DERIVATION OF A SIMPLE POLYMER/SOLVENT SYSTEM VIA THE
HYBRID MIXTURE THEORETIC APPROACH

by

Tessa F. Weinstein

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Tessa F. Weinstein
has been approved
by

L.S. Bennethum

Tom Russell

William Briggs

Date
05/02/02
Weinstein, Tessa F. (M.S., Applied Mathematics)

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Thesis directed by Assistant Professor L.S. Bennethum

ABSTRACT

A two-scale theory involving swelling polymeric media is considered. Macromolecular relaxation of polymer chains is modeled by considering the solid phase as viscoelastic and the fluid as viscous. The mesoscopic averaging procedure is laid out in detail and the mesoscopic field equations for mass, momentum, energy and entropy balance are given. Constitutive theory is developed. Independent variables are chosen and constitutive restrictions are derived for a two-phase, multi-component system with negligible interfacial effects. Non-equilibrium, equilibrium, and near-equilibrium results are obtained. The system is simplified to a two-phase, single constituent per phase scenario. An experiment is proposed and relevant governing equations are given. Appropriate assumptions are made to reduce the system to one which is reasonably solvable.

This abstract accurately represents the content of the candidate's thesis. I recommend its publication.
Signed

L.S. Bennethum
DEDICATION

This thesis is dedicated to the memory of John Lord Knight. Without his support, encouragement, and kind heart this work would not have been possible.
ACKNOWLEDGMENT

I would like to thank my advisor, Lynn Bennethum, for her time, patience, and advice over the course of the last two years.
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1. Introduction and Overview of HMT

We develop a two-scale theory for swelling polymer systems, herein called the microscale and mesoscale. Swelling polymers exhibit a hierarchy of scales due to their complex porous structure. While the author recognizes that this is naturally a three scale problem, it is the belief of the author that a full understanding of the two-scale problem must be attained before the three-scale problem is considered.

In recent years polymers have become increasingly important in technological industries. Swelling polymers have a myriad of applications including but not limited to: construction, agriculture, drug delivery, and food stuffs. For ease of exposition we will restrict our discussion to drug delivery. While several useful drug delivery systems have been developed, most have been found by trial and error. Accurate mathematical models are needed to elucidate the mechanics of drug release and to suggest new alternatives to current methodologies. Drug delivery systems are usually classified as diffusion-, swelling-, or chemically-controlled systems. Of these, swelling-controlled systems are the least understood because of the complex interactions that occur during release [37].

In order to develop a model, a basic understanding of polymer terminology, characteristics, and behavior is needed. Although there is still some debate on the subject, polymers generally have molecular weights of 25,000 g/mol or larger, and increased chain length means increased entanglement of polymer chains. Monomers are the building blocks of polymers, e.g. amino acids or
sugars. *Monomers* link together with other molecules of the same or different type to form polymers. A *homopolymer* is made up of a single monomer, whereas a *copolymer* is made up of two or more types of monomers. A *repeating unit* is a segment of a macromolecule that forms the basic unit of the macromolecule (excluding the ends). In other words, we can form a complete polymer by linking an adequate number of repeating units together. A *linear polymer* is one in which every repeating unit is attached to exactly two others. A *branched polymer* is one in which repeating units are not linked exclusively in linear fashion. See Figure 1.1 for a schematic representation. A *network polymer* is formed by chemically linking together linear or branch polymers; this process is referred to as crosslinking. This same process is known as vulcanization for rubbers. See [39, 44, 47, 42].

Polymers can be broadly classified into two groups: *amorphous polymers*, which can be further classified as crosslinked or un-crosslinked, and *crystalline polymers*. Amorphous portions of a polymer are the areas of the polymer with long chain length where the polymer tends to coil about itself; this is known as entanglement. The entanglement of amorphous regions makes polymers flexible, and helps them hold together under stress. Unvulcanized natural rubber is an example of an un-crosslinked amorphous polymer. Vulcanization of natural
rubber introduces covalent sulfur bonds so that the chains are chemically bonded to one another. Crystalline polymers exhibit a crystalline structure, however, most of them contain regions of amorphous material. Because of the complicated nature of crystalline polymers, the model developed herein would need to be extended. Thus, we restrict our discussion to polymers of the amorphous type, [17].

Different polymers exhibit a whole spectrum of behavior dependent on various properties such as degree of cross-linking, crystallinity, and surrounding temperature. In particular, some polymers are so highly sensitive to temperature that certain properties change almost discontinuously at a temperature, \( T_g \), called the glass transition temperature, [17]. Such polymers are called thermosets. Below the glass transition temperature, \( T_g \), polymers are solid, hard, even brittle and are considered to be in the glassy state. Amorphous polymers in the glassy state are sometimes called amorphous liquids or supercooled liquids. It is well known that amorphous polymers below \( T_g \) are not in thermodynamic equilibrium; they still flow, but the time scale for observing creep and flow is very long. Above \( T_g \) polymers enter the glassy transition, where the polymer softens. As the temperature increases polymers will enter a rubbery plateau, rubbery flow state, and finally a viscous flow state [42]. Diffusion properties of a polymer will change drastically as the polymer nears \( T_g \) [30].

Figure 1.2 gives a schematic representation of the problem being considered at various scales. At the microscale we can distinguish between the solid matrix of the polymer and the fluid (or solvent); this is on the order of microns. At the mesoscale the solid and fluid appear as a mixture; this is represented by the
mesoscale polymer. Figure 1.2 also depicts the the polymer particle immersed in a bulk fluid. Inclusion of the bulk fluid in our model would constitute a third scale, which would be considered the macroscale, and is not considered here.

Traditional models of drug delivery systems begin with a concentration form of Fick’s law of diffusion. Depending on the type of system modeled and geometry, Fick’s law is modified accordingly. For example, the diffusion coefficient can be modified by considering it as the mutual diffusion of the drug in the polymer, the diffusion of the drug alone, or concentration dependent. The primary problem with these models is that they are of limited applicability since they only apply to Fickian diffusion phenomena [37]. It is well known that non-Fickian diffusion occurs when polymers enter the glass-rubber transition [30]. Various authors have expanded the Fickian model to account for anomalous behavior, but these extensions are largely heuristic [37]. A variation on the traditional approach is to treat coefficients of Fick’s and Darcy’s law as stochastic processes using the Karhunen-Loeve expansion, [22]. However, this increases the dimension of the problem by treating the random aspect of the problem as a new dimension and it is not entirely clear how the resulting coefficients relate back to the physical problem. Lustig et al. [30], address the problem using continuum thermodynamics. However, they do not have a variable that directly accounts for the moisture content of the polymer. Low [29] found that the swelling pressure in smectitic clays (specifically montmorillonite), is highly dependent on moisture content. We find it reasonable to assume that the same will be true of the swelling of polymers. Hybrid mixture theory (HMT) has recently been applied to polymeric and biopolymeric systems by Singh et al.
Figure 1.2: Scales of Observation
Hybrid mixture theory has all of the advantages of classical mixture theory plus the added advantage that mesoscale variables can be directly related to microscale counterparts. This last method is the context in which our model is systematically developed.

Hassanizadeh and Gray developed hybrid mixture theory (HMT) in a series of papers, [24, 25, 26] aimed at single phase flow in granular media. In [24] the microscopic field equations are averaged once to obtain mesoscale analogues. Bowen's continuum theory of mixtures is then applied to obtain constitutive relationships [14, 15, 16]. Bowen uses the classical mixture theory framework and exploits of the entropy inequality in the sense of Coleman and Noll, [18], then linearizes about variables becoming zero at equilibrium to obtain constitutive relationships at the larger scale. Hassanizadeh further extended the theory to include a multi-component fluid phase in a granular material and obtained generalized forms of Darcy's and Fick's laws [27, 28]. Later, Gray and Hassanizadeh applied HMT to a system with three single constituent phases and included interfacial effects.

Some of the aforementioned papers contained the incorrect result that, at equilibrium, the chemical potential of two phases are equal to each other. This contradicts the classical thermodynamic result that, at equilibrium, the chemical potential of a single constituent in two phases is equal. In 1994, Achanta et al. correctly employed HMT with the additional axiom of equipresence [2], which requires that before exploiting the entropy inequality it is assumed that each phase is composed of the same $N$ constituents. Only after the entropy inequality has been exploited can the concentration of certain constituents be set to
zero. In [2], the authors derive the macroscale field equations for each phase and interface of a three-phase, multi-constituent media.

From 1994 to present HMT has been successfully employed to model swelling and shrinking behavior in gels, food stuffs, and colloidal systems where phase interactions play an important roll in the mesoscopic and macroscopic behavior, [3, 6, 7, 10, 33, 34, 35, 36]. All of these works assumed an elastic solid phase at the microscale. Thus, they are applicable to systems exhibiting macroscopic viscoelastic behavior, but not to systems in which viscoelastic behavior is observed in much smaller scales, such as the solid phase of polymers. In [41], Singh et al. propose a constitutive theory to model a two-phase polymeric system with a viscoelastic solid phase, a viscous fluid phase, and obtain novel forms of Darcy's and Fick's laws.

Despite the clear progress that has been made with the application of HMT to the study of polymers it is the opinion of the author that no one has yet correctly simplified the problems of diffusion and absorption of a solvent to a satisfactory degree. These systems are simply too complicated to solve numerically. It is the aim of this work to reduce the latter problem to one that is both tractable and comparable with current literature in polymer science.

In Chapter 2 we give the microscale governing equations, review the averaging procedure, give the definitions of mesoscale quantities in terms of their microscale counterparts, and give a detailed derivation of all of the mesoscale field equations (mass, momentum, etc.). In Chapter 3 we discuss the simplifying assumptions and constitution of the system being modeled. We obtain an entropy inequality that is valid for systems with a visco-elastic solid phase and viscous
liquid phase, then obtain non-equilibrium, equilibrium, and near-equilibrium results for that system, as well as a generalized Darcy’s law. In Chapter 4, we reduce the entropy inequality previously obtained for a two-phase system composed of a single constituent per phase. Again, we obtain non-equilibrium, equilibrium, near-equilibrium results, and a generalized Darcy’s law. We then derive a system of equations that we believe is tractable. Finally, in Chapter 5 we discuss avenues for further research both with this model, and more sophisticated ones.
2. Microscale Averaging and the Governing Field Equations

The purpose of this section is to lay out in detail the averaging procedure used in HMT for any two-scale, multi-constituent, multi-phase material. The two scales are herein called the microscale and mesoscale. At the microscale one can distinguish between phases. It is at this scale that the field equations (mass, momentum, etc.) are known to hold and properties such as density, velocity, and mass are clearly defined. The mesoscale is order of magnitudes larger than the microscale. At the mesoscale one can no longer distinguish between individual phases. Because an averaging process is performed to obtain an analogue on this larger scale, properties such as density and velocity are now viewed as somewhat blurred. Herein we develop one such technique.

Before continuing we need to mention a few basic underlying assumptions. First, we assume that the material we are modeling has negligible interfacial effects. That is, the interface has no thermodynamic properties and is massless. Thus, no constituent present gains or loses mass, momentum, or energy when crossing an interface. This will place special restrictions on each of the field equations and will be discussed in further detail in subsequent sections. Second, the material we are modeling has a representative elementary volume (REV); that is, a volume for which averaged properties will remain the same if the REV is made slightly larger or smaller. In addition we require that the REV size and shape remain the same for all space and time. Such an REV does not exist if the material under question is too heterogeneous. For a more detailed discussion of
the existence of such an REV see [5, 19]. It is important to remember that for the current discussion, the following theory is applicable to any material meeting these requirements.

2.1 Microscale Governing Equation

Each phase is denoted by small Greek letters (α, β, γ), and species (or constituents) are denoted by j, j = 1, . . . , N. For the purposes of simplicity and brevity we assume that all interfaces are massless and have no thermodynamic properties. Interfacial effects can be included by following the approach provided by [23].

Additionally, we assume that there are no internal surface discontinuities, meaning that each phase is the union of several isolated simply connected volumes, [24]. Using the notation of Eringen, [21], the constituent, microscopic field equations for a given phase, α, can be stated as

$$\frac{\partial}{\partial t}(\rho^j \psi^j) + \nabla \cdot (\rho^j \mathbf{v}^j \psi^j) - \nabla \cdot \mathbf{i}^j - \rho^j f^j = \rho^j G^j + \rho^j \ddot{\psi}^j$$  \hspace{1cm} (2.1)

where \(\rho^j\) is the mass density, \(\psi^j\) is the mass average (over the phase) thermodynamic property of constituent \(j\), \(\mathbf{v}^j\) is the mass average velocity vector, \(\mathbf{i}^j\) is the flux vector, \(f^j\) is the body source, \(G^j\) is the net production, and \(\ddot{\psi}^j\) accounts for the influx of \(\dot{\psi}\) from all other constituents (e.g. due to chemical reactions). If the medium consists of only one constituent then \(\ddot{\psi}^j\) is equal to zero. This equation holds on the microscale for mass, linear and angular momentum, energy, and entropy. Table 2.1 lists the quantities used for each field equation.

In Table 2.1, \(\mathbf{t}\) is the second-order stress tensor, \(\mathbf{g}\) is the external supply of momentum (gravity), \(\mathbf{r}\) is the position vector referenced to a fixed coordinate
Table 2.1: Quantities for Microscopic Field Equations

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$\psi$</th>
<th>$i$</th>
<th>$f$</th>
<th>$\hat{\psi}$</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>$\vec{r}$</td>
<td>0</td>
</tr>
<tr>
<td>Linear Momentum</td>
<td>$v$</td>
<td>$t$</td>
<td>$g$</td>
<td>$\vec{i} + \vec{r}v$</td>
<td>0</td>
</tr>
<tr>
<td>Angular Momentum</td>
<td>$r \times v$</td>
<td>$r \times t$</td>
<td>$r \times g$</td>
<td>$r \times (\vec{i} + \vec{r}v) - \vec{m}$</td>
<td>0</td>
</tr>
<tr>
<td>Energy</td>
<td>$e + \frac{1}{2}v^2$</td>
<td>$t \cdot v + q$</td>
<td>$g \cdot v + h$</td>
<td>$\vec{Q} + \vec{i} \cdot v + \vec{r}(e + \frac{1}{2}v^2)$</td>
<td>0</td>
</tr>
<tr>
<td>Entropy</td>
<td>$\eta$</td>
<td>$\phi$</td>
<td>$b$</td>
<td>$\vec{\eta} + \vec{r}v$</td>
<td>$\Lambda$</td>
</tr>
</tbody>
</table>

system, $e$ is the internal energy density function, $h$ is the external supply of energy, $q$ is the heat flux, $\eta$ is the entropy density, $\phi$ is the entropy flux, $b$ is the external supply of entropy, and $\Lambda$ is the entropy production.

2.2 Averaging Procedure

The averaging procedure used in HMT is based on works of various authors and was developed at approximately the same time [4, 32, 45, 46]. While many different methods are available [19], we choose to use the one which is computationally the simplest where field equations are averaged via weighted integration. Here we use the indicator function of the $\alpha$-phase as the weight, and treat the averaged quantities resulting from the weighted integration as distributions. This allows us to bypass the difficulties of defining the derivative of averaged quantities that result from the weighted integration [40, 38]. Additionally, the weighting function used here may result in averaged quantities that do not correspond to physical quantities measured. This problem can be overcome by choosing a weighting function that represents the experimental apparatus used to measure physical properties [19].
Let $\delta V$ denote the REV, $\delta V_\alpha$ denote the portion of the $\alpha$-phase within $\delta V$, and $\delta A_{\alpha\beta}$ denote the portion of the $\alpha\beta$ interface within $\delta V$. It is assumed that $\delta V_\alpha$ and $\delta A_{\alpha\beta}$ are isolated simply connected regions. Express the magnitude of $\delta V$ by $|\delta V|$, then the volume fraction can be written as
\[
\varepsilon^\alpha(x, t) = \frac{|\delta V_\alpha|}{|\delta V|},
\]
so that
\[
\sum_\alpha \varepsilon^\alpha = 1.
\]
Letting $r$ and $x$ denote the position vector and the centroid of the REV, respectively, $r$ can be written
\[
r = x + \xi,
\]
where $\xi$ is the local coordinate referenced to the centroid of the REV and varies over all of $\delta V$. The indicator function for the $\alpha$-phase is given by
\[
\gamma_\alpha(r, t) = \begin{cases} 
1 & \text{if } r \in \delta V_\alpha \\
0 & \text{if } r \in \delta V_\beta, \quad \beta \neq \alpha.
\end{cases}
\]
Then
\[
|\delta V_\alpha|(x, t) = \int_{\delta V} \gamma_\alpha(x + \xi, t) \, dv(\xi)
\]
represents the magnitude of the volume $\delta V$ in the $\alpha$-phase. Following Hassanizadeh and Gray [24], we make the following definitions:
\[
\bar{\rho}^\alpha(x, t) = \frac{1}{|\delta V_\alpha|} \int_{\delta V} \rho^\beta(r, t) \gamma_\alpha(r, t) \, dv(\xi)
\]
is the average mass over $|\delta V_\alpha|$, 
\[
\langle \psi^\beta \rangle(x, t) = \frac{1}{|\delta V_\alpha|} \int_{\delta V} \psi^\beta(r, t) \gamma_\alpha(r, t) \, dv(\xi)
\]
is the volume average property of $\psi^j$, and
\[
\overline{\psi^j}_\alpha(x, t) = \frac{1}{\rho^\alpha_{\delta V}} \int_{\delta V} \rho^j(r, t) \psi^j(r, t) \gamma_\alpha(r, t) \, d\nu(\xi) \quad (2.8)
\]
is the mass average property of $\psi^j$. We would like the mesoscale field equations to be the analogues of the microscale field equations. To ensure this we will apply the following theorem that allows us to interchange the order of differentiation and integration. This result is due to Cushman [20].

**Theorem 2.1** If $w^{\alpha\beta}$ is the microscopic velocity of the interface $\alpha\beta$ and $n^\alpha$ is the outward unit normal vector of $\partial V_\alpha$ indicating the integrand should be evaluated in the limit as the $\alpha\beta$-interface is approached from the $\alpha$-side then
\[
\frac{1}{|\delta V|} \int_{\delta V} \frac{\partial f}{\partial t} \gamma_\alpha d\nu(\xi) = \frac{\partial}{\partial t} \left[ \frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha d\nu(\xi) \right] - \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta V} f w^{\alpha\beta} \cdot n^\alpha da(\xi) \quad (2.9)
\]
\[
\frac{1}{|\delta V|} \int_{\delta V} \nabla f \gamma_\alpha d\nu(\xi) = \nabla \left[ \frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha d\nu(\xi) \right] + \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta V} f n^\alpha da(\xi) \quad (2.10)
\]

We now have everything we need to average equation (2.1) from the microscale to the mesoscale. We begin with the conservation of mass, then linear momentum, angular momentum, energy, and lastly entropy. Corresponding bulk equations are derived for each field equation and restrictions that result from the assumption that the interface has negligible thermodynamic properties are given.
2.3 Mesoscale Field Equations

2.3.1 Conservation of Mass

Substituting the appropriate quantities from Table 2.1 into equation (2.1) the conservation of mass at the microscale is

\[ \frac{\partial}{\partial t}(\rho^j) + \nabla \cdot (\rho^j \mathbf{v}^j) = \rho^j \dot{\mathbf{r}}^j. \]  

(2.11)

Formally, we multiply by the indicator function, integrate over the mesoscopic REV, and divide by the magnitude of the REV, |δV|. Using Theorem 2.1, relationships (2.6)-(2.8), and substituting back into equation (2.11), we have

\[ \frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha) + \nabla \cdot (\varepsilon^\alpha \rho^\alpha \mathbf{w}^\alpha) = \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta V} \rho^j (\mathbf{w}^{\alpha\beta^j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha d\alpha + \varepsilon^\alpha \rho^\alpha \dddot{\mathbf{r}}^\alpha. \]  

(2.12)

Now, using \( \frac{D^\alpha_j}{Dt} \), the material time derivative, which is given by

\[ \frac{D^\alpha_j}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^\alpha j \cdot \nabla, \]  

(2.13)

we obtain the mesoscopic mass balance for constituent \( j \) in phase \( \alpha \)

\[ \frac{D^\alpha_j}{Dt}(\varepsilon^\alpha \rho^\alpha) + \varepsilon^\alpha \rho^\alpha (\nabla \cdot \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} \dot{\mathbf{c}}_{\beta^j}^\alpha + \dddot{\mathbf{r}}^\alpha. \]  

(2.14)

In the equations above, \( \mathbf{v}^j \) is the microscopic velocity of constituent \( j \), \( \mathbf{w}^{\alpha\beta^j} \) is the velocity of the \( j^{th} \) constituent in the \( \alpha\beta \) interface, and \( \mathbf{n}^\alpha \) is the outward unit normal vector of \( \delta V_\alpha \). Complete nomenclature is given in Appendix A. Our motivation in defining the mesoscopic variables is twofold. First, we would like the mesoscopic variables to coincide with actual physical variables that can be measured via mesoscale experiments. Second, we would like the definition of the
mesoscopic variables to be as consistent as possible with their microscale counterparts. Unless otherwise stated, the mesoscopic variables have the following definitions:

\[ \rho^{\alpha j} \equiv \bar{\rho}^{\alpha j} \quad (2.15) \]

is the average mass over \( \delta V_a \),

\[ \mathbf{v}^{\alpha j} \equiv \bar{\mathbf{v}}^{\alpha j} \quad (2.16) \]

is the mass averaged velocity,

\[ \bar{\mathbf{c}}_{(\beta)}^{\alpha j} \equiv \sum_{\beta \neq \alpha} \frac{\varepsilon^{\alpha}}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{u}^{\alpha \beta j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha \, da \quad (2.17) \]

is the net rate of mass gained by constituent \( j \) in phase \( \alpha \) from phase \( \beta \), and

\[ \bar{\mathbf{r}}^{\alpha j} \equiv \varepsilon^{\alpha} \rho^{\alpha j} \bar{\mathbf{r}}^\alpha \quad (2.18) \]

is the rate of mass gain due to interaction with other species within the same phase.

Bulk phase variable definitions are not always intuitive and are defined so as to preserve the form and interpretation of the mesoscale equations. To obtain the bulk phase counterpart for the conservation of mass we make the following definitions:

\[ \rho^\alpha \equiv \sum_{j=1}^{N} \rho^{\alpha j} \quad (2.19) \]

is the mass density of phase \( \alpha \), and

\[ C^{\alpha j} \equiv \frac{\rho^{\alpha j}}{\rho^\alpha} \quad (2.20) \]
is the concentration of the $j^{th}$ constituent in the $\alpha$-phase. All other definitions of bulk phase variables are given in Appendix B. Using equations (2.19) and (2.20) in equation (2.12) we have:

$$\frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha C^{\alpha j}) + \nabla \cdot (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j}) = \sum_{\beta \neq \alpha} \tilde{\varepsilon}^\beta_j + \tilde{\tau}^{\alpha j}. \quad (2.21)$$

Summing over $j = 1, \ldots, N$ we obtain:

$$\frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha) + \nabla (\varepsilon^\alpha \rho^\alpha \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} \tilde{\varepsilon}^\beta. \quad (2.22)$$

Defining $\frac{D^\alpha}{Dt}$ as $\frac{\partial}{\partial t} + \mathbf{v}^\alpha \cdot \nabla$, we obtain the bulk phase counterpart for the conservation of mass,

$$\frac{D^\alpha(\varepsilon^\alpha \rho^\alpha)}{Dt} + \varepsilon^\alpha \rho^\alpha (\nabla \cdot \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} \tilde{\varepsilon}^\beta, \quad (2.23)$$

where the following restrictions apply:

$$\sum_{j=1}^{N} \tilde{\tau}^{\alpha j} = 0 \quad \forall \alpha \text{ and } \quad \tilde{\varepsilon}^\beta_j + \tilde{\varepsilon}^\alpha_j = 0 \quad j = 1, \ldots, N. \quad (2.24)$$

The meaning of equation (2.24) is that the gain of mass of the bulk phase due to chemical reactions alone must be zero. Equation (2.25) says that the rate of mass gained by phase $\alpha$ from phase $\beta$ is equal to the rate of mass gained by phase $\beta$ from phase $\alpha$, i.e. no mass is lost in the interface.

### 2.3.2 Conservation of Linear Momentum

Substituting the appropriate quantities from Table 2.1 into equation (2.1) the conservation of linear momentum at the microscale is

$$\frac{\partial}{\partial t}(\rho^j \mathbf{v}^j) + \nabla \cdot (\rho^j \mathbf{v}^j \mathbf{v}^j) - \nabla \cdot \mathbf{t}^j - \rho^j \mathbf{g}^j = \rho^j \ddot{\mathbf{t}}^j + \rho^j \tilde{\tau}^j \mathbf{v}^j. \quad (2.26)$$
Using the same method as for the conservation of mass equation we obtain:

\[
\frac{\partial}{\partial t} \left( \varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \right) - \nabla \cdot \left( \varepsilon^\alpha \left( (\mathbf{t}^j)^\alpha + \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j} - \rho^{\alpha j} \overline{\mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j}} \right) \right) \\
+ \nabla \cdot \left( \varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j} \right) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{g}^{\alpha j} \\
= \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta A_{\alpha \beta}} \left[ \mathbf{t}^j + \rho^j \mathbf{v}^j \left( \mathbf{w}^{\alpha \beta j} - \mathbf{v}^j \right) \right] \cdot \mathbf{n}^\alpha \, da \\
+ \varepsilon^\alpha \rho^{\alpha j} \left( \overline{\mathbf{t}^\alpha} + \overline{\mathbf{r}^j \mathbf{v}^j} \right), \tag{2.27}
\]

where \( \mathbf{g}^{\alpha j} \equiv \overline{\mathbf{g}^\alpha} \) is the mass average external supply of momentum and all other variables retain the meaning they were given in the previous section. Additionally, we define the mesoscopic stress tensor, also known as the Cauchy stress tensor, as:

\[
\mathbf{t}^{\alpha j} \equiv (\mathbf{t}^j)^\alpha + \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j} - \rho^{\alpha j} \overline{\mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j}}. \tag{2.28}
\]

Now, subtract \( \mathbf{v}^{\alpha j} \) times equation (2.12) from equation (2.27) to obtain

\[
\varepsilon^\alpha \rho^{\alpha j} \frac{\partial}{\partial t} (\mathbf{v}^{\alpha j}) + \varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \nabla \cdot (\mathbf{v}^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{g}^{\alpha j} \\
= \sum_{\beta \neq \alpha} \left[ \frac{1}{|\delta V|} \int_{\delta A_{\alpha \beta}} \left[ \mathbf{t}^j + \rho^j \mathbf{v}^j \left( \mathbf{w}^{\alpha \beta j} - \mathbf{v}^j \right) \right] \cdot \mathbf{n}^\alpha \, da \\
- \frac{\mathbf{v}^{\alpha j}}{|\delta V|} \int_{\delta A_{\alpha \beta}} \rho^j \left( \mathbf{w}^{\alpha \beta j} - \mathbf{v}^j \right) \cdot \mathbf{n}^\alpha \, da \right] \\
+ \varepsilon^\alpha \rho^{\alpha j} \left( \overline{\mathbf{t}^\alpha} - \overline{\mathbf{r}^j \mathbf{v}^j} \right) - \mathbf{v}^{\alpha j} \overline{\mathbf{r}^{\alpha j}}. \tag{2.29}
\]

Using (2.13) we obtain the mesoscopic linear momentum balance for constituent \( j \) in the \( \alpha \)-phase:

\[
\varepsilon^\alpha \rho^{\alpha j} \frac{D^{\alpha j}}{Dt} (\mathbf{v}^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{g}^{\alpha j} = \overline{\mathbf{t}^{\alpha j}} + \sum_{\beta \neq \alpha} \overline{\mathbf{T}^{\alpha j}} \beta, \tag{2.30}
\]
where we have made the following definitions:

\[
\hat{T}_{\beta}^{\alpha j} \equiv \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[ \mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha\beta j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, da \\
- \mathbf{v}^{\alpha j} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}^{\alpha\beta j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha \, da
\]

(2.31)

represents the effect constituent \( j \) of phase \( \beta \) has on the rate of change of mechanical momentum of the same constituent in phase \( \alpha \), and

\[
\hat{\mathbf{t}}^{\alpha j} \equiv \varepsilon^\alpha \rho^j \left( \frac{\mathbf{t}^\alpha}{t^\alpha} + \frac{\mathbf{v}^j}{v^j} - \mathbf{v}^{\alpha j} \mathbf{v}^j \right) \]

(2.32)

is an exchange term that takes into account all gain of momenta due to the presence of other species but not due to chemical reactions.

Again, we would like to obtain the bulk phase counterpart. Beginning with equation (2.27) and using (2.20) we have

\[
\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha (\mathbf{t}^{\alpha j} - \rho^\alpha \mathbf{v}^{\alpha j,\alpha} \cdot \mathbf{v}^{\alpha j,\alpha})) - \varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{g}^{\alpha j} \\
+ 2 \nabla (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j} \cdot \mathbf{v}^\alpha) - \nabla (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha) \\
= \sum_{\beta \neq \alpha} \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[ \mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha\beta j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, da \\
+ \varepsilon^\alpha \rho^\alpha \left( \hat{\mathbf{t}}^\alpha + \hat{\mathbf{r}}^\alpha \mathbf{v}^j \right).
\]

(2.33)

Subtracting \( \mathbf{v}^\alpha \) times equation (2.21) we get

\[
\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j}) - \mathbf{v}^\alpha \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^\alpha C^{\alpha j}) \\
- \nabla \cdot (\varepsilon^\alpha (\mathbf{t}^{\alpha j} - \rho^\alpha \mathbf{v}^{\alpha j,\alpha} \cdot \mathbf{v}^{\alpha j,\alpha})) \\
- \varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{g}^{\alpha j} + \nabla (2\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j} \cdot \mathbf{v}^\alpha) \\
- \nabla (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha) - \mathbf{v}^\alpha \nabla \cdot (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j}) \\
= \sum_{\beta \neq \alpha} \hat{T}_{\beta}^{\alpha j} + \sum_{\beta \neq \alpha} \frac{\varepsilon^\alpha}{\rho^\alpha} \mathbf{v}^{\alpha j} + \hat{\mathbf{t}}^{\alpha j} + \hat{\mathbf{r}}^{\alpha j} \mathbf{v}^{\alpha j} - \sum_{\beta \neq \alpha} \varepsilon^\alpha \mathbf{v}^{\alpha j} - \hat{\mathbf{r}}^{\alpha j} \mathbf{v}^\alpha. \tag{2.35}
\]
Summing from $j = 1, \ldots, N$ we obtain
\[ \varepsilon^\alpha \rho^\alpha \frac{D^\alpha v^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha t^\alpha) - \varepsilon^\alpha \rho^\alpha g^\alpha = \sum_{\beta \neq \alpha} \hat{T}^\alpha_{\beta}, \]  
(2.36)

where the following restrictions apply:
\[ \sum_{j=1}^{N} (\hat{T}^\alpha_{\beta} + \hat{\psi}^\alpha_{\beta}) = 0 \quad \forall \alpha \]  
(2.37)
\[ \hat{T}^\alpha_{\beta} + v^\alpha_{\beta} \hat{\psi}^\alpha_{\beta} + \hat{T}^\beta_{\alpha} + v^\beta_{\alpha} \hat{\psi}^\beta_{\alpha} = 0 \quad j = 1, \ldots, N. \]  
(2.38)

Equation (2.37) says that linear momentum can only be lost due to interactions with other phases. Equation (2.38) says that the interface can hold no linear momentum.

2.3.3 General Case

Equation (2.1) is the constituent, microscopic general field equation. We will find it useful to average this equation up to the mesoscale. The details of the averaging are much the same as they are for the conservation of linear momentum, so we will not repeat them here. Let us just say that the general case, after averaging from the microscale to the mesoscale, can be written as
\[ \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^\alpha \psi^\alpha) - \nabla \cdot (\varepsilon^\alpha (\psi^\alpha + \rho^\alpha \psi^\alpha - \rho^\alpha \psi^\alpha)) \]
\[ + \nabla \cdot (\varepsilon^\alpha \rho^\alpha \psi^\alpha) - \varepsilon^\alpha \rho^\alpha \overline{\psi}^\alpha \]
\[ = \sum_{\beta \neq \alpha} \varepsilon^\alpha \left[ \int_{\partial V_\alpha} \left[ \int_{\delta A_{\alpha\beta}} (\psi^\alpha \psi^\beta - \psi^\beta \psi^\alpha) \cdot n^\alpha \right. \right. \right. \]
\[ \left. \left. \left. + \varepsilon^\alpha \overline{\psi}^\alpha \right] \right] \]
\[ + \varepsilon^\alpha \rho^\alpha \overline{G}^\alpha - \varepsilon^\alpha \rho^\alpha \overline{\psi}^\alpha. \]  
(2.39)
We will find it convenient to substitute the quantities from Table 2.1 directly into equation (2.39) as the averaging procedure has already been performed.

2.3.4 Conservation of Angular Momentum

Conservation of angular momentum is probably the most difficult field equation to upscale simply because the calculations are tedious. Thus, we will go into more detail in this section than in others so that the reader may more easily reproduce these results. We begin by substituting the appropriate terms for the conservation of angular momentum from Table 2.1 into equation (2.39) and obtain

\[
\frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha \mathbf{r} \times \mathbf{v}_j^\alpha) + \nabla \cdot \left(\varepsilon^\alpha \rho^\alpha \mathbf{v}_j^\alpha \mathbf{r} \times \mathbf{v}_j^\alpha\right) - \nabla \cdot \left(\varepsilon^\alpha \left(\mathbf{r} \times \mathbf{t}_j^\alpha\right)\right)
\]

\[
+ \varepsilon^\alpha \rho^\alpha \mathbf{v}_j^\alpha \mathbf{r} \times \mathbf{v}_j^\alpha - \varepsilon^\alpha \rho^\alpha \mathbf{v}_j^\alpha \mathbf{r} \times \mathbf{v}_j^\alpha - \varepsilon^\alpha \rho^\alpha \mathbf{r} \times \mathbf{g}_j^\alpha
\]

\[
= \sum_{\beta \neq \alpha} \left[\frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[\mathbf{r} \times \mathbf{t}_j + \rho_j (\mathbf{r} \times \mathbf{v}_j) (\mathbf{w}^{\alpha\beta}_j - \mathbf{v}_j)\right] \cdot \mathbf{n}^\alpha \, da\right]
\]

\[
\pm \sum_{\beta \neq \alpha} \frac{\varepsilon^\alpha \rho^\alpha \mathbf{r} \times \mathbf{v}_j^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho_j (\mathbf{w}^{\alpha\beta}_j - \mathbf{v}_j) \cdot \mathbf{n}^\alpha \, da
\]

\[
+ \varepsilon^\alpha \rho^\alpha \mathbf{r} \times (\mathbf{l}_j + \mathbf{r}_j) - \varepsilon^\alpha \rho^\alpha \mathbf{g}_j^\alpha.
\]

The result (2.40)

Next we subtract \(\sigma\) crossed with equation (2.27) (the conservation of linear momentum at the microscale), where \(\sigma\) is the macroscale field variable. To do this we will need several identities:

\[
\mathbf{r} \times \mathbf{v}_j^\alpha = \mathbf{x} \times \mathbf{v}_j^\alpha + \xi \times \mathbf{v}_j^\alpha,
\]

\[
\mathbf{v}_j^\alpha \mathbf{r} \times \mathbf{v}_j^\alpha = \mathbf{x} \times \mathbf{v}_j^\alpha \mathbf{v}_j^\alpha + \mathbf{v}_j \xi \times \mathbf{v}_j^\alpha, \text{ and}
\]

\[
\mathbf{r} \times \mathbf{g}_j^\alpha = \mathbf{x} \times \mathbf{g}_j^\alpha + \xi \times \mathbf{g}_j^\alpha.
\]
among others similar to these. These identities can be verified by combining (2.4) with the fact that (2.6) - (2.8) are integrals with respect to $\xi$ only, and not with respect to $x$. Starting with the left hand side, for the $\frac{\partial}{\partial t}$ terms we have

$$
\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} x \times v^{\alpha j}) + \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} \xi \times v^{\alpha j}) - x \times \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} v^{\alpha j}) = \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} \xi \times v^{\alpha j}).
$$

(2.41)

For the $\nabla \cdot$ terms we have:

$$
\nabla \cdot \left[ \varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} x \times v^{\alpha j} + \varepsilon^\alpha \rho^{\alpha j} \xi \times v^{\alpha j} - \varepsilon^\alpha x \times (t^j)^\alpha 
- \varepsilon^\alpha \{x \times (t^j)^\alpha \} - \varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} \xi \times v^{\alpha j}
+ \varepsilon^\alpha \rho^{\alpha j} x \times (v^j)^\alpha
+ \varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} \xi \times v^{\alpha j}
+ x \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} v^{\alpha j} - \varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} v^{\alpha j} - \varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} v^{\alpha j})
= \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} x \times v^{\alpha j}) - x \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} v^{\alpha j})
- \nabla \cdot (\varepsilon^\alpha x \times (t^j)^\alpha) + x \times \nabla \cdot (\varepsilon^\alpha (t^j)^\alpha) - \nabla \cdot (\varepsilon^\alpha \{x \times t^j\}^\alpha)
- \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} \xi \times v^{\alpha j}) + x \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} v^{\alpha j})
+ \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} x \times (v^j)^\alpha) - x \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^j v^\alpha)
+ \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^j \xi \times v^\alpha).
$$

(2.42)

The first and third lines after the equality sign in equation (2.42) cancel. Note that if we switch to indicial notation,

$$
-\nabla \cdot (\varepsilon^\alpha x \times (t^j)^\alpha) + x \times \nabla \cdot (\varepsilon^\alpha (t^j)^\alpha)
= -(\varepsilon^\alpha x_k (t^j)_k \xi_{ijl})_{,k} + x_i (\varepsilon^\alpha t^j_{,k})_{,k} \xi_{ijl}
= -\varepsilon^\alpha x_i k (l^{\cdot j k} \xi_{ijl}) - \varepsilon^\alpha x_i (t^j_{,k})_{,k} \xi_{ijl} + \varepsilon^\alpha x_i l^{\cdot j k} \xi_{ijl}
= -\varepsilon^\alpha \delta_{ik} l^{\cdot j k} \xi_{ijl} = \varepsilon^\alpha i_{ijl} \xi_{ijl}.
$$

(2.43)
where the last equivalence is left in indicial notation because there is no equivalent in direct notation, we have

\[
\nabla \cdot (\varepsilon^\alpha \rho^{ij} \mathbf{x} \times \overline{v^j v^\alpha}) - \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \rho^{ij} \overline{v^j v^\alpha}) \\
= (\varepsilon^\alpha \rho^{ij} x_i v_j v_k \varepsilon_{ijkl})_k - x_i (\varepsilon^\alpha \rho^{ij} v_j v_k)_{j} \varepsilon_{ijkl} \\
= \varepsilon^\alpha \rho^{ij} x_i k v_j v_k \varepsilon_{ijkl} + \varepsilon^\alpha \rho^{ij} x_i (v_j v_k)_{j} \varepsilon_{ijkl} \\
- \varepsilon^\alpha \rho^{ij} x_i (v_j v_k)_{j} \varepsilon_{ijkl} \\
= \varepsilon^\alpha \rho^{ij} \delta_{ik} v_j v_k \varepsilon_{ijkl} = 0, \quad (2.44)
\]

and

\[
\nabla \cdot (\varepsilon^\alpha \rho^{ij} \mathbf{v}^a v_j \times \mathbf{v}^a v^j) - \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \rho^{ij} \mathbf{v}^a v^j) \\
= (\varepsilon^\alpha \rho^{ij} v_l x_i \varepsilon_{ijkl})_l - x_i (\varepsilon^\alpha \rho^{ij} v_l v_j)_{j} \varepsilon_{ijkl} \\
= \varepsilon^\alpha \rho^{ij} x_i l v_l v_j \varepsilon_{ijkl} + \varepsilon^\alpha \rho^{ij} x_i (v_l v_j)_{j} \varepsilon_{ijkl} \\
- \varepsilon^\alpha \rho^{ij} x_i (v_l v_j)_{j} \varepsilon_{ijkl} \\
= \varepsilon^\alpha \rho^{ij} \delta_{il} v_l v_j \varepsilon_{ijkl} = 0. \quad (2.45)
\]

If we use identities (2.43) - (2.45) and treat the external supply of momentum term, \( \mathbf{r} \times \mathbf{g}^{\alpha} \) similarly, the left-hand side becomes

\[
\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{ij} \mathbf{v}^j \times \mathbf{v}^j) + \nabla \cdot (\varepsilon^\alpha \rho^{ij} \mathbf{v}^j \mathbf{v}^j - \varepsilon^\alpha \mathbf{v} \times \mathbf{t}^\alpha) \\
- \varepsilon^\alpha \mathbf{t}_{ij} \varepsilon_{ij} - \varepsilon^\alpha \rho^{ij} \mathbf{v} \times \mathbf{g}^{\alpha}. \quad (2.46)
\]
Turning our attention to the right hand side of the equation, we examine the terms with no sum:

\[
\varepsilon^\alpha \rho^{\alpha j} \mathbf{x} \times \left( \mathbf{i}^\beta + \mathbf{\tilde{v}}^\beta \right) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{\tilde{m}}^\alpha + \varepsilon^\alpha \rho^{\alpha j} \mathbf{\tilde{m}}^\alpha \mathbf{x} \times \left( \mathbf{i}^j + \mathbf{\tilde{v}}^j \right)^\alpha \\
- \mathbf{x} \times \varepsilon^\alpha \rho^{\alpha j} \left( \mathbf{\tilde{m}}^j + \mathbf{\tilde{v}}^j \right)^\alpha \\
= -\varepsilon^\alpha \rho^{\alpha j} \mathbf{\tilde{m}}^\alpha + \varepsilon^\alpha \rho^{\alpha j} \mathbf{\tilde{m}}^\alpha \mathbf{x} \times \left( \mathbf{i}^j + \mathbf{\tilde{v}}^j \right)^\alpha .
\]  

(2.47)

Now, examining the terms on the right hand side which involve a sum, we have

\[
\sum_{\beta \neq \alpha} \left[ \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha \beta}} \left[ \mathbf{x} \times \mathbf{t}^j + \rho^j (\mathbf{x} \times \mathbf{v}^j) (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, da \right] \\
+ \sum_{\beta \neq \alpha} \left[ \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha \beta}} \left[ \mathbf{\xi} \times \mathbf{t}^j + \rho^j (\mathbf{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, da \right] \\
- \mathbf{x} \times \sum_{\beta \neq \alpha} \left[ \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha \beta}} \left[ \mathbf{t}^j + \rho^j (\mathbf{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, da \right] \\
= \sum_{\beta \neq \alpha} \left[ \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha \beta}} \left[ \mathbf{\xi} \times \mathbf{t}^j + \rho^j (\mathbf{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, da \right].
\]  

(2.48)

Combining the left and right hand side, we now have the conservation of angular momentum at the mesoscale:

\[
\frac{\partial}{\partial t} \left( \varepsilon^\alpha \rho^{\alpha j} \mathbf{\xi} \times \mathbf{v}^\alpha \right) + \nabla \cdot \left( \varepsilon^\alpha \rho^{\alpha j} \mathbf{\xi} \times \mathbf{v}^\alpha \right) - \varepsilon^\alpha \left( \mathbf{\xi} \times \mathbf{t}^\alpha \right)^\alpha \\
- \varepsilon^\alpha \mathbf{I} \times (\mathbf{t}^\alpha) = -\varepsilon^\alpha \rho^{\alpha j} \mathbf{\tilde{m}}^\alpha + \varepsilon^\alpha \rho^{\alpha j} \mathbf{\tilde{m}}^\alpha \mathbf{\xi} \times (\mathbf{i}^j + \mathbf{\tilde{v}}^j) \\
+ \sum_{\beta \neq \alpha} \left[ \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha \beta}} \left[ \mathbf{\xi} \times \mathbf{t}^j + \rho^j (\mathbf{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, da \right].
\]  

(2.49)
Equation (2.49) simplifies to

\[-\varepsilon^\alpha t^\alpha_{ji} \varepsilon_{ijl} = \mathbf{m}^\alpha_{ij} + M^\alpha_{ij} + \sum_{\beta \neq \alpha} (\mathbf{m}^\beta_{ij}),\]  

(2.50)

where we have replaced \((t^j)^\alpha\) by \(t^\alpha_{ij}\) (we can do so because of equation (2.28)) and we have made the following definitions:

\[\mathbf{m}^\alpha_{ij} \equiv \varepsilon^\alpha \rho^\alpha_{ij} \mathbf{m}^\alpha_{ij}\]  

(2.51)

is the rate of gain of angular momentum due to interaction with other species within the same phase,

\[M^\alpha_{ij} \equiv -\frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha_{ij} \mathbf{g} \times \mathbf{v}^\alpha_{ij} - \nabla \cdot (\varepsilon^\alpha \rho^\alpha_{ij} \mathbf{g} \times \mathbf{v}^\alpha_{ij})) + \nabla \cdot \varepsilon^\alpha (\mathbf{g} \times t^j)^\alpha + \varepsilon^\alpha \rho^\alpha_{ij} \mathbf{g} \times (\mathbf{g}^j + \mathbf{w}^j)\]  

(2.52)

is the rate of angular momentum gain by constituent \(j\) in phase \(\alpha\) due to the microscale angular momentum terms, and

\[\mathbf{m}^\alpha_{ij} = \frac{\varepsilon^\alpha}{[\delta V_\alpha]} \int_{\delta L_{\alpha \beta}} \left[\mathbf{g} \times t^j + \rho^j (\mathbf{g} \times \mathbf{v}) \left(\mathbf{w}^\alpha_{ij} - \mathbf{v}_{ij}\right)\right] \cdot \mathbf{n}^\alpha \, da\]  

(2.53)

is the rate of angular momentum gain by constituent \(j\) in phase \(\alpha\) due to interaction with phase \(\beta\).

Summing over \(j = 1, \ldots, N\) yields the conservation of angular momentum for the bulk phase

\[-\varepsilon^\alpha t^\alpha_{ji} \varepsilon_{ijl} = M^\alpha + \sum_{\beta \neq \alpha} \mathbf{m}^\beta_{ij},\]  

(2.54)

where the following restrictions apply:

\[\sum_{j=1}^{N} \mathbf{m}^\alpha_{ij} = 0 \quad \forall \alpha,\]  

(2.55)

\[\mathbf{m}^\alpha_{ij} + \mathbf{m}^\beta_{ij} = 0 \quad j = 1, \ldots, N.\]  

(2.56)
Equation (2.54) implies that, in general, the mesoscale stress tensor $t^\alpha$ is not symmetric for multi-phase systems. However, if $t^{\alpha j}$ is symmetric then the right hand side of (2.54) must be zero. Restriction (2.55) says that bulk-phase angular momentum can only be lost due to transfer to other phases, restriction (2.56) holds because we assume that the interface is massless.

2.3.5 Conservation of Energy

Beginning as we did for the conservation of angular momentum, by substituting the appropriate terms for the conservation of energy from Table 2.1 into equation (2.39), we obtain

$$\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} (e^j + \frac{1}{2} v^j \cdot v^j)) - \nabla \cdot (\varepsilon^\alpha ((t^j \cdot v^j + q^j)^\alpha + \rho^{\alpha j} v^{\alpha j} (e^j + \frac{1}{2} v^j \cdot v^j))$$

$$- \rho^{\alpha j} v^j (e^j + \frac{1}{2} v^j \cdot v^j) ) + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} v^{\alpha j} (e^j + \frac{1}{2} v^j \cdot v^j))$$

$$= \sum_{\beta \neq \alpha} \varepsilon^\alpha \int_{\delta A_{\alpha \beta}} \left[ t^j \cdot v^j + q^j + \rho^j (e^j + \frac{1}{2} v^j \cdot v^j) (w^{\alpha \beta j} - v^j) \right] \cdot n^\alpha \, da$$

$$\mp (e^j + \frac{1}{2} v^j \cdot v^j) \int_{\delta A_{\alpha \beta}} \rho^j (w^{\alpha \beta j} - v^j) \cdot n^\alpha \, da$$

$$+ \varepsilon^\alpha \rho^{\alpha j} (\overrightarrow{Q}^j + \overrightarrow{i} \cdot v^j + \overrightarrow{r} (e^j + \frac{1}{2} v^j \cdot v^j)).$$

(2.57)

Now, from equation (2.57), subtracting equation (2.29) times $v^{\alpha j}$ and equation (2.12) times $(e^j + \frac{1}{2} v^j \cdot v^j)$, performing massive algebraic manipulations, and again using equation (2.13), we obtain the conservation of energy equation at the mesoscale:

$$\varepsilon^\alpha \rho^{\alpha j} \frac{D^{\alpha j}}{Dt} (e^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha q^{\alpha j}) - \varepsilon^\alpha t^{\alpha j} : \nabla v^{\alpha j} - \varepsilon^\alpha \rho^{\alpha j} h^{\alpha j}$$

$$= \overrightarrow{Q}^{\alpha j} + \overrightarrow{Q}_\beta^{\alpha j},$$

(2.58)
where the colon indicates the tensor dot product \((\mathbf{a} : \mathbf{b} = \sum_{i,j} a_{ij} b_{ij})\). Here we have made the following definitions:
\[
h^\alpha_j \equiv h^\alpha_j + \mathbf{g}^j \cdot \mathbf{v}^\alpha - \mathbf{g}^\alpha_j \cdot \mathbf{v}^\alpha_j
\] (2.59)
is the external supply of energy,
\[
e^\alpha_j \equiv \bar{e}^\alpha_j + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha - \frac{1}{2} \mathbf{v}^\alpha_j \cdot \mathbf{v}^\alpha_j
\] (2.60)
is the energy density,
\[
\mathbf{q}^\alpha_j \equiv (\mathbf{q}^j)\alpha + (\mathbf{t}^j \cdot \mathbf{v}^j)\alpha - \mathbf{t}^\alpha_j \cdot \mathbf{v}^\alpha_j + \rho^\alpha_j \mathbf{v}^\alpha_j (e^\alpha_j + \frac{1}{2} \mathbf{v}^\alpha_j \cdot \mathbf{v}^\alpha_j)
- \rho^\alpha_j \mathbf{v}^j (e^\alpha_j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j)
\] (2.61)
is the partial heat flux vector for the \(j^{th}\) component of phase \(\alpha\),
\[
\mathbf{Q}_{\beta \alpha}^j \equiv e^\alpha \rho^\alpha_j (\bar{Q}^\alpha_j + \bar{t}^\alpha_j \cdot \mathbf{v}^\alpha_j - \bar{\mathbf{t}}^\alpha + \bar{\mathbf{t}}^\alpha_j \cdot \mathbf{v}^\alpha_j \mathbf{v}^\alpha_j + \bar{\mathbf{t}}^\alpha_j \mathbf{v}^\alpha_j + \bar{\mathbf{t}}^\alpha_j \mathbf{v}^\alpha_j)
- \bar{\mathbf{t}}^\alpha_j (e^\alpha_j + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha_j))
\] (2.62)
is the rate of energy gain due to interaction with other species within the same phase not due to mass or momentum transfer, and
\[
\mathbf{Q}_{\beta \alpha}^j \equiv \frac{e^\alpha}{|\partial V_{\alpha}|} \left\{ \int_{\delta A_{\alpha \beta}} \left[ \mathbf{q}^j + \mathbf{t} \cdot \mathbf{v}^j + \rho^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \mathbf{v}^\alpha_j \mathbf{v}^\alpha_j - \mathbf{v}^j \mathbf{v}^\alpha_j \mathbf{v}^\alpha_j \right] \cdot \mathbf{n}^\alpha \, da
- (e^\alpha_j - \frac{1}{2} \mathbf{v}^\alpha_j \cdot \mathbf{v}^\alpha_j) \int_{\delta A_{\alpha \beta}} \rho^j (\mathbf{v}^\alpha_j \mathbf{v}^\alpha_j - \mathbf{v}^j \mathbf{v}^\alpha_j) \cdot \mathbf{n}^\alpha \, da
- \mathbf{v}^\alpha_j \int_{\delta A_{\alpha \beta}} \left[ \mathbf{t}^j \cdot \rho^j (\mathbf{v}^\alpha_j \mathbf{v}^\alpha_j - \mathbf{v}^j \mathbf{v}^\alpha_j) \right] \cdot \mathbf{n}^\alpha \, da \right\}
\] (2.63)
is the rate of energy transfer from phase \(\beta\) to phase \(\alpha\) not due to mass or momentum transfer.
The bulk phase conservation of energy equation is found in an analogous manner to the bulk phase conservation of linear momentum by using (2.20) and subtracting \( \nu^\alpha \) times (2.33) and \( (\varepsilon^\alpha + \frac{1}{2} \nu^\alpha \cdot \nu^\alpha) \) times (2.21) and then summing over constituents. This yields

\[
\varepsilon^\alpha \rho^\alpha \frac{D\varepsilon^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha q^\alpha) - \varepsilon^\alpha t^\alpha \cdot \nabla \nu^\alpha - \varepsilon^\alpha \rho^\alpha \varepsilon^\alpha = \sum_{\beta \neq \alpha} \hat{\alpha}_\beta,
\]

where the following restrictions hold:

\[
\sum_{j=1}^{N} \left[ \hat{\alpha}_{\alpha}^{\alpha j} + \hat{\beta}_{\alpha}^{\alpha j} \cdot \nu_{\alpha j, \alpha} + \hat{\gamma}_{\alpha}^{\alpha j} \left( \varepsilon_{\alpha j} + \frac{1}{2} (\nu_{\alpha j, \alpha})^2 \right) \right] = 0 \quad \forall \alpha, \quad \text{and} \quad \text{(2.65)}
\]

\[
\left[ \hat{\alpha}_{\alpha}^{\beta j} + \hat{T}_{\beta}^{\alpha j} \cdot \nu_{\alpha j} + \hat{\gamma}_{\beta}^{\alpha j} \left( \varepsilon_{\beta j} + \frac{1}{2} (\nu_{\beta j})^2 \right) \right] + \left[ \hat{Q}_{\alpha}^{\beta j} + \hat{T}_{\alpha}^{\beta j} \cdot \nu_{\beta j} + \hat{\epsilon}_{\alpha}^{\beta j} \left( \varepsilon_{\beta j} + \frac{1}{2} (\nu_{\beta j})^2 \right) \right] = 0 \quad j = 1, \ldots, N.
\]

(2.66)

The first restriction says that bulk-phase energy can only be lost due to transfer with other phases, and the second restriction states that the interface retains no energy.
2.3.6 Entropy Balance

After substituting the appropriate quantities from Table 2.1 into (2.39) the entropy balance at the mesoscale for constituent $j$ in phase $\alpha$ is

$$
\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} \eta^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha (\langle \phi^j \rangle^\alpha + \rho^{\alpha j} \mathbf{v}^{\alpha j} \eta^{\alpha j})
- \rho^{\alpha j} \mathbf{v}^j \eta^{\alpha j}) + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \eta^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{b}^\alpha
= \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \left[ \frac{1}{\rho^{\alpha j} |\delta V_{\alpha}|} \int_{\delta A_{\alpha \beta}} \phi^j + \rho^j \eta^j (\mathbf{w}^{\alpha j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha \, da \right]
+ \frac{\eta^{\alpha j}}{\rho^{\alpha j} |\delta V_{\alpha}|} \int_{\delta A_{\alpha \beta}} \rho^j (\mathbf{w}^{\alpha j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha \, da
+ \varepsilon^\alpha \rho^{\alpha j} \Lambda^{\alpha j} + \varepsilon^\alpha \rho^{\alpha j} \Lambda^{\alpha j} + \varepsilon^\alpha \rho^{\alpha j} \mathbf{r}^j \mathbf{v}^j. \tag{2.67}
$$

Subtracting $\eta^{\alpha j}$ times (2.12) and using (2.13) we obtain

$$
\varepsilon^\alpha \rho^{\alpha j} \frac{D^{\alpha j}}{Dt} (\eta^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha \phi^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{b}^{\alpha j}
= \sum_{\beta \neq \alpha} \Phi_{\beta}^{\alpha j} + \eta^{\alpha j} + \Lambda^{\alpha j}, \tag{2.68}
$$

where we have made the following definitions:

$$
\Lambda^{\alpha j} \equiv \Lambda^{\alpha j} \tag{2.69}
$$
is the entropy production,

$$
\eta^{\alpha j} \equiv \eta^{\alpha j} \tag{2.70}
$$
is the entropy of the $j^{th}$ constituent in the $\alpha$-phase,

$$
\phi^{\alpha j} \equiv (\langle \phi^j \rangle^\alpha + \rho^j \mathbf{v}^{\alpha j} \eta^{\alpha j} - \rho^{\alpha j} \mathbf{v}^j \eta^{\alpha j}) \tag{2.71}
$$
is the partial entropy flux vector for the \( j^{th} \) component of the \( \alpha \)-phase,

\[
\overline{\phi}^\alpha_j \equiv b^\alpha_j
\]  

(2.72)

is the external entropy source,

\[
\overline{\Phi}_j^\alpha \equiv \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_{\delta A_{\alpha \beta}} \left[ \phi^j + \rho^j \eta^j (\mathbf{w}^\alpha_j - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha \, d\alpha
\]

\[
- \frac{\varepsilon^\alpha \eta^\alpha_j}{|\delta V_\alpha|} \int_{\delta A_{\alpha \beta}} \rho^j (\mathbf{w}^\alpha_j - \mathbf{v}^j) \cdot \mathbf{n}^\alpha \, d\alpha
\]  

(2.73)

is the entropy transfer to the \( j^{th} \) component in the \( \alpha \)-phase through mechanical interactions with the same component in the \( \beta \)-phase, and

\[
\overline{\eta}^\alpha_j \equiv \varepsilon^\alpha \rho^\alpha \overline{\eta}^\alpha_j + \overline{\eta}^\alpha_j \rho^\alpha_j - \eta^\alpha_j \eta^\alpha_j
\]  

(2.74)

is the net entropy gain due to interaction with other species within the same phase.

The bulk-phase counterpart is given by

\[
\varepsilon^\alpha \rho^\alpha \frac{D \eta^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \Phi^\alpha) - \varepsilon^\alpha \rho^\alpha b^\alpha = \sum_{\beta \neq \alpha} \Phi^\alpha_\beta + \Lambda^\alpha,
\]  

(2.75)

where the following restrictions apply:

\[
\sum_{j=1}^{N} (\overline{\eta}^\alpha_j + \overline{\eta}^\alpha_j \eta^\alpha_j) = 0 \quad \forall \alpha,
\]  

(2.76)

\[
\overline{\Phi}_\beta^\alpha_j + \overline{\phi}_\beta^\alpha_j \eta^\alpha_j + \overline{\phi}_\alpha^\beta_j \eta^\beta_j = 0 \quad j = 1, \ldots, N.
\]  

(2.77)

The first restriction states that entropy can only be lost due to interactions with another phase, and the second restriction states that the interface can hold no entropy.
3. Assumptions and Constitution

Thus far, the theory introduced applies to all media meeting the requirements laid out in the beginning of Chapter 2. Obviously, one of the strengths of the theory is that it has a broad scope of application. However, as outlined in the introduction, we are interested in the theory as it applies to polymeric and biopolymeric systems. First, we will make a few standard simplifying assumptions, and give the resulting form of the entropy inequality. Next, we will make constitutive assumptions as they apply to polymeric and biopolymeric systems and give definitions and identities needed to compute the entropy inequality for the system defined by our specific constitution. Lastly, we will obtain non-equilibrium, equilibrium, and near equilibrium results.

3.1 Standard Assumptions and Resulting Entropy Inequality

Henceforth we assume that the stress tensor, $t^\alpha$, is symmetric. We also assume that the system is in local thermal equilibrium. That is, because the phases are viewed as overlaying continua, we assume the temperature of all constituents in all phases at a single point is the same for all phases. This assumption can be expressed as

$$ T = T^{\alpha j} = T^{\beta j} \quad \forall \alpha, \forall \beta, \forall j. \quad (3.1) $$

Note that this does not mean that we are assuming that the temperature is constant; $T$ is still a function of time and space.
Next, we assume that the system is thermodynamically simple in the sense of Eringen [21]. This means that entropy flux and external supplies of entropy are due to heat flux and external supplies of heat alone, respectively. This assumption can be expressed as:

\[ \phi^{\alpha_j} = \frac{q^{\alpha_j}}{T} \]

\[ b^{\alpha_j} = \frac{h^{\alpha_j}}{T}. \]  

(3.2)  

(3.3)

Entropy is a mathematically useful quantity. However, experimentally it cannot be measured directly. Thus, we choose to perform a Legendre transformation to convert the internal energy \( e^{\alpha_j} \) into the Helmholtz free energy \( A^{\alpha_j} \),

\[ A^{\alpha_j} = e^{\alpha_j} + T \eta^{\alpha_j}, \]  

(3.4)

allowing us to choose temperature instead of entropy as an independent variable.

The second law of thermodynamics states that the total entropy generated by the system must be non-negative, and is maximum only when the system is in equilibrium. This statement can be expressed as:

\[ \Lambda = \sum_{\alpha} \Lambda^\alpha = \sum_{\alpha} \sum_{j=1}^{N} \Lambda^{\alpha_j} \geq 0. \]  

(3.5)

We begin by solving equation (2.68) for \( \Lambda^{\alpha_j} \), subtract \( \frac{1}{T} \) times the conservation of energy equation (2.58), to eliminate the heat source variables, \( h^{\alpha_j} \), perform the Legendre transformation with (3.4), use the identities given in Ap-
Appendix C, then sum over all constituents and phases to obtain

\[
\Lambda = \sum_{\alpha} \left\{ -\frac{\varepsilon^{\alpha} \rho^{\alpha}}{T} \left( \frac{D^{\alpha} A^{\alpha}}{Dt} + \eta^{\alpha} \frac{D^{\alpha} T}{Dt} \right) \right. \\
+ \frac{\varepsilon^{\alpha}}{T} \left( \sum_{j=1}^{N} t^{\alpha j} \right) : d^{\alpha} \\
+ \frac{\varepsilon^{\alpha}}{T^2} (\nabla T) \cdot \left\{ q^{\alpha} - \sum_{j=1}^{N} \left[ t^{\alpha j} \cdot v^{\alpha j,\alpha} - \rho^{\alpha j} v^{\alpha j,\alpha} \left( A^{\alpha j} + \frac{1}{2} (v^{\alpha j,\alpha})^2 \right) \right] \right\} \\
- \frac{1}{T} \sum_{j=1}^{N} \left[ \tilde{T}^{\alpha j} + i^{\alpha j} + (\varepsilon^{\alpha} \rho^{\alpha j} A^{\alpha j}) \cdot v^{\alpha j,\alpha} \right] \\
- \frac{1}{T} \sum_{\beta \neq \alpha} \tilde{T}^{\alpha}_{\beta} \cdot v^{\alpha,\beta} \\
- \frac{1}{2T} \sum_{j=1}^{N} (v^{\alpha j,\alpha})^2 \left[ \tilde{e}^{\alpha j}_{\beta} + \tilde{e}^{\alpha j} \right] \\
- \frac{1}{T} \sum_{\beta \neq \alpha} \tilde{e}^{\alpha}_{\beta} \left( A^{\alpha} + \frac{1}{2} (v^{\alpha,\beta})^2 \right) \right\} \geq 0,
\]

(3.6)

where \( v^{\alpha j,\alpha} \equiv v^{\alpha j} - v^{\alpha} \), and in general a comma in the superscript denotes a difference in the superscripted quantity.

### 3.2 Constitutive Assumptions

First, we assume that we have a two-phase system consisting of a solid and a liquid phase, denoted \( \alpha = s, l \), respectively. The solid phase (the polymer) is assumed to be viscoelastic and the liquid phase is assumed to be viscous. The interactions of the two phases results in viscoelastic behavior. The viscoelastic solid is modeled as a Kelvin-Voigt element, which means that the constitutive variables will depend on the time rate of change of the strain tensor. The model can be extended to a general Kelvin-Voigt type by including higher derivatives.
of the strain tensor, but initially we include only one derivative for simplicity. The unknowns of the system include:

\[ \varepsilon^{\alpha} \]  
\[ \varepsilon^{\alpha} \rho^\beta, \mathbf{v}^\beta, T, \]  
\[ \mathbf{e}^\beta, \mathbf{C}^\beta, \mathbf{T}^\beta, \mathbf{u}^\beta, A^\alpha, \mathbf{q}^\alpha, \mathbf{Q}^\alpha, \mathbf{\bar{Q}}^\alpha, \mathbf{\bar{Q}}^\alpha, \eta^\alpha, \eta^\alpha. \]  

Conservation of mass (2.14), momentum (2.30) and energy (2.58) correspond to the unknowns on line (3.8), respectively. Additional equations are obtained by considering the variables on line (3.9) as constitutive. Thus, every variable on lines (3.7)-(3.9) has a corresponding equation except for \( \varepsilon^\alpha \). This is known as the closure issue [13]. Here, we choose to follow Bowen [16] and postulate an additional dependent variable, \( \dot{\varepsilon}^\alpha \), so that we assume the evolution of the time rate of change of volume is a constitutive variable.

Constitutive variables are considered functions of the following set of independent (or constitutive independent) variables:

\[ \varepsilon^l, \varepsilon^\alpha \rho^\alpha, \nabla(\varepsilon^\alpha \rho^\alpha), \mathbf{v}^\alpha, \mathbf{v}^\alpha; \mathbf{T}, \nabla \mathbf{T}, \mathbf{E}, \nabla \mathbf{E}, \dot{\mathbf{E}}, d^l, \nabla \mathbf{v}^l. \]  

Here we include only \( \varepsilon^l \) since equation (2.3) implies that either \( \varepsilon^l \) or \( \varepsilon^s \) can vary independently but not both. In our conservation equation \( \varepsilon^\alpha \) and \( \rho^\alpha \) always appear together and account for the actual physical make-up of the material. The variable \( \nabla \varepsilon^\alpha \rho^\alpha \) accounts for non-local effects of the material make-up. Including additional gradients of any variable will increase the non-locality of the model and make it more accurate with respect to that variable. However, the more gradients we include the more complicated the model becomes. Thus, we are careful only to include gradients that we feel are relevant to our system.
We include $d$ to account for viscous effects of the fluid. $E^s$ and $\nabla E^s$ account for elastic behavior in the solid. Again, $\nabla E^s$ accounts for non-local effects. $E^s$ allows for viscoelastic behavior as evidenced by the Kelvin-Voigt model [31]. By including additional time derivatives of $E^t$, we could model Kelvin-Voigt elements in series which would allow for a better fit to data, but this would also unnecessarily complicate our model. We include $T$ because amorphous polymers exhibit a high degree of dependency on temperature as discussed in the introduction. If we do not include $\nabla T$ in our list of independent variables, exploiting the resulting entropy inequality produces the result that the heat flux is zero for all time, but this is only true of non-heat-conducting materials. On the other hand, if we include $\nabla T$ in our list of independent variables, we recover Fourier's law of heat conduction. Including $v^{\alpha,s}$ gives us information about the exchange of momentum between phases. Lastly, $v^{\alpha,j,\alpha}$ and $\nabla v^{\alpha,j,\alpha}$ are directly related to viscous diffusion and give us information about the exchange of momentum within a phase.

### 3.2.1 Entropy Inequality

To arrive at a form of the entropy inequality that is useful we will need several identities and assumptions. Next, we make the appropriate simplifying assumptions and give identities needed to obtain the entropy inequality for our system.

The axiom of equipresence requires that initially all constitutive variables be functions of the complete set of independent variables, even, for example, if one phase lacks a certain constituent. Only after the entropy inequality is
exploited can the concentration of a species be set to zero. However, it can be demonstrated that the Helmholtz free energy is not a function of all the variables in list (3.9) [26]. To simplify the following manipulations, we postulate the dependence of the Helmholtz free energy as follows:

\[ A^l = A^l(\varepsilon^l, \varepsilon^l \rho^l, T, E^s, \dot{E}^s) \]  
\[ A^s = A^s(\varepsilon^s, \varepsilon^s \rho^s, T, E^s, \dot{E}^s). \]

(See Bennethum [7] for a more generalized formulation.) Otherwise we adhere to the axiom of equipresence: all other constitutive variables are considered a function of list (3.10). Material time derivatives of \( A^l \) and \( A^s \) appear in the entropy inequality (3.4). Using the chain rule, they may be calculated as follows:

\[
\frac{D^l A^l}{Dt} = \frac{\partial A^l}{\partial \varepsilon^l} \frac{D^l \varepsilon^l}{Dt} + \sum_{j=1}^{N} \frac{\partial A^l}{\partial (\varepsilon^l \rho^l)} \frac{D^l (\varepsilon^l \rho^l)}{Dt} + \frac{\partial A^l}{\partial T} \frac{D^l T}{Dt} \\
+ \frac{\partial A^l}{\partial E^s} : \frac{D^s E^s}{Dt} + \frac{\partial A^l}{\partial \dot{E}^s} : \frac{D^l \dot{E}^s}{Dt} \\
\frac{D^s A^s}{Dt} = \frac{\partial A^s}{\partial \varepsilon^s} \frac{D^s \varepsilon^s}{Dt} + \sum_{j=1}^{N} \frac{\partial A^s}{\partial (\varepsilon^s \rho^s)} \frac{D^s (\varepsilon^s \rho^s)}{Dt} + \frac{\partial A^s}{\partial T} \frac{D^s T}{Dt} \\
+ \frac{\partial A^s}{\partial E^s} : \frac{D^s E^s}{Dt} + \frac{\partial A^s}{\partial \dot{E}^s} : \frac{D^s \dot{E}^s}{Dt}. \]  

(3.13)  
(3.14)

We will find it useful to be able to convert a material time derivative with respect to one phase (or species within a phase) into a material time derivative with respect to another phase (or species within a phase). This can be done using either of the following two identities:

\[
\frac{D^l (\cdot)}{Dt} = \frac{D^s (\cdot)}{Dt} + \nu^{i,s} \nabla (\cdot) \\
\frac{D^o_s (\cdot)}{Dt} = \frac{D^s (\cdot)}{Dt} + \nu^{o,s} \nabla (\cdot). \]

(3.15)  
(3.16)
After using the identities and techniques discussed above, performing massive algebraic calculations and grouping terms for ease of exploitation we arrive at the following form of the entropy inequality:

\[
\Lambda = -\frac{1}{T} \sum_{\alpha} \varepsilon^\alpha \rho^\alpha \left( \frac{\partial A^\alpha}{\partial T} + \eta^\alpha \right) \frac{D^s T}{D t} \\
= \frac{1}{T} \left( \varepsilon^t \rho^t \frac{\partial A^t}{\partial \dot{c}^t} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \dot{c}^s} \right) \dot{\varepsilon}^t \\
+ \frac{1}{T} \left[ \sum_{j=1}^N \left( t^j + \rho^s \rho^s \frac{\partial A^i}{\partial \rho^j} \right) \right] : d^t \\
- \frac{1}{T} \left\{ \mathbf{F}^{-1} \cdot \left[ \varepsilon^t \rho^t \frac{\partial A^t}{\partial \mathbf{E}^s} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} + \varepsilon^s \sum_{j=1}^N \left( t^j + \rho^s \rho^s \frac{\partial A^i}{\partial \rho^j} \right) \right] \cdot \mathbf{F}^{-T} \right\} : \mathbf{\dot{E}}^s \\
- \frac{1}{T} \left[ \varepsilon^t \rho^t \left( \frac{\partial A^t}{\partial \mathbf{E}^s} + \eta^t \right) \mathbf{\nabla} T + \varepsilon^s \rho^s \mathbf{\nabla} \left( \frac{\partial A^t}{\partial \mathbf{E}^s} \mathbf{\nabla} T + \frac{\partial A^s}{\partial \mathbf{E}^s} \mathbf{\nabla} \mathbf{\dot{E}}^s \right) \right. \\
\left. + \varepsilon^t \rho^t \frac{\partial A^t}{\partial \mathbf{E}^s} \mathbf{\nabla} \varepsilon^t + \mathbf{\dot{T}}^s \right] \cdot \mathbf{v}^{t,s} \\
- \frac{1}{T} \left( \varepsilon^t \rho^t \frac{\partial A^t}{\partial \mathbf{E}^s} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} \right) \mathbf{\dot{E}}^s \\
+ \sum_{\alpha} \frac{\varepsilon^\alpha \mathbf{\nabla} T}{T^2} \cdot \left\{ q^\alpha - \sum_{j=1}^N \left[ t^{\alpha j} \cdot \mathbf{v}^{\alpha j} + \rho^{\alpha j} \mathbf{v}^{\alpha j} \cdot \left( A^{\alpha j} + \frac{1}{2} \left( \mathbf{v}^{\alpha j} \right)^2 \right) \right] \right\} \\
- \frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \left[ \mathbf{T}^{\alpha j} + \mathbf{\dot{t}}^{\alpha j} + \mathbf{\nabla} \left( \varepsilon^\alpha \rho^{\alpha j} A^{\alpha j} \right) - \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} \mathbf{\nabla} \left( \varepsilon^\alpha \rho^{\alpha j} \right) \right] \cdot \mathbf{v}^{\alpha j} \\
- \frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \left[ A^{\alpha} + \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} + \frac{1}{2} \left( \mathbf{v}^{\alpha j} \right)^2 + \frac{1}{2} \left( \mathbf{v}^{\alpha j} \right)^2 \right] \mathbf{\dot{\varepsilon}}^{\alpha j} \\
- \frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \left[ \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} + \frac{1}{2} \left( \mathbf{v}^{\alpha j} \right)^2 \right] \mathbf{\dot{\varepsilon}}^{\alpha j} \\
+ \frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \varepsilon^\alpha \left[ \rho^{\alpha} \rho^{\alpha j} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} + t^{\alpha j} - \rho^{\alpha j} A^{\alpha j} \mathbf{I} \right] : \left( \mathbf{\nabla} \mathbf{v}^{\alpha j} \right) \geq 0, \quad (3.17)
\]

where \( d \equiv \frac{1}{2} (\mathbf{n} \cdot \mathbf{v}^{\alpha} + (\mathbf{n} \cdot \mathbf{v}^{\alpha})^T) \). The last term in the square brackets of line four in equation (3.17) comes from converting \( d^s \) into the independent variable
\[ \dot{E}^s \text{ via} \]
\[ d^s = F^{-T} \cdot \dot{E}^s \cdot F^{-1}, \]  
(3.18)

where \( F \) is the deformation gradient of the solid phase and is defined by (in indicial notation)
\[ F = F_{kK} = x_{k,K} = \frac{\partial x_k}{\partial X_K}, \]  
(3.19)

where \( x \) is the Eulerian coordinate and \( X \) is the Lagrangian coordinate. Note that in the entropy inequality (3.17) the terms involving \( v^{\alpha_j,\alpha} \) and \( \nabla v^{\alpha_j,\alpha} \) have only \( N - 1 \) independent variables and one dependent variable. This is because
\[ \sum_{j=1}^{N} C^{\alpha_j} = 1, \]  
(3.20)

and
\[ \sum_{j=1}^{N} C^{\alpha_j} v^{\alpha_j,\alpha} = 0. \]  
(3.21)

The difficulty arises from using intensive variables (variables that do not change with a change in quantity, e.g. concentrations) as opposed to extensive variables (variables that change with a change in quantity, e.g. mole numbers). While upscaling is possible on extensive variables the results are not physically applicable to open systems. To remove the \( N^{th} \) component dependence from \( v^{\alpha_j,\alpha} \) and \( \nabla v^{\alpha_j,\alpha} \) in equation (3.17) we will use the following identities due to Bennethum et al., [11]:
\[ \sum_{j=1}^{N} F^{\alpha_j} \cdot v^{\alpha_j,\alpha} = \sum_{j=1}^{N-1} \left( F^{\alpha_j} \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} F^{\alpha_N} \right) \cdot v^{\alpha_j,\alpha}, \]  
(3.22)
\[
\sum_{j=1}^{N} G^{\alpha j} : \nabla \mathbf{v}^{\alpha j, \alpha} = \sum_{j=1}^{N-1} \left( G^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} G^{\alpha N} \right) : \nabla \mathbf{v}^{\alpha j, \alpha} \\
- G^{\alpha N} \cdot \sum_{j=1}^{N-1} \nabla \left( \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \right) \mathbf{v}^{\alpha j, \alpha}
\] 

(3.23)

where \( F^{\alpha j} \) and \( G^{\alpha j} \) are the coefficients of \( \mathbf{v}^{\alpha j, \alpha} \) and \( \nabla \mathbf{v}^{\alpha j, \alpha} \) in (3.17), respectively. Hence, these terms of the entropy inequality become:

\[
\sum_{\alpha} \varepsilon^{\alpha} \frac{\rho^{\alpha j}}{T} \sum_{j=1}^{N} \left[ \rho^{\alpha j} \left( \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} - \frac{\partial A^{\alpha}}{\partial \rho^{\alpha N}} \right) \right. \\
\left. + t^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} t^{\alpha N} - \rho^{\alpha j} (A^{\alpha j} - A^{\alpha N}) \right] : \left( \nabla \mathbf{v}^{\alpha j, \alpha} \right) \\
\frac{1}{T} \sum_{\alpha} \sum_{j=1}^{N-1} \left[ -\varepsilon^{\alpha} t^{\alpha j} \nabla \left( \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \right) \right. \\
\left. + \left( \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \right) \left( \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} - \rho^{\alpha j} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha N}} \right) \nabla \left( \varepsilon^{\alpha} \rho^{\alpha j} \right) \right] \cdot \mathbf{v}^{\alpha j, \alpha} 
\] 

(3.24)

Before we obtain non-equilibrium, equilibrium, and near-equilibrium results we make the following definitions for ease of exposition:

\[
t^{se} = \rho^{s} \mathbf{F} \cdot \frac{\partial A^{s}}{\partial \mathbf{E}^{s}} \cdot \mathbf{F}^{T}
\] 

(3.25)

and

\[
t^{sh} = \rho^{h} \mathbf{F} \cdot \frac{\partial A^{h}}{\partial \mathbf{E}^{h}} \cdot \mathbf{F}^{T}
\]

(3.26)

where \( t^{se} \) and \( t^{sh} \) are the effective stress, and hydration stress, respectively. The effective stress accounts for the elastic component of the stress in the solid phase. The hydration stress accounts for physio-chemical forces between the liquid and solid phases.
Whenever possible we will use the following thermodynamic definitions in the following sections to simplify notation. The chemical potential, $\mu^\alpha_j$, is defined as

$$
\mu^\alpha_j = \frac{\partial A^\alpha}{\partial M^\alpha_j} \bigg|_{V^\alpha,T} = \frac{\partial (\varepsilon^\alpha \rho^\alpha A^\alpha)}{\partial (\varepsilon^\alpha \rho^\alpha)} \bigg|_{\varepsilon^\alpha,T} = A^\alpha + \rho^\alpha \frac{\partial A^\alpha}{\partial \rho^\alpha} \bigg|_{\varepsilon^\alpha,T}, \quad (3.27)
$$

and represents the amount of energy required to insert a molecule of constituent $j$. Here $M^\alpha_j$ is the mass of the $j^{th}$ constituent in the $\alpha$-phase. The classical pressure, $p^\alpha$, is

$$
p^\alpha = -\frac{\partial A^\alpha}{\partial \varepsilon^\alpha \rho^\alpha} \bigg|_{\varepsilon^\alpha, \rho^\alpha} = -(\rho^\alpha)^2 \frac{\partial A^\alpha}{\partial \rho^\alpha} \bigg|_{\varepsilon^\alpha, \rho^\alpha} = \sum_{j=1}^{N} \rho^\alpha \rho^\alpha_j \frac{\partial A^\alpha}{\partial \rho^\alpha_j} \bigg|_{\varepsilon^\alpha}, \quad (3.28)
$$

where $\varepsilon^\alpha$ is the specific volume of phase $\alpha$. In the case of a single isotropic solid phase $p^\alpha$ represents the physical pressure of the solid phase. However, for our system the classical pressure is distinct from the thermodynamic pressure, $\bar{p}^\alpha$

$$
\bar{p}^\alpha = -\frac{\partial A^\alpha}{\partial V^\alpha} \bigg|_{M^\alpha, T} = -\rho^\alpha \frac{\partial A^\alpha}{\partial \rho^\alpha} \bigg|_{\varepsilon^\alpha, \rho^\alpha, T}, \quad (3.29)
$$

which is the change in energy (extensive) of phase $\alpha$ with respect to a change in volume of phase $\alpha$ keeping the mass and temperature fixed. This coincides with the classical definition of pressure in Gibbsian thermodynamics. For a single phase, single constituent system the previous two definitions are equivalent. However, for swelling systems these pressures are distinct and related to each other through

$$
p^\alpha = \bar{p}^\alpha + \pi^\alpha, \quad (3.30)
$$

where $\pi^\alpha$, the swelling potential, is

$$
\pi^\alpha = \varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \bigg|_{\rho^\alpha, \rho^\alpha}, \quad (3.31)
$$
The derivation of (3.12) will be given in a subsequent section.

3.2.1.1 Non-Equilibrium Results

The following variables are neither constitutive nor independent:

\[ \dot{T}, \nabla v^{s, c}, \bar{E}^s. \]  

(3.32)

This means that they can vary arbitrarily, and because these variables appear linearly, to avoid violating entropy inequality (3.17), the coefficients of these variables must be identically zero. This yields the following set of non-equilibrium results:

\[ \sum_{\alpha} \varepsilon^\alpha \rho^\alpha \left( \frac{\partial A^\alpha}{\partial T} + \eta^\alpha \right) = 0, \]  

(3.33)

\[ \varepsilon^l \rho^l \frac{\partial A^l}{\partial E^s} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial E^s} = 0, \]  

(3.34)

\[ t^{s} - \frac{\rho^s}{\rho^{s'}} t^{s'} = \rho^s (A^{s} - A^{s'N} - \mu^{s'} + \mu^{s'}) I. \]  

(3.35)

Equation (3.33), the classical result for one phase, says that \( T \) and \( \eta \) are dual variables so that \( \frac{\partial A^\alpha}{\partial T} + \eta^\alpha = 0 \). We will make the simplifying assumption that

\[ \frac{\partial A^\alpha}{\partial T} = -\eta^\alpha, \quad \forall \alpha = l, s. \]  

(3.36)

In equation (3.34) the partial derivatives are taken while holding the volume fraction times density terms fixed, which means that these terms can be moved inside the partial. Defining the total Helmholtz free energy as \( A_T = \varepsilon^l \rho^l A^l + \varepsilon^s \rho^s A^s \), we can write (3.34) as

\[ \frac{\partial A_T}{\partial E^s} = 0. \]  

(3.37)
This means that the total Helmholtz free energy is not a function of $\dot{E}^s$. Equation (3.35) contains an $N^{th}$ component dependence and will be used later to obtain an equilibrium result for $\mu^{\alpha j}$.

### 3.2.1.2 Equilibrium Results

We choose to define equilibrium to be when the following variables are zero:

$$\dot{\varepsilon}^I, \dot{d}^I, \dot{E}^s, \dot{v}^{l,s}, \dot{v}^{\alpha j,\alpha}, \nabla \dot{v}^{l,s}, \dot{\varepsilon}_{\beta}^{\alpha j}, \nabla T.$$ 

At equilibrium the total entropy of the system is maximum and the net generation of entropy is minimum. Thus $\frac{\partial A}{\partial x} = 0$ and $\frac{\partial A}{\partial y} \geq 0$, where $x$ and $y$ are variables in the list (3.38). Hence, we obtain the following results:

$$\bar{p}^I = \bar{p}^s,$$ 

$$t^I = -p^I I,$$ 

$$t^s = -p^s I + t^{se} + \dot{\varepsilon}^I t^{sk},$$ 

$$\sum_{\alpha} \varepsilon^{l} q^{\alpha} = 0,$$ 

$$\tilde{T}^l_\alpha = \bar{p}^l (\nabla \varepsilon^l) - \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial \dot{E}^s} \nabla \dot{E}^s + \frac{\partial A^l}{\partial \dot{E}^s} \nabla \dot{E}^s \right),$$ 

$$\tilde{T}_\beta^{\alpha j} + \tilde{t}_\beta^{\alpha j} - \rho^{\alpha j} \left( \tilde{T}_\beta^{\alpha N} + \tilde{t}_\beta^{\alpha N} \right) = -\varepsilon^{\alpha} t^{\alpha N} \nabla \left( \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \right),$$ 

$$(\mu^{\alpha j} - \mu^{\alpha N}) \nabla (\varepsilon^{\alpha} \rho^{\alpha j}) - \nabla (\varepsilon^{\alpha} \rho^{\alpha j} (A^{\alpha j} - A^{\alpha N})).$$
\[ \rho_j^i \left( \mu_j^i - \mu_{iN}^i \right) I + t_j^i - \frac{\rho_j^i}{\rho_{iN}^i} t_{iN}^i - \rho_j^i (A_j^i - A_{iN}^i) I = 0, \quad (3.45) \]

\[ \mu_s^i = \mu_j^i. \quad (3.46) \]

Equation (3.39) says that at equilibrium the thermodynamic pressures in the liquid and solid phases are equal. The next equation says that the stress in the liquid phase is a scalar multiple of the identity. Equation (3.41) says that the stress in the solid phase is a scalar multiple of the identity and contains the effective and hydration stresses. Equation (3.42) states that the total heat flux of the system is zero at equilibrium. In equation (3.43) the last term in round brackets is new and is due to including \( \dot{E}^s \) as a constitutive independent variable.

Equations (3.44) and (3.47) contain an \( N^{th} \) component dependence and which will be discussed shortly. Finally, we used restriction (2.25) to obtain equation (3.46), which is the classical thermodynamic result that, at equilibrium, the chemical potential of a species in two different phases is equal.

To obtain an equilibrium equation for \( \mu_s^i \), first note that the non-equilibrium equation (3.35) contains an \( N^{th} \) component dependence. This implies that the way in which the species are ordered matters. To remove this dependence, sum (3.35) from \( j = 1 \) to \( N \) and use equations (3.27) and (3.28) to obtain

\[ \frac{t_s^i}{\rho_s^i} + \frac{1}{\rho_s^i} \sum_{j=1}^{N} \rho_s^j v_{s_j}^s v_{s_j}^s + \frac{\rho_s^i}{\rho_{iN}^s} I = \frac{t_{iN}^i}{\rho_{iN}^s} - A_{sN}^i I + \mu_{sN}^i I. \quad (3.47) \]

Substituting the equilibrium expression (3.41) for \( t_s^i \) into (3.47) and noting that at equilibrium \( v_{s_j}^s = 0 \) yields

\[ \frac{t_{sN}^i}{\rho_{sN}^i} - A_{sN}^i I - \mu_{sN}^i I = \frac{t_{se}^i}{\rho_s^i} + \frac{\varepsilon_s^i}{\rho_s^i} t_{se}^i. \quad (3.48) \]
Substituting (3.48) into equation (3.35) results in an equilibrium expression for \( \mu^{ij} \):

\[
\mu^{ij} I = A^{ij} I - \frac{t^{ij}}{\rho^2} + \frac{t^{se}}{\varepsilon^s \rho^s} t^{sk}.
\]  \hspace{1cm} (3.49)

Similarly, we want to remove the \( N^{th} \) component dependence from equation (3.45) to obtain an equilibrium relation for \( \mu^{lj} \). First, sum (3.45) from \( j = 1 \) to \( N \), divide by \( \rho^l \), then use (3.27), (3.28) and (3.40) to obtain

\[
\mu^{lj} I = A^{lj} I - \frac{t^{lj}}{\rho^l}.
\]  \hspace{1cm} (3.50)

This equation implies that the shear components of \( t^{lj} \) must be zero. This makes sense when we recall that equation (3.40) implies that the stress in the liquid phase is a scalar multiple of the identity.

Equation (3.44) also contains an \( N^{th} \) component dependence. Because \( u^{\alpha ij} = 0 \) at equilibrium, equation (2.37) becomes \( \sum_{j=1}^{N} \tilde{\tau}^{\alpha j} = 0 \), and (B.13) reduces to \( \tilde{T}^{\alpha}_{\beta} = \sum_{j=1}^{N} \tilde{\tau}^{\alpha j}_{\beta} \). Thus, when we sum equation (3.44) from \( j = 1 \) to \( N \) we obtain

\[
\tilde{T}^{\alpha}_{\beta} = \frac{\rho^\alpha}{\rho^N} \left( \tilde{T}^{\alpha N}_{\beta} + \tilde{\tau}^{\alpha N} \right) - \sum_{j=1}^{N} \mu^{\alpha j} \nabla \left( \varepsilon^{\alpha \rho^{\alpha j}} \right) - \varepsilon^{\alpha \rho^{\alpha N}} \nabla \left( \frac{\rho^\alpha}{\rho^N} \right)
\]

\[
- \nabla \left( \varepsilon^{\alpha \rho^{\alpha}} \left( A^{\alpha} - A^{\alpha N} \right) \right)
\]  \hspace{1cm} (3.51)

Now, taking \( \alpha = l \) and \( \beta = s \), using (3.27), (3.43) and

\[
\nabla A^l = \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l + \sum_{j=1}^{N} \frac{\partial A^l}{\partial (\varepsilon^j \rho^j)} \nabla \left( \varepsilon^j \rho^j \right) + \frac{\partial A^l}{\partial T} \nabla T + \frac{\partial A^l}{\partial E^s} \nabla E^s + \frac{\partial A^l}{\partial E^s} : \nabla \dot{E}^s,
\]  \hspace{1cm} (3.52)
which comes from using equation (3.11), we obtain the following equilibrium result:

$$\hat{T}_i^{lj} + \hat{i}^l = \mu^{lj} \nabla(e^l \rho^j) - \nabla(e^l \rho^j A^l_j).$$  \hspace{1cm} (3.53)

The above equation is an equilibrium relation for the right hand side. We will not be using this equation, thus a discussion of it is beyond the scope of this paper, but we include it here for completeness.

### 3.2.1.3 Near-Equilibrium Results

The coefficients of the variables that are zero at equilibrium (equilibrium variables) are a function of these variables. In other words, if $z_j$ are the equilibrium variables and $f_i$ are the corresponding coefficients, then for each $i$ we have $f_i(z_j)$. We linearize the coefficients to form positive quadratic terms by using a Taylor series expansion about the equilibrium variables. We truncate all second order and higher terms. For this reason the results hold only near equilibrium. Additionally, we can perform a Taylor series expansion of each of the coefficients about one or more equilibrium variables. This method of obtaining near-equilibrium results within the context of HMT was clarified by Singh et al. in [41].

We choose to perform a one variable expansion for all of the equilibrium variables in (3.38) except for $\nabla \mathbf{T}$, $\mathbf{E}^i$, and $d^i$, for which we will perform a two variable expansion.

Performing a single variable expansion for $\varepsilon^i$, $v^i$, $v^i_{\beta^j}$, $\nabla \cdot v^i_{\beta^j}$, and $\varepsilon^i_{\beta^j}$ we obtain the following near-equilibrium relationships:

$$\bar{p}^i - \bar{p}^s = \eta \varepsilon^i;$$  \hspace{1cm} (3.54)
\[ \mathbf{T}_s^l = -\mathbf{R} \cdot \mathbf{v}^N + \bar{p}^l (\nabla \varepsilon^l) \]

\[-\varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial E_s^0} (\nabla E^0_s) + \frac{\partial A^l}{\partial E^s} (\nabla \dot{E}^s) \right) - \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial T} + \eta^l \right) (\nabla T), \quad (3.55) \]

\[ \mathbf{T}_s^{lj} + \mathbf{t}_s^j = -\mathbf{R}^j \cdot \mathbf{v}^{l,j} + \mu^j \nabla (\varepsilon^l \rho^j) - \nabla (\varepsilon^l \rho^l A^{lj}), \quad (3.56) \]

\[ \mu^{lj} \mathbf{I} = C^{lj} : \nabla \mathbf{v}^{l,j} + A^{lj} \mathbf{I} - \frac{t^{lj}}{\rho^j}, \quad (3.57) \]

\[ \mu^{lj} - \mu^j = S^j \dot{\varepsilon}_s^{lj}. \quad (3.58) \]

In the above equations $\mathbf{R}$, $\mathbf{R}^j$, $C^{lj}$, and $S^j$ are the linearization coefficients. Both $\mathbf{R}$ and $\mathbf{R}^j$ are second order tensors, $C^{lj}$ is fourth order, and $S^j$ is a scalar. In equation (3.54) $\eta$ is a scalar variable. This equation states that the rate at which the polymer takes on liquid is governed (at least near equilibrium) by the difference in the thermodynamic pressures of the two phases. When the time rate of change of the volume fraction of the liquid phase is zero we recover the equilibrium relation (3.39) as expected. Equations (3.55) through (3.57) are constitutive relationships and interpretation of them is beyond the scope of this paper. The last term in brackets in equation (3.55) becomes zero after applying the non-equilibrium result (3.36). Equation (3.58) says that mass transfer of a constituent is governed by the differences in the chemical potentials of that constituent in each phase. Solid phase diffusion is assumed to be negligible, so there is no result for $\mathbf{v}^{s,j,s}$.

Next we perform a two-variable expansion of the coefficients of $\nabla T$ and $\dot{E}^s$ about $t^{s,j}$ and the coefficient of $\nabla T$. Set the coefficient of $\nabla T$ for the solid phase
equal to $Q^s$ and consider the standard decomposition

$$\left( \sum_{j=1}^{N} t^{s_j} \right)_{\text{neq}} = \left( \sum_{j=1}^{N} t^{s_j} \right)_{\text{eq}} + \left( \sum_{j=1}^{N} t^{s_j} \right)_{\text{diss}}, \tag{3.59}$$

where the subscripts $\text{eq}$, $\text{neq}$, and $\text{diss}$, mean equilibrium, non-equilibrium, and dissipative, respectively. Substituting $Q^s$ and equation (3.59) into the corresponding terms of the entropy inequality we find

$$\frac{\dot{\varepsilon}}{T} F^{-1} \cdot \left( \sum_{j=1}^{N} t^{s_j} \right)_{\text{diss}} \cdot F^{-T} : \dot{E}^s + \frac{\dot{\varepsilon}}{T^2} Q^s \cdot \nabla T \geq 0. \tag{3.60}$$

We now linearize to obtain

$$\left( \sum_{j=1}^{N} t^{s_j} \right)_{\text{diss}} = F \cdot G^s \cdot \dot{E}^s \cdot F^T + H^s \cdot \nabla T, \tag{3.61}$$

$$Q^s = K^s \cdot \nabla T + F \cdot J^s : \dot{E}^s. \tag{3.62}$$

$G^s$ is a fourth order tensor representing the effect of strain rate on stress due to relaxation processes within the solid phase. $H^s$ is a third order tensor that causes the thermal gradients to affect the stress inside the anisotropic solid phase. $J^s$ is a third order tensor that represents heat flux in the anisotropic solid due to strain rate, and $K^s$ is a second order tensor representing heat flux in the solid due to the thermal gradient. Symmetry relationships follow due to the symmetry of the stress tensor and strain rate. Substituting (3.36) and (3.61) into (3.59), and (3.62) into $Q^s$, respectively, we obtain

$$t^s = -p^s I + t^{sc} + \frac{\dot{\varepsilon}}{\varepsilon^s} t^{sh}$$

$$+ F \cdot G^s \cdot F^T : \dot{E}^s + H^s \cdot \nabla T - \sum_{j=1}^{N} \rho_j \theta_j \delta_{ij} \delta_{ij} \delta_{ij}. \tag{3.63}$$
\[ q^s = K^s \cdot \nabla T + F \cdot J^s : \dot{E}^s \]
\[ - \sum_{j=1}^{N} \left[ t^{s_j} \cdot v^{s_j,s} - \rho^{s_j} v^{s_j,s} \left( A^{s_j} + \frac{1}{2} (v^{s_j,s})^2 \right) \right]. \quad (3.64) \]

Similarly, we perform a two-variable expansion of the coefficients of \( \nabla T \) and \( \mathbf{d}' \) about these variables to obtain
\[ t^l = -p^l I + H^l \cdot \nabla T + L^l : \mathbf{d}' - \sum_{j=1}^{N} \rho^{l_j} v^{l_j,l} v^{l_j,l}, \quad (3.65) \]
\[ q^l = K^l \cdot \nabla T + M^l : \mathbf{d}' \]
\[ + \sum_{j=1}^{N} \left[ t^{l_j} \cdot v^{l_j,l} - \rho^{l_j} v^{l_j,l} \left( A^{l_j} + \frac{1}{2} (v^{l_j,l})^2 \right) \right], \quad (3.66) \]

where \( H^l \) is a third order tensor representing the stress in the liquid phase due to the thermal gradient, \( L^l \) is a fourth order tensor representing the effect on stress due to the rate of deformation, \( K^l \) is a second order tensor representing the heat flux due to the thermal gradient, and \( M^l \) is a third order tensor representing the heat flux due to rate of deformation. As before, symmetry relationships follow.

To obtain a near-equilibrium result for \( \mu^{s_j} \), substitute (3.63) into (3.47) to get
\[ \mu^{s_j} I = A^{s_j} I - \frac{t^{s_j}}{\rho^{s_j}} \]
\[ + \frac{1}{\rho^s} \left( t^{s_e} + \varepsilon^l t^{s_h} + F \cdot G^s F^T : \dot{E}^s + H^s \cdot \nabla T \right). \quad (3.67) \]

This form of the solid-phase chemical potential was first reported by Singh et al. [41]. The term containing the time rate of strain of the solid phase, \( \dot{E}^s \), is new. This implies in polymeric systems \( \mu^{s_j} \) is dependent on the strain rate of the solid phase.
4. Derivation of a Model of a Simple Polymer/Solvent System

We are interested in further simplifying our system to a two-phase, single constituent per phase system, so that we might gain insight to the applicability of this theory. The reader may ask if such systems are of interest in the scientific community. As an example of one such system consider the Poly(methyl methacrylate)-methanol (PMMA), which has a wide variety of applications. PMMA is used as a glass replacement (Plexiglas), it is found in acrylic latex paints and lubricating oils for machinery. Technically, PMMA is an amorphous polymer. As mentioned in the introduction, amorphous polymers have long chains of molecules that tend to coil about themselves. For this reason amorphous polymers tend to be flexible and hold together well when stressed. The chemical resistance of PMMA to acids is good, to alkalis is excellent, and to solvents, such as methanol, is poor. This means that acids have a difficult time penetrating PMMA, while solvents penetrate PMMA quite easily. The entangled nature of PMMA produces swelling behavior when put in a solvent like methanol. Additionally, there are existing models on the PMMA-methanol system, [43].

The remainder of this section will be organized in the following manner. First we will make the appropriate assumptions for our entropy inequality to be consistent with the system described above. This will greatly reduce the complexity of the entropy inequality (3.17). Next, we will exploit the resulting entropy inequality to obtain non-equilibrium, equilibrium, and near-equilibrium
results, as we did in the previous chapter. Following this, we propose an experiment, list the relevant equations, and reduce the system to one that should be solvable.

4.0.2 Assumptions and Entropy Inequality for a Simple Polymer/Solvent System

A species is a compound that cannot be broken down into smaller pieces by the system. We assume there is exactly one species per phase where the solid phase is the polymer. This results in a greatly simplified system. First, the diffusive velocity of the $j^{th}$ component in the $\alpha$-phase is zero. This is because there is only one component per phase and it constitutes the entire phase. For the same reason the gradients of the diffusive velocities, $\nabla v^{\alpha;j}$, are also zero. Both $\bar{\epsilon}_\beta^\alpha$ and $\bar{\tau}_\beta^{aj}$ are zero because there will be no mass transfer between species or phases. Additionally, $\bar{\tau}^{aj}$ is also zero because chemical reactions within a phase with only one constituent cannot produce more or less of that constituent.

Having made these assumption we arrive at the following entropy inequality:

\[
\begin{align*}
\Lambda &= -\sum_\alpha \frac{\varepsilon^\alpha \rho^\alpha}{T} \left( \frac{\partial A^\alpha}{\partial T} + \eta^\alpha \right) \frac{D^s T}{Dt} - \frac{1}{T} \left( \bar{p}^a - \bar{p}^l \right) \varepsilon^l \\
&\quad - \frac{1}{T} \mathbf{F}^{-1} \cdot \left[ \left( \varepsilon^s \rho^s \mathbf{I} - \varepsilon^s \mathbf{t}^{se} - \varepsilon^l \mathbf{t}^{sh} + \varepsilon^s \mathbf{t}^s \right) \right] \cdot \mathbf{F}^{-T} : \dot{\mathbf{E}}^s \\
&\quad + \frac{\varepsilon^l}{T} \left( p^l \mathbf{I} + t^l \right) : \mathbf{d}^l - \frac{1}{T} \left( \varepsilon^s \rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} \right) \dot{\mathbf{E}}^s \\
&\quad + \frac{\nabla_T}{T^2} \sum_\alpha \varepsilon^\alpha q^\alpha - \frac{1}{T} \left[ \bar{p} \left( \nabla \varepsilon^l \right) + \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial \mathbf{E}^s} \left( \nabla \mathbf{E}^s \right) + \frac{\partial A^l}{\partial \mathbf{E}^s} \left( \nabla \dot{\mathbf{E}}^s \right) \right) \right] \\
&\quad \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial T} + \eta^l \right) \left( \nabla T \right) + T^l \right] v^{l,s} \geq 0. \tag{4.1}
\end{align*}
\]
4.0.3 General Non-Equilibrium Results

The following variables are neither constitutive nor independent and can vary arbitrarily.

\[ \dot{E}^s, \frac{D^s T}{Dt}, \]

(4.2)

If the entropy inequality is to hold for all possible processes their coefficients must be identically equal to zero. This results in the following set of non-equilibrium relations:

\[ \sum_{\alpha} \varepsilon^\alpha \rho^\alpha \left( \frac{\partial A^\alpha}{\partial T} + \eta^\alpha \right) = 0 \]  

(4.3)

\[ \varepsilon^s \rho^s \frac{\partial A^s}{\partial E^s} + \varepsilon^l \rho^l \frac{\partial A^l}{\partial E^s} = 0 \]  

(4.4)

Both of these equations are identical to those obtained in Section 3.2.1.1.

4.0.4 Equilibrium Results

The equilibrium variables for this system are the variables in (3.38) that still appear in equation (4.1). They are:

\[ \dot{\varepsilon}, \dot{E}^s, d^l, v^{l,s}, \nabla T. \]  

(4.5)

Using the same argument given in Section 3.2.1.2 we obtain the following results:

\[ \bar{p}^s = \bar{p}^l \]  

(4.6)

\[ t^s = -p^s I + t^{se} + \frac{\varepsilon^t}{\varepsilon^s} t^{sh} \]  

(4.7)

\[ t^l = -p^l I \]  

(4.8)

\[ T^l_s = \bar{p}^l (\nabla \varepsilon) - \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial E^s} (\nabla E^s) + \frac{\partial A^l}{E^s} (\nabla \dot{E}^s) \right) \]  

(4.9)

\[ \sum_{\alpha} \varepsilon^\alpha q^\alpha = 0 \]  

(4.10)
These are the same equations that appear in Section 3.2.1.2 without the equations in that section that give results for $\mu^l_j, \mu^s_j,$ and $\hat{T}_s^l + \epsilon^l_j$. Because there is only one constituent per phase it does not make sense to talk about the chemical potential of species. However, it does make sense to talk about the chemical potential of a phase. This will be discussed in greater detail in later sections.

4.0.5 Near-Equilibrium Results

Near-equilibrium results are obtain as described in Section 3.2.1.3. Performing a single variable expansion for $\dot{\varepsilon}^s$ and $\mathbf{v}^{l,s}$, we obtain the following near-equilibrium relationships:

\[ \overline{\rho}^l - \overline{\rho}^s = \eta \dot{\varepsilon}^s \]  \hspace{1cm} (4.11)

\[ \mathbf{T}_s^l = -R \cdot \mathbf{v}^{l,s} + \overline{\rho}^l(\nabla \mathbf{v}^l) - \varepsilon^{l} \rho^{l} \left( \frac{\partial A^l}{\partial E^s}(\nabla E^s) + \frac{\partial A^l}{\partial E^l}(\nabla E^l) \right) \]
\[ -\varepsilon^{l} \rho^{l} \left( \frac{\partial A^l}{\partial T} + \eta^l \right)(\nabla T). \]  \hspace{1cm} (4.12)

Both equations (4.11) and (4.12) appear exactly as they do in Section 3.2.1.3. Thomas and Windle [43] investigate a similar system as the one under consideration here in and empirically obtain $\eta$ as $\eta^0 e^{[-M \varepsilon^l / \varepsilon_m]}$ for polymer solvent systems at a fixed temperature below its glassy-transition temperature, $T_g$, and refer to it as the viscosity coefficient. In this equation $\eta^0$ is the viscosity of the polymer when the volume fraction of the liquid phase is zero, $M$ is a constant, and $\varepsilon_m$ is the maximum value that $\varepsilon^l$ can attain and occurs when the polymer is saturated. Achanta [1] suggests that both $\eta^0$ and $M$ are highly dependent on temperature because amorphous polymers exhibit a wide range of behavior dependent on temperature. For our purposes we will adopt the assumptions of
Thomas and Windle described above. In equation (4.12), $\mathbf{R}$ is a second order tensor. As before, the last term in round brackets will vanish when we employ (3.36).

Next we perform a two-variable expansion of the coefficients of $\nabla T$ and $\dot{E}^s$ about these variables and obtain

$$t^s = -\rho^s I + t^{sc} + \frac{\xi^l}{\xi^s} t^{sh} - F' \cdot G' \cdot F'^T \cdot \dot{E}^s - H^s \cdot \nabla T. \quad (4.13)$$

$$q^s = F' \cdot J' \cdot \dot{E}^s + K^s \cdot \nabla T, \quad (4.14)$$

In the above equations $G^s$, $H^s$, $J^s$ and $K^s$ retain the same meaning they were given in Section 3.2.1.3. In fact, equations (4.13) and (4.14) differ from equations (3.63) and (3.64), respectively, only in that they contain no terms with diffusive velocities.

Performing a two-variable expansion of the coefficients of $\nabla T$ and $d^l$ about these variables we obtain

$$t^l = -\rho^l I + H^l \cdot \nabla T + L^l : d^l \quad (4.15)$$

$$q^l = q^l + K^l \cdot \nabla T + M^l : d^l, \quad (4.16)$$

where $H^l$, $K^l$, $M^l$, and $L^l$ also retain the meanings that they were given previously. Again, the only way that they differ from their previously obtained counterparts is that they contain no diffusive velocities.
4.0.6 Total Stress and Total Heat Flux

Following [10] we define the total stress and particle pressure as

\[ t = \varepsilon^s t^s + \varepsilon^l t^l, \]  
and

\[ p = \varepsilon^s p^s + \varepsilon^l p^l, \]  
respectively.

Substituting (4.13) and (4.15) into (4.17) and using (4.18) we obtain

\[ t = -pI - \varepsilon^s \left( \rho^s I + t^{ss} + \frac{\varepsilon^l}{\varepsilon^s} t^{sh} - G^s : \dot{E}^s_{K,K} x_{l,I,L}^s - H^s : \nabla T \right) \]

\[ + \varepsilon^l \left( H^l \cdot \nabla T + L^l : d^l \right) \]  
(4.19)

for the total stress in a particle. Similarly, we define the total heat flux of a particle to be

\[ q = \varepsilon^s q^s + \varepsilon^l q^l. \]  
(4.20)

Substituting (4.14) and (4.16) into (4.20) and using (4.10) we obtain

\[ q = \varepsilon^l \left( K^l \cdot \nabla T + M^l : d^l \right) + \varepsilon^s \left( K^s \cdot \nabla T + J^s : \dot{E}^s \right). \]  
(4.21)

4.0.7 Generalized Darcy’s Law

To obtain Darcy’s law, we begin with the conservation of momentum for the bulk phase, equation (2.36), neglect the inertial term, and substitute in equations (4.12) and (4.15). We then have

\[ R \cdot v^{l,s} = \nabla (\varepsilon^l p^l) - \nabla (\varepsilon^l (H^l \cdot \nabla T)) - \nabla (\varepsilon^l (L^l : d^l)) - \varepsilon^l \rho g^l \]

\[ + \frac{\partial}{\partial t} (\nabla \varepsilon^l) - \varepsilon^l \rho \left( \frac{\partial A^l}{\partial E^s} (\nabla E^s) + \frac{\partial A^l}{\partial \dot{E}^s} (\nabla \dot{E}^s) \right). \]  
(4.22)
This equation was originally obtained by Singh et al. [41]. \( \mathbf{R} \) is called the resistivity tensor, and we assume it is diagonalizable and invertible. Furthermore, \( \mathbf{R}^{-1} = \mathbf{K} \), where \( \mathbf{K} \) is the conductivity tensor. We will be simplifying this equation in a subsequent section, and so we leave physical interpretation for later.

4.0.8 A First Approximation

In this section we make further simplifying assumptions with the goal of arriving at a system that is solvable. To do this we will need several tools. In Section 3.2.1 we listed several definitions, including chemical potential, classical pressure, thermodynamic pressure, and swelling potential. We restate them here, as they relate to the problem under investigation for ease of exposition and clarity. The chemical potential is given by

\[
\mu^{\alpha j} = A^{\alpha} + \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} \bigg|_{\rho^{\alpha}, T}, \tag{4.23}
\]

the classical pressure, \( p^{\alpha} \), is

\[
p^{\alpha} = \sum_{j=1}^{N} \rho^{\alpha} \rho^{\alpha j} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha j}} \bigg|_{\rho^{\alpha}}. \tag{4.24}
\]

the thermodynamic pressure, \( \bar{p}^{\alpha} \), is

\[
\bar{p}^{\alpha} = -\varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \varepsilon^{\alpha j}} \bigg|_{\varepsilon^{\alpha}, \rho^{\alpha}, T}. \tag{4.25}
\]

and the swelling potential, \( \pi^{\alpha} \), is

\[
\pi^{\alpha} = \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \varepsilon^{\alpha}} \bigg|_{\rho^{\alpha}, \varepsilon^{\alpha}, T}. \tag{4.26}
\]
The last three variables are related through the following equation originally obtained by Bennethum and Weinstein, [12]:

\[ p^\alpha = \overline{p}^\alpha + \pi^\alpha. \]  

(4.27)

This relationship can be derived in the following manner. First note that we can write the Helmholtz potential of the liquid phase as

\[ A^l = A^l(\varepsilon^l, \varepsilon^l \rho^j, T, \ldots) = \overline{A}^l(\varepsilon^l, \rho^j, T, \ldots), \]  

(4.28)

that is, our two formulations coincide regardless of what combination of independent variables we use. Here the overline on the right hand side emphasized that a different combination of independent variables is being used. The total differential of \( A^l \) is given by

\[ DA^l = \frac{\partial A^l}{\partial \varepsilon^l} \varepsilon^l d\varepsilon^l + \frac{\partial A^l}{\partial \rho^j} \rho^j d\rho^j \]  

\[ = \frac{\partial \overline{A}^l}{\partial \varepsilon^l} \varepsilon^l d\varepsilon^l + \frac{\partial \overline{A}^l}{\partial \rho^j} \rho^j d\rho^j = \frac{\partial \overline{A}}{\partial \varepsilon} \varepsilon d\varepsilon + \frac{\partial \overline{A}}{\partial \rho^j} \rho^j d\rho^j + \frac{\rho^j}{\varepsilon^l} \frac{\partial \overline{A}^l}{\partial \rho^j} \varepsilon d\varepsilon. \]  

(4.29)

(4.30)

Now take the partial of equations (4.29) and (4.30) with respect to \( \varepsilon^l \) while holding \( \rho^j \) fixed to obtain

\[ \frac{\partial A^l}{\partial \varepsilon^l} = \frac{\partial A^l}{\partial \varepsilon^l} \frac{\partial \varepsilon^l}{\partial \varepsilon^l} + \frac{\partial A^l}{\partial \rho^j} \frac{\partial \rho^j}{\partial \varepsilon^l} = \frac{\partial \overline{A}}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial \varepsilon^l} + \frac{\partial \overline{A}^l}{\partial \rho^j} \frac{\partial \rho^j}{\partial \varepsilon^l} + \frac{\rho^j}{\varepsilon^l} \frac{\partial \overline{A}^l}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial \varepsilon^l}. \]  

(4.31)

After canceling the appropriate terms we have

\[ \frac{\partial A^l}{\partial \varepsilon^l} = \frac{\partial \overline{A}}{\partial \varepsilon}, \]  

(4.32)
Multiplying through by $\varepsilon' \rho'$ we recover (4.28).

Consider the following experiment. A thin polymer film is affixed to a stationary object and surrounded by solvent. Assume that changes in the volume of the polymer are due primarily to changes in the height of the polymer. Because we are interested in predicting the swelling behavior of this system, we will need Darcy's law. However, equation (4.22) is far too complicated for our present purpose. As a first approximation, we neglect gravity and all second order and higher terms. Thus, the relevant equations for the proposed experiment are

$$p^l = p^s$$  \hspace{2cm} (4.33)

$$p^l = p^l + \pi^l$$  \hspace{2cm} (4.34)

$$p^l - p^s = \eta \varepsilon'$$  \hspace{2cm} (4.35)

$$R \cdot v'^{l, s} = \bar{p}^l (\nabla \varepsilon') - \nabla (\varepsilon' p')$$  \hspace{2cm} (4.36)

$$\dot{\varepsilon}' + v'^{l, s} \cdot (\nabla \varepsilon') + \varepsilon' \nabla \cdot v'^{l, s} + \varepsilon' \nabla \cdot v^s = 0$$   \hspace{2cm} (4.37)

$$\dot{\varepsilon}^s + \varepsilon^s \nabla v^s = 0$$  \hspace{2cm} (4.38)

$$\varepsilon' + \varepsilon^s = 1,$$  \hspace{2cm} (4.39)

where equations (4.37) and (4.38) come from the mass balance for each bulk phase, (2.23) and the assumption that the density of each phase is constant. The unknowns of the system include

$$\bar{p}^l, \bar{p}^s, \pi^l, \varepsilon', v'^{l, s}, \varepsilon', \varepsilon^s, p'.$$  \hspace{2cm} (4.40)
Thus, we have six equations and eight unknowns.

As mentioned previously, equation (4.35) says that time rate of change of the volume fraction of the liquid phase is governed by the difference in the thermodynamic pressures of the two phases. Here, \( \eta \) is not considered an unknown of the system because it can be approximated by [43]

\[
\eta^0 e^{\frac{-Me^l}{\varepsilon_m^l}},
\]

(4.41)

where \( M \) is a constant, \( \varepsilon_m^l \) is the maximum volume fraction of the liquid phase, and \( \eta^0 \) is the viscosity of the dry polymer. It is this variable that accounts for the polymer structure. Consider a polymer submerged in solvent. At first, regardless of the polymer structure, the polymer is in a glassy state and polymer chains are entangled. As the polymer takes on liquid the polymer swells. If the polymer is not crosslinked, as may be the case with linear polymers, the solid phase will be unable to support tension and the pressure in the solid phase will be equal to the pressure in the liquid phase, i.e. \( p^s = p^l \). On the other hand, if the polymer is crosslinked, as in the case of network polymers, then the solid phase can support tension. The degree of crosslinking or entanglement is taken into account by \( \eta \). Initially, \( \eta \approx \eta^0 \), which means polymers with small \( \eta^0 \) like to swell, and are therefore not terribly entangled nor highly crosslinked. Polymers with large \( \eta^0 \) have more difficulty swelling, and are thus either very entangled or highly crosslinked. This can be seen by comparing the two two values of \( \varepsilon^l \) that result from using \( \eta \) greater than one, \( \eta \) less than one, and the same left hand side in equation (4.35). Using (4.41) and calculating \( M \) at equilibrium we find that \( M = -\ln(\frac{\eta}{\eta^0}) \), and because \( \eta < \eta^0 \), we know that \( M \) is always positive. According to [43] \( M \) controls the sharpness of the diffusion front, with
low values representing little to no diffusion front and high values representing a sharp diffusion front.

It has been argued in various ways [1, 41] that $\bar{p}^s \approx 0$, or at least that $\bar{p}^s \ll \pi^l$. If we adopt this assumption, and use (4.34) and (4.35) in (4.36) we arrive at the following form of Darcy’s law:

$$
R \cdot \mathbf{v}^{l,s} = -\nabla (\varepsilon^l \pi^l) - \varepsilon^l \nabla (\eta \varepsilon^l),
$$

(4.42)

which resembles the form of Darcy’s Law used by Achanta et al. [1]. An important feature of this equation is that fluid flow is dependent on both the gradient of the volume fraction of the liquid phase and the time rate of change of the same variable. Additionally, $\eta$ is a function of the volume fraction of the liquid phase. In other words, the system is highly dependent on $\varepsilon^l$.

If we think of the swelling potential, $\pi^l$, as a function of $\varepsilon^l$ only, then

$$
\nabla (\varepsilon^l \pi^l) = \frac{d(\varepsilon^l \pi^l)}{d\varepsilon^l} (\nabla \varepsilon^l).
$$

Replacing $R^{-1}$ with $K$, and using the approximation for $\eta$ given above we can rewrite (4.42) as

$$
\mathbf{v}^{l,s} = -K \left( \frac{d(\varepsilon^l \pi^l)}{d\varepsilon^l} (\nabla \varepsilon^l) + \varepsilon^l \nabla (\eta^0 \varepsilon^{(\pi - \pi^l)} \varepsilon^l) \right). \quad (4.43)
$$

Add (4.37) and (4.38) and using (4.39) we get

$$
\nabla \cdot \mathbf{v}^s = -\nabla \cdot (\varepsilon^l \mathbf{v}^{l,s}). \quad (4.44)
$$

Substituting this back into (4.37) we obtain

$$
\dot{\varepsilon}^l + (1 - \varepsilon^l) \nabla \cdot (\varepsilon^l \mathbf{v}^{l,s}) = 0 \quad (4.45)
$$

We will need to transform our system of equations from Eulerian to Lagrangian coordinates and back again because it is computationally easier to
Figure 4.1: Proposed Experiment and Corresponding Geometry
model solids in Lagrangian coordinates. See Figure 4.1 for a schematic representation of the experiment and proposed change of coordinates. Here, $z$ is the Eulerian coordinate and $Z$ is the Lagrangian coordinate. Suppose that $V$ is the Eulerian REV and that $V_s$ is the solid in the REV; then

$$
epsilon^s = \frac{V_s}{V} = \frac{A(\Delta Z)}{A(\Delta z)}, \quad (4.46)$$

where $A$ is the cross-sectional area. Taking the limit of this equation as $\Delta$ approaches zero, we have

$$\frac{\partial Z}{\partial z} = \epsilon^s = 1 - \epsilon^t. \quad (4.47)$$

This equation defines the transformation between coordinate systems.

In terms of the Eulerian coordinates (4.43) and (4.45) are

$$\nu^{l,s} = -K \left( \frac{d(\epsilon^t \pi^t)}{d\epsilon^t} \frac{\partial \epsilon^t}{\partial z} + \eta^0 \epsilon^t \frac{\partial (\epsilon^{(-M \epsilon^t / \epsilon^t)})}{\partial z} \right) \quad (4.48)$$

$$\epsilon^t + (1 - \epsilon^t) \frac{\partial (\epsilon^t \nu^{l,s})}{\partial z} = 0. \quad (4.49)$$

Because of (4.47) we can change from Eulerian to Lagrangian coordinates using

$$\frac{\partial (\cdot)}{\partial z} = \frac{\partial (\cdot)}{\partial Z} \frac{\partial Z}{\partial z} = (1 - \epsilon^t) \frac{\partial (\cdot)}{\partial Z}. \quad (4.50)$$

Thus, in Lagrangian coordinates (4.48) and (4.49) become

$$\nu^{l,s} = -K \left( (1 - \epsilon^t) \frac{d(\epsilon^t \pi^t)}{d\epsilon^t} \frac{\partial \epsilon^t}{\partial Z} + \eta^0 \epsilon^t (1 - \epsilon^t) \frac{\partial (\epsilon^{(-M \epsilon^t / \epsilon^t)})}{\partial Z} \right), \quad (4.51)$$

$$\epsilon^t + (1 - \epsilon^t)^2 \frac{\partial (\epsilon^t \nu^{l,s})}{\partial Z} = 0. \quad (4.52)$$
The primary stumbling block in this analysis is that we do not have an explicit expression for $\pi^l$ in terms of $\varepsilon^l$. In [12] the authors rigorously derive an empirical relationship originally obtained by Low [29], allowing them to derive an equation in which $\pi^l$ is explicitly dependent on the thickness of the water layers in a well-ordered clay. One of the primary assumptions that leads to this expression is that the sample of clay is assumed to be well-ordered, and therefore there is a balance of forces. This is not the case in most polymeric and biopolymeric systems. In particular, polymer gels are cross-linked, and therefore permanently entangled. Additionally, uncross-linked polymers can behave as if they are cross-linked when swelling occurs quickly. Thus, the well-ordered assumption does not apply to these systems and there is no balance of forces between the solid and liquid phases. The author still believes that it is reasonable to assume that $\pi^l$ is a strong function of $\varepsilon^l$. However, it is not clear how to measure this variable experimentally independent of the other pressures. Achanta, [1], assumes that we can use the elastic modulus of the dry polymer to approximate $\frac{d(\varepsilon^l\pi^l)}{d\varepsilon^l}$, but does not give any formal derivation.
5. Discussion and Future Work

A numerical solution to this problem that can be compared to current literature is needed. However, it is not always clear how the variables presented in this analysis, as well as others like it, are related to quantities measured in physical experiments. A clear connection needs to be made between the physical properties measured experimentally and the variables that appear in the governing equations, (e.g. $\pi^l$ in equation (4.42)) before a comparison can be made in a meaningful way. The geometry proposed in the previous chapter was chosen because it is one-dimensional and therefore $\varepsilon^l$ is easily measured. Once an equation of state is obtained for the swelling pressure, that is not a function of the equilibrium variables, the problem can be non-dimensionalized, and appropriate initial and boundary conditions can be imposed, and the problem can be solved numerically. The problem is similar to a class of moving boundary value problems known a Stefan and Stefan-Neumann boundary value problems.

In addition, there is a plethora of future work to be done with respect to diffusion, temperature dependence, phase change, and electroquasistatic problems. While Darcy’s law governs fluid flow, modeling drug delivery requires a Fickian type equation to predict diffusion of species. A generalized Fick’s law of diffusion can be obtained by substituting (3.56) and $t^l$ from (3.57) into the momentum balance (2.30). However, a detailed analysis of such an equation is beyond the scope of this work, and is left for future study. As mentioned before, polymers are highly sensitive to temperature. A model including the effects of temperature that could accurately predict the change in diffusive and swelling
behavior associated with the polymer nearing $T_g$ would constitute a major advance in polymer modeling. To this end, we would include the $\nabla T$ term (second term) of (4.22), and any other relevant equations. Entangled polymers that are not crosslinked and swollen at a reasonably slow rate will eventually disentangle and dissolve into the solvent. This is a phase change problem and is usually modeled by considering a jump in coefficients. Finally, swelling is affected by the pH of water (i.e. concentrations of hydrogen in the liquid phase) indicating that the solid phase is chargee. The foundations of the application of electroquasistatics to swelling porous media is laid out in [9, 8]. Future research in these areas is required to gain a comprehensive understanding of polymer behavior.
Appendix A. Complete Nomenclature

Superscripts, Subscripts, and Other Notations

\( \alpha_j \)  \( j^{th} \) component of \( \alpha \)-phase on mesoscale

\( \cdot \alpha \) \( \alpha \)-phase on mesoscale

\( \cdot \) denotes exchange from other interface or phase

\( \cdot_{kl} \) difference of the two quantities, i.e. \( \cdot_k - \cdot_l \)

\( \cdot_{\alpha_j} \) microscopic property of constituent \( j \) in phase [subscript] (non-averaged)

Latin Symbols

\( \delta A_{\alpha\beta} \): Portion of \( \alpha\beta \)-interface in representative elementary volume (REV)

\( A^{\alpha_j}, A^{\alpha} \): Helmholtz free energy density [J/Kg]

\( b^{\alpha_j}, b^{\alpha} \): External entropy source [J/(Kg·s·K)]

\( C^{\alpha_j} \): Mass fraction of \( j^{th} \) component [-]

\( d^{\alpha} \): Rate of deformation tensor, approximately equal to the symmetric part of \( \nu^{\alpha} \) [1/s]

\( e^{\alpha_j}, e^{\alpha} \): energy density [J/Kg]

\( \dot{e}_{\alpha\beta}^{\alpha_j} \): Rate of mass transfer from phase [subscript] to phase [superscript] per unit mass density [1/s]
\( E^\alpha: \) Strain tensor of the solid phase [-]

\( F: \) Deformation Gradient of the solid phase [-]

\( g^{\alpha i}, g^\alpha: \) External supply of momentum (gravity) [m/s^2]

\( G^\alpha: \) Fourth order tensor, effect of strain rate on stress due to relaxation processes in the solid phase

\( h^{\alpha i}, h^\alpha: \) External supply of energy [J/(Kg-s)]

\( H^i, H^\alpha: \) Third order tensors representing the effect of thermal gradients on the stress

\( \tilde{\nu}^\alpha: \) Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

\( \tilde{\nu}^\alpha: \) Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

\( J^\alpha: \) Third order tensor representing the heat flux in the anisotropic solid due to strain rate

\( K^i, K^\alpha: \) Second order tensors representing heat flux in the liquid and solid phases, respectively, due to the thermal gradient

\( K: \) Second order tensor representing the permeability of the solid matrix

\( L^\alpha: \) Fourth order tensor representing the effect on stress due to the rate of deformation [-]
\( \dot{m}^{(\alpha j)} \): Rate of angular momentum gain due to interaction with other species within the same phase per unit mass density [N-m/Kg]

\( \dot{m}^{(\alpha j)}_{\beta} \): Rate of angular momentum gain by constituent \( j \) in phase \( \alpha \) due to interaction with phase \( \beta \) [N-m/Kg]

\( M^{\alpha j} \): Rate of angular momentum gain due to the microscale angular momentum terms - see Appendix C [N-m/Kg]

\( M^I \): Third order tensor representing the heat flux due to the rate of deformation

\( n^\alpha \): Unit normal vector pointing out of \( \alpha \)-phase within mesoscopic REV [-]

\( \dot{m}^{(\alpha j)} \): Rate of gain of angular momentum of constituent \( j \) from other constituents in phase \( \alpha \) [m^2/s^2]

\( q^{(\alpha j)} \): Partial heat flux vector for the \( j^{th} \) component of phase [J/(m^2-s)]

\( q^\alpha \): Heat flux vector for phase \( \alpha \) [J/(m^2-s)]

\( \dot{Q}^{(\alpha j)} \): Rate of energy gain due to interaction with other species within the same phase per unit mass density not due to mass or momentum transfer [J/(Kg-s)]

\( \dot{Q}^{(\alpha j)}_{\beta} , \dot{Q}^{(\alpha j)}_{\beta} \): Energy transfer rate from phase [subscript] to phase [superscript] per unit mass density not due to mass or momentum transfer [J/(Kg-s)]

\( r \): Microscale spatial variable [m]
$\tau^\alpha$: Rate of mass gain due to interaction with other species within the same phase per unit mass density [1/s]

$R$: Second order tensor called the resistivity tensor

t: Time [s]

$T$: Temperature [$^\circ$K]

t$^\alpha$: Partial stress tensor for the $j^{th}$ component for phase [N/m$^2$]

$\mathbf{t}^\alpha$: Total stress tensor for the phase [N/m$^2$]

$\hat{T}_{\beta}^\alpha, \hat{T}_{\beta}^\alpha$: Rate of momentum transfer through mechanical interactions from phase [subscript] to phase [superscript] per unit mass density [N/Kg]

$\mathbf{v}^{\alpha}, \mathbf{v}^\alpha$: Velocity [m/s]

$\delta V$: Representative elementary volume (REV)

$\delta V_\alpha$: Portion of $\alpha$-phase in REV

$\mathbf{w}^{\alpha\beta}_j$: Velocity of constituent $j$ at interface between phases $\alpha$ and $\beta$ [m/s]

$\mathbf{x}$: Macroscale spatial variable [m]

Greek Symbols

$\gamma^\alpha$: Indicator function which is 1 if in mesoscopic region $\alpha$ and zero otherwise

$\varepsilon^\alpha$: Volume fraction of $\alpha$-phase in mesoscale REV [-]

$\Lambda^{\alpha\beta}$, $\Lambda^\alpha$: Entropy production per unit mass density [J/(Kg-s-$^\circ$K)]
\( \xi \): Microscale spatial variable which varies over REV for fixed \( x: r = x + \xi \) [m]

\( \eta^{(a)}, \eta^{(a)} \): Entropy [J/(Kg\cdot K)]

\( \tilde{\eta}^{(a)} \): Entropy gain due to interaction with other species within the same phase/interface per unit mass density [J/(Kg-s\cdot K)]

\( \phi^{(a)} \): Partial entropy flux vector for the \( j^{th} \) component for phase [J/(m\(^2\)-s\cdot K)]

\( \phi^{(a)} \): Total entropy flux vector for the phase [J/(m\(^2\)-s\cdot K)]

\( \tilde{\Phi}^{(a)}_{\beta}, \tilde{\Phi}^{(a)}_{\beta} \): Entropy transfer through mechanical interactions from phase [subscript] to phase [superscript] per unit mass [J/(kg-s\cdot K)]

\( \rho^{(a)} \): Partial mass density of \( j^{th} \) component of \( \alpha \)-phase [Kg/m\(^3\)] so that \( \epsilon^{(a)} \rho^{(a)} \) is the total mass of \( j^{th} \) constituent in phase \( \alpha \) divided by the volume of REV

\( \rho^{(a)} \): Mass density of \( \alpha \)-phase averaged over /\( a \)-phase [Kg/m\(^3\)]
Appendix B. Relations between Phase and Species Variables

\[ A^\alpha = \sum_{j=1}^{N} C^{\alpha_j} A^{\alpha_j} \]  \hspace{1cm} (B.1)

\[ b^\alpha = \sum_{j=1}^{N} C^{\alpha_j} b^{\alpha_j} \]  \hspace{1cm} (B.2)

\[ C^{\alpha_j} \equiv \frac{\rho^{\alpha_j}}{\rho^\alpha} \]  \hspace{1cm} (B.3)

\[ e^\alpha \equiv \sum_{j=1}^{N} C^{\alpha_j} (e^{\alpha_j} \frac{1}{2} v^{\alpha_j,\alpha} \cdot v^{\alpha_j,\alpha}) \]  \hspace{1cm} (B.4)

\[ \tilde{e}_\beta^{\alpha} \equiv \sum_{j=1}^{N} \tilde{e}_{\beta}^{\alpha_j} \]  \hspace{1cm} (B.5)

\[ g^\alpha \equiv \sum_{j=1}^{N} C^{\alpha_j} g^{\alpha_j} \]  \hspace{1cm} (B.6)

\[ h^\alpha \equiv \sum_{j=1}^{N} C^{\alpha_j} (h^{\alpha_j} + g^{\alpha_j} v^{\alpha_j,\alpha}) \]  \hspace{1cm} (B.7)

\[ \tilde{m}_{\beta}^{\alpha} \equiv \sum_{j=1}^{N} \tilde{m}_{\beta}^{\alpha_j} \]  \hspace{1cm} (B.8)

\[ M^\alpha \equiv \sum_{j=1}^{N} M^{\alpha_j} \]  \hspace{1cm} (B.9)
\[ q^\alpha = \sum_{j=1}^{N} [q^\alpha_j + t^\alpha_j \cdot v'^\alpha_j,\alpha - \rho^\alpha_j (e^\alpha_j + \frac{1}{2} v'^\alpha_j,\alpha \cdot v'^\alpha_j,\alpha) v'^\alpha_j,\alpha] \] (B.10)

\[ \hat{Q}^\alpha_\beta \equiv \sum_{j=1}^{N} [\hat{Q}^\alpha_\beta_j + \hat{T}^\alpha_\beta_j \cdot v'^\alpha_j,\alpha + \hat{e}_\beta^\alpha_j (e^\alpha_j + \frac{1}{2} v'^\alpha_j,\alpha \cdot v'^\alpha_j,\alpha)] \] (B.11)

\[ t^\alpha \equiv \sum_{j=1}^{N} (t^\alpha_j - \rho^\alpha_j v'^\alpha_j,\alpha v'^\alpha_j,\alpha) \] (B.12)

\[ \hat{T}^\alpha_\beta \equiv \sum_{j=1}^{N} (\hat{T}^\alpha_\beta_j + \hat{e}_\beta^\alpha_j v'^\alpha_j,\alpha) \] (B.13)

\[ v^\alpha = \sum_{j=1}^{N} C^\alpha_j v'^\alpha_j \] (B.14)

\[ \eta^\alpha = \sum_{j=1}^{N} C^\alpha_j \eta^\alpha_j \] (B.15)

\[ \Lambda^\alpha = \sum_{j=1}^{N} \Lambda^\alpha_j \] (B.16)

\[ \rho^\alpha = \sum_{j=1}^{N} \rho^\alpha_j \] (B.17)

\[ \phi^\alpha = \sum_{j=1}^{N} (\phi^\alpha_j - \rho^\alpha_j v'^\alpha_j,\alpha \eta^\alpha_j) \] (B.18)

\[ \hat{\Phi}^\alpha_\beta = \sum_{j=1}^{N} (\hat{\Phi}^\alpha_\beta_j + \hat{e}_\beta^\alpha_j \eta^\alpha_j,\alpha) \] (B.19)
Appendix C. Identities Needed to Obtain Entropy Equation (3.4)

\[
\sum_{j=1}^{N} \left( \frac{\varepsilon^{\alpha} \rho^{\alpha_j}}{T} \frac{D^{\alpha_j} A^{\alpha_j}}{Dt} \right) = \frac{\varepsilon^{\alpha} \rho}{T} \frac{D^{\alpha}}{Dt} + \frac{A^{\alpha}}{T} \varepsilon^{\alpha} + \sum_{j=1}^{N} \left\{ \frac{1}{T} \mathbf{v}^{\alpha_j, \alpha} \cdot \nabla (\varepsilon^{\alpha} \rho^{\alpha_j} A^{\alpha_j}) \right\}
\]

\[
+ \sum_{j=1}^{N} \left\{ \frac{A^{\alpha_j}}{T} \varepsilon^{\alpha_j} - \frac{A^{\alpha_j}}{T} \delta^{\alpha_j} \right\}
\]

\[
- \frac{\varepsilon^{\alpha} \rho^{\alpha_j}}{T} A^{\alpha_j} \left( \mathbf{\nabla} \cdot \mathbf{v}^{\alpha_j, \alpha} \right)
\]

(C.1)

\[
\sum_{j=1}^{N} \frac{\varepsilon^{\alpha} \rho^{\alpha_j}}{T} \frac{D^{\alpha_j} T}{Dt} = \frac{\varepsilon^{\alpha} \rho^{\alpha}}{T} \frac{D^{\alpha}}{Dt} + \sum_{j=1}^{N} \frac{\varepsilon^{\alpha} \rho^{\alpha_j}}{T} \eta^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{\nabla} T
\]

(C.2)

\[
\sum_{j=1}^{N} \frac{\alpha^{\alpha_j}}{T} \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j} = \sum_{j=1}^{N} \left\{ \frac{\varepsilon^{\alpha}}{T} \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j, \alpha} + \frac{\varepsilon^{\alpha}}{T} \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha} \right\}
\]

(C.3)

\[
\sum_{j=1}^{N} \sum_{\beta \neq \alpha} \Phi^{\alpha_j}_{\beta} = - \sum_{j=1}^{N} \sum_{\beta \neq \alpha} \varepsilon^{\alpha_j}_{\beta} \eta^{\alpha_j}_{\beta}
\]

(C.4)

\[
\sum_{j=1}^{N} \tilde{Q}^{\alpha_j} = - \sum_{\beta \neq \alpha} \left[ \varepsilon^{\alpha_j}_{\beta} \cdot \mathbf{v}^{\alpha_j, \alpha} + \delta^{\alpha_j}_{\beta} \left( A^{\alpha_j} + T \eta^{\alpha_j} \left( \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \right)^2 \right) \right]
\]

(C.5)

\[
\sum_{j=1}^{N} \sum_{\beta \neq \alpha} \tilde{Q}^{\alpha_j}_{\beta} = - \sum_{\alpha} \sum_{\beta \neq \alpha} \left\{ \tilde{T}^{\alpha}_{\beta} \cdot \mathbf{v}^{\alpha, \alpha} + \frac{1}{2} \varepsilon^{\alpha}_{\beta} (\mathbf{v}^{\alpha, \alpha})^2 \right\}
\]

\[
+ \sum_{j=1}^{N} \left[ \tilde{T}^{\alpha_j}_{\beta} \cdot \mathbf{v}^{\alpha_j, \alpha} + \frac{1}{2} \varepsilon^{\alpha_j}_{\beta} (\mathbf{v}^{\alpha_j, \alpha})^2 \right] \right\}
\]

\[
+ \sum_{\beta \neq \alpha} \sum_{j=1}^{N} \tilde{e}^{\alpha_j}_{\beta} (A^{\alpha_j} + T \eta^{\alpha_j})
\]

(C.6)
References


