

THREE-PHASE HYBRID MIXTURE THEORY FOR SWELLING DRUG
DELIVERY SYSTEMS

by

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Thesis directed by Associate Professor Lynn S. Bennenthum

ABSTRACT

Drug delivery systems are composed of a polymeric carrier, such as hydroxypropyl methylcellulose (HPMC), and a drug or active agent, such as naproxen, the drug found in brands names such as Aleve. When such a device is ingested, the polymer swells and the pore-space increases in size, the drug diffuses out of the device. Some of these devices are swelling-controlled, meaning that the rate of swelling is the controlling factor in release kinetics. Modeling swelling-controlled polymeric drug delivery systems presents unique problems. As the solid drug undergoes phase transfer, the density of the solid phase, composed of polymer and drug, changes. As such, the usual incompressibility condition, that the density of the solid phase does not change in time, no longer applies. To overcome this difficulty we modify a two-phase mixture theoretic model to a three-phase model where the polymer and drug are modeled as separate solid phases, and the liquid phase remains water and drug. A two-scale and three-scale theory for such a three-phase model is developed. First, it is shown how a new choice of independent variables yields a physically meaningful interpretation of the solid phase stress, pressure, and Terzaghi stress tensors. We present the

three-phase theory modeling the polymer as viscoelastic, the drug as elastic, and the liquid as a viscous fluid. We present constitutive theory, non-equilibrium results, equilibrium results, near-equilibrium results, as well as Darcy's and Fick's laws for both the two-scale and three-scale scenarios. Appropriate simplifications that are specifically applicable to swelling-controlled drug delivery systems are presented and used to combine the Darcy's and Fick's laws with the conservation of mass equations to obtain a system of equations which models the transport of the drug in terms of liquid volume fraction and the concentration of the drug in the liquid phase.

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

Signed _____
Lynn S. Bennenthum

DEDICATION

This thesis is dedicated to my mother, Suzanne Ruth Weinstein, my ex-husband, David Brown. They provided an endless supply of emotional support, without which this would not have been possible.

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1. Introduction

Porous materials consisting of a porous solid with fluid filled or gas filled pores appear in a wide variety of applications. In particular, polymers have become increasingly important in technological industries. Polymers have a myriad of applications including but not limited to: construction, agriculture, drug delivery, and food stuffs. The focus of this thesis will be on the swelling polymers - polymers that swell (shrink) upon wetting (drying) - used in drug delivery applications.

Swelling polymers exhibit a hierarchy of scales due to their complex porous structure. Herein, we develop both a two-scale and a three-scale theory for swelling polymer systems. We call these scales the microscale, mesoscale, and macroscale. Figure 1 depicts the relevant scales of polymer particle immersed in a bulk fluid.

1.1 Terminology

Before we discuss the complex interplay of forces at work in these systems, 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

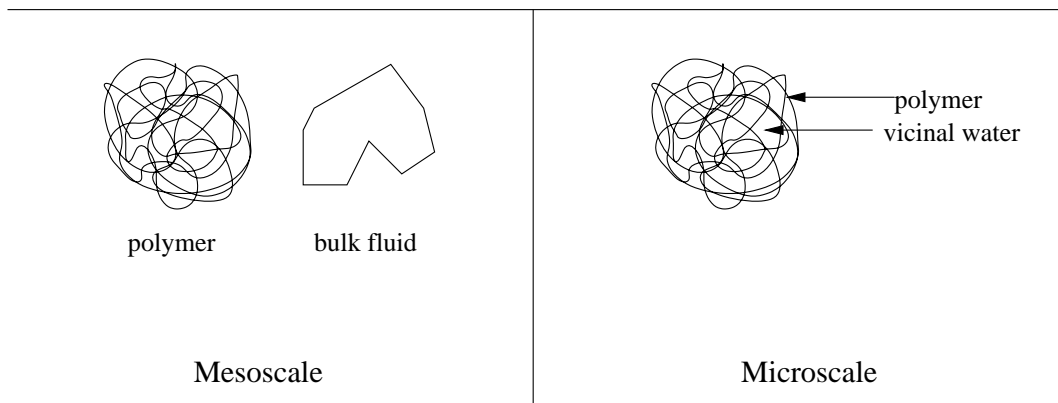
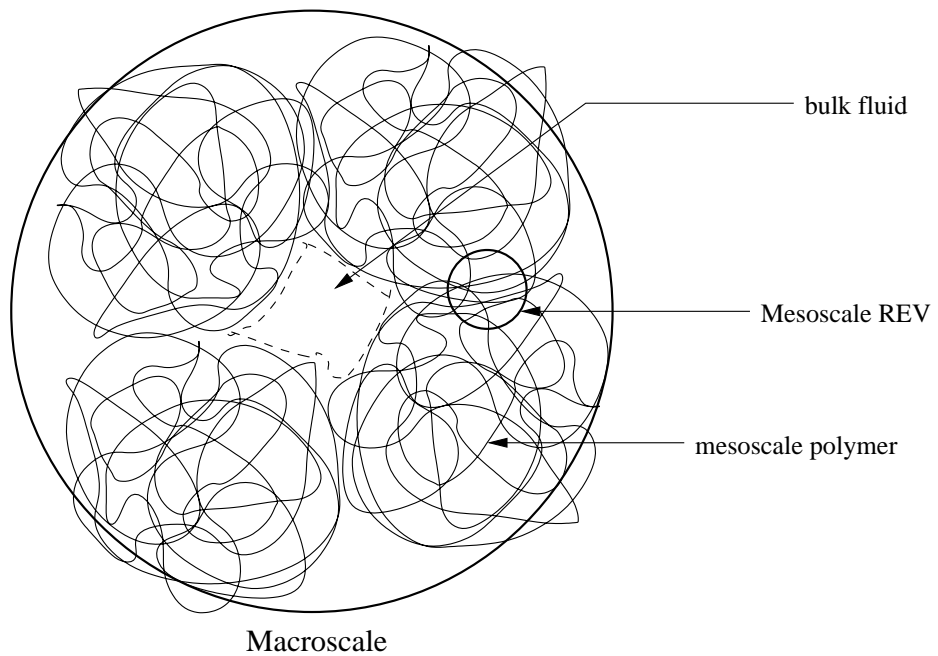


Figure 1.1: Scales of Observation

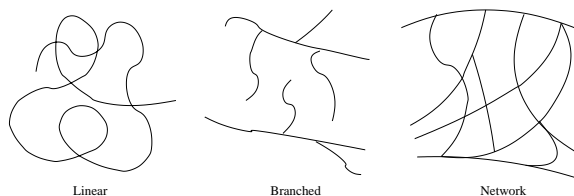


Figure 1.2: Different types of polymer molecules

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 [45, 55, 58, 54].

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 randomly with no apparent order. 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.

Polymers exhibit a wide spectrum of behavior dependent on various properties such as degree of crystallinity, crystal size, cross-linking, molecular weight of the polymer, and surrounding temperature, all of which can affect diffusive behavior. In systems with fluid filled pores on the order of $200 - 500 \text{ \AA}$, molecular diffusion occurs due to concentration gradients. In less porous systems molecular diffusion of the drug may happen throughout the entire polymer phase, and dissolution of the polymer matrix may be necessary to accomplish release of the active agent (drug). Some polymers are so highly sensitive to temperature that certain properties change almost discontinuously at a temperature, T_g , called the *glass transition temperature*, [18]. Such polymers are called thermosets. Below the glass transition temperature 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, as is the case with common glass. Above T_g polymers enter the *glass-rubber transition*, where the polymer softens. As the temperature increases polymers will enter a rubbery plateau, rubbery flow state, and finally a viscous flow state [54]. Diffusion properties of a polymer change drastically as the polymer nears T_g [36].

Hydroxypropyl methylcellulose (HMPC) is the prevalent polymer carrier used in oral drug delivery systems, [47]. Because of the hydrophilic nature of HMPC, it displays strongly time-dependent behavior when exposed to water, swelling considerably, and eventually dissolving. In a recent experiment performed by Colombo et al., [20], cylindrical disks containing HMPC and varying

initial loadings of fluorescein sodium (a water soluble dye used as a detection agent in visible images) were clamped between transparent Plexiglass slabs, introduced to water filled vessels, removed at different times, and photographed. The results showed that, depending on the initial loading of the active agent, three distinct fronts were observed. Consider figure 1.1. The swelling front is denoted by S. As water penetrates the polymer matrix it acts as a plasticizer by increasing the free volume, reducing the glass transition temperature of the system, T_g . Eventually, T_g will equal the experimental temperature, T , the polymer enters the glass transition, as discussed above, and swells. Thus, inside front S, $T_g > T$ and the polymer remains in a glassy state, and outside front S, $T_g < T$ and the polymer is in a swollen, rubbery state. As water penetrates the matrix, drug dissolves and diffuses out of the material. The rate at which the drug diffuses out of the material is directly proportional to the amount of water that has penetrated the material. At high enough drug loadings a diffusion front, D, is observed because when the maximum solubility of the drug is reached both dissolved drug, and non-dissolved drug (which is not available for diffusion) exist within the polymer matrix. Lastly, an erosion front, E, is observed due to polymer disentanglement caused by the molecular-level snake like motion of the polymer chains (reptation) [47]. The effects of the erosion front on release kinetics depends largely on whether or not all of the drug has diffused out of the polymer matrix by the time the erosion starts to occur. The effects of the erosion front become of greater concern in systems where the drug has a low solubility. Then the dissolution of the polymer matrix becomes the controlling factor in release kinetics.

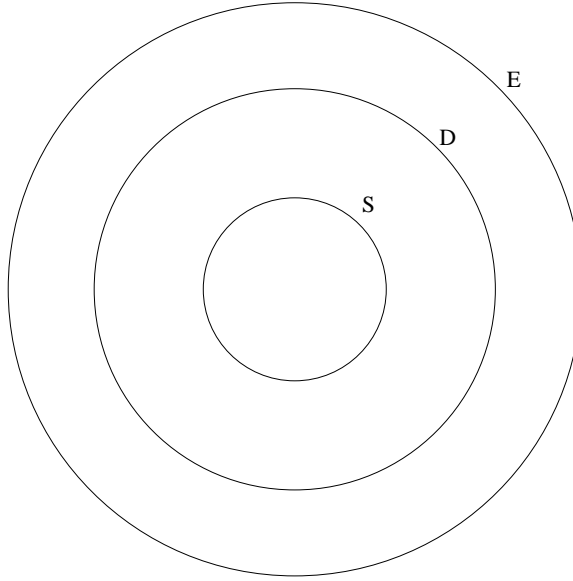


Figure 1.3: Observed Fronts

1.2 Previous Work

Traditional models of drug delivery systems begin with a concentration form of Fick's law of diffusion, such as

$$\mathbf{q} = -D_{eff}\nabla C, \quad (1.1)$$

where \mathbf{q} is the mass flux and C is the concentration of the active agent. Depending on the type of system modeled and geometry, Fick's law is modified accordingly. Classical models use the effective diffusion coefficient

$$D_{eff} = D_{iw} \frac{\epsilon}{\tau}, \quad (1.2)$$

where D_{iw} is the diffusion coefficient of the drug when the pores are filled with a solution of the drug, ϵ is the porosity, and τ is the tortuosity. The diffusion

coefficient can be modified by considering it as the mutual diffusion of the drug in the polymer, which measures the change in the concentration of a species from its average concentration with respect to time, the diffusion of the drug alone, or making it concentration dependent. The primary problem with these variations is that they are of limited applicability since they only apply to Fickian diffusion phenomena [43]. For swelling-controlled drug delivery systems, it is well known that non-Fickian diffusion occurs when polymers enter the glass-rubber transition [36]. Various authors have expanded the Fickian model to account for anomalous behavior, but these extensions are largely heuristic [43]. More rigorous mechanistic models exist, such as that proposed in [48]. However, they assume a priori that the diffusion coefficient of the drug is a function of the water content (liquid volume fraction) of the system to capture the dependency of the rate of drug dissolution on water content. Our analysis will show that a gradient in volume fraction should be used to account for this behavior.

The author notes here that it is common in the drug delivery literature for authors to refer to equations for the fluid phase penetration into the polymer as Fick's law. The bulk fluid is made up of species including: water, active agent, and perhaps dissolved polymer. We will adopt the hydrology convention and use Fick's law to refer to diffusion of these species within the fluid phase, and use Darcy's law to refer to penetration of the bulk fluid into the polymer matrix.

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, [27]. 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. [36], address the problem using continuum thermodynamics. However, they do not have a variable that directly accounts for the moisture content of the polymer. Low [34] 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. [49, 50, 51]. 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.

HMT consists of averaging the microscopic conservation and balance equations (mass, momentum, energy) to obtain macroscale analogues, then applying Bowen's continuum theory of mixtures to obtain constitutive relationships [15, 16, 17] by exploiting the entropy in the sense of Coleman and Noll [19]. The approach was pioneered by Hassanizadeh and Gray in a series of papers [29, 30, 31]. 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 role in the mesoscopic and macroscopic behavior [2, 7, 8, 12, 39, 40, 41, 42, 49, 50, 51]. Most of these works assumed that the solid phase is composed of an elastic material and a viscous liquid phase at the microscale. Using HMT the resulting macroscopic models exhibited viscoelastic behavior due to phase interactions. In [50, 51], a model was developed in which the solid itself is modeled as viscoelastic, and the result-

ing bulk transport equation is an integro-differential equation in terms of the volume fraction which has been successfully used to model the drying of food stuffs.

Some the aforementioned papers [2, 7, 8] 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 [1], 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 [1], the authors derive the macroscale field equations for each phase and interface of a three-phase, multi-constituent media.

The purpose of this thesis is many fold. One of the goals of this thesis is to re-examine the assumptions used in [49] and in the process develop thermodynamic quantities which are physically meaningful. However, the primary aim of this thesis is to extend the results of Singh et al. [49, 50, 51] to include constituent transport so that we can accurately model swelling-controlled drug delivery systems using a polymer carrier such as HMPC. Doing so presents some unique problems which are outlined below and discussed in great detail throughout this thesis.

1.3 Thesis Outline

For the sake of completeness, Chapter 2 will give an overview of HMT. We will start by summarizing the averaging procedure and giving a detailed deriva-

tion of the mesoscale conservation and balance equations. We will discuss some standard assumptions, give the resulting entropy inequality, discuss how the independent variables are chosen, and clarify the process of exploiting the entropy inequality in the sense of Coleman and Noll [19] by using two demonstrative examples.

A common result of using HMT is that the thermodynamic definition of solid phase pressure does not coincide with the actual physical stress exerted on the solid phase. In Chapter 3 we present a solution this problem. First, we present the constitutive assumptions for a two-scale, two-phase system consisting of a viscoelastic solid phase and a viscous liquid phase, motivate our new choice of independent variables, and derive the entropy inequality using our new choice of independent variables. We will present only the novel results which give rise to a physically meaningful interpretation of the solid phase stress, pressure, and Terzaghi stress tensors. To show the usefulness of this new set of independent variables, we will derive a transport equation analogous to that found in [51]. Using Darcy's law and Flory-Huggins theory we will develop another transport equation specifically applicable to polymers.

A few problems arise when trying to apply two-phase HMT to drug-delivery applications. In [50], Singh et al. assume that the solid phase is incompressible, which is perfectly reasonable for the system under consideration in that paper since it was aimed at systems in which no mass transfer takes place between phases. However, when considering mass transfer of constituents between phases the incompressibility condition for the solid phase no longer holds since the density of the phase changes with time as drug leaves the solid phase. Furthermore,

experimental literature often refers to the volume fraction of drug present in the system, and unfortunately two-phase HMT has no way straight forward way of expressing this variable. Using three phases instead of two phases has the ability to overcome both of these problems. In Chapter 4 we will present the constitutive theory for a two-scale, three-phase system consisting of a viscoelastic solid (polymer), an elastic solid (drug), and a viscous fluid (bulk fluid), keeping the theory as general as possible. We will then derive the entropy inequality for this system, and present non-equilibrium, equilibrium, near-equilibrium results, as well as Darcy's and Fick's laws.

In Chapter 5 we will present the model assumptions specifically applicable to swelling-controlled drug delivery systems, using them to combine the constitutive equations with the mesoscale conservation and balance equations from the previous chapter to derive a novel bulk fluid transport equation and constituent transport equation. Additionally, we will discuss the experimental data needed to solve these equations.

In Chapter 6 we will present the constitutive theory for a three-scale, three-phase system consisting of a particle composed of viscoelastic solid, an elastic solid, a viscous fluid and two additional bulk fluids. We will then derive the entropy inequality for this system, and present non-equilibrium, equilibrium, near equilibrium results, as well as Darcy's and Fick's laws. Chapter 7 will mirror Chapter 5 but for the three-scale system. We will discuss avenues of further research in the final chapter.

2. Overview of Hybrid Mixture Theory

The purpose of this chapter is to give a comprehensive overview of 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 (conservation of mass, momentum balance, 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.

We assume that the material we are modeling has negligible interfacial effects; that is, the interface has no thermodynamic properties and is massless. As such, 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, 21]. 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 Equations

Each phase is denoted by small Greek letters (α, β, γ), and species (or constituents) are denoted by j , $j = 1, \dots, N$. In general, a subscript Greek letter indicates a macroscale quantity from that phase. Superscript minuscules indicate the constituent, so that, e.g. $\mathbf{v}^{\alpha j}$ is the macroscopic velocity of constituent j in the α -phase. A carrot over the symbol, $\hat{}$, is used to emphasize that the quantity represents a transfer from either another phase or from other constituents. A complete nomenclature for the microscale to mesoscale averaging and mesoscale variables can be found in Appendix A. 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 [28].

Additionally, we assume that there are no internal surface discontinuities, meaning that each phase is the union of several isolated simply connected volumes, [29]. Using the notation of Eringen, [24], the constituent, microscopic field equations for a given phase, α , can be stated as

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

where ρ^j is the mass density, ψ^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 $\hat{\psi}^j$ accounts for

Table 2.1: Quantities for Microscopic Field Equations

Quantity	ψ	\mathbf{i}	f	$\widehat{\psi}$	G
Mass	1	$\mathbf{0}$	0	\widehat{r}	0
Linear Momentum	\mathbf{v}	\mathbf{t}	\mathbf{g}	$\widehat{\mathbf{i}} + \widehat{r}\mathbf{v}$	0
Angular Momentum	$\mathbf{r} \times \mathbf{v}$	$\mathbf{r} \times \mathbf{t}$	$\mathbf{r} \times \mathbf{g}$	$\mathbf{r} \times (\widehat{\mathbf{i}} + \widehat{r}\mathbf{v}) - \widehat{\mathbf{m}}$	0
Energy	$e + \frac{1}{2}v^2$	$\mathbf{t} \cdot \mathbf{v} + \mathbf{q}$	$\mathbf{g} \cdot \mathbf{v} + h$	$\widehat{Q} + \widehat{\mathbf{i}} \cdot \mathbf{v} + \widehat{r}(e + \frac{1}{2}v^2)$	0
Entropy	η	ϕ	b	$\widehat{\eta} + \widehat{r}\mathbf{v}$	Λ

the influx of $\widehat{\psi}$ from all other constituents (e.g. due to chemical reactions). If the medium consists of only one constituent then $\widehat{\psi}^j$ 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 system, e is the internal energy density function, h is the external supply of energy, \mathbf{q} is the heat flux, η is the entropy density, ϕ is the entropy flux, b is the external supply of entropy, and Λ 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 [3, 38, 56, 57]. While many different methods are available [21], 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 α -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 [46, 44]. 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 [21].

Let δV denote the REV, δV_α denote the portion of the α -phase within δV , and $\delta A_{\alpha\beta}$ denote the portion of the $\alpha\beta$ interface within δV . It is assumed that δV_α and $\delta A_{\alpha\beta}$ are isolated simply connected regions. Expressing the magnitude of δV by $|\delta V|$, the volume fraction can be written as

$$\varepsilon^\alpha(\mathbf{x}, t) = \frac{|\delta V_\alpha|}{|\delta V|}, \quad (2.2)$$

so that

$$\sum_\alpha \varepsilon^\alpha = 1. \quad (2.3)$$

Letting \mathbf{r} and \mathbf{x} denote the position vector and the centroid of the REV, respectively, \mathbf{r} can be written

$$\mathbf{r} = \mathbf{x} + \boldsymbol{\xi}, \quad (2.4)$$

where $\boldsymbol{\xi}$ is the local coordinate referenced to the centroid of the REV and varies over all of δV . The indicator function for the α -phase is given by

$$\gamma_\alpha(\mathbf{r}, t) = \begin{cases} 1 & \text{if } \mathbf{r} \in \delta V_\alpha \\ 0 & \text{if } \mathbf{r} \in \delta V_\beta, \quad \beta \neq \alpha. \end{cases}$$

Then

$$|\delta V_\alpha|(\mathbf{x}, t) = \int_{\delta V} \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dv(\boldsymbol{\xi}) \quad (2.5)$$

represents the magnitude of the volume δV in the α -phase. Following Hasanizadeh and Gray [29], we make the following definitions:

$$\overline{\rho^j}^\alpha(\mathbf{x}, t) \equiv \frac{1}{|\delta V_\alpha|} \int_{\delta V} \rho^j(\mathbf{r}, t) \gamma_\alpha(\mathbf{r}, t) dv(\boldsymbol{\xi}) \quad (2.6)$$

is the average mass over $|\delta V_\alpha|$,

$$\langle \psi^j \rangle(\mathbf{x}, t) \equiv \frac{1}{|\delta V_\alpha|} \int_{\delta V} \psi^j(\mathbf{r}, t) \gamma_\alpha(\mathbf{r}, t) dv(\boldsymbol{\xi}) \quad (2.7)$$

is the volume average property of ψ^j , and

$$\overline{\psi^j}^\alpha(\mathbf{x}, t) \equiv \frac{1}{\overline{\rho^j}^\alpha |\delta V_\alpha|} \int_{\delta V} \rho^j(\mathbf{r}, t) \psi^j(\mathbf{r}, t) \gamma_\alpha(\mathbf{r}, t) dv(\boldsymbol{\xi}) \quad (2.8)$$

is the mass average property of ψ^j . We would like the mesoscale field equations to be 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 [22].

Theorem 2.1 *If $\mathbf{w}^{\alpha\beta}$ is the microscopic velocity of the interface $\alpha\beta$ and \mathbf{n}^α is the outward unit normal vector of ∂V_α indicating the integrand should be evaluated in the limit as the $\alpha\beta$ -interface is approached from the α -side then*

$$\begin{aligned} \frac{1}{|\delta V|} \int_{\delta V} \frac{\partial f}{\partial t} \gamma_\alpha dv(\boldsymbol{\xi}) &= \frac{\partial}{\partial t} \left[\frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha dv(\boldsymbol{\xi}) \right] \\ &\quad - \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_A f \mathbf{w}^{\alpha\beta} \cdot \mathbf{n}^\alpha da(\boldsymbol{\xi}) \end{aligned} \quad (2.9)$$

$$\begin{aligned} \frac{1}{|\delta V|} \int_{\delta V} \boldsymbol{\nabla} f \gamma_\alpha dv(\boldsymbol{\xi}) &= \boldsymbol{\nabla} \left[\frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha dv(\boldsymbol{\xi}) \right] \\ &\quad + \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_A f \mathbf{n}^\alpha da(\boldsymbol{\xi}) \end{aligned} \quad (2.10)$$

We now have everything we need to average equation (2.1) from the microscale to the mesoscale.

2.3 Mesoscale Field Equations

In this section we will derive the mesoscale field equations. We begin with the conservation of mass, linear momentum balance, angular momentum balance, energy balance, 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.

2.3.1 Conservation of Mass

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

$$\frac{\partial}{\partial t}(\rho^j) + \nabla \cdot (\rho^j \mathbf{v}^j) = \rho^j \widehat{r}^j. \quad (2.11)$$

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

$$\begin{aligned} \frac{\partial}{\partial t}(\varepsilon^\alpha \overline{\rho^j}^\alpha) + \nabla \cdot (\varepsilon^\alpha \overline{\rho^j}^\alpha \overline{\mathbf{v}^j}^\alpha) \\ = \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_A \rho^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da + \varepsilon^\alpha \overline{\rho^j}^\alpha \widehat{r}^{\alpha_j}. \end{aligned} \quad (2.12)$$

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

$$\frac{D^{\alpha_j}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^{\alpha_j} \cdot \nabla, \quad (2.13)$$

we obtain the mesoscopic mass balance for constituent j in phase α

$$\frac{D^{\alpha_j}(\varepsilon^\alpha \rho^{\alpha_j})}{Dt} + \varepsilon^\alpha \rho^{\alpha_j} (\nabla \cdot \mathbf{v}^{\alpha_j}) = \sum_{\beta \neq \alpha} \widehat{e}_\beta^{\alpha_j} + \widehat{r}^{\alpha_j}. \quad (2.14)$$

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}^α is the outward unit normal vector of δV_α . 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:

$$\rho^{\alpha_j} \equiv \overline{\rho^j}^\alpha \quad (2.15)$$

is the average mass over δV_a ,

$$\mathbf{v}^{\alpha_j} \equiv \overline{\mathbf{v}^j}^\alpha \quad (2.16)$$

is the mass averaged velocity,

$$\widehat{e}_\beta^{\alpha_j} \equiv \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A \rho^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \quad (2.17)$$

is the net rate of mass gained by constituent j in phase α from phase β , and

$$\widehat{r}^{\alpha_j} \equiv \varepsilon^\alpha \rho^{\alpha_j} \widehat{r}^j{}^\alpha \quad (2.18)$$

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 α , and

$$C^{\alpha_j} \equiv \frac{\rho^{\alpha_j}}{\rho^\alpha} \quad (2.20)$$

is the concentration of the j^{th} constituent in the α -phase. All other definitions of bulk phase variables are given in Appendix A. Using equations (2.19) and (2.20) in equation (2.12) we have:

$$\frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha C^{\alpha_j}) + \nabla \cdot (\varepsilon^\alpha \rho^\alpha C^{\alpha_j} \mathbf{v}^{\alpha_j}) = \sum_{\beta \neq \alpha} \widehat{e}_\beta^{\alpha_j} + \widehat{r}^{\alpha_j}. \quad (2.21)$$

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

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

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,

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

where the following restrictions apply:

$$\sum_{j=1}^N \widehat{r}^{\alpha_j} = 0 \quad \forall \alpha, \text{ and} \quad (2.24)$$

$$\sum_{\alpha, \beta \neq \alpha} \widehat{e}_\beta^{\alpha_j} = 0 \quad j = 1, \dots, N. \quad (2.25)$$

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 α from phase β is equal to the rate of mass gained by phase β from phase α , i.e. no mass is lost in the interface.

2.3.2 Linear Momentum Balance

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

$$\frac{\partial}{\partial t}(\rho^j \mathbf{v}^j) + \nabla \cdot (\rho^j \mathbf{v}^j \mathbf{v}^j) - \nabla \cdot \mathbf{t}^j - \rho^j \mathbf{g}^j = \rho^j \widehat{\mathbf{i}}^j + \rho^j \widehat{\mathbf{r}}^j \mathbf{v}^j. \quad (2.26)$$

Using the same method as for the conservation of mass equation we obtain:

$$\begin{aligned} & \frac{\partial}{\partial t}(\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha (\langle \mathbf{t}^j \rangle^\alpha + \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j} - \rho^{\alpha j} \overline{\mathbf{v}^j \mathbf{v}^j}^\alpha)) \\ & + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{g}^{\alpha j} \\ & = \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_A [\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \\ & + \varepsilon^\alpha \rho^{\alpha j} (\widehat{\mathbf{i}}^j{}^\alpha + \widehat{\mathbf{r}}^j \mathbf{v}^j{}^\alpha), \end{aligned} \quad (2.27)$$

where $\mathbf{g}^{\alpha j} \equiv \overline{\mathbf{g}^j}^\alpha$ 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:

$$\mathbf{t}^{\alpha j} \equiv \langle \mathbf{t}^j \rangle^\alpha + \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j} - \rho^{\alpha j} \overline{\mathbf{v}^j \mathbf{v}^j}^\alpha. \quad (2.28)$$

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

$$\begin{aligned} & \varepsilon^\alpha \rho^{\alpha j} \frac{\partial}{\partial t}(\mathbf{v}^{\alpha j}) + \varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \nabla \cdot (\mathbf{v}^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{g}^{\alpha j} \\ & = \sum_{\beta \neq \alpha} \left[\frac{1}{|\delta V|} \int_A [\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right. \\ & \quad \left. - \frac{\mathbf{v}^{\alpha j}}{|\delta V|} \int_A \rho^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \right] \\ & + \varepsilon^\alpha \rho^{\alpha j} (\widehat{\mathbf{i}}^j{}^\alpha - \widehat{\mathbf{r}}^j \mathbf{v}^j{}^\alpha) - \mathbf{v}^{\alpha j} \widehat{\mathbf{r}}^{\alpha j}. \end{aligned} \quad (2.29)$$

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

$$\varepsilon^\alpha \rho^{\alpha j} \frac{D^{\alpha j}}{Dt}(\mathbf{v}^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{g}^{\alpha j} = \widehat{\mathbf{i}}^{\alpha j} + \sum_{\beta \neq \alpha} \widehat{\mathbf{T}}_\beta^{\alpha j}, \quad (2.30)$$

where we have made the following definitions:

$$\begin{aligned} \widehat{\mathbf{T}}_\beta^{\alpha j} \equiv & \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \left[\int_A [\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right. \\ & \left. - \mathbf{v}^{\alpha j} \int_A \rho^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \right] \end{aligned} \quad (2.31)$$

represents the effect constituent j of phase β has on the rate of change of mechanical momentum of the same constituent in phase α , and

$$\widehat{\mathbf{i}}^{\alpha j} \equiv \varepsilon^\alpha \rho^{\alpha j} (\widehat{\mathbf{i}}^{j\alpha} + \overline{\widehat{\mathbf{r}}^j \mathbf{v}^j}^\alpha - \mathbf{v}^{\alpha j} \overline{\widehat{\mathbf{r}}^j}^\alpha) \quad (2.32)$$

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

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j}) - \nabla \cdot (\varepsilon^\alpha (\mathbf{t}^{\alpha j} - \rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha} \cdot \mathbf{v}^{\alpha j, \alpha})) - \varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{g}^{\alpha j} \\ & + 2 \nabla (\varepsilon^\alpha \rho^{\alpha j} C^{\alpha j} \mathbf{v}^{\alpha j} \cdot \mathbf{v}^\alpha) - \nabla (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha) \\ & = \sum_{\beta \neq \alpha} \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \\ & + \varepsilon^\alpha \rho^{\alpha j} (\widehat{\mathbf{i}}^{j\alpha} + \overline{\widehat{\mathbf{r}}^j \mathbf{v}^j}^\alpha). \end{aligned} \quad (2.33)$$

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

$$\begin{aligned}
& \frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^{\alpha j}) - \mathbf{v}^\alpha \frac{\partial}{\partial t}(\varepsilon^\alpha \rho^\alpha C^{\alpha j}) \\
& - \nabla \cdot (\varepsilon^\alpha (\mathbf{t}^{\alpha j} - \rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha} \cdot \mathbf{v}^{\alpha j, \alpha})) \\
& - \varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{g}^{\alpha j} + \nabla (2\varepsilon^\alpha \rho^{\alpha j} C^{\alpha j} \mathbf{v}^{\alpha j} \cdot \mathbf{v}^\alpha) \\
& - \nabla (\varepsilon^\alpha \rho^\alpha C^{\alpha j} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha) - \mathbf{v}^\alpha \nabla \cdot (\varepsilon^\alpha \rho^\alpha c^{\alpha j} \mathbf{v}^{\alpha j}) \\
& = \sum_{\beta \neq \alpha} \widehat{\mathbf{T}}_\beta^{\alpha j} + \sum_{\beta \neq \alpha} \widehat{e}_\beta^{\alpha j} \mathbf{v}^{\alpha j} + \widehat{\mathbf{i}}^{\alpha j} + \widehat{r}^{\alpha j} \mathbf{v}^{\alpha j} - \sum_{\beta \neq \alpha} \widehat{e}_\beta^{\alpha j} \mathbf{v}^\alpha - \widehat{r}^{\alpha j} \mathbf{v}^\alpha.
\end{aligned} \tag{2.34}$$

$$\tag{2.35}$$

Summing from $j = 1, \dots, N$ we obtain

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^\alpha) - \varepsilon^\alpha \rho^\alpha \mathbf{g}^\alpha = \sum_{\beta \neq \alpha} \widehat{\mathbf{T}}_\beta^\alpha, \tag{2.36}$$

where the following restrictions apply:

$$\sum_{j=1}^N (\widehat{\mathbf{i}}^{\alpha j} + \widehat{r}^{\alpha j} \mathbf{v}^{\alpha j, \alpha}) = 0 \quad \forall \alpha, \text{ and} \tag{2.37}$$

$$\sum_{\alpha, \beta \neq \alpha} (\widehat{\mathbf{T}}_\beta^{\alpha j} + \mathbf{v}^{\alpha j} \widehat{e}_\beta^{\alpha j}) = 0 \quad j = 1, \dots, N. \tag{2.38}$$

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

$$\begin{aligned}
& \frac{\partial}{\partial t}(\varepsilon^\alpha \rho^{\alpha_j} \overline{\psi^{j^\alpha}}) - \nabla \cdot (\varepsilon^\alpha (\langle \mathbf{i}^j \rangle^\alpha + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\psi^{j^\alpha}} - \rho^{\alpha_j} \overline{\mathbf{v}^j \psi^{j^\alpha}})) \\
& \quad + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\psi^{j^\alpha}}) - \varepsilon^\alpha \rho^{\alpha_j} \overline{f^{j^\alpha}} \\
& = \sum_{\beta \neq \alpha} \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \left[\int_A [\mathbf{i}^j + \rho^j \psi^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right. \\
& \quad \left. \pm \varepsilon^\alpha \overline{\psi^{j^\alpha}} \int_A \rho^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \right] \\
& \quad + \varepsilon^\alpha \rho^{\alpha_j} \overline{G^{j^\alpha}} - \varepsilon^\alpha \rho^{\alpha_j} \widehat{\psi^{j^\alpha}}, \tag{2.39}
\end{aligned}$$

where the \pm means that we are subtracting and adding this quantity as it will be needed for certain variable definitions. 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 Angular Momentum Balance

Angular momentum balance 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) to obtain

$$\begin{aligned}
& \frac{\partial}{\partial t}(\varepsilon^\alpha \rho^{\alpha_j} \overline{\mathbf{r} \times \mathbf{v}^{j^\alpha}}) + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\mathbf{r} \times \mathbf{v}^{j^\alpha}}) - \nabla \cdot (\varepsilon^\alpha \langle \mathbf{r} \times \mathbf{t}^j \rangle^\alpha \\
& \quad + \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\mathbf{r} \times \mathbf{v}^{j^\alpha}} - \varepsilon^\alpha \rho^{\alpha_j} \overline{\mathbf{v}^j (\mathbf{r} \times \mathbf{v}^j)^\alpha}) - \varepsilon^\alpha \rho^{\alpha_j} \overline{\mathbf{r} \times \mathbf{g}^{j^\alpha}} \\
& = \sum_{\beta \neq \alpha} \left[\frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\mathbf{r} \times \mathbf{t}^j + \rho^j (\mathbf{r} \times \mathbf{v}^j) (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right.
\end{aligned}$$

$$\begin{aligned}
& \pm \sum_{\beta \neq \alpha} \frac{\varepsilon^\alpha \overline{\mathbf{r} \times \mathbf{v}^{j\alpha}}}{|\delta V_\alpha|} \int_A \rho^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \\
& + \varepsilon^\alpha \overline{\rho^{\alpha_j} \mathbf{r} \times (\widehat{\mathbf{i}}^j + \widehat{\mathbf{r}}^j \mathbf{v}^j)}^\alpha - \varepsilon^\alpha \rho^{\alpha_j} \overline{\widehat{\mathbf{m}}^{j\alpha}}.
\end{aligned} \tag{2.40}$$

Next we subtract \mathbf{x} crossed with equation (2.27) (the conservation of linear momentum at the microscale), where \mathbf{x} is the macroscale field variable. To do this we will need several identities which can be verified by combining (2.4) with the fact that (2.6) - (2.8) are integrals with respect to $\boldsymbol{\xi}$ only, and not with respect to \mathbf{x} :

$$\begin{aligned}
\overline{\mathbf{r} \times \mathbf{v}^{j\alpha}} &= \mathbf{x} \times \mathbf{v}^{\alpha_j} + \overline{\boldsymbol{\xi} \times \mathbf{v}^{j\alpha}}, \\
\overline{\mathbf{v}^j (\mathbf{r} \times \mathbf{v}^{j\alpha})} &= \mathbf{x} \times \overline{\mathbf{v}^j \mathbf{v}^{j\alpha}} + \overline{\mathbf{v}^j (\boldsymbol{\xi} \times \mathbf{v}^j)}^\alpha, \text{ and} \\
\overline{\mathbf{r} \times \mathbf{g}^{j\alpha}} &= \mathbf{x} \times \mathbf{g}^{\alpha_j} + \overline{\boldsymbol{\xi} \times \mathbf{g}^{j\alpha}},
\end{aligned}$$

among others similar to these. Starting with the left hand side, for the $\frac{\partial}{\partial t}$ terms we have

$$\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha_j} \mathbf{x} \times \mathbf{v}^{\alpha_j}) + \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{v}^{j\alpha}}) - \mathbf{x} \times \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j}) = \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{v}^{j\alpha}}). \tag{2.41}$$

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

$$\begin{aligned}
& \nabla \cdot [\varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{x} \times \mathbf{v}^{\alpha_j} + \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{v}^{j\alpha}} - \varepsilon^\alpha \mathbf{x} \times \langle \mathbf{t}^j \rangle^\alpha \\
& - \varepsilon^\alpha \langle \boldsymbol{\xi} \times \mathbf{t}^j \rangle^\alpha - \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{x} \times \mathbf{v}^{\alpha_j} - \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{v}^{j\alpha}} \\
& + \varepsilon^\alpha \rho^{\alpha_j} \mathbf{x} \times \overline{\mathbf{v}^j \mathbf{v}^j} + \varepsilon^\alpha \rho^{\alpha_j} \overline{\mathbf{v}^j \boldsymbol{\xi} \times \mathbf{v}^j}] \\
& + \mathbf{x} \times \nabla \cdot [\varepsilon^\alpha \langle \mathbf{t}^j \rangle^\alpha + \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{v}^{\alpha_j} - \varepsilon^\alpha \rho^{\alpha_j} \overline{\mathbf{v}^j \mathbf{v}^j} - \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{v}^{\alpha_j}] \\
& = \nabla \cdot (\varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{x} \times \mathbf{v}^{\alpha_j}) - \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{v}^{\alpha_j})
\end{aligned}$$

$$\begin{aligned}
& -\nabla \cdot (\varepsilon^\alpha \mathbf{x} \times \langle \mathbf{t}^j \rangle^\alpha) + \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \langle \mathbf{t}^j \rangle^\alpha) - \nabla \cdot (\varepsilon^\alpha \langle \boldsymbol{\xi} \times \mathbf{t}^j \rangle^\alpha) \\
& -\nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{x} \times \mathbf{v}^{\alpha j}) + \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j}) \\
& + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{x} \times \overline{\mathbf{v}^j \mathbf{v}^{j\alpha}}) - \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \overline{\mathbf{v}^j \mathbf{v}^{j\alpha}}) \\
& + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \overline{\mathbf{v}^j \boldsymbol{\xi}} \times \mathbf{v}^{j\alpha}).
\end{aligned} \tag{2.42}$$

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

$$\begin{aligned}
& -\nabla \cdot (\varepsilon^\alpha \mathbf{x} \times \langle \mathbf{t}^j \rangle^\alpha) + \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \langle \mathbf{t}^j \rangle^\alpha) \\
& = -(\varepsilon^\alpha x_i t_{jk} \varepsilon_{ijl})_{,k} + x_i (\varepsilon^\alpha t_{jk})_{,k} \varepsilon_{ijl} \\
& = -\varepsilon^\alpha x_{i,k} t_{jk} \varepsilon_{ijl} - \varepsilon^\alpha x_i t_{jk,k} \varepsilon_{ijl} + \varepsilon^\alpha x_i t_{jk,k} \varepsilon_{ijl} \\
& = -\varepsilon^\alpha \delta_{ik} t_{jk} \varepsilon_{ijl} = \varepsilon^\alpha t_{ji} \varepsilon_{ijl},
\end{aligned} \tag{2.43}$$

where the last equivalence is left in indicial notation because there is no equivalent in direct notation. We also have

$$\begin{aligned}
& \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{x} \times \overline{\mathbf{v}^j \mathbf{v}^{j\alpha}}) - \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \overline{\mathbf{v}^j \mathbf{v}^{j\alpha}}) \\
& = (\varepsilon^\alpha \rho^{\alpha j} x_i v_j v_k \varepsilon_{ijl})_{,k} - x_i (\varepsilon^\alpha \rho^{\alpha j} v_j v_k)_{,j} \varepsilon_{ijl} \\
& = \varepsilon^\alpha \rho^{\alpha j} x_{i,k} v_j v_k \varepsilon_{ijl} + \varepsilon^\alpha \rho^{\alpha j} x_i (v_j v_k)_{,k} \varepsilon_{ijl} \\
& \quad - \varepsilon^\alpha \rho^{\alpha j} x_i (v_j v_k)_{,j} \varepsilon_{ijl} \\
& = \varepsilon^\alpha \rho^{\alpha j} \delta_{ik} v_j v_k \varepsilon_{ijl} = 0,
\end{aligned} \tag{2.44}$$

and finally

$$\begin{aligned}
& \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} (\mathbf{x} \times \mathbf{v}^{\alpha j})) - \mathbf{x} \times \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} \mathbf{v}^{\alpha j}) \\
& = (\varepsilon^\alpha \rho^{\alpha j} v_l x_i v_j \varepsilon_{ijk})_{,l} - x_i (\varepsilon^\alpha \rho^{\alpha j} v_l v_j)_{,j} \varepsilon_{ijk}
\end{aligned}$$

$$\begin{aligned}
&= \varepsilon^\alpha \rho^{\alpha j} x_{i,l} v_l v_j \varepsilon_{ijk} + \varepsilon^\alpha \rho^{\alpha j} x_i (v_l v_j)_{,l} \varepsilon_{ijk} - \varepsilon^\alpha \rho^{\alpha j} x_i (v_l v_j)_{,j} \varepsilon_{ijk} \\
&= \varepsilon^\alpha \rho^{\alpha j} \delta_{il} v_l v_j \varepsilon_{ijk} = 0.
\end{aligned} \tag{2.45}$$

Using identities (2.43) - (2.45) and treating the external supply of momentum term, $\overline{\mathbf{r} \times \mathbf{g}^j}^\alpha$ similarly, the left hand side of equations (2.40) becomes

$$\begin{aligned}
&\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} \overline{\boldsymbol{\xi} \times \mathbf{v}^j}^\alpha) + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \overline{\mathbf{v}^j (\boldsymbol{\xi} \times \mathbf{v}^j)}^\alpha) - \varepsilon^\alpha \langle \boldsymbol{\xi} \times \mathbf{t}^j \rangle^\alpha \\
&\quad - \varepsilon^\alpha t_{ji} \varepsilon_{ijl} - \varepsilon^\alpha \rho^{\alpha j} \overline{\boldsymbol{\xi} \times \mathbf{g}^j}^\alpha.
\end{aligned} \tag{2.46}$$

Turning our attention to the right hand side of equation (2.40), and examining the terms with no sum, we have

$$\begin{aligned}
&\varepsilon^\alpha \rho^{\alpha j} \mathbf{x} \times (\widehat{\mathbf{i}}^{\alpha j} + \overline{\widehat{\mathbf{r}}^j \mathbf{v}^j}^\alpha) - \varepsilon^\alpha \rho^{\alpha j} \overline{\widehat{\mathbf{m}}^j}^\alpha + \varepsilon^\alpha \rho^{\alpha j} \overline{\boldsymbol{\xi} \times (\mathbf{i}^j + \widehat{\mathbf{r}}^j \mathbf{v}^j)}^\alpha \\
&\quad - \mathbf{x} \times \varepsilon^\alpha \rho^{\alpha j} \overline{(\widehat{\mathbf{i}}^j \widehat{\mathbf{r}}^j + \mathbf{v}^j)}^\alpha \\
&= -\varepsilon^\alpha \rho^{\alpha j} \overline{\widehat{\mathbf{m}}^j}^\alpha + \varepsilon^\alpha \rho^{\alpha j} \overline{\boldsymbol{\xi} \times (\widehat{\mathbf{i}}^j + \widehat{\mathbf{r}}^j \mathbf{v}^j)}^\alpha.
\end{aligned} \tag{2.47}$$

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

$$\begin{aligned}
&\sum_{\beta \neq \alpha} \left[\frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\mathbf{x} \times \mathbf{t}^j + \rho^j (\mathbf{x} \times \mathbf{v}^j) (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right] \\
&+ \sum_{\beta \neq \alpha} \left[\frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\boldsymbol{\xi} \times \mathbf{t}^j + \rho^j (\boldsymbol{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right] \\
&- \mathbf{x} \times \sum_{\beta \neq \alpha} \left[\frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right] \\
&= \sum_{\beta \neq \alpha} \left[\frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\boldsymbol{\xi} \times \mathbf{t}^j + \rho^j (\boldsymbol{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right].
\end{aligned} \tag{2.48}$$

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

$$\begin{aligned}
& \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{v}^{j\alpha}}) + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha_j} \overline{\mathbf{v}^j \boldsymbol{\xi} \times \mathbf{v}^{j\alpha}} - \varepsilon^\alpha \langle \boldsymbol{\xi} \times \mathbf{t}^j \rangle^\alpha) \\
& - \varepsilon^\alpha \mathbf{I} \times \langle \mathbf{t}^j \rangle^\alpha - \varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{g}^{j\alpha}} \\
& = -\varepsilon^\alpha \rho^{\alpha_j} \overline{\widehat{\mathbf{m}}^{j\alpha}} + \varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times (\widehat{\mathbf{i}}^j + \widehat{\mathbf{r}}^j \mathbf{v}^j)}^\alpha \\
& + \sum_{\beta \neq \alpha} \left[\frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\boldsymbol{\xi} \times \mathbf{t}^j + \rho^j (\boldsymbol{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right].
\end{aligned} \tag{2.49}$$

Equation (2.49) simplifies to

$$-\varepsilon^\alpha \mathbf{t}_{ji}^{\alpha_j} \varepsilon_{ijl} = \widehat{\mathbf{m}}^{\alpha_j} + \mathbf{M}^{\alpha_j} + \sum_{\beta \neq \alpha} (\widehat{\mathbf{m}}_\beta^{\alpha_j}), \tag{2.50}$$

where we have replaced $\langle \mathbf{t}^j \rangle^\alpha$ by \mathbf{t}^{α_j} (we can do so because of equation (2.28)) and we have made the following definitions:

$$\overline{\widehat{\mathbf{m}}^{j\alpha}} \equiv \varepsilon^\alpha \rho^{\alpha_j} \widehat{\mathbf{m}}^{\alpha_j} \tag{2.51}$$

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

$$\begin{aligned}
\mathbf{M}^{\alpha_j} & \equiv -\frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{v}^{j\alpha}}) - \nabla \cdot (\varepsilon^\alpha \rho^{\alpha_j} \overline{\mathbf{v}^j \boldsymbol{\xi} \times \mathbf{v}^{j\alpha}}) + \nabla \cdot \varepsilon^\alpha \langle \boldsymbol{\xi} \times \mathbf{t}^j \rangle^\alpha \\
& + \varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times \mathbf{g}^{j\alpha}} + \varepsilon^\alpha \rho^{\alpha_j} \overline{\boldsymbol{\xi} \times (\widehat{\mathbf{i}}^j + \widehat{\mathbf{r}}^j \mathbf{v}^j)}^\alpha
\end{aligned} \tag{2.52}$$

is the rate of angular momentum gain by constituent j in phase α due to the microscale angular momentum terms, and

$$\widehat{\mathbf{m}}_\beta^{\alpha_j} \equiv \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\boldsymbol{\xi} \times \mathbf{t}^j + \rho^j (\boldsymbol{\xi} \times \mathbf{v}^j) (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \tag{2.53}$$

is the rate of angular momentum gain by constituent j in phase α due to interaction with phase β .

Summing over $j = 1, \dots, N$ yields the conservation of angular momentum for the bulk phase

$$-\varepsilon^\alpha \mathbf{t}_{ji}^\alpha \varepsilon_{ijl} = \mathbf{M}^\alpha + \sum_{\beta \neq \alpha} \widehat{\mathbf{m}}_\beta^\alpha, \quad (2.54)$$

where the following restrictions apply:

$$\sum_{j=1}^N \widehat{\mathbf{m}}^{\alpha j} = 0 \quad \forall \alpha, \quad (2.55)$$

$$\sum_{\alpha, \beta \neq \alpha} \widehat{\mathbf{m}}_\beta^{\alpha j} = 0 \quad j = 1, \dots, N. \quad (2.56)$$

Equation (2.54) implies that, in general, the mesoscale stress tensor \mathbf{t}^α is not symmetric for multi-phase systems. However, if $\mathbf{t}^{\alpha j}$ 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

$$\begin{aligned} & \frac{\partial}{\partial t} (\varepsilon^\alpha \rho^{\alpha j} (\overline{e^j} + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha)) - \nabla \cdot (\varepsilon^\alpha (\langle \mathbf{t}^j \cdot \mathbf{v}^j + \mathbf{q}^j \rangle^\alpha + \rho^{\alpha j} \mathbf{v}^{\alpha j} (\overline{e^j} + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha) \\ & - \overline{\rho^{\alpha j} \mathbf{v}^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j)}^\alpha)) + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha j} \mathbf{v}^{\alpha j} (\overline{e^j} + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha)) \\ & - \varepsilon^\alpha \rho^{\alpha j} (\overline{\mathbf{g}^j \cdot \mathbf{v}^j}^\alpha + \overline{h^j}^\alpha) \\ & = \sum_{\beta \neq \alpha} \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \left[\int_A [\mathbf{t}^j \cdot \mathbf{v}^j + \mathbf{q}^j + \rho^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \right] \end{aligned}$$

$$\begin{aligned} & \overline{\mp(e^j + \frac{1}{2}\mathbf{v}^j \cdot \mathbf{v}^j)}^\alpha \int_A \rho^j(\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \Big] \\ & + \varepsilon^\alpha \rho^{\alpha_j} (\widehat{Q}^j{}^\alpha + \overline{\mathbf{i}^j \cdot \mathbf{v}^j}^\alpha + \widehat{r}^j(e^j + \frac{1}{2}\mathbf{v}^j \cdot \mathbf{v}^j)^\alpha). \end{aligned} \quad (2.57)$$

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

$$\begin{aligned} \varepsilon^\alpha \rho^{\alpha_j} \frac{D^{\alpha_j}}{Dt}(e^{\alpha_j}) - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^{\alpha_j}) - \varepsilon^\alpha \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j} - \varepsilon^\alpha \rho^{\alpha_j} h^{\alpha_j} \\ = \widehat{Q}^{\alpha_j} + \widehat{Q}_\beta^{\alpha_j}, \end{aligned} \quad (2.58)$$

where the colon indicates the tensor dot product ($\underline{\mathbf{a}} : \underline{\mathbf{b}} = \sum_{i,j} a_{ij} b_{ij}$). Here we have made the following definitions:

$$h^{\alpha_j} \equiv \overline{h^j}^\alpha + \overline{\mathbf{g}^j \cdot \mathbf{v}^j}^\alpha - \mathbf{g}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \quad (2.59)$$

is the external supply of energy,

$$e^{\alpha_j} \equiv \overline{e^j}^\alpha + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \quad (2.60)$$

is the energy density,

$$\begin{aligned} \mathbf{q}^{\alpha_j} \equiv \langle \mathbf{q}^j \rangle^\alpha + \langle \mathbf{t}^j \cdot \mathbf{v}^j \rangle^\alpha - \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} (e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}) \\ - \overline{\rho^{\alpha_j} \mathbf{v}^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j)}^\alpha \end{aligned} \quad (2.61)$$

is the partial heat flux vector for the j^{th} component of phase α ,

$$\begin{aligned} \widehat{Q}^{\alpha_j} \equiv \varepsilon^\alpha \rho^{\alpha_j} (\widehat{Q}^j{}^\alpha + \overline{\mathbf{i}^j \cdot \mathbf{v}^j}^\alpha - (\overline{\mathbf{i}^j}^\alpha + \overline{\widehat{r}^j \mathbf{v}^j}^\alpha - \mathbf{v}^{\alpha_j} \overline{\widehat{r}^j}^\alpha) \cdot \mathbf{v}^{\alpha_j} + \overline{\widehat{r}^j (e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j)}^\alpha \\ - \overline{\widehat{r}^j}^\alpha (\overline{e^j}^\alpha + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha)) \end{aligned} \quad (2.62)$$

is the rate of energy gain due to interaction with other species within the same phase not due to mass or momentum transfer, and

$$\begin{aligned} \widehat{Q}_\beta^{\alpha_j} \equiv & \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \left\{ \int_A \left[\mathbf{q}^j + \mathbf{t}^j \cdot \mathbf{v}^j + \rho^j \left(e^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j \right) (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha da \right. \\ & - \left(e^{\alpha_j} - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \right) \int_A \rho^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \\ & \left. - \mathbf{v}^{\alpha_j} \int_A \left[\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \right] \cdot \mathbf{n}^\alpha da \right\} \end{aligned} \quad (2.63)$$

is the rate of energy transfer from phase β to phase α 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 \mathbf{v}^α times (2.33) and $(e^\alpha + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha)$ times (2.21) and then summing over constituents. This yields

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha e^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^\alpha) - \varepsilon^\alpha \mathbf{t}^\alpha : \nabla \mathbf{v}^\alpha - \varepsilon^\alpha \rho^\alpha h^\alpha = \sum_{\beta \neq \alpha} \widehat{Q}_\beta^\alpha,$$

where the following restrictions hold:

$$\sum_{j=1}^N \left[\widehat{Q}_j^{\alpha_j} + \widehat{\mathbf{i}}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} + \widehat{r}^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) \right] = 0 \quad \forall \alpha, \text{ and} \quad (2.64)$$

$$\sum_{\alpha, \beta \neq \alpha} \left[\widehat{Q}_\beta^{\alpha_j} + \widehat{\mathbf{T}}_\beta^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \widehat{e}_\beta^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j})^2 \right) \right] = 0 \quad j = 1, \dots, N. \quad (2.65)$$

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 α is

$$\begin{aligned}
& \frac{\partial}{\partial t}(\varepsilon^\alpha \rho^{\alpha_j} \overline{\eta^j}^\alpha) - \nabla \cdot (\varepsilon^\alpha \langle \phi^j \rangle^\alpha + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\eta^j}^\alpha \\
& \quad - \rho^{\alpha_j} \overline{\mathbf{v}^j} \overline{\eta^j}^\alpha) + \nabla \cdot (\varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \overline{\eta^j}^\alpha) - \varepsilon^\alpha \rho^{\alpha_j} \overline{b^j}^\alpha \\
& = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha_j} \left[\frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_A \phi^j + \rho^j \eta^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \right. \\
& \quad \mp \frac{\overline{\eta^j}^\alpha}{\rho^{\alpha_j} |\delta V_\alpha|} \int_A \rho^j (\mathbf{w}^{\alpha\beta_j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \\
& \quad \left. + \varepsilon^\alpha \rho^{\alpha_j} \overline{\Lambda^j}^\alpha + \varepsilon^\alpha \rho^{\alpha_j} \overline{\hat{\eta}^j} + \overline{\hat{r}^j} \mathbf{v}^j \right]. \tag{2.66}
\end{aligned}$$

Subtracting η^{α_j} times (2.12) and using (2.13) we obtain

$$\begin{aligned}
\varepsilon^\alpha \rho^{\alpha_j} \frac{D^{\alpha_j}}{Dt}(\eta^{\alpha_j}) - \nabla \cdot (\varepsilon^\alpha \phi^{\alpha_j}) - \varepsilon^\alpha \rho^{\alpha_j} b^{\alpha_j} \\
= \sum_{\beta \neq \alpha} \widehat{\Phi}_\beta^{\alpha_j} + \widehat{\eta}^{\alpha_j} + \Lambda^{\alpha_j}, \tag{2.67}
\end{aligned}$$

where we have made the following definitions:

$$\Lambda^{\alpha_j} \equiv \overline{\Lambda^j}^\alpha \tag{2.68}$$

is the entropy production,

$$\eta^{\alpha_j} \equiv \overline{\eta^j}^\alpha \tag{2.69}$$

is the entropy of the j^{th} constituent in the α -phase,

$$\phi^{\alpha_j} \equiv \langle \phi^j \rangle^\alpha + \rho^j \mathbf{v}^{\alpha_j} \eta^{\alpha_j} - \rho^{\alpha_j} \overline{\mathbf{v}^j} \overline{\eta^j}^\alpha \tag{2.70}$$

is the partial entropy flux vector for the j^{th} component of the α -phase,

$$\overline{b^j}^\alpha \equiv b^{\alpha j} \quad (2.71)$$

is the external entropy source,

$$\begin{aligned} \widehat{\Phi}_\beta^{\alpha j} &\equiv \frac{\varepsilon^\alpha}{|\delta V_\alpha|} \int_A [\phi^j + \rho^j \eta^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j)] \cdot \mathbf{n}^\alpha da \\ &\quad - \frac{\varepsilon^\alpha \eta^{\alpha j}}{|\delta V_\alpha|} \int_A \rho^j (\mathbf{w}^{\alpha \beta j} - \mathbf{v}^j) \cdot \mathbf{n}^\alpha da \end{aligned} \quad (2.72)$$

is the entropy transfer to the j^{th} component in the α -phase through mechanical interactions with the same component in the β -phase, and

$$\widehat{\eta}^{\alpha j} \equiv \varepsilon^\alpha \rho^{\alpha j} (\overline{\widehat{\eta}^j}^\alpha + \overline{\widehat{r}^j}^\alpha - \overline{\widehat{r}^j}^\alpha \eta^{\alpha j}) \quad (2.73)$$

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

The bulk-phase counterpart is given by

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha \eta^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \phi^\alpha) - \varepsilon^\alpha \rho^\alpha b^\alpha = \sum_{\beta \neq \alpha} \widehat{\Phi}_\beta^\alpha + \Lambda^\alpha, \quad (2.74)$$

where the following restrictions apply:

$$\sum_{j=1}^N (\widehat{\eta}^{\alpha j} + \widehat{r}^{\alpha j} \eta^{\alpha j}) = 0 \quad \forall \alpha, \text{ and} \quad (2.75)$$

$$\sum_{\alpha, \beta \neq \alpha} (\widehat{\Phi}_\beta^{\alpha j} + \widehat{e}_\beta^{\alpha j} \eta^{\alpha j}) = 0 \quad j = 1, \dots, N. \quad (2.76)$$

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.

2.4 Standard Assumptions and Resulting Entropy Inequality

In this section we make a few standard simplifying assumptions, and give the resulting form of the entropy inequality. Henceforth we assume that the stress tensor, \mathbf{t}^α , 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

$$T = T^{\alpha_j} = T^{\beta_j} \quad \forall \alpha, \forall \beta, \forall j. \quad (2.77)$$

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 [24]. 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:

$$\phi^{\alpha_j} = \frac{\mathbf{q}^{\alpha_j}}{T}, \quad (2.78)$$

$$b^{\alpha_j} = \frac{h^{\alpha_j}}{T}. \quad (2.79)$$

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^{α_j} into the Helmholtz free energy A^{α_j} ,

$$A^{\alpha_j} = e^{\alpha_j} + T\eta^{\alpha_j}, \quad (2.80)$$

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:

$$\Lambda = \sum_{\alpha} \Lambda^{\alpha} = \sum_{\alpha} \sum_{j=1}^N \Lambda^{\alpha_j} \geq 0. \quad (2.81)$$

We begin by solving equation (2.67) for Λ^{α_j} , subtract $\frac{1}{T}$ times the conservation of energy equation (2.58), to eliminate the heat source variables, h^{α_j} , perform the Legendre transformation with (2.80), then sum over all constituents and phases to obtain

$$\begin{aligned} \Lambda = & \sum_{\alpha} \left\{ -\frac{\varepsilon^{\alpha} \rho^{\alpha}}{T} \left(\frac{D^{\alpha} A^{\alpha}}{Dt} + \eta^{\alpha} \frac{D^{\alpha} T}{Dt} \right) \right. \\ & + \frac{\varepsilon^{\alpha}}{T} \left(\sum_{j=1}^N \mathbf{t}^{\alpha_j} \right) : \mathbf{d}^{\alpha} \\ & + \frac{\varepsilon^{\alpha}}{T^2} (\nabla T) \cdot \left\{ \mathbf{q}^{\alpha} - \sum_{j=1}^N \left[\mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \left(A^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) \right] \right\} \\ & - \frac{1}{T} \sum_{j=1}^N \left[\widehat{\mathbf{T}}_{\beta}^{\alpha_j} + \widehat{\mathbf{i}}^{\alpha_j} + \nabla (\varepsilon^{\alpha} \rho^{\alpha_j} A^{\alpha_j}) \right] \cdot \mathbf{v}^{\alpha_j, \alpha} \\ & + \sum_{j=1}^N \frac{\varepsilon^{\alpha}}{T} (\mathbf{t}^{\alpha_j} - \rho^{\alpha_j} A^{\alpha_j} \mathbf{I}) : \nabla \mathbf{v}^{\alpha_j, \alpha} \\ & - \frac{1}{T} \sum_{\beta \neq \alpha} \widehat{\mathbf{T}}_{\beta}^{\alpha} \cdot \mathbf{v}^{\alpha, s} \\ & - \frac{1}{2T} \sum_{j=1}^N (\mathbf{v}^{\alpha_j, \alpha})^2 [\widehat{\mathbf{e}}_{\beta}^{\alpha_j} + \widehat{\mathbf{r}}^{\alpha_j}] \\ & \left. - \frac{1}{T} \sum_{\beta \neq \alpha} \widehat{\mathbf{e}}_{\beta}^{\alpha} \left(A^{\alpha} + \frac{1}{2} (\mathbf{v}^{\alpha, s})^2 \right) \right\} \geq 0, \quad (2.82) \end{aligned}$$

where $\mathbf{v}^{\alpha_j, \alpha} \equiv \mathbf{v}^{\alpha_j} - \mathbf{v}^{\alpha}$, and in general a comma in the superscript denotes a difference in the superscripted quantity. Identities needed to obtain equation (2.82) can be found in Appendix A.3.

2.5 Choosing Constitutive Independent Variables and Exploiting the Entropy Inequality

Thus far, the theory introduced applies to all media meeting the requirements laid out in the beginning of this chapter and the previous section. What distinguishes one material from another is the set of variables upon which all other variables depend; these are called constitutive independent variables, or more simply, independent variables. How we choose the independent variables is informed by knowledge of the material we wish to model, experience, and experiments. It is important to note that the choice of independent variables *defines* the material.

Once the constitutive independent variables are chosen, we expand the Helmholtz potential term found in (2.82) in terms of these variables, perform various algebraic manipulations and collect terms. 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, [31]. Failure to adhere to the axiom of equipresence can produce erroneous results. However, it can be shown that the Helmholtz free energy is not a function of all the independent variables, as will be demonstrated momentarily.

To illustrate how we chose the independent variables and exploit the entropy inequality in the sense of Coleman and Noll, [19], we will present two illustrative examples. The first example will be for a single-phase elastic solid composed of a single constituent. The second example will be a single-phase thermo-viscous fluid, also composed of a single constituent.

2.5.1 Example: Elastic Solid

Mechanics of materials tells us that linear elastic bodies exhibit different behavior depending on the strain and temperature of the material, denoted \mathbf{E}^s and T , respectively. Expanding the derivative of the Helmholtz potential as a function of these variables we have:

$$\frac{DA^s}{Dt} = \frac{\partial A^s}{\partial \mathbf{E}^s} \frac{D\mathbf{E}^s}{Dt} + \frac{\partial A^s}{\partial T} \frac{DT}{Dt}, \quad (2.83)$$

where we have dropped the superscript on the derivative terms since there is only one phase. Substituting this into entropy inequality (2.82) and collecting like terms we obtain:

$$\begin{aligned} \Lambda = & -\frac{\rho^s}{T} \left(\frac{\partial A^s}{\partial T} + \eta^s \right) \dot{T} \\ & - \frac{1}{T} \left(\rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} - (\mathbf{F}^s)^{-1} \cdot \mathbf{t}^s \cdot (\mathbf{F}^s)^{-T} \right) : \dot{\mathbf{E}}^s \\ & + \frac{\nabla T}{T^2} \cdot \mathbf{q}^s \geq 0, \end{aligned} \quad (2.84)$$

where we have converted \mathbf{d}^s into the independent variable \mathbf{E}^s via the identity $\mathbf{d}^s = (\mathbf{F}^s)^{-T} \cdot \dot{\mathbf{E}}^s \cdot (\mathbf{F}^s)^{-1}$.

Variables which appear linearly in the entropy inequality which are neither constitutive nor independent can vary independently, thus their coefficients must

be set to zero to avoid violating the entropy inequality. In this example, the following variables satisfy these requirements:

$$\dot{T}, \dot{\mathbf{E}}^s, \nabla T. \quad (2.85)$$

The resulting equations are called *non-equilibrium* results as they must hold both at equilibrium as well as away from equilibrium. Since the coefficient of \dot{T} must be zero, we obtain the classical result

$$\frac{\partial A^s}{\partial T} = -\eta^s, \quad (2.86)$$

which means that temperature and entropy are dual variables. For the coefficient of $\dot{\mathbf{E}}^s$, we obtain

$$\mathbf{t}^s = \rho^s \mathbf{F}^s \cdot \frac{\partial A^s}{\partial \mathbf{E}^s} \cdot (\mathbf{F}^s)^T, \quad (2.87)$$

which is a classical Hooke's law. Finally, for the coefficient of ∇T we obtain the result that

$$\mathbf{q}^s = \mathbf{0}. \quad (2.88)$$

This last result says that there is no heat flux. As such, the material that we have defined by our choice of independent variables does not conduct heat. This is perfectly acceptable if we mean to model an insulating solid or we know a priori that the system has a constant temperature. However, we may wish to model an elastic solid that conducts heat, that is, a thermo-elastic solid. To accomplish this, we add ∇T to our list of independent variables, resulting in an

additional term in entropy inequality. Equation (2.84) becomes

$$\begin{aligned} \Lambda = & -\frac{\rho^s}{T} \left(\frac{\partial A^s}{\partial T} + \eta^s \right) \dot{T} \\ & -\frac{1}{T} \left(\rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} - (\mathbf{F}^s)^{-1} \cdot \mathbf{t}^s \cdot (\mathbf{F}^s)^{-T} \right) : \dot{\mathbf{E}}^s \\ & + \frac{\nabla T}{T^2} \cdot \mathbf{q}^s - \frac{\rho^s}{T} \frac{\partial A^s}{\partial(\nabla T)} \frac{D(\nabla T)}{Dt} \geq 0. \end{aligned} \quad (2.89)$$

The variable ∇T no longer appears in list (2.85) because now it is independent. In its place $\frac{D(\nabla T)}{Dt}$ appears, leading to the non-equilibrium result that

$$\frac{\partial A^s}{\partial(\nabla T)} = 0, \quad (2.90)$$

meaning that the Helmholtz free energy is not a function of ∇T . Where it can be demonstrated that Helmholtz free energy is not a function of certain variables, as above, the Helmholtz free energy will be taken as a function of a subset of the complete list of independent variables to simplify calculations, otherwise we will adhere to the axiom of equipresence.

We now have a heat conducting elastic solid, that is, a thermo-elastic solid. Equilibrium for this systems is guaranteed to occur when $\nabla T = \mathbf{0}$. At equilibrium the net generation of entropy is minimum, so that $\frac{\partial \Lambda}{\partial(\nabla T)} = \mathbf{0}$ and $\frac{\partial^2 \Lambda}{\partial(\nabla T)^2} \geq 0$. Taking the partial derivative of equation (2.89) with respect to ∇T and setting it equal to zero yields

$$\mathbf{q}^s = \mathbf{0}, \quad (2.91)$$

that is, there is no heat flux at equilibrium, which makes sense for a thermo-elastic body.

The coefficients of the variables that are zero at equilibrium are a function of these variables. To clarify, if x and y are variables becoming zero at equilibrium,

then the coefficients of x and y are functions of x and y . One way of obtaining *near-equilibrium results* is to linearize the coefficients to form positive quadratic terms by using a Taylor series expansion about the variables becoming zero at equilibrium, and then truncating all second-order and higher terms. In this simple example, we have that $\mathbf{q}^s = \mathbf{q}^s(\nabla T)$, so that

$$\mathbf{q}^s = \mathbf{q}^s|_{eq} + \mathbf{K}^s \cdot \nabla T, \quad (2.92)$$

where eq stands for equilibrium, and \mathbf{K}^s is a second-order tensor resulting from the linearization process. Equation (2.91) tells us that $\mathbf{q}^s|_{eq} = \mathbf{0}$, thus

$$\mathbf{q}^s = \mathbf{K}^s \cdot \nabla T. \quad (2.93)$$

Equation (2.93) is Fourier's law of heat conduction, which is known to hold for thermo-elastic solids near equilibrium.

2.5.2 Example: Thermo-viscoelastic Fluid

If we want to model a thermo-viscous fluid we would include in the list of independent variables the density, the temperature, the gradient of the velocity, and the gradient of the temperature, denoted ρ^l , T , $\nabla \mathbf{v}^l$, and ∇T , respectively. However, it can be shown that $\nabla \mathbf{v}^l$ is not frame invariant, where as the symmetric part of $\nabla \mathbf{v}^l$, $\mathbf{d}^l = 1/2(\nabla \mathbf{v}^l + (\mathbf{v}^l)^T)$ is frame invariant, [24]. Thus, we include \mathbf{d}^l in our list of independent variables instead. Including gradient of various variables produces flow in those variables. For example, just as including ∇T produces heat flow, including a gradient in the volume fraction, $\nabla \varepsilon^l$, produces a material which has flow dependent on the moisture content, which is the case in swelling materials. Including higher-order gradients of a variable

yields non-local effects due to that variable. It is important to remember to include only those variables which will enrich our model without unnecessarily complicating it.

Expanding the derivative of the Helmholtz potential as a function of the independent variables discussed above except ∇T (since, as demonstrated above, the Helmholtz potential is not a function of ∇T) we have:

$$\frac{DA^l}{Dt} = \frac{\partial A^l}{\partial \rho^l} \frac{D\rho^l}{Dt} + \frac{\partial A^l}{\partial \mathbf{d}^l} \frac{D\mathbf{d}^l}{Dt} + \frac{\partial A^l}{\partial T} \frac{DT}{Dt}, \quad (2.94)$$

where we have dropped the superscript l on the derivatives terms since there is only one phase. Note that because of the conservation of mass, equation (2.23), we have

$$\frac{D\rho^l}{Dt} = -\rho^l \nabla \cdot \mathbf{v}^l. \quad (2.95)$$

Substituting this into equation (2.94), then substituting the result into entropy inequality (2.82), and collecting like terms we obtain

$$\begin{aligned} \Lambda = & -\frac{\rho^l}{T} \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \dot{T} \\ & + \frac{1}{T} \left(\mathbf{t}^l + (\rho^l)^2 \frac{\partial A^l}{\partial \rho^l} \mathbf{I} \right) : \mathbf{d}^l \\ & - \frac{\rho^l}{T} \frac{\partial A^l}{\partial \mathbf{d}^l} \frac{D\mathbf{d}^l}{Dt} + \frac{\nabla T}{T^2} \cdot \mathbf{q}^l \geq 0, \end{aligned} \quad (2.96)$$

where we have used the fact that $\nabla \cdot \mathbf{v}^l = \mathbf{d}^l : \mathbf{I}$ since $\mathbf{d}^l = \frac{1}{2}(\nabla \mathbf{v}^l + (\nabla \mathbf{v}^l)^T)$. The variables which appear linearly and are neither constitutive nor independent are:

$$\dot{T}, \frac{D\mathbf{d}^l}{Dt}. \quad (2.97)$$

Using the method outlined in the previous example, we obtain the following *non-equilibrium results*

$$\frac{\partial A^l}{\partial T} = -\eta^l, \quad (2.98)$$

which states that entropy and temperature are dual variables, and

$$\frac{\partial A^l}{\partial \mathbf{d}^l} = 0, \quad (2.99)$$

which means that the Helmholtz free energy is not a function of \mathbf{d}^l .

We define equilibrium to be when both \mathbf{d}^l and ∇T are zero. If x is a variable becoming zero at equilibrium, then $\frac{\partial \Lambda}{\partial x} = 0$ because the net generation of entropy of the system must be minimum at equilibrium. Thus, we obtain the following *equilibrium results*. For the coefficient of \mathbf{d}^l we have:

$$\mathbf{t}^l = -p^l \mathbf{I}, \quad (2.100)$$

where we have used the thermodynamic definition of pressure

$$p^l = (\rho^l)^2 \frac{\partial A^l}{\partial \rho^l}. \quad (2.101)$$

Pressures will be discussed at great length in subsequent chapters. Equation (2.100) is a standard result and states that at equilibrium the stress in the liquid is equal to minus the pressure in the liquid phase. For the coefficient of ∇T we have

$$\mathbf{q}^l = \mathbf{0}, \quad (2.102)$$

which states that at equilibrium the heat flux is zero. Since we now have more than one variable defining equilibrium, the condition on the second partial derivative of Λ in the previous example is replaced by the requirement that

the Jacobian of Λ be positive definite. This assures that entropy production is minimum.

Once again, we would like to obtain near-equilibrium results for the system. The situation is different than the previous example because now we have more than one variable that defines equilibrium. We will still use a Taylor series expansion about the variables which define equilibrium and truncate all second-order and higher terms. However, there is now more than one way to accomplish this. First, we can choose to do single variable expansions. Setting the coefficient of \mathbf{d}^l to \mathbf{Q}^l , we have that $\mathbf{q}^l = \mathbf{q}^l(\nabla T)$ and $\mathbf{Q}^l = \mathbf{q}^l(\mathbf{d}^l)$, analogous to the previous example. Thus, single variable expansions yield

$$\mathbf{q}^l = \mathbf{K}^l \cdot \nabla T \quad (2.103)$$

$$\mathbf{t}^l = -p^l \mathbf{I} + \mathbf{L}^l : \mathbf{d}^l, \quad (2.104)$$

where $\mathbf{q}^l|_{eq} = \mathbf{0}$ because of equation (2.102), and $\mathbf{Q}^l|_{eq} = \mathbf{0}$ because of equation (2.100). In the above equations \mathbf{K}^l and \mathbf{L}^l are second-order and fourth-order tensors, respectively, resulting from the linearization process. We note that because we choose to do single variable expansions that \mathbf{K}^l and \mathbf{L}^l must be evaluated as functions of \mathbf{d}^l and ∇T , respectively. In general, whenever single variable expansions are performed the coefficients resulting from the linearization process must be evaluated as functions of all the other variables which define equilibrium. Of course, having constant coefficients is preferable and can be achieved by using expansions in all of the variables that define equilibrium. In this example we can perform two variable expansions by taking $\mathbf{q}^l = \mathbf{q}^l(\nabla T, \mathbf{d}^l)$

and $\mathbf{Q}^l = \mathbf{Q}^l(\mathbf{d}^l, \nabla T)$. Doing so yields

$$\mathbf{q}^l = \mathbf{K}^l \cdot \nabla T + \mathbf{H}^l : \mathbf{d}^l, \quad (2.105)$$

$$\mathbf{t}^l = -p^l \mathbf{I} + \mathbf{L}^l : \mathbf{d}^l + \mathbf{M}^l \cdot \nabla T, \quad (2.106)$$

where \mathbf{K}^l and \mathbf{M}^l are second-order tensors, and \mathbf{H}^l and \mathbf{L}^l are fourth-order tensors resulting from equilibrium expansion, all of which are only functions of independent variables not becoming zero at equilibrium. Unfortunately, using Taylor series expansions in all the variable defining equilibrium can produce cumbersome expressions. We will be careful to the use expansions that are relevant to the system we want to model but significantly enrich the resulting equations.

In subsequent chapters we will use the techniques described in this section to obtain non-equilibrium, equilibrium, and near-equilibrium results for far more complex systems.

3. A New Choice of Independent Variables

Deriving a physically meaningful transport equation for porous swelling materials that undergo finite deformations depends largely on our ability to relate thermodynamically defined variables to physically interpretable quantities. In this chapter we present a novel and judicious choice of independent variables for the solid phase that clarifies the relationship between thermodynamically defined pressure and actual physical stress. To further show the usefulness of this new set of independent variables, we will show how it elucidates and simplifies the assumptions and the derivation of the transport equation previously investigated by Singh et al., [51], while continuing to capture the important features. We then show how this framework can be used to derive a transport equation used to model swelling polymers, and compare the result with another transport equation derived using the Flory-Huggins theory.

3.1 Motivation

In this chapter we will restrict our discussion to a two-phase system consisting of a viscoelastic solid and viscous liquid phase, each composed of a single constituent, and neglect all interfacial effects, though the theory can be used to incorporate such effects, [7, 8]. Results for non-swelling media may be obtained by making simplifying assumptions.

To capture the viscoelastic nature of the solid phase and phase interaction effects, the independent variables should include variables upon which the solid phase behavior depends, the liquid phase behavior depends, and the interaction

of phases depend. The intuitive choice for independent solid variables include but are not limited to: the solid phase volume fraction, ε^s , solid phase density, ρ^s , and smeared-out solid strain, \mathbf{E}^s . These variables are not independent. To see this, consider the continuity equation for the solid phase assuming no loss of solid material to the liquid phase, see equation (2.23):

$$\frac{D^s(\varepsilon^s \rho^s)}{Dt} + \varepsilon^s \rho^s \nabla \cdot \mathbf{v}^s = 0. \quad (3.1)$$

Let \mathbf{F}^s denote the deformation gradient. Then the right Cauchy-Green tensor can be expressed as

$$\mathbf{C}^s = (\mathbf{F}^s)^T \cdot \mathbf{F}^s, \quad (3.2)$$

where \mathbf{F}^s is the deformation gradient of the solid phase and is defined by (in indicial notation)

$$\mathbf{F}^s = F_{kK}^s = x_{k,K}^s = \frac{\partial x_k^s}{\partial X_K^s}, \quad (3.3)$$

where \mathbf{x}^s is the Eulerian coordinate and \mathbf{X}^s is the Lagrangian coordinate, and where the strain tensor is expressed as

$$\mathbf{E}^s = 1/2(\mathbf{C}^s - \mathbf{I}). \quad (3.4)$$

Let V be the total volume of the smeared-out solid phase, and let V_0 be the initial volume of the (smeared-out) solid phase. Equation (3.1) can be expressed in integral form as [14]

$$\int_V \varepsilon^s \rho^s dv = \int_{V_0} \varepsilon^s \rho^s J^s dv_0 = \int_{V_0} \varepsilon_0^s \rho_0^s dv_0, \quad (3.5)$$

where the jacobian, $J^s = \det(\mathbf{F}^{sT} \cdot \mathbf{F}^s) = \det(\mathbf{C}^s) = \det(2\mathbf{E}^s + \mathbf{I})$. From (3.5), we have $J^s = \frac{\varepsilon_0^s \rho_0^s}{\varepsilon^s \rho^s}$. Combining these results, we obtain the following relationship

$$\det(2\mathbf{E}^s + \mathbf{I}) = J^s = \frac{\varepsilon_0^s \rho_0^s}{\varepsilon^s \rho^s}. \quad (3.6)$$

Thus, we see clearly that \mathbf{E}^s , ρ^s and ε^s are dependent. In particular, the first equality tells us that all six components of $2\mathbf{E}^s + \mathbf{I}$ are not independent of J^s .

Because of this coupling it is not straight forward as to how to choose independent variables which lead to physically meaningful variables. A first choice might be to eliminate volume fraction or density as one of the independent variables. However, density is dual to the thermodynamic definition of pressure, and volume fraction measures liquid content, and hence both are essential quantities in determining macroscopic behavior.

One way of handling this coupling is to enforce the continuity equation using a Lagrange multiplier [33]. The Lagrange multiplier then becomes an unknown of the system to be determined by boundary conditions [24]. Using a Lagrange multiplier, derivatives with respect to \mathbf{E}^s (or \mathbf{C}^s) can be evaluated letting ρ^s and ε^s vary without restriction. However, it then becomes unclear what the physical representation of the dual variables are. To see this, consider the following result obtained via HMT using ρ^s , ε^s , and \mathbf{E}^s in the list of independent variables [49]:

$$\mathbf{t}^s = -p^s \mathbf{I} + \mathbf{t}^{se} + \frac{\varepsilon^l}{\varepsilon^s} \mathbf{t}^{sh}, \quad (3.7)$$

where

$$\mathbf{t}^{se} = \rho^s \mathbf{F}^s \cdot \frac{\partial A^s}{\partial \mathbf{E}^s} \cdot (\mathbf{F}^s)^T, \quad (3.8)$$

and

$$\mathbf{t}^{sh} = \rho^l \mathbf{F}^s \cdot \frac{\partial A^l}{\partial \mathbf{E}^s} \cdot (\mathbf{F}^s)^T. \quad (3.9)$$

In equation (3.7), \mathbf{t}^s is the stress of the solid phase and is related to the stress of the entire medium via $\mathbf{t} = \varepsilon^s \mathbf{t}^s + \varepsilon^l \mathbf{t}^l$. The variable p^s is the thermodynamic pressure and is defined by

$$p^s = (\rho^s)^2 \frac{\partial A^s}{\partial \rho^s}, \quad (3.10)$$

and \mathbf{t}^{se} and \mathbf{t}^{sh} are labeled the Terzaghi stress and the hydration stress, respectively [11, 12]. As $-1/3tr(\mathbf{t}^s)$ represents the physical pressure exerted on the solid phase it is not clear what portion of pressure p^s represents, since neither \mathbf{t}^{se} nor \mathbf{t}^{sh} have zero trace.

Another way of dealing with this coupling is to make simplifying assumptions. For example, in [49], Singh et al. proposed a constitutive theory to model a two-phase polymeric system with a viscoelastic solid phase and viscous fluid phase. By including strain, time derivative of strain, and a gradient in strain as constitutive independent variables, they developed a theory applicable to viscoelastic systems. Therein, they obtained novel forms of Darcy's law. In [50], they extended the two-scale theory to three scales, and then in [51], a transport theory was developed based on their work in [50]. The development of the transport model required the assumption that the strain of the solid phase and rates of strain, were a function of volumetric changes only, that is, a function of J^s , and not a function of shear.

This brings us to another issue we address in this chapter. The form of Darcy's law used to derive the transport equation in [51], which we will derive

in a subsequent section, is written in terms of gradients in the classical pressure, volume fraction, and time derivatives of volume fraction. However, as we will see later, this form of Darcy's law can be written in an equivalent form expressed in terms of a gradient in the Gibbs free energy (or chemical potential) of the liquid phase. Either form of Darcy's law, when combined with the bulk conservation of mass equation for the liquid and solid phases, yields a transport equation. However, we need different constitutive equations and employ different assumptions depending on the form of Darcy's law that we use. We will derive two such transport equations and discuss the similarities, differences, and usefulness of these equations.

In this chapter we will first introduce a new set of constitutive independent variables that give rise to a physically meaningful interpretation of the solid phase stress, solid pressure, and Terzaghi stress tensors. We will present the necessary techniques and methodology to obtain the entropy inequality and then present only the novel results stemming from this choice of variables. Then, based on this choice of independent variables we derive a transport equation analogous to that found in [51]. Next, using an equivalent form of Darcy's law, we will use Flory-Huggins theory to develop another transport equation specifically applicable to polymers. Lastly, it is worth mentioning that we are able to reproduce the three pressure relationship of Bennethum et al. [14] in terms of these new variables.

3.2 Constitution

As discussed above, complications arise from the dependence of the variables ε^s , ρ^s , and \mathbf{E}^s through the solid phase continuity equation. In choosing

an appropriate set of independent variables consider the properties of swelling clays and polymeric materials. Swelling clays, as well as many polymeric materials, have markedly different behavior at low and high moisture contents. At high moisture contents the liquid phase cannot support shear. Thus shearing has little effect on flow, and macroscopic behavior is dominated by volumetric changes due to changes in moisture content. In contrast, a swelling clay with low moisture content will have very few layers of vicinal water (water residing close to the solid phase), and the liquid phase supports shear and the effects of shearing become of greater concern when modeling deformation and transport [23]. For these reasons, it becomes appropriate to consider splitting the deformation of the (smeared-out) solid phase into volumetric (dilatational) and isochoric (distortional) parts. Ideally it would be nice to decompose strain, \mathbf{E}^s , into volumetric and isochoric components, however mathematically this makes the problem quite complicated due to the relationship between ε^s , ρ^s , and \mathbf{E}^s . Consequently, we follow Holzaphfel [32], and consider a multiplicative decomposition of \mathbf{F}^s and \mathbf{C}^s as follows:

$$\mathbf{C}^s = (J^s)^{2/3} \overline{\mathbf{C}}^s, \quad (3.11)$$

$$\mathbf{F}^s = (J^s)^{1/3} \overline{\mathbf{F}}^s, \quad (3.12)$$

where $J^{s1/3} \mathbf{I}$ and $J^{s2/3} \mathbf{I}$ represent volumetric deformation, $\overline{\mathbf{F}}^s$ and $\overline{\mathbf{C}}^s$ are the modified deformation gradient and the modified right Cauchy-Green tensor, respectively. These variables account for distortional deformation. They are related in the same way \mathbf{F}^s and \mathbf{C}^s are, that is,

$$\overline{\mathbf{C}}^s = (\overline{\mathbf{F}}^s)^T \cdot \overline{\mathbf{F}}^s. \quad (3.13)$$

With this decomposition in mind, we assume the following independent variables:

$$\begin{aligned} \varepsilon^l, \nabla \varepsilon^l, \overset{(m)}{\varepsilon}{}^l, \nabla \overset{(m)}{\varepsilon}{}^l, T, \nabla T, \\ \rho^l, C^{lj}, \overline{\mathbf{C}}^s, \overset{(n)}{\overline{\mathbf{C}}}{}^s, J^s, C^{sj}, \mathbf{v}^{\alpha,s}, \mathbf{v}^{\alpha_j,\alpha}, \mathbf{d}^l, \end{aligned} \quad (3.14)$$

where $m = 1, \dots, p$ and $n = 1, \dots, q$ denote material time derivatives of order m and order n , and $j = 1, \dots, N - 1$ represent $N - 1$ constituents throughout this thesis unless otherwise noted. This choice of independent variables differs from that found in [49] in that we have replaced \mathbf{E}^s and ρ^s with $\overline{\mathbf{C}}^s$ and J^s . Additionally, we have replaced higher order derivatives of \mathbf{E}^s with derivatives of ε^l and $\overline{\mathbf{C}}^s$.

3.3 The Entropy Inequality

In this section we will present the necessary methodology to obtain a form of the entropy inequality that is exploitable.

To simplify the following manipulations, we postulate the dependence of the Helmholtz free energy as follows:

$$A^l = A^l(\varepsilon^l, \overset{(m)}{\varepsilon}{}^l, \rho^l, C^{lj}, T, \overline{\mathbf{C}}^s, \overset{(n)}{\overline{\mathbf{C}}}{}^s), \quad (3.15)$$

$$A^s = A^s(\varepsilon^l, \overset{(m)}{\varepsilon}{}^l, J^s, C^{sj}, T, \overline{\mathbf{C}}^s, \overset{(n)}{\overline{\mathbf{C}}}{}^s), \quad (3.16)$$

where $m = 1, \dots, p$ and $n = 1, \dots, q$ are material time derivatives of order p and q , C^{α_j} is the concentration of the j^{th} species in phase α and $j = 1, \dots, N$. Otherwise, we adhere to the axiom of equipresence, that is, all other variables are considered a function of the complete list (3.14). Material time derivatives

of A^l and A^s appear in the entropy inequality (2.82). Using the chain rule, they may be calculated as follows:

$$\begin{aligned} \frac{D^l A^l}{Dt} &= \frac{\partial A^l}{\partial \varepsilon^l} \frac{D^l \varepsilon^l}{Dt} + \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \frac{D^l \varepsilon^{(m)l}}{Dt} + \frac{\partial A^l}{\partial \rho^l} \frac{D^l \rho^l}{Dt} + \sum_{j=1}^{N-1} \tilde{\mu}^{lj} \frac{D^l (C^{lj})}{Dt} \\ &\quad + \frac{\partial A^l}{\partial T} \frac{D^l T}{Dt} + \frac{\partial A^l}{\partial \bar{C}^s} : \frac{D^l \bar{C}^s}{Dt} + \sum_{n=1}^q \frac{\partial A^l}{\partial \bar{C}^{(n)s}} : \frac{D^l \bar{C}^{(n)s}}{Dt}, \end{aligned} \quad (3.17)$$

$$\begin{aligned} \frac{D^s A^s}{Dt} &= \frac{\partial A^s}{\partial \varepsilon^l} \frac{D^s \varepsilon^l}{Dt} + \sum_{m=1}^p \frac{\partial A^s}{\partial \varepsilon^{(m)l}} \frac{D^s \varepsilon^{(m)l}}{Dt} + \frac{\partial A^s}{\partial J^s} \frac{D^s J^s}{Dt} + \sum_{j=1}^{N-1} \tilde{\mu}^{sj} \frac{D^s (C^{sj})}{Dt} \\ &\quad + \frac{\partial A^s}{\partial T} \frac{D^s T}{Dt} + \frac{\partial A^s}{\partial \bar{C}^s} : \frac{D^s \bar{C}^s}{Dt} + \sum_{n=1}^q \frac{\partial A^s}{\partial \bar{C}^{(n)s}} : \frac{D^s \bar{C}^{(n)s}}{Dt}, \end{aligned} \quad (3.18)$$

Because $j = 1, \dots, N$ in (3.15) and (3.16), the concentrations, C^{α_j} , are a dependent variables since

$$\sum_{j=1}^N C^{\alpha_j} = 1, \quad (3.19)$$

which implies for example

$$\frac{D^\alpha C^{\alpha_N}}{Dt} = - \sum_{j=1}^{N-1} \frac{D^\alpha C^{\alpha_j}}{Dt}, \quad (3.20)$$

giving rise to the relative chemical potential [13]

$$\tilde{\mu}^{\alpha_j} \equiv \mu^{\alpha_j} - \mu^{\alpha_N}, \quad (3.21)$$

where

$$\mu^{\alpha_j} \equiv \frac{\partial A^\alpha}{\partial C^{\alpha_j}}. \quad (3.22)$$

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:

$$\frac{D^\alpha(\cdot)}{Dt} = \frac{D^s(\cdot)}{Dt} + \mathbf{v}^{\alpha,s} \nabla(\cdot), \quad (3.23)$$

$$\frac{D^{\alpha_j}(\cdot)}{Dt} = \frac{D^\alpha(\cdot)}{Dt} + \mathbf{v}^{\alpha_j,\alpha} \nabla(\cdot). \quad (3.24)$$

Since \mathbf{d}^s is not in the list of independent variables (3.14), it is necessary to convert \mathbf{d}^s into the independent variables $\dot{\mathbf{C}}^s$ and J^s . We use the following calculation:

$$\begin{aligned} \mathbf{d}^s &= (\mathbf{F}^s)^{-T} \cdot \dot{\mathbf{E}}^s \cdot (\mathbf{F}^s)^{-1} \\ &= \frac{1}{2} (\mathbf{F}^s)^{-T} \cdot \dot{\mathbf{C}}^s \cdot (\mathbf{F}^s)^{-1} \\ &= \frac{1}{2} (\mathbf{F}^s)^{-T} \cdot \left(\frac{2}{3} (J^s)^{-1/3} \dot{J}^s \bar{\mathbf{C}}^s + (J^s)^{2/3} \dot{\bar{\mathbf{C}}}^s \right) \cdot (\mathbf{F}^s)^{-1} \\ &= \frac{1}{3} (J^s)^{-1} \dot{J}^s (\bar{\mathbf{F}}^s)^{-T} \cdot \bar{\mathbf{C}}^s \cdot (\bar{\mathbf{F}}^s)^{-1} + \frac{1}{2} (\bar{\mathbf{F}}^s)^{-T} \cdot \dot{\bar{\mathbf{C}}}^s \cdot (\bar{\mathbf{F}}^s)^{-1} \\ &= \frac{1}{3} (J^s)^{-1} \dot{J}^s \mathbf{I} + \frac{1}{2} (\bar{\mathbf{F}}^s)^{-T} \cdot \dot{\bar{\mathbf{C}}}^s \cdot (\bar{\mathbf{F}}^s)^{-1}. \end{aligned} \quad (3.25)$$

In the above calculation the first equality is an identity, see [37], the second equality is due to the definition of the strain tensor, the third and fourth equalities are due to equations (3.11) and (3.12), respectively, and the fifth equality holds because of (3.2).

Hence it follows from (3.25) that

$$\mathbf{d}^s : \mathbf{I} = \frac{1}{2} ((\bar{\mathbf{F}}^s)^{-1} \cdot (\bar{\mathbf{F}}^s)^{-T}) : \dot{\bar{\mathbf{C}}}^s + \frac{\dot{J}^s}{J^s}. \quad (3.26)$$

and

$$\begin{aligned} \left(\sum_{j=1}^N \mathbf{t}^{s_j} \right) : \mathbf{d}^s &= \frac{1}{2} \left((\overline{\mathbf{F}}^s)^{-1} \cdot \sum_{j=1}^N \mathbf{t}^{s_j} \cdot (\overline{\mathbf{F}}^s)^{-T} \right) : \dot{\overline{\mathbf{C}}}^s \\ &+ \frac{1}{3} \frac{j^s}{J^s} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_j}). \end{aligned} \quad (3.27)$$

Using the identities given in the entropy inequality (2.82) above and collecting terms, we obtain the following form of the entropy inequality:

$$\begin{aligned} \Lambda &= -\frac{1}{T} \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \left(\frac{\partial A^{\alpha}}{\partial T} + \eta^{\alpha} \right) \frac{D^s T}{Dt} \\ &- \frac{1}{T} \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} - \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^s} \right) \dot{\varepsilon}^l \\ &- \frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \varepsilon^{\alpha} \rho^{\alpha} \tilde{\mu}^{\alpha_j} \dot{C}^{\alpha_j} - \frac{1}{T} \varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^l} \dot{\rho}^l \\ &- \frac{1}{T} \left(\varepsilon^s \rho^s \frac{\partial A^{s_e}}{\partial J^s} - \frac{\varepsilon^s}{3} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_j}) \right) j^s \\ &- \frac{1}{T} \left[\varepsilon^l \rho^l \frac{\partial A^l}{\partial \overline{\mathbf{C}}^s} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \overline{\mathbf{C}}^s} - \frac{\varepsilon^s}{2} (\overline{\mathbf{F}}^s)^{-1} \cdot \left(\sum_{j=1}^N \mathbf{t}^{s_j} \right) \cdot (\overline{\mathbf{F}}^s)^{-T} \right] : \dot{\overline{\mathbf{C}}}^s \\ &+ \frac{\varepsilon^l}{T} \left(\sum_{j=1}^N \mathbf{t}^{l_j} \right) : \mathbf{d}^l \\ &- \frac{1}{T} \sum_{\alpha} \left(\sum_{n=1}^q \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^s} \right) : \overline{\mathbf{C}}^s \\ &- \frac{1}{T} \left[\varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial \varepsilon^l} + \eta^l \right) \nabla T + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l + \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \overline{\mathbf{C}}^s} : \nabla \overline{\mathbf{C}}^s \right. \\ &\left. + \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \cdot \nabla \varepsilon^{(m)l} + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^l} \nabla \rho^l + \varepsilon^l \rho^l \sum_{j=1}^N \tilde{\mu}^{l_j} \nabla C^{l_j} + \widehat{\mathbf{T}}_s^l \right] \cdot \mathbf{v}^{l,s} \end{aligned}$$

$$\begin{aligned}
& -\frac{1}{T} \sum_{m=1}^p \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^s} \right) \varepsilon^{(m+1)l} \\
& + \sum_{\alpha} \frac{\varepsilon^{\alpha} \nabla T}{T^2} \cdot \left\{ \mathbf{q}^{\alpha} + \sum_{j=1}^N \left[\rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \left(A^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) - \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} \right] \right\} \\
& - \frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \left[\widehat{\mathbf{T}}_{\beta}^{\alpha_j} + \widehat{\mathbf{i}}^{\alpha_j} + \nabla (\varepsilon^{\alpha} \rho^{\alpha_j} A^{\alpha_j}) \right] \cdot \mathbf{v}^{\alpha_j, \alpha} \\
& + \sum_{\alpha} \sum_{j=1}^N \frac{\varepsilon^{\alpha}}{T} (\mathbf{t}^{\alpha_j} - \rho^{\alpha_j} A^{\alpha_j} \mathbf{I}) : (\nabla \mathbf{v}^{\alpha_j, \alpha}) \\
& - \frac{1}{2T} \sum_{j=1}^N (\mathbf{v}^{\alpha_j, \alpha})^2 (\widehat{e}_{\beta}^{\alpha_j} + \widehat{r}^{\alpha_j}) \\
& - \frac{1}{T} \sum_{\beta \neq \alpha} \widehat{e}_{\beta}^{\alpha} \left(A^{\alpha} + \frac{1}{2} (\mathbf{v}^{\alpha, s})^2 \right) \geq 0. \tag{3.28}
\end{aligned}$$

We choose to use Lagrange multipliers to weakly enforce the continuity equations, see [33]. The entropy inequality is modified as follows:

$$\begin{aligned}
\Lambda_{new} = \Lambda_{old} & + \sum_{\alpha} \frac{\lambda^{\alpha}}{T} \left[\frac{D^{\alpha}(\varepsilon^{\alpha} \rho^{\alpha})}{Dt} + \varepsilon^{\alpha} \rho^{\alpha} \nabla \cdot \mathbf{v}^{\alpha} - \sum_{\alpha, \alpha \neq \beta} \widehat{e}_{\beta}^{\alpha} \right] \\
& + \sum_{\alpha} \sum_{j=1}^N \frac{\lambda^{\alpha_j}}{T} \left[\varepsilon^{\alpha} \rho^{\alpha} \frac{D^{\alpha} C^{\alpha_j}}{Dt} + \nabla \cdot (\varepsilon^{\alpha} \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha}) \right. \\
& \quad \left. - \left(\sum_{\alpha, \alpha \neq \beta} \widehat{e}_{\beta}^{\alpha_j} + \widehat{r}^{\alpha_j} - C^{\alpha_j} \sum_{\alpha, \alpha \neq \beta} \widehat{e}_{\beta}^{\alpha} \right) \right] \geq 0, \tag{3.29}
\end{aligned}$$

where Λ_{old} is given by (3.28). This yields the following form of the entropy inequality:

$$\begin{aligned}
\Lambda = & -\frac{1}{T} \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \left(\frac{\partial A^{\alpha}}{\partial T} + \eta^{\alpha} \right) \frac{D^s T}{Dt} \\
& - \frac{1}{T} \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} - \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^s} - \rho^l \lambda^l \right) \varepsilon^l
\end{aligned}$$

$$\begin{aligned}
& -\frac{1}{T} \sum_{\alpha} \left(\sum_{j=1}^N \varepsilon^{\alpha} \rho^{\alpha} \tilde{\mu}^{\alpha_j} - \varepsilon^{\alpha} \rho^{\alpha} \lambda^{\alpha_j} \right) \dot{C}^{\alpha_j} \\
& -\frac{1}{T} \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^l} - \varepsilon^l \lambda^l \right) \dot{\rho}^l \\
& -\frac{1}{T} \left[\varepsilon^s \rho^s \frac{\partial A^s}{\partial J^s} - \frac{1}{3} \frac{\varepsilon^s}{J^s} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_j}) \right] \dot{J}^s \\
& -\frac{1}{T} \left[\varepsilon^l \rho^l \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} \right. \\
& \left. - \frac{\varepsilon^s}{2} (\bar{\mathbf{F}}^s)^{-1} \cdot \left(\sum_{j=1}^N \mathbf{t}^{s_j} \right) \cdot (\bar{\mathbf{F}}^s)^{-T} - \frac{\varepsilon^s \rho^s \lambda^s}{2} (\bar{\mathbf{F}}^s)^{-1} \cdot (\bar{\mathbf{F}}^s)^{-T} \right] : \dot{\bar{\mathbf{C}}}^s \\
& + \frac{\varepsilon^l}{T} \left(\sum_{j=1}^N \mathbf{t}^{l_j} + \rho^l \lambda^l \mathbf{I} \right) : \dot{\mathbf{d}}^l \\
& - \frac{1}{T} \sum_{\alpha} \left(\sum_{n=1}^q \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \bar{\mathbf{C}}^s} \right)^{(n+1)} : \dot{\bar{\mathbf{C}}}^s \\
& - \frac{1}{T} \left[\varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial \varepsilon^l} + \eta^l \right) \nabla T + \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial \varepsilon^l} - \frac{\lambda^l}{\varepsilon^l} \right) \nabla \varepsilon^l \right. \\
& \left. + \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : \nabla \bar{\mathbf{C}}^s + \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l \right. \\
& \left. + \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial \rho^l} - \frac{\lambda^l}{\rho^l} \right) \nabla \rho^l + \varepsilon^l \rho^l \left(\sum_{j=1}^{N-1} \tilde{\mu}^{l_j} - \lambda^{\alpha_j} \right) \nabla C^{l_j} + \hat{\mathbf{T}}_s^l \right] \cdot \mathbf{v}^{l,s} \\
& - \frac{1}{T} \sum_{m=1}^p \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^l} \right)^{(m+1)} \varepsilon^l \\
& + \sum_{\alpha} \frac{\varepsilon^{\alpha} \nabla T}{T^2} \cdot \left\{ \mathbf{q}^{\alpha} - \sum_{j=1}^N \left[\mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \left(A^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) \right] \right\} \\
& + \sum_{\alpha} \frac{\varepsilon^{\alpha}}{T} \sum_{j=1}^{N-1} \left[\mathbf{t}^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \mathbf{t}^{\alpha_N} - \rho^{\alpha_j} (A^{\alpha_j} - A^{\alpha_N}) + \rho^{\alpha_j} (\lambda^{\alpha_j} - \lambda^{\alpha_N}) \right] : \nabla \mathbf{v}^{\alpha_j, \alpha} \\
& - \frac{1}{T} \sum_{\alpha} \sum_{j=1}^{N-1} \left\{ (\hat{\mathbf{T}}_{\beta}^{\alpha_j} + \hat{\mathbf{i}}^{\alpha_j}) - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} (\hat{\mathbf{T}}_{\beta}^{\alpha_N} + \hat{\mathbf{i}}^{\alpha_N}) + \varepsilon^{\alpha} \mathbf{t}^{\alpha_N} \nabla \left(\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \right) \right\}
\end{aligned}$$

$$\begin{aligned}
& \left. \begin{aligned}
& -(\lambda^{\alpha_j} - \lambda^{\alpha_N}) \nabla(\varepsilon^\alpha \rho^{\alpha_j}) + \nabla[\varepsilon^\alpha \rho^{\alpha_j} (A^{\alpha_j} - A^{\alpha_N})] \\
& -\frac{1}{T} \sum_{j=1}^N \widehat{r}^{\alpha_j} \left[\lambda^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right] \\
& -\frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \sum_{\beta \neq \alpha} \widehat{e}_{\beta}^{\alpha_j} \left[\lambda^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right] \\
& -\frac{1}{T} \sum_{\alpha} \sum_{\beta \neq \alpha} \widehat{e}_{\beta}^{\alpha} \left[A^{\alpha} + \frac{1}{2} (\mathbf{v}^{\alpha, s_v})^2 + \lambda^{\alpha} - \sum_{j=1}^{N-1} \lambda^{\alpha_j} C^{\alpha_j} \right]
\end{aligned} \right\} \geq 0, \quad (3.30)
\end{aligned}$$

where we have used the following two identities

$$\sum_{j=1}^N F^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} = \sum_{j=1}^{N-1} \left(F^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} F^{\alpha_N} \right) \cdot \mathbf{v}^{\alpha_j, \alpha}, \quad (3.31)$$

$$\begin{aligned}
\sum_{j=1}^N G^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j, \alpha} &= \sum_{j=1}^{N-1} \left(G^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} G^{\alpha_N} \right) : \nabla \mathbf{v}^{\alpha_j, \alpha} \\
&\quad - G^{\alpha_N} \sum_{j=1}^{N-1} \nabla \left(\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \right) \cdot \mathbf{v}^{\alpha_j, \alpha}, \quad (3.32)
\end{aligned}$$

to remove the N^{th} component dependence from terms involving $\mathbf{v}^{\alpha_j, \alpha}$, and $\nabla \mathbf{v}^{\alpha_j, \alpha}$, [13].

3.3.1 Two Phase Pressures

In Gibbsian thermodynamics, pressure is defined as follows:

$$\bar{p}^{\alpha} = - \left. \frac{\partial A_T^{\alpha}}{\partial V^{\alpha}} \right|_{M^{\alpha_j}, \dots} \quad (3.33)$$

where M^{α_j} is the mass of constituent j in the α -phase, V^{α} is the volume of the α -phase, and A_T^{α} is the total (extensive) Helmholtz free energy. Dividing the top and bottom of the partial by the magnitude of the REV, we obtain

$$\bar{p}^{\alpha} = - \left. \frac{\partial(\varepsilon^{\alpha} \rho^{\alpha} A^{\alpha})}{\partial \varepsilon^{\alpha}} \right|_{\varepsilon^{\alpha} \rho^{\alpha_j}, \dots} = - \varepsilon^{\alpha} \rho^{\alpha} \left. \frac{\partial A^{\alpha}}{\partial \varepsilon^{\alpha}} \right|_{\varepsilon^{\alpha} \rho^{\alpha_j}, \dots}, \quad (3.34)$$

so that we now have an expression for the *thermodynamic pressure* in terms of intensive variables. Another thermodynamic variable with arises is

$$p^\alpha = \sum_{j=1}^N \rho^\alpha \rho^{\alpha_j} \left. \frac{\partial A^\alpha}{\partial \rho^{\alpha_j}} \right|_{\varepsilon^\alpha, \dots}. \quad (3.35)$$

Bennethum and Weinstein showed that [14]

$$\bar{p}^\alpha = p^\alpha \quad (3.36)$$

for a single-phase material made up of one constituent by converting to extensive variables. However, as we will see, these pressures differ for a swelling porous media. Exploitation of the entropy inequality in the sense of Coleman and Noll, [19] yields the following equilibrium result for the coefficient of \mathbf{d}^l :

$$\mathbf{t}^l = -p^l \mathbf{I}, \quad (3.37)$$

which implies that

$$\frac{1}{3} \text{tr}(\mathbf{t}^l) = -p^l. \quad (3.38)$$

The stress tensor is a physical quantity, and since one third the trace of the stress tensor is the actual physical pressure exerted on an isotropic system, equation (3.38) indicates that p^l coincides with the physical pressure in the liquid phase. Thus, it is called the *classical pressure* (see also [14]).

The relationship between the thermodynamic pressure and classical pressure was elucidated in [14] by considering the Helmholtz potential to be a function of two different combinations of the same set of independent variables. As such, they are not different potentials; an overline is used to distinguish between the

sets of variables being used and will be dropped later. Consider the following relationship for the liquid phase:

$$A^l(\varepsilon^l, \varepsilon^l \rho^{l_j}, \dots) = \bar{A}^l(\varepsilon^l, \rho^l, C^{l_j}, \dots), \quad (3.39)$$

where $j = 1, \dots, N$ for $\varepsilon^l \rho^{l_j}$ and $j = 1, \dots, N - 1$ for C^{l_j} , with the total differential given by

$$\begin{aligned} DA^l &= \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^{l_j}, \dots} d\varepsilon^l + \sum_{j=1}^N \left. \frac{\partial A^l}{\partial (\varepsilon^l \rho^{l_j})} \right|_{\varepsilon^l, \dots} d(\varepsilon^l \rho^{l_j}) \\ &= \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{l_j}} d\varepsilon^l + \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l, C^{l_j}, \dots} d\rho^l + \sum_{j=1}^{N-1} \left. \frac{\partial \bar{A}^l}{\partial C^{l_j}} \right|_{\varepsilon^l, \rho^l, \dots} dC^{l_j} \end{aligned} \quad (3.40)$$

Then, for example

$$\begin{aligned} \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{l_j}, \dots} &= \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^{l_j}, \dots} + \sum_{j=1}^N \left. \frac{\partial A^l}{\partial (\varepsilon^l \rho^{l_j})} \right|_{\varepsilon^l, \dots} \left. \frac{\partial (\varepsilon^l \rho^{l_j})}{\partial \varepsilon^l} \right|_{\rho^l, C^{l_j}, \dots} \\ &= \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^{l_j}, \dots} + \sum_{j=1}^N \frac{\rho^{l_j}}{\varepsilon^l} \left. \frac{\partial A^l}{\partial (\varepsilon^l \rho^{l_j})} \right|_{\varepsilon^l, \dots}. \end{aligned} \quad (3.41)$$

Multiplying (3.41) through by $-\varepsilon^l \rho^l$ we obtain the *three pressure relationship* in [14]

$$p^l(\varepsilon^l, \rho^l, C^{l_j}) = \bar{p}^l(\varepsilon^l, \varepsilon^l \rho^{l_j}) + \pi^l(\varepsilon^l, \rho^l, C^{l_j}), \quad (3.42)$$

where

$$\pi^l = \varepsilon^l \rho^l \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{l_j}, \dots}, \quad (3.43)$$

is called the *swelling potential* since it represents the degree to which the energy of the phase is changed with respect to a change in the liquid content. Equation (3.42) states that the classical pressure is equal to the pressure obtained by

changing the volume of the liquid phase keeping the mass fixed plus the pressure obtained by changing the volume fraction keeping the density fixed.

In a similar fashion, one can show that

$$p^l(\varepsilon^l, \varepsilon^l \rho^{l_j}) = \sum_{j=1}^N \rho^l \rho^{l_j} \frac{\partial A^l}{\partial \rho^{l_j}} \Big|_{\varepsilon^l, \dots} = (\rho^l)^2 \frac{\partial \bar{A}^l}{\partial \rho^l} \Big|_{\varepsilon^l, C^{l_j}, \dots} = p^l(\varepsilon^l, \rho^l, C^{l_j}), \quad (3.44)$$

so that the definition of the classical pressure coincides regardless of which set of independent variables is used.

Using similar calculations one can show that equations (3.42) and (3.43) hold with l replaced by s , so that we obtain the general relationships

$$\pi^\alpha = \varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \Big|_{\rho^{\alpha_j}, C^{\alpha_j}, \dots}, \quad \alpha = l, s, \quad (3.45)$$

and

$$p^\alpha(\varepsilon^\alpha, \rho^{\alpha_j}, C^{\alpha_j}) = \bar{p}^\alpha(\varepsilon^\alpha, \varepsilon^\alpha \rho^{\alpha_j}) + \pi^\alpha(\varepsilon^\alpha, \rho^\alpha, C^{\alpha_j}), \quad \alpha = l, s. \quad (3.46)$$

The liquid phase pressures remain the same as in previous works [14], since the independent variables have not been changed. However, in the solid phases we have replaced the variable ρ^s with J^s . Consider, the following relationship

$$A^s(\varepsilon^l, \rho^s, C^{s_j}, \dots) = \bar{A}^s(\varepsilon^l, \varepsilon^s \rho^{s_j}, \dots) = \tilde{A}^s(\varepsilon^l, J^s, C^{s_j}, \dots), \quad (3.47)$$

where $j = 1, \dots, N - 1$ for C^{s_j} , and $j = 1, \dots, N$ for $\varepsilon^s \rho^{s_j}$. As before, the overline and tilde are used to distinguish between the different combinations of

the same set independent variables. The total differential is given by

$$\begin{aligned}
DA^s &= \left. \frac{\partial A^s}{\partial \varepsilon^l} \right|_{\rho^s, C^{sj}} d\varepsilon^l + \left. \frac{\partial A^s}{\partial \rho^s} \right|_{\varepsilon^l, C^{sj}} d\rho^s + \sum_{j=1}^{N-1} \left. \frac{\partial A^s}{\partial C^{sj}} \right|_{\varepsilon^l, \rho^s} dC^{sj} \\
&= \left. \frac{\partial \bar{A}^s}{\partial \varepsilon^l} \right|_{\varepsilon^s \rho^{sj}} d\varepsilon^l + \sum_{j=1}^N \left. \frac{\partial \bar{A}^s}{\partial (\varepsilon^s \rho^{sj})} \right|_{\varepsilon^l} d(\varepsilon^s \rho^{sj}) \\
&= \left. \frac{\partial \tilde{A}^s}{\partial \varepsilon^l} \right|_{J^s, C^{sj}} d\varepsilon^l + \left. \frac{\partial \tilde{A}^s}{\partial J^s} \right|_{\varepsilon^l, C^{sj}} dJ^s + \sum_{j=1}^{N-1} \left. \frac{\partial \tilde{A}^s}{\partial C^{sj}} \right|_{\varepsilon^l, J^s} dC^{sj}. \quad (3.48)
\end{aligned}$$

Then, for example

$$\left. \frac{\partial A^s}{\partial \varepsilon^s} \right|_{\rho^s, C^{sj}} = \left. \frac{\partial \bar{A}^s}{\partial \varepsilon^s} \right|_{\varepsilon^s \rho^{sj}} + \sum_{j=1}^N \left. \frac{\rho^{sj}}{\varepsilon^s} \frac{\partial \bar{A}^s}{\partial \rho^{sj}} \right|_{\varepsilon^s} = \left. \frac{\partial \tilde{A}^s}{\partial \varepsilon^s} \right|_{\rho^s, C^{sj}} - \left. \frac{J^s}{\varepsilon^s} \frac{\partial \tilde{A}^s}{\partial J^s} \right|_{\varepsilon^s, C^{sj}}, \quad (3.49)$$

where we have used the following calculation

$$\begin{aligned}
\left. \frac{\partial J^s}{\partial \varepsilon^s} \right|_{\rho^s, C^{sj}} &= \left. \frac{\partial \left(\frac{\varepsilon_0^s \rho_0^s}{\varepsilon^s \rho^s} \right)}{\partial \varepsilon^s} \right|_{\rho^s, C^{sj}} = \left. \frac{\varepsilon_0^s \rho_0^s}{\rho^s} \frac{\partial (1/\varepsilon^s)}{\partial \varepsilon^s} \right|_{\rho^s, C^{sj}} \\
&= -\frac{\varepsilon_0^s \rho_0^s}{(\varepsilon^s)^2 \rho^s} = -\frac{J^s}{\varepsilon^s}. \quad (3.50)
\end{aligned}$$

Multiplying equation (3.49) through by $-\varepsilon^s \rho^s$ we obtain

$$-\pi^s = \bar{p}^s - p^s = \bar{p}^s + \rho^s J^s \left. \frac{\partial A^s}{\partial J^s} \right|_{\varepsilon^s, C^{sj}}, \quad (3.51)$$

where the first equality is the three pressure relationship (3.46) with $\alpha = s$, and the second equality yields the following identity for the classical pressure of the solid phase in terms of the new set of independent variables

$$p^s(\varepsilon^s, J^s, C^{sj}) = -\rho^s J^s \left. \frac{\partial A^s}{\partial J^s} \right|_{\varepsilon^s, C^{sj}}. \quad (3.52)$$

Using similar calculations one can show that

$$\pi^s(J^s, \rho^s, C^{sj}) = -\rho^s J^s \left. \frac{\partial A^s}{\partial J^s} \right|_{\rho^s, C^{sj}}, \quad (3.53)$$

where we note the difference in the variables being held fixed, and that

$$\bar{p}^s(\varepsilon^s, J^s, C^{sj}) = -\varepsilon^s \rho^s \left. \frac{\partial A^s}{\partial \varepsilon^s} \right|_{J^s, C^{sj}}. \quad (3.54)$$

3.4 Novel Results

Rather than present the entire constitutive theory associated with the exploitation of entropy inequality (3.30) we will present only those results which are novel and relevant to the current discussion. A comprehensive discussion of these results can be found in [49]. We begin by addressing how the choice of independent variables, list (3.14), affects the form of the solid phase stress. Next we present two equivalent forms of Darcy's law. One form of Darcy's law will be used to derive a transport equation that is analogous to the transport equation derived by Singh et al., [51], but where the new choice of independent variables simplifies and elucidates the derivation and assumptions necessary to obtain said equation. Using a second form of Darcy's law, we will derive another transport equation using Flory-Huggins theory for polymer solutions. We end this section by comparing and contrasting the resulting transport equations.

3.4.1 Solid Phase Stress

After exploiting the entropy inequality in the sense of Coleman and Noll, this choice of independent variables produces the novel *non-equilibrium* result for the coefficient of \dot{J}^s :

$$\frac{1}{3} \text{tr}(\mathbf{t}^s) = -p^s, \quad (3.55)$$

where we have assumed that the diffusive velocities in the solid phase are negligible and p^s is given by (3.52). This result indicates that p^s now coincides with

the classical pressure in the solid phase, whereas before it was unclear what portion of the pressure p^s represented (see equations (3.7)-(3.9)).

We obtain the following *equilibrium* result for the coefficient of $\dot{\bar{\mathbf{C}}}^s$:

$$\mathbf{t}^s = -\rho^s \lambda^s \mathbf{I} + 2 \frac{\varepsilon^l}{\varepsilon^s} \rho^l \bar{\mathbf{F}}^s \cdot \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}}^s)^T + 2 \rho^s \bar{\mathbf{F}}^s \cdot \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}}^s)^T, \quad (3.56)$$

where λ^s is a Lagrange multiplier used to enforce the continuity equation. Taking one-third the trace of equation (3.56), using (3.55) to eliminate \mathbf{t}^s , and solving for $\rho^s \lambda^s$ we obtain

$$\rho^s \lambda^s = p^s + \frac{2}{3} \frac{\varepsilon^l \rho^l}{\varepsilon^s} \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s + \frac{2}{3} \rho^s \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s. \quad (3.57)$$

Substituting this equation back into (3.56) we have

$$\mathbf{t}^s = -p^s \mathbf{I} + \frac{\varepsilon^l}{\varepsilon^s} \bar{\mathbf{t}}^{sh} + \bar{\mathbf{t}}^{se} - \frac{2}{3} \frac{\varepsilon^l \rho^l}{\varepsilon^s} \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s - \frac{2}{3} \rho^s \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s, \quad (3.58)$$

where

$$\bar{\mathbf{t}}^{se} = 2 \rho^s \bar{\mathbf{F}}^s \cdot \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}}^s)^T, \quad (3.59)$$

$$\bar{\mathbf{t}}^{sh} = 2 \rho^l \bar{\mathbf{F}}^s \cdot \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}}^s)^T. \quad (3.60)$$

While it is possible to lump the last two terms of (3.58) into the definitions of $\bar{\mathbf{t}}^{sh}$ and $\bar{\mathbf{t}}^{se}$ so that they both have zero trace, we choose to keep with convention and define equations (3.59) and (3.60) in an analogous manner as equations (3.8) and (3.9). Note that now, when we take one third the trace of equation (3.58) we recover equation (3.55).

3.4.2 Darcy's Law

Darcy's Law is obtained by combining the linear momentum equation for the liquid phase, equation (2.36), with constitutive equations for the stress tensor and the exchange of momentum term, $\widehat{\mathbf{T}}_s^l$. A complete mesoscale nomenclature is given in Appendix A. Exploiting the entropy inequality results in the equilibrium result

$$\widehat{\mathbf{T}}_s^l = \bar{p}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^{(m)l} - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : (\nabla \bar{\mathbf{C}}^s)^T, \quad (3.61)$$

where \bar{p}^l is defined by equation (3.34) with $\alpha = l$. Thus, linearizing about the variable $\mathbf{v}^{l,s} = \mathbf{v}^l - \mathbf{v}^s$, we obtain

$$\begin{aligned} \widehat{\mathbf{T}}_s^l = & -\mathbf{R}^l \cdot (\varepsilon^l \mathbf{v}^{l,s}) + \bar{p}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^{(m)l} \\ & - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : (\nabla \bar{\mathbf{C}}^s)^T. \end{aligned} \quad (3.62)$$

To eliminate $\widehat{\mathbf{T}}_s^l$ and \mathbf{t}^l , equation (3.62) along with the near-equilibrium result for \mathbf{t}^l

$$\mathbf{t}^l = -p^l \mathbf{I} + \mathbf{L}^l : \mathbf{d}^l + \mathbf{H}^l \cdot \nabla T \quad (3.63)$$

(see [49]), are substituted into the conservation of linear momentum equation (3.61). The result is Darcy's Law:

$$\begin{aligned} \mathbf{R}^l \cdot (\varepsilon^l \mathbf{v}^{l,s}) = & -\nabla (\varepsilon^l p^l) + \bar{p}^l \nabla \varepsilon^l + \nabla \cdot (\varepsilon^l \mathbf{L}^l : \mathbf{d}^l) + \nabla \cdot (\varepsilon^l \mathbf{H}^l \cdot \nabla T) \\ & + \varepsilon^l \rho^l \mathbf{g} - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : (\nabla \bar{\mathbf{C}}^s)^T - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^{(m)l}, \end{aligned} \quad (3.64)$$

where \mathbf{R}^l is called the resistivity tensor and is second order. On the right hand side of the equation the first term is responsible for flow due to a gradient in pressure and is the primary driving force in the classical Darcy's law. The second term accounts for flow due to a gradient in volume fraction. These terms have previously been reported in [49]. The third is known as the Brinkman correction factor and is often neglected for slow velocity flows. The coefficient \mathbf{L}^l is a fourth-order tensor resulting from the linearization process, and could be a function of any independent variable that is not zero at equilibrium. The last term on the first line accounts for flow due to thermal gradients and was also reported in [49]; a comprehensive discussion of its impact can be found there. The coefficient \mathbf{H}^l is a third-order tensor arising from the linearization process and could be a function of the same variables as \mathbf{L}^l . It should be noted that there are no isotropic third-order tensors, so that this term vanishes for isotropic materials.

The first term on the second line accounts for gravitational effects. The second term is previously unreported, although it resembles a term reported by Singh et al. [49]. The first-order component is responsible for flow induced by the change in energy of the liquid phase due to (pure) shearing of the solid phase, which is of interest at low moisture contents when only a few layers of water are present. A similar term was originally reported by Murad and Cushman [40] and Bennethum and Giorgi [11]. The second-order and higher-order components are novel. They are non-linear in $\overset{(n)}{\mathbf{C}}^s$ and account for flow induced by the changes in the liquid phase energy due to the rates of shearing. It is similar to $\partial A^l / \partial \overset{(n)}{\mathbf{E}}^s$, a term reported in [49], however \mathbf{E}^s incorporates changes due to shear and

volumetric changes and it is unclear what volumetric changes are being captured by ε^l and what by \mathbf{E}^s . Here we clearly distinguish between shearing effects and changes due to moisture content, which are captured by the last term. The first-order component of the last term was previously reported by Achanta, [2], and accounts for swelling in the normal directions and it has been speculated that this term is responsible, in part, for non-Fickian fluid transport. The second and higher-order components of the last term are previously unreported, and are non-linear in time derivatives of volume fraction. As the polymer takes on fluid the fluid acts as a plasticizer, lowering the glass transition temperature and causing viscous relaxation and swelling. As these last terms are related to the change in energy with respect to the time derivatives of the volume fraction of the liquid phase, they are related to the normal components of strain; thus they account for the effect of relaxation of the polymer matrix on fluid transport.

We now derive an equivalent form of equation (3.64) written in terms of the Gibbs free energy which is related to the chemical potential of the species by [13]

$$G^l = \sum_{j=1}^N C^{lj} \mu^{lj} = A^l + \frac{p^l}{\rho^l}, \quad (3.65)$$

where the chemical potential is defined thermodynamically as [13]

$$\mu^{\alpha j} = \left. \frac{\partial(\varepsilon^\alpha \rho^\alpha A^\alpha)}{\partial(\varepsilon^\alpha \rho^{\alpha j})} \right|_{\varepsilon^\alpha, T} = A^\alpha + \rho^\alpha \left. \frac{\partial A^\alpha}{\partial \rho^{\alpha j}} \right|_{\varepsilon^\alpha, T}. \quad (3.66)$$

Writing (3.15) in terms of the independent variables $\rho^{lj} = C^{lj} \rho^l$ (instead of C^{lj} and ρ^l), we have

$$A^l = A^l(\varepsilon^l, \overset{(m)}{\varepsilon}^l, \rho^{lj}, T, \overline{\mathbf{C}}^s, \overset{(n)}{\overline{\mathbf{C}}}^s), \quad (3.67)$$

where $m = 1, \dots, p$, $n = 1, \dots, q$, and $j = 1, \dots, N$. Thus, we have

$$\begin{aligned} -\varepsilon^l \rho^l \nabla A^l &= -\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \Big|_{\rho^{lj}} \nabla \varepsilon^l - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \nabla \varepsilon^{(m)l} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial T} \nabla T \\ &\quad - \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^{lj}} \Big|_{\varepsilon^l} \nabla \rho^{lj} - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : (\nabla \bar{\mathbf{C}}^s)^T. \end{aligned} \quad (3.68)$$

Recall the definition of the swelling potential (3.43), and the three pressure relationship (3.42). Combining these results to eliminate π^l and then using this to eliminate $\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l}$ in (3.68) results in

$$\begin{aligned} \bar{p}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \nabla \varepsilon^{(m)l} - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : (\nabla \bar{\mathbf{C}}^s)^T \\ = -\varepsilon^l \rho^l \nabla A^l + p^l \nabla \varepsilon^l + \varepsilon^l \rho^l \frac{\partial A^l}{\partial T} \nabla T + \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^{lj}} \Big|_{\varepsilon^l} \nabla \rho^{lj}. \end{aligned} \quad (3.69)$$

The left-hand side of (3.69) can be substituted into equation (3.64) to obtain

$$\begin{aligned} \mathbf{R}^l \cdot (\varepsilon^l \mathbf{v}^{l,s}) &= -\varepsilon^l \rho^l \nabla A^l - \nabla(\varepsilon^l p^l) + p^l \nabla \varepsilon^l + \varepsilon^l \rho^l \frac{\partial A^l}{\partial T} \nabla T \\ &\quad + \varepsilon^l \rho^l \mathbf{g} + \nabla \cdot (\varepsilon^l \mathbf{L}^l : \mathbf{d}^l) + \nabla \cdot (\varepsilon^l \mathbf{H}^l \cdot \nabla T) + \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^{lj}} \Big|_{\varepsilon^l} \nabla \rho^{lj}. \end{aligned} \quad (3.70)$$

With the goal of writing equation (3.70) in terms of a gradient in the Gibbs free energy, note that because $\rho^{lj} = C^{lj} \rho^l$

$$\nabla \rho^{lj} = \rho^l \nabla C^{lj} + C^{lj} \nabla \rho^l, \quad (3.71)$$

so that

$$\sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^{lj}} \Big|_{\varepsilon^l} \nabla \rho^{lj} = \sum_{j=1}^N \varepsilon^l (\rho^l)^2 \frac{\partial A^l}{\partial \rho^{lj}} \Big|_{\varepsilon^l} \nabla C^{lj} + \frac{\varepsilon^l p^l}{\rho^l} \nabla \rho^l, \quad (3.72)$$

where we have used the definition of the classical pressure, equation (3.35), with $\alpha = l$. Using (3.72) in (3.70), combining terms and rearranging, we obtain the

following form of Darcy's Law

$$\begin{aligned} \mathbf{R}^l \cdot (\varepsilon^l \mathbf{v}^{l,s}) = & -\varepsilon^l \rho^l \nabla G^l + \varepsilon^l \rho^l \frac{\partial A^l}{\partial T} \nabla T + \sum_{j=1}^N \varepsilon^l (\rho^l)^2 \frac{\partial A^l}{\partial \rho^{l_j}} \Big|_{\varepsilon^l} \nabla C^{l_j} \\ & + \varepsilon^l \rho^l \mathbf{g} + \nabla(\varepsilon^l (\mathbf{L}^l : \mathbf{d}^l)) + \nabla(\varepsilon^l (\mathbf{H}^l \cdot \nabla T)). \end{aligned} \quad (3.73)$$

The first term on the right-hand side is the generalized Darcy's law term which says that flow is induced by a gradient in the Gibbs free energy. The second term accounts for temperature effects due to re-writing Darcy's law in terms of the Gibbs potential (G^l is a function of temperature). The third term appears because the gradient in the Gibbs free energy accounts for effects on the bulk flow, but not entirely for contribution of species, which still may have an effect on flow. The last three terms remain the same as in equation (3.64).

3.5 Transport Models

The goal is to derive a transport equation which can be used for swelling soils and for swelling polymers. As such, we neglect higher-order terms and neglect gravity since we expect the contribution of these terms to be small in comparison with other terms, assume constant temperature, and assume negligible shearing effects since in relevant experiments and applications fluid penetration occurs in the normal directions. Thus, equations (3.64) and (3.73) simplify to the two following equivalent forms of Darcy's law

$$\begin{aligned} \mathbf{R}^l \cdot (\varepsilon^l \mathbf{v}^{l,s}) = & -\nabla(\varepsilon^l p^l) + \bar{p}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^s} : (\nabla \bar{\mathbf{C}}^s)^T \\ & - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l \end{aligned} \quad (3.74)$$

$$\mathbf{R}^l \cdot (\varepsilon^l \mathbf{v}^{l,s}) = -\varepsilon^l \rho^l \nabla G^l + \sum_{j=1}^N \varepsilon^l (\rho^l)^2 \frac{\partial A^l}{\partial \rho^{l_j}} \Big|_{\varepsilon^l} \nabla C^{l_j}. \quad (3.75)$$

Either form of Darcy's law, equation (3.74) or (3.75), can be used to derive a transport equation. To avoid confusion we will call equation (3.74) the *pressure form* of Darcy's law, since the first term involves a pressure gradient, and we will call equation (3.75) the *Gibbs form*. Both are valid for any two-phase porous medium that meets the requirements laid out in the introduction, where, as mentioned above, gravitational and thermal effects have been neglected. In what follows we restrict our derivation to materials in which each phase is composed of only one species and where no mass transfer between phases takes place. For such a system, the last term of equation (3.75) is zero. This means that the lone term containing the gradient in Gibbs free energy accounts for all of the information contained in the four terms of equation (3.74).

The same form of the continuity equations are used for both transport equations. Assuming an incompressible liquid phase and re-writing the liquid phase continuity equation in terms of $\dot{\varepsilon}^l = D^s \varepsilon^l / Dt$ we have

$$\dot{\varepsilon}^l + (1 - \varepsilon^l) \nabla \cdot (\varepsilon^l \mathbf{v}^{l,s}) = 0, \quad (3.76)$$

where $\nabla \cdot \mathbf{v}^s$ was eliminated via $\nabla \cdot \mathbf{v}^s = \dot{\varepsilon}^l / \varepsilon^s$, which comes from equation (3.1) assuming that the solid phase is incompressible.

3.5.1 Transport Equation in Terms of Pressures

The goal of this section is to obtain a transport equation that can be expressed entirely in terms of the volume fraction of the liquid phase. To this end, note that the first two terms on the right-hand side of (3.74) can be written as

$$-\nabla(\varepsilon^l p^l) + \bar{p}^l \nabla \varepsilon^l = -\varepsilon^l \nabla \bar{p}^l - \varepsilon^l \nabla \pi^l - \pi^l \nabla \varepsilon^l, \quad (3.77)$$

where we have used the three pressure relationship, (3.42). Now, we assuming that π^l is primarily a function of ε^l , that is

$$\frac{\partial \pi^l}{\partial \rho^l} \nabla \rho^l \ll \frac{\partial \pi^l}{\partial \varepsilon^l} \nabla \varepsilon^l, \quad (3.78)$$

equation (3.77) becomes

$$-\nabla(\varepsilon^l p^l) + \bar{p}^l \nabla \varepsilon^l = - \left(\pi^l + \varepsilon^l \frac{\partial \pi^l}{\partial \varepsilon^l} \right) \nabla \varepsilon^l - \varepsilon^l \nabla \bar{p}^l. \quad (3.79)$$

Note that this assumption would not be valid for a non-swelling porous medium, but it is reasonable for a porous medium composed of a highly interacting solid and liquid phase.

Let K' be the unjacketed compressibility for a porous media with incompressible liquid and solid phases, [6]

$$K' = -\varepsilon^s \frac{\partial p^l}{\partial \varepsilon^l} \Bigg|_{\rho^l} - \frac{\varepsilon^s}{\varepsilon^l} \pi^l, \quad (3.80)$$

then

$$\frac{\varepsilon^l}{\varepsilon^s} K' = - \left(\pi^l + \varepsilon^l \frac{\partial \pi^l}{\partial \varepsilon^l} \Bigg|_{\rho^l} \right) - \varepsilon^l \frac{\partial \bar{p}^l}{\partial \varepsilon^l} \Bigg|_{\rho^l}, \quad (3.81)$$

where we have used equation (3.42) again. Substituting into (3.79) we obtain

$$\begin{aligned} -\nabla(\varepsilon^l p^l) + \bar{p}^l \nabla \varepsilon^l &= \frac{\varepsilon^l}{\varepsilon^s} K' \nabla \varepsilon^l + \varepsilon^l \frac{\partial \bar{p}^l}{\partial \varepsilon^l} \Bigg|_{\rho^l} \nabla \varepsilon^l - \varepsilon^l \nabla \bar{p}^l \\ &= \frac{\varepsilon^l}{\varepsilon^s} K' \nabla \varepsilon^l - \varepsilon^l \frac{\partial \bar{p}^l}{\partial \rho^l} \Bigg|_{\varepsilon^l} \nabla \rho^l, \end{aligned} \quad (3.82)$$

where we have assumed $\bar{p}^l = \bar{p}^l(\varepsilon^l, \rho^l)$ to calculate $\nabla \bar{p}^l$. If we impose a constant pressure along the boundaries then the density gradient $\nabla \rho^l$ will be negligible.

Neglecting $\nabla \rho^l$ and using (3.82) in the pressure form Darcy's law, (3.74) we have

$$\varepsilon^l \mathbf{v}^{l,s} = \frac{K^l}{\mu^l} \left[\frac{\varepsilon^l}{\varepsilon^s} K' \nabla \varepsilon^l - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \overline{\mathbf{C}}^s} : (\nabla \overline{\mathbf{C}}^s)^T - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l \right], \quad (3.83)$$

where we have assumed that the resistivity tensor \mathbf{R}^l is isotropic, so that we can write

$$(\mathbf{R}^l)^{-1} = \frac{K^l}{\mu_v^l} \mathbf{I}, \quad (3.84)$$

where K^l is the permeability and μ_v^l is the viscosity of the liquid phase. Substituting $\varepsilon^l \mathbf{v}^{l,s}$ from (3.83) into (3.76) gives the first form of the general transport equation

$$\dot{\varepsilon}^l + (1 - \varepsilon^l) \nabla \cdot \left(\varepsilon^l \frac{K^l}{\mu_v^l} \left[\frac{\varepsilon^l}{\varepsilon^s} K' \nabla \varepsilon^l - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l \right] \right) = 0, \quad (3.85)$$

where we have chosen to neglect the terms involving $\overline{\mathbf{C}}^s$ and its derivatives. This means that the model will only be applicable to systems with relatively slow flows with a moderate to high fluid content.

This closely resembles an equation obtained by Singh et al. in [51] for a three scale system but with a few key differences. First, the equation obtained in [51] contains a coefficient E^{wA} , which is obtained in an ad hoc manner and is related to the equilibrium elasticity of the material. Alternatively, in this formulation we have used K^l , which is a macroscale physically measurable compressibility possessing a rigorous thermodynamic definition. Second, the terms containing $\nabla \varepsilon^l$ appear naturally as a result of the constitutive independent variables; there is no need to preform a change of variables from gradients in strain and

its time derivative to gradients in volume fraction and its time derivatives as in [51]. To make the change of variables from \mathbf{E}^s to $\varepsilon^{(m)s}$, Singh et al. assumed that their system has moderate to high fluid contents. This assumption, as mentioned before, means that shear forces are being neglected, and as this choice of independent variables for the solid phase shows is equivalent to neglecting terms involving $\overline{\mathbf{C}}^s$. Applying subsequent arguments of Singh et al. [51] to (3.85), we obtain the following integro-differential equation

$$\dot{\varepsilon}^l + (1 - \varepsilon^l) \nabla \cdot \left(D \nabla \varepsilon^l - \int_0^t B_v(t - \tau) \nabla \dot{\varepsilon}^l d\tau \right) = 0, \quad (3.86)$$

where

$$D = \frac{(\varepsilon^l)^2 K^l K'}{\varepsilon^s \mu_v^l} \quad (3.87)$$

$$B_v(t) = \frac{\varepsilon^{l2} \rho^l K^l}{\mu_v^l} \sum_{m=1}^p M_{(m)}^l \delta^{(m-1)}(t), \quad (3.88)$$

where

$$\delta^{(m-1)}(t) = \frac{d^{(m-1)} \delta(t)}{dt^{(m-1)}}, \quad (3.89)$$

is the time derivative of the dirac delta function, and where

$$M_{(m)}^l = \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \quad (3.90)$$

are constant as long as A^l is a linear function of ε^l and its time derivatives. The primary difference between (3.85) and the transport equation derived in [51] is in the interpretation of coefficients D and $B_v(t)$, and the ease with which this equation is obtained. Appropriate choice of $B_v(t - \tau)$ allows this transport equation to capture a wide range of viscoelastic material behavior. A comprehensive discussion of its modeling capabilities can be found in [51].

3.5.2 Transport Model in Terms of the Chemical Potential

Next we turn to equation (3.75) and show how to combine it with the classical Flory-Huggins model used to model swelling polymers. To use equation (3.75) we need to obtain an expression for the Gibbs free energy for the specific system we wish to model. In this case we will seek an expression for the Gibbs free energy that is valid for a polymer/solvent system. We use the standard Flory-Huggins theory for a polymer/solvent system, [26]. According to the theory the chemical potential for the solvent (water) and solute (polymer) phases are given by

$$\mu^l = \mu_0^l + RT[\ln(1 - v^s) + (1 - 1/x)v^s + \chi(v^s)^2] \quad (3.91)$$

$$\mu^s = \mu_0^s + RT[\ln(v^s) + (x - 1)(1 - v^s) + \chi x(1 - v^s)^2], \quad (3.92)$$

respectively, [26]. Here, R is the gas constant and x is the ratio of molar volumes of the solute and solvent. The interaction parameter, χ , is as a measure of how good a particular solvent is for a particular polymer, and is set to zero for good solvents. The molar volume fraction parameters v^l and v^s are given by

$$v^l = \frac{n^l}{n^l + xn^s}, \quad (3.93)$$

$$v^s = \frac{xn^s}{n^l + xn^s}, \quad (3.94)$$

where n^α represents the number of α -phase molecules. The units of v^l are $\frac{\text{vol } l}{\text{vol } l + \text{vol } s}$. Dividing the top and bottom by the total volume we find that v^l has the same units as ε^l . This suggests that we may take $v^l = \varepsilon^l$. In fact, this is precisely what is accomplished by using x , the ratio of molar volumes of the solute to solvent in the denominator of (3.93) and (3.94), because x has the effect

of scaling the size of a solid phase molecule to take up the appropriate volume of liquid phase molecules. Similarly, $v^s = \varepsilon^s$. Thus, we can write equations (3.91) and (3.92) in terms of volume fraction

$$\mu^l = \mu_0^l + RT[\ln(1 - \varepsilon^s) + (1 - 1/x)\varepsilon^s + \chi(\varepsilon^s)^2] \quad (3.95)$$

$$\mu^s = \mu_0^s + RT[\ln(\varepsilon^s) + (x - 1)(1 - \varepsilon^s) + \chi x(1 - \varepsilon^s)^2]. \quad (3.96)$$

Assuming a good solvent, we take $\chi = 0$, and equations (3.95) and (3.96) become

$$\mu^l = \mu_0^l + RT[\ln(\varepsilon^l) + (1 - 1/x)\varepsilon^s] \quad (3.97)$$

$$\mu^s = \mu_0^s + RT[\ln(\varepsilon^s) + (x - 1)\varepsilon^l]. \quad (3.98)$$

For phases composed of only one species, the Gibbs potential of the phase is equal to the chemical potential of the phase, so that we may take $G^l = \mu^l$ in (3.75).

If x is sufficiently large, which is a valid assumption for polymer solvent systems since the molar volume of most polymers is quite large in comparison to the molar volume of solutes like water, equation (3.97) can be approximated as follows

$$\begin{aligned} \mu^l &\approx \mu_0^l + RT[\ln(\varepsilon^l) + \varepsilon^s] \\ &= \mu_0^l + RT[\ln(\varepsilon^l) + \ln e^{\varepsilon^s}] \\ &= \mu_0^l + RT[\ln(\varepsilon^l e^{1-\varepsilon^l})] \\ &= \mu_0^l + RT[\ln(a)], \end{aligned} \quad (3.99)$$

where $a = \varepsilon^l e^{1-\varepsilon^l}$ is called the activity, and has been used in [4] to model a penetrant into a glassy polymer. If the solution were instead composed of two

polymers we might take $x \approx 1$. Substituting (3.99) into equation (3.75) we obtain

$$\varepsilon^l \mathbf{v}^{l,s} = -\frac{RT\rho^l K^l}{\mu_v^l} (1 - \varepsilon^l) \nabla \varepsilon^l. \quad (3.100)$$

Substituting equation (3.100) into (3.76) we obtain the following transport equation

$$\dot{\varepsilon}^l + (1 - \varepsilon^l) \nabla \cdot (D \nabla \varepsilon^l) = 0, \quad (3.101)$$

where

$$D = \frac{RT\rho^l K^l}{\mu_v^l} (\varepsilon^l - 1). \quad (3.102)$$

3.5.3 Model Comparison

The derivation of equations (3.86) and (3.101) used equivalent forms of Darcy's law and the same conservation of mass equations. However, the similarity between equations (3.86) and (3.101) is surprising because the development of these equations came from two completely different perspectives. Equation (3.101) simply lacks the integral term of (3.86), and the coefficient D of equation (3.102) takes a slightly different form than that of equation (3.86). Moreover, if we choose an appropriate form for $B_v(t)$, as discussed in [51], equation (3.86) reduces to equation (3.101) for polymers in the glassy state and in the rubbery state. For polymers in the glassy or the rubbery state the decision to use the coefficient associated with either equation should be determined by the application and the available experimental data for a given material. Equation (3.86) is capable of capturing the complex behavior of polymers undergoing the transition between the glassy state and rubbery state. The discussion of the necessary experimental data to use equation (3.86) can be found in [53, 52].

3.6 Conclusions

In this chapter, we have shown that a judicious choice of independent variables for the solid phase yields a physically meaningful expression for the solid phase stress, validating the assumptions made by Bennethum and Weinstein in [14]. We have shown how this choice of independent variables can be used to elucidate the assumptions necessary to derive a transport equation applicable to swelling viscoelastic materials analogous to that of Singh et al. [51]. Using Flory-Huggins theory we derived another transport equation which is specifically applicable to polymers. We then compared the resulting transport equations (3.86) and (3.101) and argued that the latter should be thought of as a simplification of the former to be used specifically when a polymer is in a glassy or rubbery state, and the former should be used when the polymer is undergoing a transition from one state to the other.

4. Three-Phase HMT for Swelling Porous Systems

Obtaining bulk and species transport equations that are capable of modeling viscoelastic swelling systems in which mass transfer between phases takes place requires special consideration. In this chapter we develop constitutive theory for a system composed of a viscoelastic solid phase, an elastic solid phase, and a viscous fluid that is capable of dealing with the unique difficulties that arise in modeling such systems.

4.1 Motivation

In the context of HMT, fluid transport for swelling porous systems has been investigated by a number of authors. Bennethum and Cushman presented theory for such a system in [8]. In this work, they modeled the solid phase as elastic and the liquid phase as viscous. The resulting model exhibited viscoelastic behavior due to phase interactions. Singh et al. extended these results, modeling the solid phase as viscoelastic, [49, 50]. These papers were aimed at biopolymeric systems which display viscoelastic behavior at the microscale. In Chapter 3 we revisited the transport theory for biopolymeric systems developed by Singh et al. [51], in which they used the constitutive theory in [50] and the balance laws in [7]. However, this transport theory did not include constituent transport, only transport of bulk fluid, that is, transport of the liquid phase with respect to the solid phase, but not transport of species within a phase. They also assumed that no mass transfer takes place between phases. Because we wish to develop

a model that represents viscoelastic drug delivery systems, we must take into account mass transfer between phases.

When attempting to model such systems using two-phase HMT we encounter a couple of difficulties. First, to obtain the bulk transport equation (3.85) we assumed that both the solid and the liquid phases are incompressible, that is

$$\frac{D^s \rho^s}{Dt} = 0, \quad (4.1)$$

and

$$\frac{D^l \rho^l}{Dt} = 0. \quad (4.2)$$

Unfortunately, because mass transfer between phases takes place, these conditions no longer hold. While we can make the argument that equation (4.2) is approximately true by assuming that the dissolved drug in the liquid phase is sufficiently dilute, we cannot make the same argument for the solid phase, especially at high drug loadings.

Often, experiments in the literature measure the volume fraction of drug, [20]. In two-phase HMT the variables that describe the constitution of the solid phase are: the concentration of species within the phase, $C^{sj} = [\text{mass } s_j / \text{mass } s]$, the density of species within the phase, $\rho^{sj} = [\text{mass } s_j / \text{vol } s]$, the density of the bulk phase, $\rho^s = [\text{mass } s / \text{vol } s]$, and the volume fraction of the phase, $\varepsilon^s = [\text{vol } s / \text{vol}]$. Since none of these variables account for the volume of j in the solid phase, two-phase HMT lacks the ability to represent the volume fraction of drug. This makes it difficult to compare the results of a two-phase HMT model to the available experimental data.

These considerations lead us to consider an alternative method of modeling swelling drug delivery systems. In particular, a three-phase model with a viscoelastic solid phase (the polymer), an elastic solid phase (the drug), and a viscous liquid phase, where we specify that mass transfer takes place between the drug and liquid phases only, has the potential of overcoming the aforementioned difficulties. This allows us to consider both solid phases as incompressible, where equation (4.1) is the mathematical representation of this condition. We can also argue that equation (4.2) is approximately true for the liquid phase, as we did above. Furthermore, using three phases allows us to make more direct comparisons with experiments since we now have a variable that represents the volume fraction of drug in the solid phase.

In this chapter we will present the constitutive theory for such a system. The details involved in deriving the entropy inequality are analogous to that found in Chapter 3, so we will present only those details which differ significantly due to the presence of three phases. The resulting entropy inequality will be given, then we will present non-equilibrium, equilibrium, and near-equilibrium results, as well as Darcy's and Fick's laws.

4.2 Constitution

We assume the following independent variables:

$$\begin{aligned} \varepsilon^l, \varepsilon^{sv}, \nabla \varepsilon^l, \nabla \varepsilon^{sv}, \overset{(m)}{\varepsilon}{}^l, \nabla \overset{(m)}{\varepsilon}{}^l, T, \nabla T, \rho^l, C^{lj} \\ J^{se}, C^{sej}, \overline{C}^{sv}, \overline{C}^{sv(n)}, \overline{C}^{se}, J^{sv}, C^{svj}, \mathbf{v}^{\alpha,s}, \mathbf{v}^{\alpha_j,\alpha}, \nabla \mathbf{v}^{lj,l}, \mathbf{d}^l \end{aligned} \quad (4.3)$$

where $m = 1, \dots, p$ denote material time derivatives of order m , $n = 1, \dots, q$, denote material time derivatives of order n , and $j = 1, \dots, N - 1$ represent

$N - 1$ constituents, l denotes the liquid phase, s_v denotes the viscoelastic solid phase, and s_e denotes the elastic solid phase. We do not include all three volume fractions since they are related through

$$\varepsilon^l + \varepsilon^{s_v} + \varepsilon^{s_e} = 1, \quad (4.4)$$

and therefore are not independent. We choose to use ε^l since it measures liquid content of the system and this plays an important role in the swelling behavior of the system. We choose to use ε^{s_v} as opposed to ε^{s_e} because we want the polymer phase to be the reference phase. We include T since the behavior of most polymers is a function of temperature, and we include ∇T so that we recover Fourier's law of heat conduction, that is, without it we obtain no heat flux. The relative velocities $\mathbf{v}^{\alpha,s}$ and $\mathbf{v}^{\alpha_j,\alpha}$ give us information about exchange of momentum within a phase and viscous diffusion. For the liquid phase we include in our list of independent variables: ρ^l , and C^{l_j} , which account for the material makeup, $\mathbf{d}^l = 1/2(\nabla \mathbf{v}^l + (\nabla \mathbf{v}^l)^T)$ to account for the viscous nature of the liquid, $\nabla \varepsilon^l$ to account flow due to moisture content, and $\nabla \mathbf{v}^{l_j,l}$ to account for viscous diffusion within the phase. For the viscoelastic solid we include: J^{s_v} and $C^{s_v j}$ to account for the material makeup of the viscoelastic solid phase, derivatives of order $m = 1$ to p for ε^l (derivatives in the volume fraction of the liquid phase are related to the derivatives in the normal components of strain) and derivatives of order 0 through q for \overline{C}^{s_v} to account for (as well as J^{s_v}) the viscoelastic nature of the material (combined they take the place of the usual higher order derivatives in strain), $\nabla \varepsilon^{s_v}$ to account for flow due to polymer content, and $\nabla \varepsilon^{(m)l}$ to account flow due to changes in moisture content. Finally, for the elastic solid phase we include: J^{s_e} and $C^{s_e j}$ to account for material make-up, and \overline{C}^{s_e}

(along with J^{s_e}) to account for elastic behavior.

4.3 Entropy Inequality

To simplify calculations, we postulate the dependence of the Helmholtz free energies as follows:

$$A^l = A^l(\varepsilon^l, \varepsilon^{s_v}, \varepsilon^{(m)l}, \rho^l, C^{lj}, T, \overline{C}^{s_v}, \overline{C}^{(n)s_v}, \overline{C}^{s_e}), \quad (4.5)$$

$$A^{s_v} = A^{s_v}(\varepsilon^l, \varepsilon^{s_v}, \varepsilon^{(m)l}, J^{s_v}, C^{s_vj}, T, \overline{C}^{s_v}, \overline{C}^{(n)s_v}, \overline{C}^{s_e}), \quad (4.6)$$

$$A^{s_e} = A^{s_e}(\varepsilon^l, \varepsilon^{s_v}, \varepsilon^{(m)l}, J^{s_e}, C^{s_ej}, T, \overline{C}^{s_v}, \overline{C}^{(n)s_v}, \overline{C}^{s_e}), \quad (4.7)$$

where $C^{\alpha j}$ is the concentration of the j^{th} species in phase α , and $j = 1, \dots, N$. Otherwise we adhere to the axiom of equipresence: all other constitutive variables are considered a function of list (4.3). Material time derivatives of A^l , A^{s_v} , and A^{s_e} appear in the entropy inequality (2.82). Using the chain rule, they may be calculated as follows:

$$\begin{aligned} \frac{D^l A^l}{Dt} &= \frac{\partial A^l}{\partial \varepsilon^l} \frac{D^l \varepsilon^l}{Dt} + \frac{\partial A^l}{\partial \varepsilon^{s_v}} \frac{D^l \varepsilon^{s_v}}{Dt} + \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \frac{D^l \varepsilon^{(m)l}}{Dt} + \frac{\partial A^l}{\partial \rho^l} \frac{D^l \rho^l}{Dt} \\ &+ \sum_{j=1}^{N-1} \tilde{\mu}^{lj} \frac{D^l(C^{lj})}{Dt} + \frac{\partial A^l}{\partial T} \frac{D^l T}{Dt} + \frac{\partial A^l}{\partial \overline{C}^{s_v}} : \frac{D^l \overline{C}^{s_v}}{Dt} \\ &+ \sum_{n=1}^q \frac{\partial A^l}{\partial \overline{C}^{(n)s_v}} : \frac{D^l \overline{C}^{(n)s_v}}{Dt} + \frac{\partial A^l}{\partial \overline{C}^{s_e}} : \frac{D^l \overline{C}^{s_e}}{Dt}, \end{aligned} \quad (4.8)$$

$$\begin{aligned}
\frac{D^{s_v} A^{s_v}}{Dt} &= \frac{\partial A^{s_v}}{\partial \varepsilon^l} \frac{D^{s_v} \varepsilon^l}{Dt} + \frac{\partial A^{s_v}}{\partial \varepsilon^{s_v}} \frac{D^{s_v} \varepsilon^{s_v}}{Dt} + \sum_{m=1}^p \frac{\partial A^{s_v}}{\partial \varepsilon^{(m)l}} \frac{D^{s_v} \varepsilon^{(m)l}}{Dt} + \frac{\partial A^{s_v}}{\partial J^{s_v}} \frac{D^{s_v} J^{s_v}}{Dt} \\
&+ \sum_{j=1}^{N-1} \tilde{\mu}^{s_v j} \frac{D^{s_v} (C^{s_v j})}{Dt} + \frac{\partial A^{s_v}}{\partial T} \frac{D^{s_v} T}{Dt} + \frac{\partial A^{s_v}}{\partial \bar{C}^{s_v}} : \frac{D^{s_v} \bar{C}^{s_v}}{Dt} \\
&+ \sum_{n=1}^q \frac{\partial A^{s_v}}{\partial \bar{C}^{s_v (n)}} : \frac{D^{s_v} \bar{C}^{s_v (n)}}{Dt} + \frac{\partial A^{s_v}}{\partial \bar{C}^{s_e}} : \frac{D^{s_v} \bar{C}^{s_e}}{Dt}, \tag{4.9}
\end{aligned}$$

$$\begin{aligned}
\frac{D^{s_e} A^{s_e}}{Dt} &= \frac{\partial A^{s_e}}{\partial \varepsilon^l} \frac{D^{s_e} \varepsilon^l}{Dt} + \frac{\partial A^{s_e}}{\partial \varepsilon^{s_v}} \frac{D^{s_e} \varepsilon^{s_v}}{Dt} + \sum_{m=1}^p \frac{\partial A^{s_e}}{\partial \varepsilon^{(m)l}} \frac{D^{s_e} \varepsilon^{(m)l}}{Dt} + \frac{\partial A^{s_e}}{\partial J^{s_e}} \frac{D^{s_e} J^{s_e}}{Dt} \\
&+ \sum_{j=1}^{N-1} \tilde{\mu}^{s_e j} \frac{D^{s_e} (C^{s_e j})}{Dt} + \frac{\partial A^{s_e}}{\partial T} \frac{D^{s_e} T}{Dt} + \frac{\partial A^{s_e}}{\partial \bar{C}^{s_v}} : \frac{D^{s_e} \bar{C}^{s_v}}{Dt} \\
&+ \sum_{n=1}^q \frac{\partial A^{s_e}}{\partial \bar{C}^{s_v (n)}} : \frac{D^{s_e} \bar{C}^{s_v (n)}}{Dt} + \frac{\partial A^{s_e}}{\partial \bar{C}^{s_e}} : \frac{D^{s_e} \bar{C}^{s_e}}{Dt}. \tag{4.10}
\end{aligned}$$

We can choose either solid phase to be the reference solid phase. We choose the viscoelastic solid phase because in the case of drug delivery the elastic solid phase will undergo phase transfer. As such, equation (3.23) is replaced by

$$\frac{D^\alpha(\cdot)}{Dt} = \frac{D^{s_v}(\cdot)}{Dt} + \mathbf{v}^{\alpha, s_v} \nabla(\cdot) \tag{4.11}$$

Enforcing the conservation of mass equations using the Lagrange multipliers given by equation (3.29) we arrive at the following form of the entropy inequality:

$$\begin{aligned}
\Lambda &= -\frac{1}{T} \sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \left(\frac{\partial A^{\alpha}}{\partial T} + \eta^{\alpha} \right) \frac{D^s T}{Dt} \\
&- \frac{1}{T} \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} + \varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_v}}{\partial \varepsilon^l} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} - \rho^l \lambda^l \right) \dot{\varepsilon}^l
\end{aligned}$$

$$\begin{aligned}
& -\frac{1}{T} \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^{s_v}} + \varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_v}}{\partial \varepsilon^{s_v}} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^{s_v}} \right) \dot{\varepsilon}^{s_v} \\
& -\frac{1}{T} \sum_{\alpha} \sum_{j=1}^N \varepsilon^{\alpha} \rho^{\alpha} (\tilde{\mu}^{\alpha_j} - \lambda^{\alpha_j}) \dot{C}^{\alpha_j} \\
& -\frac{1}{T} \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \rho^l} - \varepsilon^l \lambda^l \right) \dot{\rho}^l \\
& -\frac{1}{T} \left[\varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial J^{s_e}} - \frac{1}{3} \frac{\varepsilon^{s_e}}{J^{s_e}} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_e j}) \right] \dot{J}^{s_e} \\
& -\frac{1}{T} \left[\varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_e}}{\partial J^{s_v}} - \frac{1}{3} \frac{\varepsilon^{s_v}}{J^{s_v}} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_v j}) \right] \dot{J}^{s_v} \\
& -\frac{1}{T} \left[\varepsilon^l \rho^l \frac{\partial A^l}{\partial \bar{\mathbf{C}}^{s_e}} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \bar{\mathbf{C}}^{s_e}} + \varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_v}}{\partial \bar{\mathbf{C}}^{s_e}} \right. \\
& \left. - \frac{\varepsilon^{s_e}}{2} (\bar{\mathbf{F}}^{s_e})^{-1} \cdot \left(\sum_{j=1}^N \mathbf{t}^{s_e j} \right) \cdot (\bar{\mathbf{F}}^{s_e})^{-T} - \frac{\varepsilon^{s_e} \rho^{s_e} \lambda^{s_e}}{2} (\bar{\mathbf{F}}^{s_e})^{-1} \cdot (\bar{\mathbf{F}}^{s_e})^{-T} \right] : \dot{\bar{\mathbf{C}}}^{s_e} \\
& -\frac{1}{T} \left[\varepsilon^l \rho^l \frac{\partial A^l}{\partial \bar{\mathbf{C}}^{s_v}} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \bar{\mathbf{C}}^{s_v}} + \varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_v}}{\partial \bar{\mathbf{C}}^{s_v}} \right. \\
& \left. - \frac{\varepsilon^{s_v}}{2} (\bar{\mathbf{F}}^{s_v})^{-1} \cdot \left(\sum_{j=1}^N \mathbf{t}^{s_v j} \right) \cdot (\bar{\mathbf{F}}^{s_v})^{-T} - \frac{\varepsilon^{s_v} \rho^{s_v} \lambda^{s_v}}{2} (\bar{\mathbf{F}}^{s_v})^{-1} \cdot (\bar{\mathbf{F}}^{s_v})^{-T} \right] : \dot{\bar{\mathbf{C}}}^{s_v} \\
& + \frac{\varepsilon^l}{T} \left(\sum_{j=1}^N \mathbf{t}^{l j} + \rho^l \lambda^l \mathbf{I} \right) : \mathbf{d}^l \\
& -\frac{1}{T} \sum_{\alpha} \left(\sum_{n=1}^q \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \bar{\mathbf{C}}^{s_v(n)}} \right) : \bar{\mathbf{C}}^{s_v(n+1)} \\
& -\frac{1}{T} \left[\varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \bar{\mathbf{C}}^{s_e}} : \nabla \bar{\mathbf{C}}^{s_e} + \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial \varepsilon^l} - \frac{\lambda^l}{\varepsilon^l} \right) \nabla \varepsilon^l \right. \\
& \left. + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^{s_v}} \nabla \varepsilon^{s_v} + \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^{s_v(n)}} : \nabla \bar{\mathbf{C}}^{s_v(n)} + \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \cdot \nabla \varepsilon^{(m)l} \right. \\
& \left. + \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial \rho^l} - \frac{\lambda^l}{\rho^l} \right) \nabla \rho^l + \varepsilon^l \rho^l \left(\sum_{j=1}^N \tilde{\mu}^{l j} - \lambda^{\alpha_j} \right) \nabla C^{l j} + \hat{\mathbf{T}}_{s_v}^l + \hat{\mathbf{T}}_{s_e}^l \right] \cdot \mathbf{v}^{l,s}
\end{aligned}$$

$$\begin{aligned}
& -\frac{1}{T} \left[\varepsilon^{s_e} \rho^{s_e} \left(\frac{\partial A^{s_e}}{\partial T} + \eta^{s_e} \right) \nabla T + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \bar{C}^{s_e}} : \nabla \bar{C}^{s_e} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \nabla \varepsilon^l \right. \\
& + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^{s_v}} \nabla \varepsilon^{s_v} + \varepsilon^{s_e} \rho^{s_e} \sum_{n=0}^q \frac{\partial A^{s_e}}{\partial \bar{C}^{s_v(n)}} : \nabla \bar{C}^{s_v(n)} + \varepsilon^{s_e} \rho^{s_e} \sum_{m=1}^p \frac{\partial A^{s_e}}{\partial \varepsilon^{(m)l}} \cdot \nabla \varepsilon^{(m)l} \\
& + \varepsilon^{s_e} \rho^{s_e} \left(\frac{\partial A^{s_e}}{\partial \rho^{s_e}} + \frac{\lambda^{s_e}}{J^{s_e}} \right) \nabla J^{s_e} + \varepsilon^{s_e} \rho^{s_e} \left(\sum_{j=1}^N \tilde{\mu}^{s_e j} - \lambda^{s_e j} \right) \nabla C^{s_e j} \\
& \quad \left. + \hat{T}_{s_v}^{s_e} + \hat{T}_l^{s_e} \right] \cdot \mathbf{v}^{s_e, s_v} \\
& - \frac{1}{T} \sum_{m=1}^p \left(\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^{(m)l}} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^{(m)l}} + \varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_v}}{\partial \varepsilon^{(m)l}} \right) \varepsilon^{(m+1)l} \\
& + \sum_{\alpha} \frac{\varepsilon^{\alpha} \nabla T}{T^2} \cdot \left\{ \mathbf{q}^{\alpha} + \sum_{j=1}^N \left[\rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha} \left(A^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2 \right) - \mathbf{t}^{\alpha j} \cdot \mathbf{v}^{\alpha j, \alpha} \right] \right\} \\
& + \sum_{\alpha} \frac{\varepsilon^{\alpha}}{T} \sum_{j=1}^{N-1} \left[\mathbf{t}^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \mathbf{t}^{\alpha N} - \rho^{\alpha j} (A^{\alpha j} - A^{\alpha N}) + \rho^{\alpha j} (\lambda^{\alpha j} - \lambda^{\alpha N}) \right] : \nabla \mathbf{v}^{\alpha j, \alpha} \\
& + \sum_{\alpha} \frac{1}{T} \sum_{j=1}^{N-1} \left\{ \frac{\rho^{\alpha j}}{\rho^{\alpha N}} (\hat{\mathbf{T}}_{\beta}^{\alpha N} + \hat{\mathbf{i}}^{\alpha N}) - (\hat{\mathbf{T}}_{\beta}^{\alpha j} + \hat{\mathbf{i}}^{\alpha j}) - \varepsilon^{\alpha} \mathbf{t}^{\alpha N} \nabla \left(\frac{\rho^{\alpha j}}{\rho^{\alpha N}} \right) \right. \\
& \left. + (\lambda^{\alpha j} - \lambda^{\alpha N}) \nabla (\varepsilon^{\alpha} \rho^{\alpha j}) - \nabla [\varepsilon^{\alpha} \rho^{\alpha j} (A^{\alpha N} - A^{\alpha j})] \right\} \cdot \mathbf{v}^{\alpha j, \alpha} \\
& - \frac{1}{T} \sum_{j=1}^N \hat{r}^{\alpha j} \left[\lambda^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2 \right] \\
& - \frac{1}{T} \sum_{\alpha} \sum_{j=1}^{N-1} \sum_{\beta \neq \alpha} \hat{e}_{\beta}^{\alpha j} \left[\lambda^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2 \right] \\
& - \frac{1}{T} \sum_{\alpha} \sum_{\beta \neq \alpha} \hat{e}_{\beta}^{\alpha} \left[A^{\alpha} + \frac{1}{2} (\mathbf{v}^{\alpha, s_v})^2 + \lambda^{\alpha} - \sum_{j=1}^{N-1} \lambda^{\alpha j} C^{\alpha j} \right] \left. \right\} \geq 0. \tag{4.12}
\end{aligned}$$

where we have used identities (3.31) and (3.32) to remove the N^{th} component dependence from terms involving $\mathbf{v}^{\alpha j, \alpha}$, and $\nabla \mathbf{v}^{\alpha j, \alpha}$, [13], and used (3.26)-(3.27) to eliminate \mathbf{d}^{s_v} and \mathbf{d}^{s_e} , as we did in Chapter 3, in favor of the independent

variables \dot{C}^{s_v} and \dot{J}^{s_v} , and \dot{C}^{s_e} and \dot{J}^{s_e} , respectively.

4.3.1 Three Phase Pressures

Because our system now contains three phases instead of two, it is necessary to revisit the subject of defining pressures for the liquid and solid phases. The changes in pressure definitions result from the fact that we now have two independent volume fractions as opposed to one. For the liquid phase we make the following definitions, $s = s_v, s_e$:

$$p^l(\varepsilon^l, \varepsilon^s, \rho^l, C^{l_j}) = (\rho^l)^2 \frac{\partial A^l}{\partial \rho^l} \Big|_{\varepsilon^l, \varepsilon^s, C^{l_j}} \quad (4.13)$$

is the classical pressure. Because two out of three of the volume fractions are held fixed and the sum of the volume fractions is one, that is, $\varepsilon^l + \varepsilon^{s_e} + \varepsilon^{s_v} = 1$, we can write p^l as a function of any two of the three volume fractions.

$$\bar{p}_s^l(\varepsilon^l, \varepsilon^s, \varepsilon^l \rho^{l_j}) = -\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \Big|_{\varepsilon^l \rho^{l_j}, \varepsilon^s} \quad (4.14)$$

is the thermodynamic pressure of the liquid phase holding the volume fraction of the s phase fixed,

$$\pi_s^l(\varepsilon^l, \varepsilon^s, \rho^l, C^{l_j}) = \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \Big|_{\varepsilon^s, \rho^l, C^{l_j}} \quad (4.15)$$

is the swelling potential of the liquid phase holding the volume fraction of the s phase fixed. These pressures are related through:

$$p^l(\varepsilon^l, \varepsilon^{s_v}, \rho^l, C^{l_j}) = \bar{p}_s^l(\varepsilon^l, \varepsilon^s, \varepsilon^l \rho^{l_j}) + \pi_s^l(\varepsilon^l, \varepsilon^s, \rho^l, C^{l_j}), \quad (4.16)$$

which is analogous to equation (3.42). In equations (4.5)-(4.7) we chose the Helmholtz potentials to be functions of ε^l and ε^{s_v} . Thus, we expect the thermodynamic pressure and swelling potential holding ε^{s_v} fixed to appear. Another

important relationship between the swelling potentials exists

$$\pi_{s_v}^l = \pi_{s_e}^l - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^{s_e}} \Bigg|_{\varepsilon^l, \rho^l, C^{lj}}. \quad (4.17)$$

This means that if the liquid phase and the s_e phase are non-interacting then $\pi_{s_v}^l = \pi_{s_e}^l$, which implies $\bar{p}_{s_v}^l = \bar{p}_{s_e}^l$ because of equation (4.16).

For the solid phases, $s = s_v, s_e$, we make the following definitions:

$$p^s(\varepsilon^l, \varepsilon^s, J^s, C^{sj}) = -\rho^s J^s \frac{\partial A^s}{\partial J^s} \Bigg|_{\varepsilon^l, \varepsilon^s, C^{sj}} \quad (4.18)$$

as the classical pressure of the s phase. Analogous to p^l , we note that p^s can be defined using any two of the three volume fractions.

$$\bar{p}_\beta^s(\varepsilon^\beta, \varepsilon^s, J^s, C^{sj}) = -\varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^s} \Bigg|_{\varepsilon^\beta, J^s, C^{sj}} \quad (4.19)$$

is the thermodynamic pressure of the s phase holding the volume fraction of the β phase fixed, where $\beta \neq s$.

$$\pi_\beta^s(\varepsilon^\beta, J^s, \rho^s, C^{sj}) = -\rho^s J^s \frac{\partial A^s}{\partial J^s} \Bigg|_{\varepsilon^\beta, \rho^s, C^{sj}} \quad (4.20)$$

is the swelling potential of the s phase holding the volume fraction of the β phase fixed, where $\beta \neq s$. These pressures related through:

$$p^s(\varepsilon^l, \varepsilon^s, J^s, C^{sj}) = \bar{p}_\beta^s(\varepsilon^\beta, \varepsilon^s, J^s, C^{sj}) + \pi_\beta^s(\varepsilon^\beta, J^s, \rho^s, C^{sj}), \quad (4.21)$$

which can be derived the same way as equation (3.46). We note that the difference between equations (4.18) and (4.20) is in the variables that are being held fixed. Again, we have a relationship between the swelling potentials

$$\pi_l^s = \pi_\beta^s - \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^\beta} \Bigg|_{\varepsilon^s, J^s, C^{sj}}, \quad (4.22)$$

where $\beta \neq s, l$, that is, β is the other solid phase. This means that if the solid phases are non-interacting then $\pi_l^s = \pi_\beta^s$, which implies that $\bar{p}_l^s = \bar{p}_\beta^s$ because of equation (4.21).

Because the Helmholtz potential of the s_e phase is not a function of its own volume fraction the pressure variable \bar{p}^{s_e} does not appear naturally, and instead we have terms involving $(\partial A^{s_e})/(\partial \varepsilon^l)|_{\varepsilon^{s_v}, \dots}$ and $(\partial A^{s_e})/(\partial \varepsilon^{s_v})|_{\varepsilon^l, \dots}$. Consider the following two choices of independent variables for the s_e phase:

$$A^{s_e}(\varepsilon^l, \varepsilon^{s_v}, \dots) = \bar{A}^{s_e}(\varepsilon^l, \varepsilon^{s_e}, \dots). \quad (4.23)$$

We note that because of the relationship between the volume fractions, equation (4.4), both sets of variables contain the same information, A^{s_e} and \bar{A}^{s_e} are not two different potentials, but rather the same potential with two different representations of the same set of independent variables. The total differential of equation (4.23) is given by

$$\begin{aligned} DA^{s_e} &= \left. \frac{\partial A^{s_e}}{\partial \varepsilon^l} \right|_{\varepsilon^{s_v}} d\varepsilon^l + \left. \frac{\partial A^{s_e}}{\partial \varepsilon^{s_v}} \right|_{\varepsilon^l} d\varepsilon^{s_v} + \dots \\ &= \left. \frac{\partial \bar{A}^{s_e}}{\partial \varepsilon^l} \right|_{\varepsilon^{s_e}} d\varepsilon^l + \left. \frac{\partial \bar{A}^{s_e}}{\partial \varepsilon^{s_e}} \right|_{\varepsilon^l} d\varepsilon^{s_e} + \dots \end{aligned} \quad (4.24)$$

Then, for example

$$\left. \frac{\partial A^{s_e}}{\partial \varepsilon^l} \right|_{\varepsilon^{s_v}} = \left. \frac{\partial \bar{A}^{s_e}}{\partial \varepsilon^l} \right|_{\varepsilon^{s_e}} - \left. \frac{\partial \bar{A}^{s_e}}{\partial \varepsilon^{s_e}} \right|_{\varepsilon^l}, \quad (4.25)$$

where

$$\left. \frac{\partial \varepsilon^{s_e}}{\partial \varepsilon^l} \right|_{\varepsilon^{s_v}} = -1, \quad (4.26)$$

because of the relationship between volume fractions, equation (4.4). Similarly,

$$\left. \frac{\partial A^{s_e}}{\partial \varepsilon^{s_v}} \right|_{\varepsilon^l} = - \left. \frac{\partial \bar{A}^{s_e}}{\partial \varepsilon^{s_e}} \right|_{\varepsilon^l}. \quad (4.27)$$

Equations (4.25) allows us to make conversions such as

$$\varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_v}, J^{s_e}, C^{s_e j}} = \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_e}, J^{s_e}, C^{s_e j}} + \bar{p}_l^{s_e}, \quad (4.28)$$

where we have used definition (4.19). In the following sections we will use calculations such as these to simplify our results.

4.3.2 Non-Equilibrium Results

The following variables are neither constitutive nor independent and appear linearly in the entropy inequality:

$$\dot{T}, \dot{\rho}^l, \dot{C}^{\alpha_j}, \dot{J}^{s_e}, \dot{J}^{s_v}, \nabla \mathbf{v}^{s_j, s}, \dot{\bar{C}}^{s_e}, \frac{(q+1)}{\bar{C}^{s_v}}, \frac{(p+1)l}{\varepsilon}, \quad (4.29)$$

where $s = s_v, s_e$. This means that they can vary arbitrarily, and because these variables appear linearly, to avoid violating entropy inequality (4.12), the coefficients of these variables must be identically zero. This yields the following set of non-equilibrium results:

$$\sum_{\alpha} \left(\frac{\partial A^{\alpha}}{\partial T} + \eta^{\alpha} \right) = 0, \quad (4.30)$$

$$\lambda^l = \frac{p^l}{\rho^l}, \quad (4.31)$$

$$\lambda^{\alpha_j} = \tilde{\mu}^{l_j}, \quad (4.32)$$

$$\frac{1}{3} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_e j}) = -p^{s_e}, \quad (4.33)$$

$$\frac{1}{3} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_v j}) = -p^{s_v}, \quad (4.34)$$

$$\mathbf{t}^{s_j} - \frac{\rho^{s_j}}{\rho^{s_N}} \mathbf{t}^{s_N} = \rho^{s_j} (A^{s_j} - A^{s_N} - \tilde{\mu}^{s_j}) \mathbf{I}, \quad s = s_v, s_e, \quad (4.35)$$

$$\sum_{j=1}^N \mathbf{t}^{s_{e_j}} = 2(\bar{\mathbf{F}}^{s_e}) \cdot \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_e}} \frac{\partial A^{\alpha}}{\partial \bar{\mathbf{C}}^{s_e}} \cdot (\bar{\mathbf{F}}^{s_e})^T - \rho^{s_e} \lambda^{s_e} \mathbf{I}, \quad (4.36)$$

$$\sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \bar{\mathbf{C}}^{(q)s_v}} = 0. \quad (4.37)$$

$$\sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \varepsilon^{(p)l}} = 0. \quad (4.38)$$

Consider equation (4.30). A classical result for a single material was demonstrated in Chapter 2, and says that T and η are dual variables. In this case we will make the simplifying assumption that

$$\frac{\partial A^{\alpha}}{\partial T} = -\eta^{\alpha}, \quad \forall \alpha. \quad (4.39)$$

Equation (4.31) gives an identity for the Lagrange multiplier and for the remainder of this section we will use it wherever λ^l appears. Equation (4.32) gives an identity for λ^{α_j} . It has been used to obtain (4.35) and will also be used throughout this chapter. Equations (4.33) and (4.34) are novel. They are a direct consequence of the new choice of independent variables. Since it is reasonable to expect the diffusive velocities in the solid phases to be negligible, see equation (A.12), we can rewrite these two equations as:

$$\frac{1}{3} \text{tr}(\mathbf{t}^{s_e}) = -p^{s_e}, \quad (4.40)$$

$$\frac{1}{3} \text{tr}(\mathbf{t}^{s_v}) = -p^{s_v}. \quad (4.41)$$

Equation (4.35) contains an N^{th} -component dependence which we will remove later since we do not want a result which depends on the labeling of the constituents. Equation (4.36) is novel and allows us to solve for the Lagrange multiplier λ^{s_e} . Again assuming the diffusive velocities in the s_e -phase are small, we have

$$\mathbf{t}^{s_e} = -\rho^{s_e} \lambda^{s_e} \mathbf{I} + 2(\overline{\mathbf{F}}^{s_e}) \cdot \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_e}} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^{s_e}} \cdot (\overline{\mathbf{F}}^{s_e})^T. \quad (4.42)$$

Taking 1/3 the trace of (4.42), using (4.40) to eliminate \mathbf{t}^{s_e} , and then solving for λ^{s_e} we obtain

$$\lambda^{s_e} = \frac{p^{s_e}}{\rho^{s_e}} + \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_e} \rho^{s_e}} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^{s_e}} : \overline{\mathbf{C}}^{s_e}. \quad (4.43)$$

Substituting this back into equation (4.42) yields

$$\mathbf{t}^{s_e} = -p^{s_e} \mathbf{I} + \mathbf{t}_{s_e}^{s_e} + \frac{\varepsilon^l}{\varepsilon^{s_e}} \mathbf{t}_{sh}^{s_e} - \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_e}} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^{s_e}} : \overline{\mathbf{C}}^{s_e}, \quad (4.44)$$

where

$$\mathbf{t}_{s_e}^{s_e} = 2\rho^{s_e} \overline{\mathbf{F}}^{s_e} \cdot \frac{\partial A^{s_e}}{\partial \overline{\mathbf{C}}^{s_e}} \cdot (\overline{\mathbf{F}}^{s_e})^T + 2 \frac{\varepsilon^{s_v} \rho^{s_v}}{\varepsilon^{s_e}} \overline{\mathbf{F}}^{s_e} \cdot \frac{\partial A^{s_v}}{\partial \overline{\mathbf{C}}^{s_e}} \cdot (\overline{\mathbf{F}}^{s_e})^T \quad (4.45)$$

and

$$\mathbf{t}_{sh}^{s_e} = 2\rho^l \overline{\mathbf{F}}^{s_e} \cdot \frac{\partial A^l}{\partial \overline{\mathbf{C}}^{s_e}} \cdot (\overline{\mathbf{F}}^{s_e})^T, \quad (4.46)$$

where $\mathbf{t}_{s_e}^{s_e}$ and $\mathbf{t}_{sh}^{s_e}$ are the Terzaghi and hydration stress tensors for the s_e -phase, respectively. Note that when we take one third the trace of (4.44) we recover (4.40) so that the physical pressure in the s_e phase, $-1/3\text{tr}(\mathbf{t}^{s_e})$, coincides with the classical pressure of that phase, p^{s_e} .

In equation (4.37) and (4.38) $\varepsilon^\alpha \rho^\alpha$ is begin held fixed, therefore we can bring it inside the partial derivative. Doing so yields

$$\frac{\partial A_T}{\partial \overline{\mathbf{C}}^{(q)s_v}} = 0, \quad (4.47)$$

and

$$\frac{\partial A_T}{\partial \varepsilon^{(p)l}} = 0, \quad (4.48)$$

where $\varepsilon^l \rho^l A^l + \varepsilon^{s_e} \rho^{s_e} A^{s_e} + \varepsilon^{s_v} \rho^{s_v} A^{s_v} = A_T$ is the total Helmholtz free energy. This means that the total Helmholtz free energy is not a function of the q^{th} derivative of the right Cauchy-Green tensor nor a function of the p^{th} derivative of the volume fraction of the liquid phase.

4.3.3 Equilibrium Results

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

$$\dot{\varepsilon}^l, \dot{\varepsilon}^{s_v}, \dot{\overline{\mathbf{C}}}^{s_v}, \mathbf{d}^l, \overline{\mathbf{C}}^{(n+1)s_v}, \mathbf{v}^{l,s_v}, \mathbf{v}^{s_e,s_v}, \varepsilon^{(m+1)l}, \nabla T, \nabla \mathbf{v}^{l_j,l}, \mathbf{v}^{\alpha_j,\alpha}, \widehat{e}_\beta^{\alpha_j}, \widehat{e}_\beta^\alpha, \quad (4.49)$$

where $n = 1, \dots, q - 1$ and $m = 1, \dots, p - 1$. Using the method for obtaining equilibrium results outlined in Chapter 2, we obtain the following results:

$$p^l = \sum_\alpha \varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial \varepsilon^l}, \quad (4.50)$$

$$\sum_\alpha \varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial \varepsilon^{s_v}} = 0, \quad (4.51)$$

$$\mathbf{t}^{s_v} = -\rho^{s_v} \lambda^{s_v} \mathbf{I} + 2\overline{\mathbf{F}}^{s_v} \cdot \left(\sum_\alpha \frac{\varepsilon^\alpha \rho^\alpha}{\varepsilon^{s_v}} \frac{\partial A^\alpha}{\partial \overline{\mathbf{C}}^{s_v}} \right) \cdot (\overline{\mathbf{F}}^{s_v})^T, \quad (4.52)$$

$$\mathbf{t}^l = -p^l \mathbf{I}, \quad (4.53)$$

$$\sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^{(n)sv}} = 0, \quad n = 1, \dots, q-1, \quad (4.54)$$

$$\begin{aligned} \widehat{\mathbf{T}}_{s_v}^l + \widehat{\mathbf{T}}_{s_e}^l &= \overline{p}_{s_v}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^{sv}} \nabla \varepsilon^{sv} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \overline{\mathbf{C}}^{s_e}} : (\nabla \overline{\mathbf{C}}^{s_e})^T \\ &- \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \overline{\mathbf{C}}^{(n)sv}} : (\nabla \overline{\mathbf{C}}^{(n)sv})^T - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^{(m)l}, \end{aligned} \quad (4.55)$$

$$\begin{aligned} \widehat{\mathbf{T}}_{s_v}^{s_e} + \widehat{\mathbf{T}}_l^{s_e} &= -\varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \nabla \varepsilon^l - \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^{sv}} \nabla \varepsilon^{sv} \\ &- \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \overline{\mathbf{C}}^{s_e}} : (\nabla \overline{\mathbf{C}}^{s_e})^T - \varepsilon^{s_e} \rho^{s_e} \sum_{n=0}^q \frac{\partial A^{s_e}}{\partial \overline{\mathbf{C}}^{(n)sv}} : (\nabla \overline{\mathbf{C}}^{(n)sv})^T \\ &- \varepsilon^{s_e} \rho^{s_e} \sum_{m=1}^p \frac{\partial A^{s_e}}{\partial \varepsilon^l} \nabla \varepsilon^{(m)l} - \varepsilon^{s_e} \rho^{s_e} \left(\frac{\partial A^{s_e}}{\partial J^{s_e}} + \frac{\lambda^{s_e}}{J^{s_e}} \right) \nabla J^{s_e}, \end{aligned} \quad (4.56)$$

$$\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} + \varepsilon^{sv} \rho^{sv} \frac{\partial A^{sv}}{\partial \varepsilon^l} = 0, \quad m = 1, \dots, p-1, \quad (4.57)$$

$$\sum_{\alpha} \varepsilon^{\alpha} \mathbf{q}^{\alpha} = 0, \quad (4.58)$$

$$\mathbf{t}^{lj} - \frac{\rho^{lj}}{\rho^{lN}} \mathbf{t}^{lN} = \rho^{lj} (A^{lj} - A^{lN} - \tilde{\mu}^{lj}), \quad (4.59)$$

$$\begin{aligned} (\widehat{\mathbf{T}}_{\beta}^{\alpha_j} + \widehat{\mathbf{i}}^{\alpha_j}) - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} (\widehat{\mathbf{T}}_{\beta}^{\alpha_N} + \widehat{\mathbf{i}}^{\alpha_N}) &= -\varepsilon^{\alpha} \mathbf{t}^{\alpha N} \nabla \left(\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \right) \\ &+ (\lambda^{\alpha_j} - \lambda^{\alpha_N}) \nabla (\varepsilon^{\alpha} \rho^{\alpha_j}) - \nabla [\varepsilon^{\alpha} \rho^{\alpha_j} (A^{\alpha_j} - A^{\alpha_N})], \end{aligned} \quad (4.60)$$

$$\tilde{\mu}^{lj} = \tilde{\mu}^{svj} = \tilde{\mu}^{s_ej}, \quad (4.61)$$

$$A^\alpha + \lambda^\alpha - \sum_{j=1}^{N-1} \tilde{\mu}^{\alpha_j} C^{\alpha_j} = A^\beta + \lambda^\beta - \sum_{j=1}^{N-1} \tilde{\mu}^{\beta_j} C^{\beta_j}, \quad \forall \alpha, \beta, \beta \neq \alpha, \quad (4.62)$$

Writing equation (4.50) holding the appropriate variables fixed we have

$$\begin{aligned} p^l = & \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_v}, \rho^l, C^{l_j}} + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_v}, J^{s_e}, C^{s_e j}} \\ & + \varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_v}}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_v}, J^{s_v}, C^{s_v j}}. \end{aligned} \quad (4.63)$$

Using the definition of the swelling potential for the liquid phase, equation (4.15), the three pressure relationship, equation (4.16), and combining equations (4.27) and (4.19) with $s = s_e$, we obtain

$$\bar{p}_{s_v}^l - \bar{p}_l^{s_e} = \varepsilon^{s_e} \rho^{s_e} \left(\frac{\partial A^{s_e}}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_e}, J^{s_e}, C^{s_e j}} + \frac{\partial A^{s_v}}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_v}, J^{s_v}, C^{s_v j}} \right). \quad (4.64)$$

To interpret this result, assume for the moment that the s_e phase is inert with respect to both the liquid and s_v phase. Then equation (4.64) becomes

$$\bar{p}^l - \bar{p}^{s_e} = \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_v}}{\partial \varepsilon^l} \Big|_{\varepsilon^{s_v}, J^{s_v}, C^{s_v j}}, \quad (4.65)$$

which means that there is a difference in the thermodynamic pressures of the liquid and drug phase if the viscoelastic solid phase has a preference for the either of the other phases. If there is no elastic solid phase, equation (4.63) becomes

$$p^l = \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \Big|_{\rho^l, C^{l_j}} - \varepsilon^{s_v} \rho^{s_v} \frac{\partial A^{s_v}}{\partial \varepsilon^{s_v}} \Big|_{J^{s_v}, C^{s_v j}}, \quad (4.66)$$

or

$$\bar{p}^l = \bar{p}^{s_v}, \quad (4.67)$$

which is the standard two-phase result. For a non-interacting system the swelling potential of the liquid phase is zero, that is, $\pi^l = 0$. Using the three pressure relationship, equation (4.67) becomes

$$p^l = p^{s_v} - \pi^{s_v}, \quad (4.68)$$

which says that at equilibrium, the pressure in the liquid phase is the pressure in the solid phase minus the pressure due to configurational changes.

Equation (4.51) can be written

$$\bar{p}_l^{s_v} - \bar{p}_l^{s_e} = \varepsilon^l \rho^l \left. \frac{\partial A^l}{\partial \varepsilon^{s_v}} \right|_{\varepsilon^l, \rho^l, C^{lj}} \quad (4.69)$$

where we have used equation (4.19) for both solid phases and used (4.27) to obtain the elastic solid phase pressure. This states that there is a difference in the thermodynamic pressures of the solid phases (keeping the volume fraction of the liquid phase fixed) if the liquid prefers one solid phase over the other.

Taking 1/3 the trace of equation (4.52), using equation (4.41), and solving for λ^{s_v} yields

$$\lambda^{s_v} = \frac{p^{s_v}}{\rho^{s_v}} + \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_v} \rho^{s_v}} \frac{\partial A^{\alpha}}{\partial \bar{\mathbf{C}}^{s_v}} : \bar{\mathbf{C}}^{s_v}. \quad (4.70)$$

We then substitute back into (4.52) to get

$$\mathbf{t}^{s_v} = -p^{s_v} \mathbf{I} + \mathbf{t}_{se}^{s_v} + \frac{\varepsilon^l}{\varepsilon^{s_v}} \mathbf{t}_{sh}^{s_v} - \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_v}} \frac{\partial A^{\alpha}}{\partial \bar{\mathbf{C}}^{s_v}} : \bar{\mathbf{C}}^{s_v}, \quad (4.71)$$

where

$$\mathbf{t}_{se}^{s_v} = 2\rho^{s_v} \bar{\mathbf{F}}^{s_v} \cdot \frac{\partial A^{s_v}}{\partial \bar{\mathbf{C}}^{s_v}} \cdot (\bar{\mathbf{F}}^{s_v})^T + 2 \frac{\varepsilon^{s_e}}{\varepsilon^{s_v}} \rho^{s_e} \bar{\mathbf{F}}^{s_v} \cdot \frac{\partial A^{s_e}}{\partial \bar{\mathbf{C}}^{s_v}} \cdot (\bar{\mathbf{F}}^{s_v})^T, \quad (4.72)$$

and

$$\mathbf{t}_{sh}^{s_v} = 2\rho^l \overline{\mathbf{F}}^{s_v} \cdot \frac{\partial A^l}{\partial \overline{\mathbf{C}}^{s_v}} \cdot (\overline{\mathbf{F}}^{s_v})^T, \quad (4.73)$$

where $\mathbf{t}_{se}^{s_v}$ and $\mathbf{t}_{sh}^{s_v}$ are the Terzaghi and hydration stress tensors for the s_v -phase, respectively. Analogous to the s_e phase, we note that by taking one-third the trace of equation (4.71), we recover equation (4.41).

Equation (4.53) says that the liquid phase stress coincides with the classical pressure for that phase at equilibrium.

In order to interpret the meaning of equation (4.54), we can take the $\varepsilon^\alpha \rho^\alpha$ inside the partial derivative because it is being held fixed, thus equation (4.54) can be written

$$\frac{\partial A_T}{\partial \overline{\mathbf{C}}^{s_v(n)}} = 0, \quad n = 1, \dots, q-1, \quad (4.74)$$

where we have used $\varepsilon^l \rho^l A^l + \varepsilon^{s_e} \rho^{s_e} A^{s_e} + \varepsilon^{s_v} \rho^{s_v} A^{s_v} = A_T$. This means that at equilibrium, the total Helmholtz free energy is not a function of rates of shear, and thus behaves elastically at equilibrium as opposed to viscoelastically.

Equation (4.55) simplifies to

$$\begin{aligned} \widehat{\mathbf{T}}_{s_v}^l + \widehat{\mathbf{T}}_{s_e}^l &= \overline{p}_{s_v}^l \nabla \varepsilon^l - (\overline{p}_{s_v}^{s_v} - \overline{p}_{s_e}^{s_e}) \nabla \varepsilon^{s_v} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \overline{\mathbf{C}}^{s_e}} : (\nabla \overline{\mathbf{C}}^{s_e})^T \\ &\quad - \varepsilon^l \rho^l \sum_{q=0}^p \frac{\partial A^l}{\partial \overline{\mathbf{C}}^{s_v(n)}} : (\nabla \overline{\mathbf{C}}^{s_v(n)})^T - \varepsilon^l \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^l(m)} \nabla \varepsilon^l(m), \end{aligned} \quad (4.75)$$

where we have used definition (4.69). Later this will be used in the momentum balance equation to derive a generalized Darcy's Law.

Equation (4.56) can be significantly simplified as well. First we use equation (4.28), and combine (4.27) with (4.19) with $s = s_e$ to rewrite the first two terms

of (4.56) in terms of $\bar{p}_l^{s_e}$. The last term in brackets is simplified using equation (4.18) to replace the partial derivative term with a pressure term, and λ^{s_e} is eliminated using (4.43). The result is that

$$\begin{aligned} \widehat{\mathbf{T}}_l^{s_e} + \widehat{\mathbf{T}}_{s_v}^{s_e} &= \bar{p}_l^{s_e} \nabla \varepsilon^{s_e} - \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \bigg|_{\varepsilon^{s_e}, J^{s_e}, \mathbf{C}^{s_e j}} \nabla \varepsilon^l - \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \bar{\mathbf{C}}^{s_e}} : (\nabla \bar{\mathbf{C}}^{s_e})^T \\ &- \varepsilon^{s_e} \rho^{s_e} \sum_{n=0}^q \frac{\partial A^{s_e}}{\partial \bar{\mathbf{C}}^{s_e (n)}} : (\nabla \bar{\mathbf{C}}^{s_e (n)})^T - \varepsilon^{s_e} \rho^{s_e} \sum_{m=1}^p \frac{\partial A^{s_e}}{\partial \varepsilon^{(m)l}} \nabla \varepsilon^{(m)l} \\ &- \frac{2}{3} \left(\sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{J^{s_e}} \frac{\partial A^{\alpha}}{\partial \bar{\mathbf{C}}^{s_e}} : \bar{\mathbf{C}}^{s_e} \right) \nabla J^{s_e}. \end{aligned} \quad (4.76)$$

Similar to equation (4.54), equation (4.57) can be written

$$\frac{\partial A_T}{\partial \varepsilon^{(m)l}} = 0, \quad m = 1, \dots, p-1, \quad (4.77)$$

which means that the total Helmholtz free energy is a function of ε^l at equilibrium and not a function of its derivatives.

Equation (4.58) says that at equilibrium there is no net heat flux.

The rest of the equilibrium results contain N^{th} component dependencies, which we address in the next section.

4.3.4 Removing N^{th} Component Dependencies

Equations (4.35), (4.59), (4.60), and (4.61) contain N^{th} component dependencies which result from using the concentration of species as independent variables. Classical Gibbsian thermodynamics does not encounter this problem because extensive variables, such as the number of molecules, as opposed to intensive variables, such as concentrations, are used as independent variables. However, physically meaningful upscaling is not possible using extensive variables. In classical Gibbsian thermodynamics the chemical potential (1) is scalar

and measures the amount of energy needed to insert a particle into the system, (2) has its gradient as the driving force for diffusive flow (Fick's law), and (3) is constant for a single constituent coexisting in two phases at equilibrium. In [13], Bennethum et al. found that a judicious choice for the $\mu^{\alpha N}$ satisfies these requirements. Following Bennethum et al. [13], we take

$$\mu^{lN} = A^{lN} - \frac{\mathbf{t}^{lN}}{\rho^{lN}}, \quad (4.78)$$

$$\mu^{sN} = A^{sN} - \frac{\mathbf{t}^{sN}}{\rho^{sN}} + \frac{\mathbf{t}_{se}^s}{\rho^s} + \frac{\varepsilon^l \mathbf{t}_{sh}^s}{\varepsilon^s \rho^s}, \quad s = s_v, s_e. \quad (4.79)$$

Substituting equation (4.78) into (4.59), and equation (4.79) into (4.35), we obtain

$$\mu^{lj} \mathbf{I} = A^{lj} \mathbf{I} - \frac{\mathbf{t}^{lj}}{\rho^{lj}}, \quad (4.80)$$

$$\mu^{sj} \mathbf{I} = A^{sj} \mathbf{I} - \frac{\mathbf{t}^{sj}}{\rho^{sj}} + \frac{\mathbf{t}_{se}^s}{\rho^s} + \frac{\varepsilon^l \mathbf{t}_{sh}^s}{\varepsilon^s \rho^s}, \quad s = s_v, s_e, \quad (4.81)$$

respectively. Multiplying (4.80) and (4.81) by $C^{\alpha j}$ and summing j from 1 to N , then eliminating \mathbf{t}^l with equation (4.53), and \mathbf{t}^s with equations (4.44) and (4.71), we obtain the following expressions for the Gibbs free energy

$$G^l = \sum_{j=1}^N \mu^{lj} C^{lj} = A^l + \frac{p^l}{\rho^l}, \quad (4.82)$$

$$G^s = \sum_{j=1}^N \mu^{sj} C^{sj} = A^s + \frac{p^s}{\rho^s} + \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^s \rho^s} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^s} : \overline{\mathbf{C}}^s, \quad s = s_v, s_e. \quad (4.83)$$

Rewriting equation (4.62) as

$$\begin{aligned} & A^{\alpha} + \lambda^{\alpha} - \sum_{j=1}^N \mu^{\alpha j} C^{\alpha j} + \mu^{\alpha N} \\ &= A^{\beta} + \lambda^{\beta} - \sum_{j=1}^N \mu^{\beta j} C^{\beta j} + \mu^{\beta N}, \quad \forall \alpha, \beta, \beta \neq \alpha, \end{aligned} \quad (4.84)$$

then substituting (4.31) for λ^l , (4.43) for λ^{s_e} , (4.70) for λ^{s_v} , and using (4.82) and (4.83), we obtain

$$\mu^{\alpha_N} = \mu^{\beta_N}, \quad \forall \alpha, \beta, \beta \neq \alpha. \quad (4.85)$$

Substituting this result into equation (4.61), yields the classical result

$$\mu^{\alpha_j} = \mu^{\beta_j}, \quad \forall \alpha, \beta, \beta \neq \alpha, \quad (4.86)$$

which states that the chemical potential of a species in different phases is equal at equilibrium.

To remove the N^{th} component dependence from equation (4.60) we first consider $\alpha = s_e$. Summing from j from 1 to N we obtain:

$$\begin{aligned} & \left(\widehat{\mathbf{T}}_l^{s_e} + \widehat{\mathbf{T}}_{s_v}^{s_e} \right) - \frac{\rho^{s_e}}{\rho^{s_e N}} \left(\widehat{\mathbf{T}}_l^{s_e N} + \widehat{\mathbf{T}}_{s_v}^{s_e N} + \widehat{\mathbf{i}}^{s_e N} \right) \\ &= -\varepsilon^{s_e} \mathbf{t}^{s_e N} \cdot \nabla \left(\frac{\rho^{s_e}}{\rho^{s_e N}} \right) + \sum_{j=1}^N \tilde{\mu}^{s_e j} \nabla (\varepsilon^{s_e} \rho^{s_e j}) \\ & - \varepsilon^{s_e} \rho^{s_e} \nabla A^{s_e} - A^{s_e} \nabla (\varepsilon^{s_e} \rho^{s_e}) + \nabla (\varepsilon^{s_e} \rho^{s_e} A^{s_e N}), \end{aligned} \quad (4.87)$$

where $\sum_{j=1}^N \widehat{\mathbf{i}}^{s_e j} = 0$ and $\sum_{j=1}^N \left(\widehat{\mathbf{T}}_l^{s_e j} + \widehat{\mathbf{T}}_{s_v}^{s_e j} \right) = \widehat{\mathbf{T}}_l^{s_e} + \widehat{\mathbf{T}}_{s_v}^{s_e}$ due to restrictions (2.37) and (2.38), respectively. Using equation (4.76) to eliminate $\widehat{\mathbf{T}}_l^{s_e} + \widehat{\mathbf{T}}_{s_v}^{s_e}$ from the left-hand side of equation (4.87), expanding ∇A^{s_e} using the following calculation

$$\begin{aligned} \nabla A^{s_e} &= \frac{\partial A^{s_e}}{\partial \varepsilon^l} \nabla \varepsilon^l + \frac{\partial A^{s_e}}{\partial \varepsilon^{s_v}} \nabla \varepsilon^{s_v} + \sum_{m=1}^p \frac{\partial A^{s_e}}{\partial \varepsilon^{(m)l}} \nabla \varepsilon^{(m)l} + \frac{\partial A^{s_e}}{\partial J^{s_e}} \nabla J^{s_e} \\ & + \sum_{j=1}^{N-1} \tilde{\mu}^{s_e j} \nabla (C^{s_e j}) + \frac{\partial A^{s_e}}{\partial T} \nabla T + \frac{\partial A^{s_e}}{\partial \overline{\mathbf{C}}^{s_v}} : (\nabla \overline{\mathbf{C}}^{s_v})^T \\ & + \sum_{n=1}^q \frac{\partial A^{s_e}}{\partial \overline{\mathbf{C}}^{(n) s_v}} : (\nabla \overline{\mathbf{C}}^{(n) s_v})^T + \frac{\partial A^{s_e}}{\partial \overline{\mathbf{C}}^{s_e}} : (\nabla \overline{\mathbf{C}}^{s_e})^T, \end{aligned} \quad (4.88)$$

and then canceling like terms we get

$$\begin{aligned}
& \bar{p}_l^{s_e} - \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \nabla \varepsilon^l - \frac{2}{3} \left(\sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{J^{s_e}} \frac{\partial A^{\alpha}}{\partial \bar{C}^{s_e}} : \bar{C}^{s_e} \right) \nabla J^{s_e} \\
& - \frac{\rho^{s_e}}{\rho^{s_{eN}}} (\widehat{\mathbf{T}}_l^{s_{eN}} + \widehat{\mathbf{T}}_{s_v}^{s_{eN}} + \widehat{\mathbf{i}}^{s_{eN}}) = -\varepsilon^{s_e} \mathbf{t}^{s_{eN}} \cdot \nabla \left(\frac{\rho^{s_e}}{\rho^{s_{eN}}} \right) + \sum_{j=1}^N \tilde{\mu}^{s_{ej}} \nabla (\varepsilon^{s_e} \rho^{s_{ej}}) \\
& - A^{s_e} \nabla (\varepsilon^{s_e} \rho^{s_e}) - \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^l} \nabla \varepsilon^l - \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial \varepsilon^{s_v}} \nabla \varepsilon^{s_v} \\
& - \varepsilon^{s_e} \rho^{s_e} \sum_{j=1}^{N-1} \tilde{\mu}^{s_{ej}} \nabla C^{s_{ej}} + \nabla (\varepsilon^{s_e} \rho^{s_e} A^{s_{eN}}) - \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial J^{s_e}} \nabla J^{s_e}. \tag{4.89}
\end{aligned}$$

In the previous calculation we have dropped the term involving ∇T since it is zero at equilibrium. The first two terms on the left-hand side are equivalent to the fourth and fifth terms of the right-hand side as described in the paragraph preceding equation (4.76). Furthermore, if we expand the gradient portion of the second term on the right-hand side $\nabla (\varepsilon^{s_e} \rho^{s_{ej}}) = \varepsilon^{s_e} \rho^{s_e} \nabla C^{s_{ej}} + C^{s_{ej}} \nabla (\varepsilon^{s_e} \rho^{s_e})$ we can eliminate the first term of the last line as well. Collecting all the terms involving the N^{th} component on one side and all other terms on the other side, we are left with

$$\begin{aligned}
& \frac{\rho^{s_e}}{\rho^{s_{eN}}} (\widehat{\mathbf{T}}_l^{s_{eN}} + \widehat{\mathbf{T}}_{s_v}^{s_{eN}} + \widehat{\mathbf{i}}^{s_{eN}}) - \varepsilon^{s_e} \mathbf{t}^{s_{eN}} \cdot \nabla \left(\frac{\rho^{s_e}}{\rho^{s_{eN}}} \right) \\
& + \nabla (\varepsilon^{s_e} \rho^{s_e} A^{s_{eN}}) - \mu^{s_{eN}} \nabla (\varepsilon^{s_e} \rho^{s_e}) \\
& = A^{s_e} \nabla (\varepsilon^{s_e} \rho^{s_e}) + \varepsilon^{s_e} \rho^{s_e} \frac{\partial A^{s_e}}{\partial J^{s_e}} \nabla J^{s_e} - \sum_{j=1}^N \mu^{s_{ej}} C^{s_{ej}} \nabla (\varepsilon^{s_e} \rho^{s_e}) \\
& - \frac{2}{3} \left(\sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{J^{s_e}} \frac{\partial A^{\alpha}}{\partial \bar{C}^{s_e}} : \bar{C}^{s_e} \right) \nabla J^{s_e}. \tag{4.90}
\end{aligned}$$

Substituting equation (4.20) for the second term on the right-hand side and using (4.83) with $s = s_e$ for the third term, the right-hand side of equation

(4.90) becomes

$$\begin{aligned}
& A^{s_e} \nabla(\varepsilon^{s_e} \rho^{s_e}) + \frac{\varepsilon^{s_e}}{J^{s_e}} p^{s_e} \nabla J^{s_e} - \frac{2}{3} \left(\sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{J^{s_e}} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^{s_e}} : \overline{\mathbf{C}}^{s_e} \right) \nabla J^{s_e} \\
& - \left(A^{s_e} + \frac{p^{s_e}}{\rho^{s_e}} + \frac{2}{3} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_e} \rho^{s_e}} \frac{\partial A^{\alpha}}{\partial \overline{\mathbf{C}}^{s_e}} : \overline{\mathbf{C}}^{s_e} \right) \nabla(\varepsilon^{s_e} \rho^{s_e}) = 0,
\end{aligned} \tag{4.91}$$

since $\nabla(\varepsilon^{s_e} \rho^{s_e}) = -\frac{\varepsilon^{s_e} \rho^{s_e}}{J^{s_e}} \nabla J^{s_e}$. Thus,

$$\begin{aligned}
& \frac{\rho^{s_e}}{\rho^{s_e N}} (\widehat{\mathbf{T}}_{s_v}^{s_e N} + \widehat{\mathbf{T}}_l^{s_e N} + \widehat{\mathbf{i}}^{s_e N}) - \varepsilon^{s_e} \mathbf{t}^{s_e N} \cdot \nabla \left(\frac{\rho^{s_e}}{\rho^{s_e N}} \right) \\
& + \nabla(\varepsilon^{s_e} \rho^{s_e} A^{s_e N}) - \mu^{s_e N} \nabla(\varepsilon^{s_e} \rho^{s_e}) = 0.
\end{aligned} \tag{4.92}$$

Substituting equation (4.92) back into equation (4.87), and undoing the summation prior to equation (4.87), we obtain

$$\sum_{\beta \neq s_e} \widehat{\mathbf{T}}_{\beta}^{s_e j} + \widehat{\mathbf{i}}^{s_e j} = \mu^{s_e j} \nabla(\varepsilon^{s_e} \rho^{s_e j}) - \nabla(\varepsilon^{s_e} \rho^{s_e} A^{s_e j}). \tag{4.93}$$

Removing the N^{th} component dependence from (4.60) with $\alpha = l$ is done in an analogous manner and yields

$$\begin{aligned}
& \frac{\rho^l}{\rho^{l N}} (\widehat{\mathbf{T}}_{s_e}^{l N} + \widehat{\mathbf{T}}_{s_v}^{l N} + \widehat{\mathbf{i}}^{l N}) - \varepsilon^l \mathbf{t}^{l N} \cdot \nabla \left(\frac{\rho^l}{\rho^{l N}} \right) \\
& + \nabla(\varepsilon^l \rho^l A^{l N}) - \mu^{l N} \nabla(\varepsilon^l \rho^l) = 0,
\end{aligned} \tag{4.94}$$

whence,

$$\sum_{\beta \neq l} \widehat{\mathbf{T}}_{\beta}^{l j} + \widehat{\mathbf{i}}^{l j} = \mu^{l j} \nabla(\varepsilon^l \rho^{l j}) - \nabla(\varepsilon^l \rho^l A^{l j}). \tag{4.95}$$

4.3.5 Near-Equilibrium Results

We obtain near-equilibrium results using the method described in Chapter 2. We choose to perform a one variable expansion for all of the variables in (4.49).

In what follows we use indicial notation so that the order of the coefficients resulting from the linearization process and the contractions are clear. For the variables $\dot{\varepsilon}^l$ and $\dot{\varepsilon}^{sv}$ we obtain following near-equilibrium relationships:

$$\bar{p}_{s_v}^l - \bar{p}_l^{s_e} - \sum_{s=s_v, s_e} \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^l} \Big|_{\varepsilon^s, J^s, C^{s_j}} = -\eta^l \dot{\varepsilon}^l, \quad (4.96)$$

$$\bar{p}_l^{s_v} - \bar{p}_l^{s_e} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^{s_v}} \Big|_{\varepsilon^l, \rho^l, C^{l_j}} = -\eta^s \dot{\varepsilon}^{s_v}, \quad (4.97)$$

respectively. The coefficients η^l and η^s are scalar material parameters that may contain information such as: the stiffness of the solid matrix, the ease (or difficulty) with which the solid phase swells, and the connectedness of the two solid phases. For the coefficients of $\dot{\bar{C}}^{s_v}$, \mathbf{d}^l , and $\bar{C}^{(n+1)s_v}$, where $n = 1, \dots, q-1$, we obtain the following near-equilibrium relationships:

$$\begin{aligned} t_{lk}^{s_v} &= -p^{s_v} \delta_{lk} + (t_{se}^{s_v})_{lk} + \frac{\varepsilon^l}{\varepsilon^{s_v}} (t_{sh}^{s_v})_{lk} - \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{\varepsilon^{s_v}} \frac{\partial A^{s_v}}{\partial \bar{C}_{LK}^{s_v}} : \bar{C}_{LK}^{s_v} \delta_{lk} \\ &\quad - \sum_{j=1}^N \rho^{s_v j} v_l^{s_v j, s_v} v_k^{s_v j, s_v} + \bar{F}_{kK}^{s_v} G_{LKMN}^{s_v} \dot{\bar{C}}_{MN}^{s_v} \bar{F}_{lL}^{s_v}, \end{aligned} \quad (4.98)$$

$$t_{lk}^l = -p^l \delta_{lk} - \sum_{j=1}^N \rho^{l_j} v_l^{l_j, l} v_k^{l_j, l} + G_{lkmn}^l d_{mn}^l, \quad (4.99)$$

$$\sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \bar{C}_{LK}^{(n)s_v}} = Q_{LKMN}^n \bar{C}_{MN}^{(n+1)s_v}, \quad n = 1, \dots, q-1, \quad (4.100)$$

where the components of $\mathbf{t}_{se}^{s_v}$ are given by $(t_{se}^{s_v})_{lk}$ and the components of $\mathbf{t}_{sh}^{s_v}$ $(t_{sh}^{s_v})_{lk}$. Here $G_{LKMN}^{s_v}$, G_{lkmn}^l , and Q_{LKMN}^n are all fourth-order positive semi-definite tensors. $G_{LKMN}^{s_v}$ accounts for the viscoelastic solid stress dissipation due

to relaxation in shearing of the viscoelastic solid. G_{lkmn}^l is a viscous dissipation tensor. And lastly, Q_{LKMN}^n are material coefficients of the n^{th} derivative of the shear rate, $\overline{C}^{sv(n)}$, and like G_{LKMN}^{sv} , represent stress dissipation due to relaxation in shearing of the viscoelastic solid. For the coefficients of $\mathbf{v}^{l,sv}$ and $\mathbf{v}^{se,sv}$ we obtain the following near-equilibrium results:

$$\begin{aligned} (\widehat{T}_{s_e}^l)_k + (\widehat{T}_{s_v}^l)_k &= -R_{km}^l v_m^{l,sv} + \bar{p}_{s_v}^l \varepsilon_{,k}^l - (\bar{p}_{s_v}^{sv} - \bar{p}_{s_e}^{se}) \varepsilon_{,k}^{sv} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \overline{C}_{LK}^{se}} \overline{C}_{LK,k}^{se} \\ &\quad - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \overline{C}_{LK}^{sv(n)}} \overline{C}_{LK,k}^{sv(n)} - \sum_{m=1}^p \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon_{,k}^{(m)l}} \varepsilon_{,k}^{(m)l}, \end{aligned} \quad (4.101)$$

$$\begin{aligned} (\widehat{T}_l^{se})_k + (\widehat{T}_{s_v}^{se})_k &= -R_{km}^{se} v_m^{se,sv} + \bar{p}_l^{se} \varepsilon_{,k}^{se} - \varepsilon^{se} \rho^{se} \frac{\partial A^{se}}{\partial \varepsilon^l} \varepsilon_{,k}^l - \varepsilon^{se} \rho^{se} \frac{\partial A^{se}}{\partial \overline{C}_{LK}^{se}} \overline{C}_{LK,k}^{se} \\ &\quad - \varepsilon^{se} \rho^{se} \sum_{n=0}^q \frac{\partial A^{se}}{\partial \overline{C}_{LK}^{sv(n)}} \overline{C}_{LK,k}^{sv(n)} - \varepsilon^{se} \rho^{se} \sum_{m=1}^p \frac{\partial A^{se}}{\partial \varepsilon_{,k}^{(m)l}} \varepsilon_{,k}^{(m)l} \\ &\quad - \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha} \rho^{\alpha}}{J^{se}} \frac{\partial A^{\alpha}}{\partial \overline{C}_{LK}^{se}} \overline{C}_{LK}^{se} J_{,k}^{se}. \end{aligned} \quad (4.102)$$

Here, both R_{km}^l and R_{km}^{se} are second-order resistivity tensors. However, since the elastic solid phase does not flow inside the viscoelastic solid phase R_{km}^{se} is taken sufficiently large so that when we invert it and solve for $\mathbf{v}^{se,sv}$ we get that $\mathbf{v}^{se,sv} = 0$, as expected. For the coefficient of $\varepsilon^{(m+1)l}$ and ∇T , we obtain the following near-equilibrium results:

$$\sum_{\alpha} \varepsilon^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \varepsilon_{,k}^{(m)l}} = -\eta^m \varepsilon_{,k}^{(m+1)l}, \quad m = 1, \dots, p-1, \quad (4.103)$$

$$\begin{aligned} q_k^s &= \sum_{j=1}^N \left[t_{km}^{sj} v_m^{sj,s} - \rho^{sj} v_k^{sj,s} \left(A^{sj} + \frac{1}{2} v_m^{sj,s} v_m^{sj,s} \right) \right] \\ &\quad + K_{km}^s T_{,m}, \quad s = s_v, s_e, \end{aligned} \quad (4.104)$$

and

$$q_k^l = \sum_{j=1}^N \left[t_{km}^{l_j} v_m^{l_j,l} - \rho^{l_j} v_k^{l_j,l} \left(A^{l_j} + \frac{1}{2} v_m^{l_j,l} v_m^{l_j,l} \right) \right] + K_{km}^l T_{,m}, \quad (4.105)$$

respectively. Here, η^m are scalar coefficients, and K_{km}^s and K_{km}^l are second-order tensors. Most often it is reasonable to assume that $\mathbf{v}^{s_j,s} \approx 0$, in which case equation (4.104) reduces to $\mathbf{q} = \mathbf{K}^s \cdot \nabla T$, so that we recover Fourier's law of heat conduction for the solid phases. The coefficients of $\nabla \mathbf{v}^{l_j,l}$ and $\mathbf{v}^{l_j,l}$ produce the following near-equilibrium results:

$$\mu^{l_j} \delta_{mn} = S_{mnkl}^{l_j} v_{k,l}^{l_j,l} + A^{l_j} \delta_{mn} - \frac{t_{mn}^{l_j}}{\rho^{l_j}}, \quad (4.106)$$

and

$$\sum_{\beta \neq l} (\widehat{T}_\beta^{l_j})_k + \widehat{i}_k^{l_j} = -R_{km}^{l_j} v_m^{l_j,l} + \mu^{l_j} (\varepsilon^l \rho^{l_j})_{,k} - (\varepsilon^l \rho^{l_j} A^{l_j})_{,k}, \quad (4.107)$$

where $S_{klmn}^{l_j}$ are a fourth-order symmetric positive semi-definite tensors representing the effects of the gradient in diffusive velocity in the liquid phase on the chemical potential, and $R_{km}^{l_j}$ are a second-order tensors. In this system we do not linearize about $\mathbf{v}^{s_j,s}$, $s = s_v, s_e$, because solid phase diffusion is assumed to be negligible. As such, $\mathbf{v}^{s_j,s}$ is not an independent variable, and thus the coefficient of $\mathbf{v}^{s_j,s}$ cannot be a function of $\mathbf{v}^{s_j,s}$. Finally, for the coefficient of $\widehat{e}_\beta^{\alpha_j}$ we obtain:

$$\mu^{\alpha_j} - \mu^{\beta_j} = M^{\alpha\beta_j} \widehat{e}_\beta^{\alpha_j} - \frac{1}{2} \mathbf{v}^{\alpha_j,\alpha} \cdot \mathbf{v}^{\alpha_j,\alpha} - \frac{1}{2} \mathbf{v}^{\beta_j,\beta} \cdot \mathbf{v}^{\beta_j,\beta}, \quad (4.108)$$

where $\alpha, \beta = l, s_v, s_e$, $\beta \neq \alpha$, and $M^{\alpha\beta_j}$ are scalar coefficients.

4.3.6 Darcy's Law

Darcy's Law is obtained from the bulk linear momentum equation for the liquid phase, equation (2.36), by using constitutive equations to eliminate the stress tensor, equation (4.99), and equation (4.101) to eliminate the exchange of momentum terms, $\widehat{\mathbf{T}}_{s_v}^l + \widehat{\mathbf{T}}_{s_e}^l$. The result is

$$\begin{aligned} \mathbf{R}^l \cdot \mathbf{v}^{l,s_v} &= -\varepsilon^l \nabla p^l - \pi_{s_v}^l \nabla \varepsilon^l + \nabla \cdot (\varepsilon^l \mathbf{G}^l : \mathbf{d}^l) - \varepsilon^l \rho^l \mathbf{g} \\ &\quad - (\bar{p}_l^{s_v} - \bar{p}_l^{s_e}) \nabla \varepsilon^{s_v} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \bar{\mathbf{C}}^{s_e}} : (\nabla \bar{\mathbf{C}}^{s_e})^T \\ &\quad - \varepsilon^l \rho^l \sum_{n=0}^q \frac{\partial A^l}{\partial \bar{\mathbf{C}}^{(n)s_v}} : (\nabla \bar{\mathbf{C}}^{(n)s_v})^T - \sum_{m=1}^p \varepsilon^l \rho^l \frac{\partial A^l}{\partial \bar{\varepsilon}^{(m)l}} \nabla \bar{\varepsilon}^{(m)l}, \end{aligned} \quad (4.109)$$

where we have rewritten the first two terms of equation (4.99) using the three-pressure relationship, equation (4.21). Equation (4.109) contains novel terms due to the presence of three phases. All of the terms on the first line have been reported previously. The first term resembles the classical Darcy's law which states the flow is produced due to a minus gradient in pressure. The second term states that if the system is swelling then there is flow due to a gradient in volume fraction. Since π^l is zero for non-swelling system, this term disappears for non-swelling system and we recover the classical Darcy's law. The rest of the terms on the first line are discussed in Section 3.4.2. The first term on the second line, which is novel, says that if there is a difference in the solid phase pressures flow will be driven due to a gradient in the viscoelastic solid phase volume fraction. The second term on the second line says that flow can be driven due to a gradient in (pure) shear of the elastic phase. The first term on the last line is also novel and accounts for flow induced by shearing and rates of shearing of the viscoelastic solid phase. It is similar to a term reported by Singh

et al. in [50], where \mathbf{E}^s appears in place of $\overline{\mathbf{C}}^{sv}$. However, strain includes effects due to both shearing and changes in volume, whereas here we clearly distinguish between the effects of shearing and the effects of the volume fraction, which are captured by the last term. The last term also appears in equation (3.64) and is discussed there.

4.3.7 Fick's Law

Fick's law is obtained from the species linear momentum equation for the liquid phase, equation (2.30), by using the near-equilibrium result for the chemical potential of the liquid phase, equation (4.106), to eliminate the species stress tensor, \mathbf{t}^{lj} , and using equation (4.107) to eliminate $\widehat{\mathbf{T}}_{se}^{lj} + \widehat{\mathbf{i}}^{lj}$. The result is

$$\mathbf{R}^{lj} \cdot \mathbf{v}^{lj,l} = -\varepsilon^l \rho^l \nabla \mu^{lj} + \nabla \cdot (\varepsilon^l \rho^{lj} \mathbf{S}^{lj} : \nabla \mathbf{v}^{lj,l}) + \varepsilon^l \rho^{lj} \mathbf{g}, \quad (4.110)$$

where we have neglected the inertial term in the momentum equation. The first term is the generalized Fick's law, and says the diffusion is caused by a the gradient in chemical potential. This equations is similar to an equation obtained by Bennethum et al. in [12]. The second terms is often neglected as it is of second order.

5. Two-Scale Polymeric Drug Delivery Systems

The theory presented in Chapter 4 is generally applicable to a three-phase system composed of a viscoelastic solid, elastic solid, and viscous liquid that meets the general requirements of HMT. We now want to make the appropriate simplifying assumptions so that we may combine the conservation and balance equations of Chapter 2 with results of Chapter 4 to model drug delivery systems. To this end we assume that the viscoelastic solid phase is composed of a polymer, denoted p , and the elastic solid is composed of a drug, denoted d . Both the polymer and drug phases are each composed of a single constituent. Furthermore, mass transfer takes place only between the drug phase and viscous liquid phase, which is composed of water (or biological fluid) and drug. As such, we can write the restriction on mass transfer between phases, equation (2.25), as

$$\widehat{e}_d^l + \widehat{e}_l^d = 0. \quad (5.1)$$

We will begin by presenting the equations related to bulk fluid transport, that is, conservation of mass for each bulk phase and Darcy's law. Next, we will present the equations relevant to species transport, that is, conservation of mass for the drug in the liquid phase and Fick's law.

5.1 Bulk Transport

To begin, we assume that the polymer and drug are both incompressible, so that $D^s \rho^s / Dt = 0$, $s = p, d$. We also assume that the liquid phase is incompressible and the drug in the liquid phase is sufficiently dilute so that $D^l \rho^l / Dt \approx 0$,

as well. By assuming the concentration of the drug in the liquid phase is sufficiently dilute we are implying that the drug is transported quickly out of the device. This may not be the case for poorly soluble drugs or for initially high drug loadings. As such, we would not expect the diffusion front, D , in figure 1.3 to appear. Under these conditions, the conservation of mass equations (2.23) for each phase can be written:

$$\dot{\varepsilon}^l + \nabla \cdot (\varepsilon^l \mathbf{v}^{l,p}) + \varepsilon^l \nabla \cdot \mathbf{v}^p = \frac{\widehat{e}_d^l}{\rho^l}, \quad (5.2)$$

$$\dot{\varepsilon}^d + \nabla \cdot (\varepsilon^d \mathbf{v}^{d,p}) + \varepsilon^d \nabla \cdot \mathbf{v}^p = \frac{\widehat{e}_d^d}{\rho^d}, \quad (5.3)$$

$$\dot{\varepsilon}^p + \varepsilon^p \nabla \cdot \mathbf{v}^p = 0, \quad (5.4)$$

where we have used equation (4.11) to convert to material time derivatives. Solving for $\nabla \cdot \mathbf{v}^p$ in equation (5.4), substituting back into equations (5.2) and (5.3), and using the relationship between volume fractions, equation (4.4), to convert derivatives of ε^d into derivatives of ε^l and ε^p , we obtain

$$\dot{\varepsilon}^l - \frac{\varepsilon^l}{\varepsilon^p} \dot{\varepsilon}^p + \nabla \cdot (\varepsilon^l \mathbf{v}^{l,p}) = \frac{\widehat{e}_d^l}{\rho^l}, \quad (5.5)$$

$$-\dot{\varepsilon}^l - \frac{(1 - \varepsilon^l)}{\varepsilon^p} \dot{\varepsilon}^p = -\frac{\widehat{e}_d^l}{\rho^d}, \quad (5.6)$$

where we note that we have dropped the term involving $\nabla \cdot (\varepsilon^d \mathbf{v}^{d,p})$ since on the time scales of concern it is reasonable to assume that $\mathbf{v}^{d,p} \approx 0$. We have also used the restriction on mass transfer between phases, equation (5.1), to

eliminate \widehat{e}_l^d . Solving for ε^p in equation (5.6) and substituting into equation (5.5), we obtain

$$\varepsilon^l + (1 - \varepsilon^l) \nabla \cdot (\varepsilon^l \mathbf{v}^{l,p}) = \left(\frac{(1 - \varepsilon^l)}{\rho^l} + \frac{\varepsilon^l}{\rho^d} \right) \widehat{e}_d^l. \quad (5.7)$$

As expected, equation (5.7) reduces to equation (3.76) when there is no mass transfer between phases.

Darcy's law, equation (4.109), is needed to model bulk fluid penetration into the delivery device. We choose to neglect all second-order terms and gravity. Furthermore, in recent experiments, such as that described in Chapter 1 performed by Colombo et al., [20], we expect infiltration of liquid into the device to occur in the normal directions, meaning that shear forces should have little affect on flow, so we neglect shear forces as well. Finally, we assume that the liquid phase does not have a preference for either the drug or polymer phase so that pressures in the elastic and viscoelastic solid phases will be equal (see equation (4.69)), thus we take $\bar{p}^p - \bar{p}^d = 0$. The resulting Darcy's law is given by

$$\mathbf{R}^l \cdot \mathbf{v}^{l,p} = -\nabla(\varepsilon^l p^l) + \bar{p}_{s_v}^l \nabla \varepsilon^l - \sum_{m=1}^p \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \nabla \varepsilon^{(m)l}. \quad (5.8)$$

Following the discussion given in Section 3.5.1 we can rewrite Darcy's law as follows:

$$\mathbf{v}^{l,p} = \frac{\varepsilon^l K^l}{\mu_v^l} \left(\frac{K'}{1 - \varepsilon^l} \nabla \varepsilon^l - \rho^l \sum_{m=1}^p \frac{\partial A^l}{\partial \varepsilon^{(m)l}} \nabla \varepsilon^{(m)l} \right). \quad (5.9)$$

We remind the reader that K^l is the permeability, μ_v^l is the viscosity of the liquid phase, and that K' is theunjacketed compressibility for a porous medium with incompressible solid and liquid phases. To simplify the last term of equation

(5.9) we will use a Laplace transform. To that end, we assume that A^l is a linear function of $\varepsilon^{(m)l}$ for $m = 1$ to p , which means that $\frac{\partial A^l}{\partial \varepsilon^{(m)l}}$ is independent of $\varepsilon^{(m)l}$; thus we can set

$$M_{(m)}^l = \frac{\partial A^l}{\partial \varepsilon^{(m)l}}. \quad (5.10)$$

We can now write the last term of (5.9) as

$$\xi(t) = \sum_{m=1}^p M_{(m)}^l \nabla \varepsilon^{(m)l}. \quad (5.11)$$

Taking the Laplace transform of (5.11), we have

$$\begin{aligned} \tilde{\xi}(s) &= \sum_{m=1}^p M_{(m)}^l \widetilde{(\nabla \varepsilon^{(m)l})} \\ &= \sum_{m=1}^p M_{(m)}^l s^m \widetilde{(\nabla \varepsilon^l)}, \end{aligned} \quad (5.12)$$

where $\tilde{}$ denotes the Laplace transform, and s denotes the frequency. To go from the first to the second equality in the above calculation we have assumed that initially there are no gradients in the liquid volume fraction. Taking the inverse Laplace transform of equation (5.12) and using a convolution theorem for Laplace transforms, we obtain

$$\xi(t) = \int_0^t \left(\sum_{m=1}^p M_{(m)}^l \delta^{(m-1)}(t-\tau) \right) \nabla \varepsilon^l(\tau) d\tau, \quad (5.13)$$

where

$$\delta^{(m-1)}(t) = \frac{d^{(m-1)}\delta(t)}{dt^{(m-1)}}. \quad (5.14)$$

Substituting (5.12) into equation (5.9), we obtain

$$\mathbf{v}^{l,p} = \frac{\varepsilon^l K^l}{\mu_v^l} \left[\frac{K^l}{1-\varepsilon^l} \nabla \varepsilon^l - \rho^l \int_0^t \left(\sum_{m=1}^p M_{(m)}^l \delta^{(m-1)}(t-\tau) \right) \nabla \varepsilon^l(\tau) d\tau \right], \quad (5.15)$$

Substituting this into equation (5.7) yields

$$\dot{\varepsilon}^l + (1 - \varepsilon^l) \nabla \cdot \left[D_1 \nabla \varepsilon^l - \int_0^t B_v(t - \tau) \nabla \dot{\varepsilon}^l(\tau) d\tau \right] = \left(\frac{1 - \varepsilon^l}{\rho^l} + \frac{\varepsilon^l}{\rho^d} \right) \widehat{e}_d^l \quad (5.16)$$

where

$$D_1 = \frac{(\varepsilon^l)^2 K^l K^d}{(1 - \varepsilon^l) \mu_v^l}, \quad (5.17)$$

$$B_v(t) = \frac{(\varepsilon^l)^2 \rho^l K^l}{\mu_v^l} \sum_{m=1}^p M_{(m)}^l \delta^{(m-1)}(t). \quad (5.18)$$

Equation (5.16) is identical to equation (3.86), except that now we have a right hand side, as would be expected once species transport is taken into account. Furthermore, equation (3.86) is recovered when we assume that there is no mass transfer between phases. According to Singh et al., [51], $B_v(t)$ can be determined experimentally by measuring the bulk relaxation function for the polymer matrix and mass uptake curves as a function of temperature and liquid concentration. One can get both Darcian and non-Darcian flow by choosing the functional form of $B_v(t)$ appropriately, [51].

5.1.1 Species Transport

Conservation of mass for the drug in the liquid phase, denoted by l_d , is given by equation (2.14) with $\alpha = l$ and $j = d$

$$\frac{D^{l_d}(\varepsilon^l \rho^{l_d})}{Dt} + \varepsilon^l \rho^{l_d} \nabla \cdot \mathbf{v}^{l_d} = \widehat{e}_d^l. \quad (5.19)$$

Converting derivatives in l_d into derivatives in p using equations (3.24) and (4.11), using equation (2.20) to convert terms involving ρ^{l_d} into concentrations, and using the incompressibility condition for the liquid phase, $D^l(\rho^l)/Dt =$

0, and the fact that $\nabla \rho^l = 0$ since we assume a constant pressure along the boundaries, we have

$$C^{l_d} \dot{\varepsilon}^l + \varepsilon^l \dot{C}^{l_d} + \nabla \cdot (\varepsilon^l C^{l_d} \mathbf{v}^{l,p}) + \nabla \cdot (\varepsilon^l C^{l_d} \mathbf{v}^{l_d,l}) + \varepsilon^l C^{l_d} \nabla \cdot \mathbf{v}^p = \frac{\widehat{e}_d^l}{\rho^l}. \quad (5.20)$$

Solving equation (5.4) for $\nabla \cdot \mathbf{v}^p$ and substituting into the above equation, then solving equation (5.6) for $\dot{\varepsilon}^p$ and substituting into the result yields

$$\begin{aligned} & C^{l_d} \dot{\varepsilon}^l + (1 - \varepsilon^l) \left[\varepsilon^l \dot{C}^{l_d} + \nabla \cdot (\varepsilon^l C^{l_d} \mathbf{v}^{l,p}) + \nabla \cdot (\varepsilon^l C^{l_d} \mathbf{v}^{l_d,l}) \right] \\ &= \widehat{e}_d^l \left(\frac{1 - \varepsilon^l}{\rho^l} + \frac{\varepsilon^l C^{l_d}}{\rho^d} \right). \end{aligned} \quad (5.21)$$

Fick's law, equation (4.110), is needed to model diffusion of the drug in the liquid phase. Again we neglect second-order terms. Furthermore, we assume that the chemical potential of the drug in the liquid phase is a function of the concentration of the drug in the liquid phase. The resulting Fick's law is given by

$$\mathbf{v}^{l_d,l} = -\varepsilon^l \rho^l F_C \nabla C^{l_d}, \quad (5.22)$$

where

$$F_C \mathbf{I} = (\mathbf{R}^{l_d})^{-1} \frac{\partial \mu^{l_d}}{\partial C^{l_d}}, \quad (5.23)$$

is the mutual diffusion coefficient.

Substituting equations (5.22) and (5.15) into equation (5.21), we obtain

$$\begin{aligned} & C^{l_d} \dot{\varepsilon}^l + (1 - \varepsilon^l) \left[\varepsilon^l \dot{C}^{l_d} + \nabla \cdot \left(D_2 \nabla \varepsilon^l - D_3 \nabla C^{l_d} - \int_0^t B_u(t - \tau) \nabla \dot{\varepsilon}^l(\tau) d\tau \right) \right] \\ &= \widehat{e}_d^l \left(\frac{1 - \varepsilon^l}{\rho^l} + \frac{\varepsilon^l C^{l_d}}{\rho^d} \right), \end{aligned} \quad (5.24)$$

where

$$D_2 = C^{l_d} D_1, \quad (5.25)$$

$$B_u(t) = C^{l_d} B_v(t), \quad (5.26)$$

and

$$D_3 = (\varepsilon^l)^2 \rho^l C^{l_d} F_C. \quad (5.27)$$

5.2 Discussion

Equations (5.16) and (5.24) constitute a system of two equations in three unknowns: the volume fraction of the liquid phase, ε^l , the concentration of drug in the liquid phase, C^{l_d} , and the rate of mass transfer of drug into the liquid phase, \tilde{e}_d^l . The rate of mass transfer must be determined experimentally as a function of volume fraction and concentration of drug in the liquid phase. This can be accomplished by performing two experiments. In one experiment the volume fraction would be held fixed, and \tilde{e}_d^l is measured as a function of concentration. The other experiment would measure \tilde{e}_d^l as a function of volume fraction at constant concentration. Naturally, several of these experiments would need to be performed at various fixed values of volume fraction and concentration, then an interpolation scheme could be used to fill in the missing values.

We note that D_2 must be negative and that D_3 must be positive for this problem to be well-posed. Since D_3 has the same sign as the diffusion coefficient in a classical Fick's law D_3 is indeed positive. In many drug delivery models the term involving D_2 does not appear. In these other drug delivery models,

authors postulate that D_3 is a function of volume fraction. Indeed, according to equation (5.26), D_3 is a function of volume fractions. However, as this analysis shows, a term involving $\nabla \varepsilon^l$ is needed to fully describe the system, and that means obtaining a measurement of D_1 .

6. Three-Scale HMT for Swelling Porous Systems

In the first section we will discuss the macroscale averaging procedure. We have made minor modifications to the definitions which resolve several issues resulting in slightly different variable definitions, but leave the basic form of the macroscale balance and conservation equations unchanged. In the following section we will summarize the macroscale conservation and balance equations. In the next section, we will present some standard assumptions and the resulting entropy inequality. In the third section we present the constitution of the system by discussing the unknowns, constitutive (dependent), and independent variables. In the final section of this chapter will derive the resulting entropy inequality, non-equilibrium, equilibrium, and near-equilibrium results, as well as Darcy's and Fick's laws.

6.1 Macroscale Notation and Averaging Procedure

In this section we will discuss the macroscale notation and averaging procedure. The definitions that follow apply only to macroscopic volumes composed of more than one phase, denoted by the capital letter A . The corresponding macroscale equations for regions composed of strictly a single phase are the same as the mesoscopic equations with capital letters replacing the Greek letters. This will be made clear in what follows.

A particle A is viewed as a homogeneous mixture of solid polymer matrix, solid drug, and vicinal fluid, denoted $s_v A$, $s_e A$, and lA , respectively. At the macroscale particles exist with two bulk fluids, denoted B and C , which form

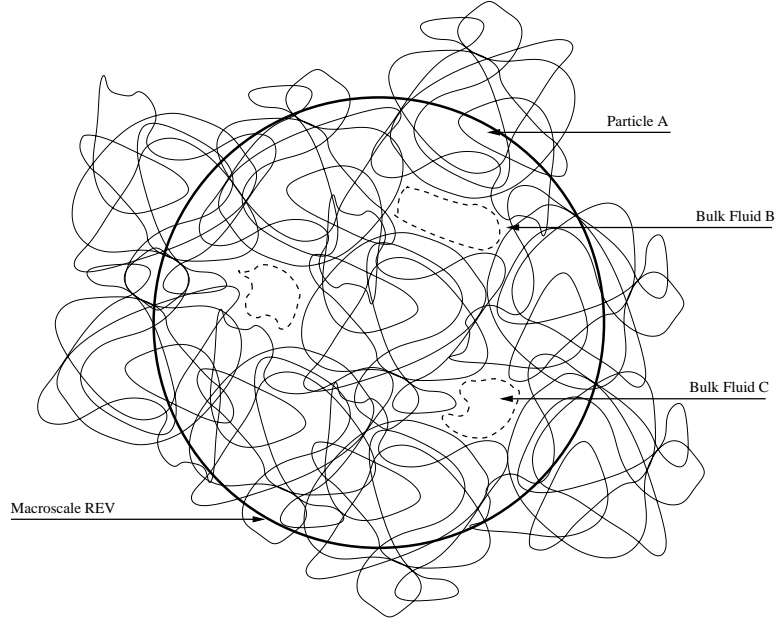


Figure 6.1: Macroscale REV

another homogeneous mixture. At this scale of the particle phases interacts with fluids B and C , see Figure 6.1. Macroscale volume fractions are denoted ε^K , where $K = s_v A, s_e A, lA, B, C$.

In [7], the following definitions were made for a particle A composed of a solid phase, sA , and a liquid phase lA :

$$\varepsilon^A \equiv \frac{1}{|\Delta V|} \int_{\Delta V} \gamma_A(\mathbf{r}, t) dv \quad (6.1)$$

as the volume fraction of the bulk region,

$$\langle \varepsilon^\alpha \rho^\alpha \rangle^A \equiv \frac{1}{\varepsilon^A |\Delta V|} \int_{\Delta V} \varepsilon^\alpha \rho^\alpha \gamma_A(\mathbf{r}, t) dv \quad (6.2)$$

as the volume average mass,

$$\langle \psi^{\alpha j} \rangle^A \equiv \frac{1}{\varepsilon^A |\Delta V|} \int_{\Delta V} \varepsilon^\alpha \psi^{\alpha j} \gamma_A(\mathbf{r}, t) dv \quad (6.3)$$

as the volume average of ψ^{α_j} , and

$$\overline{\psi^{\alpha_j}}^A \equiv \frac{1}{\varepsilon^A \langle \varepsilon^\alpha \rho^{\alpha_j} \rangle^A |\Delta V|} \int_{\Delta V} \varepsilon^\alpha \rho^{\alpha_j} \psi^{\alpha_j} \gamma_A(\mathbf{r}, t) dv \quad (6.4)$$

as the mass average of ψ^{α_j} , where

$$\gamma_A(\mathbf{r}, t) = \begin{cases} 1 & \text{if } \mathbf{r} \in \Delta V_A \\ 0 & \text{if } \mathbf{r} \in \text{otherwise,} \end{cases} \quad \beta \neq \alpha. \quad (6.5)$$

In [7] density is defined as

$$\rho^{\alpha A} = \langle \varepsilon^\alpha \rho^\alpha \rangle^A, \quad (6.6)$$

which can be interpreted physically as $\frac{\text{mass } \alpha}{|\Delta V_A|}$, where ΔV_A is the volume of the region A in the macroscale REV. Unfortunately, this is not a true density, which has dimensions of $\frac{\text{mass } \alpha}{\text{volume } \alpha}$

In Appendix A of [51], Singh et al. mentioned that the density as defined by equation (6.6) is hard to measure since ε^α likely changes continuously during fluid transport. As such, they redefine $\rho^{\alpha A}$ as follows:

$$\rho^{\alpha A} \equiv \frac{1}{\varepsilon^\alpha} \langle \varepsilon^\alpha \rho^\alpha \rangle^A. \quad (6.7)$$

The problem with this definition is that we are using the mesoscale parameter ε^α as input to a macroscale variable. This definition also requires that we assume

$$\varepsilon^{\alpha A} = \varepsilon^\alpha \varepsilon^A. \quad (6.8)$$

Once again, equation (6.8) is using a mesoscale variable to define a macroscale quantity.

Furthermore, it does not make sense to define

$$\varepsilon^{\alpha A} \equiv \frac{1}{|\Delta V|} \int_{\Delta V} \gamma_{\alpha A}(\mathbf{r}, t) dv \quad (6.9)$$

since at the macroscale the particle has already been homogenized and one cannot specify the state of being in the αA phase in terms of macroscale coordinates, as would be needed to define the indicator function in (6.9).

To overcome this problem, we propose the following definitions:

$$\varepsilon^{\alpha A} \equiv \frac{1}{|\Delta V|} \int_{\Delta V} \varepsilon^\alpha \gamma_A(\mathbf{r}, t) dv, \quad (6.10)$$

which can be interpreted physically as $\frac{|\Delta V_{\alpha A}|}{|\Delta V|}$,

$$\langle \varepsilon^\alpha \rho^\alpha \rangle^A \equiv \frac{1}{\varepsilon^{\alpha A} |\Delta V|} \int_{\Delta V} \varepsilon^\alpha \rho^\alpha \gamma_A(\mathbf{r}, t) dv \quad (6.11)$$

as the volume average mass,

$$\langle \psi^{\alpha j} \rangle^A \equiv \frac{1}{\varepsilon^{\alpha A} |\Delta V|} \int_{\Delta V} \varepsilon^\alpha \psi^{\alpha j} \gamma_A(\mathbf{r}, t) dv \quad (6.12)$$

as the volume average of $\psi^{\alpha j}$, and

$$\overline{\psi^{\alpha j}}^A \equiv \frac{1}{\varepsilon^{\alpha A} \langle \varepsilon^\alpha \rho^{\alpha j} \rangle^A |\Delta V|} \int_{\Delta V} \varepsilon^\alpha \rho^{\alpha j} \psi^{\alpha j} \gamma_A(\mathbf{r}, t) dv \quad (6.13)$$

as the mass average of $\psi^{\alpha j}$. Now we can define $\rho^{\alpha A}$:

$$\rho^{\alpha A} = \langle \varepsilon^\alpha \rho^\alpha \rangle^A, \quad (6.14)$$

which can be interpreted physically as $\frac{\text{mass } \alpha A}{|\Delta V_{\alpha A}|}$, and which corresponds to true density. Furthermore, definition (6.10) yields the expected relation

$$\varepsilon^{svA} + \varepsilon^{seA} + \varepsilon^{lA} = \varepsilon^A. \quad (6.15)$$

The macroscale averaging procedure is analogous to the mesoscale averaging procedure outlined in Chapter 2, and can be found in [7]. We summarize the results in the next section for future reference, where we have made the aforementioned modifications.

6.2 Macroscale Field Equations

In this section we summarize the macroscale conservation and balance equations. As in Chapter 2, we begin with the conservation of mass, linear momentum balance, energy balance and lastly entropy.

Throughout this section $\alpha = l, s_v, s_e, j = 1, \dots, N, L = s_v A, s_e A, lA, B, C$ and $K = B, C$, unless otherwise noted. For example,

$$\sum_{L, L \neq \alpha A} \widehat{e}_L^{\alpha A_j} \quad (6.16)$$

means for each $\alpha = l, s_v, s_e$, and for each $j = 1, \dots, N$, take the sum over $L = s_v A, s_e A, lA, B, C$, where $L \neq \alpha A$.

6.2.1 Conservation of Mass

For the j^{th} species in the particle, conservation of mass is given by:

$$\frac{D^{\alpha A_j}(\varepsilon^{\alpha A} \rho^{\alpha A_j})}{Dt} + \varepsilon^{\alpha A} \rho^{\alpha A_j} (\nabla \cdot \mathbf{v}^{\alpha A_j}) = \sum_{L, L \neq \alpha A} \widehat{e}_L^{\alpha A_j} + \widehat{r}^{\alpha A_j}, \quad (6.17)$$

where the macroscale variables in (6.17) are related to their mesoscale counterparts in the following way:

$$\rho^{\alpha A_j} = \langle \varepsilon^{\alpha} \rho^{\alpha_j} \rangle^A, \quad (6.18)$$

$$\mathbf{v}^{\alpha A_j} = \overline{\mathbf{v}^{\alpha_j A}}, \quad (6.19)$$

$$\widehat{e}_{\beta A}^{\alpha A_j} \equiv \varepsilon^{\alpha A} \rho^{\alpha A_j} \overline{\left(\frac{\widehat{e}_{\beta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A}, \quad \alpha, \beta = s_v A, s_e A, lA, \alpha \neq \beta, \quad (6.20)$$

$$\begin{aligned} \widehat{e}_L^{\alpha A_j} &= \frac{1}{|\Delta V|} \int_{\Delta A_{AL}} \varepsilon^{\alpha} \rho^{\alpha_j} (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j}) \cdot \mathbf{n}^A da \\ L &= B, C, \quad \alpha = s_v, s_e, l, \end{aligned} \quad (6.21)$$

and

$$\widehat{r}^{\alpha A_j} \equiv \varepsilon^{\alpha A} \rho^{\alpha A_j} \overline{\left(\frac{\widehat{r}^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A}. \quad (6.22)$$

Summing (6.17) from $j = 1$ to N yields

$$\frac{D^{\alpha A}(\varepsilon^{\alpha A} \rho^{\alpha A})}{Dt} + \varepsilon^{\alpha A} \rho^{\alpha A} (\nabla \cdot \mathbf{v}^{\alpha A}) = \sum_{L, L \neq \alpha A} \widehat{e}_L^{\alpha A}. \quad (6.23)$$

Relationships between the macroscopic species variables and their bulk phase counterparts can be found in Appendix B. Conservation of mass for species in the bulk phase is given by

$$\frac{D^{K_j}(\varepsilon^K \rho^{K_j})}{Dt} + \varepsilon^K \rho^{K_j} (\nabla \cdot \mathbf{v}^{K_j}) = \sum_{L, L \neq K} \widehat{e}_L^{K_j} + \widehat{r}^{K_j}. \quad (6.24)$$

Summing (6.24) from $j = 1$ to N yields

$$\frac{D^K(\varepsilon^K \rho^K)}{Dt} + \varepsilon^K \rho^K (\nabla \cdot \mathbf{v}^K) = \sum_{L, L \neq K} \widehat{e}_L^K. \quad (6.25)$$

Additionally, we have the following restrictions

$$\varepsilon^A + \varepsilon^B + \varepsilon^C = 1, \quad (6.26)$$

$$\sum_{j=1}^N \widehat{r}^{K_j} = 0, \quad (6.27)$$

$$\sum_{j=1}^N C^{K_j} = 1, \quad (6.28)$$

and

$$\widehat{e}_L^{K_j} + \widehat{e}_K^{L_j} = 0, \quad (6.29)$$

where $K \neq L$, and $K, L = s_v A, s_e A, lA, B, C$ for restrictions (6.27), (6.28) and (6.29).

6.2.2 Conservation of Linear Momentum

For the j^{th} species in the particle, momentum balance is given by

$$\begin{aligned} \varepsilon^{\alpha A} \rho^{\alpha A_j} \frac{D^{\alpha A_j} \mathbf{v}^{\alpha A_j}}{Dt} - \nabla \cdot (\varepsilon^{\alpha A} \mathbf{t}^{\alpha A_j}) - \varepsilon^{\alpha A} \rho^{\alpha A_j} \mathbf{g}^{\alpha A} \\ = \sum_{L, L \neq K} \widehat{\mathbf{T}}_L^{\alpha A_j} + \widehat{\mathbf{i}}^{\alpha A_j}, \end{aligned} \quad (6.30)$$

where the macroscale variables in (6.30) are related to their mesoscale counterparts in the following way:

$$\widehat{\mathbf{i}}^{\alpha A_j} \equiv \varepsilon^{\alpha A} \rho^{\alpha A_j} \left[\overline{\left(\frac{\widehat{\mathbf{i}}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\mathbf{v}^{\alpha_j} \widehat{\mathbf{r}}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} - \mathbf{v}^{\alpha A_j} \overline{\left(\frac{\widehat{\mathbf{r}}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} \right], \quad (6.31)$$

$$\mathbf{g}^{\alpha A_j} \equiv \overline{\mathbf{g}^{\alpha_j A}}, \quad (6.32)$$

$$\mathbf{t}^{\alpha A_j} \equiv \left(\langle \varepsilon^{\alpha} \mathbf{t}^{\alpha_j} \rangle^A + \langle \varepsilon^{\alpha} \rho^{\alpha_j} \rangle^A \mathbf{v}^{\alpha A_j} \mathbf{v}^{\alpha A_j} - \langle \varepsilon^{\alpha} \rho^{\alpha_j} \rangle^A \overline{\mathbf{v}^{\alpha_j} \mathbf{v}^{\alpha_j A}} \right), \quad (6.33)$$

$$\begin{aligned} \widehat{\mathbf{T}}_{\beta A}^{\alpha A_j} \equiv \varepsilon^{\alpha A} \rho^{\alpha A_j} \left[\overline{\left(\frac{\widehat{\mathbf{T}}_{\beta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\mathbf{v}^{\alpha_j} \widehat{\mathbf{e}}_{\beta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} - \mathbf{v}^{\alpha A_j} \overline{\left(\frac{\widehat{\mathbf{e}}_{\beta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} \right], \\ \alpha, \beta = s_v A, s_e A, l A, \quad \alpha \neq \beta, \end{aligned} \quad (6.34)$$

and

$$\begin{aligned} \widehat{\mathbf{T}}_L^{\alpha A_j} \equiv \frac{1}{|\Delta V|} \left[\int_{\Delta A_{AL}} (\mathbf{t}^{\alpha_j} + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j})) \cdot \mathbf{n}^A da \right. \\ \left. - \mathbf{v}^{\alpha_j} \int_{\Delta A_{AL}} \rho^{\alpha_j} (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j}) \mathbf{n}^A da \right], \\ L = B, C, \quad \alpha = s_v, s_e, l. \end{aligned} \quad (6.35)$$

Summing (6.30) from $j = 1$ to N yields

$$\varepsilon^{\alpha A} \rho^{\alpha A} \frac{D^{\alpha A} \mathbf{v}^{\alpha A}}{Dt} - \nabla \cdot (\varepsilon^{\alpha A} \mathbf{t}^{\alpha A}) - \varepsilon^{\alpha A} \rho^{\alpha A} \mathbf{g}^{\alpha A} = \sum_{L, L \neq \alpha A} \widehat{\mathbf{T}}_L^{\alpha A}. \quad (6.36)$$

Momentum balance for species in the bulk phase is given by

$$\varepsilon^K \rho^{K_j} \frac{D^{K_j}(\mathbf{v}^{K_j})}{Dt} - \nabla \cdot (\varepsilon^K \mathbf{t}^{K_j}) - \varepsilon^K \rho^{K_j} \mathbf{g}^{K_j} = \sum_{L, L \neq K} \widehat{\mathbf{T}}_L^{K_j} + \widehat{\mathbf{i}}^{K_j}. \quad (6.37)$$

Summing (6.37) from $j = 1$ to N yields:

$$\varepsilon^K \rho^K \frac{D^K \mathbf{v}^K}{Dt} - \nabla \cdot (\varepsilon^K \mathbf{t}^K) - \varepsilon^K \rho^K \mathbf{g}^K = \sum_{L, L \neq K} \widehat{\mathbf{T}}_L^K. \quad (6.38)$$

Additionally, we have the following restrictions

$$\sum_{j=1}^N \left(\widehat{\mathbf{i}}^{K_j} + \widehat{\mathbf{r}}^{K_j} \mathbf{v}^{K_j, K} \right) = 0, \quad (6.39)$$

and

$$\widehat{\mathbf{T}}_L^{K_j} + \widehat{\mathbf{e}}_L^{K_j} \cdot \mathbf{v}^{K_j} + \widehat{\mathbf{T}}_K^{L_j} + \widehat{\mathbf{e}}_K^{L_j} \cdot \mathbf{v}^{L_j} = 0, \quad (6.40)$$

where $K \neq L$, and $K, L = s_v A, s_e A, lA, B, C$ for restrictions (6.39) and (6.40).

6.2.3 Conservation of Energy

For the j^{th} species in the particle, conservation of energy is given by:

$$\begin{aligned} \varepsilon^{\alpha A} \rho^{\alpha A_j} \frac{D^{\alpha A_j}(e^{\alpha A_j})}{Dt} - \nabla \cdot (\varepsilon^{\alpha A} \mathbf{q}^{\alpha A_j}) - \varepsilon^{\alpha A} \mathbf{t}^{\alpha A_j} : \nabla \mathbf{v}^{\alpha A_j} - \varepsilon^{\alpha A} \rho^{\alpha A_j} h^{\alpha A_j} \\ = \sum_{L, L \neq \alpha A} \widehat{Q}_L^{\alpha A_j} + \widehat{Q}^{\alpha A_j}, \end{aligned} \quad (6.41)$$

where the macroscale variables in (6.41) are related to their mesoscale counterparts in the following way:

$$e^{\alpha A_j} \equiv \overline{e^{\alpha A}} + \frac{1}{2} \overline{\mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j A}} - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}, \quad (6.42)$$

$$h^{\alpha A_j} \equiv \overline{h^{\alpha_j A}} + \overline{\mathbf{g}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j A}} - \mathbf{g}^{\alpha A_j} \cdot \mathbf{v}^{\alpha A_j}, \quad (6.43)$$

$$\begin{aligned}
\mathbf{q}^{\alpha A_j} \equiv & \left(\langle \mathbf{q}^{\alpha_j} \rangle^A + \langle \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \rangle^A - \mathbf{t}^{\alpha A_j} \cdot \mathbf{v}^{\alpha A_j} \right. \\
& + \langle \varepsilon^\alpha \rho^{\alpha_j} \rangle^A \mathbf{v}^{\alpha A_j} \left(e^{\alpha A_j} + \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha} \right) \\
& \left. - \overline{\langle \varepsilon^\alpha \rho^{\alpha_j} \rangle^A \mathbf{v}^{\alpha_j} \left(e^\alpha + \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha} \right)^A} \right), \tag{6.44}
\end{aligned}$$

$$\begin{aligned}
\widehat{Q}_{\beta A}^{\alpha A_j} \equiv & \varepsilon^{\alpha A} \rho^{\alpha A_j} \left\{ \overline{\left(\frac{\widehat{Q}_\beta^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\mathbf{v}^{\alpha_j} \cdot \widehat{\mathbf{T}}_\beta^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} \right. \\
& - \mathbf{v}^{\alpha_j} \left[\overline{\left(\frac{\widehat{\mathbf{T}}_\beta^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\mathbf{v}^{\alpha_j} \widehat{e}_\beta^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} - \mathbf{v}^{\alpha_j} \overline{\left(\frac{\widehat{e}_\beta^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} \right] \\
& \left. + \overline{\left(\frac{\widehat{e}_\beta^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \right)}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} - \left(e^{\alpha A_j} + \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha} \right) \overline{\left(\frac{\widehat{e}_\beta^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} \right\}, \\
& \alpha, \beta = s_v A, s_e A, l A, \alpha \neq \beta, \tag{6.45}
\end{aligned}$$

$$\begin{aligned}
\widehat{Q}_L^{\alpha A_j} \equiv & \frac{1}{|\Delta V|} \int_{\Delta A_{AL}} \left(\mathbf{q}^{\alpha_j} + \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \right. \\
& + \rho^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \right) (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j}) \cdot \mathbf{n}^a da \\
& - \frac{\mathbf{v}^{\alpha A_j}}{\Delta V} \int_{\Delta A_{AL}} (\mathbf{t}^{\alpha_j} + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j})) \cdot \mathbf{n}^A da \\
& \left. - \frac{e^{\alpha A_j} - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}}{|\Delta V|} \int_{\Delta A_{AL}} \varepsilon^\alpha \rho^{\alpha_j} (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j}) \cdot \mathbf{n}^A da, \right. \\
& L = B, C, \alpha = s_v, s_e, l, \tag{6.46}
\end{aligned}$$

and

$$\begin{aligned} \widehat{Q}^{\alpha A_j} \equiv & \varepsilon^{\alpha A} \rho^{\alpha A_j} \left\{ \overline{\left(\frac{\widehat{Q}^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\mathbf{v}^{\alpha_j} \cdot \widehat{\mathbf{i}}^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} \right. \\ & - \mathbf{v}^{\alpha_j} \cdot \left[\overline{\left(\frac{\widehat{\mathbf{i}}^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\mathbf{v}^{\alpha_j} \widehat{\mathbf{r}}^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} - \mathbf{v}^{\alpha_j} \overline{\left(\frac{\widehat{\mathbf{r}}^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} \right] \\ & \left. + \overline{\left(\frac{\widehat{\mathbf{r}}^{\alpha_j} (e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j})}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} - \left(e^{\alpha A_j} + \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha} \right) \overline{\left(\frac{\widehat{\mathbf{r}}^{\alpha_j}}{\varepsilon^\alpha \rho^{\alpha_j}} \right)^A} \right\}. \end{aligned}$$

Summing (6.41) from $j = 1$ to N yields

$$\begin{aligned} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{D^{\alpha A} e^{\alpha A}}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^{\alpha A}) - \varepsilon^{\alpha A} \mathbf{t}^{\alpha A} : \nabla \mathbf{v}^{\alpha A} - \varepsilon^{\alpha A} \rho^{\alpha A} h^{\alpha A} \\ = \sum_{L, L \neq \alpha A} \widehat{Q}_L^{\alpha A}. \end{aligned} \quad (6.47)$$

For the j^{th} species in the bulk phase, conservation of energy is given by

$$\begin{aligned} \varepsilon^K \rho^{K_j} \frac{D^{K_j} (e^{K_j})}{Dt} - \nabla \cdot (\varepsilon^K \mathbf{q}^{K_j}) - \varepsilon^K \mathbf{t}^{K_j} : \nabla \mathbf{v}^{K_j} - \varepsilon^K \rho^{K_j} h^{K_j} \\ = \sum_{L, L \neq \alpha A} \widehat{Q}_L^{K_j} + \widehat{Q}^{K_j}. \end{aligned} \quad (6.48)$$

Summing (6.48) from $j = 1$ to N yields

$$\varepsilon^K \rho^K \frac{D^K e^K}{Dt} - \nabla \cdot (\varepsilon^K \mathbf{q}^K) - \varepsilon^K \mathbf{t}^K : \nabla \mathbf{v}^K - \varepsilon^K \rho^K h^K = \sum_{L, L \neq K} \widehat{Q}_L^K. \quad (6.49)$$

Additionally, we have following restrictions

$$\sum_{j=1}^N \left[\widehat{Q}^{K_j} + \widehat{\mathbf{i}}^{K_j} \cdot \mathbf{v}^{K_j, K} + \widehat{\mathbf{r}}^{K_j} \left(\widehat{e}^{K_j} + \frac{1}{2} \mathbf{v}^{K_j, K} \cdot \mathbf{v}^{K_j, K} \right) \right] = 0, \quad (6.50)$$

and

$$\sum_{L, L \neq K} \left[\widehat{Q}_L^{K_j} + \widehat{\mathbf{T}}_L^{K_j} \cdot \mathbf{v}^{K_j} + \widehat{e}_L^{K_j} \left(e^{K_j} + \frac{1}{2} \mathbf{v}^{K_j} \cdot \mathbf{v}^{K_j} \right) \right] = 0, \quad (6.51)$$

where $K \neq L$, and $K, L = s_v A, s_e A, lA, B, C$ for restrictions (6.50) and (6.51).

6.2.4 Entropy Production

For the j^{th} species in the particle, the entropy balance is given by

$$\begin{aligned} \varepsilon^{\alpha A} \rho^{\alpha A_j} \frac{D^{\alpha A_j} \eta^{\alpha A_j}}{Dt} - \nabla \cdot (\varepsilon^{\alpha A} \phi^{\alpha A_j}) - \varepsilon^{\alpha A} \rho^{\alpha A_j} b^{\alpha A_j} \\ = \sum_{L, L \neq \alpha A} \widehat{\Phi}_L^{\alpha A_j} + \widehat{\eta}^{\alpha A_j} + \Lambda^{\alpha A_j}, \end{aligned} \quad (6.52)$$

where the macroscale variables in (6.52) are related to their mesoscale counterparts in the following way:

$$b^{\alpha A_j} \equiv \overline{b^{\alpha_j A}}, \quad (6.53)$$

$$\eta^{\alpha A_j} \equiv \overline{\eta^{\alpha_j A}}, \quad (6.54)$$

$$\widehat{\eta}^{\alpha A_j} \equiv \varepsilon^{\alpha A} \rho^{\alpha A_j} \left[\overline{\left(\frac{\widehat{\eta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\eta^{\alpha_j} \widehat{r}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} - \eta^{\alpha A_j} \overline{\left(\frac{\widehat{r}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} \right], \quad (6.55)$$

$$\phi^{\alpha A_j} \equiv \left(\langle \phi^{\alpha_j} \rangle^A - \langle \varepsilon^{\alpha} \rho^{\alpha_j} \rangle^A \overline{\mathbf{v}^{\alpha_j} \eta^{\alpha_j A}} + \langle \varepsilon^{\alpha} \rho^{\alpha_j} \rangle^A \mathbf{v}^{\alpha_j} \eta^{\alpha A_j} \right), \quad (6.56)$$

$$\begin{aligned} \widehat{\Phi}_{\beta A}^{\alpha A_j} \equiv \varepsilon^{\alpha A} \rho^{\alpha A_j} \left[\overline{\left(\frac{\widehat{\Phi}_{\beta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} + \overline{\left(\frac{\eta^{\alpha_j} \widehat{e}_{\beta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} - \eta^{\alpha A_j} \overline{\left(\frac{\widehat{e}_{\beta}^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A} \right], \\ \alpha, \beta = s_v A, s_e A, l A, \alpha \neq \beta, \end{aligned} \quad (6.57)$$

$$\begin{aligned} \widehat{\Phi}_L^{\alpha A_j} \equiv \frac{1}{|\Delta V|} \int_{\Delta A_{AL}} (\varepsilon^{\alpha} \phi^{\alpha_j} + \varepsilon^{\alpha} \rho^{\alpha_j} \eta^{\alpha_j} (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j})) \cdot \mathbf{n}^A da \\ - \eta^{\alpha A_j} \int_{\Delta A_{AL}} \varepsilon^{\alpha} \rho^{\alpha_j} (\mathbf{w}^{AL_j} - \mathbf{v}^{\alpha_j}) \cdot \mathbf{n}^A da \\ L = B, C, \alpha = s_v, s_e, l, \end{aligned} \quad (6.58)$$

$$\Lambda^{\alpha A_j} \equiv \varepsilon^{\alpha A} \rho^{\alpha A_j} \overline{\left(\frac{\Lambda^{\alpha_j}}{\varepsilon^{\alpha} \rho^{\alpha_j}} \right)^A}. \quad (6.59)$$

Summing (6.52) from $j = 1$ to N yields

$$\varepsilon^{\alpha A} \rho^{\alpha A} \frac{D^{\alpha A} \eta^{\alpha A}}{Dt} - \nabla \cdot (\varepsilon^{\alpha A} \phi^{\alpha A}) - \varepsilon^{\alpha A} \rho^{\alpha A} b^{\alpha A} = \sum_{L, L \neq \alpha A} \widehat{\Phi}_L^{\alpha A} + \widehat{\Lambda}^{\alpha A}. \quad (6.60)$$

For the j^{th} species in the bulk phase, the entropy balance is given by

$$\varepsilon^K \rho^{K_j} \frac{D^{K_j} \eta^{K_j}}{Dt} - \nabla \cdot (\varepsilon^K \phi^{K_j}) - \varepsilon^K \rho^{K_j} b^{K_j} = \sum_{L, L \neq K} \widehat{\Phi}_L^{K_j} + \widehat{\eta}^{K_j} + \Lambda^{K_j}. \quad (6.61)$$

Summing (6.61) from $j = 1$ to N yields

$$\varepsilon^K \rho^K \frac{D^K \eta^K}{Dt} - \nabla \cdot (\varepsilon^K \phi^K) - \varepsilon^K \rho^K b^K = \sum_{L, L \neq K} \widehat{\Phi}_L^K + \widehat{\Lambda}^K. \quad (6.62)$$

Additionally, we have the following restrictions

$$\sum_{j=1}^N (\widehat{\eta}^{K_j} + \widehat{r}^{K_j} \eta^{K_j, K}) = 0, \quad \forall K, \quad (6.63)$$

and

$$\sum_{L, L \neq K} (\widehat{\Phi}_L^{K_j} + \eta^{K_j} \widehat{e}_L^{K_j}) = 0, \quad j = 1, \dots, N, \quad (6.64)$$

where $K \neq L$, and $K, L = s_v A, s_e A, lA, B, C$ for restrictions (6.63) and (6.64).

6.3 Standard Assumptions and Resulting Entropy Inequality

The assumptions that we make in this section are analogous to those made in Section 2.4. To simplify the notation, we will now take $L, K = s_v A, s_e A, lA, B, C$, so that, for example, equation (6.24) holds for all K not just $K = B, C$. As before, the second law of thermodynamics requires that the total entropy generated by a system must be non-negative, and is maximum only when the system is in equilibrium. Mathematically, we can express this as

$$\Lambda = \sum_K \Lambda^K = \sum_K \sum_{j=1}^N \Lambda^{K_j} \geq 0, \quad (6.65)$$

where $K = s_v A, s_e A, lA, B, C$. Assuming that the system is in local thermodynamic equilibrium, we have

$$T = T^{lA_j} = T^{s_v A_j} = T^{s_e A_j} = T^B = T^C. \quad (6.66)$$

Solving equation (6.61) for Λ^{K_j} , assuming that the system is thermodynamically simple, that is,

$$\phi^{K_j} = \frac{\mathbf{q}^{K_j}}{T} \quad (6.67)$$

$$\beta^{K_j} = \frac{h^{K_j}}{T}, \quad (6.68)$$

performing Legendre transformation to convert the internal energy e^{K_j} into the Helmholtz free energy A^{K_j} ,

$$A^{K_j} = e^{K_j} + T\eta^{K_j}, \quad (6.69)$$

and using the conservation of energy equation (6.48), we obtain

$$\begin{aligned} \Lambda^{K_j} = & \frac{\varepsilon^K \rho^{K_j}}{T} \left[-\frac{D^{K_j} A^{K_j}}{Dt} - \eta^{K_j} \frac{D^{K_j} T}{Dt} \right] + \frac{\varepsilon^K}{T} \mathbf{t}^{K_j} : \nabla \mathbf{v}^{K_j} \\ & + \frac{1}{T} \sum_{L, L \neq K} \widehat{Q}_L^{K_j} + \frac{1}{T} \widehat{Q}^{K_j} + \frac{\varepsilon^K}{T^2} \cdot \nabla T - \sum_{L, L \neq K} \widehat{\Phi}_L^{K_j} - \widehat{\eta}^{K_j}. \end{aligned} \quad (6.70)$$

Summing this equation over species and phases and canceling appropriate terms, we obtain:

$$\begin{aligned}
T\Lambda = & \sum_K \left\{ -\varepsilon^K \rho^K \left[\frac{D^K A^K}{Dt} + \eta^K \frac{D^K T}{Dt} \right] \right. \\
& + \varepsilon^K \mathbf{d}^K : \left(\mathbf{t}^K + \sum_{j=1}^N \rho^K \mathbf{v}^{K_j, K} \mathbf{v}^{K_j, K} \right) \\
& + \sum_{j=1}^N \varepsilon^K \nabla \mathbf{v}^{K_j, K} : (\mathbf{t}^{K_j} - \rho^{K_j} A^{K_j} \mathbf{I}) \\
& + \frac{\varepsilon^K}{T} \nabla T \cdot \left\{ \mathbf{q}^K + \sum_{j=1}^N \left[\rho^{K_j} \mathbf{v}^{K_j, K} \left(A^{K_j} + \frac{1}{2} \mathbf{v}^{K_j, K} \mathbf{v}^{K_j, K} \right) - \mathbf{t}^{K_j} \cdot \mathbf{v}^{K_j, K} \right] \right\} \\
& - \sum_{j=1}^N \mathbf{v}^{K_j, K} \cdot \left[\widehat{\mathbf{i}}^{K_j} + \sum_{L, L \neq K} \widehat{\mathbf{T}}_L^{K_j} + \nabla \cdot (\varepsilon^K \rho^{K_j} A^{K_j}) \right] \\
& - \frac{1}{2} \sum_{j=1}^N \mathbf{v}^{K_j, K} \cdot \mathbf{v}^{K_j, K} \left[\widehat{r}^{K_j} + \sum_{L, L \neq K} \widehat{e}_L^{K_j} \right] \\
& \left. - \sum_{L, L \neq K} \widehat{\mathbf{T}}_L^K \mathbf{v}^{K, sA} - \sum_{L, L \neq K} \widehat{e}_L^K \left(A^K + \frac{1}{2} \mathbf{v}^{K, sA} \cdot \mathbf{v}^{K, sA} \right) \right\} \geq 0. \tag{6.71}
\end{aligned}$$

6.4 Constitution

The unknowns of this system include:

$$\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}, \tag{6.72}$$

$$\rho^K, C^{K_j}, \mathbf{v}^{K_j}, T \tag{6.73}$$

$$\widehat{e}_L^{K_j}, \widehat{r}^{K_j}, \mathbf{t}^{K_j}, \widehat{\mathbf{T}}_L^{K_j}, \widehat{\mathbf{i}}^{K_j}, A^{K_j}, \mathbf{q}^{K_j}, \widehat{Q}^{K_j}, \widehat{Q}_L^{K_j}, \eta^{K_j}, \widehat{\eta}^{K_j}, \widehat{\phi}_L^{K_j}, \tag{6.74}$$

where $j = 1, \dots, N$ except for C^{K_j} , for which $j = 1, \dots, N-1$ because of restriction (6.28), and $K, L = lA, sA, B, C, K \neq L$. We consider four of the six volume fractions as unknowns since they are related through equations (6.15)

and (6.26). The conservation of mass equation (6.24) corresponds to the unknown C^{Kj} . The momentum balance (6.37) and the energy conservation (6.48) correspond to \mathbf{v}^{Kj} and T , respectively. Because we assume that the system is in local thermodynamic equilibrium only one energy equation is needed.

Additional equations are obtained by considering the following variables as constitutive (dependent):

$$\dot{\varepsilon}^A, \dot{\varepsilon}^B, \dot{\varepsilon}^{lA}, \dot{\varepsilon}^{svA}, \quad (6.75)$$

$$\widehat{e}_L^{Kj}, \widehat{r}^{Kj}, \widehat{\mathbf{T}}_L^{Kj}, \mathbf{t}^{Kj}, \widehat{\mathbf{i}}^{Kj}, A^{Kj}, \mathbf{q}^{Kj}, \widehat{Q}^{Kj}, \widehat{Q}_L^{Kj}, \eta^{Kj}, \widehat{\eta}^{Kj}, \widehat{\phi}_L^{Kj}, \quad (6.76)$$

$K, L = lA, sA, B, C, K \neq L$.

Constitutive variables are considered to be a function of the following list of independent variables:

$$\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}, \nabla \varepsilon^A, T, \nabla T, \quad (6.77)$$

$$J^{svA}, C^{svA_j}, \overline{C}^{svA}, \overline{C}^{(n)svA}, \nabla \varepsilon^{svA}, \varepsilon^{(m)lA}, \nabla \varepsilon^{(m)lA}, \quad (6.78)$$

$$J^{seA}, C^{seA_j}, \overline{C}^{seA}, \quad (6.79)$$

$$\rho^{lA}, C^{lA_j}, \mathbf{v}^{lA,svA}, \mathbf{v}^{lA_j,lA}, \mathbf{d}^{lA}, \nabla \mathbf{v}^{lA_j,lA}, \nabla \varepsilon^{lA} \quad (6.80)$$

$$\rho^B, C^{Bj}, \mathbf{v}^{B,svA}, \mathbf{v}^{B_j,B}, \mathbf{d}^B, \nabla \mathbf{v}^{B_j,B}, \nabla \varepsilon^B, \quad (6.81)$$

$$\rho^C, C^{Cj}, \mathbf{v}^{C,svA}, \mathbf{v}^{C_j,C}, \mathbf{d}^C, \nabla \mathbf{v}^{C_j,C}, \quad (6.82)$$

where $m = 1, \dots, p$ denote material time derivatives of order m , $n = 1, \dots, q$, denote material time derivatives of order n , and $j = 1, \dots, N - 1$ represent $N - 1$ constituents. We do not include all three macroscale volume fractions since they are related through equation (6.26), and we do not include all three mesoscale volume fractions since they are related through equation (6.15). We

have chosen ε^{lA} since it measures the liquid content of the particle and it plays an significant role in the swelling behavior of the particles. As in Chapter 4, we choose to use ε^{svA} because we want to use the polymer portion of the particle as the reference phase. Furthermore, we choose ε^A and ε^B , since we need only two out of the three macroscale volume fractions since they are related through equation (6.26). We include T since the behavior of most polymers is a strong function of temperature, and we include ∇T so that we recover Fourier's law of heat conduction. The variables in list (6.78) account for the behavior of the viscoelastic solid phase. The variables J^{svA} and C^{svAj} account for the material make up, derivatives of order 0 through q of \overline{C}^{svA} combined with derivatives of order 1 through p of ε^{lA} and J^{svA} account for the viscoelastic nature of the material by taking the place of the usual higher-order derivatives in strain. Finally, $\nabla \varepsilon^{svA}$ accounts for flow due to polymer content and $\nabla \varepsilon^{(m)lA}$ accounts for flue due to changes in moisture content. The variables in list (6.79) are included to model the elastic solid phase. The variables J^{seA} and C^{seAj} account for the material make up, and \overline{C}^{seA} combined with J^{seA} account for elastic behavior. The variables in lists (6.80), (6.81) and (6.82) represent the liquid contained in the particle, and the fluids of the bulk phases. We include ρ^{Kj} and C^{Kj} , where $K = lA, B, C$, to account for the material make up of these phases, and \mathbf{d}^K to account for the viscous nature of the liquids. We include $\nabla \varepsilon^{lA}$ and $\nabla \varepsilon^B$ to account for flow due to moisture content, but do not include gradients of all the volume fractions because they are related through equations (6.26) and (6.15). The variables $\mathbf{v}^{Kj,K}$ and $\nabla \mathbf{v}^{Kj,K}$, where $K = lA, B, C$, account for viscous diffusion within the phase. Finally, the variables $\mathbf{v}^{K,svA}$ give us information

about the exchange of momentum within a phase.

6.5 Entropy Inequality

As in Chapter 2, to simplify calculations, we postulate the dependence of the Helmholtz free energies as follows:

$$A^{lA} = A^{lA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}, T, \rho^{lA}, C^{lA_j}, \overset{(m)}{\varepsilon}^{lA}, \overline{C}^{svA}, \overline{C}^{svA}, \overline{C}^{seA}), \quad (6.83)$$

$$A^{svA} = A^{svA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}, T, J^{svA}, C^{svA_j}, \overset{(m)}{\varepsilon}^{lA}, \overline{C}^{svA}, \overline{C}^{svA}, \overline{C}^{seA}), \quad (6.84)$$

$$A^{seA} = A^{seA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}, T, J^{seA}, C^{seA_j}, \overset{(m)}{\varepsilon}^{lA}, \overline{C}^{svA}, \overline{C}^{svA}, \overline{C}^{seA}), \quad (6.85)$$

$$A^B = A^B(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}, T, \rho^B, C^{B_j}), \quad (6.86)$$

$$A^C = A^C(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}, T, \rho^C, C^{C_j}), \quad (6.87)$$

otherwise we adhere to the axiom of equipresence [24]: all other constitutive variables are considered a function of lists (6.77) - (6.82). Material time derivatives of the Helmholtz free energies appear in entropy inequality (6.71). Using the chain rule, they may be calculated as follows:

$$\begin{aligned} \frac{D^{lA} A^{lA}}{Dt} &= \frac{\partial A^{lA}}{\partial \varepsilon^A} \frac{D^{lA} \varepsilon^A}{Dt} + \frac{\partial A^{lA}}{\partial \varepsilon^B} \frac{D^{lA} \varepsilon^B}{Dt} + \frac{\partial A^{lA}}{\partial \varepsilon^{lA}} \frac{D^{lA} \varepsilon^{lA}}{Dt} + \frac{\partial A^{lA}}{\partial \varepsilon^{svA}} \frac{D^{lA} \varepsilon^{svA}}{Dt} \\ &+ \frac{\partial A^{lA}}{\partial T} \frac{D^{lA} T}{Dt} + \frac{\partial A^{lA}}{\partial \rho^{lA}} \frac{D^{lA} \rho^{lA}}{Dt} + \sum_{j=1}^{N-1} \tilde{\mu}^{lA_j} \frac{D^{lA} (C^{lA_j})}{Dt} + \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \overset{(m)}{\varepsilon}^{lA}} \frac{D^{lA} \overset{(m)}{\varepsilon}^{lA}}{Dt} \\ &+ \frac{\partial A^{lA}}{\partial \overline{C}^{svA}} : \frac{D^{lA} \overline{C}^{svA}}{Dt} + \sum_{n=1}^q \frac{\partial A^{lA}}{\partial \overset{(n)}{\overline{C}^{svA}}} : \frac{D^{lA} \overset{(n)}{\overline{C}^{svA}}}{Dt} + \frac{\partial A^{lA}}{\partial \overline{C}^{seA}} : \frac{D^{lA} \overline{C}^{seA}}{Dt}, \quad (6.88) \end{aligned}$$

$$\begin{aligned}
\frac{D^{s_v A} A^{s_v A}}{Dt} &= \frac{\partial A^{s_v A}}{\partial \varepsilon^A} \frac{D^{s_v A} \varepsilon^A}{Dt} + \frac{\partial A^{s_v A}}{\partial \varepsilon^B} \frac{D^{s_v A} \varepsilon^B}{Dt} + \frac{\partial A^{s_v A}}{\partial \varepsilon^{lA}} \frac{D^{s_v A} \varepsilon^{lA}}{Dt} \\
&+ \frac{\partial A^{s_v A}}{\partial \varepsilon^{s_v A}} \frac{D^{s_v A} \varepsilon^{s_v A}}{Dt} + \frac{\partial A^{s_v A}}{\partial T} \frac{D^{s_v A} T}{Dt} + \frac{\partial A^{s_v A}}{\partial J^{s_v A}} \frac{D^{s_v A} J^{s_v A}}{Dt} \\
&+ \sum_{j=1}^{N-1} \tilde{\mu}^{s_v A_j} \frac{D^{s_v A} (C^{s_v A_j})}{Dt} + \sum_{m=1}^p \frac{\partial A^{s_v A}}{\partial \varepsilon^{(m)lA}} \frac{D^{s_v A} \varepsilon^{(m)lA}}{Dt} + \frac{\partial A^{s_v A}}{\partial \overline{C}^{s_v A}} : \frac{D^{s_v A} \overline{C}^{s_v A}}{Dt} \\
&+ \sum_{n=1}^q \frac{\partial A^{s_v A}}{\partial \overline{C}^{s_v A}{}^{(n)}} : \frac{D^{s_v A} \overline{C}^{s_v A}{}^{(n)}}{Dt} + \frac{\partial A^{s_v A}}{\partial \overline{C}^{s_e A}} : \frac{D^{s_v A} \overline{C}^{s_e A}}{Dt}, \tag{6.89}
\end{aligned}$$

$$\begin{aligned}
\frac{D^{s_e A} A^{s_e A}}{Dt} &= \frac{\partial A^{s_e A}}{\partial \varepsilon^A} \frac{D^{s_e A} \varepsilon^A}{Dt} + \frac{\partial A^{s_e A}}{\partial \varepsilon^B} \frac{D^{s_e A} \varepsilon^B}{Dt} + \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \frac{D^{s_e A} \varepsilon^{lA}}{Dt} \\
&+ \frac{\partial A^{s_e A}}{\partial \varepsilon^{s_v A}} \frac{D^{s_e A} \varepsilon^{s_v A}}{Dt} + \frac{\partial A^{s_e A}}{\partial T} \frac{D^{s_e A} T}{Dt} + \frac{\partial A^{s_e A}}{\partial J^{s_e A}} \frac{D^{s_e A} J^{s_e A}}{Dt} \\
&+ \sum_{j=1}^{N-1} \tilde{\mu}^{s_e A_j} \frac{D^{s_e A} (C^{s_e A_j})}{Dt} + \sum_{m=1}^p \frac{\partial A^{s_e A}}{\partial \varepsilon^{(m)lA}} \frac{D^{s_e A} \varepsilon^{(m)lA}}{Dt} + \frac{\partial A^{s_e A}}{\partial \overline{C}^{s_v A}} : \frac{D^{s_e A} \overline{C}^{s_v A}}{Dt} \\
&+ \sum_{n=1}^q \frac{\partial A^{s_e A}}{\partial \overline{C}^{s_v A}{}^{(n)}} : \frac{D^{s_e A} \overline{C}^{s_v A}{}^{(n)}}{Dt} + \frac{\partial A^{s_e A}}{\partial \overline{C}^{s_e A}} : \frac{D^{s_e A} \overline{C}^{s_e A}}{Dt}, \tag{6.90}
\end{aligned}$$

$$\begin{aligned}
\frac{D^K A^K}{Dt} &= \frac{\partial A^K}{\partial \varepsilon^A} \frac{D^K \varepsilon^A}{Dt} + \frac{\partial A^K}{\partial \varepsilon^B} \frac{D^K \varepsilon^B}{Dt} + \frac{\partial A^K}{\partial \varepsilon^{lA}} \frac{D^K \varepsilon^{lA}}{Dt} + \frac{\partial A^{s_v A}}{\partial \varepsilon^{s_v A}} \frac{D^K \varepsilon^{s_v A}}{Dt} \\
&+ \frac{\partial A^K}{\partial T} \frac{D^K T}{Dt} + \frac{\partial A^K}{\partial \rho^K} \frac{D^K \rho^K}{Dt} + \sum_{j=1}^{N-1} \tilde{\mu}^{K_j} \frac{D^K C^{K_j}}{Dt}, \quad K = B, C. \tag{6.91}
\end{aligned}$$

We will enforce conservation of mass weakly using a Lagrange multiplier technique:

$$\begin{aligned}
\Lambda_{new} &= \Lambda_{old} + \sum_K \lambda^K \left[\frac{D^K (\varepsilon^K \rho^K)}{Dt} + \varepsilon^K \rho^K (\nabla \cdot \mathbf{v}^K) - \sum_{L, L \neq K} \widehat{e}_L^K \right] \\
&+ \sum_K \sum_{j=1}^{N-1} \lambda^{K_j} \left[\varepsilon^K \rho^K \frac{D^K C^{K_j}}{Dt} + \nabla \cdot (\varepsilon^K \rho^{K_j} \mathbf{v}^{K_j, K}) \right. \\
&\left. + C^{K_j} \sum_{L, L \neq K} \widehat{e}_L^K - \sum_{L, L \neq K} \widehat{e}_L^{K_j} - \widehat{r}^{K_j} \right], \tag{6.92}
\end{aligned}$$

where we have converted the conservation of mass for species from density to concentration form.

We choose the viscoelastic solid phase of the particle as the reference phase. As such, we use the following equation to convert to material time derivatives:

$$\frac{D^K(\cdot)}{Dt} = \frac{D^{s_v A}(\cdot)}{Dt} + \mathbf{v}^{K, s_v A} \nabla(\cdot). \quad (6.93)$$

Using the identities and methods described above, we obtain the following form of the entropy inequality:

$$\begin{aligned} T\Lambda = & - \sum_K \varepsilon^K \rho^K \left(\frac{\partial A^K}{\partial T} + \eta^K \right) \dot{T} \\ & - \left(\sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^A} + \lambda^C \rho^C \right) \dot{\varepsilon}^A \\ & - \left(\sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^B} - \lambda^B \rho^B + \lambda^C \rho^C \right) \dot{\varepsilon}^B \\ & - \left(\sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{lA}} - \lambda^{lA} \rho^{lA} \right) \dot{\varepsilon}^{lA} \\ & - \left(\sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{s_v A}} \right) \dot{\varepsilon}^{s_v A} \\ & - \sum_{K=lA, B, C} \left(\varepsilon^K \rho^K \frac{\partial A^K}{\partial \rho^K} - \varepsilon^K \lambda^K \right) \dot{\rho}^K \\ & - \sum_K \sum_{j=1}^{N-1} \varepsilon^K \rho^K (\tilde{\mu}^{K_j} - \lambda^{K_j}) \dot{C}^{K_j} \\ & - \left(\varepsilon^{s_v A} \rho^{s_v A} \frac{\partial A^{s_v A}}{\partial J^{s_v A}} - \frac{1}{3} \frac{\varepsilon^{s_v A}}{J^{s_v A}} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_v A_j}) \right) \dot{J}^{s_v A} \\ & - \left(\varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial J^{s_e A}} - \frac{1}{3} \frac{\varepsilon^{s_e A}}{J^{s_e A}} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_e A_j}) \right) \dot{J}^{s_e A} \\ & - \left[\sum_{\alpha=l, s_v, s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \bar{\mathbf{C}}^{s_v A}} - \frac{\varepsilon^{s_v A}}{2} (\bar{\mathbf{F}}^{s_v A})^{-1} \cdot \left(\sum_{j=1}^N \mathbf{t}^{s_v A_j} \right) \cdot (\bar{\mathbf{F}}^{s_v A})^{-T} \right] \end{aligned}$$

$$\begin{aligned}
& - \left[\frac{\varepsilon^{s_v A} \rho^{s_v A} \lambda^{s_v A}}{2} (\bar{\mathbf{F}}^{s_v A})^{-1} \cdot (\bar{\mathbf{F}}^{s_v A})^{-T} \right] : \dot{\bar{\mathbf{C}}}^{s_v A} \\
& - \left[\sum_{\alpha=l, s_v, s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \bar{\mathbf{C}}^{s_e A}} - \frac{\varepsilon^{s_e A}}{2} (\bar{\mathbf{F}}^{s_e A})^{-1} \cdot \left(\sum_{j=1}^N \mathbf{t}^{s_e A_j} \right) \cdot (\bar{\mathbf{F}}^{s_e A})^{-T} \right. \\
& \quad \left. - \frac{\varepsilon^{s_e A} \rho^{s_e A} \lambda^{s_e A}}{2} (\bar{\mathbf{F}}^{s_e A})^{-1} \cdot (\bar{\mathbf{F}}^{s_e A})^{-T} \right] : \dot{\bar{\mathbf{C}}}^{s_e A} \\
& - \sum_{\alpha=l, s_v, s_e} \sum_{m=1}^p \left(\varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \varepsilon^{(m)lA}} \right)^{(m+1)lA} \\
& + \sum_{K=lA, B, C} \varepsilon^K \left(\sum_{j=1}^N \mathbf{t}^{Kj} + \lambda^K \rho^K \mathbf{I} \right) : \mathbf{d}^K \\
& - \sum_{\alpha=l, s_v, s_e} \sum_{n=1}^q \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \bar{\mathbf{C}}^{s_v A (n)}} : \bar{\mathbf{C}}^{s_v A (n+1)} \\
& - \left[\varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla_{\varepsilon^A} + \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla_{\varepsilon^B} + \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial \varepsilon^{lA}} - \frac{\lambda^{lA}}{\varepsilon^{lA}} \right) \nabla_{\varepsilon^{lA}} \right. \\
& + \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^{s_v A}} \nabla_{\varepsilon^{s_v A}} + \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial T} + \eta^{lA} \right) \nabla T \\
& + \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial \rho^{lA}} - \frac{\lambda^{lA}}{\rho^{lA}} \right) \nabla \rho^{lA} + \varepsilon^{lA} \rho^{lA} \sum_{j=1}^N (\tilde{\mu}^{lA_j} - \lambda^{lA_j}) \nabla C^{lA_j} \\
& + \varepsilon^{lA} \rho^{lA} \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \varepsilon^{(m)lA}} \nabla_{\varepsilon^{(m)lA}} + \varepsilon^{lA} \rho^{lA} \sum_{n=0}^q \frac{\partial A^{lA}}{\partial \bar{\mathbf{C}}^{s_v A (n)}} : \nabla \bar{\mathbf{C}}^{s_v A (n)} \\
& \left. + \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \bar{\mathbf{C}}^{s_e A}} : \nabla \bar{\mathbf{C}}^{s_e A} + \sum_{L, L \neq lA} \hat{\mathbf{T}}_L^{lA} \right] \cdot \mathbf{v}^{lA, s_v A} \\
& - \left[\varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^A} \nabla_{\varepsilon^A} + \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^B} \nabla_{\varepsilon^B} + \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \nabla_{\varepsilon^{lA}} \right. \\
& + \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^{s_v A}} \nabla_{\varepsilon^{s_v A}} + \varepsilon^{s_e A} \rho^{s_e A} \left(\frac{\partial A^{s_e A}}{\partial T} + \eta^{s_e A} \right) \nabla T \\
& \left. + \varepsilon^{s_e A} \rho^{s_e A} \left(\frac{\partial A^{s_e A}}{\partial J^{s_e A}} + \frac{\lambda^{s_e A}}{J^{s_e A}} \right) \nabla J^{s_e A} + \varepsilon^{s_e A} \rho^{s_e A} \sum_{j=1}^N (\tilde{\mu}^{s_e A_j} - \lambda^{s_e A_j}) \nabla C^{s_e A_j} \right]
\end{aligned}$$

$$\begin{aligned}
& +\varepsilon^{s_e A} \rho^{s_e A} \sum_{m=1}^p \frac{\partial A^{s_e A}}{\partial \varepsilon^{(m)lA}} \nabla_{\varepsilon^{(m)lA}} + \varepsilon^{s_e A} \rho^{s_e A} \sum_{n=0}^q \frac{\partial A^{s_e A}}{\partial \overline{C}^{(n)s_v A}} : \nabla \overline{C}^{(n)s_v A} \\
& +\varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \overline{C}^{s_e A}} : \nabla \overline{C}^{s_e A} + \left[\sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A} \right] \cdot \mathbf{v}^{s_e A, s_v A} \\
& - \left[\varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} \nabla_{\varepsilon^A} + \varepsilon^B \rho^B \left(\frac{\partial A^B}{\partial \varepsilon^B} - \frac{\lambda^B}{\varepsilon^B} \right) \nabla_{\varepsilon^B} + \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{lA}} \nabla_{\varepsilon^{lA}} \right. \\
& + \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{s_v A}} \nabla_{\varepsilon^{s_v A}} + \varepsilon^B \rho^B \left(\frac{\partial A^B}{\partial T} + \eta^B \right) \nabla T + \varepsilon^B \rho^B \left(\frac{\partial A^B}{\partial \rho^B} - \frac{\lambda^B}{\rho^B} \right) \nabla \rho^B \\
& \left. + \varepsilon^B \rho^B \sum_{j=1}^N (\tilde{\mu}^{Bj} - \lambda^{Bj}) \nabla C^{Bj} + \sum_{L, L \neq B} \widehat{\mathbf{T}}_L^B \right] \cdot \mathbf{v}^{B, s_v A} \\
& - \left[\varepsilon^C \rho^C \left(\frac{\partial A^C}{\partial \varepsilon^A} + \frac{\lambda^C}{\varepsilon^C} \right) \nabla_{\varepsilon^A} + \varepsilon^C \rho^C \left(\frac{\partial A^C}{\partial \varepsilon^B} + \frac{\lambda^C}{\varepsilon^C} \right) \nabla_{\varepsilon^B} \right. \\
& + \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{lA}} \nabla_{\varepsilon^{lA}} + \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{s_v A}} \nabla_{\varepsilon^{s_v A}} + \varepsilon^C \rho^C \left(\frac{\partial A^C}{\partial T} + \eta^C \right) \nabla T \\
& \left. + \varepsilon^C \rho^C \left(\frac{\partial A^C}{\partial \rho^C} - \frac{\lambda^C}{\rho^C} \right) \nabla \rho^C + \varepsilon^C \rho^C \sum_{j=1}^N (\tilde{\mu}^{Cj} - \lambda^{Cj}) \nabla C^{Cj} + \sum_{L, L \neq C} \widehat{\mathbf{T}}_L^C \right] \cdot \mathbf{v}^{C, s_v A} \\
& + \sum_K \frac{\varepsilon^K (\nabla T)}{T} \cdot \left\{ \mathbf{q}^K + \sum_{j=1}^N \left[\rho^{Kj} \mathbf{v}^{Kj, K} \left(A^{Kj} + \frac{1}{2} (\mathbf{v}^{Kj, K})^2 \right) - \mathbf{t}^{Kj} \mathbf{v}^{Kj, K} \right] \right\} \\
& + \sum_K \sum_{j=1}^{N-1} \varepsilon^K \left(\mathbf{t}^{Kj} - \frac{\rho^{Kj}}{\rho^{KN}} \mathbf{t}^{KN} - \rho^{Kj} (A^{Kj} - A^{KN}) \mathbf{I} \right. \\
& \left. + \rho^{Kj} (\lambda^{Kj} - \lambda^{KN}) \mathbf{I} \right) : (\nabla \mathbf{v}^{Kj, K}) \\
& + \sum_K \sum_{j=1}^{N-1} \left[- \left(\sum_{L, L \neq K} \widehat{\mathbf{T}}_L^{Kj} + \widehat{\mathbf{i}}^{Kj} \right) + \frac{\rho^{Kj}}{\rho^{KN}} \left(\sum_L \widehat{\mathbf{T}}_L^{KN} + \widehat{\mathbf{i}}^{KN} \right) \right. \\
& \quad - \nabla \cdot (\varepsilon^K \rho^{Kj} (A^{Kj} - A^{KN})) - \varepsilon^K \mathbf{t}^{KN} \cdot \nabla \left(\frac{\rho^{Kj}}{\rho^{KN}} \right) \\
& \quad \left. + (\lambda^{Kj} - \lambda^{KN}) \nabla (\varepsilon^K \rho^{Kj}) \right] \cdot \mathbf{v}^{Kj, K} \\
& - \sum_K \sum_{j=1}^N \left(\frac{1}{2} (\mathbf{v}^{Kj, K})^2 + \lambda^{Kj} \right) \widehat{\mathbf{r}}^{Kj}
\end{aligned}$$

$$\begin{aligned}
& - \sum_K \sum_{L, L \neq K} \widehat{e}_L^K \left(\lambda^K + A^K + \frac{1}{2} (\mathbf{v}^{K, sA})^2 - \sum_{j=1}^{N-1} \lambda^{K_j} C^{K_j} \right) \\
& - \sum_K \sum_{L, L \neq K} \sum_{j=1}^{N-1} \widehat{e}_L^{K_j} \left(\lambda^{K_j} + \frac{1}{2} (\mathbf{v}^{K_j, K})^2 \right) \geq 0, \tag{6.94}
\end{aligned}$$

where we have used identities (3.31) and (3.32), but replaced α with K , to remove the N^{th} component dependence from terms involving $\mathbf{v}^{K_j, K}$, and $\nabla \mathbf{v}^{K_j, K}$. We have also used equations (3.26)-(3.27), with $s_v A$ and $s_e A$ replacing s , to eliminate $\mathbf{d}^{s_v A}$ and $\mathbf{d}^{s_e A}$ in favor of the independent variables $\dot{\mathbf{C}}^{s_v}$ and $\dot{\mathbf{J}}^{s_v A}$, and $\dot{\mathbf{C}}^{s_e}$ and $\dot{\mathbf{J}}^{s_e A}$, respectively.

6.5.1 Macroscale Pressures

The macroscale pressures are essentially analogous to the definitions given in Section 4.3.1. We give them and some essential relations here for future reference. We note that, as in Section 4.3.1, it is possible to define other pressures based on using different combinations of the volume fractions. We chose to define the pressures below using the same set of independent variables given for the Helmholtz free energies given in equations (6.83) - (6.87). For the lA -phase, we make the following definitions:

$$p^{lA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{s_v A}, \rho^{lA}, C^{lA_j}) = (\rho^{lA})^2 \frac{\partial A^{lA}}{\partial \rho^{lA}} \Bigg|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{s_v A}, C^{lA_j}} \tag{6.95}$$

as the classical pressure,

$$\bar{p}^{lA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{s_v A}, \varepsilon^{lA} \rho^{lA_j}) = -\varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^{lA}} \Bigg|_{\varepsilon^A, \varepsilon^B, \varepsilon^{s_v A}, \varepsilon^{lA} \rho^{lA_j}} \tag{6.96}$$

as the thermodynamic pressure,

$$\pi^{lA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{s_v A}, \rho^{lA}, C^{lA_j}) = \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^{lA}} \Bigg|_{\varepsilon^A, \varepsilon^B, \varepsilon^{s_v A}, \rho^{lA}, C^{lA_j}} \tag{6.97}$$

as the swelling potential. Equations (6.95)-(6.97) are related through

$$p^{lA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{s_v A}, \rho^{lA}, C^{lA_j}) = \bar{p}^{lA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{s_v A}, \varepsilon^{lA} \rho^{lA_j}) \\ + \pi^{lA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{s_v A}, \rho^{lA}, C^{lA_j}). \quad (6.98)$$

For the solid particle phases, $sA = s_v A, s_e A$, we make the following definitions:

$$p^{sA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{sA}, J^{sA}, C^{sA_j}) = -\rho^{sA} J^{sA} \left. \frac{\partial A^{sA}}{\partial J^{sA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{sA}, C^{sA_j}} \quad (6.99)$$

as the classical pressure,

$$\bar{p}^{sA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{sA}, J^{sA}, C^{sA_j}) = -\varepsilon^{sA} \rho^{sA} \left. \frac{\partial A^{sA}}{\partial \varepsilon^{sA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, J^{sA}, C^{sA_j}} \quad (6.100)$$

as the thermodynamic pressure,

$$\pi^{sA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, J^{sA}, \rho^{sA}, C^{sA_j}) = -\rho^{sA} J^{sA} \left. \frac{\partial A^{sA}}{\partial J^{sA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \rho^{sA}, C^{sA_j}} \quad (6.101)$$

as the swelling potential. Equations (6.99)-(6.101) are related through

$$p^{sA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{sA}, J^{sA}, C^{sA_j}) = \bar{p}^{sA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, \varepsilon^{sA}, J^{sA}, C^{sA_j}) \\ + \pi^{sA}(\varepsilon^A, \varepsilon^B, \varepsilon^{lA}, J^{sA}, \rho^{sA}, C^{sA_j}). \quad (6.102)$$

Note that the difference between equations (6.99) and (6.101) is in the variables that are being held fixed.

As we noted in Chapter 4, the thermodynamic pressure, $\bar{p}^{s_e A}$, of the $s_e A$ -phase does not appear naturally as the Helmholtz potential of this phase is not a function of its own volume fraction. Using calculations analogous to those in Section 4.3.1, we can derive the following relationships:

$$\left. \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{s_v A}} = \left. \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{s_e A}} - \left. \frac{\partial A^{s_e A}}{\partial \varepsilon^{s_e A}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}}, \quad (6.103)$$

and

$$\left. \frac{\partial A^{seA}}{\partial \varepsilon^{svA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} = - \left. \frac{\partial A^{seA}}{\partial \varepsilon^{seA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}}, \quad (6.104)$$

where

$$\left. \frac{\partial \varepsilon^{seA}}{\partial \varepsilon^{svA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} = -1, \quad (6.105)$$

because of the relationship between volume fractions, equation (6.15).

For the bulk phases, $K = B, C$ we make the following definitions:

$$p^K(\varepsilon^A, \varepsilon^K, \varepsilon^{lA}, \varepsilon^{svA}, \rho^K, C^{Kj}) = (\rho^K)^2 \left. \frac{\partial A^K}{\partial \rho^K} \right|_{\varepsilon^A, \varepsilon^K, \varepsilon^{lA}, \varepsilon^{svA}, C^{Kj}} \quad (6.106)$$

as the classical pressure,

$$\bar{p}^K(\varepsilon^A, \varepsilon^K, \varepsilon^{lA}, \varepsilon^{svA}, \varepsilon^K \rho^{Kj}) = -\varepsilon^K \rho^K \left. \frac{\partial A^K}{\partial \varepsilon^K} \right|_{\varepsilon^A, \varepsilon^{lA}, \varepsilon^{svA}, \varepsilon^K \rho^{Kj}} \quad (6.107)$$

as the thermodynamic pressure,

$$\pi^K(\varepsilon^A, \varepsilon^K, \varepsilon^{lA}, \varepsilon^{svA}, \rho^K, C^{Kj}) = \varepsilon^K \rho^K \left. \frac{\partial A^K}{\partial \varepsilon^K} \right|_{\varepsilon^A, \varepsilon^{lA}, \varepsilon^{svA}, \rho^K, C^{Kj}} \quad (6.108)$$

as the swelling potential. Equations (6.106)-(6.108) are related through

$$p^K(\varepsilon^A, \varepsilon^K, \varepsilon^{lA}, \varepsilon^{svA}, \rho^K, C^{Kj}) = \bar{p}^K(\varepsilon^A, \varepsilon^K, \varepsilon^{lA}, \varepsilon^{svA}, \varepsilon^K \rho^{Kj}) + p^K(\varepsilon^A, \varepsilon^K, \varepsilon^{lA}, \varepsilon^{svA}, \rho^K, C^{Kj}). \quad (6.109)$$

The three pressure relationships (6.98), (6.102) and (6.109) can be derived using the same method that was used to derive equation (3.46).

The thermodynamic pressure \bar{p}^C does not appear naturally as the Helmholtz potential of this phase is not a function of its own volume fraction. Using

calculations analogous to those in Section 4.3.1, we can derive the following relationships:

$$\left. \frac{\partial A^C}{\partial \varepsilon^A} \right|_{\varepsilon^B, \varepsilon^{lA}, \varepsilon^{svA}} = \left. \frac{\partial A^C}{\partial \varepsilon^A} \right|_{\varepsilon^C, \varepsilon^{lA}, \varepsilon^{svA}} - \left. \frac{\partial A^C}{\partial \varepsilon^C} \right|_{\varepsilon^A, \varepsilon^{lA}, \varepsilon^{svA}}, \quad (6.110)$$

and

$$\left. \frac{\partial A^C}{\partial \varepsilon^B} \right|_{\varepsilon^A, \varepsilon^{lA}, \varepsilon^{svA}} = - \left. \frac{\partial A^C}{\partial \varepsilon^C} \right|_{\varepsilon^A, \varepsilon^{lA}, \varepsilon^{svA}}, \quad (6.111)$$

where

$$\left. \frac{\partial \varepsilon^C}{\partial \varepsilon^B} \right|_{\varepsilon^A, \varepsilon^{lA}, \varepsilon^{svA}} = -1, \quad (6.112)$$

because of the relationship between volume fractions, equation (6.26).

6.5.2 Non-Equilibrium Results

Λ , the rate of entropy production, is a linear function of the following list of variables, which are neither independent nor constitutive, thus arbitrary:

$$\dot{T}, \dot{\rho}^K, \dot{C}^{Kj}, \dot{j}^{svA}, \dot{j}^{seA}, \nabla \mathbf{v}^{seAj, seA}, \nabla \mathbf{v}^{svAj, svA}, \dot{\mathbf{C}}^{seA}, \frac{(q+1)}{\varepsilon^{svA}} \varepsilon^{(p+1)lA} \quad (6.113)$$

where $K = lA, B, C$ for $\dot{\rho}^K$ and $K = lA, svA, seA, B, C$ for \dot{C}^{Kj} . To avoid violating the entropy inequality, equation (6.94), for all possible processes their coefficients must be identically zero. This yields the following set of non-equilibrium results:

$$\sum_K \varepsilon^K \rho^K \left(\frac{\partial A^K}{\partial T} + \eta^K \right) = 0, \quad (6.114)$$

$$\lambda^K = \frac{p^K}{\rho^K}, \quad K = lA, B, C, \quad (6.115)$$

$$\lambda^{K_j} = \tilde{\mu}^{K_j}, \quad K = lA, s_v A, s_e A, B, C, \quad (6.116)$$

$$\frac{1}{3} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_v A_j}) = -p^{s_v A}, \quad (6.117)$$

$$\frac{1}{3} \sum_{j=1}^N \text{tr}(\mathbf{t}^{s_e A_j}) = -p^{s_e A}, \quad (6.118)$$

$$\mathbf{t}^{s A_j} - \frac{\rho^{s A_j}}{\rho^{s A_N}} \mathbf{t}^{s A_N} = \rho^{s A_j} (A^{s A_j} - A^{s A_N} - \tilde{\mu}^{s A_j}) \mathbf{I}, \quad s = s_v, s_e, \quad (6.119)$$

$$\sum_{j=1}^N \mathbf{t}^{s_e A_j} = 2(\overline{\mathbf{F}}^{s_e A}) \cdot \sum_{\alpha=l, s_v, s_e} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_e A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{s_e A}} \cdot (\overline{\mathbf{F}}^{s_e A})^T - \rho^{s_e A} \lambda^{s_e A} \mathbf{I}, \quad (6.120)$$

$$\sum_{\alpha=l, s_v, s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{(q) s_v A}} = 0, \quad (6.121)$$

$$\sum_{\alpha=l, s_v, s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \varepsilon^{(p) l A}} = 0. \quad (6.122)$$

Consider equation (6.114). A classical result for a single material was demonstrated in Chapter 2, and says that T and η are dual variables. In this case we will make the simplifying assumption that

$$\frac{\partial A^K}{\partial T} = -\eta^K, \quad \forall K. \quad (6.123)$$

Equation (6.115) gives identities for the Lagrange multipliers and for the remainder of this section we will use them wherever λ^K , $K = lA, B, C$, appear. Equation (6.116) gives an identity for λ^{α_j} . It has been used to obtain (6.119) and will also be used throughout this chapter. Equations (6.117) and (6.118) are

novel. They are a direct consequence of the new choice of independent variables. Since it is reasonable to expect the diffusive velocities in the solid phases to be negligible, see equation (B.12), we can rewrite these two equations as

$$\frac{1}{3}\text{tr}(\mathbf{t}^{s_e A}) = -p^{s_e A}, \text{ and} \quad (6.124)$$

$$\frac{1}{3}\text{tr}(\mathbf{t}^{s_v A}) = -p^{s_v A}, \quad (6.125)$$

respectively. Equation (6.119) contains an N^{th} -component dependence. Since we do not want a result which depends on the labeling of the constituents we will remove this dependence in a subsequent section. Equation (6.120) is novel and allows us to solve for the Lagrange multiplier $\lambda^{s_e A}$. Again assuming the diffusive velocities in the $s_e A$ -phase are small, we have

$$\mathbf{t}^{s_e A} = -\rho^{s_e A} \lambda^{s_e A} \mathbf{I} + 2(\overline{\mathbf{F}}^{s_e A}) \cdot \sum_{\alpha=l, s_v, s_e} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_e A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{s_e A}} \cdot (\overline{\mathbf{F}}^{s_e A})^T. \quad (6.126)$$

Taking 1/3 the trace of (6.126), using (6.124) to eliminate $\mathbf{t}^{s_e A}$, and then solving for $\lambda^{s_e A}$ we obtain

$$\lambda^{s_e A} = \frac{p^{s_e A}}{\rho^{s_e A}} + \frac{2}{3} \sum_{\alpha=l, s_v, s_e} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_e A} \rho^{s_e A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{s_e A}} : \overline{\mathbf{C}}^{s_e A}. \quad (6.127)$$

Substituting this back into equation (6.126) yields

$$\mathbf{t}^{s_e A} = -p^{s_e A} \mathbf{I} + \mathbf{t}_{se}^{s_e A} + \frac{\varepsilon^{lA}}{\varepsilon^{s_e A}} \mathbf{t}_{sh}^{s_e A} - \frac{2}{3} \sum_{\alpha=l, s_v, s_e} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_e A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{s_e A}} : \overline{\mathbf{C}}^{s_e A}, \quad (6.128)$$

where

$$\begin{aligned} \mathbf{t}_{se}^{s_e A} &= 2\rho^{s_e A} \overline{\mathbf{F}}^{s_e A} \cdot \frac{\partial A^{s_e A}}{\partial \overline{\mathbf{C}}^{s_e A}} \cdot (\overline{\mathbf{F}}^{s_e A})^T \\ &+ 2 \frac{\varepsilon^{s_v A} \rho^{s_v A}}{\varepsilon^{s_e A}} \overline{\mathbf{F}}^{s_e A} \cdot \frac{\partial A^{s_v A}}{\partial \overline{\mathbf{C}}^{s_e A}} \cdot (\overline{\mathbf{F}}^{s_e A})^T \end{aligned} \quad (6.129)$$

and

$$\mathbf{t}_{sh}^{s_e A} = 2\rho^{lA} \overline{\mathbf{F}}^{s_e A} \cdot \frac{\partial A^{lA}}{\partial \overline{\mathbf{C}}^{s_e A}} \cdot (\overline{\mathbf{F}}^{s_e A})^T, \quad (6.130)$$

where $\mathbf{t}_{s_e}^{s_e A}$ and $\mathbf{t}_{sh}^{s_e A}$ are the Terzaghi and hydration stress tensors for the $s_e A$ -phase, respectively. Note that when we take one third the trace of (6.128) we recover (6.124) so that the physical pressure in the $s_e A$ phase, $-1/3\text{tr}(\mathbf{t}^{s_e A})$, coincides with the thermodynamic definition of pressure of that phase, $p^{s_e A}$.

In equation (6.121) and (6.122) $\varepsilon^{\alpha A} \rho^{\alpha A}$ is begin held fixed, therefore we can bring it inside the partial derivative. Doing so yields

$$\frac{\partial A_T^A}{\partial \overline{\mathbf{C}}^{s_e A}{}^{(q)}} = 0, \quad (6.131)$$

and

$$\frac{\partial A_T^A}{\partial \varepsilon^{lA}{}^{(p)}} = 0, \quad (6.132)$$

where $\varepsilon^{lA} \rho^{lA} A^{lA} + \varepsilon^{s_e A} \rho^{s_e A} A^{s_e A} + \varepsilon^{s_v A} \rho^{s_v A} A^{s_v A} = A_T^A$ is the total Helmholtz free energy of the particle. This means that the total Helmholtz free energy of the particle is not a function of the q^{th} derivative of the right Cauchy-Green tensor nor a function of the p^{th} derivative of the volume fraction of the liquid phase.

6.5.3 Equilibrium Results

We define equilibrium to be when the following set of variables is equal to zero:

$$\begin{aligned} \dot{\varepsilon}^A, \dot{\varepsilon}^B, \dot{\varepsilon}^{(m+1)lA}, \dot{\varepsilon}^{s_v A}, \dot{\overline{\mathbf{C}}}^{s_v A}, \mathbf{d}^K, \overline{\mathbf{C}}^{s_v A}{}^{(n+1)}, \mathbf{v}^{lA, s_v A}, \mathbf{v}^{s_e A, s_v A}, \mathbf{v}^{B, s_v A}, \\ \mathbf{v}^{C, s_v A}, \nabla T, \nabla \mathbf{v}^{K_j, K}, \mathbf{v}^{K_j, K}, \hat{e}_L^{K_j}, \hat{e}_L^K, \end{aligned} \quad (6.133)$$

where $n = 1, \dots, q-1$, $m = 0, \dots, p-1$, $K = lA, B, C$ for \mathbf{d}^K and $\nabla \mathbf{v}^{K_j, K}$, and $K = lA, s_v A, s_e A, B, C$ for $\mathbf{v}^{K_j, K}$. Using the method for obtaining equilibrium results outlined in Chapter 2, we obtain the following set of equilibrium results:

$$p^C = - \sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^A}, \quad (6.134)$$

$$p^B - p^C = \sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^B}, \quad (6.135)$$

$$p^{lA} = \sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{lA}}, \quad (6.136)$$

$$\sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{s_v A}} = 0, \quad (6.137)$$

$$\mathbf{t}^{s_v A} = 2(\overline{\mathbf{F}}^{s_v A}) \cdot \sum_{\alpha=l, s_v, s_e} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_v A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{s_v A}} \cdot (\overline{\mathbf{F}}^{s_v A})^T - \rho^{s_v A} \lambda^{s_v A} \mathbf{I}, \quad (6.138)$$

$$\sum_{\alpha=l, s_v, s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \varepsilon^{(m) lA}} = 0, \quad m = 1, \dots, p-1, \quad (6.139)$$

$$\mathbf{t}^K = -p^K \mathbf{I}, \quad K = lA, B, C, \quad (6.140)$$

$$\sum_{\alpha=l, s_v, s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{(n) s_v A}} = 0, \quad n = 1, \dots, q-1, \quad (6.141)$$

$$\begin{aligned} \sum_{L, L \neq lA} \widehat{\mathbf{T}}_L^{lA} &= -\varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B \\ &\quad - \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial \varepsilon^{lA}} - \frac{p^{lA}}{\varepsilon^{lA} \rho^{lA}} \right) \nabla \varepsilon^{lA} - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} \\ &\quad - \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial \rho^{lA}} - \frac{p^{lA}}{(\rho^{lA})^2} \right) \nabla \rho^{lA} - \varepsilon^{lA} \rho^{lA} \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \varepsilon^{(m) lA}} \nabla \varepsilon^{(m) lA} \\ &\quad - \varepsilon^{lA} \rho^{lA} \sum_{n=0}^q \frac{\partial A^{lA}}{\partial \overline{\mathbf{C}}^{(n) s_v A}} : \nabla \overline{\mathbf{C}}^{(n) s_v A} - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \overline{\mathbf{C}}^{s_e A}} : \nabla \overline{\mathbf{C}}^{s_e A} \end{aligned} \quad (6.142)$$

$$\begin{aligned}
\sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A} &= -\varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^B} \nabla \varepsilon^B \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \left(\frac{\partial A^{s_e A}}{\partial J^{s_e A}} + \frac{\lambda^{s_e A}}{J^{s_e A}} \right) \nabla J^{s_e A} - \varepsilon^{s_e A} \rho^{s_e A} \sum_{m=1}^p \frac{\partial A^{s_e A}}{\partial \varepsilon^{(m)lA}} \nabla \varepsilon^{(m)lA} \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \sum_{n=0}^q \frac{\partial A^{s_e A}}{\partial \overline{\mathbf{C}}^{s_v A (n)}} : \nabla \overline{\mathbf{C}}^{s_v A (n)} - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \overline{\mathbf{C}}^{s_e A}} : \nabla \overline{\mathbf{C}}^{s_e A} \quad (6.143)
\end{aligned}$$

$$\begin{aligned}
\sum_{L, L \neq B} \widehat{\mathbf{T}}_L^B &= -\varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^B \rho^B \left(\frac{\partial A^B}{\partial \varepsilon^B} - \frac{p^B}{\varepsilon^B \rho^B} \right) \nabla \varepsilon^B \\
&\quad - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} \\
&\quad - \varepsilon^B \rho^B \left(\frac{\partial A^B}{\partial \rho^B} - \frac{p^B}{(\rho^B)^2} \right) \nabla \rho^B \quad (6.144)
\end{aligned}$$

$$\begin{aligned}
\sum_{L, L \neq C} \widehat{\mathbf{T}}_L^C &= -\varepsilon^C \rho^C \left(\frac{\partial A^C}{\partial \varepsilon^A} + \frac{p^C}{\varepsilon^C \rho^C} \right) \nabla \varepsilon^A - \varepsilon^C \rho^C \left(\frac{\partial A^C}{\partial \varepsilon^C} + \frac{p^C}{\varepsilon^C \rho^C} \right) \nabla \varepsilon^B \\
&\quad - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} \\
&\quad - \varepsilon^C \rho^C \left(\frac{\partial A^C}{\partial \rho^C} - \frac{p^C}{(\rho^C)^2} \right) \nabla \rho^C \quad (6.145)
\end{aligned}$$

$$\sum_K \varepsilon^K \mathbf{q}^K = 0, \quad (6.146)$$

$$\mathbf{t}^{K_j} - \frac{\rho^{K_j}}{\rho^{K_N}} \mathbf{t}^{K_N} = \rho^{K_j} (A^{K_j} - A^{K_N} - \tilde{\mu}^{K_j}) \mathbf{I}, \quad K = lA, B, C, \quad (6.147)$$

$$\begin{aligned}
\sum_{L, L \neq K} \widehat{\mathbf{T}}_L^{K_j} + \widehat{\mathbf{i}}^{K_j} - \frac{\rho^{K_j}}{\rho^{K_N}} \left(\sum_{L, L \neq K} \widehat{\mathbf{T}}_L^{K_N} + \widehat{\mathbf{i}}^{K_N} \right) = \\
\tilde{\mu}^{K_j} \nabla (\varepsilon^K \rho^{K_j}) - \nabla \cdot (\varepsilon^K \rho^{K_j} (A^{K_j} - A^{K_N})) - \varepsilon^K \mathbf{t}^{K_N} \cdot \nabla \left(\frac{\rho^{K_j}}{\rho^{K_N}} \right), \quad (6.148)
\end{aligned}$$

$$\tilde{\mu}^{LA_j} = \tilde{\mu}^{s_e A_j} = \tilde{\mu}^{s_v A_j} = \tilde{\mu}^{B_j} = \tilde{\mu}^{C_j}, \quad (6.149)$$

$$A^K + \lambda^K - \sum_{j=1}^{N-1} \tilde{\mu}^{K_j} C^{K_j} = A^L + \lambda^L - \sum_{j=1}^{N-1} \tilde{\mu}^{L_j} C^{L_j} \quad (6.150)$$

Equation (6.134) can be rewritten

$$p^C = \sum_K \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^C}, \quad (6.151)$$

where we have used the fact that

$$\left. \frac{\partial \varepsilon^A}{\partial \varepsilon^C} \right|_{\varepsilon^B, \dots} = -1 \quad (6.152)$$

because of the relationship between the volume fractions, equation (6.26). It can also be written as

$$\bar{p}^C = \sum_{K, K \neq C} \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^C}, \quad (6.153)$$

where we have used definition (6.108), and the three pressure relationship (6.109) with $K = C$.

Equation (6.135) can be written

$$\bar{p}^B - \bar{p}^C = \sum_{\alpha=l, s_v, s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \varepsilon^B}, \quad (6.154)$$

where we have used definition (6.108) and the three pressure relationship, (6.109) with $K = B$ to obtain the \bar{p}^B term, and we have used equation (6.111) to convert a derivative with respect to ε^B into a derivative with respect to ε^C , and used equations (6.108) and (6.109) with $K = C$ to obtain the \bar{p}^C term. If we convert derivatives with respect to ε^C into derivatives with respect to ε^B in equation

(6.153) using equation (6.111) then add the result to equation (6.154) we recover the definition of the thermodynamic pressure, equation (6.107) with $K = B$.

Equation (6.136) can be written as

$$\bar{p}^{lA} = \sum_{K, K \neq lA} \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{lA}}, \quad (6.155)$$

where we have used definition (6.97), and the three pressure relationship, equation (6.98).

Equation (6.137) can be written as

$$\bar{p}^{s_v A} = \sum_{K, K \neq s_v A} \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{s_v A}}, \quad (6.156)$$

where we have used definition (6.100) with $s = s_v$.

Taking 1/3 the trace of equation (6.138), using equation (6.125) to eliminate $\mathbf{t}^{s_v A}$, and solving for $\lambda^{s_v A}$ yields

$$\lambda^{s_v A} = \frac{p^{s_v A}}{\rho^{s_v A}} + \frac{2}{3} \sum_{\alpha=l, s_v, s_e} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_v A} \rho^{s_v A}} \frac{\partial A^{\alpha A}}{\partial \bar{\mathbf{C}}^{s_v A}} : \bar{\mathbf{C}}^{s_v A}. \quad (6.157)$$

We then substitute back into (6.138) to get

$$\mathbf{t}^{s_v A} = -p^{s_v A} \mathbf{I} + \mathbf{t}_{s_e}^{s_v A} + \frac{\varepsilon^{lA}}{\varepsilon^{s_v A}} \mathbf{t}_{sh}^{s_v A} - \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_v A}} \frac{\partial A^{\alpha A}}{\partial \bar{\mathbf{C}}^{s_v A}} : \bar{\mathbf{C}}^{s_v A}, \quad (6.158)$$

where

$$\begin{aligned} \mathbf{t}_{s_e}^{s_v A} &= 2\rho^{s_v A} \bar{\mathbf{F}}^{s_v A} \cdot \frac{\partial A^{s_v A}}{\partial \bar{\mathbf{C}}^{s_v A}} \cdot (\bar{\mathbf{F}}^{s_v A})^T \\ &+ 2 \frac{\varepsilon^{s_e A}}{\varepsilon^{s_v A}} \rho^{s_e A} \bar{\mathbf{F}}^{s_v A} \cdot \frac{\partial A^{s_e A}}{\partial \bar{\mathbf{C}}^{s_v A}} \cdot (\bar{\mathbf{F}}^{s_v A})^T, \end{aligned} \quad (6.159)$$

and

$$\mathbf{t}_{sh}^{s_v A} = 2\rho^{lA} \bar{\mathbf{F}}^{s_v A} \cdot \frac{\partial A^{lA}}{\partial \bar{\mathbf{C}}^{s_v A}} \cdot (\bar{\mathbf{F}}^{s_v A})^T, \quad (6.160)$$

where $\mathbf{t}_{se}^{s_v A}$ and $\mathbf{t}_{sh}^{s_v A}$ are the Terzaghi and hydration stress tensors for the $s_v A$ -phase, respectively. Analogous to the $s_e A$ phase, we note that by taking one-third the trace of equation (6.158), we recover equation (6.125).

In order to interpret the meaning of equation (6.139), we can take the $\varepsilon^{\alpha A} \rho^{\alpha A}$ inside the partial derivative because it is being held fixed, thus equation (6.139) can be written

$$\frac{\partial A_T^A}{\partial \varepsilon^{(m)lA}} = 0, \quad m = 1, \dots, p-1, \quad (6.161)$$

where we have used $\varepsilon^{lA} \rho^{lA} A^{lA} + \varepsilon^{s_e A} \rho^{s_e A} A^{s_e A} + \varepsilon^{s_v A} \rho^{s_v A} A^{s_v A} = A_T^A$. This means that at equilibrium, the total Helmholtz free energy of the particle A is a function of ε^{lA} at equilibrium, but not its derivatives.

Equation (6.140) says that the liquid phase stress of phases lA, B and C coincides with the classical pressure for that phase at equilibrium.

Similar to equation (6.139), equation (6.141) can be written

$$\frac{\partial A_T^A}{\partial \bar{\mathbf{C}}^{s_v A (n)}} = 0, \quad n = 1, \dots, q-1, \quad (6.162)$$

which means that the total Helmholtz free energy of the particle A is not a function of rates of shear at equilibrium. This means that at equilibrium the particle behaves elastically as opposed to viscoelastically.

Equation (6.142) simplifies to

$$\begin{aligned} \sum_{L, L \neq lA} \hat{\mathbf{T}}_L^{lA} &= \bar{p}^{lA} \nabla \varepsilon^{lA} - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B \\ &\quad - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} - \varepsilon^{lA} \rho^{lA} \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \varepsilon^{(m)lA}} \nabla \varepsilon^{(m)lA} \\ &\quad - \varepsilon^{lA} \rho^{lA} \sum_{n=0}^q \frac{\partial A^{lA}}{\partial \bar{\mathbf{C}}^{s_v A (n)}} : \nabla \bar{\mathbf{C}}^{s_v A (n)} - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \bar{\mathbf{C}}^{s_e A}} : \nabla \bar{\mathbf{C}}^{s_e A} \quad (6.163) \end{aligned}$$

where we have used definition (6.97) and the three pressure relationship (6.98). Later this will be used in the momentum balance equation to derive a generalized Darcy's Law for the liquid in the particle.

Equation (6.143) can be significantly simplified as well. First we use equations (6.103) and (6.104), to convert derivatives with respect to ε^{lA} and ε^{svA} into derivatives in ε^{seA} , respectively. We then use definition (6.100) with $s = s_e$, and the relationship between volume fractions, equation (6.15), to obtain the first two terms in the equation below. The last term in brackets is simplified using equation (6.99) to replace the partial derivative term with a pressure term, and λ^{seA} is eliminated using (6.127). The result is that

$$\begin{aligned}
\sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A} &= \bar{p}^{s_e A} \nabla \varepsilon^{s_e A} + \left(\bar{p}^{s_e A} - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^A} \right) \nabla \varepsilon^A \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^B} \nabla \varepsilon^B - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \bigg|_{\varepsilon^A, \varepsilon^B, \varepsilon^{s_e A}, \dots} \nabla \varepsilon^{lA} \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \sum_{m=1}^p \frac{\partial A^{s_e A}}{\partial \varepsilon^{(m)lA}} \nabla \varepsilon^{(m)lA} - \varepsilon^{s_e A} \rho^{s_e A} \sum_{n=0}^q \frac{\partial A^{s_e A}}{\partial \overline{\mathcal{C}}^{svA(n)}} : \nabla \overline{\mathcal{C}}^{svA(n)} \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \overline{\mathcal{C}}^{s_e A}} : \nabla \overline{\mathcal{C}}^{s_e A} - \frac{2}{3} \sum_{\alpha=l, sv, s_e} \left(\frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{J^{s_e A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathcal{C}}^{s_e A}} : \overline{\mathcal{C}}^{s_e A} \right) \nabla J^{s_e A}. \quad (6.164)
\end{aligned}$$

Equation (6.144) simplifies to

$$\begin{aligned}
\sum_{L, L \neq B} \widehat{\mathbf{T}}_L^B &= \bar{p}^B \nabla \varepsilon^B - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} \\
&\quad - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{svA}} \nabla \varepsilon^{svA}, \quad (6.165)
\end{aligned}$$

where we have used definition (6.108) combined with the three pressure relationship (6.109), with $K = B$, to obtain the first term of the preceding equation, and used equation (6.106) to eliminate the last term in brackets of (6.144).

To simplify equation (6.145) use equations (6.110) and (6.111) to convert derivatives with respect to ε^A and ε^B into derivatives with respect to ε^C , respectively. Then using the definition of the swelling potential, equation (6.108), and the three pressure relationship, equation (6.109), with $K = C$, and converting gradients in ε^A and ε^B into gradients in ε^C using the relationship between volume fractions, equation (6.26), we have

$$\begin{aligned} \sum_{L, L \neq C} \widehat{\mathbf{T}}_L^C &= \bar{p}^C \nabla \varepsilon^C - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} \\ &\quad - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{svA}} \nabla \varepsilon^{svA}. \end{aligned} \quad (6.166)$$

Equation (6.146) says that at equilibrium there is no net heat flux.

The rest of the equilibrium results contain N^{th} component dependencies, which we address in the next section.

6.5.4 Removing N^{th} Component Dependencies

Equations (6.119), (6.147), (6.148), and (6.149) contain an N^{th} resulting from using the concentrations of species as independent variables. These dependencies are removed in an analogous way as in Chapter 4. As such, we take [13]

$$\mu^{K_N} = A^{K_N} - \frac{\mathbf{t}^{K_N}}{\rho^{K_N}}, \quad K = lA, B, C, \quad (6.167)$$

$$\mu^{sA_N} = A^{sA_N} - \frac{\mathbf{t}^{sA_N}}{\rho^{sA_N}} + \frac{\mathbf{t}_{se}^{sA}}{\rho^{sA}} + \frac{\varepsilon^{lA} \mathbf{t}_{sh}^{sA}}{\varepsilon^{sA} \rho^{sA}}, \quad s = s_v, s_e. \quad (6.168)$$

Substituting equation (6.167) into (6.147), and equation (6.168) into (6.119), we obtain

$$\mu^{K_j} \mathbf{I} = A^{K_j} \mathbf{I} - \frac{\mathbf{t}^{K_j}}{\rho^{K_j}}, \quad K = lA, B, C, \quad (6.169)$$

$$\mu^{sA_j} \mathbf{I} = A^{sA_j} \mathbf{I} - \frac{\mathbf{t}^{sA_j}}{\rho^{sA_j}} + \frac{\mathbf{t}_{se}^{sA}}{\rho^{sA}} + \frac{\varepsilon^{lA} \mathbf{t}_{sh}^{sA}}{\varepsilon^{sA} \rho^{sA}}, \quad s = s_v, s_e, \quad (6.170)$$

respectively. Multiplying (6.169) and (6.170) by C^{K_j} and C^{sA_j} , respectively, and summing j from 1 to N , then eliminating \mathbf{t}^K , $K = lA, B, C$ with equation (6.140), and \mathbf{t}^{sA} with equations (6.128) and (6.158), we obtain the following expressions for the Gibbs free energy

$$G^K = \sum_{j=1}^N \mu^{K_j} C^{K_j} = A^K + \frac{p^K}{\rho^K}, \quad K = lA, B, C, \quad (6.171)$$

$$G^{sA} = \sum_{j=1}^N \mu^{sA_j} C^{sA_j} = A^{sA} + \frac{p^{sA}}{\rho^{sA}} + \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{sA} \rho^{sA}} \frac{\partial A^{\alpha A}}{\partial \overline{C}^{sA}} : \overline{C}^{sA},$$

$$s = s_v, s_e. \quad (6.172)$$

Rewriting equation (6.150) as

$$\begin{aligned} & A^K + \lambda^K - \sum_{j=1}^N \mu^{K_j} C^{K_j} + \mu^{K_N} \\ &= A^L + \lambda^L - \sum_{j=1}^N \mu^{L_j} C^{L_j} + \mu^{L_N}, \quad \forall K, L, L \neq K, \end{aligned} \quad (6.173)$$

then substituting (6.115) for λ^L , $L = lA, B, C$, (6.127) for $\lambda^{s_e A}$, (6.157) for $\lambda^{s_v A}$, and using (6.171) and (6.172), we obtain

$$\mu^{K_N} = \mu^{L_N}, \quad \forall K, L, L \neq K. \quad (6.174)$$

Substituting this result into equation (6.149), yields the classical result

$$\mu^{K_j} = \mu^{L_j}, \quad \forall K, L, L \neq K, \quad (6.175)$$

which states that the chemical potential of a species in different phases is equal at equilibrium.

To remove the N^{th} component dependence from equation (6.148) we first consider $K = s_e A$. Summing from j from 1 to N we obtain

$$\begin{aligned}
& \sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A} - \frac{\rho^{s_e A}}{\rho^{s_e A_N}} \left(\sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A_N} + \widehat{\mathbf{i}}^{s_e A_N} \right) \\
&= -\varepsilon^{s_e A} \mathbf{t}^{s_e A_N} \cdot \nabla \left(\frac{\rho^{s_e A}}{\rho^{s_e A_N}} \right) + \sum_{j=1}^N \tilde{\mu}^{s_e A_j} \nabla (\varepsilon^{s_e A} \rho^{s_e A_j}) \\
& - \varepsilon^{s_e A} \rho^{s_e A} \nabla A^{s_e A} - A^{s_e A} \nabla (\varepsilon^{s_e A} \rho^{s_e A}) + \nabla (\varepsilon^{s_e A} \rho^{s_e A} A^{s_e A_N}), \quad (6.176)
\end{aligned}$$

where $\sum_{j=1}^N \widehat{\mathbf{i}}^{s_e A_j} = 0$ and $\sum_{L, L \neq s_e A} \sum_{j=1}^N \widehat{\mathbf{T}}_L^{s_e A_j} = \sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A}$ due to restrictions (6.39) and (6.40), respectively. Using equation (6.143) to eliminate $\sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A}$ from the left-hand side of equation (6.176), expanding $\nabla A^{s_e A}$ using the following calculation

$$\begin{aligned}
\nabla A^{s_e A} &= \frac{\partial A^{s_e A}}{\partial \varepsilon^A} \nabla \varepsilon^A + \frac{\partial A^{s_e A}}{\partial \varepsilon^B} \nabla \varepsilon^B + \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} + \frac{\partial A^{s_e A}}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} \\
&+ \sum_{m=1}^p \frac{\partial A^{s_e A}}{\partial \varepsilon^{(m)lA}} \nabla \varepsilon^{(m)lA} + \frac{\partial A^{s_e A}}{\partial J^{s_e A}} \nabla J^{s_e A} \\
&+ \sum_{j=1}^{N-1} \tilde{\mu}^{s_e A_j} \nabla (C^{s_e A_j}) + \frac{\partial A^{s_e A}}{\partial T} \nabla T + \frac{\partial A^{s_e A}}{\partial \overline{C}^{s_v A}} : (\nabla \overline{C}^{s_v A})^T \\
&+ \sum_{n=1}^q \frac{\partial A^{s_e A}}{\partial \overline{C}^{(n)s_v A}} : (\nabla \overline{C}^{(n)s_v A})^T + \frac{\partial A^{s_e A}}{\partial \overline{C}^{s_e A}} : (\nabla \overline{C}^{s_e A})^T, \quad (6.177)
\end{aligned}$$

and then canceling like terms we get

$$\begin{aligned}
& -\frac{\varepsilon^{seA}}{J^{seA}} p^{se} \nabla J^{seA} - \frac{2}{3} \left(\sum_{\alpha} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{J^{seA}} \frac{\partial A^{\alpha A}}{\partial \overline{C}^{seA}} : \overline{C}^{seA} \right) \nabla J^{seA} \\
& - \frac{\rho^{seA}}{\rho^{seA_N}} \left(\sum_{L, L \neq seA} \widehat{\mathbf{T}}_L^{seA_N} + \widehat{\mathbf{i}}^{seA_N} \right) = -\varepsilon^{seA} \mathbf{t}^{seA_N} \cdot \nabla \left(\frac{\rho^{seA}}{\rho^{seA_N}} \right) \\
& + \sum_{j=1}^N \widetilde{\mu}^{seA_j} \nabla (\varepsilon^{seA} \rho^{seA_j}) - A^{seA} \nabla (\varepsilon^{seA} \rho^{seA}) \\
& - \varepsilon^{seA} \rho^{seA} \sum_{j=1}^{N-1} \widetilde{\mu}^{seA_j} \nabla C^{seA_j} + \nabla (\varepsilon^{seA} \rho^{seA} A^{seN}). \tag{6.178}
\end{aligned}$$

In the previous calculation we have dropped the term involving ∇T since it is zero at equilibrium, and used equation (6.127) for λ^{seA} . If we expand the gradient portion of the second term on the right-hand side $\nabla (\varepsilon^{seA} \rho^{seA_j}) = \varepsilon^{seA} \rho^{seA} \nabla C^{seA_j} + C^{seA_j} \nabla (\varepsilon^{seA} \rho^{seA})$ we can eliminate the fourth term on the right-hand side. Collecting all the terms involving the N^{th} component on one side and all other terms on the other side, we have

$$\begin{aligned}
& \frac{\rho^{seA}}{\rho^{seA_N}} (\widehat{\mathbf{T}}_L^{seA_N} + \widehat{\mathbf{i}}^{seA_N}) - \varepsilon^{seA} \mathbf{t}^{seA_N} \cdot \nabla \left(\frac{\rho^{seA}}{\rho^{seA_N}} \right) \\
& + \nabla (\varepsilon^{seA} \rho^{seA} A^{seA_N}) - \mu^{seA_N} \nabla (\varepsilon^{seA} \rho^{seA}) \\
& = A^{seA} \nabla (\varepsilon^{seA} \rho^{seA}) - \frac{\varepsilon^{seA}}{J^{seA}} p^{se} \nabla J^{seA} \\
& - \frac{2}{3} \left(\sum_{\alpha} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{J^{seA}} \frac{\partial A^{\alpha A}}{\partial \overline{C}^{seA}} : \overline{C}^{seA} \right) \nabla J^{seA} \\
& - \sum_{j=1}^N \mu^{seA_j} C^{seA_j} \nabla (\varepsilon^{seA} \rho^{seA}). \tag{6.179}
\end{aligned}$$

Substituting equation (6.172) with $s = s_e$ for the last term, the right-hand side becomes

$$A^{s_e A} \nabla(\varepsilon^{s_e A} \rho^{s_e A}) - \frac{\varepsilon^{s_e A}}{J^{s_e A}} p^{s_e} \nabla J^{s_e A} - \frac{2}{3} \left(\sum_{\alpha} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{J^{s_e A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{s_e A}} : \overline{\mathbf{C}}^{s_e A} \right) \nabla J^{s_e A} - \left(A^{s_e A} + \frac{p^{s_e A}}{\rho^{s_e A}} + \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_e A} \rho^{s_e A}} \frac{\partial A^{\alpha A}}{\partial \overline{\mathbf{C}}^{s_e A}} : \overline{\mathbf{C}}^{s_e A} \right) \nabla(\varepsilon^{s_e A} \rho^{s_e A}) = 0 \quad (6.180)$$

since $\nabla(\varepsilon^{s_e A} \rho^{s_e A}) = -\frac{\varepsilon^{s_e A} \rho^{s_e A}}{J^{s_e A}} \nabla J^{s_e A}$. Thus,

$$\frac{\rho^{s_e A}}{\rho^{s_e A_N}} \left(\sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_{s_v}^{s_e A_N} + \widehat{\mathbf{i}}^{s_e A_N} \right) - \varepsilon^{s_e} \mathbf{t}^{s_e A_N} \cdot \nabla \left(\frac{\rho^{s_e A}}{\rho^{s_e A_N}} \right) + \nabla(\varepsilon^{s_e A} \rho^{s_e A} A^{s_e A_N}) - \mu^{s_e A_N} \nabla(\varepsilon^{s_e A} \rho^{s_e A}) = 0. \quad (6.181)$$

Substituting equation (6.181) back into equation (6.176) and undoing the summation prior to equation (6.176), we obtain

$$\sum_{L, L \neq s_e A} \widehat{\mathbf{T}}_L^{s_e A_j} + \widehat{\mathbf{i}}^{s_e A_j} = \mu^{s_e A_j} \nabla(\varepsilon^{s_e A} \rho^{s_e A_j}) - \nabla(\varepsilon^{s_e A} \rho^{s_e A} A^{s_e A_j}). \quad (6.182)$$

Removing the N^{th} component dependence from (6.148) for $K = lA, s_v A, B, C$ is done in an analogous manner and yields

$$\sum_{L, L \neq K} \widehat{\mathbf{T}}_L^{K_j} + \widehat{\mathbf{i}}^{K_j} = \mu^{K_j} \nabla(\varepsilon^K \rho^{K_j}) - \nabla \cdot (\varepsilon^K \rho^{K_j} A^{K_j}), \forall K. \quad (6.183)$$

6.5.5 Near-Equilibrium Relations

We obtain near-equilibrium results using the method described in Chapter 2. We choose to perform a one variable expansion for all of the variables in (6.133). In what follows we use indicial notation so that the order of the coefficients resulting from the linearization process and the contractions are clear. For the variables $\dot{\varepsilon}^A, \dot{\varepsilon}^B, \dot{\varepsilon}^{lA}$, and $\dot{\varepsilon}^{s_v A}$ we obtain following near-equilibrium relationships

$$\bar{p}^C - \sum_{K, K \neq C} \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^C} = -\eta^C \dot{\varepsilon}^A, \quad (6.184)$$

$$\bar{p}^B - \bar{p}^C - \sum_{\alpha=l,s_v,s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \varepsilon^B} = -\eta^B \dot{\varepsilon}^B, \quad (6.185)$$

$$\bar{p}^{lA} - \sum_{K,K \neq lA} \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{lA}} = -\eta^{lA} \dot{\varepsilon}^{lA}, \quad (6.186)$$

and

$$\bar{p}^{s_v A} - \sum_{K,K \neq s_v A} \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^{s_v A}} = -\eta^{s_v A} \dot{\varepsilon}^{s_v A}, \quad (6.187)$$

respectively. The coefficients η^C , η^B , η^{lA} , and $\eta^{s_v A}$ are scalar material parameters that may contain information such as: the stiffness of the solid matrix, the ease (or difficulty) with which the solid phase swells, and the connectedness of the two solid phases. For the coefficients of $\dot{\bar{C}}^{s_v A}$, \mathbf{d}^K , where $K = lA, s_v A, s_e A$, and $\bar{C}^{s_v A}$, where $n = 1, \dots, q-1$, we obtain the following near-equilibrium relationships:

$$\begin{aligned} t_{lk}^{s_v A} = & -p^{s_v A} \delta_{lk} + (t_{se}^{s_v A})_{lk} + \frac{\varepsilon^{lA}}{\varepsilon^{s_v A}} (t_{sh}^{s_v A})_{lk} - \frac{2}{3} \sum_{\alpha} \frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{\varepsilon^{s_v A}} \frac{\partial A^{s_v A}}{\partial \bar{C}_{LK}^{s_v A}} : \bar{C}_{LK}^{s_v A} \delta_{lk} \\ & - \sum_{j=1}^N \rho^{s_v A_j} v_l^{s_v A_j, s_v A} v_k^{s_v A_j, s_v A} + \bar{F}_{kK}^{s_v A} G_{LKMN}^{s_v A} \dot{\bar{C}}_{MN}^{s_v A} \bar{F}_{lL}^{s_v A}, \end{aligned} \quad (6.188)$$

$$\mathbf{t}_{lk}^K = -p^K \delta_{lk} - \sum_{j=1}^N \rho^{K_j} v_l^{K_j, K} v_k^{K_j, K} + G_{lkmn}^K d_{mn}^K, \quad K = lA, B, C, \quad (6.189)$$

$$\sum_{\alpha=l,s_v,s_e} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \bar{C}_{LK}^{s_v A}} = Q_{LKMN}^n \bar{C}_{MN}^{s_v A}, \quad n = 1, \dots, q-1. \quad (6.190)$$

Here $G_{LKMN}^{s_v}$, G_{lkmn}^l , and Q_{LKMN}^n are all fourth-order positive semi-definite tensors. $G_{LKMN}^{s_v A}$ accounts for the viscoelastic solid stress dissipation due to relaxation in shearing of the viscoelastic solid. G_{lkmn}^K is a viscous dissipation

tensor. And lastly, Q_{LKMN}^n are material coefficients of the n^{th} derivative of the shear rate, $\overline{C}^{s_v A}$, and like $G_{LKMN}^{s_v A}$, represent stress dissipation due to relaxation in shearing of the viscoelastic solid. For the coefficients of $\mathbf{v}^{LA, s_v A}$, $\mathbf{v}^{s_e A, s_v A}$, $\mathbf{v}^{B, s_v A}$, and $\mathbf{v}^{B, s_v A}$ we obtain the following near-equilibrium results:

$$\begin{aligned}
\sum_{L, L \neq lA} (\widehat{T}_L^{lA})_k &= -R_{km}^{lA} v_m^{lA, s_v A} + \bar{p}^{lA} \varepsilon_{,k}^{lA} - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \varepsilon_{,k}^A - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \varepsilon_{,k}^B \\
&\quad - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^{s_v A}} \varepsilon_{,k}^{s_v A} - \sum_{m=1}^p \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^{(m)lA}} \varepsilon_{,k}^{(m)lA} \\
&\quad - \varepsilon^{lA} \rho^{lA} \frac{\partial A^{lA}}{\partial \overline{C}_{LK}^{s_e A}} \overline{C}_{LK,k}^{s_e A} - \varepsilon^{lA} \rho^{lA} \sum_{n=0}^q \frac{\partial A^{lA}}{\partial \overline{C}_{LK}^{(n) s_v A}} \overline{C}_{LK,k}^{(n) s_v A}, \quad (6.191)
\end{aligned}$$

$$\begin{aligned}
\sum_{L, L \neq s_e A} (\widehat{T}_L^{s_e A})_k &= -R_{km}^{s_e A} v_m^{s_e A, s_v A} + \bar{p}^{s_e A} \varepsilon_{,k}^{s_e A} + \left(\bar{p}^{s_e A} - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^A} \right) \varepsilon_{,k}^A \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^B} \varepsilon_{,k}^B - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^{lA}} \varepsilon_{,k}^{lA} \\
&\quad - \sum_{m=1}^p \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \varepsilon^{(m)lA}} \varepsilon_{,k}^{(m)lA} - \varepsilon^{s_e A} \rho^{s_e A} \sum_{n=0}^q \frac{\partial A^{s_e A}}{\partial \overline{C}_{LK}^{(n) s_v A}} \overline{C}_{LK,k}^{(n) s_v A} \\
&\quad - \varepsilon^{s_e A} \rho^{s_e A} \frac{\partial A^{s_e A}}{\partial \overline{C}_{LK}^{s_e A}} \overline{C}_{LK,k}^{s_e A} - \frac{2}{3} \sum_{\alpha=l, s_v, s_e} \left(\frac{\varepsilon^{\alpha A} \rho^{\alpha A}}{J^{s_e A}} \frac{\partial A^{s_e A}}{\partial \overline{C}_{LK}^{s_e A}} \overline{C}_{LK}^{s_e A} \right) J_{,k}^{s_e A}, \quad (6.192)
\end{aligned}$$

$$\begin{aligned}
\sum_{L, L \neq B} (\widehat{T}_L^B)_k &= -R_{km}^B v_m^{B, s_v A} + \bar{p}^B \varepsilon_{,k}^B - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} \varepsilon_{,k}^A \\
&\quad - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{lA}} \varepsilon_{,k}^{lA} - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^{s_v A}} \varepsilon_{,k}^{s_v A} \quad (6.193)
\end{aligned}$$

$$\begin{aligned}
\sum_{L, L \neq C} (\widehat{T}_L^C)_k &= -R_{km}^C v_m^{C, s_v A} + \bar{p}^C \varepsilon_{,k}^C - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^A} \varepsilon_{,k}^A \\
&\quad - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{lA}} \varepsilon_{,k}^{lA} - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^{s_v A}} \varepsilon_{,k}^{s_v A} \quad (6.194)
\end{aligned}$$

Here, R_{km}^{lA} , R_{km}^{seA} , R_{km}^B , and R_{km}^C are all second-order resistivity tensors. Since the elastic solid phase does not flow inside the viscoelastic solid phase R_{km}^{seA} is taken sufficiently large so that when we invert it and solve for $\mathbf{v}^{seA,svA}$ we get that $\mathbf{v}^{seA,svA} = 0$, as expected. For the coefficient of $\varepsilon^{(m+1)lA}$ and ∇T , we obtain the following near-equilibrium result:

$$\sum_{\alpha=l,sv,se} \varepsilon^{\alpha A} \rho^{\alpha A} \frac{\partial A^{\alpha A}}{\partial \varepsilon^{(m)lA}} = -\eta^m \varepsilon^{(m+1)lA}, \quad m = 1, \dots, p-1, \quad (6.195)$$

$$\begin{aligned} q_k^{sA} = \sum_{j=1}^N \left[t_{km}^{sA_j} v_m^{sA_j,sA} - \rho^{sA_j} v_k^{sA_j,sA} \left(A^{sA_j} + \frac{1}{2} v_m^{sA_j,sA} v_m^{sA_j,sA} \right) \right] \\ + K_{km}^{sA} T_{,m}, \quad s = sv, se, \end{aligned} \quad (6.196)$$

and

$$\begin{aligned} q_k^K = \sum_{j=1}^N \left[t_{km}^{K_j} v_m^{K_j,K} - \rho^{K_j} v_k^{K_j,K} \left(A^{K_j} + \frac{1}{2} v_m^{K_j,K} v_m^{K_j,K} \right) \right] \\ + K_{km}^K T_{,m}, \quad K = lA, B, C, \end{aligned} \quad (6.197)$$

respectively. Here, η^m are scalar coefficients, and K_{km}^{sA} and K_{km}^K are second-order tensors. Most often it is reasonable to assume that $\mathbf{v}^{sA_j,sA} \approx 0$, in which case equation (6.196) reduces to $\mathbf{q} = \mathbf{K}^{sA} \cdot \nabla T$, so that we recover Fourier's law of heat conduction for the solid phases. The coefficients of $\nabla \mathbf{v}^{K_j,K}$ and $\mathbf{v}^{K_j,K}$ produce the following near-equilibrium results:

$$\mu^{K_j} \delta_{mn} = S_{mnkl}^{K_j} v_{k,l}^{K_j,K} + A^{K_j} \delta_{mn} - \frac{t_{mn}^{K_j}}{\rho^{K_j}} \quad (6.198)$$

and

$$\sum_{L, L \neq K} (\widehat{T}_L^{K_j})_k + \widehat{i}_k^{K_j} = -R_{km}^{K_j} v_m^{K_j,K} + \mu^{K_j} (\varepsilon^K \rho^{K_j})_{,k} - (\varepsilon^K \rho^{K_j} A^{K_j})_{,k}, \quad (6.199)$$

where $K = lA, B, C,$, and where $S_{klmn}^{K_j}$ are a fourth-order symmetric positive semi-definite tensors representing the effects of the gradient in diffusive velocity in the liquid phase on the chemical potential, and $R_{km}^{K_j}$ are a second-order tensors. In this system we do not linearize about $\mathbf{v}^{sA_j, sA}$, $s = s_v, s_e$, because solid phase diffusion is assumed to be negligible. As such, $\mathbf{v}^{sA_j, sA}$ is not an independent variable, and thus the coefficient of $\mathbf{v}^{sA_j, s}$ cannot be a function of $\mathbf{v}^{sA_j, sA}$. Finally, for the coefficient of $\widehat{e}_\beta^{K_j}$ we obtain:

$$\mu^{K_j} - \mu^{L_j} = M^{KLj} \widehat{e}_L^{K_j} - \frac{1}{2} \mathbf{v}^{K_j, K} \cdot \mathbf{v}^{K_j, K} - \frac{1}{2} \mathbf{v}^{L_j, L} \cdot \mathbf{v}^{L_j, L}, \quad (6.200)$$

where $K, L = lA, s_v A, s_e A, B, C$, $L \neq K$, and M^{KLj} are scalar coefficients.

6.5.6 Darcy's Laws

Darcy's Laws are obtained from the bulk linear momentum equation for the liquid phase, equation (6.38), by using constitutive equations to eliminate the stress tensor, equation (6.189), and equations (6.191), (6.193), and (6.194) to eliminate the exchange of momentum terms, $\sum_{L, L \neq lA} \widehat{\mathbf{T}}_L^{lA}$, $\sum_{L, L \neq B} \widehat{\mathbf{T}}_L^B$, and $\sum_{L, L \neq C} \widehat{\mathbf{T}}_L^C$, respectively. We obtain the following forms of Darcy's law:

$$\begin{aligned} \mathbf{R}^{lA} \cdot \mathbf{v}^{lA, s_v A} &= -\varepsilon^{lA} \nabla p^{lA} - \pi^{lA} \nabla \varepsilon^{lA} + \nabla \cdot (\varepsilon^{lA} \mathbf{G}^{lA} : \mathbf{d}^{lA}) + \varepsilon^{lA} \rho^{lA} \mathbf{g}^{lA} \\ &\quad - \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A + \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B + \frac{\partial A^{lA}}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} \right) \\ &\quad - \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial \overline{\mathbf{C}}^{s_e A}} : (\nabla \overline{\mathbf{C}}^{s_e A})^T + \sum_{n=0}^q \frac{\partial A^{lA}}{\partial \overline{\mathbf{C}}^{s_v A}^{(n)}} : (\nabla \overline{\mathbf{C}}^{s_v A})^T \right. \\ &\quad \left. + \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \varepsilon^{(m)lA}} \nabla \varepsilon^{(m)lA} \right), \end{aligned} \quad (6.201)$$

and

$$\begin{aligned} \mathbf{R}^K \cdot \mathbf{v}^{K,s_v A} = & -\varepsilon^K \nabla p^K - \pi^K \nabla \varepsilon^K + \nabla \cdot (\varepsilon^K \mathbf{G}^K : \mathbf{d}^K) + \varepsilon^K \rho^K \mathbf{g}^K \\ & - \varepsilon^K \rho^K \left(\frac{\partial A^K}{\partial \varepsilon^A} \nabla \varepsilon^A + \frac{\partial A^K}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} + \frac{\partial A^K}{\partial \varepsilon^{s_v A}} \nabla \varepsilon^{s_v A} \right), \end{aligned} \quad (6.202)$$

for $K = B, C$, respectively, where we have used the three pressure relationships (6.98) and (6.109) to obtain the first two terms of both equations. \mathbf{R}^{lA} and \mathbf{R}^K , $K = B, C$, are resistivity tensors. The first lines of equations (6.201) and (6.202) have been discussed in previously. The first two terms in parentheses on the second line of equation (6.201) have been previously reported in [50]. In [50], Singh et al. defined the swelling potential as

$$\pi^{lA} = \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \Bigg|_{\rho^{lA}, C^{lAj}, T, \dots}, \quad (6.203)$$

where they used the macroscale definitions given by equations (6.1)-(6.6). Using the macroscale definitions given by equations (6.10)-(6.14) allow us to make the more consistent definition of swelling potential given by equation (6.97). The last term in parentheses of the second line of equation (6.201) is novel and is due to defining $\varepsilon^{s_v A}$ as an independent variable. The last term in parentheses on the last lines of equations (6.201) and (6.202) are analogous to those of equation (4.109) and were discussed in Section 4.3.6.

6.5.7 Fick's Law

Fick's law is obtained from the species linear momentum equation for the liquid phase, equation (6.37), by using the near-equilibrium result for the chemical potential of the liquid phase, equation (6.198), to eliminate the species stress tensor, \mathbf{t}^{Kj} , and using equation (6.199) to eliminate $\widehat{\mathbf{T}}_{s_e}^{lj} + \widehat{\mathbf{i}}^{lj}$. The result is

$$\mathbf{R}^{Kj} \cdot \mathbf{v}^{Kj,K} = -\varepsilon^K \rho^K \nabla \mu^{Kj} + \nabla \cdot (\varepsilon^K \rho^{Kj} \mathbf{S}^{Kj} \cdot \nabla \mathbf{v}^{Kj,K}) + \varepsilon^K \rho^{Kj} \mathbf{g}, \quad (6.204)$$

where we have neglected the inertial term in the momentum equation. The first term is the generalized Fick's law, and says the diffusion is caused by a the gradient in chemical potential. This equations is similar to an equation obtained by Bennethum et al. in [12]. The second terms is often neglected as it is of second order.

7. Three-Scale Polymeric Drug Delivery Systems

In this chapter we combine the macroscale balance laws and constitutive equations from the previous section to obtain bulk fluid and species transport equations. Macroscale fluid and species transport is affected by physical processes taking place at all three scales. At the mesoscale solid polymer, drug, and vicinal fluid form a homogeneous mixture, particle A . Imperfect processing of the drug delivery device may leave pockets of bulk fluids B and C inside the polymer matrix, see figure 6.1. We assume that fluid B and the vicinal fluid are composed of the same constituents, water and drug. Fluid C can be thought of as a gas trapped inside the particle. In swelling-controlled devices the drug will have diffused out of the device before the polymer matrix begins to erode. Thus, on the time scale of concern any pockets of gas trapped within the device will be surrounded by walls containing micropores which are impenetrable to the gas unless the system is under a massive amount of pressure. Interactions between the structure-sensitive polymer and vicinal fluid lower the free energy of the vicinal fluid [35], causing fluid to flow from the bulk fluid to the vicinal fluid and which causes the particle to swell. At the macroscale, particles and fluids B and C are viewed as overlying continua, forming another homogeneous mixture. Exchange of thermodynamic properties, such as mass and momentum, take place between phases. This exchange is taken into account by the source/sink terms in the balance laws.

Throughout this chapter the viscoelastic solid phase is assumed to be composed of polymer, denoted pA , and the elastic solid phase is assumed to be the drug, denoted dA . We will begin by presenting equations related to the vicinal fluid, bulk fluid, B , and fluid C . We will then derive the wetting bulk phase transport equation by combining the equations from the previous three sections. Next, we will present equations relating to species diffusion and derive a system of equations governing species transport.

7.1 Vicinal Fluid

In Darcy's law, equation (6.201), the effects of gravity, shearing, and quadratic terms are neglected as the effects of these terms are expected to be negligible in comparison to other force terms. Dropping these terms, we obtain

$$\begin{aligned} \mathbf{R}^{lA} \cdot \mathbf{v}^{lA,pA} = & -\nabla(\varepsilon^{lA} p^{lA}) + \bar{p}^{lA} \nabla \varepsilon^{lA} + \varepsilon^{lA} \rho^{lA} \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \varepsilon^{(m)lA}} \nabla \varepsilon^{(m)lA} \\ & - \varepsilon^{lA} \rho^{lA} \left(\frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A + \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B + \frac{\partial A^{lA}}{\partial \varepsilon^{pA}} \nabla \varepsilon^{pA} \right). \end{aligned} \quad (7.1)$$

Following the discussion in Section 3.5.1, we can rewrite this equation as

$$\begin{aligned} \mathbf{v}^{lA,pA} = & \frac{\varepsilon^{lA} K^{lA}}{\mu_v^{lA}} \left(\frac{K'}{1 - \varepsilon^{lA}} \nabla \varepsilon^{lA} - \rho^{lA} \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \varepsilon^{(m)lA}} \nabla \varepsilon^{(m)lA} \right) \\ & - \frac{\varepsilon^{lA} \rho^{lA} K^{lA}}{\mu_v^{lA}} \left(\frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A + \frac{\partial A^{lA}}{\partial \varepsilon^{pA}} \nabla \varepsilon^{pA} \right), \end{aligned} \quad (7.2)$$

where we have assumed that the free energy of the vicinal fluid is not affected by the volume fraction of the bulk fluid, B , since the bulk fluid interacts with the vicinal fluid only through the boundaries. K^{lA} is the permeability of the particle, K' is the unjacketed compressibility for a porous medium with incompressible solid and liquid phases, and μ_v^{lA} is the viscosity of the vicinal fluid.

The vicinal fluid exchanges mass with the drug phase and the bulk fluid phase B , but not with the polymer phase ($\widehat{e}_{pA}^{lA} = 0$) nor with the fluid phase C ($\widehat{e}_C^{lA} = 0$). Thus, conservation of mass for the vicinal fluid is given by

$$\frac{D^{lA}(\varepsilon^{lA}\rho^{lA})}{Dt} + \varepsilon^{lA}\rho^{lA}\nabla \cdot \mathbf{v}^{lA} = \widehat{e}_B^{lA} + \widehat{e}_{dA}^{lA}. \quad (7.3)$$

Assuming that the drug in the vicinal fluid is sufficiently dilute and that the liquid is incompressible allow us to use the incompressibility condition for the vicinal fluid ($D^{lA}\rho^{lA}/Dt = 0$). Applying this condition to equation (7.3) yields

$$\rho^{lA}\left(\dot{\varepsilon}^{lA} + \nabla \cdot (\varepsilon^{lA}\mathbf{v}^{lA,pA}) + \varepsilon^{lA}\nabla \cdot \mathbf{v}^{pA}\right) = \widehat{e}_B^{lA} + \widehat{e}_{dA}^{lA}, \quad (7.4)$$

where we have converted the derivative in lA to a material time derivative using equation (6.93).

The drug phase may exchange mass with both the vicinal fluid and the bulk fluid B , but not with the polymer phase ($\widehat{e}_{pA}^{dA} = 0$) nor with the fluid phase C ($\widehat{e}_C^{dA} = 0$). Thus, the conservation of mass for the drug phase is given by

$$\frac{D^{dA}(\varepsilon^{dA}\rho^{dA})}{Dt} + \varepsilon^{dA}\rho^{dA}\nabla \cdot \mathbf{v}^{dA} = \widehat{e}_{lA}^{dA} + \widehat{e}_B^{dA}. \quad (7.5)$$

Using the incompressibility condition for the drug phase ($D^{dA}\rho^{dA}/Dt = 0$), we obtain

$$\rho^{dA}\left(\dot{\varepsilon}^{dA} + \nabla \cdot (\varepsilon^{dA}\mathbf{v}^{dA,pA}) + \varepsilon^{dA}\nabla \cdot \mathbf{v}^{pA}\right) = \widehat{e}_{lA}^{dA} + \widehat{e}_B^{dA}, \quad (7.6)$$

where we have converted the material time derivative with respect to dA to material time derivative with respect to pA using equation (6.93).

Because the drug has diffused out of the device by the time the polymer matrix begins to erode, the polymer phase is assumed not to exchange mass

with any other phase. Thus the conservation of mass for the polymer phase can be written as

$$\dot{\varepsilon}^{pA} + \varepsilon^{pA} \nabla \cdot \mathbf{v}^{pA} = 0, \quad (7.7)$$

where we have used the incompressibility condition for the polymer phase ($D^{pA} \rho^{dA} / Dt = 0$). Using equation (7.7) to eliminate $\nabla \cdot \mathbf{v}^{pA}$ from equations (7.4) and (7.6) yields

$$\rho^{lA} \left(\dot{\varepsilon}^{lA} - \frac{\varepsilon^{lA}}{\varepsilon^{pA}} \dot{\varepsilon}^{pA} + \nabla \cdot (\varepsilon^{lA} \mathbf{v}^{lA,pA}) \right) = \widehat{e}_B^{lA} + \widehat{e}_{dA}^{lA} \quad (7.8)$$

and

$$\rho^{dA} \left(\dot{\varepsilon}^{dA} - \frac{\varepsilon^{dA}}{\varepsilon^{pA}} \dot{\varepsilon}^{pA} \right) = \widehat{e}_{lA}^{dA} + \widehat{e}_B^{dA}, \quad (7.9)$$

respectively.

7.2 Bulk Fluid, B

Neglecting gravity and higher-order terms, Darcy's law for the bulk fluid B is given by

$$\begin{aligned} \mathbf{R}^B \cdot \mathbf{v}^{B,pA} &= -\nabla \cdot (\varepsilon^B p^B) + \bar{p}^B \nabla \varepsilon^B \\ &\quad - \varepsilon^B \rho^B \left(\frac{\partial A^B}{\partial \varepsilon^A} \nabla \varepsilon^A + \frac{\partial A^B}{\partial \varepsilon^{lA}} \nabla \varepsilon^{lA} + \frac{\partial A^B}{\partial \varepsilon^{pA}} \nabla \varepsilon^{pA} \right). \end{aligned} \quad (7.10)$$

Bennethum and Weinstein [14] showed that for a material composed of a single constituent the classical pressure and the thermodynamic pressure are the same. While the bulk fluid B is composed of both liquid and drug, we are already assuming that the solution is dilute enough so that the incompressibility condition holds. As such, we find it reasonable to assume that $\bar{p}^B \approx p^B$ as well.

Furthermore, we assume that the free energy of the bulk phase B is not a strong function of the volume fractions ε^{IA} , ε^A , and ε^{pA} . Thus, equation (7.10) can be written as

$$\mathbf{v}^{B,pA} = -\frac{\varepsilon^B K^B}{\mu_v^B} \nabla p^B, \quad (7.11)$$

where, assuming that the bulk fluid behaves isotopically

$$(\mathbf{R}^B)^{-1} = \frac{K^B}{\mu_v^B} \mathbf{I}, \quad (7.12)$$

where K^B is the permeability, and μ_v^B is the viscosity of the bulk fluid.

The bulk fluid exchanges mass with the vicinal fluid and the drug phase, but not with the polymer phase ($\widehat{e}_{pA}^B = 0$) nor with the fluid phase C ($\widehat{e}_C^B = 0$). Thus, the conservation of mass for phase B is given by

$$\frac{D^B(\varepsilon^B \rho^B)}{Dt} + \varepsilon^B \rho^B \nabla \cdot \mathbf{v}^B = \widehat{e}_{lA}^B + \widehat{e}_{dA}^B. \quad (7.13)$$

Using the incompressibility condition for the bulk phase ($D^B \rho^B / Dt = 0$) we obtain

$$\rho^B \left(\dot{\varepsilon}^B - \frac{\varepsilon^B}{\varepsilon^{pA}} \dot{\varepsilon}^{pA} + \nabla \cdot (\varepsilon^B \mathbf{v}^{B,pA}) \right) = \widehat{e}_{lA}^B + \widehat{e}_{dA}^B, \quad (7.14)$$

where we have used equation (7.7) to eliminate $\nabla \cdot \mathbf{v}^{pA}$, and used equation (6.93) to convert the derivative in B into a material derivative.

7.3 Fluid Phase, C

The fluid phase C does not exchange mass with any other phase. Following the derivation used in the previous section we can write the conservation of mass for the fluid phase C as

$$\dot{\varepsilon}^C - \frac{\varepsilon^C}{\varepsilon^{pA}} \dot{\varepsilon}^{pA} + \nabla \cdot (\varepsilon^C \mathbf{v}^{C,pA}) = 0. \quad (7.15)$$

As discussed in the introduction, on the time scale of concern fluid C is trapped by walls containing micropores. Thus, fluid C does not move relative to the solid polymer. As such, $\mathbf{v}^{C,pA}$ is taken to be zero. Thus, equation (7.15) becomes

$$\frac{\dot{\varepsilon}^C}{\varepsilon^C} = \frac{\dot{\varepsilon}^{pA}}{\varepsilon^{pA}}, \quad (7.16)$$

which can be solved analytically by integrating

$$\int_{\varepsilon_{t=0}^C}^{\varepsilon^C} \frac{d\varepsilon^C}{\varepsilon^C} = \int_{\varepsilon_{t=0}^{pA}}^{\varepsilon^{pA}} \frac{d\varepsilon^{pA}}{\varepsilon^{pA}}. \quad (7.17)$$

The solution to (7.15) is given by

$$\frac{\varepsilon^C}{\varepsilon_0^C} = \frac{\varepsilon^{pA}}{\varepsilon_0^{pA}}, \quad (7.18)$$

which is equivalent to

$$\frac{\varepsilon^C}{\varepsilon^{pA}} = \frac{\varepsilon_0^C}{\varepsilon_0^{pA}} = C_1, \quad (7.19)$$

where C_1 is a constant. This means that the ratio $\varepsilon^C/\varepsilon^{pA}$ is unaffected by fluid sorption/desorption or by mass transfer taking place within the system.

7.4 Bulk Transport

Because the vicinal water is more structured than the bulk fluid we expect the density of the vicinal water to be less dense than the bulk water, [25]. The data suggests that the vicinal fluid is approximately 4% less dense than the bulk fluid. Since this difference is small, we assume that ρ^{lA} is equal to ρ^B , and denote it ρ^f . Adding equations (7.8) and (7.14), we obtain

$$\rho^f \left(\dot{\varepsilon}^f - \frac{\varepsilon^f}{\varepsilon^{pA}} \dot{\varepsilon}^{pA} + \nabla \cdot (\varepsilon^{lA} \mathbf{v}^{lA,pA}) + \nabla \cdot (\varepsilon^B \mathbf{v}^{B,pA}) \right) = \widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B, \quad (7.20)$$

where

$$\varepsilon^f = \varepsilon^{lA} + \varepsilon^B \quad (7.21)$$

is the total volume fraction of the wetting phase. To obtain equation (7.20) we have used macroscale restriction (6.29) with $K = lA$ and $L = B$, that is, $\widehat{e}_B^{lA} = -\widehat{e}_{lA}^B$. The sum of the macroscale volume fractions is one, that is, if we substitute equation (6.15) into equation (6.26), we obtain

$$\varepsilon^{pA} + \varepsilon^{dA} + \varepsilon^{lA} + \varepsilon^B + \varepsilon^C = 1. \quad (7.22)$$

Substituting equation (7.21) into equation (7.22) yields

$$\varepsilon^{pA} + \varepsilon^{dA} + \varepsilon^f + \varepsilon^C = 1. \quad (7.23)$$

Solving equation (7.19) for ε^C , substituting the result into equation (7.23), and solving for ε^{pA} yields

$$\varepsilon^{pA} = \frac{1 - \varepsilon^f - \varepsilon^{dA}}{1 + C_1}, \quad (7.24)$$

which implies that

$$\frac{\dot{\varepsilon}^{pA}}{\varepsilon^{pA}} = \frac{-\dot{\varepsilon}^f - \dot{\varepsilon}^{dA}}{1 - \varepsilon^f - \varepsilon^{dA}}. \quad (7.25)$$

Using equation (7.25) to eliminate $\dot{\varepsilon}^{pA}/\varepsilon^{pA}$ from equations (7.9) and (7.20), and simplifying, we obtain

$$\dot{\varepsilon}^{dA} \left(\frac{1 - \varepsilon^f}{1 - \varepsilon^f - \varepsilon^{dA}} \right) + \dot{\varepsilon}^f \left(\frac{\varepsilon^{dA}}{1 - \varepsilon^f - \varepsilon^{dA}} \right) = \frac{-\widehat{e}_{dA}^{lA} - \widehat{e}_{dA}^B}{\rho^{dA}}, \quad (7.26)$$

and

$$\begin{aligned} \dot{\varepsilon}^f \left(\frac{1 - \varepsilon^{dA}}{1 - \varepsilon^f - \varepsilon^{dA}} \right) + \dot{\varepsilon}^{dA} \left(\frac{\varepsilon^f}{1 - \varepsilon^f - \varepsilon^{dA}} \right) + \nabla \cdot (\varepsilon^{lA} \mathbf{v}^{lA,pA}) + \nabla \cdot (\varepsilon^B \mathbf{v}^{B,pA}) \\ = \frac{\widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B}{\rho^f}, \end{aligned} \quad (7.27)$$

respectively. To obtain equation (7.26) we have used the fact that $\widehat{e}_{lA}^{dA} = -\widehat{e}_{dA}^{lA}$ and $\widehat{e}_B^{dA} = -\widehat{e}_{dA}^B$. Solving equation (7.26) for $\dot{\varepsilon}^{dA}/(1 - \varepsilon^f - \varepsilon^{dA})$, substituting the result into equation (7.27), and simplifying, we obtain

$$\begin{aligned} & \dot{\varepsilon}^f + (1 - \varepsilon^f) (\nabla \cdot (\varepsilon^{lA} \mathbf{v}^{lA,pA}) + \nabla \cdot (\varepsilon^B \mathbf{v}^{B,pA})) \\ &= (\widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B) \left(\frac{1 - \varepsilon^f}{\rho^f} + \frac{\varepsilon^f}{\rho^{dA}} \right). \end{aligned} \quad (7.28)$$

Substituting equations (7.2) and (7.11) into equation (7.28) yields

$$\begin{aligned} & \dot{\varepsilon}^f + (1 - \varepsilon^f) \left[\nabla \cdot \left(\frac{K^3 K^{lA} K^f (\varepsilon^f)^2}{(1 - K\varepsilon^f) \mu_v^{lA}} \nabla \varepsilon^f - \frac{K^2 K^{lA} \rho^f}{\mu_v^{lA}} \sum_{m=1}^p \frac{\partial A^{lA}}{\partial \varepsilon^{(m)f}} \nabla \varepsilon^{(m)f} \right. \right. \\ & \quad \left. \left. - \frac{K K^{lA} \varepsilon^f \rho^f}{\mu_v^{lA}} \left(\frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A + \frac{\partial A^{lA}}{\partial \varepsilon^{pA}} \nabla \varepsilon^{pA} \right) \right) - \nabla \cdot \left(\frac{K^B (\varepsilon^B)^2}{\mu_v^B} \nabla p^B \right) \right] \\ &= (\widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B) \left(\frac{1 - \varepsilon^f}{\rho^f} + \frac{\varepsilon^f}{\rho^{dA}} \right), \end{aligned} \quad (7.29)$$

where, like Singh et al. [51], we have assumed a linear relationship between the volume fraction of the vicinal fluid and the volume fraction of the wetting phase

$$\varepsilon^{lA} = K \varepsilon^f. \quad (7.30)$$

The first term in parentheses on the second line of equation (7.29) can be simplified as follows. First, rewrite it as

$$\begin{aligned} & \left. \frac{\partial A^{lA}}{\partial \varepsilon^A} \right|_{\varepsilon^B, \varepsilon^{lA}, \varepsilon^{pA}} \nabla \varepsilon^A + \left. \frac{\partial A^{lA}}{\partial \varepsilon^{pA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} \nabla \varepsilon^{pA} \\ &= \left. \frac{\partial A^{lA}}{\partial \varepsilon^{dA}} \right|_{\varepsilon^B, \varepsilon^{lA}, \varepsilon^{pA}} \frac{\partial \varepsilon^{dA}}{\partial \varepsilon^A} \bigg|_{\varepsilon^B, \varepsilon^{lA}, \varepsilon^{pA}} \nabla \varepsilon^A + \left. \frac{\partial A^{lA}}{\partial \varepsilon^{dA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} \frac{\partial \varepsilon^{dA}}{\partial \varepsilon^{pA}} \bigg|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} \nabla \varepsilon^{pA} \end{aligned} \quad (7.31)$$

Substituting equations (7.30) and (7.24) into equation (6.15) and solving for ε^{dA} yields

$$\varepsilon^{dA} = \left(\frac{1 + C_1}{C_1} \right) \varepsilon^A + \left(\frac{K(1 - C_1) - 1}{C_1} \right) \varepsilon^f + C_1, \quad (7.32)$$

which implies that

$$\left. \frac{\partial \varepsilon^{dA}}{\partial \varepsilon^A} \right|_{\varepsilon^{lA}, \varepsilon^B, \varepsilon^{pA}} = \frac{1 + C_1}{C_1}. \quad (7.33)$$

Taking the gradient of (7.24), we have

$$\nabla \varepsilon^{pA} = \frac{-\nabla \varepsilon^f - \nabla \varepsilon^{dA}}{1 + C_1}. \quad (7.34)$$

Taking the gradient of equation (6.15) and substituting equation (7.34) into the result, we obtain

$$\nabla \varepsilon^A = \left(\frac{C_1}{1 + C_1} \right) \nabla \varepsilon^{dA} + \left(\frac{K(1 + C_1) - 1}{1 + C_1} \right) \nabla \varepsilon^f. \quad (7.35)$$

Substituting equations (7.33), (7.34), and (7.35) into equation (7.31) and simplifying, we obtain

$$\begin{aligned} & \left. \frac{\partial A^{lA}}{\partial \varepsilon^A} \right|_{\varepsilon^B, \varepsilon^{lA}, \varepsilon^{pA}} \nabla \varepsilon^A + \left. \frac{\partial A^{lA}}{\partial \varepsilon^{pA}} \right|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} \nabla \varepsilon^{pA} = \\ & \left[\left(\frac{1}{1 + C_1} \frac{\partial A^{lA}}{\partial \varepsilon^{dA}} \right) \Big|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} + \frac{\partial A^{lA}}{\partial \varepsilon^{dA}} \Big|_{\varepsilon^B, \varepsilon^{lA}, \varepsilon^{pA}} \right] \nabla \varepsilon^{dA} \\ & + \left[\left(\frac{1}{1 + C_1} \frac{\partial A^{lA}}{\partial \varepsilon^{dA}} \right) \Big|_{\varepsilon^A, \varepsilon^B, \varepsilon^{lA}} + (K(1 + C_1) - 1) \frac{\partial A^{lA}}{\partial \varepsilon^{dA}} \Big|_{\varepsilon^B, \varepsilon^{lA}, \varepsilon^{pA}} \right] \nabla \varepsilon^f. \end{aligned} \quad (7.36)$$

Consider equation (7.36). All of the terms involve a partial derivative of the vicinal fluid Helmholtz free energy with respect to the volume fraction of the drug phase. Since we do not expect the energy of the vicinal fluid to be a strong function of the volume fraction of drug, that is, the drug and vicinal fluid are non-interacting, we expect both terms of equation (7.36) to be negligible.

Using the Laplace transform derivation outlined in Chapter 5, we can write equation (7.29) as

$$\begin{aligned} \dot{\varepsilon}^f + (1 - \varepsilon^f) \left[\nabla \cdot \left(D_1 \nabla \varepsilon^f - \int_0^t B_v(t - \tau) \nabla \dot{\varepsilon}^f(\tau) d\tau \right) \right] \\ = (\widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B) \left(\frac{1 - \varepsilon^f}{\rho^f} + \frac{\varepsilon^f}{\rho^{dA}} \right), \end{aligned} \quad (7.37)$$

where

$$D_1 = \frac{K^3 K^{lA} K'(\varepsilon^f)^2}{(1 - K\varepsilon^f) \mu_v^{lA}}, \quad (7.38)$$

and

$$B_v(t) = \frac{(\varepsilon^l)^2 \rho^l K^l}{\mu_v^l} \sum_{m=1}^p M_{(m)}^{lA} \delta^{(m-1)}(t), \quad (7.39)$$

where

$$M_{(m)}^{lA} = \frac{\partial A^{lA}}{\partial \varepsilon^{(m)} f}. \quad (7.40)$$

To obtain equation (7.37), we have assumed that the classical pressure of the bulk phase, B , is primarily a function of density, that is

$$\nabla p^B = \frac{\partial p^B}{\partial \rho^B} \nabla \rho^B. \quad (7.41)$$

If the pressure is constant along the boundaries then the density gradient, $\nabla \rho^B$ is negligible.

Equation (7.37) is very similar in form to the two-scale equation (5.16). As expected, we have acquired an additional exchange term on the right-hand side, so that now the total mass transfer from the drug phase to the wetting phase must be determined. The coefficients naturally take a different form.

7.5 Species Transport

The conservation of mass equations for drug in the vicinal water, denoted lA_d , and for drug in the bulk fluid B , denoted B_d , are given by equation (6.24) with $K = lA, B$, and $j = d$

$$\frac{D^{lA_d}(\varepsilon^{lA}\rho^{lA_d})}{Dt} + \varepsilon^{lA}\rho^{lA_d}\nabla \cdot \mathbf{v}^{lA_d} = \widehat{e}_{dA}^{lA} + \widehat{e}_B^{lA}, \quad (7.42)$$

$$\frac{D^{B_d}(\varepsilon^B\rho^{B_d})}{Dt} + \varepsilon^B\rho^{B_d}\nabla \cdot \mathbf{v}^{B_d} = \widehat{e}_{dA}^B + \widehat{e}_{lA}^B. \quad (7.43)$$

Converting derivatives in lA_d and B_d into derivatives in pA using equation (3.24) with $K = lA, B$ replacing α , and equation (6.93), and using the relationship between density and concentration, equation (B.3), we obtain

$$\begin{aligned} \rho^{lA} \left(C^{lA_d} \dot{\varepsilon}^{lA} + \varepsilon^{lA} \dot{C}^{lA_d} + \nabla \cdot (\varepsilon^{lA} C^{lA_d} \mathbf{v}^{lA_d, lA}) + \nabla \cdot (\varepsilon^{lA} C^{lA_d} \mathbf{v}^{lA, pA}) \right. \\ \left. + \varepsilon^{lA} C^{lA_d} \nabla \cdot \mathbf{v}^{pA} \right) = \widehat{e}_{dA}^{lA} + \widehat{e}_B^{lA} \end{aligned} \quad (7.44)$$

$$\begin{aligned} \rho^B \left(C^{B_d} \dot{\varepsilon}^B + \varepsilon^B \dot{C}^{B_d} + \nabla \cdot (\varepsilon^B C^{B_d} \mathbf{v}^{B_d, B}) + \nabla \cdot (\varepsilon^B C^{B_d} \mathbf{v}^{B, pA}) \right. \\ \left. + \varepsilon^B C^{B_d} \nabla \cdot \mathbf{v}^{pA} \right) = \widehat{e}_{lA}^B + \widehat{e}_{dA}^B. \end{aligned} \quad (7.45)$$

To obtain equations (7.44) and (7.45) we have used the incompressibility conditions $D^{lA}\rho^{lA}/Dt = 0$ and $D^B\rho^B/Dt = 0$ since the densities of the vicinal water and bulk fluid, B , are assumed to be constant, as well as the fact that $\nabla\rho^{lA} = 0$ and $\nabla\rho^B = 0$ since the pressure is assumed to be constant along the boundaries.

Since we have assumed a linear relationship between the volume fraction vicinal fluid and the total wetting phase volume fraction, equation (7.30), we can substitute this equation into equation (7.21) to obtain

$$\varepsilon^B = \varepsilon^f(1 - K) \quad (7.46)$$

Using equations (7.30) and (7.46) to eliminate ε^{lA} and ε^B in favor of ε^f , and adding equations (7.44) and (7.45), we obtain

$$\begin{aligned} & \rho^f \left(C^{lA_d} K \dot{\varepsilon}^f + K \varepsilon^f \dot{C}^{lA_d} + \nabla \cdot (K \varepsilon^f C^{lA_d} \mathbf{v}^{lA_d, lA}) + \nabla \cdot (K \varepsilon^f C^{lA_d} \mathbf{v}^{lA, pA}) \right. \\ & - K \varepsilon^f C^{lA_d} \frac{\dot{\varepsilon}^{pA}}{\varepsilon^{pA}} + C^{B_d} (1 - K) \dot{\varepsilon}^f + (1 - K) \varepsilon^f \dot{C}^{B_d} + \nabla \cdot ((1 - K) \varepsilon^f C^{B_d} \mathbf{v}^{B_d, B}) \\ & \left. + \nabla \cdot ((1 - K) \varepsilon^f C^{B_d} \mathbf{v}^{B, pA}) - (1 - K) \varepsilon^f C^{B_d} \frac{\dot{\varepsilon}^{pA}}{\varepsilon^{pA}} \right) = \widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B, \end{aligned} \quad (7.47)$$

where, the variable $\nabla \cdot \mathbf{v}^{pA}$ has been eliminated using equation (7.7). Eliminating $\dot{\varepsilon}^{pA}/\varepsilon^{pA}$ from equation (7.47) using equation (7.25), then eliminating $\dot{\varepsilon}^{dA}/(1 - \varepsilon^f - \varepsilon^{dA})$ from the result using equation (7.26), and simplifying yields

$$\begin{aligned} & (C^{lA_d} K + C^{B_d} (1 - K)) \dot{\varepsilon}^f + \varepsilon^f (1 - \varepsilon^f) \left(K \dot{C}^{lA_d} + (1 - K) \dot{C}^{B_d} \right) \\ & + (1 - \varepsilon^f) \left(\nabla \cdot (K \varepsilon^f C^{lA_d} \mathbf{v}^{lA_d, lA}) + \nabla \cdot (K \varepsilon^f C^{lA_d} \mathbf{v}^{lA, pA}) \right. \\ & \left. + \nabla \cdot ((1 - K) \varepsilon^f C^{B_d} \mathbf{v}^{B_d, B}) + \nabla \cdot ((1 - K) \varepsilon^f C^{B_d} \mathbf{v}^{B, pA}) \right) \\ & = (\widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B) \left(\frac{1 - \varepsilon^f}{\rho^f} + \frac{\varepsilon^f (K C^{lA_d} + (1 - K) C^{B_d})}{\rho^{dA}} \right) \end{aligned} \quad (7.48)$$

Fick's law for diffusion is given by equation (6.204). Neglecting higher-order terms and gravity, Fick's law for the drug in both fluid phases can be written

$$\mathbf{R}^{K_d} \cdot \mathbf{v}^{K_d, K} = -\varepsilon^K \rho^K \nabla \mu^{K_d}, \quad (7.49)$$

where $K = lA, B$. We assume that the chemical potential of the drug in both the vicinal water or the bulk fluid, B , is a function of the concentration of the drug in that phase and the volume fraction of that phase, that is

$$\mu^{lA_d} = \mu^{lA_d}(\varepsilon^{lA}, C^{lA_d}) = \mu^{lA_d}(K \varepsilon^f, C^{lA_d}), \quad (7.50)$$

$$\mu^{B_d} = \mu^{B_d}(\varepsilon^B, C^{B_d}) = \mu^{B_d}((1 - K) \varepsilon^f, C^{B_d}). \quad (7.51)$$

Using these equations to calculate $\nabla\mu^{K_d}$, we obtain the following form of Fick's law

$$\mathbf{v}^{lA_d,lA} = -\varepsilon^f \rho^f F_1 \nabla C^{lA_d} - \varepsilon^f \rho^f F_2 \nabla \varepsilon^f, \quad (7.52)$$

$$\mathbf{v}^{B_d,B} = -\varepsilon^f \rho^f F_3 \nabla C^{B_d} - \varepsilon^f \rho^f F_4 \nabla \varepsilon^f, \quad (7.53)$$

where

$$F_1 \mathbf{I} = K(\mathbf{R}^{lA_d})^{-1} \frac{\partial \mu^{lA_d}}{\partial C^{lA_d}}, \quad (7.54)$$

$$F_2 \mathbf{I} = K(\mathbf{R}^{lA_d})^{-1} \frac{\partial \mu^{lA_d}}{\partial \varepsilon^f}, \quad (7.55)$$

$$F_3 \mathbf{I} = (1 - K)(\mathbf{R}^{B_d})^{-1} \frac{\partial \mu^{B_d}}{\partial C^{B_d}}, \quad (7.56)$$

and

$$F_4 \mathbf{I} = (1 - K)(\mathbf{R}^{B_d})^{-1} \frac{\partial \mu^{B_d}}{\partial \varepsilon^f}, \quad (7.57)$$

In a single-phase theory the coefficient appearing in front of the gradient of the concentration is the mutual diffusion coefficient. Thus, F_1 and F_2 should be related to the mutual diffusion coefficient. The parameters F_3 and F_4 are material parameters that need to be determined experimentally.

Substituting equations (7.52) and (7.53) into equation (7.48), and using the same methods as in the previous section to substitute (7.2) and (7.11) into

equation (7.48) as well, we obtain

$$\begin{aligned}
& (C^{lA_d}K + C^{B_d}(1 - K))\dot{\varepsilon}^f + \varepsilon^f(1 - \varepsilon^f)(K\dot{C}^{lA_d} + (1 - K)\dot{C}^{B_d}) \\
& + (\varepsilon^f - 1)\nabla \cdot (D_2\nabla C^{lA_d} + D_3\nabla C^{B_d}) \\
& + (1 - \varepsilon^f) \left[\nabla \cdot \left(D_4\nabla \varepsilon^f - \int_0^t B_u(t - \tau)\nabla \dot{\varepsilon}^f(\tau)d\tau \right) \right] \\
& = (\widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B) \left(\frac{1 - \varepsilon^f}{\rho^f} + \frac{\varepsilon^f(KC^{lA_d} + (1 - K)C^{B_d})}{\rho^{dA}} \right)
\end{aligned} \tag{7.58}$$

where

$$D_2 = K(\varepsilon^f)^2 C^{lA_d} \rho^f F_1, \tag{7.59}$$

$$D_3 = (1 - K)(\varepsilon^f)^2 C^{B_d} \rho^f F_3, \tag{7.60}$$

$$D_4 = C^{lA_d} D_1 - (\varepsilon^f)^2 \rho^f (K C^{lA_d} F_2 + (1 - K) C^{B_d} F_4), \tag{7.61}$$

and

$$B_u(t) = C^{lA_d} B_v(t). \tag{7.62}$$

Note that if there was no bulk fluid phase B then $K = 1$, $C^{B_d} = 0$ and $\varepsilon^f = \varepsilon^l$ and equation (7.58) simplifies to the two-scale transport equation (5.24).

7.6 Discussion

Equations (7.37) and (7.58) constitute a system of two equations and five unknowns. The second upscaling has produced an additional two unknowns. The additional rate of mass transfer, \widehat{e}_{dA}^B , was discussed at the end of Section 7.4. The concentration of the drug in the bulk phase is the additional variable

that appears in (7.58). This variable could be eliminated via the assumption that the concentration in the vicinal water and bulk phases are the same, but this significantly reduces the applicability of this system of equations. The total mass transfer of drug to the fluid phase, $\widehat{e}_{dA}^f = \widehat{e}_{dA}^{lA} + \widehat{e}_{dA}^B$, could be measured in the same way as described at the end of Chapter 5.

For this problem to be well posed we must have that D_2 and D_3 are positive and that D_4 is negative. The coefficients D_2 and D_3 represent the diffusion coefficients in a classical Fick's law if the other phase is not present. As such, it seems reasonable to assume that these coefficients are indeed positive. The complex form of D_1 makes it difficult to speculate on the sign of this parameter prior to actually determining at least a few of the constants for the system in question, such as K and C_1 . As was the case in the two-scale scenario, many models have no term that corresponds to the term involving D_4 . Instead, such models postulate the dependence of the coefficient D_2 on the volume fraction of the fluid phase. In this model D_2 is a function of the volume fraction of the fluid phase and yet the gradient in volume fraction still appears, suggesting that this term is needed to fully account for the physics.

8. Discussion and Avenues for Future Work

Most traditional fluid transport equations modeling swelling polymeric systems, including drug delivery systems, employ a single-scale theory. Both multiscale interactions and phase interactions are either ignored or the effects of these interaction are incorporated into the coefficients. As such, the physics of multiscale and phase interactions are not fully accounted. Experiments have been designed to collect data in an attempt to reconcile observation and theory and as a result there is a lack of experimental data corresponding to variables which account for these interactions. The next step is to perform the experiments needed to have a clear connection to the variables that appear in the governing equations discussed in Chapters 5 and 7. For example, there is a dearth of information concerning the rate of mass transfer from one phase to another. The discussion at the end of Chapter 5 offers a way of resolving this variable.

Theory also needs to attempt to accommodate empirical data. It was necessary to modify the two-phase theory of Singh et al. [50, 51] to a three-phase theory to accommodate experiments that measure the volume fraction of the drug in solid form. In this thesis we have developed a two-scale and a three-scale theory that takes a step forward to mathematically account for experimental data which measures drug volume fraction.

Despite the theoretical advances made in this thesis and the complicated form of these equations, we have not accounted for some very simple scenarios.

For example, the compressibility condition for the liquid phase restricts the application of these equations to systems in which the drug is transported quickly out of the polymer matrix. This is not always the case, especially when the initial drug loading is very high. Another scenario that is not accounted for is when polymer matrix erosion affects release kinetics, as is the case with some poorly soluble drugs. Modeling a system that is highly dependent on the polymer matrix erosion requires that we consider the rate of mass transfer of polymer to the liquid phase.

Numerical solutions of the systems of equations laid out in Chapters 5 and 7 need to be obtained and compared to experimental data. In [52], Singh et al. used the finite element method in Lagrangian coordinates to obtain a numerical solution to a similar problem involving the drying of seeds. Lagrangian coordinates are employed in the material reference frame because the material deforms as it swells (shrinks). A similar method needs to be applied to the aforementioned equations to validate the application of this theory to drug delivery systems.

The foundations of the application of electroquasistatics to swelling porous media is laid out in [10, 9], but has yet to be applied to systems in which the solid phase is known to be viscoelastic at the microscale. Such a theory would allow us to model the effect of oscillating electromagnetic fields on chemical transport in three-dimensional hydrogel-based scaffolds that have been designed to treat spinal cord injuries.

Appendix A. Mesoscale Appendix

A.1 Nomenclature

Superscripts, Subscripts, and Other Notations

\cdot^{α_j} j^{th} component of α -phase on mesoscale

\cdot^α α -phase on mesoscale

$\hat{\cdot}$ denotes exchange from other interface or phase

$\cdot^{k,l}$ 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^{α_j}, A^α : Helmholtz free energy density [J/Kg]

b^{α_j}, b^α : External entropy source [J/(Kg-s $^\circ$ K)]

C^{α_j} : Mass fraction of j^{th} component [-]

\mathbf{C}^s : Right Cauchy-Green tensor = $(\mathbf{F}^s)^T \cdot \mathbf{F}^s$

$\overline{\mathbf{C}}^s$: Modified right Cauchy-Green tensor = $(\overline{\mathbf{F}}^s)^T \cdot \overline{\mathbf{F}}^s$

\mathbf{d}^α : Rate of deformation tensor, equal to the symmetric part of $\nabla \mathbf{v}^\alpha$ [1/s]

e^{α_j}, e^α : energy density [J/Kg]

$\widehat{e}_\beta^{\alpha_j}$: Rate of mass transfer from phase [subscript] to phase [superscript] per unit mass density [1/s]

\mathbf{E}^s : Strain tensor of the solid phase [-]

\mathbf{F}^s : Deformation gradient of the solid phase [-]

$\overline{\mathbf{F}}^s$: Modified deformation gradient of the solid phase [-]

$\mathbf{g}^{\alpha_j}, \mathbf{g}^\alpha$: External supply of momentum (gravity) [m/s²]

G^α : Gibbs free energy [J/Kg]

\mathbf{G}^s : Fourth order tensor, effect of strain rate on stress due to relaxation processes in the solid phase

h^{α_j}, h^α : External supply of energy [J/(Kg-s)]

$\mathbf{H}^l, \mathbf{H}^s$: Third order tensors representing the effect of thermal gradients on the stress

$\widehat{\mathbf{i}}^{\alpha_j}$: Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

$\widehat{\mathbf{i}}^{\alpha_j}$: Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

J^s : Jacobian of the sold phase [-]

\mathbf{J}^s : Third order tensor representing the heat flux in the anisotropic solid due to strain rate

K' : Unjacketed compressibility [N/m²]

K^l : Permeability, see (3.84)

$\mathbf{K}^l, \mathbf{K}^s$: Second order tensors representing heat flux in the liquid and solid phases, respectively, due to the thermal gradient

\mathbf{K} : Second order tensor representing the permeability of the solid matrix

\mathbf{L}^l : Fourth order tensor representing the effect on stress due to the rate of deformation [-]

$\widehat{\mathbf{m}}^{\alpha j}$: Rate of angular momentum gain due to interaction with other species within the same phase per unit mass density [N-m/Kg]

$\widehat{\mathbf{m}}_{\beta}^{\alpha j}$: Rate of angular momentum gain by constituent j in phase α due to interaction with phase β [N-m/Kg]

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

\mathbf{M}^l : Third order tensor representing the heat flux due to the rate of deformation

n^{α} : Number of α -phase molecules [mols]

p^{α} : Classical pressure [N/m²]

- \bar{p}^α : Thermodynamic pressure [N/m²]
- \mathbf{n}^α : Unit normal vector pointing out of α -phase within mesoscopic REV [-]
- $\widehat{\mathbf{m}}^{\alpha j}$: Rate of gain of angular momentum of constituent j from other constituents in phase α [m²/s²]
- $\mathbf{q}^{\alpha j}$: Partial heat flux vector for the j^{th} component of phase [J/(m²-s)]
- \mathbf{q}^α : Heat flux vector for phase α [J/(m²-s)]
- $\widehat{Q}^{\alpha j}$: 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)]
- $\widehat{Q}_\beta^{\alpha j}, \widehat{Q}_\beta^\alpha$: Energy transfer rate from phase [subscript] to phase [superscript] per unit mass density not due to mass or momentum transfer [J/(Kg-s)]
- \mathbf{r} : Microscale spatial variable [m]
- $\widehat{r}^{\alpha j}$: Rate of mass gain due to interaction with other species within the same phase per unit mass density [1/s]
- R : Gas constant [J/(m T)]
- \mathbf{R} : Second order tensor called the resistivity tensor
- t : Time [s]
- T : Temperature [°K]
- $\mathbf{t}^{\alpha j}$: Partial stress tensor for the j^{th} component for phase [N/m²]

\mathbf{t}^α : Total stress tensor for the phase [N/m²]

\mathbf{t} : Total stress tensor = $\varepsilon^l \mathbf{t}^l + \varepsilon^s \mathbf{t}^s$ (for a two-phase system [N/m²])

\mathbf{t}^{se} : Terzaghi stress [N/m²], see (3.8)

\mathbf{t}^{sh} : Hydration stress [N/m²], see (3.9)

$\bar{\mathbf{t}}^{se}$: Terzaghi stress, [N/m²], see (3.60)

$\bar{\mathbf{t}}^{sh}$: Hydration stress [N/m²], see (3.59)

$\hat{\mathbf{T}}_\beta^{\alpha_j}, \hat{\mathbf{T}}_\beta^\alpha$: Rate of momentum transfer through mechanical interactions from phase [subscript] to phase [superscript] per unit mass density [N/m³]

v^α : Molar volume fraction of phase α = vol α / total volume

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

δV : Representative elementary volume (REV)

δV_α : Portion of α -phase in REV

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

x : Ratio of molar volumes of solute to solvent [-]

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

Greek Symbols

γ^α : Indicator function which is 1 if in mesoscopic region α and zero otherwise

$\delta(t)$: Dirac delta function [-]

ε^α : Volume fraction of α -phase in mesoscale REV = $|\delta V_\alpha|/|\delta V|$ [-]

$\eta^{\alpha j}, \eta^\alpha$: Entropy [J/(Kg-°K)]

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

λ^α : Lagrange multiplier for the continuity equation of phase α

$\Lambda^{\alpha j}, \Lambda^\alpha$: Entropy production per unit mass density [J/(Kg-s-°K)]

$\mu^{\alpha j}$: Scalar chemical potential of j^{th} constituent in phase α [J/Kg]

μ^α : Scalar chemical potential of phase α [J/Kg]

μ_v^l : Viscosity of the liquid phase, see (3.84)

$\boldsymbol{\xi}$: Microscale spatial variable which varies over REV for fixed \boldsymbol{x} : $\boldsymbol{r} = \boldsymbol{x} + \boldsymbol{\xi}$
[m]

π^α : Swelling potential, [N/m²]

$\rho^{\alpha j}$: Partial mass density of j^{th} component of α -phase [Kg/m³] so that $\varepsilon^\alpha \rho^{\alpha j}$ is the total mass of j^{th} constituent in phase α divided by the volume of REV

ρ^α : Mass density of α -phase averaged over / a -phase [Kg/m³]

$\boldsymbol{\phi}^{\alpha j}$: Partial entropy flux vector for the j^{th} component for phase [J/(m²-s-°K)]

$\boldsymbol{\phi}^\alpha$: Total entropy flux vector for the phase [J/(m²-s-°K)]

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

χ : Flory-Huggins interaction parameter [-]

A.2 Bulk Phase Definitions

Bulk phase variable definitions are not always intuitive and are defined so as to preserve the form and interpretation of the mesoscale equations.

$$A^\alpha \equiv \sum_{j=1}^N C^{\alpha_j} A^{\alpha_j} \quad (\text{A.1})$$

$$b^\alpha \equiv \sum_{j=1}^N C^{\alpha_j} b^{\alpha_j} \quad (\text{A.2})$$

$$C^{\alpha_j} \equiv \frac{\rho^{\alpha_j}}{\rho^\alpha} \quad (\text{A.3})$$

$$e^\alpha \equiv \sum_{j=1}^N C^{\alpha_j} (e^{\alpha_j} \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha}) \quad (\text{A.4})$$

$$\widehat{e}_\beta^\alpha \equiv \sum_{j=1}^N \widehat{e}_\beta^{\alpha_j} \quad (\text{A.5})$$

$$\mathbf{g}^\alpha \equiv \sum_{j=1}^N C^{\alpha_j} \mathbf{g}^{\alpha_j} \quad (\text{A.6})$$

$$h^\alpha \equiv \sum_{j=1}^N C^{\alpha_j} (h^{\alpha_j} + \mathbf{g}^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha}) \quad (\text{A.7})$$

$$\widehat{\mathbf{m}}_\beta^\alpha \equiv \sum_{j=1}^N \widehat{\mathbf{m}}_\beta^{\alpha_j} \quad (\text{A.8})$$

$$M^\alpha \equiv \sum_{j=1}^N M^{\alpha_j} \quad (\text{A.9})$$

$$\mathbf{q}^\alpha \equiv \sum_{j=1}^N [\mathbf{q}^{\alpha_j} + \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} - \rho^{\alpha_j} (e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha}) \mathbf{v}^{\alpha_j, \alpha}] \quad (\text{A.10})$$

$$\widehat{Q}_\beta^\alpha \equiv \sum_{j=1}^N [\widehat{Q}_\beta^{\alpha_j} + \widehat{\mathbf{T}}_\beta^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} + \widehat{e}_\beta^{\alpha_j} (e^{\alpha_j, \alpha} \frac{1}{2} \mathbf{v}^{\alpha_j, \alpha} \cdot \mathbf{v}^{\alpha_j, \alpha})] \quad (\text{A.11})$$

$$\mathbf{t}^\alpha \equiv \sum_{j=1}^N (\mathbf{t}^{\alpha_j} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \mathbf{v}^{\alpha_j, \alpha}) \quad (\text{A.12})$$

$$\widehat{\mathbf{T}}_\beta^\alpha \equiv \sum_{j=1}^N (\widehat{\mathbf{T}}_\beta^{\alpha_j} + \widehat{e}_\beta^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha}) \quad (\text{A.13})$$

$$\mathbf{v}^\alpha \equiv \sum_{j=1}^N C^{\alpha_j} \mathbf{v}^{\alpha_j} \quad (\text{A.14})$$

$$\eta^\alpha \equiv \sum_{j=1}^N C^{\alpha_j} \eta^{\alpha_j} \quad (\text{A.15})$$

$$\Lambda^\alpha \equiv \sum_{j=1}^N \Lambda^{\alpha_j} \quad (\text{A.16})$$

$$\rho^\alpha \equiv \sum_{j=1}^N \rho^{\alpha_j} \quad (\text{A.17})$$

$$\phi^\alpha \equiv \sum_{j=1}^N (\phi^{\alpha_j} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \eta^{\alpha_j}) \quad (\text{A.18})$$

$$\widehat{\Phi}_\beta^\alpha \equiv \sum_{j=1}^N (\widehat{\phi}_\beta^{\alpha_j} + \widehat{e}_\beta^{\alpha_j} \eta^{\alpha_j, \alpha}) \quad (\text{A.19})$$

A.3 Identities Needed to Obtain Entropy Inequality 2.82

$$\begin{aligned} \sum_{j=1}^N \frac{\varepsilon^\alpha \rho^{\alpha_j}}{T} \frac{D^{\alpha_j} A^{\alpha_j}}{Dt} &= \frac{\varepsilon^\alpha \rho}{T} \frac{D^\alpha A^\alpha}{Dt} + \frac{A^\alpha}{T} \widehat{e}_\beta^\alpha \\ &+ \sum_{j=1}^N \left\{ \frac{1}{T} \mathbf{v}^{\alpha_j, \alpha} \cdot \nabla (\varepsilon^\alpha \rho^{\alpha_j} A^{\alpha_j}) - \frac{A^{\alpha_j}}{T} \widehat{e}_\beta^{\alpha_j} - \frac{A^{\alpha_j}}{T} \widehat{r}^{\alpha_j} \right. \\ &\left. - \frac{\varepsilon^\alpha \rho^{\alpha_j}}{T} A^{\alpha_j} (\nabla \cdot \mathbf{v}^{\alpha_j, \alpha}) \right\} \end{aligned} \quad (\text{A.20})$$

$$\sum_{j=1}^N \frac{\varepsilon^\alpha \rho^{\alpha_j}}{T} \eta^{\alpha_j} \frac{D^{\alpha_j} T}{Dt} = \frac{\varepsilon^\alpha \rho^\alpha}{T} \frac{D^\alpha T}{Dt} + \sum_{j=1}^N \frac{\varepsilon^\alpha \rho^{\alpha_j}}{T} \eta^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \cdot \nabla T \quad (\text{A.21})$$

$$\sum_{j=1}^N \frac{\alpha}{T} \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j} = \sum_{j=1}^N \left\{ \frac{\varepsilon^\alpha}{T} \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j, \alpha} + \frac{\varepsilon^\alpha}{T} \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^\alpha \right\} \quad (\text{A.22})$$

$$\sum_{j=1}^N \sum_{\beta \neq \alpha} \widehat{\Phi}_\beta^{\alpha_j} = - \sum_{j=1}^N \sum_{\beta \neq \alpha} \widehat{e}_\beta^{\alpha_j} \eta^{\alpha_j} \quad (\text{A.23})$$

$$\sum_{j=1}^N \widehat{Q}^{\alpha_j} = - \sum_{\beta \neq \alpha} \left[\widehat{\mathbf{i}}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} + \widehat{r}^{\alpha_j} \left(A^{\alpha_j} + T \eta^{\alpha_j} \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) \right] \quad (\text{A.24})$$

$$\begin{aligned} \sum_{j=1}^N \sum_{\beta \neq \alpha} \widehat{Q}_\beta^{\alpha_j} &= - \sum_{\alpha} \sum_{\beta \neq \alpha} \left\{ \widehat{\mathbf{T}}_\beta^\alpha \cdot \mathbf{v}^{\alpha, s} + \frac{1}{2} \widehat{e}_\beta^\alpha (\mathbf{v}^{\alpha, s})^2 \right. \\ &\left. + \sum_{j=1}^N \left[\widehat{\mathbf{T}}_\beta^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} + \frac{1}{2} \widehat{e}_\beta^{\alpha_j} (\mathbf{v}^{\alpha_j, \alpha})^2 \right] \right\} + \sum_{\beta \neq \alpha} \sum_{j=1}^N \widehat{e}_\beta^{\alpha_j} (A^{\alpha_j} + T \eta^{\alpha_j}) \end{aligned} \quad (\text{A.25})$$

Appendix B. Macroscale Appendix

B.1 Nomenclature

Superscripts, Subscripts, and Other Notations

\cdot^{K_j} j^{th} component of K -phase on mesoscale

\cdot^K K -phase on mesoscale

$\hat{\cdot}$ denotes exchange from other interface or phase

$\cdot^{K,L}$ difference of the two quantities, i.e. $\cdot^K - \cdot^L$

$\cdot|_{K_j}$ microscopic property of constituent j in phase [subscript] (non-averaged)

Latin Symbols

δA_{KL} : Portion of KL -interface in representative elementary volume (REV)

A^{K_j}, A^K : Helmholtz free energy density [J/Kg]

b^{K_j}, b^K : External entropy source [J/(Kg-s-°K)]

C^{K_j} : Mass fraction of j^{th} component [-]

\mathbf{C}^{sA} : Right Cauchy-Green tensor = $(\mathbf{F}^{sA})^T \cdot \mathbf{F}^{sA}$

$\overline{\mathbf{C}}^{sA}$: Modified right Cauchy-Green tensor = $(\overline{\mathbf{F}}^s)^T \cdot \overline{\mathbf{F}}^s$

\mathbf{d}^K : Rate of deformation tensor, equal to the symmetric part of $\nabla \mathbf{v}^K$ [1/s]

e^{K_j}, e^K : energy density [J/Kg]

$\hat{e}_L^{K_j}$: Rate of mass transfer from phase [subscript] to phase [superscript] per unit mass density [1/s]

\mathbf{E}^{sA} : Strain tensor of the solid phase [-]

\mathbf{F}^{sA} : Deformation gradient of the solid phase [-]

$\overline{\mathbf{F}}^{sA}$: Modified deformation gradient of the solid phase [-]

$\mathbf{g}^{K_j}, \mathbf{g}^K$: External supply of momentum (gravity) [m/s²]

G^K : Gibbs free energy [J/Kg]

\mathbf{G}^{sA} : Fourth order tensor, effect of strain rate on stress due to relaxation processes in the solid phase

h^{K_j}, h^K : External supply of energy [J/(Kg-s)]

$\mathbf{H}^L, \mathbf{H}^{sA}$: Third order tensors representing the effect of thermal gradients on the stress

$\hat{\mathbf{i}}^{K_j}$: Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

$\hat{\mathbf{i}}^{K_j}$: Rate of momentum gain due to interaction with other species within the same phase per unit mass density [N/Kg]

J^{sA} : Jacobian of the sold phase [-]

\mathbf{J}^{sA} : Third order tensor representing the heat flux in the anisotropic solid due to strain rate

K' : Unjacketed compressibility [N/m²]

K^{lA} : Permeability, see (7.2)

$\mathbf{K}^L, \mathbf{K}^{sA}$: Second order tensors representing heat flux in the liquid and solid phases, respectively, due to the thermal gradient

\mathbf{K} : Second order tensor representing the permeability of the solid matrix

\mathbf{L}^L : Fourth order tensor representing the effect on stress due to the rate of deformation [-]

$\widehat{\mathbf{m}}^{Kj}$: Rate of angular momentum gain due to interaction with other species within the same phase per unit mass density [N-m/Kg]

$\widehat{\mathbf{m}}_L^{Kj}$: Rate of angular momentum gain by constituent j in phase K due to interaction with phase L [N-m/Kg]

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

\mathbf{M}^L : Third order tensor representing the heat flux due to the rate of deformation

n^K : Number of K -phase molecules [mols]

p^K : Classical pressure [N/m²]

- \bar{p}^K : Thermodynamic pressure [N/m²]
- \mathbf{n}^K : Unit normal vector pointing out of K -phase within mesoscopic REV [-]
- $\widehat{\mathbf{m}}^{K_j}$: Rate of gain of angular momentum of constituent j from other constituents in phase K [m²/s²]
- \mathbf{q}^{K_j} : Partial heat flux vector for the j^{th} component of phase [J/(m²-s)]
- \mathbf{q}^K : Heat flux vector for phase K [J/(m²-s)]
- \widehat{Q}^{K_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)]
- $\widehat{Q}_L^{K_j}, \widehat{Q}_L^K$: Energy transfer rate from phase [subscript] to phase [superscript] per unit mass density not due to mass or momentum transfer [J/(Kg-s)]
- \mathbf{r} : Microscale spatial variable [m]
- \widehat{r}^{K_j} : Rate of mass gain due to interaction with other species within the same phase per unit mass density [1/s]
- R : Gas constant [J/(m T)]
- \mathbf{R}^K : Second order tensor called the resistivity tensor
- t : Time [s]
- T : Temperature [°K]
- \mathbf{t}^{K_j} : Partial stress tensor for the j^{th} component for phase [N/m²]

\mathbf{t}^K : Total stress tensor for the phase [N/m²]

\mathbf{t}_{se}^{sA} : Terzaghi stress [N/m²], see (6.129) and (6.159)

\mathbf{t}_{sh}^{sA} : Hydration stress [N/m²], see (6.130) and (6.160)

$\widehat{\mathbf{T}}_L^{K_j}, \widehat{\mathbf{T}}_L^K$: Rate of momentum transfer through mechanical interactions from phase [subscript] to phase [superscript] per unit mass density [N/m³]

v^K : Molar volume fraction of phase K = vol K / total volume

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

$\mathbf{v}^{K_j, K}$: Diffusive velocity, $\mathbf{v}^{K_j} - \mathbf{v}^K$ [m/s]

δV : Representative elementary volume (REV)

δV_K : Portion of K -phase in REV

\mathbf{w}^{KL_j} : Velocity of constituent j at interface between phases K and L [m/s]

Greek Symbols

γ^K : Indicator function which is 1 if in mesoscopic region K and zero otherwise

$\delta(t)$: Dirac delta function [-]

ε^K : Volume fraction of K -phase in mesoscale REV = $|\delta V_K|/|\delta V|$ [-]

η^{K_j}, η^K : Entropy [J/(Kg-°K)]

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

λ^K : Lagrange multiplier for the continuity equation of phase K

Λ^{K_j}, Λ^K : Entropy production per unit mass density [J/(Kg-s-°K)]

μ^{K_j} : Scalar chemical potential of j^{th} constituent in phase K [J/Kg]

μ^K : Scalar chemical potential of phase K [J/Kg]

μ_v^{LA} : Viscosity of the liquid phase, see (7.2)

π^K : Swelling potential, [N/m²]

ρ^{K_j} : Partial mass density of j^{th} component of K -phase [Kg/m³] so that $\varepsilon^K \rho^{K_j}$ is the total mass of j^{th} constituent in phase K divided by the volume of REV

ρ^K : Mass density of K -phase averaged over $/a$ -phase [Kg/m³]

ϕ^{K_j} : Partial entropy flux vector for the j^{th} component for phase [J/(m²-s-°K)]

ϕ^K : Total entropy flux vector for the phase [J/(m²-s-°K)]

$\widehat{\Phi}_L^{K_j}, \widehat{\Phi}_L^K$: Entropy transfer through mechanical interactions from phase [subscript] to phase [superscript] per unit mass [J/(kg-s-°K)]

B.2 Bulk Phase Definitions

Bulk phase variable definitions are not always intuitive and are defined so as to preserve the form and interpretation of the mesoscale equations.

$$A^K \equiv \sum_{j=1}^N C^{K_j} A^{K_j} \quad (\text{B.1})$$

$$b^K \equiv \sum_{j=1}^N C^{K_j} b^{K_j} \quad (\text{B.2})$$

$$C^{K_j} \equiv \frac{\rho^{K_j}}{\rho^K} \quad (\text{B.3})$$

$$e^K \equiv \sum_{j=1}^N C^{K_j} (e^{K_j} \frac{1}{2} \mathbf{v}^{K_j, K} \cdot \mathbf{v}^{K_j, K}) \quad (\text{B.4})$$

$$\widehat{e}_L^K \equiv \sum_{j=1}^N \widehat{e}_L^{K_j} \quad (\text{B.5})$$

$$\mathbf{g}^K \equiv \sum_{j=1}^N C^{K_j} \mathbf{g}^{K_j} \quad (\text{B.6})$$

$$h^K \equiv \sum_{j=1}^N C^{K_j} (h^{K_j} + \mathbf{g}^{K_j} \mathbf{v}^{K_j, K}) \quad (\text{B.7})$$

$$\widehat{\mathbf{m}}_L^K \equiv \sum_{j=1}^N \widehat{\mathbf{m}}_L^{K_j} \quad (\text{B.8})$$

$$M^K \equiv \sum_{j=1}^N M^{K_j} \quad (\text{B.9})$$

$$\mathbf{q}^K \equiv \sum_{j=1}^N [\mathbf{q}^{K_j} + \mathbf{t}^{K_j} \cdot \mathbf{v}^{K_j, K} - \rho^{K_j} (e^{K_j} + \frac{1}{2} \mathbf{v}^{K_j, K} \cdot \mathbf{v}^{K_j, K}) \mathbf{v}^{K_j, K}] \quad (\text{B.10})$$

$$\widehat{Q}_L^K \equiv \sum_{j=1}^N [\widehat{Q}_L^{K_j} + \widehat{\mathbf{T}}_L^{K_j} \cdot \mathbf{v}^{K_j, K} + \widehat{e}_L^{K_j} (e^{K_j, K} \frac{1}{2} \mathbf{v}^{K_j, K} \cdot \mathbf{v}^{K_j, K})] \quad (\text{B.11})$$

$$\mathbf{t}^K \equiv \sum_{j=1}^N (\mathbf{t}^{K_j} - \rho^{K_j} \mathbf{v}^{K_j, K} \mathbf{v}^{K_j, K}) \quad (\text{B.12})$$

$$\widehat{\mathbf{T}}_L^K \equiv \sum_{j=1}^N (\widehat{\mathbf{T}}_L^{K_j} + \widehat{e}_L^{K_j} \mathbf{v}^{K_j, K}) \quad (\text{B.13})$$

$$\mathbf{v}^K \equiv \sum_{j=1}^N C^{K_j} \mathbf{v}^{K_j} \quad (\text{B.14})$$

$$\eta^K \equiv \sum_{j=1}^N C^{K_j} \eta^{K_j} \quad (\text{B.15})$$

$$\Lambda^K \equiv \sum_{j=1}^N \Lambda^{K_j} \quad (\text{B.16})$$

$$\rho^K \equiv \sum_{j=1}^N \rho^{K_j} \quad (\text{B.17})$$

$$\boldsymbol{\phi}^K \equiv \sum_{j=1}^N (\boldsymbol{\phi}^{K_j} - \rho^{K_j} \mathbf{v}^{K_j, K} \eta^{K_j}) \quad (\text{B.18})$$

$$\widehat{\boldsymbol{\Phi}}_L^K \equiv \sum_{j=1}^N (\widehat{\boldsymbol{\phi}}_L^{K_j} + \widehat{e}_L^{K_j} \eta^{K_j, K}) \quad (\text{B.19})$$

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