Use of mixture theory to represent a cohesive elastic-viscoplastic material
by Michael James Barber

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering
Montana State University
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Abstract:
The analysis of material properties depends upon detailed information of the physical, geometric, and chemical properties of the materials. Relating these properties to a set of mathematical models is the principle objective of mechanics. Mixtures of materials made up of several constituents require special consideration since the constituent behavior must be reconciled with the overall behavior of the mixture. Mathematical models and their validity must be established to represent these materials.

This thesis establishes a methodology whereby a logical sequence of considerations may be followed to represent complex mixtures adequately. Several existing theories of mechanics are assimilated into a cohesive theory to demonstrate the validity of the mathematical model used to represent mixtures. A structured development of the second law of thermodynamics is constructed to allow additional constraint equations which will restrict the form of new parameters.

An example of a wood-snow mixture is used to show how the analysis is to be completed. Laboratory tests were run to use as a means of constructing the values of the new constitutive parameters. Proposed ways of including more constituents and spatial dimensions suggested.
USE OF MIXTURE THEORY TO REPRESENT A
COHESIVE ELASTIC-VISCOPLASTIC MATERIAL

by

Michael James Barber

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Michael James Barber

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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# TABLE OF CONTENTS

## 1. INTRODUCTION ................................................. 1

Applications ................................................. 4
Methodology ................................................. 5
  Volume Fraction Mixture Theory ......................... 6
  Internal State Variables .................................. 7

## 2. CONTINUUM PRINCIPLES OF MIXTURES ....................... 8

Introduction .................................................................. 8
  Theories of Mixtures ........................................... 9
  Kinematics .................................................................. 12
    Deformation ..................................................... 13
    Strain ............................................................. 15
    Volume Change .................................................. 17
  Stress ............................................................... 18
  Balance of Mass .................................................. 22
  Balance of Linear Momentum .................................... 24
  Balance of Angular Momentum ................................ 27
  Balance of Energy ............................................... 30
  Second Law of Thermodynamics ................................. 34
  Summing Rules .................................................... 37
    Summed Balance of Mass ..................................... 38
    Summed Balance of Linear Momentum ..................... 39
    Summed Balance of Angular Momentum .................. 40
    Summed Balance of Energy .................................. 40
    Summed Second Law .......................................... 41
  Field Equation Variables ...................................... 41

## 3. CONSTITUTIVE PRINCIPLES ..................................... 43

  Restrictions Based Upon the First Derivative of the Second Law 49
  Restrictions Based Upon the Second Derivative of the Second Law 57
  Restrictions based upon arbitrary perturbations in temperature 61
  Restriction based upon arbitrary perturbations in strain 64
  Restriction based upon arbitrary perturbations in the extent of reaction 68
TABLE OF CONTENTS-Continued

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Restrictions based upon arbitrary perturbations in the internal state vector</td>
<td>71</td>
</tr>
<tr>
<td>4. PRINCIPLES APPLIED TO A VISCO-PLASTIC MATERIAL</td>
<td>75</td>
</tr>
<tr>
<td>Assumptions Used in Deriving Constitutive Equations</td>
<td>75</td>
</tr>
<tr>
<td>Derivation of Constitutive Equations</td>
<td>77</td>
</tr>
<tr>
<td>Restrictions based upon the Second Law</td>
<td>80</td>
</tr>
<tr>
<td>Linear Momentum Interaction</td>
<td>83</td>
</tr>
<tr>
<td>Angular Momentum Interaction</td>
<td>84</td>
</tr>
<tr>
<td>Internal Energy Interaction</td>
<td>84</td>
</tr>
<tr>
<td>Evolution Equations</td>
<td>85</td>
</tr>
<tr>
<td>Material Frame Indifference</td>
<td>85</td>
</tr>
<tr>
<td>Material Frame Indifference for Stress and Strain</td>
<td>87</td>
</tr>
<tr>
<td>Material Frame Indifference for Balance Law Interaction Terms</td>
<td>89</td>
</tr>
<tr>
<td>5. APPLICATION TO A SNOW-WOOD MIXTURE</td>
<td>91</td>
</tr>
<tr>
<td>Introduction</td>
<td>91</td>
</tr>
<tr>
<td>Constitutive Equations for a Snow-Wood Mixture</td>
<td>91</td>
</tr>
<tr>
<td>Evolution Equations for the Ice-Ice Interaction</td>
<td>92</td>
</tr>
<tr>
<td>Evolution Equations for the Wood - Snow Interaction</td>
<td>94</td>
</tr>
<tr>
<td>Identification of constant coefficients</td>
<td>98</td>
</tr>
<tr>
<td>Constitutive Equations for Mass Interaction Supply</td>
<td>100</td>
</tr>
<tr>
<td>Constitutive Equations for Linear Momentum Supply</td>
<td>101</td>
</tr>
<tr>
<td>Model for a 1-Dimension Example</td>
<td>103</td>
</tr>
<tr>
<td>Identification of Model Coefficients</td>
<td>106</td>
</tr>
<tr>
<td>Consideration of Additional Variables and Higher Order Dimensions</td>
<td>112</td>
</tr>
<tr>
<td>6. DISCUSSION</td>
<td>114</td>
</tr>
<tr>
<td>Future Research</td>
<td>115</td>
</tr>
<tr>
<td>Conclusions</td>
<td>116</td>
</tr>
<tr>
<td>7. REFERENCES CITED</td>
<td>117</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>1. Internal State Variables Used for a Snow-Wood Mixture</td>
<td>92</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Graphical Representation of Mixture Theory.</td>
<td>8</td>
</tr>
<tr>
<td>2.</td>
<td>Cauchy Stress Vector and Tensor.</td>
<td>20</td>
</tr>
<tr>
<td>3.</td>
<td>First Piola Stress Tensor, $T_{\alpha R}$</td>
<td>21</td>
</tr>
<tr>
<td>4.</td>
<td>Second Piola Stress Tensor, $\tilde{T}_{\alpha}$</td>
<td>21</td>
</tr>
<tr>
<td>5.</td>
<td>Two Reference Frames Demonstrating Material Frame Indifference.</td>
<td>86</td>
</tr>
<tr>
<td>7.</td>
<td>Characterization of the Snow Surface: Black Pore Space, White Ice.</td>
<td>96</td>
</tr>
<tr>
<td>8.</td>
<td>Typical Stress-Strain Diagram of a Snow-Wood Mixture.</td>
<td>107</td>
</tr>
<tr>
<td>9.</td>
<td>Plot of Displacement Versus Psi Value for Different Compositions at a Constant $A$ Parameter Value.</td>
<td>110</td>
</tr>
<tr>
<td>10.</td>
<td>Plot of Displacement Versus Psi Value as the Parameter $A$ in the Linear Momentum Supply Term is Changed.</td>
<td>111</td>
</tr>
</tbody>
</table>
ABSTRACT

The analysis of material properties depends upon detailed information of the physical, geometric, and chemical properties of the materials. Relating these properties to a set of mathematical models is the principle objective of mechanics. Mixtures of materials made up of several constituents require special consideration since the constituent behavior must be reconciled with the overall behavior of the mixture. Mathematical models and their validity must be established to represent these materials.

This thesis establishes a methodology whereby a logical sequence of considerations may be followed to represent complex mixtures adequately. Several existing theories of mechanics are assimilated into a cohesive theory to demonstrate the validity of the mathematical model used to represent mixtures. A structured development of the second law of thermodynamics is constructed to allow additional constraint equations which will restrict the form of new parameters.

An example of a wood-snow mixture is used to show how the analysis is to be completed. Laboratory tests were run to use as a means of constructing the values of the new constitutive parameters. Proposed ways of including more constituents and spatial dimensions suggested.
CHAPTER 1

INTRODUCTION

Composite mixtures of materials contain different elements, each of which has its own material properties. In some industries this is called composite materials while in others it is called chemical mixtures. There is a whole range of materials from fluids to solids which have viscous, elastic, to visco-plastic material behavior. Each of these has a specialized field of study which tries to identify, model, and measure the properties in some way.

In the study of mechanics or more particularly, continuum mechanics, these material behaviors are approached from a more generic point of view. The equations are established which govern the physics of material objects, hypotheses are made regarding the influence the material has upon the properties, then a model is constructed, tested, and validated in the laboratory to be used in industry. Some materials are very predictable while others are more difficult since they depend upon so many different variables.

The constituent parts may have a distinctive form or may be rather haphazard or random in nature. Consider the mixture of several chemical fluids such as water and oil. Due to the material properties, these elements will not mix but will stay separated depending upon the physical conditions such as mixing, heat, and pressure. Other fluids may mix quite readily such as water and dyes. Other types of materials such as solids have a definite physical structure to them. They may be laminated or formed in some specific way such as an airplane wing laminated with carbon fibers. These types of structures are
more easily modeled due to the predictability of geometric form, structure and material interaction.

We will assume the material structure is large compared to the atomic or molecular scale of the material. It is assumed that we can represent this material with some very small but finite volume that is very much larger than the molecular structure of the material.

With this in mind we would like to consider the representation of a somewhat random geometric structure of materials that have the possibility of interacting with each other while remaining separate in the whole. This could represent such common things as soil and water, biofilm and water, or snow and soil. In general many constituents could be integrated into the whole of the material. It is also assumed that there does exist the possibility of the material interacting with the other constituents. There may be some mass change due to a chemical reaction. There may be a force or momentum interaction between the constituents. Using Newton’s laws we can derive some additional relationships from these interactions.

Mixture theory as a topic has raised many a discussion of the possible ways of representing the material behavior. It has a long history of analysis from some of the best minds in mechanics. As with any scientific model, there will be new insights and theories as the investigations continue in future generations. One thing is sure, the largest impediment to analysis and discovery of this particular topic hinges largely upon the use of some means of theory validation. With more powerful computers, researchers have better computational tools available and analysis has become a more tractable problem. With more powerful computers and by using perturbation theory and notions of chaos theory to construct numerical models, the analysis to these problems will have better solutions. The continuing problem is one of scale. Different constituents within a mixture may behave at different time scales, a formidable computational task.
With the development of the theories of mechanics for a single material beginning with Hooke (1678), Euler (1769), Cauchy (1823), to Truesdell, Toupin, Coleman, Rivlin, Green, Ericksen, Gurtin, and Noll in the 1950’s through the mid 1960’s, mechanics was rigorously developed as an applied science with which to develop new products, processes, and facilities. It was on these shoulders and many more that allowed us to develop the world infrastructure, space travel, and improved product development. One underlying problem was always how to make materials lighter yet stronger. While much attention was placed upon geometric configuration, some investigated the use of different materials. Once this notion became usable the need for new models of analysis of mixtures was required.

Beginning with Biot (1941) the concepts of mixtures were considered. Bedford and Drumheller (1983) give a thorough account of the different philosophies of mixture theories developed during those years. With the development of chemical processes the chemical industry became more involved in using these mixture models to conduct their analysis. This required not only the use of balance equations but also consideration of interactions between components.

Truesdell and Toupin (1960) established a solid foundation for the development of models used in mixture theory mechanics. Bowen (1976) gives a rigorous development of what has come to be known as classical mixture theory. He examines the restrictions imposed by equilibrium, thermodynamics, material symmetry, and material frame-indifference. He applies these results to mixtures of gases and solids. The theory of mixtures has now been established as a method for creating analytical models to represent materials made up of more than one constituent.
Applications

The theory of mixtures is used for many different types of material. Traditional uses include mixtures that are structured, mixtures that are random, and mixtures that are of a chemical nature.

The chemical industry uses mixtures to model interactions, rate of reactions, and production rates. These applications require models that allow for constituent reactions, with rates of changes that may be of a much smaller time scale than the macroscopic equations of equilibrium. More modern applications use colloids and suspensions in the mixtures. This combines the mechanics of solids, fluids, and reactions into one model. Often the notion of interfaces is used in these models so each colloid has a set of jump conditions. Bird, Stewart, and Lightfoot (1960) contains a development of mixture theory intended for the chemical engineer.

Early in the engineering field a need to model soil and its interactions with air and water were needed. Some early models of mixture theory were used to model the soils as particulates. The principle notion was one of granules or particulates with a set of fluids flowing through the porous matrix. Several theories were developed which included additional kinematic variables to account for rate of change between initial points of constituents and their position with respect to each other at some future point in time. People such as Biot (1956), Goodman and Cowin (1972), and Bear (1972) used the fundamental notions of mixture theory to develop specific models for their problems.

Adams and Brown (1989) used mixture theory to model a snow pack. A granular matrix was used through which water vapor was allowed to travel. This included the snow pack or ice matrix, water vapor, and air. Here the reactions, energy exchanges, and temperature gradients became important considerations. The primary notion of this study was to determine how the ice grains within a snow pack change geometrically,
mechanically, and thermally as a function of time and temperature. The external forces and strains were not the primary consideration.

Through personal communication with Cunningham we saw mixture theory as a method to model the behavior of a biofilm matrix. While much is to be developed in this area, the general notion is promising. Here the structure consists of a matrix of a reacting growing cell structure, fluid containing reacting constituents (food), and fluid flowing with a changing interface and velocities, portions which have both low and high Reynolds' numbers. As has been found in biomechanics, the inclusion of growing things with lifeforms further complicates many of the mechanisms.

The particular application we will address is the use of mixture theory to model the mechanisms of a snow-wood constituent mixture. The particular application is to mix wood chips with a snow matrix to increase the strength of the whole matrix. This has particular applications in cold regions where snow and ice are used as travel ways. Due to the densities of snow after compaction, the water vapor within the snow matrix is not accounted for. This is because the primary mechanisms are stresses induced by the loading.

Methodology

The normal approach to establishing the equations with which to solve applied problems in mixture theory is to write the conservation equations of each constituent. This is a series of five equations including the conservations of mass, conservation of linear momentum, conservation of angular momentum, first law of thermodynamics, and the second law of thermodynamics. Each of the constituents is treated separately. In order to connect each constituent to the whole, interactions of constituents for each of the balance equations must be considered. This introduces new variables which require additional
equations. This is achieved by requiring the sum of all constituents to behave in the manner the total mixture behaves. This gives what is called the summing equations.

An additional component of this model is the inclusion of what is called the internal state variables. Coleman and Gurtin (1967), Bowen (1989) and Hansen (1985) have used internal state variables to model relaxation phenomena. This includes such applications as slip mechanisms, crack propagation, and visoplasticity. Since snow has a viscous and elastic behavior the theory of internal state variables is combined with mixture theory to represent this snow-wood mixture.

**Volume Fraction Mixture Theory**

Classical mixture theory as presented by the mechanicians up to 1989 used the fundamental principle that the total mixture velocity is determined by taking the density of each constituent times the constituent velocity, summing then dividing by the sum of the densities. With this definition comprehensive theories were developed which when matched with experimental data required the introduction of additional kinematic variables. As shown in the next chapter, Hansen (1989) showed how this definition uses a non-kinematic variable, density, to determine a kinematic variable, velocity. Because of the apparent inconsistency we proceeded to develop a theory which we call the volume fraction mixture theory which uses as its definition of total mixture velocity the volume fraction of the constituent times the constituent velocity, summed then divided by the total volume fraction which for a saturated mixture will be unity.

With this change a different theory evolves. The additional kinematic variables introduced in the classical theories now disappear.
Internal State Variables

The internal state variables are used to represent the ice within the snow matrix, Hansen (1985). This is combined with existing work done by Edens and Brown (1990) to determine the appropriate internal state variables to use. Several variables have been introduced through the years. Some have been found to have more significance than others and some have been easily measured while others are not measurable with current technology.

The purpose of the additional variables is to represent the visco-plastic behavior of the mixture in question. Internal state variables were introduced by Coleman and Gurtin (1967), which postulated internal variables that will account for dissipative phenomena. Lubliner (1990) develops the general theory of internal variables and relates the theory to plasticity and visco-plasticity while Bowen (1989) uses internal state variable theory to develop the constitutive relations for the class of materials with internal state variables. These variables can be physically relevant or some mathematical construct. Examples of how internal state variables are used are dislocation densities, chemical affinities or yield surface parameters. In particular this theory allows for creep and relaxation when deformation, deformation rate, temperature and temperature gradients remain constant.

The combination of theories of mechanics, theories of mixtures, and theories of internal state variables allows us to construct a complex model which represents the behavior of complex materials. We use much of what has gone before us to construct this model. At each stage specific assumptions are made from which there is no return. To change the model at one point would require a reconstruction of the assumptions and the theories. With that we will begin.
CHAPTER 2

CONTINUUM PRINCIPLES OF MIXTURES

Introduction

A body which is composed of more than one constituent is difficult to model unless some simplifying assumptions are made. Truesdell and Toupin (1960) assumed that a body may be made up of more than one constituent with each point $X$ of the body $B$ occupying an equivalent point $X$ in each constituent's Euclidean space $B_\alpha \subset \mathbb{R}^3$, see Figure 1.

Figure 1. Graphical Representation of Mixture Theory.
This chapter will investigate some possible theories of mixtures which result from different assumptions. A choice of assumptions will be made, and then the resulting field equations will be derived for formulation specifically adopted for this study.

Theories of Mixtures

Assume a mixture is made up of $n$ components. Denote each constituent by a subscript $\alpha$, $\beta$, $\gamma$, ... where $\alpha$, $\beta$, $\gamma$, ... may vary from 1 to $n$. In order to associate the Euclidean spaces of each constituent with that of the body, it is necessary to specify how each space is connected. Truesdell and Toupin (1960) introduce the notion of baricentric velocity given by

$$
\dot{x} = \frac{\sum_{\alpha=1}^{n} \omega_\alpha \dot{x}_\alpha}{\sum_{\alpha=1}^{n} \omega_\alpha}
$$

(1)

where $\omega_\alpha \in R$ is a weighting factor and $\sum_{\alpha=1}^{n} \omega_\alpha \neq 0$. The baricentric velocity will sometimes be referred to as the mixture velocity. The restriction in this paper will be for $\omega_\alpha \geq 0, \forall \alpha$. $\dot{x}_\alpha$, the velocity vector of the $\alpha^{th}$ constituent, the constituent velocity, is defined by

$$
\dot{x}_\alpha = \frac{\partial}{\partial t} x_\alpha (X_\alpha, t) |_{X_\alpha = \text{fixed}}
$$

(2)

The choice of the weighting function, $\omega_\alpha$, will determine the mixture theory derived.

Consider first $\omega_\alpha = c_\alpha$, where $c_\alpha = \frac{\rho_\alpha}{\rho}$ is the mass fraction of the mixture density due to constituent $\alpha$ and is called the constituent concentration. $\rho_\alpha$ is the partial density of the constituent $\alpha$, constituent mass per unit mixture volume. $\rho$ is the mixture density of the total mixture, total mass per unit mixture volume. Then, the velocity of the mixture, $\dot{x}$, is
\[
\dot{x} = \frac{\sum_{\alpha=1}^{n} c_{\alpha} \dot{x}_{\alpha}}{\sum_{\alpha=1}^{n} c_{\alpha}} 
\]

(3)

\[
\dot{x} = \frac{\sum_{\alpha=1}^{n} \rho_{\alpha} \dot{x}_{\alpha}}{\sum_{\alpha=1}^{n} \rho_{\alpha}} 
\]

(4)

\[
\dot{x} = \frac{\sum_{\alpha=1}^{n} \rho_{\alpha} \dot{x}_{\alpha}}{\rho} 
\]

(5)

where \( \rho = \sum_{\alpha=1}^{n} \rho_{\alpha} \). This gives the definition used in classical mixture theory for the mean mixture velocity, Truesdell and Toupin (1960) and Bowen (1976).

Another possible choice made by Hansen (1989) is for \( \omega_{\alpha} = \phi_{\alpha} \), where \( \phi_{\alpha} \) is the volume fraction of constituent \( \alpha \), i.e. the fraction of the mixture volume occupied by constituent \( \alpha \). This results in the following definition for the mixture velocity,

\[
\dot{x} = \frac{\sum_{\alpha=1}^{n} \phi_{\alpha} \dot{x}_{\alpha}}{\sum_{\alpha=1}^{n} \phi_{\alpha}} 
\]

(6)

where

\[
\sum_{\alpha=1}^{n} \phi_{\alpha} \leq 1. 
\]

(7)

If we impose the restriction that for a saturated mixture,

\[
\sum_{\alpha=1}^{n} \phi_{\alpha} = 1
\]

(8)

then the denominator in equation (7) reduces to unity and we have

\[
\dot{x} = \sum_{\alpha=1}^{n} \phi_{\alpha} \dot{x}_{\alpha}.
\]

(9)
By a saturated mixture we mean that all constituents are accounted for in the analysis and the space occupied by $B$ is fully occupied by the constituents, therefore the sum of the volume fractions of all constituents must add to 1.

Equations (5) and (9) give very different results for the mixture velocity, $\mathbf{x}$, in both magnitude and direction. Equation (9) forms the mixture theory proposed by Hansen (1989), which is called the volume fraction theory, while the theory based upon equation (5) will be called the classical mixture theory. In each theory, there are different assumptions which must be made.

Truesdell (1984) lists the three metaphysical principles to be followed when considering mixtures.

- All properties of the mixture must be mathematical consequences of properties of the constituents.
- So as to describe the motion of a constituent, we may in imagination isolate it from the rest of the mixture, provided we allow properly for the actions of the other constituents upon it.
- The motion of the mixture is governed by the same equations as is a single body.

These fundamental principles relate the properties and field equations of each constituent to the properties and field equations of the body as a whole.

Classical mixture theory is derived from the choice of weighting function $\omega_\alpha = c_\alpha$ and the last metaphysical principle. These assumptions give the following principles.

- The mass weighted mean velocity of the mixture is given by equation (5).
- The sum of the constituent equations must result in the equations of the mixture.

These assumptions give the complete classical mixture theory.

Hansen (1989) has pointed out that in the classical mixture theory the definition for the mean velocity of the mixture $\mathbf{x}$ contains the notion of linear momentum. Since velocity is
a purely kinematic notion, it does not seem reasonable to define kinematics in terms of linear momentum, a kinetic term.

Hansen (1989) proposed what is called the volume fraction theory. In this theory the choice of weighting function is $\omega_\alpha = \phi_\alpha$. Additionally, the third metaphysical principle is altered giving the following principles.

- The mean velocity of the mixture is given by

$$\dot{x} = \sum_{\alpha = 1}^{n} \phi_\alpha \dot{x}_\alpha.$$  \hfill (10)

- The behavior of the mixture is governed by the summed constituent balance equations which reduces to the balance equations of a single constituent as a special case.

Notice, the kinematic definition for the velocity now contains only terms that are kinematic in nature and the mixture behaves in accordance with the summed field equations. Based on this analysis, the volume fraction theory will be utilized to model mixtures of cohesive elastic-viscoplastic materials.

**Kinematics**

The fundamental notion common to all mixture theories postulated so far is the concept of separate particles $X_\alpha$ for each constituent $\alpha$, which scaled and related in some way make up the particle $X$ in the body $B$. Truesdell and Toupin (1960) indicate the relations that must be defined so as to specify interactions between particles. It is assumed that particle $X_\alpha$ does not occupy the position of particle $Y_\alpha$, where $X_\alpha$ and $Y_\alpha$ belong to the same body $B_\alpha$. However, particles of different constituents $X_\alpha$ and $X_\beta$ of body $B_\alpha$ and $B_\beta$ respectively can occupy the same point simultaneously. Classical and modified mixture theories do not preclude particle $X_\alpha(t_1)$ from occupying the position of particle $Y_\alpha(t_2)$ at different times. Thus, while each constituent $\alpha$ may not interpenetrate with
itself, different constituents may interpenetrate with each other, so each constituent and
the mixture must have kinematic relations.

**Deformation**

Let $X_\alpha$ denote the particle in $B_\alpha$. Since $B_\alpha$ is a deformable body, $B_\alpha$ is a function of
time which is written as $B_\alpha(t)$. At some time $t = t_0$, $B_\alpha(t_0)$ is called the reference
configuration. In this reference configuration, the position of particle $X_\alpha$ is

$$X_\alpha = \kappa_\alpha(X_\alpha) .$$

This mapping is assumed to be one-to-one and onto, so that it possesses a unique inverse

$$X_\alpha = \kappa^{-1}_\alpha(X_\alpha) .$$

$\kappa_\alpha$ is called a bijective mapping.

At some other time $t$, the position of $X_\alpha$ is given as

$$x_\alpha = \chi_\alpha(x_\alpha, t) = \chi_\alpha(\kappa_\alpha(X_\alpha), t) .$$

When it is assumed the reference configuration $B_\alpha(t_0)$ is fixed at time $t_0$ then the Eulerian
coordinate $x_\alpha$ is written in terms of the Lagrangian coordinate $X_\alpha$ and time $t$,

$$x_\alpha = \chi_\alpha(X_\alpha, t) .$$

The velocity $v_\alpha$ of constituent $\alpha$ is then written as

$$v_\alpha = \frac{\partial}{\partial t} \chi_\alpha(X_\alpha, t)$$

with acceleration written as

$$a_\alpha = \frac{\partial^2}{\partial t^2} \chi_\alpha(X_\alpha, t)$$

since $X_\alpha$ is not a function of time.
Consider an arbitrary scalar, vector or tensor function $\Gamma_\alpha$. This function $\Gamma_\alpha$ may be a function of Eulerian or Lagrangian coordinates,

$$
\Gamma_\alpha = \Gamma_\alpha(x_\alpha, t)
$$

$$
\Gamma^*_\alpha = \Gamma^*_\alpha(X_\alpha, t).
$$

Taking the time derivative of equation (17) we get

$$
\dot{\Gamma}_\alpha(x_\alpha, t) = \frac{\partial}{\partial t} \Gamma_\alpha(x_\alpha, t) + \frac{\partial}{\partial x_\alpha} \Gamma_\alpha(x_\alpha, t) \frac{\partial x_\alpha}{\partial t}
$$

$$
\dot{\Gamma}_\alpha(x_\alpha, t) = \frac{\partial}{\partial t} \Gamma_\alpha(x_\alpha, t) + grad(\Gamma_\alpha(x_\alpha, t)) \dot{x}_\alpha
$$

where

$$
grad(\Gamma_\alpha(x_\alpha, t)) = \frac{\partial}{\partial x_\alpha} \Gamma_\alpha(x_\alpha, t)
$$

and

$$
\dot{x}_\alpha = \frac{\partial}{\partial t}(x_\alpha(X_\alpha, t))
$$

Equations (15), (16), and (18) give the Lagrangian description while equations (17) and (20) give the Eulerian description.

Now consider the incremental change in deformation at nearby points. By a Taylor expansion we have

$$
x_\alpha(X_\alpha + dX_\alpha, t) = x_\alpha(X_\alpha, t) + F_\alpha(x_\alpha(X_\alpha, t)) dX_\alpha + \varepsilon(X_\alpha, dX_\alpha)
$$

where $dX_\alpha$ is some small increment and $F_\alpha$ denotes the total derivative as used in Marsden (1974) and $\varepsilon(X_\alpha, dX_\alpha)$ is the error term of the expansion.

By rearranging terms in equation (23) and taking the limit we now define the deformation gradient, $F_\alpha$ by the following,
\[ F_\alpha(X_\alpha, t) = \lim_{dX_\alpha \to 0} \frac{x_\alpha(X_\alpha + dX_\alpha, t) - x_\alpha(X_\alpha, t)}{dX_\alpha} = GRAD(x_\alpha(X_\alpha, t)) \]  

(24)

where

\[ GRAD(x_\alpha(X_\alpha, t)) = \frac{\partial}{\partial X_\alpha} x_\alpha(X_\alpha, t). \]  

(25)

This also gives the relation between a spatial incremental vector and the corresponding increment in the referential description,

\[ dx_\alpha = F_\alpha(X_\alpha, t) dX_\alpha. \]  

(26)

The velocity gradient is defined by

\[ L_\alpha(x_\alpha, t) = grad(\dot{x}_\alpha(x_\alpha, t)). \]  

(27)

Observing the deformation gradient \( F_\alpha \) and taking the time derivative yields

\[ \dot{F}_\alpha = \frac{\partial}{\partial x_\alpha} (\dot{x}_\alpha) \frac{dx_\alpha}{dX_\alpha} = L_\alpha \dot{F}_\alpha. \]  

(28)

\[ \dot{F}_\alpha = \frac{\partial}{\partial x_\alpha} (\dot{x}_\alpha) \frac{dx_\alpha}{dX_\alpha} = L_\alpha \dot{F}_\alpha. \]  

(29)

thus,

\[ \dot{F}_\alpha(X_\alpha, t) = L_\alpha(x_\alpha, t) F_\alpha(X_\alpha, t). \]  

(30)

**Strain**

Here the investigation turns to line elements and how they deform. Consider the square of the length of a differential line element \( dx_\alpha \) in the spatial configuration,

\[ (ds)^2 = dx_\alpha \cdot dx_\alpha \]  

(31)

and the length squared in the reference configuration given by

\[ (dS)^2 = dX_\alpha \cdot dX_\alpha. \]  

(32)
The difference between the square of these lengths is computed to be

\[(ds)^2 - (dS)^2 = dx_\alpha \cdot dx_\alpha - dX_\alpha \cdot dX_\alpha \]  \hspace{1cm} (33)

which is rewritten as

\[(ds)^2 - (dS)^2 = F_\alpha dX_\alpha \cdot F_\alpha dX_\alpha - dX_\alpha \cdot dX_\alpha \]  \hspace{1cm} (34)

thus

\[(ds)^2 - (dS)^2 = dX_\alpha (F_\alpha^T F_\alpha - 1) dX_\alpha \]  \hspace{1cm} (35)

where 1 is the identity tensor which is the tensor that maps a vector onto itself, i.e.

\[1v = v, \forall v \in V.\]  \hspace{1cm} (36)

The Lagrangian strain tensor \(E_\alpha\) is defined to be

\[E_\alpha = \frac{1}{2} (F_\alpha^T F_\alpha - 1)\]  \hspace{1cm} (37)

thus the defining relation.

\[(ds)^2 - (dS)^2 = 2dX_\alpha E_\alpha dX_\alpha \]  \hspace{1cm} (38)

Furthermore, the right Cauchy-Green tensor \(C_\alpha\) is defined to be

\[C_\alpha = F_\alpha^T F_\alpha\]  \hspace{1cm} (39)

so that

\[E_\alpha = \frac{1}{2} (C_\alpha - 1)\]  \hspace{1cm} (40)

The Eulerian formulation follows a similar development and is given by

\[(ds)^2 - (dS)^2 = 2dx_\alpha e_\alpha dx_\alpha\]  \hspace{1cm} (41)

where \(e_\alpha\) is called the Eulerian strain with the definition

\[e_\alpha = \frac{1}{2}(1 - B_\alpha^{-1})\]  \hspace{1cm} (42)

where \(B_\alpha^{-1}\) is the inverse tensor of \(B_\alpha\), the left Cauchy-Green tensor defined by
\[ B_\alpha = F_\alpha F_\alpha^T. \] (43)

The inverse of any tensor \( T \) is denoted by \( T^{-1} \), such that \( T^{-1}T = TT^{-1} = I \).

The time derivative of the Lagrangian strain tensor \( \dot{E}_\alpha \) is defined by

\[
\dot{E}_\alpha = \frac{1}{2}(F_\alpha^T F_\alpha + F_\alpha^T \dot{F}_\alpha)
\]

by substituting equation (30). This yields

\[
\dot{E}_\alpha = \frac{1}{2} F_\alpha^T (L_\alpha^T + L_\alpha) F_\alpha.
\] (45)

Defining the rate of deformation \( D_\alpha \) to be

\[
D_\alpha = \frac{1}{2}(L_\alpha^T + L_\alpha)
\] (46)

then substituting into the above equation yields,

\[
\dot{E}_\alpha = F_\alpha^T D_\alpha F_\alpha.
\] (47)

Malvern (1969) shows that the Eulerian strain rate \( \dot{e}_\alpha \) can be related to the rate of deformation tensor, \( D_\alpha \), by

\[
\dot{e}_\alpha = D_\alpha - L_\alpha^T e_\alpha - e_\alpha L_\alpha.
\] (48)

**Volume Change**

Consider the effect of the deformation gradient upon the volume. Recall the differential volume elements \( dV_\alpha \) or \( dv_\alpha \) are given by

\[
dV_\alpha = |dx_{1\alpha} \cdot (dx_{2\alpha} \times dx_{3\alpha})| \] (49)

for the Lagrangian case and

\[
dv_\alpha = |dx_{1\alpha} \cdot (dx_{2\alpha} \times dx_{3\alpha})| \] (50)
for the Eulerian case. $dX_{1\alpha}$, $dX_{2\alpha}$, and $dX_{3\alpha}$ are three non-aligned differential position vectors emanating from the same point of $B_{\alpha}$ in the reference configuration. $dx_{i\alpha}$ are the corresponding position vectors in the deformed configuration as defined by equation (26). Now recall from equation (26) that we have
\begin{align}
dx_{1\alpha} &= F_{\alpha} dX_{1\alpha} \\
dx_{2\alpha} &= F_{\alpha} dX_{2\alpha} \\
dx_{3\alpha} &= F_{\alpha} dX_{3\alpha}
\end{align}
(51)

thus from equation (50) and (51) we have
\begin{equation}
dv_{\alpha} = |F_{\alpha} dX_{1\alpha} \cdot (F_{\alpha} dX_{2\alpha} \times F_{\alpha} dX_{3\alpha})|
\end{equation}
(52)

so as Bowen (1989) shows, the Eulerian differential volume element is,
\begin{equation}
dv_{\alpha} = |F_{\alpha}| dv_{\alpha}.
\end{equation}
(53)

Thus, the volume change from the Lagrangian to the Eulerian state is given by the deformation gradient $F$.

**Stress**

Associated with the idea of displacement and strain are the notions of force and pressure. Stress is defined as the force per unit area that resists particles from being separated. Since this occurs in $R^3$, the stress $t_{\alpha}^n$ is a vector. This vector $t_{\alpha}^n$ is called the Cauchy stress vector for constituent $\alpha$. For an arbitrary plane cutting through the point $X_{\alpha}$, the vector has both normal and tangential components. Considering the unit normal vector $n_{\alpha}$ to this plane, the tensor $T_{\alpha}$ may be formulated by
\begin{equation}
t_{\alpha}^n = T_{\alpha} n_{\alpha}
\end{equation}
(54)

where the tensor $T_{\alpha}$ is called the Cauchy stress tensor for constituent $\alpha$. It should be noted that this gives the surface traction at $x_{\alpha}$ that occurs in the deformed configuration
per unit deformed area. The Cauchy stress tensor is a member of the forces per unit area that are called surface stresses or tractions.

Stress tensors may also be reckoned in terms of other stress vectors and surface areas. The first Piola stress tensor $T_{αR}$ is the actual force on the deformed area reckoned per undeformed area as seen in Figure 3. The second Piola stress tensor $\tilde{T}_α$ is the actual force transformed by the inverse deformation gradient reckoned per undeformed area which is shown in Figure 4. This can be made more precise by considering the nature of the forces and areas involved. Consider the following spatial relationships,

\begin{equation}
  dA = ndS \tag{55}
\end{equation}

and

\begin{equation}
  dA_0 = N dS_0. \tag{56}
\end{equation}

Equation (55) represents the deformed area while equation (56) represents the original area. Now relating the Piola stress tensors to these areas the first Piola stress is the actual force on the deformed area, reckoned per unit area of the undeformed area. The second Piola stress tensor is projected in the same manner as a material vector is changed to the spatial vector to represent a deformed stress. The following mathematical relationships exist in terms of the Cauchy stress tensor and deformation gradient,

\begin{equation}
  T_{αR} = \frac{ρ_0}{ρ} (F^{-1}_α \cdot T_α) \tag{57}
\end{equation}

for the first Piola stress tensor and

\begin{equation}
  \tilde{T}_α = \frac{ρ_0}{ρ} (F^{-1}_α \cdot T_α \cdot F^{-T}_α) \tag{58}
\end{equation}

or,

\begin{equation}
  \tilde{T}_α = T_{αR} \cdot F^{-T}_α \tag{59}
\end{equation}

for the second Piola stress tensor.
Due to gravity or other physical phenomena, another type of force must be considered. These are described as the internal forces such as gravitational, magnetic or polar forces. These forces would be present in such applications as magnetic analysis, materials which have non-local interactions, and materials which have long fibers which cause local phenomena due to phenomena far from the point of analysis. The primary force we will consider is the body force vector $b_\alpha$, which describes the mass-gravity interaction. These have the units of force per unit mass.
Figure 3. First Piola Stress Tensor, $T_{αR}$.

Figure 4. Second Piola Stress Tensor, $\tilde{T}_{α}$. 
Balance of Mass

Given a body $B_\alpha$ of constituent $\alpha$, define $\gamma_\alpha$ as the intrinsic density, the mass $m_\alpha$ of constituent $\alpha$ divided by the unit volume of constituent $\alpha$. The dispersed density is identified by $\rho_\alpha$ where the mass of constituent $\alpha$, $m_\alpha$ is divided by the unit volume of the mixture. These are related by the volume fraction $\phi_\alpha$, which denotes the volume fraction of each constituent,

$$\rho_\alpha = \phi_\alpha \gamma_\alpha .$$  \hspace{1cm} (60)$$

In a multiconstituent mixture we must also consider mass interaction between constituents. This will be represented by $\hat{c}_\alpha$, the mass supply between constituents. $\hat{c}_\alpha$ represents the rate at which constituent $\alpha$ is acquiring mass from the other $n-1$ constituents, either by chemical reaction or by phase changes. $\hat{c}_\alpha$ is positive when constituent $\alpha$ is gaining mass. The density of the mixture is defined by $\rho$ where

$$\rho = \sum_{\alpha=1}^{n} \rho_\alpha = \sum_{\alpha=1}^{n} \phi_\alpha \gamma_\alpha$$ \hspace{1cm} (61)$$

where $\gamma_\alpha$ is the intrinsic density (mass per unit volume of constituent $\alpha$). For a saturated mixture, an additional relation for the volume fraction is

$$\sum_{\alpha=1}^{n} \phi_\alpha = 1 .$$ \hspace{1cm} (62)$$

Consider an arbitrary region $R_\alpha$ in body $B_\alpha$ fixed in space. The mass of the region $R_\alpha$, $M_\alpha$ is given by

$$M_\alpha = \int_{R_\alpha} \rho_\alpha dv .$$ \hspace{1cm} (63)$$
where the notation follows that used by Malvern (1969). The time rate of change of the 
mass $M_\alpha$ must equal the rate of inflow through the surface of $R_\alpha$, denoted as $\partial R_\alpha$. From 
equation (63), we can write

$$\frac{\partial M_\alpha}{\partial t} = \frac{\partial}{\partial t} \int_{R_\alpha} \rho_\alpha dv.$$  \hspace{1cm} (64)

This must equal the rate of mass growth due to the mass supply minus the flux of mass 
across the boundary, $\partial R_\alpha$, of $R_\alpha$. The flux of mass across $\partial R_\alpha$ may be expressed as

$$- \int_{\partial R_\alpha} \rho_\alpha \hat{x}_\alpha \cdot n_\alpha ds = - \int_{R_\alpha} \text{div}(\rho_\alpha \hat{x}_\alpha) dv$$  \hspace{1cm} (65)

where $\hat{x}_\alpha \cdot n_\alpha$ is positive if $x_\alpha$ is directed outward from the interior of $R_\alpha$. Therefore

$$\frac{\partial}{\partial t} \int_{R_\alpha} \rho_\alpha dv = \int_{R_\alpha} (- \text{div}(\rho_\alpha \hat{x}_\alpha) + \hat{c}_\alpha) dv$$  \hspace{1cm} (66)

where we have used the divergence theorem (Malvern, 1969) in equation (65). Rearranging terms we get

$$\int_{R_\alpha} \left( \frac{\partial \rho_\alpha}{\partial t} + \text{div}(\rho_\alpha \hat{x}_\alpha) - \hat{c}_\alpha \right) dv = 0$$  \hspace{1cm} (67)

but since $R_\alpha$ is an arbitrary volume and is assumed to meet the continuity assumptions, 
the kernel of the integrand must be zero, thus the local form becomes

$$\frac{\partial \rho_\alpha}{\partial t} + \text{div}(\rho_\alpha \hat{x}_\alpha) = \hat{c}_\alpha.$$  \hspace{1cm} (68)

Relating the Eulerian to the Lagrangian form and recalling that $dv = |F_\alpha| dV$, where 
$|F_\alpha|$ is the absolute value of the determinant of the deformation gradient $F_\alpha$, we get
Upon combining terms this yields

\[ \int_{R_{\alpha}} \left( \rho_{\alpha 0} - |\rho_{\alpha}|F_{\alpha} + |F_{\alpha}|\int_{t_0}^{t} \hat{c} \, dt \right) dV = 0 \]  

(70)

thus since \( R_{\alpha} \) is an arbitrary volume and is assumed to meet the continuity assumptions we get

\[ \rho_{\alpha 0} - |\rho_{\alpha}|F_{\alpha} + |F_{\alpha}|\int_{t_0}^{t} \hat{c} \, dt = 0 \]  

(71)

\[ \rho_{\alpha 0} = |F_{\alpha}|\left( \rho_{\alpha} - \int_{t_0}^{t} \hat{c} \, dt \right). \]  

(72)

which is the Lagrangian form for the balance of mass. This may also be written as

\[ \rho_{\alpha} = \rho_{\alpha 0}|F_{\alpha}|^{-1} + \int_{t_0}^{t} \hat{c} \, dt. \]  

(73)

Balance of Linear Momentum

Consider now the interaction between mass and velocity which is described as linear momentum. Fixing a spatial region \( R_{\alpha} \) contained in the body \( B_{\alpha} \) we get the following relation,

\[ \frac{\partial}{\partial t} \int_{R_{\alpha}} \rho_{\alpha} \dot{x}_{\alpha} \, dv = - \int_{\partial R_{\alpha}} \rho_{\alpha} \dot{x}_{\alpha} (\dot{x}_{\alpha} \cdot n_{\alpha}) \, ds + \int_{\partial R_{\alpha}} (T_{\alpha} \cdot n_{\alpha}) \, ds \]

\[ + \int_{R_{\alpha}} (\rho_{\alpha} b_{\alpha} + \hat{\rho}_{\alpha} + \hat{c}_{\alpha} \dot{x}_{\alpha}) \, dv. \]  

(74)
Here we introduce the linear momentum supply \( \hat{p}_\alpha \) which accounts for the momentum interaction between constituents. The term,

\[
- \int_{\partial R_\alpha} \rho_\alpha \hat{x}_\alpha (\hat{x}_\alpha \cdot n_\alpha) ds
\]  \hspace{1cm} (75)

represents the flux of the linear momentum out of the fixed region \( R_\alpha \) across its boundary \( \partial R_\alpha \),

\[
\int_{R_\alpha} (\rho_\alpha \dot{b}_\alpha) dv
\]  \hspace{1cm} (76)

represents the rate at which the body force is producing linear momentum in the region \( R_\alpha \),

\[
\int_{R_\alpha} (\hat{p}_\alpha) dv
\]  \hspace{1cm} (77)

represents the rate at which the linear momentum supply is generating linear momentum in the region \( R_\alpha \),

\[
\int_{R_\alpha} (\hat{c}_\alpha \hat{x}_\alpha) dv
\]  \hspace{1cm} (78)

is the rate at which the mass interaction is producing linear momentum in the region \( R_\alpha \), and

\[
\int_{\partial R_\alpha} (T_\alpha \cdot n_\alpha) ds
\]  \hspace{1cm} (79)

is the flux of linear momentum in the region \( R_\alpha \) across its boundary \( \partial R_\alpha \) due to the surface stresses.

Utilizing the divergence theorem to transform the surface integrals we get
\[
\int_{R_a} \left( \frac{\partial}{\partial t} (\rho_\alpha \dot{x}_\alpha) + \text{div}(\rho_\alpha \dot{x}_\alpha \dot{x}_\alpha) - \text{div}(T_\alpha) - \rho_\alpha b_\alpha - \hat{p}_\alpha - \hat{c}_\alpha \dot{x}_\alpha \right) dv = 0. \tag{80}
\]

Now notice that equation (68) is embedded in (80), so substitution yields,
\[
\int_{R_a} (\rho_\alpha \dot{x}_\alpha - \text{div}(T_\alpha) - \rho_\alpha b_\alpha - \hat{p}_\alpha) dv = 0 \tag{81}
\]
from which we get the local form
\[
\rho_\alpha \ddot{x}_\alpha - \text{div}(T_\alpha) - \rho_\alpha b_\alpha = \hat{p}_\alpha \tag{82}
\]
which gives the Eulerian form for linear momentum.

Multiplying equation (82) by \(|F_\alpha|\) we get
\[
|F_\alpha| \rho_\alpha \ddot{x}_\alpha - |F_\alpha| \text{div}(T_\alpha) - |F_\alpha| \rho_\alpha b_\alpha = |F_\alpha| \hat{p}_\alpha. \tag{83}
\]
Introducing the first Piola stress tensor \(T_{\alpha R}\), Bowen (1989) shows that equation (83) may be rewritten as
\[
|F_\alpha| \rho_\alpha \ddot{x}_\alpha - \text{DIV}(T_{\alpha R}) - |F_\alpha| \rho_\alpha b_\alpha = |F_\alpha| \hat{p}_\alpha. \tag{84}
\]
Substituting for the dispersed density from equation (73) we get
\[
|F_\alpha| (\ddot{x}_\alpha - b_\alpha) (\rho_\alpha |F_\alpha|^{-1} + \int_{t_0}^{t} \dot{c} d\tau) - \text{DIV}(T_{\alpha R}) = |F_\alpha| \hat{p}_\alpha. \tag{85}
\]
This may in turn be written using the second Piola stress tensor \(T_\alpha\)
\[
|F_\alpha| (\ddot{x}_\alpha - b_\alpha) (\rho_\alpha |F_\alpha|^{-1} + \int_{t_0}^{t} \dot{c} d\tau) - \text{DIV}(F_\alpha \tilde{T}_\alpha) = |F_\alpha| \hat{p}_\alpha \tag{86}
\]
which gives the Lagrangian form of the linear momentum.
Balance of Angular Momentum

In a manner similar to that used with linear momentum, we establish the balance law for angular momentum using an arbitrary fixed spatial region \( R_\alpha \). Taking the cross product of equation (82) with the position vector \( x_\alpha \) we get

\[
\frac{\partial}{\partial t} \int_{R_\alpha} \rho_\alpha x_\alpha \times \dot{x}_\alpha dv = - \int_{\partial R_\alpha} \rho_\alpha x_\alpha \times \dot{x}_\alpha (\dot{x}_\alpha \cdot n_\alpha) ds + \int_{\partial R_\alpha} x_\alpha \times (T_\alpha \cdot n_\alpha) ds \\
+ \int_{R_\alpha} x_\alpha \times (\rho_\alpha b_\alpha + \dot{p}_\alpha + \ddot{c}_\alpha x_\alpha) dv. \tag{87}
\]

\( \hat{m}_\alpha \) is introduced to account for the interaction of angular momentum between constituents. The term

\[
- \int_{\partial R_\alpha} \rho_\alpha x_\alpha \times \dot{x}_\alpha (\dot{x}_\alpha \cdot n_\alpha) ds \tag{88}
\]

represents the angular momentum of the momentum flux out of the boundary \( \partial R_\alpha \),

\[
\int_{\partial R_\alpha} x_\alpha \times (T_\alpha \cdot n_\alpha) ds \tag{89}
\]

is the angular momentum produced by the surface tractions on the boundary \( \partial R_\alpha \), and

\[
\int_{R_\alpha} x_\alpha \times (\rho_\alpha b_\alpha + \dot{p}_\alpha + \ddot{c}_\alpha x_\alpha) dv \tag{90}
\]

represents the angular momentum produced by the body force, linear momentum interactions, and mass interaction terms, respectively, in the region \( R_\alpha \).

By the divergence theorem we get
\[
\int_{R_\alpha} \left\{ \frac{\partial}{\partial t} (\rho_\alpha x_\alpha \times \dot{x}_\alpha) + \text{div}(x_\alpha \times \rho_\alpha \ddot{x}_\alpha \dot{x}_\alpha) - \text{div}(x_\alpha \times T_\alpha) \right\} dv = 0. \tag{91}
\]

The local form is given by
\[
\frac{\partial}{\partial t} (\rho_\alpha x_\alpha \times \dot{x}_\alpha) + \text{div}(x_\alpha \times \rho_\alpha \ddot{x}_\alpha \dot{x}_\alpha) - \text{div}(x_\alpha \times T_\alpha) - x_\alpha \times (\rho_\alpha \ddot{b}_\alpha + \ddot{p}_\alpha + \dot{c}_\alpha \ddot{x}_\alpha) = m_\alpha, \tag{92}
\]

since \( R_\alpha \) is an arbitrary fixed region and the assumed continuity. Noting that the balance of mass is contained within equation (92) we may rewrite equation (92) in the simplified form
\[
\rho_\alpha(x_\alpha \times \dot{x}_\alpha) - \text{div}(x_\alpha \times T_\alpha) - x_\alpha \times (\rho_\alpha \ddot{b}_\alpha + \ddot{p}_\alpha) = m_\alpha. \tag{93}
\]

As shown by Bowen (1976), we have the following identities,
\[
\text{div}(x_\alpha \times T_\alpha) = x_\alpha \times \text{div}(T_\alpha) + \begin{bmatrix} T_{\alpha 23} - T_{\alpha 32} \\ T_{\alpha 31} - T_{\alpha 13} \\ T_{\alpha 12} - T_{\alpha 21} \end{bmatrix}, \tag{94}
\]

and
\[
\frac{d}{dt}(x_\alpha \times \dot{x}_\alpha) = x_\alpha \times \ddot{x}_\alpha \tag{95}
\]

since
\[
\dot{x}_\alpha \times \dot{x}_\alpha = 0. \tag{96}
\]

Rewriting equation (93) we get
\[
x_\alpha \times (\rho_\alpha \ddot{x}_\alpha - \text{div}(T_\alpha) - \rho_\alpha \ddot{b}_\alpha - \ddot{p}_\alpha) + \begin{bmatrix} T_{\alpha 23} - T_{\alpha 32} \\ T_{\alpha 31} - T_{\alpha 13} \\ T_{\alpha 12} - T_{\alpha 21} \end{bmatrix} = m_\alpha. \tag{97}
\]
Since the first term in equation (97) contains the balance of linear momentum, equation (82), we get the following,

\[
\begin{bmatrix}
T_{\alpha 23} - T_{\alpha 32} \\
T_{\alpha 31} - T_{\alpha 13} \\
T_{\alpha 12} - T_{\alpha 21}
\end{bmatrix} = \begin{bmatrix}
\hat{m}_{\alpha 1} \\
\hat{m}_{\alpha 2} \\
\hat{m}_{\alpha 3}
\end{bmatrix} = \hat{m}_{\alpha}.
\] (98)

Thus, if we have an angular momentum supply, the Cauchy stress tensor is not symmetric. Bowen (1976) rewrites the angular momentum supply vector \( \hat{m}_{\alpha} \) as a skew-symmetric tensor \( \hat{M}_{\alpha} \) defined by

\[
T_{\alpha} - T_{\alpha}^T = \hat{M}_{\alpha}
\] (99)

where

\[
\hat{M}_{\alpha} = \begin{bmatrix}
0 & \hat{m}_{\alpha 3} & -\hat{m}_{\alpha 2} \\
-\hat{m}_{\alpha 3} & 0 & \hat{m}_{\alpha 1} \\
\hat{m}_{\alpha 2} & -\hat{m}_{\alpha 1} & 0
\end{bmatrix}.
\] (100)

Rewriting the Cauchy stress tensor \( T_{\alpha} \) as the second Piola stress tensor \( \tilde{T}_{\alpha} \) yields the Lagrangian form of the balance of angular momentum,

\[
\tilde{T}_{\alpha} - \tilde{T}_{\alpha}^T = |F_{\alpha}|F_{\alpha}^{-1}\hat{M}_{\alpha}F_{\alpha}^{-T}
\] (101)

which shows that the second Piola stress tensor is symmetric when the angular momentum supply is zero but may or may not be symmetric when there is an angular momentum supply.
Balance of Energy

The energies of a system must be in balance. This requires that the time rate of change of the kinetic and internal energy must be equal to the rate of work and heat addition. In addition to those variables defining the energy relation, we must account for the energy supply due to the interaction of the constituents. This energy supply term is denoted by \( \hat{e}_\alpha \). The balance law for energy then takes the form, after Bowen (1976),

\[
\frac{\partial}{\partial t} \int_{R_\alpha} \rho_\alpha \left( e_\alpha + \frac{1}{2} (\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) dv + \int_{\partial R_\alpha} \rho_\alpha \left( e_\alpha + \frac{1}{2} (\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) (\dot{x}_\alpha \cdot n_\alpha) ds \\
- \int_{\partial R_\alpha} (T_\alpha \dot{x}_\alpha - q_\alpha) \cdot n_\alpha ds - \int_{R_\alpha} (\rho_\alpha \dot{x}_\alpha \cdot b_\alpha + \dot{x}_\alpha \cdot \hat{p}_\alpha + \rho_\alpha r_\alpha + \hat{e}_\alpha) dv
\]

\[
= 0
\]

(102)

where the term,

\[
- \int_{\partial R_\alpha} \rho_\alpha \left( e_\alpha + \frac{1}{2} (\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) (\dot{x}_\alpha \cdot n_\alpha) ds
\]

(103)

represents the energy flux out of the boundary \( \partial R_\alpha \) of the region \( R_\alpha \) caused by the energy and kinetic energy,

\[
\int_{\partial R_\alpha} (T_\alpha \dot{x}_\alpha - q_\alpha) \cdot n_\alpha ds
\]

(104)

is the energy flux in on the boundary \( \partial R_\alpha \) in the region \( R_\alpha \) caused by the flux of stress and heat,

\[
\int_{R_\alpha} (\rho_\alpha \dot{x}_\alpha \cdot b_\alpha + \dot{x}_\alpha \cdot \hat{p}_\alpha + \rho_\alpha r_\alpha + \hat{e}_\alpha) dv
\]

(105)
in the energy change in the region $R_\alpha$ due to the body force, linear momentum interaction, heat source, and energy interaction, and

$$\int_{R_\alpha} \hat{c}_\alpha \left( e_\alpha + \frac{1}{2}(\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) dv$$  \hspace{1cm} (106)

is the energy change due to the mass interaction combined with the energy supply and a kinetic energy per unit mass in the region $R_\alpha$.

By the now standard theorems to transform the surface integrals with the appropriate continuity assumptions, we get the form

$$\int_{R_\alpha} \left[ \frac{\partial}{\partial t} \left( \rho_\alpha \left( e_\alpha + \frac{1}{2}(\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) \right) + \text{div} \left( \rho_\alpha \left( e_\alpha + \frac{1}{2}(\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) \dot{x}_\alpha \right) - \text{div}(T^T_\alpha \dot{x}_\alpha - q_\alpha) - (\rho_\alpha \dot{x}_\alpha \cdot b_\alpha + \dot{x}_\alpha \cdot \hat{p}_\alpha + \rho_\alpha r_\alpha + \hat{e}_\alpha) \right] dv = 0$$

from which we get the local form

$$\frac{\partial}{\partial t} \left( \rho_\alpha \left( e_\alpha + \frac{1}{2}(\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) \right) + \text{div} \left( \rho_\alpha \left( e_\alpha + \frac{1}{2}(\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) \dot{x}_\alpha \right) - \text{div}(T^T_\alpha \dot{x}_\alpha - q_\alpha) - (\rho_\alpha \dot{x}_\alpha \cdot b_\alpha + \dot{x}_\alpha \cdot \hat{p}_\alpha + \rho_\alpha r_\alpha + \hat{e}_\alpha) \hspace{1cm} (107)$$

Alternately, this may be written as

$$\rho_\alpha \left( e_\alpha + \frac{1}{2}(\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) - \text{div}(T^T_\alpha \dot{x}_\alpha - q_\alpha) - (\rho_\alpha \dot{x}_\alpha \cdot b_\alpha + \dot{x}_\alpha \cdot \hat{p}_\alpha + \rho_\alpha r_\alpha + \hat{e}_\alpha) - \hat{c}_\alpha \left( e_\alpha + \frac{1}{2}(\dot{x}_\alpha \cdot \dot{x}_\alpha) \right) = 0.$$  \hspace{1cm} (109)
From the balance of linear momentum we have the relation
\[ \rho_\alpha (\dot{x}_\alpha \cdot \dot{x}_\alpha) = \dot{x}_\alpha \cdot div(T_\alpha) + \rho_\alpha (\dot{\gamma}_\alpha \cdot b_\alpha) \]  
(110)
or
\[ \frac{1}{2} \rho_\alpha (\dot{x}_\alpha \cdot \dot{x}_\alpha) = \dot{x}_\alpha \cdot div(T_\alpha) + \rho_\alpha (\dot{\gamma}_\alpha \cdot b_\alpha) \]  
(111)
where we have used the identity
\[ \dot{x}_\alpha \cdot \dot{x}_\alpha = \frac{1}{2} (\dot{x}_\alpha \cdot \dot{x}_\alpha). \]  
(112)
Additionally, we can use the identity
\[ div(T_\alpha T^{\alpha}_\alpha) = \dot{x}_\alpha \cdot div(T_\alpha) + tr(T_\alpha T^{\alpha}_\alpha) \]  
(113)
and substituting equations (113), (112) and (111) into equation (109) we get
\[ \rho_\alpha \dot{\gamma}_\alpha - tr(T_\alpha T^{\alpha}_\alpha) - div(q_\alpha) - \rho_\alpha \gamma_\alpha - \dot{\gamma}_\alpha \] 
\[ + \dot{x}_\alpha \cdot (\rho_\alpha \dot{x}_\alpha - div(T_\alpha) - \rho_\alpha b_\alpha - \dot{\gamma}_\alpha) = 0. \]  
(114)
Since the last term in equation (114) is the balance of linear momentum we get
\[ \rho_\alpha \dot{\gamma}_\alpha - tr(T_\alpha T^{\alpha}_\alpha) - div(q_\alpha) - \rho_\alpha \gamma_\alpha - \dot{\gamma}_\alpha = 0. \]  
(115)
Following Bowen (1976) we can replace the Cauchy stress tensor \( T_\alpha \) with the results of equation (99) and the velocity gradient \( L_\alpha \) with its symmetric and skew-symmetric parts. Recall the symmetric part of the velocity gradient \( L_\alpha \) is called the rate of deformation tensor \( D_\alpha \) given by
\[ D_\alpha = \frac{1}{2} (L_\alpha + L^{\alpha}_\alpha) \]  
(116)
which was given in equation (46). The anti-symmetric part of the velocity gradient is given by
\[ W_\alpha = \frac{1}{2} (L_\alpha - L^{\alpha}_\alpha) \]  
(117)
which is called the spin tensor.

Since

$$L_\alpha = D_\alpha + W_\alpha$$  \hspace{1cm} (118)

and

$$\hat{M}_\alpha = T_\alpha - T_\alpha^T$$  \hspace{1cm} (119)

we can write $T_\alpha^T L_\alpha$ as $T_\alpha^T(D_\alpha + W_\alpha)$ thus yielding,

$$T_\alpha^T W_\alpha = \frac{1}{2}(T_\alpha + T_\alpha^T)W_\alpha + \frac{1}{2}(T_\alpha - T_\alpha^T)W_\alpha$$  \hspace{1cm} (120)

which may be written as

$$T_\alpha^T W_\alpha = -\frac{1}{2}\hat{M}_\alpha W_\alpha.$$  \hspace{1cm} (121)

Combining the above equations and substituting into equation (115) yields,

$$\rho_\alpha \dot{e}_\alpha - tr(T_\alpha D_\alpha) + div(q_\alpha) - \rho_\alpha r_\alpha + \hat{e}_\alpha - \frac{1}{2} tr(M_\alpha W_\alpha) = 0,$$  \hspace{1cm} (122)

which is the local form of the balance of energy.

We can now multiply equation (122) by $|F_\alpha|$ and relating $\rho_\alpha 0$ to $\rho_\alpha$ and using the Piola identity (Marsden and Hughes, 1983)

$$DIV(Q_\alpha) = |F_\alpha| div(q_\alpha)$$  \hspace{1cm} (123)

we get

$$|F_\alpha|\rho_\alpha \dot{e}_\alpha - |F_\alpha| tr(T_\alpha D_\alpha) + DIV(Q_\alpha) - |F_\alpha| \rho_\alpha r_\alpha - |F_\alpha| \hat{e}_\alpha$$

$$+ \frac{|F_\alpha|}{2} tr(M_\alpha W_\alpha) = 0.$$  \hspace{1cm} (124)

Observing that

$$D_\alpha = F_\alpha^{-T} \hat{E}_\alpha F_\alpha^{-1}$$  \hspace{1cm} (125)

we get
\[ \text{tr}(T_\alpha D_\alpha) = \text{tr}(F_\alpha^{-1} T_\alpha F_\alpha^T \dot{E}_\alpha) \]  
(126)

\[ \text{tr}(T_\alpha D_\alpha) = |F_\alpha| \text{tr}(\tilde{T}_\alpha \dot{E}_\alpha). \]  
(127)

We can now rewrite equation (122) as

\[
\left( \rho_{\alpha_0} |F_\alpha|^{-1} + \int_0^t \hat{c} dt \right) (\hat{e}_\alpha - r_\alpha) - \hat{e}_\alpha |F_\alpha| - \text{tr}(\tilde{T}_\alpha \dot{E}_\alpha) + \text{DIV}(Q_\alpha) \\
+ \frac{1}{2} \text{tr}(F_\alpha^T (\tilde{T}_\alpha - T_\alpha) F_\alpha W_\alpha) = 0,
\]
(128)

thus giving the Lagrangian form of the balance of energy.

**Second Law of Thermodynamics**

Consider now the restrictions imposed by the second law. This states that the rate of 
increase of entropy exceeds those effects due to the flux of entropy on the boundary, the 
flux of entropy due to the heat flux and the entropy production due to the heat source.

After Bowen (1976), the form for a fixed spatial region \( R_\alpha \) becomes

\[
\frac{\partial}{\partial t} \int_{R_\alpha} \rho \eta dv \geq - \int_{\partial R_\alpha} \sum_{\alpha=1}^n \rho_\alpha \eta_\alpha (\hat{x}_\alpha \cdot n_\alpha) ds - \int_{\partial R_\alpha} \sum_{\alpha=1}^n \left[ \frac{q_\alpha}{\theta_\alpha} \right] \cdot n_\alpha ds \\
+ \int_{R_\alpha} \sum_{\alpha=1}^n \left[ \frac{\rho_{\alpha_0} r_\alpha}{\theta_\alpha} \right] dv
\]
(129)

where \( \eta_\alpha \) is the entropy per unit mass. The term

\[
- \int_{\partial R_\alpha} \sum_{\alpha=1}^n \rho_\alpha \eta_\alpha (\hat{x}_\alpha \cdot n_\alpha) ds
\]
(130)

represents the flux of entropy out of the boundary \( \partial R_\alpha \) of region \( R_\alpha \).
\[- \int_{\partial R_{\alpha}} \sum_{\alpha=1}^{n} \left[ \frac{q_{\alpha}}{\theta_{\alpha}} \right] \cdot n_{\alpha} ds \]

represents the flux of entropy out of the region \( R_{\alpha} \) through the boundary \( \partial R_{\alpha} \) due to the heat flux, and

\[ \int_{R_{\alpha}} \sum_{\alpha=1}^{n} \left[ \frac{\rho_{\alpha} r_{\alpha}}{\theta_{\alpha}} \right] dv. \] (132)

is the entropy accumulation in the region \( R_{\alpha} \) due to the heat source.

Using the divergence theorem we get

\[ \frac{\partial}{\partial t} \int_{R_{\alpha}} \rho \eta dv + \int_{R_{\alpha}} \left\{ div \left( \sum_{\alpha=1}^{n} \left[ \frac{q_{\alpha}}{\theta_{\alpha}} + \rho_{\alpha} \eta_{\alpha} \dot{x}_{\alpha} \right] \right) - \sum_{\alpha=1}^{n} \left[ \frac{\rho_{\alpha} r_{\alpha}}{\theta_{\alpha}} \right] \right\} dv \geq 0. \] (133)

This may be rewritten as

\[ \int_{R_{\alpha}} \left\{ \rho \dot{\eta} + div \left( \sum_{\alpha=1}^{n} \left[ \frac{q_{\alpha}}{\theta_{\alpha}} + \rho_{\alpha} \eta_{\alpha} \dot{u}_{\alpha} \right] \right) - \sum_{\alpha=1}^{n} \left[ \frac{\rho_{\alpha} r_{\alpha}}{\theta_{\alpha}} \right] \right\} dv \geq 0, \] (134)

where \( u_{\alpha} = \dot{x}_{\alpha} - \dot{\chi} \), is called the diffusion velocity. This represents the difference in constituent velocity from the mixture velocity (baricentric center velocity from equation (6)). The local form may then be written as

\[ \rho \dot{\eta} + div \left( \sum_{\alpha=1}^{n} \left[ \frac{q_{\alpha}}{\theta_{\alpha}} + \rho_{\alpha} \eta_{\alpha} u_{\alpha} \right] \right) - \sum_{\alpha=1}^{n} \left[ \frac{\rho_{\alpha} r_{\alpha}}{\theta_{\alpha}} \right] \geq 0. \] (135)

Hansen, Crane, Damson, Donovan, Horning and Walker (1990) define the entropy for the entire mixture as

\[ \eta = \sum_{\alpha=1}^{n} c_{\alpha} \eta_{\alpha}. \] (136)

Using this relation we get
\[ \rho \dot{\eta} = \sum_{\alpha = 1}^{n} \left( \rho_\alpha \dot{\eta}_\alpha - \text{div}(\rho_\alpha \eta_\alpha \mathbf{u}_\alpha) + \hat{c}_\alpha \eta_\alpha \right) \]  

which upon substituting into equation (135) yields

\[ \sum_{\alpha = 1}^{n} \left\{ \rho_\alpha \dot{\eta}_\alpha + \text{div} \left[ \frac{\mathbf{q}_\alpha}{\theta_\alpha} \right] - \frac{\rho_\alpha r_\alpha}{\theta_\alpha} + \hat{c}_\alpha \eta_\alpha \right\} \geq 0. \]  

Substituting from the first law, equation (122), into equation (137) results in

\[ \sum_{\alpha = 1}^{n} \left\{ \rho_\alpha \dot{\eta}_\alpha + \hat{e}_\alpha - \rho_\alpha \dot{e}_\alpha + tr(T_\alpha D_\alpha) - \frac{1}{2} tr(M_\alpha W_\alpha) + \hat{c}_\alpha \theta_\alpha \eta_\alpha \right. \\
\left. - \frac{\mathbf{q}_\alpha \cdot \text{grad}(\theta_\alpha)}{\theta_\alpha} \right\} \geq 0. \]  

Introducing the Helmholtz free energy defined by

\[ \psi_\alpha = \dot{e}_\alpha - \theta_\alpha \dot{\eta}_\alpha \]  

and differentiating with respect to time yields

\[ \dot{\psi}_\alpha = \dot{\eta}_\alpha - \theta_\alpha \dot{\eta}_\alpha - \dot{\theta}_\alpha \eta_\alpha, \]  

which upon substituting in equation (139) yields the Eulerian local form for the second law,

\[ \sum_{\alpha = 1}^{n} \left\{ -\rho_\alpha (\dot{\theta}_\alpha \eta_\alpha + \psi_\alpha) + tr(T_\alpha D_\alpha) - \frac{1}{2} tr(M_\alpha W_\alpha) + \hat{c}_\alpha \theta_\alpha \eta_\alpha \\
- \frac{\mathbf{q}_\alpha \cdot \text{grad}(\theta_\alpha)}{\theta_\alpha} + \dot{e}_\alpha \right\} \geq 0. \]  

Using equations (122) through (128) yields the Lagrangian form for the second law,
\[ \sum_{\alpha=1}^{n} \left\{ -\left( \frac{\rho_{\alpha}}{|F_{\alpha}|} \right)^{-1} + \int_{t_0}^{t} \dot{c}_\alpha dt \right\} \left( \dot{\theta}_\alpha \eta_\alpha + \psi_\alpha \right) + tr(T_\alpha \dot{E}_\alpha) \]
\[ -\frac{1}{2} tr(F_{\alpha}(\tilde{T}_\alpha - \tilde{T}_\alpha^T)F_{\alpha}^T W_\alpha) \]
\[ -|F_{\alpha}|^{-1} q_\alpha \cdot grad(\theta_\alpha) + |F_{\alpha}| \hat{c}_\alpha \hat{\theta}_\alpha \eta_\alpha + |F_{\alpha}| \hat{e}_\alpha \right\} \geq 0. \] (143)

**Summing Rules**

The previous sections have developed the field equations for each constituent in a mixture. According to Hansen (1989), the behavior of the mixture must act as the sum of the behavior of the constituents. This requires the sum of the field equations and an assumption for the sum of the interaction terms.

The assumption is that there are no point sources in the mixture. If these occur they may be treated as general restrictions in the solution process. This assumption requires the following;

\[ \sum_{\alpha=1}^{n} \hat{c}_\alpha = 0, \] (144)

\[ \sum_{\alpha=1}^{n} \hat{p}_\alpha = 0, \] (145)

\[ \sum_{\alpha=1}^{n} \hat{m}_\alpha = 0 \] (146)

and

\[ \sum_{\alpha=1}^{n} \hat{e}_\alpha = 0. \] (147)

This implies that there may be mass, linear momentum, angular momentum and energy supply between constituents but there is not a point source supply for the mixture as a whole. With these assumption the summed field equations may be constructed.
Hansen, Crane, Damson, Donovan, Horning and Walker (1990) related body force, heat source, internal energy and entropy between the constituents and the mixture. Observing the units of these intensive properties they observed the following relations:

\[ b = \sum_{\alpha=1}^{n} c_{\alpha} \beta_{\alpha}, \quad (148) \]

\[ r = \sum_{\alpha=1}^{n} c_{\alpha} r_{\alpha}, \quad (149) \]

\[ e = \sum_{\alpha=1}^{n} c_{\alpha} e_{\alpha}, \quad (150) \]

and

\[ \eta = \sum_{\alpha=1}^{n} c_{\alpha} \eta_{\alpha}. \quad (151) \]

These intensive properties are related to the mixture by their concentrations since their basic unit of measurement is per unit mass. This differs from the definition of the mixture mass which is based upon unit volume so the total mixture mass is the sum of the constituent masses.

In a similar way the Cauchy stress tensor and the heat flux can be defined. These are based on surface area by definition. Hansen (1989) has shown that from quantitative stereology the area fraction and volume fraction are the same. Thus, the Cauchy stress tensor \( T_{\alpha} \) and the heat flux vector \( q_{\alpha} \) are already scaled by the volume fraction. The definition for the mixture total stress and heat flux then becomes,

\[ T = \sum_{\alpha=1}^{n} T_{\alpha}, \quad (152) \]

and

\[ q = \sum_{\alpha=1}^{n} q_{\alpha}. \quad (153) \]
Summed Balance of Mass

With equation (144) the mixture field equation becomes,

\[ \sum_{\alpha}^{n} \left[ \frac{\partial \rho_{\alpha}}{\partial t} + \text{div}(\rho_{\alpha} \dot{x}_\alpha) \right] = 0 \quad (154) \]

which may be reduced to

\[ \frac{\partial \rho}{\partial t} + \text{div} \left[ \sum_{\alpha}^{n} \rho_{\alpha} \dot{x}_\alpha \right] = 0 \quad (155) \]

by using equation (61) Using the definition for diffusion velocity, \( u_\alpha = \dot{x}_\alpha - \dot{x} \), equation (155) yields

\[ \frac{\partial \rho}{\partial t} + \text{div}(\rho \dot{x}) + \text{div}(\sum_{\alpha}^{n} \rho_{\alpha} u_\alpha) = 0 \quad (156) \]

which shows that diffusion velocity may contribute significantly to the mixture mass balance.

Summed Balance of Linear Momentum

Combining equation (145) with (82) gives the summed linear momentum equation,

\[ \sum_{\alpha}^{n} \left[ \rho_{\alpha} \ddot{x}_\alpha - \text{div}(T_\alpha) - \rho_{\alpha} b_\alpha \right] = 0, \quad (157) \]

thus

\[ \sum_{\alpha}^{n} \rho_{\alpha} \ddot{x}_\alpha - \text{div}(\sum_{\alpha}^{n} T_\alpha) - \sum_{\alpha}^{n} \rho_{\alpha} b_\alpha = 0, \quad (158) \]

\[ \sum_{\alpha}^{n} \rho_{\alpha} \ddot{x}_\alpha - \text{div}(T) - \sum_{\alpha}^{n} \rho_{\alpha} b_\alpha = 0, \quad (159) \]

where the Cauchy stress \( T \) is related to the partial stresses \( T_\alpha \) by the relation

\[ T = \sum_{\alpha}^{n} T_\alpha, \quad (160) \]

Hansen (1989). Thus, the balance equation for the mixture becomes
\[
\sum_{\alpha=1}^{n} \rho_\alpha (\ddot{x}_\alpha - b_\alpha) - \text{div}(T) = 0. \tag{161}
\]

**Summed Balance of Angular Momentum**

Recall from classical continuum mechanics that the Cauchy stress tensor is symmetric, Malvern (1969). This has the form

\[ T = T^T \tag{162} \]

which may be rewritten in mixture theory form

\[ \sum_{\alpha=1}^{n} T_\alpha = \sum_{\alpha=1}^{n} T_\alpha^T, \tag{163} \]

since by equation (146) no angular momentum supply for the mixture has been imposed. Thus, with an angular momentum supply for each constituent, the partial stress tensor may not be symmetric but the total stress for the mixture is symmetric.

**Summed Balance of Energy**

Considering equation (147) and combining with equation (122) the summed energy balance becomes,

\[
\sum_{\alpha=1}^{n} \left\{ \rho_\alpha \dot{e}_\alpha - r_\alpha(T_\alpha D_\alpha) + \text{div}(q_\alpha) - \rho_\alpha r_\alpha + \dot{e}_\alpha - \frac{1}{2} \text{tr}(M_\alpha W_\alpha) \right\} = 0 \tag{164}
\]

which upon expanding

\[
\sum_{\alpha=1}^{n} \rho_\alpha \dot{e}_\alpha - \sum_{\alpha=1}^{n} r_\alpha(T_\alpha D_\alpha) + \sum_{\alpha=1}^{n} \text{div}(q_\alpha) - \sum_{\alpha=1}^{n} \rho_\alpha r_\alpha = 0 \tag{165}
\]

where the last two terms on the left hand side are zero, thus

\[
\rho \dot{e} - \sum_{\alpha=1}^{n} r_\alpha(T_\alpha D_\alpha) + \text{div}(q) - \rho r = 0, \tag{166}
\]

or
\[
\rho \dot{\varepsilon} - tr(TD) + div(q) - \rho r = 0. 
\] (167)

**Summed Second Law**

From equation (139) it is evident that the second law restrictions developed are based upon the summed properties of all constituents of the mixture. There have been conjectures to date as to whether the second law should hold for each constituent or for the mixture as a whole. A rigorous solution to this problem has not been found, so assumptions will need to be made. As will be noted in a following chapter, the constitutive relations for the interaction terms include not only the independent variables for the constituent but also the independent variables for other constituents. Thus, the second law should be in a form to restrict these constitutive relations.

**Field Equation Variables**

The balance equations for mass (68), linear momentum (82), angular momentum (99) and energy (122) along with the restrictions imposed by the second law (142) have been developed for each constituent and the mixture as a whole. The independent variables of interest are the position vector \( x_\alpha \) and time \( t \). The variables that have been introduced in the field equations are the dispersed density \( \rho_\alpha \), constituent velocity \( \dot{x}_\alpha \), Cauchy stress tensor \( T_\alpha \), internal energy \( e_\alpha \), heat flux \( q_\alpha \), temperature \( \theta_\alpha \) and entropy \( \eta_\alpha \). It is assumed that the body force \( b_\alpha \) and heat source \( r_\alpha \) will be specified functions. These variables are the same as those for a single constituent body, although with mixture theory new variables have been introduced. These are the mass interaction \( \hat{c}_\alpha \), linear momentum interaction \( \hat{p}_\alpha \), angular momentum interaction \( \hat{M}_\alpha \) and energy interaction \( \hat{e}_\alpha \). The
interaction variables depend upon the $\alpha$ constituent and possibly all other constituents while all other variables depend only upon the properties of the $\alpha$ constituent.

One possible method of solving this system of equations is suggested by Bedford and Drumheller, (1983). Use the four balance equations to solve for $p_\alpha$, $\dot{x}_\alpha$, $\dot{M}_\alpha$ and $\theta_\alpha$. Constitutive relations are formulated relating $\hat{c}_\alpha$, $T_\alpha$, $\hat{P}_\alpha$, $e_\alpha$, $q_\alpha$, $\dot{e}_\alpha$ and $\eta_\alpha$ by using the second law (142) and the mixture balance equations, (144) through (147), (156), (161), (163) and (167). These relations are utilized in the solution of the balance equations.

The solution to this set of partial differential equations is facilitated by using internal state variables and imposing upon the constitutive relations a rigorous development of the restrictions from continuum mechanics. This will be the subject of the next two chapters.
CHAPTER 3

CONSTITUTIVE PRINCIPLES

The solution to this set of partial differential equations is facilitated by using internal state variables and imposing upon the constitutive relations a rigorous development of the restrictions from continuum mechanics. This will be the subject of the next two chapters.

Billington and Tate (1981) show the general form for a simple elastic material to be

\[(T_{\alpha}, q_{\alpha}, e_{\alpha}, \eta_{\alpha}, \psi_{\alpha})(X_{\alpha}, t) = f_{\alpha}(x_{\alpha}, F_{\alpha}, \theta_{\alpha}, GRAD(\theta_{\alpha}), X_{\alpha}, t)\] (168)

and Bowen (1976) shows that the interaction terms are functions of,

\[(\dot{\varepsilon}_{\alpha}, \dot{\rho}_{\alpha}, \dot{\varepsilon}_{\alpha})(X_{\alpha}, t) = f_{\alpha}(x_{\beta}, F_{\beta}, \theta_{\beta}, GRAD(\theta_{\beta}), X_{\beta}, t), \forall \beta \in (1, n)\] (169)

where we have specified \( \rho_{\alpha}, \dot{x}_{\alpha}, \dot{M}_{\alpha} \) and \( \theta_{\alpha} \) by using the balance equations. For a viscoplastic material, Hansen (1985) suggests the following constitutive dependencies,

\[(T_{\alpha}, q_{\alpha}, e_{\alpha}, \eta_{\alpha}, \psi_{\alpha})(X_{\alpha}, t) = g_{\alpha}(E_{\alpha}, \theta_{\alpha}, \xi_{\alpha})\] (170)

here the internal state vector is included and the constitutive relation for the internal state vector evolution equations depends upon,

\[\dot{\xi}_{\alpha} = \omega(E_{\alpha}, \theta_{\alpha}, \xi_{\alpha})\] (171)

For this paper, we intend to be as general as possible, at least initially, and then will simplify the formulation once specific applications are considered. In order to be as general as possible, some additional variables must be included as independent variables for the above constitutive relations. In a material in which chemical reactions may take place, a term referred to as the “extent of reaction” will be included to reflect the extent to
which chemical reactions have occurred and to include this effect on the constituent properties. This term will be denoted by $I_\alpha$, and will have the form:

$$I_\alpha = \frac{\rho_\alpha}{\rho_{\alpha_0}} \text{det}|F_\alpha|$$

(172)

This variable has a value of one if there has been no mass exchange between the $\alpha$ and the other $(n-1)$ constituents. Therefore any deviation of $I_\alpha$ from the value of unity indicates it has either gained or lost mass, depending on whether the value of $I_\alpha$ is greater than or less than the value of one. This is so, since for any material in which there is no chemical reaction, the ratio of the reference density to the deformed reference density is given by the expression $\frac{\rho_{\alpha_0}}{\rho_\alpha} = \text{det}|F_\alpha|$, since changes in density would be due solely to volumetric deformations as determined by $\text{det}|F_\alpha|$. If this is true for any constituent, then $I_\alpha$ has the value of unity.

Another variable which could determine some of the constitutive relations is the constituent velocity. In our case, we will assume that the diffusion velocity, $u_\alpha$, may be an independent variable upon which some of the constitutive relations will depend. Certainly, heat transfer, momentum interaction, and the mass and energy interaction terms may depend upon this variable. Since snow is a diffusing material with mass interaction between some of the constituents, this set of variables must be included initially as a potentially important independent variable.

Finally, the temperature gradient should also be included as a possibly significant independent variable. Temperature gradients are responsible for the transfer of both heat and mass within a material, and it may play an important role in many of the interactions terms.

For the sake of brevity, the Eulerian temperature gradient will be denoted by the expression $g_\alpha = \text{grad}(\theta_\alpha)$, and the Lagrangian temperature gradient will be denoted by the expression $G_\alpha = \text{GRAD}(\theta_\alpha)$. 
Part of the development of constitutive relations in continuum mechanics consists of insuring the following restrictions hold, Bowen (1989).

**Consistency:**

The constitutive relations must obey the balance equations.

**Coordinate invariance:**

They must work in any coordinate system.

**Just setting:**

Well posed mathematically.

**Material frame indifference:**

Material response is independent of the reference frame.

**Material symmetry:**

Material symmetry should be modeled by the constitutive relations.

**Equipresence:**

Independent variables should be in all constitutive relations unless it contradicts one of the above.

Each of these issues will be addressed as the constitutive laws are developed. Some will be inferred implicitly while others such as material frame indifference will be established explicitly.

To develop the explicit constitutive equations we begin by considering the second law, equation (142), which uses the Helmholtz free energy $\psi_\alpha$. We denote the constituent free energy by

$$\psi_\alpha = \psi_\alpha(E_\alpha, \theta_\alpha, s_\alpha, u_\alpha, l_\alpha, \xi_\alpha)$$

(173)

where the vector $\xi_\alpha$ denotes the internal state vector consisting of scalars which describe the microstructure of the material. This vector gives extra displacement variables which allow the state of the material to change while deformation and temperature are constant. We assume here that elastic strains occur when $\xi_\alpha$ is constant and all other variables change, while inelastic strains occur when $\xi_\alpha$ changes while the other variables are constant, Rice (1971). The other functions listed in Equation (170) will be assumed to
have the same dependency as the free energy. In addition, all of the interaction terms will be assumed to depend on all of these variables for all constituents. The evolution relation will be assumed to depend on the same variables as the free energy.

Taking the time derivative of Equation (173) yields

$$\dot{\psi}_\alpha = \frac{\partial \psi_\alpha}{\partial \theta_\alpha} \dot{\theta}_\alpha + tr \left( \frac{\partial \psi_\alpha}{\partial E_\alpha} \cdot \dot{E}_\alpha \right) + \frac{\partial \psi_\alpha}{\partial \xi_\alpha} \cdot \dot{\xi}_\alpha + \frac{\partial \psi_\alpha}{\partial \eta_\alpha} \cdot \dot{\eta}_\alpha + \frac{\partial \psi_\alpha}{\partial g_\alpha} \cdot \dot{g}_\alpha + \frac{\partial \psi_\alpha}{\partial l_\alpha} \cdot \dot{l}_\alpha$$  

(174)

In what follows, the Eulerian form of the second law will be used. Substituting equation (174) into equation (142) yields

$$\sum_{\alpha = 1}^{n} \frac{1}{\theta_\alpha} \left\{ - \rho_\alpha \left[ \eta_\alpha \dot{\theta}_\alpha + \frac{\partial \psi_\alpha}{\partial \theta_\alpha} \dot{\theta}_\alpha + tr \left( \frac{\partial \psi_\alpha}{\partial E_\alpha} \cdot \dot{E}_\alpha \right) + \frac{\partial \psi_\alpha}{\partial \xi_\alpha} \cdot \dot{\xi}_\alpha \right] + \frac{\partial \psi_\alpha}{\partial u_\alpha} \cdot \dot{u}_\alpha + \frac{\partial \psi_\alpha}{\partial g_\alpha} \cdot \dot{g}_\alpha + \frac{\partial \psi_\alpha}{\partial l_\alpha} \cdot \dot{l}_\alpha \right\} $$

$$- \frac{1}{2} tr(\dot{M}_\alpha W_\alpha) + \frac{1}{det|F_\alpha|} \rho(\ddot{T}_\alpha E_\alpha)$$

$$- q_\alpha \cdot g_\alpha \frac{\dot{\theta}_\alpha}{\theta_\alpha} + \dot{\varepsilon}_\alpha \dot{\theta}_\alpha + \varepsilon_\alpha \right\} \geq 0.$$  

(175)

The term $dl_\alpha/dt$ can be written as:

$$l_\alpha = \frac{det|F_\alpha|}{\rho_{\alpha\alpha}} \dot{\varepsilon}_\alpha$$  

(176)

Consequently, the variable $l_\alpha$ is not actually independent of the other kinematic variables, but we retain it in order to evaluate its effect on constitutive relations. The second law now acquires the form:
\[
\sum_{\alpha=1}^{n} \frac{1}{\theta_\alpha} \left[ -\rho_\alpha \left( \eta_\alpha + \frac{\partial \psi_\alpha}{\partial \theta_\alpha} \right) + tr \left( \left( \frac{1}{det \mathbf{F}_\alpha} \mathbf{F}_\alpha \partial \mathbf{F}_\alpha \right) \frac{\partial \mathbf{F}_\alpha}{\partial \mathbf{E}_\alpha} \right) \right] - \rho_\alpha \frac{\partial}{\partial \mathbf{E}_\alpha} \mathbf{E}_\alpha \\
- \rho_\alpha \frac{\partial}{\partial \mathbf{u}_\alpha} \mathbf{u}_\alpha - \rho_\alpha \frac{\partial}{\partial \mathbf{g}_\alpha} \mathbf{g}_\alpha - \frac{1}{2} tr (\mathbf{M}_\alpha \mathbf{W}_\alpha) + \dot{\varepsilon}_\alpha \\
- \frac{\mathbf{q}_\alpha \cdot \mathbf{g}_\alpha}{\theta_\alpha} + \left( \theta_\alpha \eta_\alpha - \rho_\alpha \frac{\partial \mathbf{F}_\alpha}{\partial \mathbf{l}_\alpha} \frac{\partial \mathbf{F}_\alpha}{\partial \mathbf{E}_\alpha} \right) \dot{\varepsilon}_\alpha \geq 0
\]

(177)

which for arbitrary values and jumps in \( \theta_\alpha, \dot{\varepsilon}_\alpha, \mathbf{u}_\alpha \) and \( \mathbf{g}_\alpha \) we have the following restrictions.

\[
\mathbf{T}_\alpha = \rho_\alpha det \mathbf{F}_\alpha \frac{\partial \mathbf{F}_\alpha}{\partial \mathbf{E}_\alpha} \\
\dot{\mathbf{l}}_\alpha = \mathbf{F}_\alpha \mathbf{F}_\alpha \frac{\partial \mathbf{F}_\alpha}{\partial \mathbf{E}_\alpha}
\]

(178)

\[
\eta_\alpha = -\frac{\partial \psi_\alpha}{\partial \theta_\alpha}
\]

(179)

\[
\frac{\partial \psi_\alpha}{\partial \mathbf{g}_\alpha} = 0
\]

(180)

\[
\frac{\partial \psi_\alpha}{\partial \mathbf{u}_\alpha} = 0
\]

(181)

The second law therefore reduces to:

\[
\sum_{\alpha=1}^{n} \frac{1}{\theta_\alpha} \left[ -\rho_\alpha \frac{\partial \psi_\alpha}{\partial \theta_\alpha} \cdot \dot{\varepsilon}_\alpha - \frac{1}{2} tr (\mathbf{M}_\alpha \mathbf{W}_\alpha) + \dot{\varepsilon}_\alpha \right]
\]

\[
- \frac{\mathbf{q}_\alpha \cdot \mathbf{g}_\alpha}{\theta_\alpha} + \left( \theta_\alpha \eta_\alpha - \rho_\alpha \frac{\partial \mathbf{F}_\alpha}{\partial \mathbf{l}_\alpha} \frac{\partial \mathbf{F}_\alpha}{\partial \mathbf{E}_\alpha} \right) \dot{\varepsilon}_\alpha \geq 0.
\]

(182)

The expression which prefixes the mass interaction can be expressed in terms of the chemical potential, \( \mu_\alpha \), which has been defined as (Nunziato and Walsh, 1980)

\[
\mu_\alpha = \frac{\partial}{\partial \mathbf{l}_\alpha} (l_\alpha \psi_\alpha) = \frac{\partial}{\partial \rho_\alpha} (\rho_\alpha \psi_\alpha)
\]

(183)
Using this definition, the coefficient of the mass interaction can be written as

\[
\theta_\alpha \eta_\alpha - \rho_\alpha \frac{\partial \psi_\alpha}{\partial t_\alpha} = e_\alpha - \mu_\alpha
\]

and the second law further reduces to:

\[
\delta = \sum_{\alpha = 1}^{n} \frac{1}{\theta_\alpha} \left\{ -\rho_\alpha \frac{\partial \psi_\alpha}{\partial \xi_\alpha} \cdot \hat{\xi}_\alpha - \frac{1}{2} tr(MW_\alpha) + \hat{\varepsilon}_\alpha \
- \frac{q_\alpha \cdot g_\alpha}{\theta_\alpha} + (e_\alpha - \mu_\alpha) \hat{\varepsilon}_\alpha \right\} \geq 0.
\]

This is as simplified as the second law can be without imposing assumptions or considering additional details regarding the variation of the dissipation function $\delta$. To proceed, we need to consider the thermomechanical state of equilibrium and the value of $\delta$ as this is reached.

We define as the state of thermomechanical equilibrium to be that state reached when:

\[
\theta_1 = \theta_2 = \ldots = \theta_n = \theta^e
\]

\[
\hat{\xi}_\alpha = 0
\]

\[
\hat{\varepsilon}_\alpha = 0
\]

\[
\hat{\varepsilon}_e = 0
\]

\[
\hat{\varepsilon}_e = 0
\]

The superscript “e” is used to denote the state of thermomechanical equilibrium. When these conditions are met, the dissipation function, $\delta$, goes to zero. Now consider any small perturbation from this state of equilibrium. Denote the set of variables $s_\alpha$ and $\mathbf{s}$ to be the following:
Restrictions Based Upon the First Derivative of the Second Law

At the state of thermomechanical equilibrium, the dissipation function $\delta$ is equal to zero but must be equal or greater than zero for any small departure or perturbation from equilibrium. Now let $s^p$ be any arbitrary perturbation in the variables $s$, and let $\epsilon$ be any arbitrarily small scalar. Then the following must be observed:

$$\delta(s^\epsilon) = 0$$ (188)

$$\delta' = \delta(s^\epsilon + \epsilon s^p) \geq 0$$ (189)

The prime is used to denote the value of $\delta$ in a perturbed state. In the perturbed state, the second law acquires the form:

$$\delta' = \sum_{\alpha = 1}^{n} \frac{1}{(g^\alpha + \epsilon g^p_\alpha)} \left[ \frac{\epsilon'_\alpha \cdot (g^\alpha + \epsilon g^p_\alpha)}{\epsilon'_\alpha + \epsilon g^p_\alpha} + e'_\alpha - \rho'_\alpha \sigma_\alpha \frac{\partial}{\partial \sigma_\alpha} \psi'_\alpha \cdot \xi'_\alpha \right] + \frac{1}{2} tr(\hat{M}_\alpha W_\alpha)' + (e'_\alpha - \mu'_\alpha) \xi'_\alpha \geq 0$$ (190)

As indicated earlier, the variables which are primed are evaluated at the perturbed state away from equilibrium. The functional dependency of the terms in the above relations is:
Where we have assumed the evolution equation for $\xi_\alpha$ does not have a dependency upon either the diffusion velocity or the temperature gradient, since the free energy is a function of the state variable $\xi_\alpha$, and if the evolution equation for $\xi_\alpha$ displayed a dependency upon $u_\alpha$ and $g_\alpha$, then the free energy should also. The supply terms, however, may depend upon the full collection of variables. Thus, we have the following dependencies:

\begin{align}
\dot{\psi}'_\alpha &= \psi'_\alpha (E_\alpha^e + \varepsilon E_\alpha^p, \theta^e + \varepsilon \theta_\alpha^p, \xi_\alpha + \varepsilon \xi_\alpha^p, l_\alpha^e + \varepsilon l_\alpha^p) \\
\eta'_\alpha &= \eta'_\alpha (E_\alpha^e + \varepsilon E_\alpha^p, \theta^e + \varepsilon \theta_\alpha^p, \xi_\alpha + \varepsilon \xi_\alpha^p, l_\alpha^e + \varepsilon l_\alpha^p) \\
\mu'_\alpha &= \mu'_\alpha (E_\alpha^e + \varepsilon E_\alpha^p, \theta^e + \varepsilon \theta_\alpha^p, \xi_\alpha + \varepsilon \xi_\alpha^p, l_\alpha^e + \varepsilon l_\alpha^p) \\
e'_\alpha &= e'_\alpha (E_\alpha^e + \varepsilon E_\alpha^p, \theta^e + \varepsilon \theta_\alpha^p, \xi_\alpha + \varepsilon \xi_\alpha^p, l_\alpha^e + \varepsilon l_\alpha^p) \\
T'_\alpha &= T'_\alpha (E_\alpha^e + \varepsilon E_\alpha^p, \theta^e + \varepsilon \theta_\alpha^p, \xi_\alpha + \varepsilon \xi_\alpha^p, l_\alpha^e + \varepsilon l_\alpha^p) \\
\dot{M}'_\alpha &= \dot{M}'_\alpha (E_\alpha^e + \varepsilon E_\alpha^p, \theta^e + \varepsilon \theta_\alpha^p, \xi_\alpha + \varepsilon \xi_\alpha^p, l_\alpha^e + \varepsilon l_\alpha^p) \\
\dot{x}_\alpha &= \dot{x}_\alpha (E_\alpha^e + \varepsilon E_\alpha^p, \theta^e + \varepsilon \theta_\alpha^p, \xi_\alpha + \varepsilon \xi_\alpha^p, l_\alpha^e + \varepsilon l_\alpha^p) \\
\end{align}

(191)

Equations (188) and (189) imply the following:

\begin{align}
\dot{c}'_\alpha &= \dot{c}'_\alpha (E_\beta^e + \varepsilon E_\beta^p, \theta^e + \varepsilon \theta_\beta^p, g_\beta^e + \varepsilon g_\beta^p, \xi_\beta + \varepsilon \xi_\beta^p, l_\beta^e + \varepsilon l_\beta^p, u_\beta^e + \varepsilon u_\beta^p) \\
\dot{p}'_\alpha &= \dot{p}'_\alpha (E_\beta^e + \varepsilon E_\beta^p, \theta^e + \varepsilon \theta_\beta^p, g_\beta^e + \varepsilon g_\beta^p, \xi_\beta + \varepsilon \xi_\beta^p, l_\beta^e + \varepsilon l_\beta^p, u_\beta^e + \varepsilon u_\beta^p) \tag{192}
\\
\dot{c}'_\alpha &= \dot{c}'_\alpha (E_\beta^e + \varepsilon E_\beta^p, \theta^e + \varepsilon \theta_\beta^p, g_\beta^e + \varepsilon g_\beta^p, \xi_\beta + \varepsilon \xi_\beta^p, l_\beta^e + \varepsilon l_\beta^p, u_\beta^e + \varepsilon u_\beta^p)
\end{align}

where $\beta$ is summed over all of the constituents. In addition, the heat flux vector, $q_\alpha$, has a dependence upon the same variables as the free energy plus a dependence upon the temperature gradient and the diffusion velocity, since heat transfer by vapor diffusion is a very significant part of the overall heat transfer.

Equations (188) and (189) imply the following:

\[
\frac{d}{d\varepsilon} \delta' \bigg|_{\varepsilon = 0} = 0 \tag{193}
\]
These two equations simply state that the dissipation function is positive semi-definite and reaches a local minimum at thermomechanical equilibrium. Now consider the implications of these two equations. First expand equation (193).

\[
\frac{d^2}{de^2} \delta' \bigg|_{e=0} \geq 0
\]  

(194)

Carrying out this differentiation, we get the following:

\[
\left. \frac{d}{de} \delta' \right|_{e=0} = \left[ \frac{\partial}{\partial (s^e + \varepsilon s^p)} \delta' \cdot \frac{d}{de} (s^e + \varepsilon s^p) \right]_{e=0}
\]

\[
= \frac{\partial}{\partial (s^e + \varepsilon s^p)} \delta' \bigg|_{e=0} \cdot s^p = \left( \frac{\partial \delta}{\partial s} \right)^e \cdot s^p
\]

(195)

which upon expansion of the differentiation yields the following:

\[
\frac{d}{de} \delta' \bigg|_{e=0} = \frac{\partial}{\partial s} \sum_{\alpha=1}^{n} \frac{1}{\theta_\alpha} \left\{ -\rho_\alpha \frac{\partial \psi_\alpha}{\partial \dot{\varepsilon}_\alpha} \cdot \dot{\varepsilon}_\alpha - \frac{q_\alpha \cdot g_\alpha}{\theta_\alpha} 

- \frac{1}{2} tr \hat{M}_\alpha \omega_\alpha + (e_\alpha - \mu_\alpha) \dot{c}_\alpha \right\} \cdot s^p \geq 0
\]

(196)

which upon expansion of the differentiation yields the following:
\[
\frac{d \delta'}{d \epsilon} \bigg|_{\epsilon = 0} = \sum_{\alpha = 1}^{n} \frac{-1}{\theta_{\alpha}} \left[ -\rho_{\alpha} \partial_{\xi_{\alpha}} \cdot \dot{\theta}_{\alpha} + q_{\alpha} \cdot \frac{\partial g_{\alpha}}{\partial \theta_{\alpha}} + \dot{\epsilon}_{\alpha} \right]
\]

\[
-\frac{1}{2} \text{tr} (\dot{M}_{\alpha} W_{\alpha}) + (e_{\alpha} - \mu_{\alpha}) \dot{\epsilon}_{\alpha} \right)^{\epsilon} \theta_{\alpha}^p
\]

\[
+ \sum_{\alpha = 1}^{n} \sum_{\beta = 1}^{n} \left\{ -\frac{\partial}{\partial s_{\beta}} (q_{\alpha} \cdot \frac{\partial \psi_{\alpha}}{\partial \theta_{\alpha}}) \cdot \dot{\theta}_{\alpha} - \rho_{\alpha} \frac{\partial}{\partial s_{\beta}} (\psi_{\alpha} \cdot \frac{\partial \xi_{\alpha}}{\partial \theta_{\alpha}}) \cdot \dot{\theta}_{\alpha} \right\}
\]

\[
+ \frac{1}{2} \text{tr} \left[ \frac{\partial}{\partial s_{\beta}} (\dot{M}_{\alpha} W_{\alpha}) + \dot{M}_{\alpha} \frac{\partial W_{\alpha}}{\partial s_{\beta}} \right] + \frac{\partial}{\partial s_{\beta}} (e_{\alpha} - \mu_{\alpha}) \dot{\epsilon}_{\alpha} \right)^{\epsilon} s_{\beta}^p = 0
\]

In the above, the first summation is identically zero, since this is essentially the dissipation function at equilibrium. Expanding the second set of terms, we have:

\[
\frac{d \delta'}{d \epsilon} \bigg|_{\epsilon = 0} = \sum_{\alpha = 1}^{n} \frac{1}{\theta_{\alpha \beta}} \sum_{\beta = 1}^{n} \left\{ -\frac{\partial}{\partial s_{\beta}} (q_{\alpha} \cdot \frac{\partial \psi_{\alpha}}{\partial \theta_{\alpha}}) \cdot \dot{\theta}_{\alpha} - \rho_{\alpha} \frac{\partial}{\partial s_{\beta}} (\psi_{\alpha} \cdot \frac{\partial \xi_{\alpha}}{\partial \theta_{\alpha}}) \cdot \dot{\theta}_{\alpha} \right\}
\]

\[
-\left( \rho_{\alpha} \frac{\partial}{\partial s_{\beta}} (\psi_{\alpha} \cdot \frac{\partial \xi_{\alpha}}{\partial \theta_{\alpha}}) \right)^{\epsilon} s_{\beta}^p - \left( \frac{\partial}{\partial s_{\beta}} (q_{\alpha} \cdot \frac{\partial \psi_{\alpha}}{\partial \theta_{\alpha}}) \right)^{\epsilon} s_{\beta}^p
\]

\[
-\left[ \left( \frac{\partial}{\partial s_{\beta}} (e_{\alpha} - \mu_{\alpha}) \dot{\epsilon}_{\alpha} \right)^{\epsilon} s_{\beta}^p + \left( \frac{\partial}{\partial s_{\beta}} (\dot{\epsilon}_{\alpha}) \right)^{\epsilon} s_{\beta}^p - \frac{1}{2} \text{tr} (\dot{M}_{\alpha} W_{\alpha}) \right]^{\epsilon} s_{\beta}^p = 0
\]

Imposing the equilibrium conditions in equation (186), the above reduces to:
Note that \( \theta^e_{\alpha} = \theta^e \). In addition we must have that

\[
\sum_{\alpha=1}^{n} \frac{1}{\theta^e_{\alpha}} \sum_{\beta=1}^{n} \left( \frac{\partial \dot{e}_{\alpha}}{\partial s_{\beta}} \right)^e s_{\beta}^p - \frac{1}{2} \left[ \frac{\partial}{\partial s_{\beta}} \text{tr}(\dot{M}_{\alpha} W_{\alpha}) \right] s_{\beta}^p + \left[ (e_{\alpha} - \mu_{\alpha}) \frac{\partial \dot{e}_{\alpha}}{\partial s_{\beta}} \right] s_{\beta}^p = 0
\]  

(199)

Since \( \Sigma \dot{e}_{\alpha} = 0 \) at all thermomechanical states. Then we have:

\[
\frac{d}{de} \dot{S} \bigg|_{e=0} = \sum_{\alpha=1}^{n} \frac{1}{\theta^e_{\alpha}} \sum_{\beta=1}^{n} \left\{ -\rho \frac{\partial}{\partial s_{\beta}} (\psi_{\alpha}) \cdot \frac{\partial \dot{e}_{\alpha}}{\partial s_{\beta}} \right\} s_{\beta}^p - \frac{1}{2} \left[ \frac{\partial}{\partial s_{\beta}} \text{tr}(\dot{M}_{\alpha} W_{\alpha}) \right] s_{\beta}^p + \left[ (e_{\alpha} - \mu_{\alpha}) \frac{\partial \dot{e}_{\alpha}}{\partial s_{\beta}} \right] s_{\beta}^p = 0
\]

(201)

Since \( W_{\alpha} = 0 \) at equilibrium and since \( W_{\alpha} \) is an independent kinematic variable, we must have:

\[
\frac{\partial}{\partial s_{\beta}} \text{tr}(\dot{M}_{\alpha} W_{\alpha}) = 0
\]

(202)

Collecting coefficients of the variables \( s_{\beta} \) in the above relation, one can obtain some additional restrictions. For instance, if one considers the coefficients of the increment in the temperatures, \( \theta_{\beta}, \beta = 1, 2, \ldots n \):

\[
\frac{1}{\theta^e} \sum_{\alpha=1}^{n} \left[ -\rho \frac{\partial \psi_{\alpha}}{\partial s_{\alpha}} \frac{\partial \dot{e}_{\alpha}}{\partial \theta_{\alpha}} \theta^p + (e_{\alpha} - \mu_{\alpha}) \sum_{\beta=1}^{n} \frac{\partial \dot{e}_{\alpha}}{\partial \theta_{\beta}} \theta^p \right] = 0
\]

(203)
If, for example, only one temperature increment were nonzero, say a specific \( \theta_\beta \), we would have:

\[
\left[ -\rho_{\beta} \frac{\partial \psi_{\beta}}{\partial \xi_{\beta}} \frac{\partial \xi_{\beta}}{\partial \theta_{\beta}} + \sum_{\alpha = 1}^{n} (e_\alpha - \mu_\alpha) \frac{\partial \xi_{\beta}}{\partial \theta_{\beta}} \right]^{\varepsilon_{\beta}} = 0
\] (204)

The term in brackets must then equal zero. However, since the mass supplies are functions of the independent variables for all constituents while the first set of terms in the brackets depend only on the variables for the \( \beta \)th constituent, we will apply the following restrictions:

\[
\left[ \rho_{\beta} \frac{\partial \xi_{\beta}}{\partial \xi_{\beta}} \frac{\partial \xi_{\beta}}{\partial \theta_{\beta}} \right]^{\varepsilon_{\beta}} = 0, \quad \sum_{\alpha = 1}^{n} (e_\alpha - \mu_\alpha) \frac{\partial \xi_{\beta}}{\partial \theta_{\beta}} = 0 \quad \beta = 1, \ldots, n
\] (205)

Actually, since the second set of terms in Equation (204) is a function of the set \((E_1, \ldots, E_n, \theta_1, \ldots, \theta_n, g_1, \ldots, g_n, \xi_1, \ldots, \xi_n, u_1, \ldots, u_n, l_1, \ldots, l_n)\), whereas the first set of terms depends only upon the set \((E_{\omega}, \theta_{\omega}, \xi_{\omega}, l_{\omega})\), and since Equation (205) must hold for all possible arbitrary equilibrium states, one can show that the first part of that equation must assume a unique value \( K \) at all equilibrium states and that the second part must acquire the value \(-K\), where \( K \) is a fixed constant. We have merely set \( K = 0 \).

Using a similar reasoning for the other variables, we have:

\[
\left[ \rho_{\beta} \frac{\partial \xi_{\beta}}{\partial \xi_{\beta}} \frac{\partial \xi_{\beta}}{\partial E_{\beta}} \right]^{\varepsilon_{\beta}} = 0, \quad \sum_{\alpha = 1}^{n} (e_\alpha - \mu_\alpha) \frac{\partial \xi_{\beta}}{\partial E_{\beta}} = 0 \quad \beta = 1, \ldots, n
\] (206)

\[
\left[ \rho_{\beta} \frac{\partial \xi_{\beta}}{\partial \xi_{\beta}} \frac{\partial \xi_{\beta}}{\partial u_{\beta}} \right]^{\varepsilon_{\beta}} = 0, \quad \sum_{\alpha = 1}^{n} (e_\alpha - \mu_\alpha) \frac{\partial \xi_{\beta}}{\partial u_{\beta}} = 0 \quad \beta = 1, \ldots, n
\] (207)
\[ \left[ \rho \frac{\partial \psi}{\partial t} \right] = 0, \quad \left[ \sum_{\alpha=1}^{n} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \varphi}{\partial t} \right] = 0 \quad \beta = 1, \ldots, n \quad (208) \]

\[ \left[ \rho \frac{\partial \psi}{\partial t} \right] = 0, \quad \left[ \sum_{\alpha=1}^{n} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \varphi}{\partial t} \right] = 0 \quad \beta = 1, \ldots, n \quad (209) \]

A remaining part of the entropy inequality involves the temperature gradients, and since we are assuming that the evolution equation for the state vector does not depend upon the temperature gradient, we are left with:

\[ \left[ \sum_{\alpha=1}^{n} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \varphi}{\partial g_{\beta}} - \frac{1}{\theta} \frac{\partial \varphi}{\partial q_{\beta}} \right] \cdot g_{\beta}^p = 0 \quad (210) \]

By the same line of reasoning, the following results.

\[ q_{\beta}^e = 0, \quad \left[ \sum_{\alpha=1}^{n} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \varphi}{\partial g_{\beta}} \right] = 0 \quad \beta = 1, \ldots, n \quad (211) \]

Nunziato and Walsh (1980) utilize what is referred to as strong equilibrium conditions. In this case, it is assumed that the chemical potential \( \mu_{\alpha} \) of all constituents acquire equal values at thermomechanical equilibrium. The above results imply that at thermomechanical equilibrium the second parts of equations (205), (209) and (211) are identically satisfied if the differences \( e_{\alpha} - \mu_{\alpha} \) are all equal at equilibrium. This is so since each of the second parts then involves the summation

\[ \left( \sum_{\alpha=1}^{n} \frac{\partial \varphi}{\partial g_{\beta}} \right) \cdot \left( \sum_{\alpha=1}^{n} \frac{\partial \varphi}{\partial q_{\beta}} \right) = 0, \quad (212) \]

and the second condition in the above relations is identically satisfied.
We will therefore require that the differences \((e_{\alpha} - \mu_{\alpha})\) all acquire a common value at equilibrium. Further, assuming strong equilibrium, we assume the chemical potentials all assume equal values, this implies that the internal energies \(e_{\alpha}\) of the constituents all assume the same values at equilibrium. This seems to be a reasonable result, since if the energies all become equal, the driving forces for the constituents to exchange mass and energy will be eliminated. Therefore, thermomechanical equilibrium then implies:

\[
\Delta_{\alpha}^e = (e_{\alpha} - \mu_{\alpha})^e = e^e - \mu^e, (\alpha = 1, ..., n) \quad \alpha = 1, 2, ..., n
\]

\[
\mu_{\alpha}^e = \mu^e \quad \alpha = 1, 2, ..., n
\]

\[
e_{\alpha}^e = e^e \quad \alpha = 1, 2, ..., n
\]

The restrictions imposed in the first part of equations (205) and (209) imply that one of the three conditions must be met at equilibrium:

\[
\left[ \frac{\partial \psi_{\beta}}{\partial e_{\gamma}} \right]^e = 0, \text{ or }
\]

\[
\left[ \frac{\partial \dot{e}_{\gamma}}{\partial s_{\beta}} \right]^e = 0, \text{ or }
\]

\[
\left[ \frac{\partial \psi_{\beta}}{\partial e_{\gamma}} \right]^e \perp \left[ \frac{\partial \dot{e}_{\gamma}}{\partial s_{\beta}} \right]^e
\]

We will adopt the first of these conditions, since it states that the free energy reaches a stationary value with respect to the state vector when equilibrium is reached. In almost all physical processes, stable equilibrium is reached only when potential energy is minimized in some fashion. In this case, since the Helmholtz free energy represents the elastic energy of the material, the system will attempt to evolve to an equilibrium state which minimizes the stain energy as well as the thermal energy. The first of the three conditions is a direct application of this principle. Therefore, in the following, we will assume that \(\partial \psi_{\beta}/\partial e_{\gamma} = 0\) at equilibrium. It should be emphasized that this is a sufficient but not
necessary condition for satisfying equations (205) and (209). However, it is viewed as being consistent with what has previously been observed in mechanics.

Restrictions Based Upon the Second Derivative of the Second Law

Now consider the second variation equation (194). This can be expressed as

\[
\frac{d^2}{de^2} \delta' |_{e=0} = \frac{d}{de} \left[ \frac{\partial}{\partial (s^e + \epsilon s^p)} \delta' \cdot \frac{d}{de} (s^e + \epsilon s^p) \right] |_{e=0}
\]

\[
= \frac{d}{de} \left[ \frac{\partial}{\partial (s^e + \epsilon s^p)} \delta' \cdot s^p \right] |_{e=0}
\]

\[
= \left[ s^p \cdot \frac{\partial^2}{\partial (s^e + \epsilon s^p)^2} \delta' \cdot \frac{d}{de} (s^e + \epsilon s^p) + \frac{ds^p}{de} \frac{\partial}{\partial (s^e + \epsilon s^p)} \delta' \right]
\]

\[
\frac{d^2}{de^2} \delta' |_{e=0} = s^p \left[ \frac{\partial^2}{\partial s^i \partial s^j} \delta' \right]^{e} \cdot s^p
\]

(215)

In index notation, this equation is:

\[
\frac{d^2}{de^2} \delta' |_{e=0} = s^p_i \left[ \frac{\partial^2}{\partial s^i \partial s^j} \delta' \right]^{e} s^p_j
\]

(216)

\[
= \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\alpha=1}^{n} \left[ \frac{\partial^2}{\partial s^i \partial s^j} \delta' \right]^{e} s^p_i s^p_j \geq 0
\]

(217)

Substitute for \( \delta_\alpha \):
\[ \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{\partial^2}{\partial s_i \partial s_j} \sum_{\alpha=1}^{m} \frac{1}{\theta_\alpha} \left( -\rho_\alpha \frac{\partial}{\partial s_i} \frac{\partial \psi_{\alpha i}}{\partial \xi_{\alpha}} - \frac{q_{\alpha} \cdot g_{\alpha}}{\theta_\alpha} + \dot{c}_\alpha \right) \]

\[ - \frac{1}{2} tr(\overline{M}_\alpha W_\alpha) + (e_\alpha - \mu_\alpha) \dot{c}_\alpha \right] s_i^p s_j^p \geq 0 \]

Carrying out the differentiation,

\[ \sum_{\alpha=1}^{m} \frac{2}{\theta_\alpha^3} \left\{ - \frac{\partial}{\partial \xi_{\alpha}} (\rho_\alpha \psi_{\alpha i} \dot{\xi}_{\alpha} - \frac{q_{\alpha} \cdot g_{\alpha}}{\theta_\alpha} + \dot{c}_\alpha) - \frac{1}{2} tr(\overline{M}_\alpha W_\alpha) + (e_\alpha - \mu_\alpha) \dot{c}_\alpha \right\} \theta_\alpha^2 \]

\[ -2 \sum_{i=1}^{n} \sum_{\alpha=1}^{m} \frac{1}{\theta_\alpha^2} \left\{ \frac{\partial^2}{\partial s_i \partial s_j} (\rho_\alpha \psi_{\alpha i} \dot{\xi}_{\alpha} - \frac{q_{\alpha} \cdot g_{\alpha}}{\theta_\alpha} + \dot{c}_\alpha) - \frac{\partial}{\partial s_i} (\overline{M}_\alpha W_\alpha) + \overline{M}_\alpha \frac{\partial W_\alpha}{\partial s_i} \right\} \theta_\alpha^2 \theta_\alpha^2 \]

\[ + \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\alpha=1}^{m} \frac{1}{\theta_\alpha} \left\{ - \frac{\partial}{\partial s_i} \left( \rho_\alpha \frac{\partial \psi_{\alpha i}}{\partial s_j} \right) \dot{\xi}_{\alpha} - \frac{\partial^2}{\partial s_j \partial s_i} (\rho_\alpha \psi_{\alpha i} \dot{\xi}_{\alpha}) \cdot g_{\alpha} - \frac{\partial}{\partial s_i} (\rho_\alpha \psi_{\alpha i} \dot{\xi}_{\alpha}) \cdot \frac{\partial g_{\alpha}}{\partial s_i} \right\} \theta_\alpha^2 \theta_\alpha^2 \]

\[ - \frac{\partial}{\partial s_i} \left( \frac{q_{\alpha}}{\theta_\alpha} \right) \cdot \frac{\partial q_{\alpha}}{\partial s_i} \cdot \theta_\alpha^2 \theta_\alpha^2 \]

\[ - \frac{\partial}{\partial s_j} \left( \frac{q_{\alpha}}{\theta_\alpha} \right) \cdot \frac{\partial q_{\alpha}}{\partial s_j} \cdot \theta_\alpha^2 \theta_\alpha^2 \]

\[ - \frac{\partial}{\partial s_i} \frac{\partial q_{\alpha}}{\partial s_j} \cdot \frac{\partial q_{\alpha}}{\partial s_j} \cdot \theta_\alpha^2 \theta_\alpha^2 \]

\[ + \frac{1}{2} tr \left[ \frac{\partial^2}{\partial s_i \partial s_j} (\overline{M}_\alpha W_\alpha) + \frac{\partial}{\partial s_i} (\overline{M}_\alpha \frac{\partial W_\alpha}{\partial s_i}) + \frac{\partial}{\partial s_j} (\overline{M}_\alpha \frac{\partial W_\alpha}{\partial s_j}) \right] \]

\[ + (\overline{M}_\alpha \frac{\partial W_\alpha}{\partial s_i \partial s_j}) \frac{\partial}{\partial s_i} (e_\alpha - \mu_\alpha) \dot{c}_\alpha + \frac{\partial}{\partial s_j} (e_\alpha - \mu_\alpha) \frac{\partial \dot{c}_\alpha}{\partial s_i} \]

\[ + \frac{\partial}{\partial s_i} (e_\alpha - \mu_\alpha) \frac{\partial \dot{c}_\alpha}{\partial s_j} + (e_\alpha - \mu_\alpha) \frac{\partial^2 \dot{c}_\alpha}{\partial s_i \partial s_j} \right\} \theta_\alpha^2 \theta_\alpha^2 \]

\[ s_i^p s_j^p \geq 0 \]
At equilibrium, many of the terms in the above relation vanish. Dropping these terms using Equation (186) and utilizing symmetry with respect to the indices “i” and “j”, we obtain:

\[
\left\{ -2 \cdot \sum_{i=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{i}} \left( -\rho \alpha \frac{\partial \xi_{\alpha}}{\partial s_{i}} \cdot \frac{\partial \xi_{\alpha}}{\partial s_{i}} + \frac{\partial \epsilon_{\alpha}}{\partial s_{i}} - \frac{1}{2} \text{tr} \left( \hat{M}_{\alpha} \frac{\partial W_{\alpha}}{\partial s_{i}} \right) + \left( e_{\alpha} - \mu_{\alpha} \right) \frac{\partial \xi_{\alpha}}{\partial s_{i}} \right) \right\} \theta_{i} s_{i}^{p}
\]

\[
+ \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{i}} \left[ -2 \frac{\partial^{2}}{\partial s_{i} \partial s_{j}} (\rho \alpha \Psi_{\alpha}) - \rho \alpha \frac{\partial \xi_{\alpha}}{\partial s_{i}} \cdot \frac{\partial \xi_{\alpha}}{\partial s_{j}} \right] \frac{\partial \Psi_{\alpha}}{\partial s_{i}} \frac{\partial^{2} \Psi_{\alpha}}{\partial s_{j}}
\]

\[
-2 \frac{\partial}{\partial s_{j}} \left( \frac{q_{\alpha}}{\theta_{i}} \right) \frac{\partial \Psi_{\alpha}}{\partial s_{i}} + \frac{\partial^{2}}{\partial s_{i} \partial s_{j}} \left( \frac{2}{\theta_{i}} \text{tr} \left( \hat{M}_{\alpha} \frac{\partial W_{\alpha}}{\partial s_{i}} \right) + \left( \hat{M}_{\alpha} \frac{\partial^{2} W_{\alpha}}{\partial s_{i} \partial s_{j}} \right) \right)
\]

\[
+ 2 \frac{\partial}{\partial s_{j}} \left( e_{\alpha} - \mu_{\alpha} \right) \frac{\partial \xi_{\alpha}}{\partial s_{i}} + \left( e_{\alpha} - \mu_{\alpha} \right) \frac{\partial^{2} \xi_{\alpha}}{\partial s_{i} \partial s_{j}} \right\} \theta_{i} s_{i}^{p} s_{j}^{p} \geq 0
\]

(220)

Note that, since $\theta_{i}^{e} = \theta_{i}^{e}$, $(e_{\alpha} - \mu_{\alpha})^{e} = (e - \mu)^{e}$, and since the mass and energy supplies sum to zero at all times:

\[
\sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{i}} (e_{\alpha} - \mu_{\alpha}) \frac{\partial^{2} \xi_{\alpha}}{\partial s_{i} \partial s_{j}} s_{i}^{p} s_{j}^{p} = \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{(e - \mu)^{e}}{\theta_{i}} \frac{\partial^{2} (\xi_{\alpha})}{\partial s_{i} \partial s_{j}} s_{i}^{p} s_{j}^{p} = 0
\]

(221)

\[
\left[ \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{i}} \frac{\partial^{2} \xi_{\alpha}}{\partial s_{i} \partial s_{j}} \right] s_{i}^{p} s_{j}^{p} = \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{1}{\theta_{i}} \frac{\partial^{2} (\sum_{\alpha=1}^{n} \xi_{\alpha})}{\partial s_{i} \partial s_{j}} s_{i}^{p} s_{j}^{p} = 0
\]

(222)

Eliminating these terms, the second variation of the dissipation function becomes:
\[
\left\{-2 \sum_{i=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{\alpha}^2} \left[ -\rho_{\alpha} \frac{\partial \psi_{\alpha}}{\partial s_i} \cdot \frac{\partial \tilde{e}_{\alpha}}{\partial s_i} + \frac{\partial e_{\alpha}}{\partial s_i} - \frac{1}{2} \text{tr} \left( \frac{\partial W_{\alpha}}{\partial s_i} \right) \right] + (e_{\alpha} - \mu_{\alpha}) \frac{\partial e_{\alpha}}{\partial s_i} \right\} \theta_{\alpha}^p s_i^p
\]

\[
+ \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{\alpha}} \left[ -2 \frac{\partial}{\partial s_j} \frac{\partial e_{\alpha}^2}{\partial s_i} \left( \rho_{\alpha} \psi_{\alpha} \right) \frac{\partial \tilde{e}_{\alpha}}{\partial s_i} - \rho_{\alpha} \frac{\partial \tilde{e}_{\alpha}}{\partial s_i} \cdot \frac{\partial \tilde{e}_{\alpha}}{\partial s_i} \right] \right\} \theta_{\alpha}^p s_i^p
\]

(223)

\[
-2 \frac{\partial}{\partial s_j} \left( \frac{q_{\alpha}}{\theta_{\alpha}} \right) \cdot \frac{\partial g_{\alpha}}{\partial s_i} - \frac{1}{2} \text{tr} \left[ \left( M_{\alpha} \right) \frac{\partial^2 W_{\alpha}}{\partial s_i \partial s_j} \right] - \frac{1}{2} \text{tr} \left[ \left( M_{\alpha} \right) \frac{\partial^2 W_{\alpha}}{\partial s_i \partial s_j} \right] + 2 \frac{\partial}{\partial s_j} \left( e_{\alpha} - \mu_{\alpha} \right) \frac{\partial e_{\alpha}}{\partial s_i} \right\} s_i^p s_j^p \geq 0
\]

Since \((\partial \psi_{\alpha}/\partial \tilde{e}_{\alpha})^e = 0, (q_{\alpha})^e = 0\) and \(\partial W_{\alpha}/\partial s_j = 0\), the above reduces to:

\[
\sum_{i=1}^{n} \sum_{\alpha=1}^{n} \left\{ -2 \frac{\partial}{\partial s_i} \left( \frac{\partial e_{\alpha}}{\partial s_i} \right) + (e_{\alpha} - \mu_{\alpha}) \frac{\partial e_{\alpha}}{\partial s_i} \right\} \theta_{\alpha}^p s_i^p
\]

(224)

\[
+ \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{\alpha}} \left[ 2 \frac{\partial}{\partial s_j} \left( e_{\alpha} - \mu_{\alpha} \right) \frac{\partial e_{\alpha}}{\partial s_i} - 2 \frac{\partial^2}{\partial s_j \partial s_i} \left( \rho_{\alpha} \psi_{\alpha} \right) \frac{\partial \tilde{e}_{\alpha}}{\partial s_i} - 2 \frac{\partial}{\partial s_j} \left( \frac{q_{\alpha}}{\theta_{\alpha}} \right) \cdot \frac{\partial g_{\alpha}}{\partial s_i} \right] s_i^p s_j^p \geq 0
\]

By Equations (205), (209), and (211), the second set of terms in the first summation vanish. This last relation places additional restrictions upon the form for \(\tilde{e}_{\alpha}, q_{\alpha},\) and \(e_{\alpha} - \mu_{\alpha}\). Basically, the term in brackets must be a positive definite matrix. Since \(\psi_{\alpha}, e_{\alpha}, \mu_{\alpha},\) and \(\tilde{e}_{\alpha}\) all depend only upon the independent variables of the \(\alpha\) constituent:

\[
\sum_{\alpha=1}^{n} \frac{-2}{\theta_{\alpha}^2} \left[ \frac{\partial^2}{\partial s_\alpha \partial \tilde{e}_{\alpha}} \left( \rho_{\alpha} \psi_{\alpha} \right) \frac{\partial \tilde{e}_{\alpha}}{\partial s_\alpha} \right] s^p s^p + \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \frac{-2}{\theta_{\alpha}^2} \left[ \frac{\partial e_{\alpha}}{\partial s_\beta} \right] \theta_{\alpha}^p s^p
\]

(225)

\[
+ \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{\alpha}} \left[ 2 \frac{\partial}{\partial s_\alpha} \left( e_{\alpha} - \mu_{\alpha} \right) \frac{\partial e_{\alpha}}{\partial s_\beta} - 2 \frac{\partial}{\partial s_\alpha} \left( \frac{q_{\alpha}}{\theta_{\alpha}} \right) \cdot \frac{\partial g_{\alpha}}{\partial s_\beta} \right] s^p s^p \geq 0
\]
Restrictions based upon arbitrary perturbations in temperature

We would now like to consider several special cases. In the particular case when we look at two arbitrary perturbations in the temperature, $\theta_\alpha, \theta_\beta$. Suppose all perturbations are zero except for the following:

$$s_\alpha^p = \theta_1^p \delta_{1\alpha} + \theta_2^p \delta_{2\alpha}$$

where $s_\alpha^p = 0$ if $\alpha \neq 1, 2$ and $s_\alpha^p = \theta_1^p$ if $\alpha = 1$ and $s_\alpha^p = \theta_2^p$ if $\alpha = 2$. Similarly we have

$$s_\beta^p = \theta_1^p \delta_{1\beta} + \theta_2^p \delta_{2\beta}$$

with the same definitions, $s_\beta^p = 0$ if $\beta \neq 1, 2$ and $s_\beta^p = \theta_1^p$ if $\beta = 1$ and $s_\beta^p = \theta_2^p$ if $\beta = 2$. Using these definitions and substituting into equation (225) we get,

$$
\sum_{\alpha=1}^{n} \sum_{\beta=1}^{n} \frac{2}{\theta_\alpha^e} \left( \frac{\partial^2}{\partial \xi_\alpha \partial s_\alpha} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \xi_\alpha}{\partial s_\alpha} \right)^e \left( \theta_1^p \delta_{1\alpha} + \theta_2^p \delta_{2\alpha} \right)^2 \\
- \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \left[ \frac{2}{\theta_\alpha^2 \partial s_\beta} \right]^e \left( \theta_1^p \delta_{1\alpha} + \theta_2^p \delta_{2\alpha} \right) \left( \theta_1^p \delta_{1\beta} + \theta_2^p \delta_{2\beta} \right) \\
+ \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_\alpha^e} \left( \frac{\partial}{\partial s_\alpha} \left( \theta_\alpha \right) \cdot \frac{\partial \theta_\alpha}{\partial s_\beta} \right)^e \left( \theta_1^p \delta_{1\alpha} + \theta_2^p \delta_{2\alpha} \right) \left( \theta_1^p \delta_{1\beta} + \theta_2^p \delta_{2\beta} \right) \\
+ \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_\alpha^e} \left[ 2 \frac{\partial}{\partial s_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \xi_\alpha}{\partial s_\beta} \right]^e \left( \theta_1^p \delta_{1\alpha} + \theta_2^p \delta_{2\alpha} \right) \left( \theta_1^p \delta_{1\beta} + \theta_2^p \delta_{2\beta} \right) \geq 0
$$

Now we may substitute the equilibrium temperature $\theta_\alpha^e = \theta^e$ and replacing the $\alpha = 1, \beta = 2$ and observing the subscripts we get upon expansion,
If we take this expansion and replace the subscripts with the appropriate constituent identifier we get an equation that is of the form:

\[ A(\theta_\alpha^p)^2 + B\theta_\alpha^p\theta_\beta^p + C(\theta_\beta^p)^2 \geq 0 \]  

Equation (229) can be simplified more since \( g_\alpha \) is one of the independent variables,

\[ g_\alpha = g_\alpha(\theta_\alpha, \theta_\beta) \]  

thus we have,

\[ \frac{\partial g_\alpha}{\partial \theta_\beta} = 0, \text{ for all } (\alpha, \beta). \]  

For the other perturbations in \((E_\omega, l_\omega, \ldots)\) similar simplifications will be made later in this chapter. Thus,
Consider the case of $\alpha \neq \beta$ and $\theta^p_\alpha \neq 0$ and $\theta^{p}_\beta = 0$ then,

$$\left[ \frac{\partial^2}{\partial \xi_\alpha \partial \theta_\alpha} \left( \rho_\alpha \psi_\alpha \right) \cdot \frac{\partial \xi_\alpha}{\partial \theta_\alpha} + \frac{1}{\theta^e} \frac{\partial \xi_\alpha}{\partial \theta_\alpha} - \frac{\partial}{\partial \theta_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \xi_\alpha}{\partial \theta_\alpha} \right]^e \leq 0 \quad (234)$$

If we have the case of $\alpha \neq \beta$ and $\theta^p_\alpha = 0$ and $\theta^{p}_\beta \neq 0$ then we get the same restriction.

Now consider the two cases when $\alpha \neq \beta$, $\theta^p_\alpha = -\theta^{p}_\beta$ and $\theta^p_\alpha = \theta^{p}_\beta$, $\alpha \neq \beta$, $\theta^p_\alpha \neq 0$, and $\theta^{p}_\beta \neq 0$ when combined we get

$$\frac{2}{(\theta^e)^2} \left[ \frac{\partial \xi_\beta}{\partial \theta_\alpha} + \frac{\partial \xi_\alpha}{\partial \theta_\beta} \right]^e \quad (235)$$

$$+ \frac{2}{\theta^e} \left[ \frac{\partial}{\partial \theta_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \xi_\alpha}{\partial \theta_\alpha} + \frac{\partial}{\partial \theta_\beta} (e_\beta - \mu_\beta) \frac{\partial \xi_\beta}{\partial \theta_\alpha} \right]^e = 0$$

Thus, we have the following restrictions,

$$\frac{\partial \xi_\beta}{\partial \theta_\alpha} = -\frac{\partial \xi_\alpha}{\partial \theta_\beta} \quad (236)$$
While these are not necessary conditions they are sufficient conditions to satisfy our criterion.

Now consider the case when \( \alpha = \beta \) and both \( \theta_\alpha^P \neq 0 \), \( \theta_\beta^P \neq 0 \) then

\[
- \frac{\partial^2}{\partial \xi_\alpha \partial \theta_\alpha} (\rho \alpha \psi_\alpha) \cdot \frac{\partial e_\alpha}{\partial \theta_\alpha} + \frac{\partial}{\partial \theta_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial c_\alpha}{\partial \theta_\alpha} \geq 0
\]

Since the energy terms are not functions of the temperature gradient, we can derive the following relationship:

\[
\left[ \frac{\partial q_\alpha}{\partial g_\alpha} \right]^P \leq 0
\]

**Restriction based upon arbitrary perturbations in strain**

Now we need to consider the special case of two arbitrary perturbations in the strain, \( E_{1ij}^P, E_{2mn}^P \). In particular we may suppose that the perturbation occurs in different constituents and different components of the strain tensor or in different components of the strain tensor in one constituent. Suppose all perturbations are zero except for the following:

\[
s_\alpha^P = E_{1ij}^P \delta_{1\alpha} + E_{2mn}^P \delta_{2\alpha}
\]

where \( s_\alpha^P = 0 \) if \( \alpha \neq 1, 2 \) and \( s_\alpha^P = E_{1ij}^P \) if \( \alpha = 1 \) and \( s_\alpha^P = E_{2mn}^P \) if \( \alpha = 2 \). Similarly we have

\[
s_\beta^P = E_{1ij}^P \delta_{1\beta} + E_{2mn}^P \delta_{2\beta}
\]

with the same definitions, \( s_\beta^P = 0 \) if \( \beta \neq 1, 2 \) and \( s_\beta^P = E_{1ij}^P \) if \( \beta = 1 \) and \( s_\beta^P = E_{2mn}^P \) if \( \beta = 2 \). Using these definitions and substituting into equation (225) we get,
\[
\sum_{\alpha=1}^{n} \frac{2}{\theta_{\alpha}} \left( \frac{\partial^{2}}{\partial \xi_{\alpha} \partial \delta_{\alpha}} (\rho_{\alpha} \Psi_{\alpha}) \cdot \frac{\partial \xi_{\alpha}}{\partial \delta_{\alpha}} \right)^{e} \left( E_{1ij}^{P} \delta_{1\alpha} + E_{2mn}^{P} \delta_{2\alpha} \right)^{2} \\
- \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \left[ \frac{2}{\theta_{\beta}} \frac{\partial \delta_{\alpha}}{\partial \delta_{\beta}} \right]^{e} \left( \Theta^{P}_{1} \delta_{1\alpha} + \Theta^{P}_{2} \delta_{2\alpha} \right) \left( E_{1ij}^{P} \delta_{1\beta} + E_{2mn}^{P} \delta_{2\beta} \right) \\
+ \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{\alpha}} \left[ -2 \frac{\partial}{\partial \delta_{\alpha}} \left( \frac{\partial \xi_{\alpha}}{\partial \delta_{\alpha}} \right) \cdot \frac{\partial g_{\alpha}}{\partial \delta_{\beta}} \right]^{e} \left( E_{1ij}^{P} \delta_{1\alpha} + E_{2mn}^{P} \delta_{2\alpha} \right) \left( E_{1ij}^{P} \delta_{1\beta} + E_{2mn}^{P} \delta_{2\beta} \right) \\
+ \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_{\alpha}} \left[ 2 \frac{\partial}{\partial \delta_{\alpha}} \left( e_{\alpha} - \mu_{\alpha} \right) \frac{\partial \xi_{\alpha}}{\partial \delta_{\beta}} \right]^{e} \left( E_{1ij}^{P} \delta_{1\alpha} + E_{2mn}^{P} \delta_{2\alpha} \right) \left( E_{1ij}^{P} \delta_{1\beta} + E_{2mn}^{P} \delta_{2\beta} \right) \geq 0
\]

Now we may substitute the equilibrium temperature $T^{e}_{\alpha} = \theta^{e}$ and replacing the subscripts we get upon expansion,

\[
- \frac{2}{\theta^{e}} \left[ \frac{\partial^{2}}{\partial \xi_{1} \partial E_{1ij}^{P}} (\rho_{1} \Psi_{1}) \cdot \frac{\partial \xi_{1}}{\partial E_{1ij}^{P}} \right]^{e} \left( E_{1ij}^{P} \right)^{2} - \frac{2}{\theta^{e}} \left[ \frac{\partial^{2}}{\partial \xi_{2} \partial E_{2mn}^{P}} (\rho_{2} \Psi_{2}) \cdot \frac{\partial \xi_{2}}{\partial E_{2mn}^{P}} \right]^{e} \left( E_{2mn}^{P} \right)^{2}
\]

\[
- \frac{2}{(\theta^{e})^{2}} \left\{ \left[ \frac{\partial \xi_{1}}{\partial E_{1ij}^{P}} \right]^{e} \left( \Theta^{P}_{1} \right) \left( E_{1ij}^{P} \right) + \left[ \frac{\partial \xi_{2}}{\partial E_{2mn}^{P}} \right]^{e} \left( \Theta^{P}_{2} \right) \left( E_{2mn}^{P} \right) \right\}
\]

\[
- \frac{2}{(\theta^{e})^{2}} \left[ \frac{\partial \xi_{1}}{\partial E_{1ij}^{P}} \right]^{e} \left( \Theta^{P}_{1} \right) \left( E_{1ij}^{P} \right) - \frac{2}{(\theta^{e})^{2}} \left[ \frac{\partial \xi_{2}}{\partial E_{2mn}^{P}} \right]^{e} \left( \Theta^{P}_{2} \right) \left( E_{2mn}^{P} \right)
\]

\[
+ \frac{2}{\theta^{e}} \left[ \frac{\partial}{\partial E_{1ij}^{P}} (e_{1} - \mu_{1}) \frac{\partial \xi_{1}}{\partial E_{1ij}^{P}} \right]^{e} \left( E_{1ij}^{P} \right)^{2}
\]

\[
+ \frac{2}{\theta^{e}} \left[ \frac{\partial}{\partial E_{2mn}^{P}} (e_{2} - \mu_{2}) \frac{\partial \xi_{2}}{\partial E_{2mn}^{P}} \right]^{e} \left( E_{2mn}^{P} \right)^{2}
\]

\[
+ \frac{2}{\theta^{e}} \left[ \frac{\partial \xi_{1}}{\partial E_{1ij}^{P}} \right]^{e} \left( \Theta^{P}_{1} \right) \left( E_{1ij}^{P} \right) \left( E_{2mn}^{P} \right) \geq 0
\]
If we take this expansion and replace the subscripts with the appropriate constituent identifier we get an equation that is of the form:

\[
A(E_{\alpha ij}^P)^2 + BE_{\alpha ij}^P E_{\beta mn}^P + C(E_{\beta mn}^P)^2 \geq 0
\]  

(244)

If we assume that the perturbed temperatures \( \theta^P_\alpha, \theta^P_\beta \) are both zero then the following results upon substituting the constituent letter for the constituent numbers:

\[
- \frac{2}{\theta^e} \left[ \frac{\partial^2}{\partial \xi_{\alpha} \partial E_{\alpha ij}} \left( \rho_\alpha \psi_\alpha \right) \cdot \frac{\partial \xi_{\alpha}}{\partial E_{\alpha ij}} \right] (E_{\alpha ij}^P)^2 - \frac{2}{\theta^e} \left[ \frac{\partial^2}{\partial \xi_{\beta} \partial E_{\beta mn}} \left( \rho_\beta \psi_\beta \right) \cdot \frac{\partial \xi_{\beta}}{\partial E_{\beta mn}} \right] (E_{\beta mn}^P)^2
\]

\[
\quad + \frac{2}{\theta^e} \left[ \frac{\partial}{\partial E_{\alpha ij}} (e_\alpha - \mu_\alpha) \cdot \frac{\partial \xi_{\alpha}}{\partial E_{\alpha ij}} \right] (E_{\alpha ij}^P)^2
\]

\[
\quad + \frac{2}{\theta^e} \left[ \frac{\partial}{\partial E_{\beta mn}} (e_\beta - \mu_\beta) \cdot \frac{\partial \xi_{\beta}}{\partial E_{\beta mn}} \right] (E_{\beta mn}^P)^2
\]

\[
= 2 \left[ \frac{\partial}{\partial E_{\alpha ij}} (e_\alpha - \mu_\alpha) \cdot \frac{\partial \xi_{\alpha}}{\partial E_{\alpha ij}} + \frac{\partial}{\partial E_{\alpha ij}} (e_\beta - \mu_\beta) \cdot \frac{\partial \xi_{\beta}}{\partial E_{\alpha ij}} \right] E_{\alpha ij}^P Е_{\beta mn}^P \geq 0
\]

(245)

Consider the case of \( \alpha \neq \beta \) and \( E_{\alpha ij}^P \neq 0 \) and \( E_{\beta mn}^P = 0 \) then,

\[
\left[ \frac{\partial^2}{\partial \xi_{\alpha} \partial E_{\alpha ij}} \left( \rho_\alpha \psi_\alpha \right) \cdot \frac{\partial \xi_{\alpha}}{\partial E_{\alpha ij}} - \frac{\partial}{\partial E_{\alpha ij}} (e_\alpha - \mu_\alpha) \cdot \frac{\partial \xi_{\alpha}}{\partial E_{\alpha ij}} \right] \leq 0
\]

(246)

If we have the case of \( \alpha \neq \beta \) and \( E_{\beta mn}^P = 0 \) and \( E_{\alpha ij}^P \neq 0 \) then we get the same restriction. Now consider the cases when \( \alpha \neq \beta \), \( E_{\alpha ij}^P = -E_{\beta mn}^P \), \( E_{\alpha ij}^P = E_{\beta mn}^P \), \( \alpha \neq \beta \), \( E_{\alpha ij}^P \neq 0 \), \( E_{\beta mn}^P \neq 0 \), and \( (ij) \neq (mn) \) we get
where we have assumed the temperature gradient \( g_\alpha \) is not a function of strain. Since \( \hat{c}_\alpha \) may depend upon all variables of all constituents we have,

\[
- \frac{1}{\theta^e} \left( \frac{\partial^2}{\partial E_{\alpha ij} \partial E_{\alpha ij}} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \hat{c}_\alpha}{\partial E_{\alpha ij}} \right)^e - \frac{1}{\theta^e} \left( \frac{\partial^2}{\partial E_{\beta mn} \partial E_{\beta mn}} (\rho_\beta \psi_\beta) \cdot \frac{\partial \hat{c}_\beta}{\partial E_{\beta mn}} \right)^e = 0
\]

(248)

where we have imposed additional restrictions based on the functional dependencies of the interaction variables. If we have the same strain components, \((ij) = (mn)\) then we get,

\[
- \frac{1}{\theta^e} \left( \frac{\partial^2}{\partial E_{\alpha ij} \partial E_{\alpha ij}} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \hat{c}_\alpha}{\partial E_{\alpha ij}} \right)^e - \frac{1}{\theta^e} \left( \frac{\partial^2}{\partial E_{\alpha ij} \partial E_{\alpha ij}} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \hat{c}_\alpha}{\partial E_{\alpha ij}} \right)^e \geq 0
\]

(249)

In the above development we considered the case when the perturbation was in different constituents. If we consider only perturbations within a single constituent but different components of the strain tensor then it may be shown from equation (248),


\[
\frac{1}{\theta^e_\alpha} \left( \frac{\partial^2}{\partial \xi_\alpha \partial E_{aij}} \left( \rho_\alpha \Psi_\alpha \right) \cdot \frac{\partial \xi_\alpha}{\partial E_{aij}} \right)^e - \frac{1}{\theta^e_\alpha} \left( \frac{\partial^2}{\partial \xi_\alpha \partial E_{amn}} \left( \rho_\alpha \Psi_\alpha \right) \cdot \frac{\partial \xi_\alpha}{\partial E_{amn}} \right)^e = 0
\]

\[
\left[ \frac{\partial}{\partial E_{aij}} \left( e_\alpha - \mu_\alpha \right) \frac{\partial \xi_\alpha}{\partial E_{aij}} \right] + \frac{\partial}{\partial E_{amn}} \left( e_\alpha - \mu_\alpha \right) \frac{\partial \xi_\alpha}{\partial E_{amn}} \right]^e = 0
\]

and other analogous restrictions in the terms of one constituent.

Restriction based upon arbitrary perturbations in the extent of reaction

We would now like to consider another case. In the particular, the case when we look
at two arbitrary perturbations in the extent of reaction, \( l_\alpha, l_\beta \). Suppose all perturbations are
zero except for the following:

\[
s^\alpha_\alpha = l^\alpha_1 \delta_{1\alpha} + l^\alpha_2 \delta_{2\alpha} \quad (251)
\]

where \( s^\alpha_\alpha = 0 \) if \( \alpha \neq 1,2 \) and \( s^\alpha_\alpha = l^\alpha_1 \) if \( \alpha = 1 \) and \( s^\alpha_\alpha = l^\alpha_2 \) if \( \alpha = 2 \). Similarly we
have

\[
s^\beta_\beta = l^\beta_1 \delta_{1\beta} + l^\beta_2 \delta_{2\beta} \quad (252)
\]

with the same definitions, \( s^\beta_\beta = 0 \) if \( \beta \neq 1,2 \) and \( s^\beta_\beta = l^\beta_1 \) if \( \beta = 1 \) and \( s^\beta_\beta = l^\beta_2 \) if \( \beta = 2 \). Using these definitions and substituting into equation (225) we get,
\[ \sum_{\alpha = 1}^{n} -\frac{2}{\theta_{\alpha}^{e}} \left( \frac{\partial^{2}}{\partial s_{\alpha}^{2}}(\rho_{\alpha} \psi_{\alpha}) \cdot \frac{\partial \dot{\xi}_{\alpha}}{\partial s_{\alpha}} \right)^{e} \left( l_{1}^{\rho} \delta_{1\alpha} + l_{2}^{\rho} \delta_{2\alpha} \right)^{2} \]

\[ - \sum_{\beta = 1}^{n} \sum_{\alpha = 1}^{n} \left[ \frac{2}{\theta_{\alpha}^{e}} \frac{\partial \dot{\psi}_{\alpha}}{\partial s_{\beta}} \right]^{e} \left( \theta_{1}^{\rho} \delta_{1\alpha} + \theta_{2}^{\rho} \delta_{2\alpha} \right) \left( l_{1}^{\rho} \delta_{1\beta} + l_{2}^{\rho} \delta_{2\beta} \right) \]

\[ + \sum_{\beta = 1}^{n} \sum_{\alpha = 1}^{n} \left[ \frac{1}{\theta_{\alpha}^{e}} \left( \frac{\partial (e_{\alpha} - \mu_{\alpha})}{\partial s_{\alpha}} \right) \cdot \frac{\partial \dot{c}_{\alpha}}{\partial s_{\beta}} \right]^{e} \left( l_{1}^{\rho} \delta_{1\alpha} + l_{2}^{\rho} \delta_{2\alpha} \right) \left( l_{1}^{\rho} \delta_{1\beta} + l_{2}^{\rho} \delta_{2\beta} \right) \geq 0 \]

Now we may substitute the equilibrium temperature \( \theta_{\alpha}^{e} = \theta^{e} \) and replacing the \( \alpha = 1, \beta = 2 \) and observing the subscripts we get upon expansion,

\[ -\frac{2}{\theta^{e}} \left[ \frac{\partial^{2}}{\partial s_{1}^{2}}(\rho_{1} \psi_{1}) \cdot \frac{\partial \dot{\xi}_{1}}{\partial l_{1}} \right]^{e} \left( l_{1}^{\rho} \right)^{2} - \frac{2}{\theta^{e}} \left[ \frac{\partial^{2}}{\partial s_{2}^{2}}(\rho_{2} \psi_{2}) \cdot \frac{\partial \dot{\xi}_{2}}{\partial l_{2}} \right]^{e} \left( l_{2}^{\rho} \right)^{2} \]

\[ + \frac{2}{\theta^{e}} \left[ \frac{\partial}{\partial l_{1}}(e_{1} - \mu_{1}) \cdot \frac{\partial \dot{c}_{1}}{\partial l_{1}} \right]^{e} \left( l_{1}^{\rho} \right)^{2} \]

\[ + \frac{2}{\theta^{e}} \left[ \frac{\partial}{\partial l_{2}}(e_{2} - \mu_{2}) \cdot \frac{\partial \dot{c}_{2}}{\partial l_{2}} \right]^{e} \left( l_{2}^{\rho} \right)^{2} \]

\[ + \frac{2}{\theta^{e}} \left[ \frac{\partial}{\partial l_{1}}(e_{1} - \mu_{1}) + \frac{\partial}{\partial l_{2}}(e_{2} - \mu_{2}) \right] l_{1}^{\rho} l_{2}^{\rho} \geq 0 \]

If we take this expansion and replace the subscripts with the appropriate constituent identifier and assume the temperature perturbations are zero, we get an equation that is of the form:
\[ A(l^p_\alpha) + Bl^p_\alpha l^p_\beta + C(l^p_\beta) \geq 0 \]  
\[ (255) \]

\[- \frac{2}{\theta} \left[ \frac{\partial^2}{\partial \xi_\alpha \partial l_\alpha} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \xi_\alpha}{\partial l_\alpha} \right]^e l^p_\alpha \geq 0 \]  
\[ + \frac{2}{\theta} \left[ \frac{\partial}{\partial l_\beta} (e_\alpha - \mu_\alpha) \frac{\partial e_\alpha}{\partial l_\alpha} \right]^e l^p_\beta \geq 0 \]  
\[ (256) \]

Consider the case of \( \alpha \neq \beta \) and \( l^p_\alpha \neq 0 \) and \( l^p_\beta = 0 \) then,

\[ \left[ \frac{\partial^2}{\partial \xi_\alpha \partial l_\alpha} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \xi_\alpha}{\partial l_\alpha} - \frac{\partial}{\partial l_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial e_\alpha}{\partial l_\alpha} \right]^e \leq 0 \]  
\[ (257) \]

If we have the case of \( \alpha \neq \beta \) and \( l^p_\alpha = 0 \) and \( l^p_\beta \neq 0 \) then we get the same restriction. Now consider the two cases when \( \alpha \neq \beta \), \( l^p_\alpha = -l^p_\beta \) and \( l^p_\alpha = l^p_\beta \), \( \alpha \neq \beta \), \( l^p_\alpha \neq 0 \), and \( l^p_\beta \neq 0 \) when combined we get

\[ - \frac{2}{\theta^e} \left[ \frac{\partial e_\beta}{\partial l_\alpha} + \frac{\partial e_\alpha}{\partial l_\beta} \right]^e \]  
\[ + \frac{2}{\theta^e} \left[ \frac{\partial}{\partial l_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial e_\alpha}{\partial l_\alpha} + \frac{\partial}{\partial l_\beta} (e_\beta - \mu_\beta) \frac{\partial e_\beta}{\partial l_\beta} \right]^e = 0 \]  
\[ (258) \]

Thus, we have the following restrictions,

\[ \frac{\partial e_\beta}{\partial l_\alpha} = - \left( \frac{\partial e_\alpha}{\partial l_\beta} \right) \]  
\[ (259) \]
and

$$\frac{\partial}{\partial l_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \epsilon_\alpha}{\partial l_\beta} = \frac{\partial}{\partial l_\beta} (e_\beta - \mu_\beta) \frac{\partial \epsilon_\beta}{\partial l_\alpha}$$  \hspace{1cm} (260)

While these are not necessary conditions they are sufficient conditions to satisfy our criterion.

Now consider the case when \( \alpha = \beta \) and both \( l_\alpha^P \neq 0 \), \( l_\beta^P \neq 0 \) then

$$\left[ -\frac{\partial^2}{\partial \xi_\alpha \partial l_\alpha} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \epsilon_\alpha}{\partial l_\alpha} - \frac{\partial \epsilon_\alpha}{\partial l_\alpha} + \frac{\partial}{\partial l_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \epsilon_\alpha}{\partial l_\alpha} \right] \geq 0.$$  \hspace{1cm} (261)

Restrictions based upon arbitrary perturbations in the internal state vector

Now consider the special case of two arbitrary perturbations in one arbitrary component of the internal state vector \( \xi_\alpha, \xi_\beta \). Recall that the internal state vector is a list of scalar functions represented as a vector. Therefore we will look at individual components of these vectors. As with the strain we may consider either the perturbations within one constituent or more than one constituent. We will begin by supposing we have two different constituents. Suppose all perturbations are zero except for the following:

$$s_\alpha^P = \xi_1^P s_{1\alpha} + \xi_2^P s_{2\alpha}$$  \hspace{1cm} (262)

where \( s_\alpha^P = 0 \) if \( \alpha \neq 1, 2 \) and \( s_\alpha^P = \xi_1^P \) if \( \alpha = 1 \) and \( s_\alpha^P = \xi_2^P \) if \( \alpha = 2 \). Similarly we have

$$s_\beta^P = \xi_1^P s_{1\beta} + \xi_2^P s_{2\beta}$$  \hspace{1cm} (263)

with the same definitions, \( s_\beta^P = 0 \) if \( \beta \neq 1, 2 \) and \( s_\beta^P = \xi_1^P \) if \( \beta = 1 \) and \( s_\beta^P = \xi_2^P \) if \( \beta = 2 \). Using these definitions and substituting into equation (225) we get,
Now we may substitute the equilibrium temperature $\theta_\alpha^e = \theta^e$ and replacing the $\alpha = 1, \beta = 2$ and observing the subscripts we get upon expansion,

$$
\sum_{\alpha=1}^{n} \frac{2}{\theta_\alpha^e} \left( \frac{\partial^2}{\partial \xi_\alpha \partial \xi_\alpha} (p_\alpha \psi_\alpha) \cdot \frac{\partial \xi_\alpha}{\partial \xi_\alpha} \right)^e \left( \xi_1^p \delta_{1\alpha} + \xi_2^p \delta_{2\alpha} \right)^2
$$

$$
- \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \left[ \frac{2}{\theta_\alpha^e} \left( \frac{\partial \xi_\alpha}{\partial \xi_\alpha} \right) \cdot \frac{\partial \xi_\beta}{\partial \xi_\beta} \right]^e \left( \xi_1^p \delta_{1\beta} + \xi_2^p \delta_{2\beta} \right)^2
$$

$$
+ \sum_{\beta=1}^{n} \sum_{\alpha=1}^{n} \frac{1}{\theta_\alpha^e} \left[ \frac{2}{\theta_\alpha^e} \left( \frac{\partial \xi_\alpha}{\partial \xi_\alpha} \right) \cdot \frac{\partial \xi_\alpha}{\partial \xi_\beta} \right]^e \left( \xi_1^p \delta_{1\alpha} + \xi_2^p \delta_{2\alpha} \right) \left( \xi_1^p \delta_{1\beta} + \xi_2^p \delta_{2\beta} \right) \geq 0
$$

(264)

If we take this expansion and replace the subscripts with the appropriate constituent identifier and assume the temperature perturbations are zero, we get an equation that is of the form:
\[ A(\xi_\alpha^p)^2 + B \xi_\alpha^p \xi_\beta^p + C(\xi_\beta^p)^2 \geq 0 \]  
(266)

\[ - \frac{2}{\theta^e} \left[ \frac{\partial^2}{\partial \xi_\alpha \partial \xi_\alpha} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \xi_\alpha}{\partial \xi_\alpha} \right] (\xi_\alpha^p)^2 - \frac{2}{\theta^e} \left[ \frac{\partial^2}{\partial \xi_\alpha \partial \xi_\beta} (\rho_\beta \psi_\beta) \cdot \frac{\partial \xi_\beta}{\partial \xi_\beta} \right] (\xi_\beta^p)^2 \]

\[ + \frac{2}{\theta^e} \left[ \frac{\partial}{\partial \xi_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \xi_\alpha}{\partial \xi_\alpha} \right] (\xi_\alpha^p)^2 \]

\[ + \frac{2}{\theta^e} \left[ \frac{\partial}{\partial \xi_\beta} (e_\beta - \mu_\beta) \frac{\partial \xi_\beta}{\partial \xi_\beta} \right] (\xi_\beta^p)^2 \]  
(267)

Consider the case of \( \alpha \neq \beta \) and \( \xi_\alpha^p \neq 0 \) and \( \xi_\beta^p = 0 \) then,

\[ \left[ \frac{\partial^2}{\partial \xi_\alpha \partial \xi_\alpha} (\rho_\alpha \psi_\alpha) \cdot \frac{\partial \xi_\alpha}{\partial \xi_\alpha} - \frac{\partial}{\partial \xi_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \xi_\alpha}{\partial \xi_\alpha} \right] \xi_\alpha^p \xi_\beta^p \leq 0 \]  
(268)

If we have the case of \( \alpha \neq \beta \) and \( \xi_\alpha^p = 0 \) and \( \xi_\beta^p \neq 0 \) then we get the same restriction.

Now consider the two cases when \( \alpha \neq \beta \), \( \xi_\alpha^p = -\xi_\beta^p \) and \( \xi_\alpha^p = \xi_\beta^p \), \( \alpha \neq \beta \), \( \xi_\alpha^p \neq 0 \), and \( \xi_\beta^p \neq 0 \) when combined we get

\[ - \frac{2}{(\theta^e)^2} \left[ \frac{\partial \xi_\beta}{\partial \xi_\alpha} + \frac{\partial \xi_\alpha}{\partial \xi_\beta} \right] e^p \]  
(269)

\[ + \frac{2}{\theta^e} \left[ \frac{\partial}{\partial \xi_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \xi_\alpha}{\partial \xi_\alpha} + \frac{\partial}{\partial \xi_\beta} (e_\beta - \mu_\beta) \frac{\partial \xi_\beta}{\partial \xi_\beta} \right] e^p = 0 \]

Thus, we have the following restrictions,

\[ \frac{\partial \xi_\beta}{\partial \xi_\alpha} = - \left( \frac{\partial \xi_\alpha}{\partial \xi_\beta} \right) \]  
(270)
While these are not necessary conditions they are sufficient conditions to satisfy our criterion.

Now consider the case when \( \alpha = \beta \) and both \( \xi_\alpha^P \neq 0 \) and \( \xi_\beta^P \neq 0 \) then

\[
\frac{\partial}{\partial \xi_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \xi_\alpha}{\partial \xi_\beta} = \frac{\partial}{\partial \xi_\beta} (e_\beta - \mu_\beta) \frac{\partial \xi_\beta}{\partial \xi_\alpha} \tag{271}
\]

This completes the restrictive criterion that is necessary to be compatible with the conservation of mass, conservation of linear momentum, conservation of angular momentum, first law of thermodynamics, and the additional criterion derived from the second law of thermodynamics. These conditions are generic in that any constitutive law must satisfy each of the derived equations. If the constitutive law satisfies the criterion then obviously it does not violate the physical laws, but that is not to say that it represents the materials in the most accurate of efficient manner. This must be determined by model validation with past models, experience, and experiment.
CHAPTER 4

PRINCIPLES APPLIED TO A VISCO-PLASTIC MATERIAL

In this section, we consider the material to be an assemblage of ice grains with a distribution of grain sizes along with a distribution of wood particles. Macroscopic temperature gradients and viscous flow processes are ignored. The intent is to investigate the stresses and strains for the wood-snow mixture and what phenomena may influence those relationships. Therefore we assume:

\[ E_\alpha \neq 0 \]
\[ g_\alpha = 0 \]
\[ u_\alpha = 0 \]
\[ \xi_\alpha \neq 0 \] (273)

for all of the constituents.

Assumptions Used in Deriving Constitutive Equations

Now consider the changes in mass between the different constituents which takes place in the absence of temperature gradients, velocities, etc. but which an internal state vector represents the visco-plastic changes within the materials. For each constituent we have

\[ \psi_\alpha = \psi_\alpha(E_\alpha, \theta_\alpha, l_\alpha, \xi_\alpha) \]
\[ e_\alpha = e_\alpha(E_\alpha, \theta_\alpha, l_\alpha, \xi_\alpha) \]
\[ \eta_\alpha = \eta_\alpha(E_\alpha, \theta_\alpha, l_\alpha, \xi_\alpha) \]
\[ T_\alpha = T_\alpha(E_\alpha, \theta_\alpha, l_\alpha, \xi_\alpha) \] (274)
The second law as given by Equation (182) reduces to the following:

\[ \delta = \sum_{\alpha=1}^{n} \frac{1}{\theta_{\alpha}} \left[ -\rho_{\alpha} \left( \frac{\partial \psi_{\alpha}}{\partial \xi_{\alpha}} \cdot \frac{\partial \hat{e}_{\alpha}}{\partial \xi_{\alpha}} \right) + \partial_{\alpha} + (e_{\alpha} - \mu_{\alpha}) \hat{c}_{\alpha} \right] \geq 0 \]  

(275)

The restrictions obtained in last chapter reduce to the following.

For temperature:

\[ \left[ \frac{2}{\theta_{\alpha}} \left( \frac{\partial^{2}}{\partial \xi_{\alpha} \partial \theta_{\alpha}} \rho_{\alpha} \psi_{\alpha} \cdot \frac{\partial \hat{e}_{\alpha}}{\partial \xi_{\alpha}} \right) \right]^{\epsilon} \leq 0, \quad \alpha = \beta \]  

(276)

\[ \left[ -\frac{2}{\theta_{\alpha}^{2}} \frac{\partial \hat{e}_{\alpha}}{\partial \theta_{\alpha}} \theta_{\alpha} + \frac{\partial}{\partial \theta_{\alpha}} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \hat{c}_{\alpha}}{\partial \theta_{\alpha}} \right]^{\epsilon} \geq 0, \quad \alpha = \beta \]  

(277)

\[ \left[ -\frac{2}{\theta_{\alpha}^{2}} \frac{\partial \hat{e}_{\alpha}}{\partial \theta_{\beta} \theta_{\beta}} + \frac{\partial}{\partial \theta_{\alpha}} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \hat{c}_{\alpha}}{\partial \theta_{\beta}} \right]^{\epsilon} = 0, \quad \alpha \neq \beta \]  

(278)

For the strain components:

\[ \left[ \frac{1}{\theta_{\alpha}} \frac{\partial^{2}}{\partial \xi_{\alpha} \partial \xi_{\alpha}} (\rho_{\alpha} \psi_{\alpha}) \cdot \frac{\partial \hat{e}_{\alpha}}{\partial \xi_{\alpha}} \right]^{\epsilon} \geq 0, \quad \alpha = \beta \]  

(279)

\[ \left[ \frac{\partial}{\partial \xi_{\alpha} \xi_{\alpha}} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \hat{c}_{\alpha}}{\partial \xi_{\alpha}} \right]^{\epsilon} = 0, \quad \alpha \neq \beta \]  

(280)

\[ \left[ \frac{\partial}{\partial \xi_{\alpha} \xi_{\alpha}} (e_{\alpha} - \mu_{\alpha}) \frac{\partial \hat{c}_{\alpha}}{\partial \xi_{\alpha}} \right]^{\epsilon} \geq 0, \quad \alpha = \beta \]  

(281)

For the extent of reaction:

\[ \left[ \frac{1}{\theta_{\alpha}} \frac{\partial^{2}}{\partial \xi_{\alpha} \partial \xi_{\alpha}} (\rho_{\alpha} \psi_{\alpha}) \cdot \frac{\partial \hat{e}_{\alpha}}{\partial \xi_{\alpha}} \right]^{\epsilon} \geq 0, \quad \alpha = \beta \]  

(282)
and for the internal state variables:

\[
\left[ \frac{\partial}{\partial l_\alpha} (e_\alpha - \mu_\alpha) \frac{\partial \vec{c}_\alpha}{\partial l_\rho} \right]^e \geq 0, \quad \alpha = \beta
\]  

(285)

\[
\left[ \frac{\partial}{\partial \xi_{\alpha i}} (e_\alpha - \mu_\alpha) \frac{\partial \vec{c}_\alpha}{\partial \xi_{\alpha i}} \right]^e \geq 0, \quad \alpha = \beta
\]  

(286)

\[
\left[ \frac{\partial}{\partial \xi_{\beta i}} (e_\alpha - \mu_\alpha) \frac{\partial \vec{c}_\alpha}{\partial \xi_{\beta i}} \right]^e = 0, \quad \alpha \neq \beta.
\]  

(287)

**Derivation of Constitutive Equations**

One method of developing the constitutive relations for the constituents would be to proceed in the manner of Adams and Brown (1989) and Brown, Barber, and Edens (1996) using the Helmholtz free energy represented by a Taylor series expansion in terms of the independent variables. We will first derive the generic case then specialize the equations for the particular materials used. The Helmholtz free energy then takes on the following form,
\[
\psi_\alpha = \psi_{\alpha 0} + \psi_{\alpha 1}(trE_\alpha) + \psi_{\alpha 2}(\theta_\alpha - \theta_{\alpha R}) + \psi_{\alpha 3}(l_\alpha - l_{\alpha R}) + \psi_{\alpha 4}(\xi_\alpha - \xi_{\alpha R})
\]

\[
\frac{1}{2}[\psi_{\alpha 5}(trE_\alpha)^2 + \psi_{\alpha 6}tr(E_\alpha^2) + 2\psi_{\alpha 7}(\theta_\alpha - \theta_{\alpha R})trE_\alpha + 2\psi_{\alpha 8}(l_\alpha - l_{\alpha R})trE_\alpha
\]

\[
+ 2\psi_{\alpha 9}(\xi_\alpha - \xi_{\alpha R})trE_\alpha + 2\psi_{\alpha 10}(\theta_\alpha - \theta_{\alpha R})(l_\alpha - l_{\alpha R})
\]

\[
+ 2\psi_{\alpha 11}(\theta_\alpha - \theta_{\alpha R})(\xi_\alpha - \xi_{\alpha R}) + 2\psi_{\alpha 12}(l_\alpha - l_{\alpha R})(\xi_\alpha - \xi_{\alpha R})
\]

\[
+ \psi_{\alpha 13}(\theta_\alpha - \theta_{\alpha R})^2 + \psi_{\alpha 14}(l_\alpha - l_{\alpha R})^2 + \psi_{\alpha 15}(\xi_\alpha - \xi_{\alpha R})^2]
\]

The stress tensor for each phase then becomes,

\[
\tilde{T}_\alpha = \rho_\alpha \det[F_\alpha] \frac{\partial \psi_\alpha}{\partial E_\alpha}
\]

which yields the relation,

\[
\tilde{T}_\alpha = \rho_\alpha \det[F_\alpha] \{ \psi_{\alpha 1}I + \psi_{\alpha 5}(trE_\alpha)I + \psi_{\alpha 6}E_\alpha
\]

\[
+ \psi_{\alpha 7}(\theta_\alpha - \theta_{\alpha R})I + \psi_{\alpha 8}(l_\alpha - l_{\alpha R})I + \psi_{\alpha 9}(\xi_\alpha - \xi_{\alpha R})I \}
\]

For small strains, the determinant of the deformation gradient is approximately equal to the value of one, so equation (290) will give the classical relation for a linear elastic material. By equation (179), the entropy has the form:

\[
\eta_\alpha = -\frac{\partial \psi_\alpha}{\partial \theta_\alpha}
\]

\[
\eta_\alpha = -[\psi_{\alpha 2} + \psi_{\alpha 7}(trE_\alpha) + \psi_{\alpha 10}(l_\alpha - l_{\alpha R})
\]

\[
+ \psi_{\alpha 11}(\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha 13}(\theta_\alpha - \theta_{\alpha R})]
\]

Using Equation (183), the chemical potential can be expanded to,
\[ \mu_\alpha = \frac{\partial}{\partial l_\alpha}(l_\alpha \psi_\alpha) = l_\alpha \frac{\partial \psi_\alpha}{\partial l_\alpha} + \psi_\alpha \]

\[ \mu_\alpha = l_\alpha [\psi_{\alpha 3} + \psi_{\alpha 8} \text{tr}E_\alpha + \psi_{\alpha 10}(\theta_\alpha - \theta_{\alpha R}) + \psi_{\alpha 12}(\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha 14}(l_\alpha - l_{\alpha R})] \]

\[ + \psi_{\alpha 0} + \psi_{\alpha 1}(\text{tr}E_\alpha) + \psi_{\alpha 2}(\theta_\alpha - \theta_{\alpha R}) + \psi_{\alpha 3}(l_\alpha - l_{\alpha R}) + \psi_{\alpha 4}(\xi_\alpha - \xi_{\alpha R}) \]

\[ + \psi_{\alpha 5}(l_\alpha - l_{\alpha R}) \text{tr}E_\alpha + \psi_{\alpha 6}(\theta_\alpha - \theta_{\alpha R}) \text{tr}E_\alpha + 2 \psi_{\alpha 7}(l_\alpha - l_{\alpha R}) \text{tr}E_\alpha + \psi_{\alpha 8}(l_\alpha - l_{\alpha R}) \text{tr}E_\alpha \]

\[ + \psi_{\alpha 9}(\xi_\alpha - \xi_{\alpha R}) \text{tr}E_\alpha + 2 \psi_{\alpha 10}(\theta_\alpha - \theta_{\alpha R})(l_\alpha - l_{\alpha R}) \]

\[ + 2 \psi_{\alpha 11}(\theta_\alpha - \theta_{\alpha R})(\xi_\alpha - \xi_{\alpha R}) + 2 \psi_{\alpha 12}(l_\alpha - l_{\alpha R})(\xi_\alpha - \xi_{\alpha R}) \]

\[ + \psi_{\alpha 13}(\theta_\alpha - \theta_{\alpha R})^2 + \psi_{\alpha 14}(l_\alpha - l_{\alpha R})^2 + \psi_{\alpha 15}(\xi_\alpha - \xi_{\alpha R})^2 \] \hspace{1cm} (292)

Additional information can be obtained by considering the energy, \( e_\alpha \). Using the relation \( e_\alpha = \psi_\alpha + \theta_\alpha \eta_\alpha \), we can obtain the following equation for the internal energy:

\[ e_\alpha = \psi_{\alpha 0} + \psi_{\alpha 1}(\text{tr}E_\alpha) + \psi_{\alpha 2}(\theta_\alpha - \theta_{\alpha R}) + \psi_{\alpha 3}(l_\alpha - l_{\alpha R}) + \psi_{\alpha 4}(\xi_\alpha - \xi_{\alpha R}) \]

\[ + \frac{1}{2} \psi_{\alpha 5}(\text{tr}E_\alpha)^2 + \psi_{\alpha 6}(\text{tr}E_\alpha)^2 + 2 \psi_{\alpha 7}(\theta_\alpha - \theta_{\alpha R}) \text{tr}E_\alpha + 2 \psi_{\alpha 8}(l_\alpha - l_{\alpha R}) \text{tr}E_\alpha \]

\[ + 2 \psi_{\alpha 9}(\xi_\alpha - \xi_{\alpha R}) \text{tr}E_\alpha + 2 \psi_{\alpha 10}(\theta_\alpha - \theta_{\alpha R})(l_\alpha - l_{\alpha R}) \]

\[ + 2 \psi_{\alpha 11}(\theta_\alpha - \theta_{\alpha R})(\xi_\alpha - \xi_{\alpha R}) + 2 \psi_{\alpha 12}(l_\alpha - l_{\alpha R})(\xi_\alpha - \xi_{\alpha R}) \]

\[ + \psi_{\alpha 13}(\theta_\alpha - \theta_{\alpha R})^2 + \psi_{\alpha 14}(l_\alpha - l_{\alpha R})^2 + \psi_{\alpha 15}(\xi_\alpha - \xi_{\alpha R})^2 \] \hspace{1cm} (293)

\[ - \theta_\alpha [\psi_{\alpha 2} + \psi_{\alpha 7}(\text{tr}E_\alpha) + \psi_{\alpha 10}(l_\alpha - l_{\alpha R}) \]

\[ + \psi_{\alpha 11}(\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha 13}(\theta_\alpha - \theta_{\alpha R})] \]

The time rate of change of the internal energy is given by:

\[ \dot{e}_\alpha = \frac{\partial e_\alpha}{\partial \theta_\alpha} \dot{\theta}_\alpha + \frac{\partial e_\alpha}{\partial E_\alpha} \dot{E}_\alpha + \frac{\partial e_\alpha}{\partial l_\alpha} \dot{l}_\alpha + \frac{\partial e_\alpha}{\partial \xi_\alpha} \dot{\xi}_\alpha \] \hspace{1cm} (294)
\[
\frac{\partial e_\alpha}{\partial \theta_\alpha} = (\psi_{\alpha 2} - \theta_\alpha \psi_{\alpha 13}) + \psi_{\alpha 7} t E_\alpha + \psi_{\alpha 10} (l_\alpha - l_{\alpha R}) + \psi_{\alpha 11} (\xi_\alpha - \xi_{\alpha R})
\]  
(295)

\[
\frac{\partial e_\alpha}{\partial E_\alpha} = \psi_{\alpha 1} I + \psi_{\alpha 5} (t E_\alpha I) + \psi_{\alpha 6} E_\alpha + \psi_{\alpha 7} (\theta_\alpha - \theta_{\alpha R}) I + \psi_{\alpha 8} (l_\alpha - l_{\alpha R}) I
\]
\[
+ \psi_{\alpha 9} (\xi_\alpha - \xi_{\alpha R}) I
\]  
(296)

\[
\frac{\partial e_\alpha}{\partial l_\alpha} = (\psi_{\alpha 3} - \theta_\alpha \psi_{\alpha 10}) + \psi_{\alpha 8} t E_\alpha + \psi_{\alpha 10} (\theta_\alpha - \theta_{\alpha R})
\]
\[
+ \psi_{\alpha 12} (\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha 14} (l_\alpha - l_{\alpha R})
\]  
(297)

\[
\frac{\partial e_\alpha}{\partial \xi_\alpha} = (\psi_{\alpha 4} - \theta_\alpha \psi_{\alpha 11}) + \psi_{\alpha 9} t E_\alpha + \psi_{\alpha 11} (\theta_\alpha - \theta_{\alpha R})
\]
\[
+ \psi_{\alpha 12} (l_\alpha - l_{\alpha R}) + \psi_{\alpha 15} (\xi_\alpha - \xi_{\alpha R})
\]  
(298)

Using equations (295) and (297) gives the specific heat of the material, \(C_\theta\) and the latent heat of sublimation, \(H_s\). Substituting we obtain:

\[
C_\theta = (\psi_{\alpha 2} - \theta_\alpha \psi_{\alpha 13}) + \psi_{\alpha 7} t E_\alpha + \psi_{\alpha 10} (l_\alpha - l_{\alpha R}) + \psi_{\alpha 11} (\xi_\alpha - \xi_{\alpha R})
\]  
(299)

\[
H_s = (\psi_{\alpha 3} - \theta_\alpha \psi_{\alpha 10}) + \psi_{\alpha 8} t E_\alpha + \psi_{\alpha 10} (\theta_\alpha - \theta_{\alpha R})
\]
\[
+ \psi_{\alpha 12} (\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha 14} (l_\alpha - l_{\alpha R})
\]  
(300)

**Restrictions based upon the Second Law**

Substituting the above relations into the restrictions from the last chapter we get the following, for the relationship \(e_\alpha - \mu_\alpha\) we have,
\[ e_{\alpha} - \mu_{\alpha} = -\theta_{\alpha}(\psi_{\alpha 2} + \psi_{\alpha 7}(trE_{\alpha}) + \psi_{\alpha 10}(l_{\alpha} - l_{\alpha R}) \]
\[ + \psi_{\alpha 11}(\xi_{\alpha} - \xi_{\alpha R}) + \psi_{\alpha 13}(\theta_{\alpha} - \theta_{\alpha R}) \] 
\[ - l_{\alpha}(\psi_{\alpha 3} + \psi_{\alpha 8}trE_{\alpha} + \psi_{\alpha 10}(\theta_{\alpha} - \theta_{\alpha R}) + \psi_{\alpha 12}(\xi_{\alpha} - \xi_{\alpha R}) \]
\[ + \psi_{\alpha 14}(l_{\alpha} - l_{\alpha R}) \] 
\[ (301) \]

From equation (275) we get upon substitution,
\[ \sum_{\alpha = 1}^{n} -\frac{1}{\theta_{\alpha}} \left\{ \rho_{\alpha} \left[ \psi_{\alpha 4} + \psi_{\alpha 9}trE_{\alpha} + \psi_{\alpha 11}(\theta_{\alpha} - \theta_{\alpha R}) \right. \]
\[ + \psi_{\alpha 12}(l_{\alpha} - l_{\alpha R}) + \psi_{\alpha 15}(\xi_{\alpha} - \xi_{\alpha R}) \] \[ \left. \right\} \hat{\epsilon}_{\alpha} \]
\[ - \hat{\epsilon}_{\alpha} - \left\{ \theta_{\alpha} \left[ \psi_{\alpha 2} + \psi_{\alpha 7}(trE_{\alpha}) + \psi_{\alpha 10}(l_{\alpha} - l_{\alpha R}) \right. \]
\[ + \psi_{\alpha 11}(\xi_{\alpha} - \xi_{\alpha R}) + \psi_{\alpha 13}(\theta_{\alpha} - \theta_{\alpha R}) \] \[ \left. \right\} \] 
\[ - l_{\alpha}(\psi_{\alpha 3} + \psi_{\alpha 8}trE_{\alpha} + \psi_{\alpha 10}(\theta_{\alpha} - \theta_{\alpha R}) + \psi_{\alpha 12}(\xi_{\alpha} - \xi_{\alpha R}) \]
\[ + \psi_{\alpha 14}(l_{\alpha} - l_{\alpha R}) \] \[ \} \hat{\epsilon}_{\alpha} \geq 0 \]
\[ (302) \]
which gives a restriction for the sum of all constituents. For each individual constituent we have additional restrictions. From equation (276) we get
\[ \left[ \frac{\rho_{\alpha}(\psi_{\alpha 11} \cdot \frac{\partial \hat{\epsilon}_{\alpha}}{\partial \theta_{\alpha}})}{\theta_{\alpha}} \right]^{e} \leq 0, \quad \alpha = \beta \]
\[ (303) \]

From equation (277) we get
\[ \left[ - \frac{2 \frac{\partial \hat{\epsilon}_{\alpha}}{\theta_{\alpha}^{2} \frac{\partial}{\partial \theta_{\alpha}}} + \left\{ \psi_{\alpha 2} + \psi_{\alpha 7}(trE_{\alpha}) + \psi_{\alpha 10}(l_{\alpha} - l_{\alpha R}) \right. \]
\[ + \psi_{\alpha 11}(\xi_{\alpha} - \xi_{\alpha R}) + \psi_{\alpha 13}(2\theta_{\alpha} - \theta_{\alpha R}) \] \[ \left. \right\} \frac{\partial \hat{\epsilon}_{\alpha}}{\partial \theta_{\alpha}} \right]^{e} \geq 0, \quad \alpha = \beta \]
\[ (304) \]

From equation (278) we get
\[
\left[-\frac{2}{\theta^2} \frac{\partial^2 \alpha}{\partial \theta^2} + \left\{ \psi_{\alpha_2} + \psi_{\alpha_7}(trE_\alpha + \psi_{\alpha_{10}}(l_\alpha - l_{\alpha R})
+ \psi_{\alpha_{11}}(\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha_{13}}(2\theta_\alpha - \theta_{\alpha R}) \right\} \frac{\partial \alpha}{\partial \theta} \right] = 0, \alpha \neq \beta
\]

(305)

For the strain components and from equation (279) we get,

\[
\left[ \frac{\rho_{\alpha}}{\theta_{\alpha}} \psi_{\alpha_{9}} \cdot \frac{\partial \xi_{\alpha}}{\partial E_{\alpha i j}} \right]^e \geq 0, \quad \alpha = \beta
\]

(306)

and from equations (280) and (281) we have,

\[
\left[ (\theta_{\alpha} \psi_{\alpha_{7}} + l_{\alpha} \psi_{\alpha_{8}}) \frac{\partial \alpha}{\partial E_{\beta k l}} \right]^e = 0, \quad \alpha \neq \beta
\]

(307)

\[
\left[ (\theta_{\alpha} \psi_{\alpha_{7}} + l_{\alpha} \psi_{\alpha_{8}}) \frac{\partial \alpha}{\partial E_{\alpha i j}} \right]^e \geq 0, \quad \alpha = \beta
\]

(308)

For the extent of reaction constraints and equation (282) we get

\[
\left[ \frac{\rho_{\alpha}}{\theta_{\alpha}} \psi_{\alpha_{12}} \cdot \frac{\partial \alpha}{\partial l_\alpha} \right]^e \geq 0, \quad \alpha = \beta
\]

(309)

and equations (283) and (284) yield the following,

\[
\left\{ \psi_{\alpha_3} + \psi_{\alpha_8}(trE_\alpha) + \psi_{\alpha_{10}}(\theta_\alpha - \theta_{\alpha R})
+ \psi_{\alpha_{12}}(\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha_{14}}(2l_\alpha - l_{\alpha R}) \right\} \frac{\partial \alpha}{\partial l_\alpha} \right\} \geq 0, \alpha = \beta
\]

(310)

\[
\left\{ \psi_{\alpha_3} + \psi_{\alpha_8}(trE_\alpha) + \psi_{\alpha_{10}}(\theta_\alpha - \theta_{\alpha R})
+ \psi_{\alpha_{12}}(\xi_\alpha - \xi_{\alpha R}) + \psi_{\alpha_{14}}(2l_\alpha - l_{\alpha R}) \right\} \frac{\partial \alpha}{\partial l_\beta} \right\} = 0, \alpha \neq \beta
\]

(311)
For the internal state variables and their constraints from equation (285) we have,

$$
\left[ \frac{\rho_{\alpha}}{\theta_{\alpha}} \phi_{\alpha} \cdot \frac{\partial \phi_{\alpha}}{\partial \phi_{\alpha}} \right] \geq 0, \quad \alpha = \beta \tag{312}
$$

and from the constraint equations (286) and (287) we have,

$$
\left[ (\theta_{\alpha} \phi_{\alpha} + l_{\alpha} \phi_{\alpha}) \frac{\partial \phi_{\alpha}}{\partial \phi_{\alpha}} \right] \geq 0, \quad \alpha = \beta \tag{313}
$$

$$
\left[ (\theta_{\alpha} \phi_{\alpha} + l_{\alpha} \phi_{\alpha}) \frac{\partial \phi_{\alpha}}{\partial \phi_{\beta}} \right] = 0, \quad \alpha \neq \beta \tag{314}
$$

The above constraints give the criterion which the constant parameters to the Taylor series expansion must obey in order to satisfy the Second Law of Thermodynamics. The final constitutive equations must satisfy all of the above constraints. It should be noted that the inequalities merely tell us that what we have done may be correct and that so far we have satisfied the criterion but still may not have the correct form.

**Linear Momentum Interaction**

This term specifies the force that would be necessary to influence the motion of the constituent had the other constituents not been present. This forces the constituents to have the same displacement. Since the second law does not constrain the linear momentum interaction term in volume fraction theory, we can chose or derive a constitutive relation as long as it satisfies the various continuum principles. After Hansen, Walker and Donovan (1990) we will assume the following relation for the linear momentum interaction term,

$$
\hat{p}_\alpha = -\hat{p}_\beta = C(w_\alpha - A w_\beta) \tag{315}
$$

where \( w_\alpha \) and \( w_\beta \) are the constituent displacements,
Recall equation (86), then if there is not acceleration or a body force then

\[-\text{DIV}(F_{\alpha} \mathbf{T}_{\alpha}) = |F_{\alpha}| \dot{\rho}_{\alpha}\]  

(318)

so if there is not a stress gradient then the linear momentum supply must be zero. Specific forms for the elements will be made when a specific material is selected.

**Angular Momentum Interaction**

For there to be an angular momentum supply term the material would need to be classified as a polar material. This would include materials whose stress at a point is influenced by other constituents outside of a small neighborhood of that point. The material in mind for this model does not behave in such a manner thus the Cauchy stress tensor and the second Piola stress tensor are symmetric.

**Internal Energy Interaction**

A constitutive relation for the internal energy supply that has been used by Adams (1987) relates the internal energy supply to the differences in temperature of the constituents. Here, we have already assumed an isothermal mixture in which all constituents are the same temperature and strains are not a function of temperature except
through the internal state variables. Thus, the internal energy supply term \( \dot{\varepsilon}_\alpha \) is zero since we will require the temperatures of all constituents to be the same.

**Evolution Equations**

The notion of internal state variables was introduced in a previous chapter. When we use the internal state variables we have a set of evolution equations that have the following functional dependencies for our particular application,

\[
\dot{\xi}_\alpha = \omega(E_\alpha, \theta_\alpha, \xi_\alpha).
\]  

Since the internal state variables model a visco-plastic material we require a yield function which determines the domain of validity of the constitutive relation for the evolution equations. We will need to expand the internal state vector, \( \xi_\alpha \), in terms of the actual variables selected for our materials or constituents. The evolution equations are ordinary differential equations with given initial conditions giving the time evolution of the internal variables. The stress rate depends upon the strains, strain rate, internal variables and the rate of change of the internal variables. Since the internal variables depend upon strain, it is evident that the stress rate is nonlinear in strain.

**Material Frame Indifference**

The constitutive model used to represent material behavior should not depend upon the frame of reference. Distance, time, orientation, and temporal order must agree between different frames of reference. Thus, material frame indifference applies to the constitutive model and its variables, it does not apply to the balance laws since the material behavior is intrinsic to the material property. The balance laws merely indicate how the material is
influenced by the laws of continuum physics while the constitutive behavior reflects the intrinsic properties of the material.

Now consider two reference frames, \( R^* \) and \( R \). The same point may be represented in both reference frames as shown in Figure 5.

\[
x^* = c(t) + Q(t)x
\]

which describes the translation and rotation to get from one frame to the other. The tensor \( Q \) is an orthogonal tensor such that

\[
Q^T = Q^{-1}.
\]
By definition, Malvern (1969), those scalars, vectors and tensors which depend only upon the orientation of the reference frame are objective. Thus, for objectivity to hold we must have the following relations for all scalars, vectors and tensors respectively,

\[ \Gamma^* = \Gamma \]
\[ v^* = Qv \]
\[ T^* = QTQ^T \]

with a special case for the deformation gradient, since it is a two point tensor,

\[ F^* = QF \].

**Material Frame Indifference for Stress and Strain**

Observing first the Second Piola Stress tensor we have

\[ (tr(\tilde{T}_\alpha)1)^* = tr(\tilde{T}_\alpha)1^* = tr(\tilde{T}_\alpha)(Q1Q^T) = tr(\tilde{T}_\alpha)(QQ^T) = tr(\tilde{T}_\alpha)1 \]

and

\[ (\tilde{T}_\alpha)^* = \left( \frac{\rho_0}{\rho_\alpha} F^{-1}_\alpha T_\alpha F^{-T}_\alpha \right)^* \]
\[ = \frac{\rho_0}{\rho_\alpha} (F^{-1}_\alpha)^* (T_\alpha)^* (F^{-T}_\alpha)^* \]
\[ = \frac{\rho_0}{\rho_\alpha} (F^{-1}_\alpha Q^T)(QT_\alpha Q^T)(QF^{-T}_\alpha) \]
\[ = \frac{\rho_0}{\rho_\alpha} F^{-1}_\alpha (Q^TQT_\alpha Q^TQF^{-T}_\alpha) \]
\[ = \frac{\rho_0}{\rho_\alpha} F^{-1}_\alpha T_\alpha F^{-T}_\alpha \]
\[ = \tilde{T}_\alpha \]
from equations (322) and (323). Since the internal state vector is composed of scalars it is indifferent to reference frame changes. The Lagrangian strain rate becomes,

\[
(\dot{\varepsilon}_\alpha)^* = \frac{1}{2} (F^T_\alpha F_\alpha - 1)
\]

\[
= \frac{1}{2} [(F^T_\alpha F_\alpha)^* + (F^T_\alpha \dot{F}_\alpha)^*]
\]

\[
= \frac{1}{2} \left( F^T_\alpha Q^T Q F_\alpha + F^T_\alpha Q^T \dot{Q} F_\alpha \right)
\]

\[
= \frac{1}{2} \left( F^T_\alpha Q^T Q F_\alpha + F^T_\alpha \dot{Q} \dot{Q} T F_\alpha + F^T_\alpha \dot{Q} Q F_\alpha + F^T_\alpha Q^T Q \dot{F}_\alpha \right)
\]

\[
= \frac{1}{2} F^T_\alpha Q^T Q F_\alpha + F^T_\alpha \dot{Q} \dot{Q} T F_\alpha + F^T_\alpha \dot{Q} F_\alpha F_\alpha
\]

\[
= \frac{1}{2} F^T_\alpha T F_\alpha + F^T_\alpha \dot{F}_\alpha
\]

\[
= \frac{1}{2} F^T_\alpha T F_\alpha + F^T_\alpha \dot{F}_\alpha
\]

\[
= \dot{\varepsilon}_\alpha
\]

which is material frame indifferent. Notice we have used the identity

\[
\dot{Q}^T \dot{Q} = \dot{Q}^T \dot{Q} + \dot{Q}^T \dot{Q} = 1 = 0.
\]

Now consider the time derivative of the second Piola stress tensor. Since the term \(tr(\dot{T}_\alpha)\) is a scalar, it is material frame indifferent. Material frame indifference of the tensor, \(T_\alpha\) can be observed by considering the temporal derivative and the expansion of the different terms. This then gives the following,
\[
(\dot{\mathcal{T}}_\alpha)^* = \left(\frac{\rho_0 \alpha F^{-1}_\alpha T_\alpha F^{-T}_\alpha}{\rho_\alpha}\right)^* \\
= \frac{\rho_0 \alpha}{\rho_\alpha} ((F^{-1}_\alpha)^*(T_\alpha)^*(F^{-T}_\alpha)^*) - \frac{\rho_0 \alpha \dot{\rho}_\alpha}{\rho_\alpha^2} ((F^{-1}_\alpha)^*(T_\alpha)^*(F^{-T}_\alpha)^*) \\
= \frac{\rho_0 \alpha}{\rho_\alpha} (QF_\alpha)^{-1}(QT_\alpha Q^T)(QF_\alpha)^{-T} \\
\quad - \frac{\rho_0 \alpha \dot{\rho}_\alpha}{\rho_\alpha^2} (QF_\alpha)^{-1}(QT_\alpha Q^T)(QF_\alpha)^{-T} \\
\quad - \frac{\rho_0 \alpha}{\rho_\alpha} (F^{-1}_\alpha Q^TQT_\alpha Q^TQF_\alpha)^{-T} \\
\quad - \frac{\rho_0 \alpha \dot{\rho}_\alpha}{\rho_\alpha^2} (F^{-1}_\alpha Q^TQT_\alpha Q^TQF_\alpha)^{-T} \\
\quad = \frac{\rho_0 \alpha}{\rho_\alpha} (F^{-1}_\alpha T_\alpha F^{-T}_\alpha) \quad - \frac{\rho_0 \alpha \dot{\rho}_\alpha}{\rho_\alpha^2} (F^{-1}_\alpha T_\alpha F^{-T}_\alpha) \\
\quad = \left(\frac{\rho_0 \alpha F^{-1}_\alpha T_\alpha F^{-T}_\alpha}{\rho_\alpha}\right)^* \\
= \dot{\mathcal{T}}_\alpha
\]

which shows that \( \mathcal{T}_\alpha \) is material frame indifferent.

Compiling the results of equations (324), (325), (326) and (328) the constitutive relation is material frame indifferent. Thus, any frame of reference that is chosen will yield an appropriate model for the material assumptions.

**Material Frame Indifference for Balance Law Interaction Terms**

It is important to note that material frame indifference describes how the model of material behavior responds to changes in the material frame. It does not impose upon the material how that material will behave as described by the dynamic behavior of the balance laws. Thus the balance of mass, linear momentum, angular momentum and energy do not necessarily obey the principle of material frame indifference.
Observing the balance laws, it may be seen that this implies that the interaction terms need not necessarily obey the principle of material frame indifference. Showing the validity of material frame indifference for the material constitutive relation describing material behavior is sufficient.
CHAPTER 5

APPLICATION TO A SNOW-WOOD MIXTURE

Introduction

In this chapter a specific material is chosen to use as an example. Snow is an elastic visco-plastic material that is used in the construction of roads and runways in polar regions. This is a prevalent material in polar regions, inexpensive and usable while the temperature is controlled. In designing a new South Pole Station in Antarctica it was necessary to evaluate the transportation system required for delivery of the construction materials. This included what surface materials were to be used on the roads and runways for material delivery. The use of a snow-wood mixture was postulated, and laboratory tests and mathematical models were constructed to determine the suitability of the snow-wood mixture.

Constitutive Equations for a Snow-Wood Mixture

Here we will apply the theory developed in the previous chapters to a snow-wood mixture. We will consider a two-constituent mixture which consists of snow and wood. The wood will be treated as an elastic material while the snow is considered a visco-plastic material. A mathematical model will be constructed which will then be compared with laboratory tests and data obtained in Antarctica from field tests.
Evolution Equations for the Ice-Ice Interaction

The stress was represented by equation (289) which will be specified at this point. Consider an isothermal material with temperature entering only in the evolution equations. The specific internal state variables we will use are in Table 1.

Table 1. Internal State Variables Used for a Snow-Wood Mixture.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>mean grain radius</td>
</tr>
<tr>
<td>$h$</td>
<td>neck length</td>
</tr>
<tr>
<td>$R$</td>
<td>neck radius</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>density ratio, ice to total density</td>
</tr>
<tr>
<td>$N_3^w$</td>
<td>mean number of ice bonds per wood chip (chip to chip neglected due to volume fraction of wood chips)</td>
</tr>
<tr>
<td>$N_3$</td>
<td>mean number of ice bonds per grain of snow</td>
</tr>
<tr>
<td>$\sigma_b$</td>
<td>surface energy of the bond</td>
</tr>
<tr>
<td>$\sigma_g$</td>
<td>surface energy of the grain</td>
</tr>
<tr>
<td>$\sigma_w$</td>
<td>surface energy of the wood</td>
</tr>
<tr>
<td>$T_n$</td>
<td>stress in the grain neck</td>
</tr>
<tr>
<td>$T_s$</td>
<td>stress in the bulk snow</td>
</tr>
<tr>
<td>$\alpha_w$</td>
<td>density ratio, wood to total density</td>
</tr>
<tr>
<td>$r_w$</td>
<td>neck radius of ice on wood</td>
</tr>
</tbody>
</table>

The selection of these variables arises due to several considerations. Hansen (1985) and Edens (1989) used $L$, $h$, $R$, $\alpha$ and $N_3$ for their internal state variables. In the following discussion we will base our development upon these ideas and discuss important changes. Not all of these internal state variables must be used, and some may be made functions of others. Consider first generic formulations of the evolution equations. We will simplify
and reduce the dependency as the discussion proceeds. First use the following functional relationships as part of the evolution equations,

\[ L = f_L(N_3, \alpha, L, R, h) \]  
(329)

\[ R = f_R(T_s, N_3, \alpha, L, R, h) \]  
(330)

\[ h = f_h(T_s, N_3, \alpha, L, R, h) \]  
(331)

\[ r_w = f(T_s, \sigma_b, \sigma_g, \sigma_w, r_w, N_3, N_3, \alpha, L, R, h, \alpha_w) \]  
(332)

Hansen (1985) and Edens (1989) developed the following relationships for the time rate of change of the internal state vector \( \zeta \) components in equations (329), (330), and (331),

\[ \dot{L} = -\frac{N_3 \pi \alpha}{4(\alpha - 1)} L (2R \dot{R} - \dot{h}) \]  
(333)

\[ \dot{R} = -\nu R \dot{A} \left[ T_s \alpha \left( \frac{L}{R} \right)^2 \frac{1}{2N_3} \right]^3 - \frac{(R_0 - R)}{N_3} N_3 \]  
(334)

\[ \dot{h} = h \dot{A} \left[ T_s \alpha \left( \frac{L}{R} \right)^2 \frac{1}{2N_3} \right]^3 - \frac{(h_0 - h)}{N_3} N_3 + \bar{C} \left( \frac{R}{L} \right) \dot{R} \]  
(335)

where,

\[ \alpha = \frac{\rho_i}{\rho_s} = c_i \]  
(336)

\[ \nu = 0.5 \]  
(337)

\[ \bar{A} = 3 \times 10^{-24} \text{Pa}^{-3} \text{s} \]  
(338)

\[ \bar{C} = 10 \]  
(339)

and \( N_3 \) is determined from laboratory experiments with an approximating function of

\[ N_3 = 43\rho_s^3 - 23\rho_s^2 + 4\rho_s + 2.2 \]  
(340)
where $0.2 \leq \rho_s \leq 0.7$ or the time rate of change is,

$$\dot{N}_3 = (129\rho_s^2 - 46\rho_s + 4)\dot{\rho}_s$$  \hspace{1cm} (341)

as shown by Brown and Edens (1990).

Evolution Equations for the Wood - Snow Interaction

Now consider equation (332). The bonding physics of ice on wood will be very similar to the bonding physics of ice on ice except we have different surface texture, surface energies, porosities, and physical features. In general the wood will not change geometric form in response to the energies of the ice. The water content with wood does change. Wood always retains some moisture within the cellulose cell structure. Within the void space between cells water vapor may exist and change with time. This enables wood to retain or attract moisture in response to environmental conditions. It also has an affinity for moisture, gathering up excess moisture until its moisture content matches that of the surrounding environment.

Wood interacts with the surrounding ice. It is generated by the interactions among the moisture in the vapor and moisture in the ice in contact with the wood surface. As has been shown for the case of ice grains, there are three fundamental mechanisms for water transport within and on the ice structure. Water mass may move through the air as vapor, it may migrate over the surface of the ice, and it may migrate through the internal structure of the ice. Maeno and Ebinuma (1983) referred to these mechanisms as pressure sintering (migration through the internal structure of the ice), vapor diffusion (moving through the air as vapor), surface diffusion, volume diffusion, and grain boundary diffusion (migrating over the surface of the ice and migrating through the internal structure of the ice). While each one of these may be important there may be times when a subset will dominate the interactions.
Consider the case when ice is pressed against a wood surface. If we are discussing high stresses then the vapor diffusion, surface diffusion, and grain boundary diffusion will be dominated by pressure sintering and volume diffusion. With water vapor already within the wood pore, additional moisture would need to come from the surface of the ice grain, thus from surface diffusion but not from vapor diffusion. This would be classified as surface diffusion which will be considered separately.

The grain boundary diffusion arises from interactions of the energies from two or more grains. Due to the ability of both grains to gain or lose mass, change geometry, or change energies they will have more of an interaction than two materials which are rigid and have fixed geometries. It is true that energies may be exchanged but in general this comes at a cost of temperature change, geometry change, or some other changing variable. The definition of a grain boundary with respect to interactions with another material is not clear. Therefore we will assume that this diffusion mechanism is small compared with the others considered.

In Figure 6 the general structure of the wood cells may be ascertained. Notice there are long sections of wood fiber (white) and long sections of void space (black). Wood is a nonhomogeneous and nonisotropic material which should be considered. For our case we will use randomly orientated wood chips so on average, the cell structure is distributed uniformly in all three dimensions.

Also note that one of two conditions occur, the ice is pressed against the side of the cell structure or it is pressed against the ends of the cell structure. For the first case the interactions will primarily be ice to wood while for the other case it will primarily be ice to pore space. Since the percentage of the pore space is much smaller than the percentage of wood area, the ice in contact with the wood surface will have primary influence. Thus, it seems that the primary mechanism will be the surface of the ice in contact with the surface of the wood cell or the mechanism called pressure sintering.
Figure 6. Characterization of a Wood Cellulose Structure: Black Pore Space, White Cell Wall.

Figure 7. Characterization of the Snow Surface: Black Pore Space, White Ice.

As we can see from Figure 7, the snow, which has not been subjected to temperature gradients, has a random structure similar to the wood. There will be void space and ice in contact with the wood cell wall or the cell void space between wood cell walls. Depending upon the density of the wood and density of snow the amount of contact area will vary in
accordance with those densities. It may be possible for one dominant mechanism to become a tributary mechanism in the overall process as densities change and vary. This should show the enormous complexities that snow presents to the modeler.

With this in mind and assuming one of the dominant mechanisms is the ice and snow interaction we need now to specify the relationship between the radius of the ice in contact with the wood by adopting a form similar to equation (334).

\[ r_w' = -\nu r_w \alpha_w \left[ T_s \alpha_w \left( \frac{L}{r_w} \right)^2 \frac{1}{2 r_w^3} \right]^3 + \frac{(r_w - r_w_0) \cdot r_w^w}{N_3^w} + K(\sigma_w - \sigma_s) \]

(342)

where the first term represents what effect pressure sintering has on the radius of contact or the strain rate of the bond radius, the second term gives the effect of number of contacts of ice on the wood, and the last term gives the effect the difference in surface energies have on the rate of contact growth and \( K \) will need to be identified. The energy term may not be a linear equation but for want of additional testing and hypothesis we assume a linear relationship.

It should be noted that a new term has been added to equation (342), that being the term \( \alpha_w \), the ratio of wood density to snow density,

\[ \alpha_w = \frac{\rho_w}{\rho_s} = c_w \]

(343)

Consider now the work that was done in previous chapters in regards to the stress tensor. From equations (334), (335), and (342) we see the following terms appear,

\[ T_s \alpha_i \]

\[ T_s \alpha_w \]

(344)

which from chapter 2 yields,
the concentration times the total stress. From Brown and Edens (1990) the assumption was that the ice stress was related to the bulk stress through the ratio of the densities as determined by quantitative stereology. Recalling equation (160) where we had that the total Cauchy stress was given as,

\[ T = \sum_{\alpha=1}^{n} T_{\alpha} \]  

the total Cauchy stress is the sum of the constituent stresses. In light of this observation we will use as replacements for equations (334), (335), and (342) the following,

\[ \hat{R} = -\nu R \tilde{A} \left[ T_{I} \left( \frac{L}{R} \right)^{2} \frac{1}{2N_{3}} \right]^{3} - \frac{(R_{0} - R)}{N_{3}N_{3}} \]  

\[ \hat{h} = h \tilde{A} \left[ T_{I} \left( \frac{L}{R} \right)^{2} \frac{1}{2N_{3}} \right]^{3} - \frac{(h_{0} - h)}{N_{3}N_{3}} + \tilde{C} \left( \frac{R}{L} \right) \hat{R} \]  

\[ \hat{r}_{w} = -\nu r_{w} \tilde{A} \left[ T_{w} \left( \frac{L}{r_{w}} \right)^{2} \frac{1}{2N_{3}^{w}} \right]^{3} + \frac{(r_{w} - r_{w0})}{N_{3}^{w}N_{3}} + K(\sigma_{w} - \sigma_{g}) \]  

which in theory will be more consistent with the change in philosophy from classical mixture theory to volume fraction mixture theory.

Identification of constant coefficients

Expanding the equations (288) and (289) to get an expanded form of equation (290),

\[ \hat{T}_{i} = \rho_{i} det|F_{i}| \{ \psi_{i1} I + \psi_{i5}(trE_{i}) I + \psi_{i6}E_{i} + \psi_{i7}(\theta_{i} - \theta_{IR}) I + \psi_{i8}(l_{i} - l_{IR}) I + \psi_{i9}((L - L_{0}) + (R - R_{0}) + (h - h_{0}) + (r_{w} - r_{w0})) I \} \]
which if we examine the linear elastic region of this material we will find the following values for some of the coefficients,

$$\psi_{i1} \neq 0$$  \hspace{1cm} (351)

but we will assume that the initial tensile stress due to the surface tensions is negligible when compared with the stress undertaken during the macroscopic loading process.

$$\psi_{i5} = \frac{\lambda_i}{\rho_i}$$  \hspace{1cm} (352)

$$\psi_{i6} = \frac{\mu_i}{\rho_i}$$  \hspace{1cm} (353)

where $\lambda_i$ and $\mu_i$ can be functions of the internal state vector which will be defined below. Additionally we have

$$\psi_{i7} = \frac{\alpha_i(3\lambda_i + 2\mu_i)}{\rho_i}$$  \hspace{1cm} (354)

and

$$\psi_{i8} = \sigma_{i0}$$  \hspace{1cm} (355)

where $\sigma_{i0}$ is the initial internal stress on the ice grain caused by the surface tension. This then gives

$$\bar{T}_i = \rho_i det|\bar{F}_i| \left\{ \frac{\lambda_i}{\rho_i} (trE_i) I + \frac{2\mu_i}{\rho_i} E_i \right\}$$

$$+ \frac{\alpha_i(3\lambda_i + 2\mu_i)}{\rho_i} (\theta_i - \theta_{iR}) I + \sigma_{i0}(l_i - l_{iR}) I$$

$$+ \psi_{i9}((L - L_0) + (R - R_0) + (h - h_0) + (r_w - r_{w0})) I \right\}$$  \hspace{1cm} (356)
From the wood constituent we get a similar function in the linear elastic region for the stress

\[
\tilde{T}_w = \rho_w \det |F_w| \left[ \frac{\lambda_w}{\rho_w} (\text{tr} E_w) I + \frac{2\mu_w}{\rho_w} E_w \right] + \frac{\alpha_w (3\lambda_w + 2\mu_w)}{\rho_w} (\theta_w - \theta_{wR}) I + \sigma_{w0} (l_w - l_{wR}) I
\]

(357)

where again we can have \( \lambda_w \) and \( \mu_w \) to be functions of the internal state vector. A simple model for the ice matrix gives the following if we consider two blocks of ice connected by a bond.

\[
\lambda_i = A\lambda_{i0} \left( \frac{L + h}{L + h \left( \frac{R}{L} \right)^2} \right)
\]

(358)

and

\[
\mu_i = A\mu_{i0} \left( \frac{L + h}{L + h \left( \frac{R}{L} \right)^2} \right).
\]

(359)

Since the wood is essentially in the elastic region at the encountered stresses and the volume fraction of wood compared to the ice grains and bonds is negligible, we will not develop equations for \( \lambda_w \) and \( \mu_w \).

**Constitutive Equations for Mass Interaction Supply**

In the general case the interactions would need to be considered. We outline some concepts that would be needed. The time a stress test takes to complete probably makes some of the following mechanisms negligible so we will not use them in the model.
As the wood and ice interact there will be a mass transfer from the ice to the wood. This is so due to the fact that the wood cell has a lower moisture content than the pore space within the snow. If the water vapor is neglected then this means the water must be transferred from the ice structure to the wood directly. If the water vapor is considered as a constituent, the water may be transferred through the vapor. The choice of one of these assumptions will yield different constitutive equations for this model.

The amount of water transfer will depend upon three things. The amount of time elapsed, the pressure of the ice upon the wood, and the area of ice in contact with the wood. There will be other tributary variables such as the relative difference between moisture contents but this relates back to the choice of assumptions. Based upon the above logic we could hypothesize the following constitutive relation for the mass interaction supply,

\[ \dot{\varepsilon}_i = \pi H_{iw} N^w_3 r^2_w A_w T_i \]  

where \( H_{iw} \) is a parameter approaching zero at equilibrium relating how fast the water will go from the snow phase and be absorbed by the wood cell structure, \( N^w_3 \) is the average number of grains on each piece of wood, \( r_w \) is the average radius of the grain in contact with the wood, \( A_w \) is the surface area of the wood, and \( T_i \) is the stress in the ice.

The mass interaction for the ice would be \( \dot{\varepsilon}_w = -\dot{\varepsilon}_i \) since the sum of the conservation of mass must sum to zero.

**Constitutive Equations for Linear Momentum Supply**

Recall one of the assumptions in mixture theory is that each constituent may have its own motion. This motion depends upon how the constituents interact with each other. The interaction terms are also considered constitutive relations since they describe how the materials behave with respect to each other. Hansen (1989) proposes equation (315)
\[ p_{\text{snow}} = C(w_{\text{snow}} - A w_{\text{wood}}) \]
\[ p_{\text{wood}} = -C(w_{\text{snow}} - A w_{\text{wood}}) \]  

which upon expansion becomes,

\[
\begin{bmatrix}
  p_{1s} \\
  p_{2s} \\
  p_{3s}
\end{bmatrix} =
\begin{bmatrix}
  C_{11} & C_{12} & C_{13} \\
  C_{21} & C_{22} & C_{23} \\
  C_{31} & C_{32} & C_{33}
\end{bmatrix}
\begin{bmatrix}
  w_{1s} \\
  w_{2s} \\
  w_{3s}
\end{bmatrix} -
\begin{bmatrix}
  A_{11} & A_{12} & A_{13} \\
  A_{21} & A_{22} & A_{23} \\
  A_{31} & A_{32} & A_{33}
\end{bmatrix}
\begin{bmatrix}
  w_{1w} \\
  w_{2w} \\
  w_{3w}
\end{bmatrix}
\]  

as a constitutive relation. This term is the right hand side of the balance of linear momentum equation which is not necessarily required to obey the principle of material frame indifference. Thus, the particular form of the two tensors occurring in equation (361) may be constructed without the principle of material frame indifference.

It is assumed that a snow-wood mixture constructed in the laboratory would be isotropic since the snow in a laboratory freezer does not have a temperature gradient like that found in a snow pack. A snow-wood mixture occurring in nature would be layered and would contain preferred directions due to metamorphism, Adams (1987).

As Hansen, Walker, and Donovan (1989) propose, the tensor \( C \) determines the distance from the current point at which the boundary effects occur. The tensor \( A \) determines the interaction between the different constituents. In lieu of extensive three dimensional testing we will here assume a more simplistic version of equation (362),

\[
\begin{bmatrix}
  p_{1s} \\
  p_{2s} \\
  p_{3s}
\end{bmatrix} =
\begin{bmatrix}
  C_{11} & C_{12} & C_{13} \\
  C_{21} & C_{22} & C_{23} \\
  C_{31} & C_{32} & C_{33}
\end{bmatrix}
\begin{bmatrix}
  w_{1s} - A_{11} w_{1w} - A_{12} w_{2w} - A_{13} w_{3w} \\
  w_{2s} - A_{21} w_{1w} - A_{22} w_{2w} - A_{23} w_{3w} \\
  w_{3s} - A_{31} w_{1w} - A_{32} w_{2w} - A_{33} w_{3w}
\end{bmatrix}
\]  

which by assuming isotropic behavior for both mechanisms we get,

\[
\begin{bmatrix}
  p_{1s} \\
  p_{2s} \\
  p_{3s}
\end{bmatrix} =
\begin{bmatrix}
  C_{11} & 0 & 0 \\
  0 & C_{22} & 0 \\
  0 & 0 & C_{33}
\end{bmatrix}
\begin{bmatrix}
  w_{1s} - A_{11} w_{1w} \\
  w_{2s} - A_{22} w_{2w} \\
  w_{3s} - A_{33} w_{3w}
\end{bmatrix}
\]  

(364)
Since we assume the snow has not had temperature metamorphism or temperature induced layering and that the wood is randomly and evenly distributed about the region this further reduces to,

\[
\begin{bmatrix}
  p_{1s} \\
  p_{2s} \\
  p_{3s}
\end{bmatrix}
= 
\begin{bmatrix}
  C(w_{1s} - Aw_{1w}) \\
  C(w_{2s} - Aw_{2w}) \\
  C(w_{3s} - Aw_{3w})
\end{bmatrix}
\]  

(365)

\[
\begin{bmatrix}
  p_{1w} \\
  p_{2w} \\
  p_{3w}
\end{bmatrix}
= 
\begin{bmatrix}
  -C(w_{1s} - Aw_{1w}) \\
  -C(w_{2s} - Aw_{2w}) \\
  -C(w_{3s} - Aw_{3w})
\end{bmatrix}
\]  

(366)

We are now left with finding the values for the following parameters, \(\psi_{i9}, K, A,\) and \(C\) subject to all of the above constraints, the balance equations, and the restrictions placed upon them from the first and second laws.

**Model for a 1-Dimension Example**

We begin by looking at equations (356) through (359) in a single dimension,

\[
\lambda_i = \tilde{\lambda}_{i0} \left( \frac{p}{p_i} \right) \left( \frac{L + h}{L + h \left( \frac{R}{L} \right)^2} \right)
\]  

(367)

\[
\mu_i = \tilde{\mu}_{i0} \left( \frac{p}{p_i} \right) \left( \frac{L + h}{L + h \left( \frac{R}{L} \right)^2} \right)
\]  

(368)
\[ \ddot{T}_{i11} = \frac{\partial w_{i1}}{\partial X_1} + 1 \left\{ (\lambda_i + 2\mu_i) \left[ \frac{\partial w_{i1}}{\partial X_1} + \frac{1}{2} \left( \frac{\partial w_{i1}}{\partial X_1} \right)^2 \right] \right. \\
\left. + \rho_i \sigma_{i0} (l_i - l_{iR}) + \rho_i \psi_i ((L - L_0) + (R - R_0) + (h - h_0) + (w_w - w_{w0})) \right\} \tag{369} \]

\[ \ddot{T}_{w11} = \frac{\partial w_{w1}}{\partial X_1} + 1 \left\{ (\lambda_w + 2\mu_w) \left[ \frac{\partial w_{w1}}{\partial X_1} + \frac{1}{2} \left( \frac{\partial w_{w1}}{\partial X_1} \right)^2 \right] \right. \\
\left. + \rho_w \sigma_{w0} (l_w - l_{wR}) \right\} \tag{370} \]

\[ \rho_i = \frac{\rho_{i0}}{\frac{\partial w_{i1}}{\partial X_1} + 1} \tag{371} \]

\[ \rho_w = \frac{\rho_{w0}}{\frac{\partial w_{w1}}{\partial X_1} + 1} \tag{372} \]

\[ \frac{\partial}{\partial X_1} \left( \frac{\partial w_{i1}}{\partial X_1} + 1 \right) \ddot{T}_{i11} = \frac{\partial w_{i1}}{\partial X_1} + 1 \left| C(w_{i1} - Aw_{w1}) \right| \tag{373} \]

\[ \frac{\partial}{\partial X_1} \left( \frac{\partial w_{w1}}{\partial X_1} + 1 \right) \ddot{T}_{w11} = - \frac{\partial w_{w1}}{\partial X_1} + 1 \left| C(w_{i1} - Aw_{w1}) \right| \tag{374} \]

\[ \dot{L} = - \frac{N_3 \pi \alpha}{4(\alpha - 1)} L (2R \dot{R} - \dot{R} h) \tag{375} \]

\[ \dot{R} = -vRA \left[ \frac{\ddot{T}}{\dot{R}} \right]^2 \frac{1}{2N_3} \left( \frac{R_0 - R}{N_3} \right) N_3 \tag{376} \]
\[ h = h\bar{A}\left[T_i\left(\frac{L}{R}\right)^2 \frac{1}{2N_3}\right] - \frac{(h_0 - h)}{N_3} \dot{N}_3 + \bar{C}\left(\frac{R}{L}\right)\dot{R} \]  
(377)

\[ r_w = -\nu r_w\bar{A}\left[T_w\left(\frac{L}{r_w}\right)^2 \frac{1}{2N_3^w}\right] \dot{r_w} + \left(\frac{r_w - r_{w0}}{N_3^w}\right)\dot{N}_3 + K(\sigma_w - \sigma_s) \]  
(378)

\[ N_3 = 43\rho_s^3 - 23\rho_s^2 + 4\rho_s + 2.2 \]  
(379)

\[ \dot{N}_3 = (129\rho_s^2 - 46\rho_s + 4)\dot{\rho}_s \]  
(380)

From the second law we must also consider the sign of the constant terms, \( \psi_{ij} \).

Considering equation (306) it must be of opposite sign of the term

\[ \frac{\partial \xi_{\alpha}}{\partial E_\alpha} = \frac{\partial \xi_{\alpha}}{\partial T_\alpha} \cdot \frac{\partial T_\alpha}{\partial E_\alpha} \]  
(381)

which from equations (369) through (378) we get,

\[ \frac{\partial T_\alpha}{\partial E_\alpha} = \rho_i \delta_{i\alpha}\left[\frac{\lambda_i}{\rho_i}I + \frac{2\mu_i}{\rho_i}\right] \geq 0 \]  
(382)

\[ \frac{\partial}{\partial T_i}(\dot{R}) = -3\nu R\bar{A}\left[T_i\left(\frac{L}{R}\right)^2 \frac{1}{2N_3}\right] \left(\frac{L}{R}\right)^2 \frac{1}{2N_3} \leq 0 \]  
(383)

\[ \frac{\partial}{\partial T_i}(h) = 3h\bar{A}\left[T_i\left(\frac{L}{R}\right)^2 \frac{1}{2N_3}\right] \left(\frac{L}{R}\right)^2 \frac{1}{2N_3} \geq 0 \]  
(384)

\[ \frac{\partial}{\partial T_w}(r_w) = -3\nu r_w\bar{A}\left[T_w\left(\frac{L}{r_w}\right)^2 \frac{1}{2N_3^w}\right] \left(\frac{L}{r_w}\right)^2 \frac{1}{2N_3^w} \leq 0 \]  
(385)

If \( h \leq \nu R \) then equation (381) will be negative thus,

\[ \psi_{ij} \geq 0 \]  
(386)
Identification of Model Coefficients

To determine the parameters necessary to complete the above model we need to look at the experiments that were completed to determine the relationship between stress and strain. Here we will simplify the above one dimensional model to try to determine the nature and values of the unknown parameters.

Laboratory experiments were performed to determine the stress and strain relationships for a series of snow and wood mixtures. Snow was collected from Grayling Pass near Yellowstone National Park. The samples were collected in boxes during the spring and brought to the laboratory which is kept at approximately \(-10^\circ\text{C}\). Typical grain sizes ranged from four to eight millimeters.

27 samples were constructed consisting of 10\% wood, 5\% wood, 2.5\% wood, and 100\% snow mixtures. Each sample was placed in a sonotube using a compaction process which included placing 3 layers in the tube; each layer was compacted by a 5.5 pound hammer which was dropped from a height of 12 inches, 25 times per layer. The sonotube was covered and the samples allowed to cure in the freezer for 27 days.

There were enough samples to enable testing at two displacement rates. There was a fast displacement rate which was one inch per second and a slower displacement rate which was 0.1 inch per second. The displacement rates correspond to Lagrangian strain rates of approximately 0.15 per second and 0.016 per second. While there were three samples of each configuration, not all of the samples were good samples after 27 days. The remaining samples were tested and used as data points.

An aluminum cylinder 15.5 centimeters tall with a radius of 9.6 centimeters was used to determine a stress-strain curve for the samples. The cylinder consisted of three shorter cylinders held together by small aluminum bars on the outside. This allowed for motion to occur in the lateral direction. Each sample was taken out of the sonotube and trimmed to
fit into the testing cylinder. It was placed upon an MTS testing machine platen supporting
the bottom. The top platen was placed within the testing cylinder with which the
compressive force was applied. The testing cylinder and the platens were contained within
an environmental chamber which was cooled with liquid nitrogen to the same temperature
as the freezer. A typical test with a very nonuniform displacement-load curve is shown in
Figure 8. The variations are due to the grain-bond structure changing as deformation takes
place. Of interest is the top region which approximates a linear relationship due to close
packing of grains and is more pronounced in samples with higher wood contents.

Figure 8. Typical Stress-Strain Diagram of a Snow-Wood Mixture.
The data was collected through a data acquisition computer which was then imported into Matlab for data analysis. The data consisted of the load, vertical displacement, and hoop displacement. The load and vertical displacement were gathered directly from the MTS machine. The hoop displacement was gathered from a strain gauge which returned false information due to the sudden interactions with liquid nitrogen, thus the hoop strain was not used. The data acquisition rate was on the order of 3000 data points per second or approximately 5000 data points for each sample.

Consider first equations (375) through (380). If we take and solve these ordinary differential equations using a Runge-Kutta solver within the normal ranges of the bond radius, grain radius, bond length, and bond radius upon the wood we find that the values vary from the initial condition as long as the stress remains constant. It appears that for large densities and short time frames, these values change slowly in relation to the time scale of the mechanism. This does not mean that they have less influence, since, if the coefficient $\psi_{ij}$ is extremely large, it will magnify these characteristics. It is also apparent that the surface energy term in equation (378) is sensitive and influences the overall behavior. For now we consider the other equations to determine order of magnitude estimates of some of the parameters.

If we consider the balance equations (373) and (374), the balance of linear momentum of the mixture constituents must sum to zero. By observing the right hand side we see that if the parameter $C = 1$ is selected it would satisfy the constraints for this simple case. While this may be too restrictive, let us use this to assist in determining the remaining parameters. Letting $C = 1$ we get

$$w_{i1} = A w_{w1}$$

which indicates the displacement of the two matrix constituents are related by a scalar function. Recall this may be a function of the internal state variables.
Next we consider equations (369) and (370). Here we will neglect the extent of reaction terms until we get a better idea of the coefficient to the internal state variable terms. Note that we have assumed no mass transfer between constituents. Recalling from earlier work that the sum of the constituent Cauchy stresses must total to the total Cauchy stress of the mixture we can determine the behavior of the two parameters $\psi_{i9}$ and $A$. from our experimental data. As can be seen in Figure 9, the value of $\psi_{i9}$ appears from analysis of the experimental data to be related to

$$\frac{\partial w_{i1}}{\partial X_1}$$

by some polynomial function.

Observing Figure 10 we see that the parameter $A$ has a significant influence on the value of $\psi_{i9}$. We should also note that equation (386) gave us the appropriate sign of the parameter. Upon analysis of the laboratory data we get the following relationship for $A$ and an as yet to be determined set of power terms $a$ and $b$ which would be determined by mixture makeup.

$$\psi_{i9} = -3.227 \times 10^{10} (A)^a \left( \frac{\partial w_{i1}}{\partial X_1} \right)^2 + 4.0244 \times 10^{10} (A)^b \left( \frac{\partial w_{i1}}{\partial X_1} \right) + 5.0 \times 10^7$$

(389)

Based upon the experimental data we have

$$0 < A \leq 1$$

(390)

$$a = 3$$

(391)

$$b = 0.3$$

(392)

for the types of material we are using.
This gives a relationship for $\psi_{19}$ if we know the value of $A$ and the power terms $a$ and $b$. Since the notion of mixture stress is crucial to this understanding we need to devise a method whereby the stress in the snow and the wood may be determined separately. Since we do not have a good method to date we must approximate the parameters based upon existing understanding and experimental evidence.
From equation (378) we have yet to find the coefficient $K$ which multiplies the difference in surface energies. Consider equations (375) through (378). In particular the last equation will have a stable point when we have among other relations,

$$-\nu r_w \tilde{A} \left[ T_w \left( \frac{L}{r_w} \right)^2 \frac{1}{2N_3^w} \right] + \frac{(r_w - r_{w0})_w}{N_3^w} \tilde{N}_3^w = -K(\sigma_w - \sigma_g) \quad (393)$$

at which point the mean number of bonds between the wood and snow will have reached equilibrium, thus we have at equilibrium.
so at long term equilibrium we will have a residual surface tension which will be nonzero and $K$ can be found as

$$K = \frac{\nu r_w A T_w \left(\frac{L}{r_w}\right)^2 \frac{1}{2N_3^w}}{(\sigma_w - \sigma_g)}_{\text{equilibrium}}$$

This is achieved by observing long time material phenomena of the bonds, grains, surface energies, and stresses. This can be done by conducting extensive surface analysis of the snow and wood mixture.

We have outlined the method which can be used to determine new parameters that arise when formulating the model using mixture theory. We have found the parameters $\psi_{ij}$, $K$, $A$, and $C$ using the conservation laws, first and second laws and associated restrictions, and experimental data. We could achieve much more detail by iterating the modeling process again using the newly formed relationships to establish different possible mathematical models from which we could compare with experimental data.

Consideration of Additional Variables and Higher Order Dimensions

The above analysis was made for a simplistic case. To more realistically develop the mathematical model for the wood-snow mixture we could include the water vapor. This would add more constitutive equations for the Helmholtz free energy, interactions terms, internal state variables, and material properties. This would make a much more complex set of equations which would require additional use of the restrictions developed in the previous chapter.
As can be seen from the equations above the model turns out to be highly nonlinear. Additional constitutive equations would create more nonlinear dependencies. The numerical solution to such problems becomes very difficult requiring fast efficient numerical algorithms and computational power.

We also simplified the problem by keeping the spatial dimension to one and simplifying many of the details with logical assumptions. As two and three dimensions are addressed, additional stress, strain, and other variable interactions with other coordinate axis must be considered. More dimensions will not have symmetry such as the one dimensional simplicities. Terms such as the stress and strain will be functionally integrated with the shear components. The linear momentum interactions would need to be reconsidered to see what changes the shear terms would make on the linear momentum interaction from the linear momentum equation.

Mixture theory has provided us with another tool which models these materials. It must be used in conjunction with the established procedures developed in mechanics to restrict and place a physical constriction on these approximating models.
CHAPTER 6

DISCUSSION

We introduced the combined form of the volume fraction mixture theory and internal state variables as a possible model to represent cohesive elastic-viscoplastic material. This included a development of the conservation of mass, conservation of linear momentum, conservation of angular momentum, first law of thermodynamics, and the second law of thermodynamics. We developed some expanded restrictions from the second law which yields additional constraints that the constitutive relations must obey.

With this procedure we were able to identify variables that were relevant to the solution and some that were not relevant. In other words, we found a reduced set of independent variables from which the constitutive relations could be constructed. This then gives us direction in establishing the necessary experiments to identify and determine those constitutive parameters.

We made some assumptions about the way the second law should be applied to mixtures. We used the idea that the mixture should as a whole obey the second law. This is based upon past experience and the advice of current researchers.

If we include more constituents the problem becomes more realistic but more difficult numerically. The computational power needed to solve the problems increases as the number of constituents increases. More complex mechanics arises when more spatial dimensions are considered. We saw that the simple one dimensional case gave a very nonlinear problem. This makes for a more complex parameter identification problem.
Future Research

It is apparent that the mathematical models that result from such a mixture of cohesive elastic-viscoplastic material is highly nonlinear. This causes many complications when a numerical solution is attempted. Some effort is required to identify the necessary mathematical and numerical algorithms to efficiently solve such systems. The algorithms need to be sensitive to time dependence. The evolution equations are time dependent. All time dependence is not necessarily of the same dimension. There are applications of the mixture theory where some variables occur at one time scale while others occur at orders of magnitude different time scales.

There is some ambiguity in the use and application of the second law when it comes to mixture theory. It was assumed the entropy production must increase for the whole mixture. This assumption was used in the development. This requirement needs to be shown and developed through rigorous mathematical proof. If each constituent can use its own second law a different development would result. This requirement should be investigated in the future.

This method of modeling a material with such complex behavior could be applied to living organisms such as regions of biofilm growth and decay. With the model allowing complex interactions and the demand for new and original parameter identification for the constituent equations, the model would provide a unique opportunity to visit some old assumptions regarding biofilm growth anew. The construction of such a model would require extensive experimental research to determine the respective parameters. The bulk material properties, interaction terms, and geometric dependencies need identification.
Conclusions

We have developed a methodology whereby new constitutive equations for newly represented materials may be constructed. This theory was built on the shoulders of many previous theories. The development centered upon the need to identify the necessary restrictions required by a rigorous application of the second law to mixture theory and internal state variables. This is used to assist in parameter identification.

A simple example of the use of this method was included. This shows how complex such solutions may become. It amplifies the need for research in nonlinear numerical methods, numerical methods for problems which contain time scales that are orders of magnitude different, and complex three dimensional spatial problems. With the increasing computational capabilities this will become more tractable in the near future.
REFERENCES CITED


