3} \sum_{n=1}^{2} \mu(I, mn) dI(mn)
\]

Comparison of the coefficients in (18) and (20) gives

\[
\left( \frac{\partial A}{\partial \omega(B)} \right)_{T, \omega(C), \omega(B)}, I \quad \equiv \mu(B) - \mu(N) \quad (21)
\]

as well as Euler’s equation

\[
\dot{A} = -P \dot{V} + \sum_{B=1}^{N} \mu(B) \omega(B) \quad (22)
\]

Equations (18) and (21) yield the modified Gibbs equation

\[
dA = -P dV - S dT + \sum_{B=1}^{N-1} \left( \mu(B) - \mu(N) \right) d\omega(B) + \sum_{m=1}^{3} \sum_{n=1}^{2} \mu(I, mn) dI(mn) \quad (23)
\]

The modified Gibbs-Duhem equation follow immediately by subtracting (23) from the differential of (22):

\[
\dot{S} dT - \dot{V} dP + \sum_{B=1}^{N} \omega(B) d\mu(B) - 3 \sum_{m=1}^{3} \sum_{n=1}^{2} \mu(I, mn) dI(mn) = 0 \quad (24)
\]

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 (Slattery 1999) are applicable to the materials being considered.
4 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, 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, adiabatic boundary, the velocity of which is 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. 6.

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).

4.1 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):

$$\frac{d}{dt} \int_R \rho \omega(A) \, dV = \int_R \sum_{j=1}^J r_{(A,j)} \, dV + \int_{\Sigma} \sum_{k=1}^K r_{(A,k)}^{(\sigma)} \, dA \quad (25)$$

Here $R$ denotes the region occupied by the body, $\Sigma$ 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 $j$ ($= 1, 2, \ldots, J$); $r_{(A,k)}^{(\sigma)}$ is the rate per unit area at which mass of species $A$ is produced by heterogeneous chemical reaction $k$ ($= 1, 2, \ldots, K$). 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

$$\int_R \left( \rho \frac{d\omega(A)}{dt} - \sum_{j=1}^J r_{(A,j)} \right) \, dV + \int_{\Sigma} \left( - \sum_{k=1}^K r_{(A,k)}^{(\sigma)} + [\rho \omega(A) (v - u) \cdot \xi] \right) \, dA = 0 \quad (26)$$

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

$$\frac{\partial \psi_{(j)}}{\partial t} \equiv \frac{r_{(A,j)}}{M_{(A)} \nu_{(A,j)}} \quad (27)$$

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.

In much the same manner, we can introduce the $k$th heterogeneous reaction coordinate $\psi_{(k)}^{(\sigma)}$ by defining for all $A = 1, 2, \ldots, N$ (Slattery 1990, p. 830):

$$\frac{\partial \psi_{(k)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \psi_{(k)}^{(\sigma)} \cdot u \equiv \frac{r_{(A,k)}^{(\sigma)}}{M_{(A)} \nu_{(A,k)}^{(\sigma)}} \quad (28)$$

Here $\psi_{(k)}^{(\sigma)}$ is a function of time $t$ and two surface coordinates on the moving and deforming interface (Slattery 1990, p. 1065); $\nabla_{(\sigma)}$ denotes the surface gradient operation (Slattery 1990, p. 1075); $u$ is the time rate
of position following a surface point (Slattery 1990, 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 \( k \).

In view of (27) and (28), we may express (26) as

\[
Z_{(A)} \equiv \int_R \left[ \rho \frac{d}{dt} \omega_{(A)} - \sum_{j=1}^{j} M_{(A)} \nu_{(A,j)} \frac{\partial \psi_{(j)}}{\partial t} \right] dV \\
+ \int_\Sigma \left\{ -\sum_{k=1}^{K} M_{(A)} \nu_{(A,k)}^{(\sigma)} \frac{\partial \psi_{(k)}}{\partial t} + \sum_{k=1}^{K} M_{(A)} \nu_{(A,k)}^{(\sigma)} \nabla_{(\sigma)} \psi_{(k)} \cdot \n + \left[ \rho \omega_{(A)} (v - u) \cdot \xi \right] \right\} dA
\]

\[= 0 \quad (29)\]

4.2 Momentum balance

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

\[
\frac{d}{dt} \int_R \rho v \, dV = \int_S T n \, dA + \int_R \rho F \, dV \quad (30)
\]

(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 \( v \).) Applications of the transport theorem (Slattery 1999, p. 433) and
of Green’s theorem yields

\[
Z_m \equiv \int_R \left[ \rho \frac{d}{dt} v - \text{div} \mathbf{T} - \rho F \right] dV + \int_\Sigma \left[ \rho v (v - u) \cdot \xi - T \xi \right] dA
\]

\[= 0 \quad (31)\]

4.3 Energy balance

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

\[
\frac{d}{dt} \int_R \rho \left( \bar{U} + \frac{1}{2} v^2 \right) dV
\]

\[= \int_S v \cdot T n \, dA + \int_R \sum_{A=1}^{N} \rho_{(A)} (v_{(A)} \cdot f_{(A)}) \, dV \quad (32)\]

We also neglect the possibility of mutual radiant energy transmission.

The first term on the right of (32) can be rearranged using Green’s transformation as

\[
\int_S v \cdot T n \, dA
\]

\[= \int_R [v \cdot \text{div} \mathbf{T} + \text{tr}(\mathbf{T} \nabla v)] dV + \int_\Sigma [v \cdot T \xi] \, dA \quad (33)\]

If we assume that the external or mutual force for each species A is representable by a potential

\[f_{(A)} = -\nabla \phi_{(A)} \quad (34)\]
We will assume that this potential is only a function of position and not a function of time. This assumption together with Green's transformation and (27) permit us to arrange the second term on the right of (32) as

$$\int \sum_{A=1}^{N} \rho_{(A)} \mathbf{v}_{(A)} \cdot \mathbf{f}_{(A)} \ dV$$

$$= \int \sum_{A=1}^{N} \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{f}_{(A)} \ dV + \int \rho \mathbf{v} \cdot \mathbf{f} \ dV$$

$$= \int \sum_{A=1}^{N} \left\{ -\text{div} \left[ \rho_{(A)} \phi_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \right] + \phi_{(A)} \text{div} \left[ \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \right] \right\} \ dV + \int \rho \mathbf{v} \cdot \mathbf{f} \ dV$$

$$= \int \sum_{A=1}^{N} \left\{ -\text{div} \left[ \rho_{(A)} \phi_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \right] + \phi_{(A)} \left[ -\rho \frac{d(\omega_{(A)})}{dt} + \sum_{j=1}^{J} r_{(A,j)}^j \right] \right\} \ dV + \int \rho \mathbf{v} \cdot \mathbf{f} \ dV$$

$$= \int \sum_{A=1}^{N} \left\{ -\rho \phi_{(A)} \frac{d(\omega_{(A)})}{dt} + \sum_{j=1}^{J} \phi_{(A)} M_{(A)} \nu_{(A,j)} \frac{\partial \psi_{(j)}}{\partial t} \right\} \ dV + \int \rho \mathbf{v} \cdot \mathbf{f} \ dV$$

$$+ \int \sum_{A=1}^{N} \phi_{(A)} \left[ \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{e} \right] dA \quad (35)$$

An application of the transport theorem (Slattery 1999, p. 433) allows us to express the left side of (32) as

$$\frac{d}{dt} \int \rho \left( \mathbf{U} + \frac{1}{2} \mathbf{v}^2 \right) \ dV = \int \rho \frac{d(\mathbf{v})}{dt} \left( \mathbf{U} + \frac{1}{2} \mathbf{v}^2 \right) \ dV + \int \rho \left( \mathbf{U} + \frac{1}{2} \mathbf{v}^2 \right) (\mathbf{v} - \mathbf{u}) \cdot \mathbf{e} \ dA \quad (36)$$

In view of (33), (35), and (36), equation (32) takes the form

$$\int \left[ \rho \frac{d(\mathbf{v})}{dt} \left( \mathbf{U} + \frac{1}{2} \mathbf{v}^2 \right) + \sum_{A=1}^{N} \left\{ -\sum_{j=1}^{J} \phi_{(A)} M_{(A)} \nu_{(A,j)} \frac{\partial \psi_{(j)}}{\partial t} + \rho \phi_{(A)} \frac{d(\omega_{(A)})}{dt} \right\} \right]$$

$$- \mathbf{v} \cdot (\text{div} \mathbf{T} + \rho \mathbf{f}) - \text{tr}(\mathbf{T} \nabla \mathbf{v}) \ dV + \int \left[ \rho \left( \mathbf{U} + \frac{1}{2} \mathbf{v}^2 \right) (\mathbf{v} - \mathbf{u}) \cdot \mathbf{e} \right] dA$$

$$= \int \sum_{A=1}^{N} \phi_{(A)} \left[ \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{e} \right] + \left[ \mathbf{v} \cdot \mathbf{T} \mathbf{e} \right] dA \quad (37)$$

where we have assumed that $\phi_{(A)}$ is continuous across the dividing surface. Equation (37) can be expressed more conveniently for our purposes as

$$Z_e \equiv \int \left\{ \rho \frac{d(\mathbf{v})}{dt} \mathbf{E} - \sum_{A=1}^{N} \left( \sum_{j=1}^{J} \phi_{(A)} M_{(A)} \nu_{(A,j)} \frac{\partial \psi_{(j)}}{\partial t} - \rho \phi_{(A)} \frac{d(\omega_{(A)})}{dt} \right) \right.$$

$$- \mathbf{v} \cdot (\text{div} \mathbf{T} + \rho \mathbf{f}) - \text{tr}(\mathbf{T} \nabla \mathbf{v}) \right\} dV$$

$$+ \int \left[ \rho \mathbf{E} (\mathbf{v} - \mathbf{u}) \cdot \mathbf{e} - \sum_{A=1}^{N} \phi_{(A)} \rho_{(A)} (\mathbf{v}_{(A)} - \mathbf{v}) \cdot \mathbf{e} - \mathbf{v} \cdot \mathbf{T} \mathbf{e} \right] dA$$

$$= 0 \quad (38)$$

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

$$\mathbf{E} \equiv \mathbf{U} + \frac{1}{2} \mathbf{v}^2 \quad (39)$$
4.4 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:

\[
\frac{d}{dt} \int_R \rho \dot{S} \, dV \geq 0
\]  

(40)

*Equilibrium* is achieved, when this inequality becomes an equality.

As equilibrium is approached, (40) tells us that the entropy of this isolated body is maximized and

\[
\frac{d^2}{dt^2} \int_R \rho \dot{S} \, dV \leq 0
\]  

(41)

The implications of (41) and therefore the requirements for a stable equilibrium have been explored elsewhere [Slattery (1972, 1981, 1990), (Edelen 1975)]. This will not be further investigated here.

Applying the transport theorem (Slattery 1999, p. 433), we find that this may also be written as

\[
\int_R \rho \frac{d(v)}{dt} \dot{S} \, dV + \int_\Sigma \left[ \rho \dot{S} (\mathbf{v} - \mathbf{u}) \cdot \mathbf{\xi} \right] dA \geq 0
\]  

(42)

5 Implications of equilibrium

Referring to the beginning of the prior section, we continue to restrict our attention to a multiphase, multi-component body capable of undergoing a number of simultaneous chemical reactions and totally enclosed by an impermeable, adiabatic boundary, the velocity of which is suddenly set to zero (or a constant velocity). As explained above, if equilibrium is to be achieved, the left side of (40) must be minimized and approach zero within the constraints imposed by conservation of mass for each species, by the momentum balance, and by the energy balance as developed in the prior section.

Since \(Z_{(A)}\), \(Z_m\), and \(Z_e\) are all zero by (29), (31), and (38), there is no loss in generality in writing (42) as (Slattery 1981, p. 490; Slattery 1990, p. 839)

\[
\int_R \rho \frac{d(v)}{dt} \dot{S} \, dV + \int_\Sigma \left[ \rho \dot{S} (\mathbf{v} - \mathbf{u}) \cdot \mathbf{\xi} \right] dA + \sum_{A=1}^{N} \lambda_{(A)} Z_{(A)} + \lambda_m \cdot Z_m + \lambda_e Z_e \geq 0
\]  

(43)

where \(\lambda_{(A)}\) and \(\lambda_e\) are constants or Lagrangian multipliers; \(\lambda_m\) is a constant spatial vector, the components of which are Lagrangian multipliers. In examining this result, we will require several relationships.

From (23) and the definition of \(\dot{A}\) (Slattery 1999, p. 446), we have

\[
\frac{d(v)}{dt} \dot{S} = \frac{1}{T} \frac{d(v) \dot{U}}{dt} + \frac{P}{T} \frac{d(v) \dot{V}}{dt} - \frac{1}{T} \sum_{A=1}^{N} \left( \mu_{(A)} - \mu_{(N)} \right) \frac{d(v) \omega_{(A)}}{dt} - \frac{1}{T} \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(m,n)} \frac{d(v) I_{(mn)}}{dt}
\]

\[
= \frac{1}{T} \frac{d(v) \dot{U}}{dt} + \frac{P}{T} \rho \text{div} \mathbf{v} \quad \quad - \frac{1}{T} \sum_{A=1}^{N} \left( \mu_{(A)} - \mu_{(N)} \right) \frac{d(v) \omega_{(A)}}{dt} - \frac{1}{T} \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(m,n)} \frac{d(v) I_{(mn)}}{dt}
\]

(44)

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

\[
\rho \frac{d(v)}{dt} \dot{V} = \text{div} \mathbf{v}
\]

(45)

in this last line. In a similar way, from (22), we see that

\[
\dot{S} = \frac{1}{T} \left( \dot{U} + \frac{P}{\rho} - \sum_{A=1}^{N} \mu_{(A)} \omega_{(A)} \right)
\]

(46)
Equation (39) yields
\[
\frac{d}{dt}(\mathbf{v}E) = \frac{d}{dt}(\mathbf{v}) + \mathbf{v} \cdot \frac{d}{dt} \mathbf{v}
\]  
(47)

We will also need from (7)
\[
\frac{d}{dt}(\mathbf{m}_{(m,n)}) = \nabla \mathbf{v} \mathbf{e}_{(m)} \cdot \mathbf{e}_{(n)} + \mathbf{e}_{(m)} \cdot \nabla \mathbf{v} \mathbf{e}_{(n)}
\]
\[
= \text{tr} \left[ (\mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)}) \nabla \mathbf{v} \right]
\]  
(48)

After rearranging (43) by means of (48), (44), (46), and (39), we have
\[
\begin{align*}
\int_{\Sigma} \left\{ \rho \left( \frac{1}{T} + \lambda_e \right) \left( \frac{d}{dt} \mathbf{v} + \frac{d}{dt} \mathbf{v} \right) + \sum_{A=1}^{N} \rho \left( -\frac{\mu(A)}{T} + \lambda_e \phi(A) + \lambda(A) \right) \frac{d}{dt} \omega(A) \right. \\
\left. + (\lambda_e \mathbf{v} + \lambda_m) \cdot \left( \frac{d}{dt} \mathbf{v} - \text{div} \mathbf{T} - \rho \mathbf{f} \right) \right. \\
\left. - \sum_{A=1}^{N} \sum_{j=1}^{J} \left( \lambda_e \phi(A) M(A) \nu(A,j) + \lambda(A) M(A) \nu(A,j) \right) \frac{\partial \psi_{(j)}}{\partial t} \right. \\
\left. - \sum_{A=1}^{N} \sum_{j=1}^{J} \left( \lambda_e \phi(A) M(A) \nu(A,j) + \lambda(A) M(A) \nu(A,j) \right) \frac{\partial \psi_{(j)}}{\partial t} \right. \\
\left. + \frac{1}{T} \text{tr} \left[ \left( -T \lambda_e \mathbf{T} + \rho I - \frac{3}{2} \sum_{m=1}^{2} \sum_{n=1}^{2} \left( \mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)} \right) \right) \nabla \mathbf{v} \right] \right\} dV \\
\int_{\Sigma} \left\{ \rho \left( \frac{1}{T} + \lambda_e \right) \left( \frac{d}{dt} \mathbf{v} + \frac{d}{dt} \mathbf{v} \right) + \sum_{A=1}^{N} \left( -\frac{1}{T} \mu(A) \omega(A) + \lambda(A) \omega(A) + \lambda_e \phi(A) \omega(A) \right) \\
- \lambda_e \frac{v^2}{2} \right\} (\mathbf{v} - \mathbf{u}) \cdot \mathbf{e} \\
- \sum_{A=1}^{N} \lambda_e \phi(A) \rho(A) \left( \mathbf{v}(A) - \mathbf{u} \right) \cdot \mathbf{e} + (\lambda_e \mathbf{v} + \lambda_m) \cdot \left[ \rho \mathbf{v} (\mathbf{v} - \mathbf{u}) - \mathbf{T} \right] \mathbf{e} \\
- K \sum_{k=1}^{K} \sum_{A=1}^{N} \left( \lambda(A) M(A) \nu^{(c)}(A,k) + \lambda_e \phi(A) M(A) \nu^{(c)}(A,k) \right) \left( \frac{\partial \psi^{(c)}_{(k)}}{\partial t} - \nabla_{(c)} \psi^{(c)}_{(k)} \cdot \mathbf{u} \right) \right\} dA \geq 0
\end{align*}
\]  
(49)

or
\[
\begin{align*}
\int_{\Sigma} \left\{ \rho \left( \frac{1}{T} + \lambda_e \right) \left( \frac{d}{dt} \mathbf{v} + \frac{d}{dt} \mathbf{v} \right) + \sum_{A=1}^{N} \rho \left( -\frac{\mu(A)}{T} + \lambda_e \phi(A) + \lambda(A) \right) \frac{d}{dt} \omega(A) \right. \\
\left. - \sum_{A=1}^{N} \sum_{j=1}^{J} \left( \lambda_e \phi(A) M(A) \nu(A,j) + \lambda(A) M(A) \nu(A,j) \right) \frac{\partial \psi_{(j)}}{\partial t} \right. \\
\left. + \frac{1}{T} \text{tr} \left[ \left( -T \lambda_e \mathbf{T} + \rho I - \frac{3}{2} \sum_{m=1}^{2} \sum_{n=1}^{2} \left( \mathbf{e}_{(m)} \otimes \mathbf{e}_{(n)} + \mathbf{e}_{(n)} \otimes \mathbf{e}_{(m)} \right) \right) \nabla \mathbf{v} \right] \right\} dV \\
\int_{\Sigma} \left\{ \rho \left( \frac{1}{T} + \lambda_e \right) \left( \frac{d}{dt} \mathbf{v} + \frac{d}{dt} \mathbf{v} \right) + \sum_{A=1}^{N} \left( -\frac{1}{T} \mu(A) \omega(A) + \lambda(A) \omega(A) + \lambda_e \phi(A) \omega(A) \right) \\
- \lambda_e \frac{v^2}{2} \right\} (\mathbf{v} - \mathbf{u}) \cdot \mathbf{e} \\
+ (\lambda_e \mathbf{v} + \lambda_m) \cdot \left[ \rho \mathbf{v} (\mathbf{v} - \mathbf{u}) - \mathbf{T} \right] \mathbf{e} \\
- K \sum_{k=1}^{K} \sum_{A=1}^{N} \left( \lambda(A) M(A) \nu^{(c)}(A,k) + \lambda_e \phi(A) M(A) \nu^{(c)}(A,k) \right) \left( \frac{\partial \psi^{(c)}_{(k)}}{\partial t} - \nabla_{(c)} \psi^{(c)}_{(k)} \cdot \mathbf{u} \right) \right\} dA \geq 0
\end{align*}
\]  
(50)
In arriving at this result, we have recognized the differential momentum balance, the jump mass balance for species \( A \) (Slattery 1999, p. 427), and (28).

A sufficient conditions that \((50)\) be satisfied for equilibrium is that the system be static.

Necessary and sufficient conditions for \((50)\) to be satisfied in the presence of small perturbations to the system are

\[
T = -\frac{1}{\lambda} \tag{51}
\]

\[
\text{a constant}
\]

\[
\mu(A) + \phi(A) = T\lambda(A) \tag{52}
\]

\[
\text{a constant for each species } A = 1, 2, \ldots, N
\]

\[
\sum_{A=1}^{N} \left( -\frac{1}{T} \phi(A) M(A) \nu(A,j) + \lambda(A) M(A) \nu(A,j) \right) = \sum_{A=1}^{N} \frac{\mu(A) M(A) \nu(A,j)}{T} \tag{53}
\]

\[
\text{at } \Sigma: \ P \text{ is continuous} \tag{54}
\]

\[
\text{at } \Sigma: \ v^2 = 0 \tag{55}
\]

\[
\text{on } \Sigma: \sum_{A=1}^{N} \mu(A) M(A) \nu(A,k) = 0 \tag{56}
\]

The last step is to recognize \((56)\) and the jump momentum balance (Slattery 1999, p. 34).

It is important to recognize that \((54)\) is the description of stress-deformation behavior at equilibrium.\(^2\)

The differential momentum balance must still be satisfied subject to the jump momentum balance

\[
\text{on } \Sigma: \ [T \kappa] = \left[ \rho \sum_{m=1}^{3} \sum_{n=1}^{2} \mu(I,mn) \left( e_{(m)} \otimes e_{(n)} + e_{(n)} \otimes e_{(m)} \right) \kappa \right] \tag{58}
\]

at each phase interface as well as all appropriate boundary conditions.

Equation \((54)\) also says that at equilibrium the stress distribution may be non-isotropic. If \( F = I \), the \( I_{(mn)} = 0 \), the \( \mu(I,mn) = 0 \), and the stress distribution will be isotropic.

Notice that, if we had retained scalar products of the forms \( E_{(m)}^{(0)} \cdot e_{(n)}^{(j)} \) and \( E_{(m)}^{(j)} \cdot e_{(n)}^{(j)} \) in \((6)\), the stress tensor would have been non-symmetric.

To summarize, for the isolated body described at the beginning of the previous section, the necessary and sufficient conditions that \((50)\) be satisfied and that equilibrium be achieved (under non-trivial conditions) are \((51)\) through \((57)\).

6 Phase rule

The phase rule was developed by Gibbs Denbigh 1963, p. 183 for multiphase, multicomponent systems at equilibrium with the restriction that in each phase

\[
\hat{A} = \hat{A} \left( T, \rho, \omega(1), \omega(2), \ldots, \omega(N-1) \right) \tag{59}
\]

\(^2\)Equation \((54)\) does not belong to the class of hyperelastic behavior. While Truesdell and Noll (1965, p. 296) point out that hyperelastic behavior is a sufficient condition for the differential entropy inequality to be satisfied for all processes, hyperelastic materials are non-dissipative. In our opinion, real materials always dissipate energy under nonequilibrium conditions.
For such a system in the absence of chemical reactions, the phase rule states that the maximum number of phases that can be observed is
\[ p \leq N + 2 \]  
(60)

or the number of degrees of freedom one has in observing \( p \) phases is
\[ f = N + 2 - p \]  
(61)

The degrees of freedom are the independent variables that define the domain in which \( p \) phases can be observed in an \( N \) component system.

### 6.1 With no homogeneous or heterogeneous chemical reactions

In the case where there are no homogeneous or heterogeneous chemical reactions, we see from (11) that the state of each solid crystalline phase is determined by \( N + M + 1 \) independent variables: \( T, \rho, \omega(1), \ldots, \omega(N-1) \), and \( M \) non-zero invariants described by (7) and restricted by (9), which can be no larger than 5. The state of each gas, liquid, or amorphous solid phase is fixed by \( N + 1 \) variables: \( T, \rho, \omega(1), \ldots, \omega(N-1) \).

If \( p \) is the number of phases and \( p^{(c)} \) is the number of crystalline solid phases, the system is determined by \( p(N + 1) + p^{(c)} \) 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 (51), there are \( p - 1 \) independent equations relating \( T \) in each phase.
- From (52), there are \( N(p - 1) \) independent equations relating \( \mu(A) + \phi(A) \) in each phase.
- From (55), there are \( p - 1 \) independent equations relating the pressure in each phase.
- From (58), there are \( 3Q \) independent equations relating the elastic components of stress, where \( Q \) is the number of internal solid-solid phase interfaces at which elastic components of stress exist. (Elastic components of stress are zero at solid-fluid interfaces.) In the absence of deformation, \( Q = 0 \). If there are two or more crystalline solid phases present and in contact with one another, \( Q = p^{(c)} - 1 \).

To summarize, we have \( p(N + 1) + p^{(c)} \) variables related by \((p - 1)(N + 2) + 3Q\) equations.

We know that
\[ p(N + 1) + p^{(c)}M \geq (p - 1)(N + 2) + 3Q \]
\[ p \leq N + 2 + p^{(c)}M - 3Q \]  
(62)

This tells us the maximum number of phases that might be observed in a given equilibrium experiment. Equation (62) 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:
\[ f = N + 2 - p + p^{(c)}M - 3Q \]  
(63)

Both (62) and (63) reduce to the phase rule of Gibbs, when there are no crystalline phases.

Note that, in the absence of deformation, the invariants (7) are all zero, and the \( \mu_{(j, mn)} \) are all zero. This means that \( M = 0 \) and \( Q = 0 \), and (62) and (63) reduce to the Gibbs phase rule (60) and (61).

Commonly we are concerned with systems that are subjected to \( c \) constraints such as constant temperature, composition, and constraints imposed by (58) at external boundaries. In such cases, (63) should be replaced by
\[ f = N + 2 - p + p^{(c)}M - 3Q - c \]  
(64)

Let us apply (64) to some observations that have been reported in the literature.
6.1.1 Example 1: Phase diagrams for systems with incoherent phases

In constructing $P - T$ phase diagrams, we replace $p$ by $P$, recognizing that $P$ has the advantage of being continuous across phase interfaces by (55). Phase diagrams are commonly constructed experimentally by subjecting the system to a hydrostatic pressure (constant thermodynamic pressure) exerted by a surrounding gas or liquid.

The experiments are conducted in such a way that the phases are incoherent. The jump momentum balance (58) applied to all phase interfaces ensures that the stress is a constant thermodynamic pressure throughout the system. This in turn implies that all the $\mu_{(f,mn)} = 0$ and both (59) and the original Gibbs phase rule (61) apply without change.

6.1.2 Example 2: Phase diagrams for systems with coherent phases

There have been several observations of equilibrium phase behavior in two-component systems with coherent phases. Marcinkowski et al. (1968) studied thin foils of the equi-atomic alloy of Ni-Ti; Huh et al. (1990, 1993) studied three Ti-Al alloys with different compositions; (Na et al. 1999) studied four Ni-V alloys with different compositions. In all cases, they observed, with a fixed temperature and pressure, two distinct phases. Huh et al. (1990, 1993) and Na et al. (1999), in particular, observed that the equilibrium phase compositions for systems with coherent phase interfaces are different from those for systems with incoherent phase interfaces. Na et al. (1999, p. 10) attribute this difference as "...to the elastic strain which is generated by the misfit between the matrix and precipitate in the coherent state."

The original Gibbs phase rule (61) states that, for two component systems, there would be no degrees of freedom in observing two phases; all independent variables would be fixed, including the compositions of the two phases. Equation (61) does not explain this difference between systems with coherent phases and those with incoherent phases.

For these experiments, $N = 2$, $p = p^{(c)}$, and $c = 2$ (temperature and pressure). Let us assume that the reference configurations for the solid phases are the stress-free configurations observed with incoherent phases (as seen in the common phase diagrams described in Example 1). Since the external tractions applied to these systems are attributable to a uniform pressure, we will assume that no shear stresses are created in the solids and that all stresses are attributable to a change in density within the immediate neighborhood of the phase interfaces. In view of (9), we conclude that $M = 2$, and (64) predicts that there should be one degree of freedom in observing two phases. All independent variables are fixed with the exception of one, the mole fraction of one species in one of the phases. The composition of the other phase is known, since they studied closed systems of known overall composition. This conclusion is consistent with their observations that the composition of the phases was not fixed, but depended upon whether the phases were coherent or incoherent.

Miyazaki et al. (1994) studied three-component Ni-Al-Ti alloys. They also observed two coherent phases with compositions different from those expected with incoherent phases. The original Gibbs phase rule (61) predicts one degree of freedom for such a system; one mole fraction should be sufficient to determine the equilibrium phase composition on a triangular plot at a fixed temperature, pressure, and overall composition. Miyazaki et al. (1994) show that this is not true; two mole fractions differ from those observed with incoherent phases. Equation (64) predicts that there are two degrees of freedom, in agreement with their observations.

The scatter in the experimental measurements reported by Miyazaki et al. (1994) may be attributable to more than experimental error. We believe that the variation in composition from that expected with incoherent phases may occur only within the immediate neighborhood of a phase interface and not uniformly throughout the phases. Na et al. (1999, p. 15) appears to agree: "...the coherent phase composition is a function of the volume fraction of the coherent phase."

In all of these cases, the phase rule proposed by Johnson (1987) fails, since phases of different compositions were observed, rather than the single phase assumed.

6.1.3 Example 3: Experiments of Abeyaratne et al. (1996)

Abeyaratne et al. (1996) studied single crystals of Cu-14.0wt%Al-3.9wt%Ni subjected to isothermal, biaxial dead loading, in which approximately uniform tractions were applied to the edges of the crystal. The crystal was cut and positioned in the machine in such a way that the large square face was the (001) plane and
the edges were (110) and (110 planes, all in the cubic basis seen in the natural or reference configuration for austenite. Subsequently, the temperature was maintained below that at which the austenitic crystals would begin to form, and they observed the formation and disappearance of two martensitic variants as the balanced dead loading was varied. These variants formed a “compound twin” or a “mosaic of twinned laminates.” It is not clear from their observations whether these variants should be considered to be phases (see Introduction). Let us use the phase rule to determine how many phases (rather than variants) they observed.

Since the tangential components of stress exerted on the faces of the sample are all zero, from (54) one solution would have two of the deformed lattice vectors $e_{ij}$ 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 orthorhombic crystal structure. In this case, only two of the invariants (7) restricted by (9) are different from zero in each phase, or $M = 2$ in view of (9).

Abeyaratne et al. (1996) paid particular attention to the orientation of the parent austenitic phase before lowering the temperature to convert the specimen to martensite. At least in the experiment they described, the orientation of the parent phase may have been unimportant for the following reason. When the temperature of the austenite was initially lowered to create the initial martensitic phase, the martensite likely was nucleated at the outer boundaries of the system moving in with time. To the extent that this was the case, the process automatically insured that the stresses at the outer boundaries were satisfied according to (58) and consequently that the lattice vectors were oriented as described above.

Let choose the the Cu-Al-Ni alloy as the system to be considered.

With this choice of system, $p = p^{(c)}$ and $N = 3$. The composition of the other invariant can be determined, since the overall composition and mass of the sample is known. The constraints $c = 3$: temperature, pressure, and the integral over both variants of the magnitude of the normal stress exerted by the biaxial dead loading. This latter is a constraint on the invariants (7)). From (64), we conclude that $p^{(c)} = (5 - f)/2$. While it is possible that the two variants were distinct phases, we believe that it is more likely that the two variants were the same phase (simply rotated with respect to one another) and that $f = 3$: the density and the two independent mass fractions. Unfortunately, they did not measure the compositions of the variants, which would be required to confirm our prediction.

6.2 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 (53) for homogeneous reactions or (57) for heterogeneous reactions.

Following the same reasoning as above, (64) should be replaced by

$$f = N + 2 - p + p^{(c)} M - 3Q - r - c$$

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

7 Summary of new results

Five principal results have been developed here.

1. To our knowledge, this is the first time that the Gibbs phase rule has been extended to systems that can exhibit crystalline elastic solids. The result is consistent with three illustrative examples. It is demonstrated that neither the original phase rule derived by Gibbs (1928) nor the phase rule proposed by Johnson (1987) are consistent with the experimental observations of systems with coherent phases.

2. The foundations of nonequilibrium thermodynamics of crystalline elastic solids are developed, beginning with the assumption that the Helmholtz free energy per unit mass $A$ is a function of the deformed crystallographic or lattice vectors (2) in (5), (6), and (11). In contrast, Edelen (1975) assumes that $A$ is an explicit function of the deformation gradient $F$, requiring application of the symmetry or isotropy group (Truesdell and Noll 1965, p. 310). He did not include an explicit dependence upon $\rho$, and for this reason his development was not in terms of the thermodynamic pressure.
3. While the form of Euler's equation (22) remains unchanged, the extensions of the Gibbs equation (23) and of the Gibbs-Duhem equation (24) to these systems appears to be new.

4. The predicted stress-deformation behavior at equilibrium, (54), does not belong to the class of hypere

lastic materials [Truesdell and Noll 1965, p. 302]. Because Edelen (1975) assumed that \( \hat{A} \) is an explicit function of the deformation gradient \( F \) (rather than an explicit function of \( \rho \) and and the deformed lattice vectors), he did find that equilibrium stress-deformation behavior was hypere

lastic.

5. So long as we can assume that phases in a polycrystalline structures are contiguous, the jump momen
tum balance (58) provides a relation between the deformed lattice vectors in adjoining phases. For example, it could be used to determine the angle between lattice vectors at the dividing surface.

To take advantage of (58), one would have to measure the derivatives \( \mu_{(l,mn)} \) or assume a specific functional form in (10), for example (86).

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16


9 Notation

\( \hat{\chi} \) Helmholtz free energy per unit mass
\( \hat{\chi} \) Helmholtz free energy per unit volume
\( C \) relative right Cauchy-Green strain tensor defined by (8)
\( e \) strain tensor defined in Appendix A
\( e^{(j)}_i \) deformed lattice vectors for phase \( j \) defined by (2)
\( \hat{E} \) sum of internal energy and kinetic energy per unit mass as defined in equation (39)
\( E^{(j)}_i \) unit lattice vectors in natural (equilibrium) configuration for phase \( j \)
\( E^{(0)}_i \) lattice vectors in natural (equilibrium) configuration for the parent phase 0 (as seen in the current frame of reference)
\( f \) degrees of freedom
\( f_{(A)} \) body force per unit mass acting on species \( A \)
\( \) body force per unit mass
\( F^{(j)} \) deformation gradient in phase \( j \)
\( H \) displacement gradient defined in Appendix A
\( H^{(j)} \) orthogonal transformation for phase \( j \) defined by (3)
\( I \) identity tensor
\( I^{(j)}_{(m)} \) scalar invariants for phase \( j \) defined by (7)
\( J \) number of homogeneous chemical reactions
\( K \) number of heterogeneous chemical reactions
\( M \) number of non-zero invariants described by (7)
\( M_{(A)} \) molecular weight of species \( A \)
\( N \) number of species
\( p \) number of phases
\( p^{(c)} \) number of crystalline phases
\( P \) thermodynamic pressure defined by (15)
\( Q \) number of internal solid-solid or solid-fluid 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 \( j \)
\( r^{(A)}_{(k)} \) 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 \( v \).
\( S \) bounding surface of body
\( \dot{S} \) entropy per unit mass
\( t \) time
\( T \) temperature
\( T \) stress tensor
\( u \) time rate of change of position following a surface point (Slattery 1999, p. 24); used as displacement in Appendix A
\( \dot{U} \) internal energy per unit mass
\( v \) mass average velocity
\( v_{(A)} \) velocity of species \( A \)
\( V \) volume per unit mass
\( z \) position vector
\( z_{(n)} \) position of material particle in reference configuration
\( Z_{(A)} \) defined by (29)
\( Z_{(c)} \) defined by (38)
\( Z_{(m)} \) defined by (31)
Greek letters

\( \epsilon \) dimensionless parameters representing the disturbance from equilibrium
\( \lambda_{(A)} \) Lagrangian multiplier
\( \lambda_{e} \) Lagrangian multiplier
\( \lambda_{m} \) Lagrangian multiplier
\( \mu_{(A)} \) chemical potential for species \( A \) defined by (16)
\( \mu_{(1,m,n)} \) defined by (17)
\( \nu_{(A,j)} \) 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.
\( \xi \) unit normal to phase interface
\( \Sigma \) phase interface
\( \rho \) overall mass density
\( \rho_{(A)} \) mass density of species \( A \)
\( \phi_{(A)} \) potential energy of species \( A \) introduced in (34)
\( \psi_{(j)} \) reaction coordinate of homogeneous reaction \( j \) introduced in (27)
\( \psi_{(j)}^{(\sigma)} \) reaction coordinate of heterogeneous reaction \( j \) introduced in (28)
\( \omega_{(A)} \) mass fraction of species \( A \) or \( \rho_{(A)}/\rho \)

Other

\[ [a\xi] = a^{(1)}\xi^{(1)} + a^{(2)}\xi^{(2)} \] 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 \( \Sigma \); \( \xi^{(i)} \) 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.
\( \frac{d}{dt} \) derivative following a particle that moves with the mass-averaged velocity \( \mathbf{v} \)
\( \text{grad} \) gradient with respect to reference configuration
\( \nabla_{(\sigma)} \) denotes the surface gradient operation (Slattery 1999, p. 1075)
Appendix A: Stress-deformation behavior at equilibrium in the limit of infinitesimal deformations

Since it is common to consider infinitesimal deformations, let us consider how (54) reduces in this limit:

\[
T = -PI + \rho \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(m,nn)} \left( e_{(m)} \otimes e_{(n)} + e_{(n)} \otimes e_{(m)} \right)
\]

\[
= -PI + \rho \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(m,nn)} \left( FE_{(m)} \otimes FE_{(n)} + FE_{(n)} \otimes FE_{(m)} \right)
\]

\[
= -PI + \rho \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(m,nn)} F \left( E_{(m)} \otimes E_{(n)} + E_{(n)} \otimes E_{(m)} \right) F^T
\]  
(66)

Define

\[
\mathbf{u} \equiv \mathbf{z} - \mathbf{z}_n
\]

\[
\mathbf{u} = \mathbf{x}_n - \mathbf{z}_n
\]
(67)

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

\[
\mathbf{H} \equiv \text{grad} \mathbf{u}
\]

\[
= \frac{\partial (z_i - z_{ni})}{\partial z_{nj}} e_i e_j
\]

\[
= \frac{\partial z_i}{\partial z_{nj}} e_i e_j - \delta_{ij} e_i e_j
\]

\[
= \mathbf{F} - \mathbf{I}
\]
(68)

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

\[
\mathbf{u} = \mathbf{u}_{(0)} + \epsilon \mathbf{u}_{(1)} + \epsilon^2 \mathbf{u}_{(2)} + \ldots
\]
(69)

Let us recognize that in the absence of an infinitesimal deformation or as \( \epsilon \to 0 \)

\[
\mathbf{u}_{(0)} = 0
\]
(70)

This means that

\[
\mathbf{H} = \epsilon \mathbf{H}_{(1)} + \epsilon^2 \mathbf{H}_{(2)} + \ldots
\]
(71)

\[
\mathbf{H}_{(1)} = \text{grad} \mathbf{u}_{(1)}
\]
(72)

\[
\mathbf{C} = (\mathbf{I} + \epsilon \mathbf{H}_{(1)} + \ldots)^T (\mathbf{I} + \epsilon \mathbf{H}_{(1)} + \ldots)
\]

\[
= \mathbf{I} + \epsilon \left( \mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T \right) + O(\epsilon^2)
\]
(73)
From (8) and (73) (the derivative of a determinant is discussed by Slattery (1999, p. 679)),

\[
\rho = \frac{\rho_0}{\det \mathbf{F}} = \frac{\rho_0}{\sqrt{\det \mathbf{C}}} = \sqrt{\frac{\rho_0}{\det \mathbf{I}}} \left( \mathbf{I} + \epsilon \left( \mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T \right) \right) + \ldots
\]

\[
= \rho_0 - \frac{\rho_0}{2 (\det \mathbf{I})^2} \text{tr} \left( \mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T \right) + \ldots
\]

\[
= \rho_0 - \frac{\rho_0}{2} \text{tr} \left( \mathbf{C} - \mathbf{I} \right) + \ldots
\]

(74)

Since, in the limit of small deformations, the strain

\[
e \equiv \frac{1}{2} \left[ \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right] = \frac{1}{2} \left[ \text{grad} \mathbf{u} + (\text{grad} \mathbf{u})^T \right] = \epsilon \left( \mathbf{H}_{(1)} + \mathbf{H}_{(1)}^T \right)
\]

(75)

which allows us to also express (74) as

\[
\rho = \rho_0 (1 - \text{tr} \mathbf{e}) + \ldots
\]

(76)

Equations (68), (71), and (76) also permit us to rewrite (66) to the first order in \( \epsilon \) as (for the moment not addressing the order of \( \mu_{(1,mn)} \))

\[
\mathbf{T} = -P \mathbf{I} + \rho_0 (1 - \text{tr} \mathbf{e}) \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(1,mn)} \left( \mathbf{I} + \epsilon \mathbf{H}_{(1)} \right) \left( \mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)} \right) \left( \mathbf{I} + \epsilon \mathbf{H}_{(1)} \right)^T
\]

\[
= -P \mathbf{I} + \rho_0 (1 - \text{tr} \mathbf{e}) \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(1,mn)} \left( \mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)} \right)
\]

\[
+ \rho_0 \epsilon \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(1,mn)} \left( \mathbf{H}_{(1)} \left( \mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)} \right) \right)
\]

\[
+ \left[ \mathbf{H}_{(1)} \left( \mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)} \right) \right]^T \right)
\]

(77)

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

\[
0 = \rho_0 \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(1,mn)} \left( \mathbf{E}_{(m)} \otimes \mathbf{E}_{(n)} + \mathbf{E}_{(n)} \otimes \mathbf{E}_{(m)} \right)
\]

(78)
where the \( \mu_{(i,mn)} \) are evaluated in the natural configuration. This allows us to express (77) as

\[
T = -PI + \rho_0 \sum_{m=1}^{3} \sum_{n=1}^{2} (\mu_{(i,mn)} - \mu_{(i,mn)0}) \left( E_{(m)} \otimes E_{(n)} + E_{(n)} \otimes E_{(m)} \right) \\
- \rho_0 \text{tr} e \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(i,mn)} \left( E_{(m)} \otimes E_{(n)} + E_{(n)} \otimes E_{(m)} \right) \\
+ \rho_0 \epsilon \sum_{m=1}^{3} \sum_{n=1}^{2} \mu_{(i,mn)} \left\{ \left( H_{(1)} \left( E_{(m)} \otimes E_{(n)} + E_{(n)} \otimes E_{(m)} \right) \right)^T \right\}
\]

(79)

As a special case, let us assume that \( \tilde{A} \), as described by (10), can be represented as a quadratic function of \( I_{(11)} \ldots I_{(33)} \) (Truesdell and Noll 1965, pp. 311-312):

\[
\tilde{A} = c_{(0)} + \sum_{i=1}^{3} \sum_{j=1}^{2} c_{(ij)} I_{(ij)} + \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{2} \sum_{m=1}^{3} \sum_{n=1}^{2} c_{(ijmn)} I_{(ij)} I_{(mn)} + \ldots
\]

(80)

It should be understood here that \( c_{(0)}, c_{(ij)} = c_{(ji)}, \) and \( c_{(ijmn)} \) are functions of \( T, \rho, \) and \( \omega(A) \) (\( A = 1, \ldots, N - 1 \)) with the additional restrictions

\[
c_{(ij)} = c_{(ji)}
\]

(81)

and

\[
c_{(ijmn)} = c_{(mnij)}
\]

\[
c_{(ijmn)} = c_{(ijnm)}
\]

\[
c_{(ijmn)} = c_{(jimn)}
\]

(82)

For this special case, from (17)

\[
\mu_{(i,mn)} = c_{(mn)} + \sum_{i=1}^{3} \sum_{j=1}^{2} c_{(ijmn)} I_{(ij)}
\]

(83)

and

\[
\mu_{(i,mn)} - \mu_{(i,mn)0} = \sum_{i=1}^{3} \sum_{j=1}^{2} c_{(ijmn)} I_{(ij)}
\]

(84)

From (7), (73), and (75), we see that

\[
I_{(ij)} = \left( E_{(i)} \right) \cdot \left( C - I \right) E_{(j)}
\]

\[
= 2E_{(i)} \cdot eE_{(j)}
\]

(85)

To the first order in \( \epsilon \), we find that (79) reduces to

\[
T = -PI + 2\rho_0 \sum_{m=1}^{3} \sum_{n=1}^{2} \sum_{i=1}^{3} \sum_{j=1}^{2} c_{(ijmn)} \left( E_{(i)} \cdot eE_{(j)} \right) \left( E_{(m)} \otimes E_{(n)} + E_{(n)} \otimes E_{(m)} \right)
\]

\[
- \rho_0 \text{tr} e \sum_{m=1}^{3} \sum_{n=1}^{2} c_{(mn)} \left( E_{(m)} \otimes E_{(n)} + E_{(n)} \otimes E_{(m)} \right)
\]

\[
+ \rho_0 \epsilon \sum_{m=1}^{3} \sum_{n=1}^{2} \left\{ H_{(1)} \left( E_{(m)} \otimes E_{(n)} + E_{(n)} \otimes E_{(m)} \right) \right\}^T
\]

(86)