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A Model for Flow and Deformation in Unsaturated Swelling Porous Media

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Abstract A thermomechanical theory for multiphase transport in unsaturated swelling porous media is developed on the basis of Hybrid Mixture Theory (saturated systems can also be modeled as a special case of this general theory). The aim is to comprehensively and non-empirically describe the effect of viscoelastic deformation on fluid transport (and vice versa) for swelling porous materials. Three phases are considered in the system: the swelling solid matrix s, liquid l, and air a. The Coleman–Noll procedure is used to obtain the restrictions on the form of the constitutive equations. The form of Darcy's law for the fluid phase, which takes into account both Fickian and non-Fickian transport, is slightly different from the forms obtained by other researchers though all the terms have been included. When the fluid phases interact with the swelling solid porous matrix, deformation occurs. Viscoelastic large deformation of the solid matrix is investigated. A simple form of differential-integral equation is obtained for the fluid transport under isothermal conditions, which can be coupled with the deformation of the solid matrix to solve for transport in an unsaturated system. The modeling theory thus developed, which involves two-way coupling of the viscoelastic solid deformation and fluid transport, can be applied to study the processing of biopolymers, for example, soaking of foodstuffs and stress-crack predictions. Moreover, extension and modification of this modeling theory can be applied to study a vast variety of problems, such as drying of gels, consolidation of clays, drug delivery, and absorption of liquids in diapers.

Keywords Unsaturated · Swelling · Porous · Thermodynamics · Large deformation · Viscoelasticity

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Nomenclature

Latin Symbols

$\mathbf{A}^n$	Fourth order material coefficient tensor
$A^{\alpha j}$	Helmholtz free energy of the jth component in α phase
A^{α}	Helmholtz free energy of the α phase
$b^{\alpha j}$	External entropy source for the jth component in α phase
b^{α}	External entropy source for the α phase
B	Material coefficient related to the bulk relaxation function
$\mathbf{B}$	Material coefficient
$\mathbf{B}^{\alpha}$	Fourth order viscous dissipation tensor
$C^{\alpha j}$	Mass fraction of the jth component in α phase
$\mathbf{C}^{\mathrm{s}}$	Right Cauchy-Green strain tensor of the solid phase
$\bar{\mathbf{C}}^{\mathrm{s}}$	Right Cauchy-Green strain tensor associated with $\bar{\mathbf{F}}^{s}$
$\mathbf{d}^{\alpha}$	Rate of deformation tensor of the α phase
d_{α}	Material constant related to the initial bulk modulus of α phase
$e^{\alpha j}$	Energy density of the jth component in α phase
e^{α}	Energy density of the α phase
$\hat{e}^{\beta}_{\alpha_j}$	Rate of mass transfer from phase β to the jth component in α phase
$\hat{e}^{\beta}_{\alpha}$	Rate of mass transfer from β phase to the α phase
$\mathbf{E}^{\mathrm{s}}$	Lagrangian strain tensor of the solid phase
$\mathbf{F}^{\mathrm{s}}$	Deformation gradient of the solid phase
$\bar{\mathbf{F}}^{\mathrm{s}}$	The multiplicative decomposition of the deformation gradient
$\mathbf{g}^{\alpha j}$	Gravitational force on the jth component in α phase
$\mathbf{g}^{\alpha}$	Gravitational force on the α phase
$\mathbf{G(t)}$	Relaxation function in shear
$h^{\alpha j}$	External supply of energy to the jth component in α phase
h^{α}	External supply of energy to α phase
$\mathbf{H}^{\alpha}$	Third order material coefficient tensor
$\hat{\mathbf{i}}^{\alpha j}$	Rate of momentum gain to the jth component in α phase due to interaction with other species in the same phase
$\mathbf{I}$	Identity tensor
I_k	Principal invariants of the right Cauchy-Green tensor $\mathbf{C}^{s}$
$\bar{I}_k$	Principal invariants of $\bar{\mathbf{C}}^{s}$
J^{s}	Determinant of the deformation gradient
K^{α}	Initial bulk modulus of α phase
$\mathbf{K}^{\alpha}$	Second rank coefficient tensor from linearization
L	Laplace transform operator
M^{α}	Material coefficient
p^{α}	Physical pressure in the α phase
$\mathbf{q}^{\alpha j}$	Heat flux vector for the jth component in α phase
$\mathbf{q}^{\alpha}$	Heat flux vector for α phase
$\hat{Q}^{\alpha j}$	Rate of energy gain to the jth component in α phase due to interaction with other species in the same phase
$\hat{Q}^{\beta}_{\alpha_j}$	Rate of energy transfer from phase β to the jth component in α phase
$\hat{Q}^{\beta}_{\alpha}$	Rate of energy transfer from phase β to α phase
$\hat{r}^{\alpha j}$	Rate of mass gain to the jth component in α phase due to interaction with other species in the same phase

$\mathbf{R}^{\mathrm{a}}$	Resistivity tensor
$\mathbf{R}^{\mathrm{l}}$	Resistivity tensor
$\mathbf{S}$	Material coefficient related to the shear relaxation function
$\mathbf{S}^{\mathrm{s}}$	Second Piola-Kirchhoff stress tensor
t	Time
$\mathbf{t}^{\alpha_j}$	Stress tensor of the jth component in α phase
$\mathbf{t}^{\alpha}$	Stress tensor of the α phase
$\mathbf{t}^{\mathrm{se}}$	Terzaghi stress for the solid phase
$\mathbf{t}^{\mathrm{sh}}$	Hydration stress for the solid phase
T	Temperature
$\hat{\mathbf{T}}_{\alpha_j}^{\beta}$	Rate of momentum transfer to the jth component in α phase from β phase
$\hat{\mathbf{T}}_{\alpha}^{\beta}$	Rate of momentum transfer to α phase from β phase
$\mathbf{u}^{\mathrm{s}}$	Displacement of the solid phase
$\mathbf{v}^{\alpha_j}$	Velocity of the jth component in α phase
$\mathbf{v}^{\alpha}$	Velocity of the α phase
$\mathbf{v}^{\alpha,\beta}$	Relative velocity between phase α and phase β

Greek Symbols

δ	Dirac's delta function
ϵ^{α}	Volume fraction of the α phase
η^{α_j}	Entropy of the jth component in α phase
η^{α}	Entropy of the α phase
$\hat{\eta}^{\alpha_j}$	Entropy gain by the jth component in α phase due to interaction with other species in the same phase
λ^{α}	Lagrange multiplier for the continuity equation of α phase
Λ^{α_j}	Entropy production per unit mass density for the jth component in α phase
Λ^{α}	Entropy production per unit mass density for α phase
μ	Viscosity of the liquid phase
μ^{α_j}	Chemical potential of the jth component in α phase
μ^{α}	Chemical potential of α phase
μ_{α}	Initial shear modulus of α phase
π^{1}	Swelling pressure due to interaction of the solid phase and the bulk fluid
ρ^{α_j}	Density of the jth component in the α phase
ρ^{α}	Density of the α phase
$\boldsymbol{\phi}^{\alpha_j}$	Entropy flux vector for the jth component in α phase
$\boldsymbol{\phi}^{\alpha}$	Entropy flux vector for α phase
$\hat{\Phi}_{\alpha_j}^{\beta}$	Entropy transfer to the jth component in α phase from β phase
$\hat{\Phi}_{\alpha}^{\beta}$	Entropy transfer to α phase from β phase

Superscripts, Subscripts, and Other Notations

a	Air phase
A	Particle composed of solid phase and the vicinal fluid
wA	Vicinal water in the particle
sA	Solid phase in the particle
f	Fluid composed of vicinal water and the bulk phase fluid
j	jth component of species

l	Liquid phase
s	Solid phase
vs	The viscoelastic part
$(\cdot)_0$	Initial value of $(\cdot)$
α	α phase
$\hat{(\cdot)}_{\alpha}^{\beta}$	Exchange from β phase to α phase
$(\cdot)^{\alpha,s}$	Difference of two quantities $((\cdot)^{\alpha} - (\cdot)^{s})$
$\frac{D^{\alpha_j}(\cdot)}{Dt}$	Material time derivative of a variable with respect to velocity of jth component in the α phase

1 Introduction

A porous medium in this study is a solid matrix with fluid-filled pores. A deforming porous medium is one that swells or shrinks upon liquid absorption or desorption. Examples of swelling porous media include clays, biopolymers, and cell membranes. A porous medium is considered saturated with a fluid phase when its pores are completely filled with that fluid phase. When two or more fluid phases are present in the pores, the material is called unsaturated. In many practical applications, swelling systems can be unsaturated, e.g., in the case of drying of wood and food materials (Datta 2007; Perre and Turner 1999), and transport in soils (Carminati et al. 2008; Purandara et al. 2008). The swelling behavior of a porous medium (saturated or unsaturated) results from interactions at different spatial scales, and therefore, researchers have developed multiscale thermomechanical models to study heat and mass transport in multiphase swelling porous systems (Achanta 1995; Bennethum and Cushman 1996b; Murad et al. 1995; Murad and Cushman 1996, 1997, 2000; Bennethum et al. 2000; Schrefler 2002; Singh et al. 2003a,b; Weinstein et al. 2008).

Approaches used to develop macroscopic theories can be broadly classified into three categories—averaging or macroscopization theories, theory of mixtures, and hybrid theories of the first two. In macroscopization theories, conservation laws as well as empirical constitutive relations are introduced at the microscale, and then, averaging is done to obtain relationships at the macroscale. In the theory of mixtures, conservation laws are stated at the macroscale, and then, the entropy inequality (from second law of thermodynamics) is exploited to obtain constitutive relations at the macroscale. Since the entropy inequality is not used by the macroscopization theories, relationships among macroscopic thermodynamic variables cannot be obtained (Hassanizadeh and Gray 1990). On the contrary, mixture theories may overlook the essential features of multiphase systems as little information of the microscale is used (Hassanizadeh and Gray 1990). The third category contains various theories which are hybrids of the first two. As the name suggests, Hybrid Mixture Theory (HMT), introduced by Hassanizadeh and Gray (1979a,b), is one of the approaches from the third category, which has been extensively used to study swelling porous systems. In this approach, conservation laws are written at the microscale before introducing the constitutive relations, and then, an averaging procedure is performed to obtain conservation equations at higher scales. The entropy inequality is then applied at the macroscale to derive constitutive relations such as Fick's law of gas diffusion and Darcy's law of water flow. While developing HMT for a swelling system, interactions at two or three spatial scales are considered depending on the requirements and complexity of the modeling system. The advantages of HMT over all the other approaches are explained in detail by Achanta (1995).

1.1 Viscoelastic Deformation of the Solid

Several swelling porous materials, such as biologic tissues, food materials, and polymer foams, exhibit viscoelastic behavior. This viscoelastic behavior can result either from interaction between the elastic solid skeleton and the viscous fluid(s) present in the pores, or from viscoelasticity of the solid skeleton itself. For example, in the multiscale fluid transport model developed by Achanta and Cushman (1994); Achanta et al. (1994) and Achanta (1995), the solid phase is assumed to be elastic at the microscale, and the interaction between the elastic solid and the viscous fluid results in only short memory at the macroscale. This short memory may not be adequate to fully capture the viscoelastic effects in all situations. Therefore, in Singh's study (Singh et al. 2003a,b; Singh 2002), the viscoelastic effects are captured by including higher order material time derivatives of the macroscopic Green strain tensor of the solid phase, $\overset{(n)s}{\mathbf{E}}$, to enable a generalized Kelvin–Voigt model.

Many of the detailed transport studies on swelling porous media have been on saturated systems, where the deformation of the solid is given by change in fluid volume fraction only, and the solid deformation equation is not required. Few researchers discuss the deformation of the solid phase or the coupling between the liquid transport and the solid deformation. Singh et al. (2003a,b) considered an unsaturated system; however, the second fluid phase is assumed to be immobile. The immobility of one fluid phase makes the system essentially saturated; and under these conditions, the ratio of volume fraction of the immobile phase to the volume fraction of the solid skeleton remains constant. Many simplifications can be made on the basis of this constant ratio. If we assume that the second bulk phase is able to move freely, then this constant ratio relationship does not hold anymore. In such a case, the fluid transport equation needs to be solved simultaneously with the solid phase equations.

Murad and Cushman (1996) considered deformation for an elastic solid and assumed linearity, which only allows for small strain. Schrefler (2002) proposed a constitutive model for the solid deformation; however, elastoplasticity has been assumed. Bennethum (2007) discussed deformation and derived a generalized Terzaghi stress principle for swelling porous materials considering a saturated swelling porous system. However, a detailed study on the deformation of the nonlinear viscoelastic solid in unsaturated swelling systems is not available in the literature.

1.2 Three-scale Swelling Systems

While applying HMT to a particular system, many studies consider phenomena at three spatial scales: micro-, meso-, and macro-scales. At the microscale, the vicinal fluid and the solid matrix exist as separate phases. At the mesoscale, the solid matrix and the vicinal fluid are considered together as a homogenous mixture representing a particle; and the liquid(s) and/or gaseous bulk fluid(s) are separated from this particle. At the macroscale, the particle and the bulk fluid(s) form overlaying continua. Although a three-scale theory seems to be a more general approach of developing a model for swelling systems, complexities arise in the treatment of vicinal and bulk phases of a fluid, and while coupling the transport equation with the deformation of the solid in an unsaturated case.

In the three-scale model developed by Singh (2002) and Singh et al. (2003a,b), the vicinal phase and the bulk phase conservation equations of a mobile fluid were added to obtain a combined transport equation for the fluid. This addition of equations is necessary as only overall transport properties of the fluid can be obtained through experiments. Separate information about the vicinal phase and the bulk phase is not available. The major assumptions made to obtain a single transport equation for the mobile fluid are that the micro- and macropores drain at the same rate, i.e., the permeabilities of the micro- and the macro-pores are equal, and the volume fraction of the vicinal phase of the fluid is always proportional to the volume fraction of the bulk fluid. However, both the assumptions are difficult to justify. For example, in plants, the permeability of cell wall (micropores) is of the order of 10^{-21} m^2, while the permeability of extracellular space (macropores) is 10^{-17} m^2. Similarly, in the wood drying literature, it is well established that until the moisture content reaches the Fiber Saturation Point (FSP), all the moisture is in a vicinal state. Another problem with the three-scale model is that the separation of the volume fractions of the solid phase and the vicinal fluid cannot be achieved as the volume fraction of the particle (composed of the solid phase and the vicinal water) is chosen as an independent variable. The upscaling technique is slightly modified in Cushman et al. (2004) and, in the conservation equations, whenever the volume fraction and the density of the vicinal fluid appear as a product, the volume fraction of vicinal water is separated. However, in all other cases, it remains difficult to separate them without making further assumptions, which are not always justifiable (Refer to Appendix B for details).

To summarize, although the three-scale theory is more general, it also has more parameters, and thus, its implementation requires much more information about the system than what is available from experiments. Current applications of the three-scale theory make assumptions to simplify the system, some of which are not justified under all conditions. (See Appendix B)

1.3 Objectives of the Study

We develop a two-scale thermomechanical theory for an unsaturated swellable porous system, which includes a solid porous skeleton, a liquid, and an air phase. The solid skeleton is considered as viscoelastic of generalized Kelvin–Voigt type, while both the liquid and air phases are considered as viscous. Large deformation of the solid is considered and discussed in detail in this manuscript.

In the first part of this article, modified constitutive equations, Darcy's law for the liquid and Cauchy stress–strain relationship for the solid are derived. In the second part of this article, we develop a model for isothermal conditions in which the viscoelastic deformation of the solid phase and the flow of the fluid are fully coupled. We present a derivation of the transport equation by combining the conservation of mass of the liquid phase and Darcy's law. An investigation of the constitutive relationship between the stress and the strain of the solid phase is also presented in detail.

2 Model Development: Constitutive Relations

The methodology followed to arrive at the constitutive relations is outlined in Fig. 1. Mass, momentum, energy, and entropy conservation equations are written for all the phases at the microscale, and are then, upscaled to the macroscale. Then, we select a set of macroscopic independent variables which is assumed to fully capture the behavior of the system. Helmholtz free energy of each of the phases is assumed to be dependent on a subset of the independent variables. Using these dependencies, the total entropy for the system is then obtained by adding the entropies of all the constituents. Restrictions on the constitutive relationships are then obtained by exploiting the entropy inequality in the sense of Coleman and Noll (1963). Some of these restrictions hold only at equilibrium and are, thus, called equilibrium restrictions; while some others are true regardless of the state of the system and are called nonequilibrium restrictions. New forms of Darcy's law and Cauchy stress–strain relationship are then obtained when a near-equilibrium state is considered.

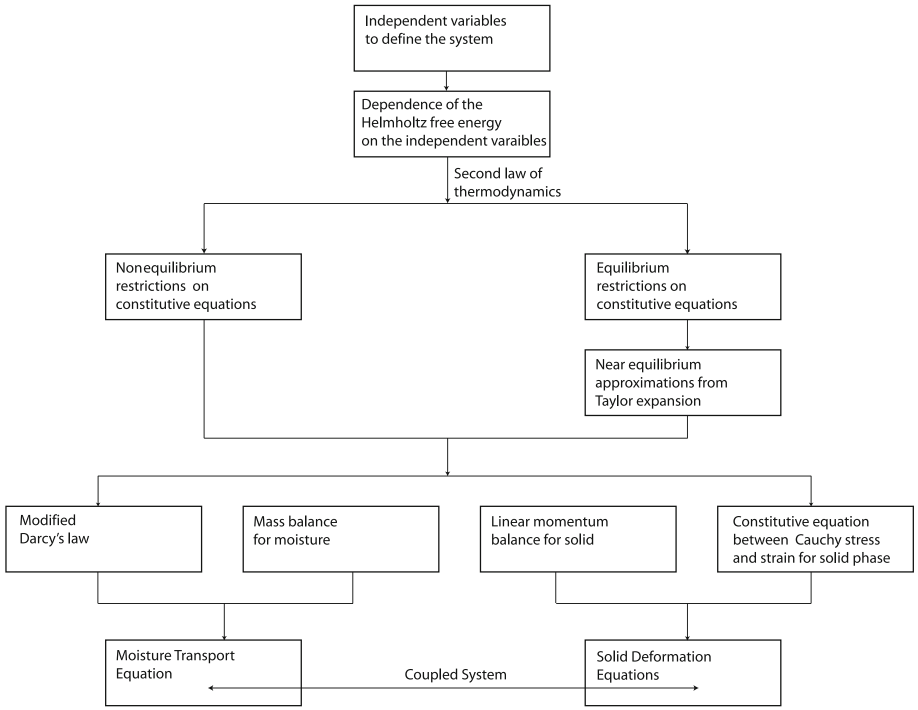

Fig. 1 Methodology followed to derive the coupled model

The conservation laws for all the three phases, solid, liquid, and air, are listed in Appendix A. These conservation laws are obtained from Bennethum and Cushman (1996a). In this section, we use the Coleman and Noll (1963) procedure to impose restrictions on the constitutive relations.

2.1 Development of Expressions for Free Energies and Entropy

We consider three phases in the system: the solid phase denoted by s, fluid l, and air a (Fig. 2). The solid is considered as viscoelastic, and both fluids are taken as viscous in nature. We make the following assumptions:

1. Both the solid and the liquid phases are incompressible.
2. All constituents are chemically nonreacting, and dissolution of air in the fluid is assumed to be negligible.
3. Local thermodynamic equilibrium exists so that only one temperature and one energy equation are needed.
4. The system is thermodynamically simple following Eringen (1994), which means that the entropy flux is due to heat flux alone and the external supplies (sources) are due to heat alone.
5. There are no interfacial effects.

The starting point of constitutive modeling is the selection of a set of independent variables to describe the system. The choice is based on the nature of the system as well as experience.

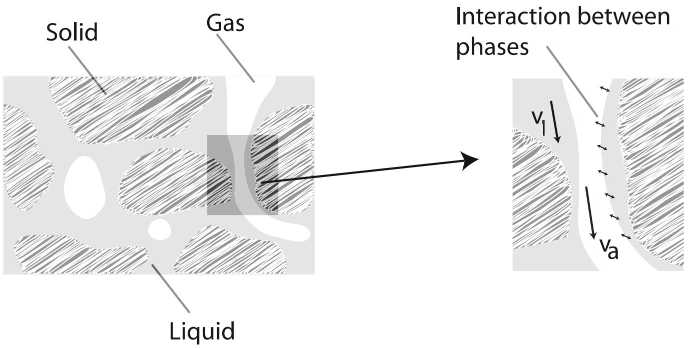

Fig. 2 Schematic of the porous medium showing the three phases and interactions between the phases

We choose the following independent variables to define the system:

$$\begin{aligned}&\epsilon^{l}, \nabla\epsilon^{l}, \overset{(m)l}{\epsilon}, \nabla \overset{(m)l}{\epsilon}, \epsilon^{s}, \nabla\epsilon^{s}, J^{s}, \bar{\mathbf{C}}^{s}, \overset{(n)s}{\bar{\mathbf{C}}}, C^{s_j}, T, \nabla T,\\ &\rho^{l}, \mathbf{d}^{l}, C^{l_j}, \mathbf{v}^{\alpha,s}, \mathbf{v}^{\alpha_j,s}, \nabla\mathbf{v}^{\alpha_j,s}, \rho^{a}, \mathbf{d}^{a}, C^{a_j}\end{aligned} \tag{2.1}$$

where $m = 1, \ldots p$ and $n = 1, \ldots q$ denote the material time derivatives of order m and n. The complete list of variables along with descriptions is available in the nomenclature.

Here, only ϵ^{l} and ϵ^{s}, volume fractions of liquid and solid, respectively, are chosen because ϵ^{a}, volume fraction of air, is related through

$$\epsilon^{s} + \epsilon^{l} + \epsilon^{a} = 1 \tag{2.2}$$

As is discussed by Weinstein and Bennethum (2006), the Green strain tensor $\mathbf{E}^{s}$, the density ρ^{s}, and the solid phase volume fraction ϵ^{s} are dependent due to mass conservation of the solid phase. Therefore, instead of choosing $\mathbf{E}^{s}$, ρ^{s}, and ϵ^{s} as independent variables, we follow Weinstein and Bennethum (2006) and consider the multiplicative decomposition of the deformation gradient F^{s}:

$$\bar{\mathbf{F}}^{s} = J^{s-\frac{1}{3}}\mathbf{F}^{s} \tag{2.3}$$

Then, we consider a new strain measure given by:

$$\bar{\mathbf{C}}^{s} = (\bar{\mathbf{F}}^{s})^{T}\bar{\mathbf{F}}^{s} \tag{2.4}$$

This multiplicative decomposition of the deformation gradient was originally proposed by Flory (1961) and successful applications include Simo and Hughes (1997) in the context of finite strain viscoelasticity. We use J^{s} and $\bar{\mathbf{C}}^{s}$ to replace $\mathbf{E}^{s}$ and ρ^{s}, respectively. More discussion on the advantage of this replacement could be found in Weinstein et al. (2008). The higher order derivatives of $\bar{\mathbf{C}}^{s}$ and ϵ^{l} are also included to ensure that the solid phase is modeled as a Kelvin–Voigt solid. The viscous nature of the two fluids are represented by the rate of deformation tensors, $\mathbf{d}^{l}$ and $\mathbf{d}^{a}$ respectively, which are all macroscopic variables. We choose temperature instead of entropy as an independent variable because entropy could hardly be measured, while we could easily measure temperature. Moreover, we could perform a Legendre transformation to convert the internal energy into the Helmhotlz free energy (Atkins and de Paula 2002).

Table 1 Dependence of Helmholz free energies on independent variables

Helmholtz free energy	Volume fraction	Density	Mass concentration	Deformation	Temperature	Viscoelastic effects
Liquid, A^{l}	$\epsilon^{l}, \epsilon^{s}$	ρ^{l}	C^{lj}	$\bar{\mathbf{C}}^{s}$	T	$\overset{(n)s}{\bar{\mathbf{C}}}, \overset{(m)l}{\epsilon}$
Solid, A^{s}	$\epsilon^{l}, \epsilon^{s}$	None	C^{sj}	$J^{s}, \bar{\mathbf{C}}^{s}$	T	$\overset{(n)s}{\bar{\mathbf{C}}}, \overset{(m)l}{\epsilon}$
Gas, A^{a}	$\epsilon^{l}, \epsilon^{s}$	ρ^{a}	C^{aj}	None	T	None

Note that we are taking the solid phase as the reference phase and in what follows the time derivatives follow the velocity of the solid phase:

$$\dot{(\cdot)} = \frac{D^{s}(\cdot)}{Dt} = \frac{\partial(\cdot)}{\partial t} + \mathbf{v}^{s} \cdot \nabla(\cdot) \tag{2.5}$$

$$\overset{(m)}{(\cdot)} = \frac{D^{sm}(\cdot)}{Dt^{m}} \tag{2.6}$$

We postulate the forms of the Helmholtz free energies as being dependent only on a subset of the independent variables based on the physical characteristic of the system:

$$A^{s} = A^{s}(\epsilon^{s}, J^{s}, \bar{\mathbf{C}}^{s}, \overset{(n)s}{\bar{\mathbf{C}}}, \epsilon^{l}, \overset{(m)l}{\epsilon}, C^{sj}, T) \tag{2.7}$$

$$A^{l} = A^{l}(\epsilon^{s}, \bar{\mathbf{C}}^{s}, \overset{(n)s}{\bar{\mathbf{C}}}, \epsilon^{l}, \overset{(m)l}{\epsilon}, \rho^{l}, C^{lj}, T) \tag{2.8}$$

$$A^{a} = A^{a}(\epsilon^{s}, \epsilon^{l}, \rho^{a}, C^{aj}, T) \tag{2.9}$$

Here, the liquid and the solid Helmholtz energies are functions of the state of the system (volume fractions, densities, mass fractions of constituents, deformation, and temperature) as well as some of their histories (viscoelastic effects). The interactions between the solid and the liquid are accounted for by the dependence of the solid and liquid Helmholtz energies on cross terms, ϵ^{l}, $\overset{(m)l}{\epsilon}$ and $\bar{\mathbf{C}}^{s}$, $\overset{(n)s}{\bar{\mathbf{C}}}$, respectively. Helmholtz energy of air does not have any viscoelastic effects (Table 1).

Total derivatives of the free energies are involved in the entropy inequality. Therefore, to explore the entropy inequality, we need to calculate the total derivatives of the free energies using the chain rule. We use the following identities to obtain the material derivatives of the free energies:

$$\frac{D^{\alpha}(\cdot)}{Dt} = \frac{D^{s}(\cdot)}{Dt} + \mathbf{v}^{\alpha,s} \cdot \nabla(\cdot) \tag{2.10}$$

where

$$\mathbf{v}^{\alpha,s} = \mathbf{v}^{\alpha} - \mathbf{v}^{s} \tag{2.11}$$

denotes the relative velocity of the α phase with respect to the solid phase.

Since $C^{\alpha N}$ is a dependent variable as listed in Appendix A (A.136), this gives rise to the relative chemical potential:

$$\tilde{\mu}^{\alpha j} \equiv \mu^{\alpha j} - \mu^{\alpha N} \tag{2.12}$$

where

$$\mu^{\alpha_j} \equiv \frac{\partial A^\alpha}{\partial C^{\alpha_j}} \tag{2.13}$$

Then, the material time derivatives of the free energies are given as

$$\begin{aligned}\frac{D^{\mathrm{s}} A^{\mathrm{s}}}{Dt} &= \frac{\partial A^{\mathrm{s}}}{\partial \epsilon^{\mathrm{l}}}\dot{\epsilon}^{\mathrm{l}} + \frac{\partial A^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}}\dot{\epsilon}^{\mathrm{s}} + \frac{\partial A^{\mathrm{s}}}{\partial T}\dot{T} + \frac{\partial A^{\mathrm{s}}}{\partial J^{\mathrm{s}}}\dot{J}^{\mathrm{s}} + \sum_{j=1}^{N-1} \tilde{\mu}^{\mathrm{s}_j} \dot{C}^{\mathrm{s}_j} + \sum_{m=1}^{p} \frac{\partial A^{\mathrm{s}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}} \overset{(m+1)\mathrm{l}}{\epsilon} \\ &\quad + \frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \dot{\bar{\mathbf{C}}}^{\mathrm{s}} + \sum_{n=1}^{q} \frac{\partial A^{\mathrm{s}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \overset{(n+1)\mathrm{s}}{\bar{\mathbf{C}}}\end{aligned} \tag{2.14}$$

$$\begin{aligned}\frac{D^{\mathrm{l}} A^{\mathrm{l}}}{Dt} &= \frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\dot{\epsilon}^{\mathrm{l}} + \frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}\dot{\epsilon}^{\mathrm{s}} + \frac{\partial A^{\mathrm{l}}}{\partial T}\dot{T} + \frac{\partial A^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}}\dot{\rho}^{\mathrm{l}} + \sum_{j=1}^{N-1} \tilde{\mu}^{\mathrm{l}_j} \dot{C}^{\mathrm{l}_j} + \sum_{m=1}^{p} \frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}} \overset{(m+1)\mathrm{l}}{\epsilon} \\ &\quad + \frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \dot{\bar{\mathbf{C}}}^{\mathrm{s}} + \sum_{n=1}^{q} \frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \overset{(n+1)\mathrm{s}}{\bar{\mathbf{C}}} + \frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\mathbf{v}^{\mathrm{l,s}} \cdot \nabla \epsilon^{\mathrm{l}} + \frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}\mathbf{v}^{\mathrm{l,s}} \cdot \nabla \epsilon^{\mathrm{s}} \\ &\quad + \frac{\partial A^{\mathrm{l}}}{\partial T}\mathbf{v}^{\mathrm{l,s}} \cdot \nabla T + \frac{\partial A^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}}\mathbf{v}^{\mathrm{l,s}} \cdot \nabla \rho^{\mathrm{l}} + \sum_{j=1}^{N-1} \tilde{\mu}^{\mathrm{l}_j} \mathbf{v}^{\mathrm{l,s}} \cdot \nabla C^{\mathrm{l}_j} \\ &\quad + \frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \nabla \bar{\mathbf{C}}^{\mathrm{s}} \cdot \mathbf{v}^{\mathrm{l,s}} + \sum_{n=1}^{q} \frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} \cdot \mathbf{v}^{\mathrm{l,s}} + \sum_{m=1}^{p} \frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}} \mathbf{v}^{\mathrm{l,s}} \cdot \nabla \overset{(m)\mathrm{l}}{\epsilon}\end{aligned} \tag{2.15}$$

$$\begin{aligned}\frac{D^{\mathrm{a}} A^{\mathrm{a}}}{Dt} &= \frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{l}}}\dot{\epsilon}^{\mathrm{l}} + \frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{s}}}\dot{\epsilon}^{\mathrm{s}} + \frac{\partial A^{\mathrm{a}}}{\partial T}\dot{T} + \frac{\partial A^{\mathrm{a}}}{\partial \rho^{\mathrm{a}}}\dot{\rho}^{\mathrm{a}} + \sum_{j=1}^{N-1} \tilde{\mu}^{\mathrm{a}_j} \dot{C}^{\mathrm{a}_j} + \frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{l}}}\mathbf{v}^{\mathrm{a,s}} \cdot \nabla \epsilon^{\mathrm{l}} \\ &\quad + \frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{s}}}\mathbf{v}^{\mathrm{a,s}} \cdot \nabla \epsilon^{\mathrm{s}} + \frac{\partial A^{\mathrm{a}}}{\partial T}\mathbf{v}^{\mathrm{a,s}} \cdot \nabla T + \frac{\partial A^{\mathrm{a}}}{\partial \rho^{\mathrm{a}}}\mathbf{v}^{\mathrm{a,s}} \cdot \nabla \rho^{\mathrm{a}} \\ &\quad + \sum_{j=1}^{N-1} \tilde{\mu}^{\mathrm{a}_j} \mathbf{v}^{\mathrm{a,s}} \cdot \nabla C^{\mathrm{a}_j}\end{aligned} \tag{2.16}$$

The material time derivatives of the free energies are then inserted in the total entropy inequality for the system (given by A.168). Mass conservation equations are weakly imposed in the entropy inequality using Lagrange multipliers in the sense of Liu (1972):

$$\begin{aligned}\Lambda_{\text{new}} = \Lambda_{\text{old}} &+ \sum_{\alpha} \frac{\lambda^\alpha}{T} \left[\frac{D^\alpha (\epsilon^\alpha \rho^\alpha)}{Dt} + \epsilon^\alpha \rho^\alpha \nabla \cdot \mathbf{v}^\alpha - \sum_{\alpha, \alpha \neq \beta} \hat{e}_\alpha^\beta \right] \\ &+ \sum_{\alpha} \sum_{j=1}^{N} \frac{\lambda^{\alpha_j}}{T} \left[\epsilon^\alpha \rho^\alpha \frac{D^\alpha C^{\alpha_j}}{Dt} + \nabla \cdot (\epsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha}) \right] \\ &- \sum_{\alpha} \sum_{j=1}^{N} \frac{\lambda^{\alpha_j}}{T} \left[\left(\sum_{\alpha, \alpha \neq \beta} \hat{e}_{\alpha_j}^\beta + \hat{r}^{\alpha_j} - C^{\alpha_j} \sum_{\alpha, \alpha \neq \beta} \hat{e}_\alpha^\beta \right) \right] \geq 0\end{aligned} \tag{2.17}$$

where Λ_{old} is given in Appendix A (A.168).

The entropy inequality is then given as

$$
\begin{aligned}
\Lambda = & -\frac{1}{T}\left(\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial T}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial T}+\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial T}+\eta^{\mathrm{s}}+\eta^{\mathrm{l}}+\eta^{\mathrm{a}}\right)\dot{T} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{s}}\rho^{s}\frac{\partial A^{\mathrm{s}}}{\partial \epsilon^{\mathrm{l}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}+\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{l}}}-\lambda^{\mathrm{l}}\rho^{\mathrm{l}}+\lambda^{\mathrm{a}}\rho^{\mathrm{a}}\right)\dot{\epsilon}^{\mathrm{l}} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \epsilon^{\mathrm{s}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}+\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{s}}}+\lambda^{\mathrm{a}}\rho^{\mathrm{a}}\right)\dot{\epsilon}^{\mathrm{s}} \\
& -\frac{1}{T}\left[\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial J^{\mathrm{s}}}-\frac{1}{3}\epsilon^{\mathrm{s}}\frac{1}{J^{\mathrm{s}}}\sum tr(\mathbf{t}^{\mathrm{s}j})\right]\dot{J}^{\mathrm{s}} \\
& -\frac{1}{T}\sum_{\alpha}\sum_{j=1}^{N}\epsilon^{\alpha}\rho^{\alpha}(\tilde{\mu}^{\alpha j}-\lambda^{\alpha j})\dot{C}^{\alpha j} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{s}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}\right)\overset{(m+1)\mathrm{l}}{\epsilon} \\
& -\frac{1}{T}\left[\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{s}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}}\right]:\overset{(n+1)\mathrm{s}}{\bar{\mathbf{C}}} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}}-\lambda^{\mathrm{l}}\epsilon^{\mathrm{l}}\right)\dot{\rho}^{\mathrm{l}} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \rho^{\mathrm{a}}}-\lambda^{\mathrm{a}}\epsilon^{\mathrm{a}}\right)\dot{\rho}^{\mathrm{a}} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{j=1}^{N-1}\tilde{\mu}^{\mathrm{l}j}\nabla C^{\mathrm{l}j}\right. \\
& +\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}:\nabla\bar{\mathbf{C}}^{\mathrm{s}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}}:\nabla\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} \\
& \left.+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}-\lambda^{\mathrm{l}}\rho^{\mathrm{l}}\nabla\epsilon^{\mathrm{l}}+\sum_{\beta\neq\mathrm{l}}\hat{\mathbf{T}}_{\mathrm{l}}^{\beta}-\lambda^{\mathrm{l}j}\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\nabla C^{\mathrm{s}j}\right)\mathbf{v}^{\mathrm{l,s}} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}}+\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}}-\lambda^{\mathrm{a}}\rho^{\mathrm{a}}\nabla\epsilon^{\mathrm{a}}+\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\sum_{j=1}^{N-1}\tilde{\mu}^{\mathrm{a}j}\nabla C^{\mathrm{a}j}\right. \\
& \left.+\sum_{\beta\neq\mathrm{a}}\hat{\mathbf{T}}_{\mathrm{a}}^{\beta}-\lambda^{\mathrm{a}j}\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\nabla C^{\mathrm{a}j}\right)\mathbf{v}^{\mathrm{a,s}} \\
& -\frac{1}{T}\left(\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}-\frac{\epsilon^{\mathrm{s}}}{2}(\bar{\mathbf{F}}^{\mathrm{s}})^{-1}\sum_{j=1}^{N}\mathbf{t}^{\mathrm{s}j}(\bar{\mathbf{F}}^{\mathrm{s}})^{-T}-\frac{\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\lambda^{\mathrm{s}}}{2}(\bar{\mathbf{F}}^{\mathrm{s}})^{-1}(\bar{\mathbf{F}}^{\mathrm{s}})^{-T}\right):\dot{\bar{\mathbf{C}}}^{\mathrm{s}} \\
& +\frac{\epsilon^{\mathrm{l}}}{T}\left(\sum_{j=1}^{N}\mathbf{t}^{\mathrm{l}j}+\lambda^{\mathrm{l}}\rho^{\mathrm{l}}\mathbf{I}\right):\mathbf{d}^{\mathrm{l}}
\end{aligned}
$$

$$
\begin{aligned}
&+\frac{\epsilon^{\mathrm{a}}}{T}\left(\sum_{j=1}^{N}\mathbf{t}^{\mathrm{a}_j}+\lambda^{\mathrm{a}}\rho^{\mathrm{a}}\mathbf{I}\right):\mathbf{d}^{\mathrm{a}}\\
&+\sum_{\alpha}\frac{\epsilon^{\alpha}}{T}\left(\mathbf{q}^{\alpha}-\sum_{j=1}^{N}\left[\mathbf{t}^{\alpha_j}\cdot\mathbf{v}^{\alpha_j,\alpha}-\rho^{\alpha_j}\mathbf{v}^{\alpha_j,\alpha}(A^{\alpha_j}+\frac{1}{2}(\mathbf{v}^{\alpha_j,\alpha})^2)\right]\right)\cdot\nabla T\\
&+\sum_{\alpha}\sum_{j=1}^{N-1}\frac{\epsilon^{\alpha}}{T}\left(\mathbf{t}^{\alpha_j}-\rho^{\alpha_j}A^{\alpha_j}\mathbf{I}-\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}}\mathbf{t}^{\alpha_N}+\rho^{\alpha_j}A^{\alpha_N}\mathbf{I}+\rho^{\alpha_j}\lambda^{\alpha_j}\mathbf{I}-\rho^{\alpha_j}\lambda^{\alpha_N}\mathbf{I}\right)\cdot\nabla\mathbf{v}^{\alpha_j,\alpha}\\
&+\frac{1}{T}\sum_{j=1}^{N-1}\left[\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}}(\hat{\mathbf{T}}^{\beta}_{\alpha_N}+\hat{\mathbf{i}}^{\alpha_N})-(\hat{\mathbf{T}}^{\beta}_{\alpha_j}+\hat{\mathbf{i}}^{\alpha_j})-\nabla[\epsilon^{\alpha}\rho^{\alpha_j}(A^{\alpha_N}-A^{\alpha_j})]\right.\\
&\left.+(\lambda^{\alpha_j}-\lambda^{\alpha_N})\nabla(\epsilon^{\alpha}\rho^{\alpha_j})-\epsilon^{\alpha}\mathbf{t}^{\alpha_N}\nabla(\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}})\right]\cdot\mathbf{v}^{\alpha_j,\alpha}\\
&-\frac{1}{T}\sum_{j=1}^{N}\hat{\mathbf{r}}^{\alpha_j}\left[\lambda^{\alpha_j}+\frac{1}{2}(\mathbf{v}^{\alpha_j,\alpha})^2\right]\\
&-\frac{1}{T}\sum_{\alpha}\sum_{\beta\neq\alpha}\hat{e}^{\beta}_{\alpha}\left[-\sum_{j=1}^{N-1}\lambda^{\alpha_j}C^{\alpha_j}+\lambda^{\alpha}+A^{\alpha}+\frac{1}{2}(\mathbf{v}^{\mathrm{a,s}})^2+\frac{1}{2}(\mathbf{v}^{\mathrm{a,s}})^2\right]\\
&-\frac{1}{T}\sum_{\alpha}\sum_{j=1}^{N-1}\hat{e}^{\beta}_{\alpha_j}\left[\lambda^{\alpha_j}+\frac{1}{2}(\mathbf{v}^{\alpha_j,\alpha})^2\right]\geq 0
\end{aligned}
\tag{2.18}
$$

Since ρ^{s} is not chosen as an independent variable, we have used the determinant of the deformation gradient tensor, J^{s}:

$$
\rho^{\mathrm{s}}\epsilon^{\mathrm{s}}=\frac{\epsilon^{\mathrm{s}}_0\rho^{\mathrm{s}}_0}{J^{\mathrm{s}}}
\tag{2.19}
$$

in the entropy inequality above, to express $\dot{\rho}^{\mathrm{s}}$ in terms of other independent variables:

$$
\begin{aligned}
&\frac{\lambda^{\mathrm{s}}}{T}\left[\frac{D^{\mathrm{s}}(\rho^{\mathrm{s}}\epsilon^{\mathrm{s}})}{Dt}+\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\nabla\cdot\mathbf{v}^{\mathrm{s}}-\sum_{\beta\neq\mathrm{s}}\hat{e}^{\beta}_{\mathrm{s}}\right]\\
&\quad=\frac{\lambda^{\mathrm{s}}}{T}\left[\frac{D^{\mathrm{s}}(\frac{\epsilon^{\mathrm{s}}_0\rho^{\mathrm{s}}_0}{J^{\mathrm{s}}})}{Dt}+\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\nabla\cdot\mathbf{v}^{\mathrm{s}}-\sum_{\beta\neq\mathrm{s}}\hat{e}^{\beta}_{\mathrm{s}}\right]\\
&\quad=\frac{\lambda^{\mathrm{s}}}{T}\left[-\frac{\epsilon^{\mathrm{s}}_0\rho^{\mathrm{s}}_0\dot{J}^{\mathrm{s}}}{(J^{\mathrm{s}})^2}+\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\mathbf{d}^{\mathrm{s}}:\mathbf{I}-\sum_{\beta\neq\mathrm{s}}\hat{e}^{\beta}_{\mathrm{s}}\right]\\
&\quad=\frac{\lambda^{\mathrm{s}}}{T}\left[-\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\dot{J}^{\mathrm{s}}}{J^{\mathrm{s}}}+\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{1}{2}((\bar{\mathbf{F}}^{\mathrm{s}})^{-1}(\bar{\mathbf{F}}^{\mathrm{s}})^{-T}):\dot{\bar{\mathbf{C}}}^{\mathrm{s}}+\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\dot{J}^{\mathrm{s}}}{J^{\mathrm{s}}}-\sum_{\beta\neq\mathrm{s}}\hat{e}^{\beta}_{\mathrm{s}}\right]\\
&\quad=\frac{\lambda^{\mathrm{s}}}{T}\left[\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{1}{2}((\bar{\mathbf{F}}^{\mathrm{s}})^{-1}(\bar{\mathbf{F}}^{\mathrm{s}})^{-T}):\dot{\bar{\mathbf{C}}}^{\mathrm{s}}-\sum_{\beta\neq\mathrm{s}}\hat{e}^{\beta}_{\mathrm{s}}\right]
\end{aligned}
\tag{2.20}
$$

where $\mathbf{d}^{\mathrm{s}} : \mathbf{I}$ is calculated as

$$\mathbf{d}^{\mathrm{s}} : \mathbf{I} = \frac{1}{2}((\bar{\mathbf{F}}^{\mathrm{s}})^{-1}(\bar{\mathbf{F}}^{\mathrm{s}})^{-T}) : \dot{\bar{\mathbf{C}}}^{\mathrm{s}} + \frac{\dot{J}^{\mathrm{s}}}{J^{\mathrm{s}}} \tag{2.21}$$

The details of this calculation can be found in Weinstein et al. (2008), where $\mathbf{d}^{\mathrm{s}}$ is rewritten in terms of J^{s} and $\bar{\mathbf{C}}^{\mathrm{s}}$.

In order to remove dependence on velocities of the Nth components of the phases (more later), we have used (Holzapfel 2000):

$$\sum_{j=1}^{N} \mathbf{F}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j,\alpha} = \sum_{j=1}^{N-1} \left(\mathbf{F}^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \mathbf{F}^{\alpha_N} \right) \cdot \mathbf{v}^{\alpha_j,\alpha} \tag{2.22}$$

$$\sum_{j=1}^{N} \mathbf{G}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j,\alpha} = \sum_{j=1}^{N-1} \left(\mathbf{G}^{\alpha_j} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \mathbf{G}^{\alpha_N} \right) : \nabla \mathbf{v}^{\alpha_j,\alpha} - \mathbf{G}^{\alpha_N} \sum_{j=1}^{N-1} \nabla \left(\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}} \right) \cdot \mathbf{v}^{\alpha_j,\alpha} \tag{2.23}$$

2.2 Nonequilibrium Restrictions

We first consider that the system is in a stationary state far from thermodynamic equilibrium. Following the procedure of Coleman and Noll (1963), the variables $\dot{T}$, $\dot{J}^{\mathrm{s}}$, $\nabla \mathbf{v}^{\mathrm{s}_j,\mathrm{s}}$, $\dot{C}^{\alpha_j}$, $\dot{\rho}^{\alpha}$, $\overset{(q+1)\mathrm{s}}{\bar{\mathbf{C}}}$, and $\overset{(p+1)l}{\epsilon}$ in the entropy inequality are not in our list of dependent variables or in that of independent variables, and thus, they are neither dependent nor independent. Since they could vary arbitrarily, the coefficients of these variables in the entropy inequality must vanish. Thus, the following nonequilibrium results are obtained:

$$\sum_{\alpha} \left(\frac{\partial A^{\alpha}}{\partial T} + \eta^{\alpha} \right) = 0 \tag{2.24}$$

$$\frac{1}{3} \sum_{j=1}^{N} tr(\mathbf{t}^{\mathrm{s}_j}) = -p^{\mathrm{s}} \tag{2.25}$$

where

$$tr(\mathbf{x}) = \sum_{i} \mathbf{x}_{ii} \tag{2.26}$$

and the physical pressure is given by (Bennethum and Weinstein 2004)

$$p^{\mathrm{s}} = -\rho^{\mathrm{s}} J^{\mathrm{s}} \frac{\partial A^{\mathrm{s}}}{\partial J^{\mathrm{s}}}\bigg|_{\epsilon^{\mathrm{s}}} \tag{2.27}$$

$$\sum_{j=1}^{N} \mathbf{t}^{\mathrm{s}_j} = \rho^{\mathrm{s}_j} (A^{\mathrm{s}_j} - A^{\mathrm{s}_N} - \tilde{\mu}^{\mathrm{s}_j}) \mathbf{I} + \frac{\rho^{\mathrm{s}_j}}{\rho^{\mathrm{s}_N}} \mathbf{t}^{\mathrm{s}_N} \tag{2.28}$$

$$\tilde{\mu}^{\alpha_j} = \lambda^{\alpha_j} \tag{2.29}$$

$$\lambda^{\mathrm{l}} = \rho^{\mathrm{l}} \frac{\partial A^{\mathrm{l}}}{\partial \rho^{\mathrm{l}}}|_{\epsilon^{\mathrm{l}}} = \frac{p^{\mathrm{l}}}{\rho^{\mathrm{l}}} \tag{2.30}$$

$$\lambda^{\mathrm{a}} = \rho^{\mathrm{a}} \frac{\partial A^{\mathrm{a}}}{\partial \rho^{\mathrm{a}}}|_{\epsilon^{\mathrm{a}}} = \frac{p^{\mathrm{a}}}{\rho^{\mathrm{a}}} \tag{2.31}$$

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \overset{(q)\mathrm{s}}{\bar{\mathbf{C}}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(q)\mathrm{s}}{\bar{\mathbf{C}}}}=0 \tag{2.32}$$

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \overset{(p)\mathrm{l}}{\epsilon}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(p)\mathrm{l}}{\epsilon}}=0 \tag{2.33}$$

Since temperature and entropy are conjugate thermodynamic variables for a single phase, for Eq. 2.24, we further assume that entropy of each phase is related to temperature through

$$\eta^{\alpha}=-\frac{\partial A^{\alpha}}{\partial T},\quad \alpha=s,\ l,\ a \tag{2.34}$$

If we assume that there is only one species in the solid phase or if we assume that the diffusive velocity in the solid phase is negligible, then Eq. 2.25 would become

$$\frac{1}{3}tr(\mathbf{t}^{\mathrm{s}})=-p^{\mathrm{s}} \tag{2.35}$$

Eqs. 2.30 and 2.31 will be used throughout this article. In this section and hereafter, not all the relationships are listed as some are not needed in the model development.

2.3 Equilibrium Restrictions

Next we explore information from the entropy inequality when the system is at an equilibrium state. The total rate of entropy production, Λ, reaches its minimum value at equilibrium. When the system is in thermodynamic equilibrium, the state variables do not change with time, and therefore, the following variables are zero at thermodynamic equilibrium:

$$\dot{\epsilon}^{\mathrm{l}},\ \dot{\epsilon}^{\mathrm{s}},\ \overset{(m)\mathrm{l}}{\epsilon},\ \overset{(n+1)\mathrm{s}}{\bar{\mathbf{C}}},\ \mathbf{v}^{\mathrm{l,s}},\ \mathbf{v}^{\mathrm{a,s}},\ \mathbf{d}^{\mathrm{l}},\ \mathbf{d}^{\mathrm{a}},\ \nabla T,\ \mathbf{v}^{\alpha_j,\alpha},\ \nabla\mathbf{v}^{\mathrm{l}_j,\mathrm{l}},\ \nabla\mathbf{v}^{\mathrm{a}_j,\mathrm{a}},\ \hat{e}^{\beta}_{\alpha_j},\ \hat{e}^{\beta}_{\alpha},\ \dot{\bar{\mathbf{C}}}^{\mathrm{s}} \tag{2.36}$$

If we denote these variables as x and y, then the necessary and sufficient conditions for Λ to be at a minimum at thermodynamic equilibrium is

$$\left(\frac{\partial\Lambda}{\partial x}\right)_{\mathrm{eq}}=0 \tag{2.37}$$

and

$$\left\|\left(\frac{\partial^2\Lambda}{\partial x\partial y}\right)_{\mathrm{eq}}\right\| \text{be positive semi-definite} \tag{2.38}$$

Using these conditions, we can obtain the following relations at equilibrium:

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial\epsilon^{\mathrm{l}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}}+\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial\epsilon^{\mathrm{l}}}-p^{\mathrm{l}}+p^{\mathrm{a}}=0 \tag{2.39}$$

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial\epsilon^{\mathrm{s}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{s}}}+\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{a}}{\partial\epsilon^{\mathrm{s}}}+p^{\mathrm{a}}=0 \tag{2.40}$$

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}=0 \tag{2.41}$$

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}}+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}}=0 \tag{2.42}$$

$$\mathbf{t}^{\mathrm{l}} = -p^{\mathrm{l}}\mathbf{I} \tag{2.43}$$

$$\mathbf{t}^{\mathrm{a}} = -p^{\mathrm{a}}\mathbf{I} \tag{2.44}$$

$$\begin{aligned}&\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}} + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}} - p^{\mathrm{l}}\nabla\epsilon^{\mathrm{l}} + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} \\ &+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}\nabla \overset{(m)\mathrm{l}}{\epsilon} + \sum_{\beta\neq \mathrm{l}}\hat{\mathbf{T}}_{\mathrm{l}}^{\beta} = 0\end{aligned} \tag{2.45}$$

$$\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}} + \epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}} - p^{\mathrm{a}}\nabla\epsilon^{\mathrm{a}} + \sum_{\beta\neq \mathrm{a}}\hat{\mathbf{T}}_{\mathrm{a}}^{\beta} = 0 \tag{2.46}$$

$$\sum_{\alpha}\epsilon^{\alpha}\mathbf{q}^{\alpha} = 0 \tag{2.47}$$

$$\begin{aligned}&\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}}(\hat{\mathbf{T}}^{\beta}_{\alpha_N} + \hat{\mathbf{i}}^{\alpha_N}) - (\hat{\mathbf{T}}^{\beta}_{\alpha_j} + \hat{\mathbf{i}}^{\alpha_j}) - \nabla[\epsilon^{\alpha}\rho^{\alpha_j}(A^{\alpha_N} - A^{\alpha_j})] \\ &+(\lambda^{\alpha_j} - \lambda^{\alpha_N})\nabla(\epsilon^{\alpha}\rho^{\alpha_j}) - \epsilon^{\alpha}\mathbf{t}^{\alpha_N}\nabla\left(\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}}\right) = 0\end{aligned} \tag{2.48}$$

$$\mathbf{t}^{\alpha_j} - \rho^{\alpha_j}A^{\alpha_j}\mathbf{I} - \frac{\rho^{\alpha_j}}{\rho^{\alpha_N}}\mathbf{t}^{\alpha_N} + \rho^{\alpha_j}A^{\alpha_N}\mathbf{I} + \rho^{\alpha_j}\lambda^{\alpha_j}\mathbf{I} = 0, \quad \alpha = l, a \tag{2.49}$$

$$-\sum_{j=1}^{N-1}\lambda^{\alpha_j}C^{\alpha_j} + \lambda^{\alpha} + A^{\alpha} + \frac{1}{2}(\mathbf{v}^{\mathrm{a,s}})^2 + \frac{1}{2}(\mathbf{v}^{\mathrm{l,s}})^2 = 0 \tag{2.50}$$

$$\tilde{\mu}^{\mathrm{s}_j} = \tilde{\mu}^{\mathrm{l}_j} = \tilde{\mu}^{\mathrm{a}_j} \tag{2.51}$$

$$\mathbf{t}^{\mathrm{s}} = -\lambda^{\mathrm{s}}\rho^{\mathrm{s}}\mathbf{I} + 2\frac{\epsilon^{\mathrm{l}}}{\epsilon^{\mathrm{s}}}\rho^{\mathrm{l}}\bar{\mathbf{F}}^{\mathrm{s}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}(\bar{\mathbf{F}}^{\mathrm{s}})^{T} + 2\rho^{\mathrm{s}}\bar{\mathbf{F}}^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}(\bar{\mathbf{F}}^{\mathrm{s}})^{T} \tag{2.52}$$

$$A^{\alpha} + \lambda^{\alpha} - \sum_{j=1}^{N-1}\tilde{\mu}^{\alpha_j}C^{\alpha_j} = A^{\beta} + \lambda^{\beta} - \sum_{j=1}^{N-1}\tilde{\mu}^{\beta_j}C^{\beta_j}, \quad \alpha \neq \beta \tag{2.53}$$

Since ρ^{s} is not taken as an independent variable, we have replaced the term involving $\dot{\rho}^{\mathrm{s}}$ in the entropy inequality. Thus, there is no equation for λ^{s}. We take $\frac{1}{3}$ of the trace of (2.52), use (2.35), and solve for λ^{s} (Weinstein and Bennethum 2006):

$$\lambda^{\mathrm{s}} = \frac{p^{\mathrm{s}}}{\rho^{\mathrm{s}}} + \frac{2}{3}\frac{\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}}{\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \bar{\mathbf{C}}^{\mathrm{s}} + \frac{2}{3}\frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \bar{\mathbf{C}}^{\mathrm{s}} \tag{2.54}$$

Then,

$$\begin{aligned}\mathbf{t}^{\mathrm{s}} = &-p^{\mathrm{s}}\mathbf{I} + 2\frac{\epsilon^{\mathrm{l}}}{\epsilon^{\mathrm{s}}}\rho^{\mathrm{l}}\bar{\mathbf{F}}^{\mathrm{s}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}(\bar{\mathbf{F}}^{\mathrm{s}})^{T} + 2\rho^{\mathrm{s}}\bar{\mathbf{F}}^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}(\bar{\mathbf{F}}^{\mathrm{s}})^{T} \\ &-\frac{2}{3}\frac{\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}}{\epsilon^{\mathrm{s}}}\left(\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \bar{\mathbf{C}}^{\mathrm{s}}\right)\mathbf{I} - \frac{2}{3}\rho^{\mathrm{s}}\left(\frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \bar{\mathbf{C}}^{\mathrm{s}}\right)\mathbf{I}\end{aligned} \tag{2.55}$$

We write out the Terzaghi stress $\mathbf{t}^{\mathrm{se}}$ and the hydration stress $\mathbf{t}^{\mathrm{sh}}$ as

$$\mathbf{t}^{\mathrm{se}} = 2\left[\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\bar{\mathbf{F}}^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}(\bar{\mathbf{F}}^{\mathrm{s}})^{T} - \frac{1}{3}\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\left(\frac{\partial A^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \bar{\mathbf{C}}^{\mathrm{s}}\right)\mathbf{I}\right] \tag{2.56}$$

$$\mathbf{t}^{\mathrm{sh}} = 2\left[\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\bar{\mathbf{F}}^{\mathrm{s}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}}(\bar{\mathbf{F}}^{\mathrm{s}})^{T} - \frac{1}{3}\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\left(\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \bar{\mathbf{C}}^{\mathrm{s}}\right)\mathbf{I}\right] \tag{2.57}$$

Then the equilibrium result for the Cauchy stress is of the following form:

$$\epsilon^{s}\mathbf{t}^{s} = -\epsilon^{s} p^{s}\mathbf{I} + \mathbf{t}^{sh} + \mathbf{t}^{se} \tag{2.58}$$

2.4 Removing *N*th Component Dependence

The relationships we obtained based on HMT for the species are expressed relative to the Nth constituent. In classical Gibbsian thermodynamics, however, since extensive variables, such as number of molecules of each constituent, rather than intensive variables, such as concentrations, are chosen as independent variables, Nth components do not appear in the species equations. Here, we follow Bennethum et al. (1997) and find out the results that are in accordance with the classic Gibbsian thermodynamics. In order to do so, we use the definition of the Nth chemical potential μ^{α_N} by Bennethum et al. (1996) and remove the Nth component dependence. We take:

$$\mu^{\alpha_N}\mathbf{I} = A^{\alpha_N}\mathbf{I} - \frac{\mathbf{t}^{\alpha_N}}{\rho^{\alpha_N}}, \quad \alpha = l, a \tag{2.59}$$

$$\mu^{s_N}\mathbf{I} = A^{s_N}\mathbf{I} - \frac{\mathbf{t}^{s_N}}{\rho^{s_N}} + \frac{\mathbf{t}^{se}}{\rho^{s}} + \frac{\epsilon^{l}}{\epsilon^{s}}\frac{\mathbf{t}^{sh}}{\rho^{s}} \tag{2.60}$$

Substituting Eqs. 2.59 and 2.60 into Eqs. 2.49 and 2.50, respectively, we obtain:

$$\mu^{\alpha_j}\mathbf{I} = A^{\alpha_j}\mathbf{I} - \frac{\mathbf{t}^{\alpha_j}}{\rho^{\alpha_j}}, \quad \alpha = l, a \tag{2.61}$$

$$\mu^{s_j}\mathbf{I} = A^{s_j}\mathbf{I} - \frac{\mathbf{t}^{s_j}}{\rho^{s_j}} + \frac{\mathbf{t}^{se}}{\rho^{s}} + \frac{\epsilon^{l}}{\epsilon^{s}}\frac{\mathbf{t}^{sh}}{\rho^{s}} \tag{2.62}$$

Multiplying Eqs. 2.61 and 2.62 by C^{α_j} and C^{s_j}, respectively, summing over all species and substituting $\mathbf{t}^{\alpha}$ with Eqs. 2.43, 2.44, and 2.58, we obtain the Gibbs free energies:

$$G^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j}\mu^{\alpha_j} = A^{\alpha} + \frac{p^{\alpha}}{\rho^{\alpha}} \tag{2.63}$$

$$G^{s} = \sum_{j=1}^{N} C^{s_j}\mu^{s_j} = A^{s} + \frac{p^{s}}{\rho^{s}} \tag{2.64}$$

We rewrite Eq. 2.53 as:

$$A^{\alpha} + \lambda^{\alpha} - \sum_{j=1}^{N}\mu^{\alpha_j}C^{\alpha_j} + \mu^{\alpha_N} = A^{\beta} + \lambda^{\beta} - \sum_{j=1}^{N}\mu^{\beta_j}C^{\beta_j} + \mu^{\beta_N} \tag{2.65}$$

Substituting λ^{α} using Eqs. 2.30, 2.31, and 2.54 and using Eqs. 2.63 and 2.64, we obtain:

$$\mu^{\alpha_N} = \mu^{\beta_N}, \quad \alpha \neq \beta \tag{2.66}$$

Therefore, the classical result is obtained as

$$\mu^{\alpha_j} = \mu^{\beta_j}, \quad \alpha \neq \beta \tag{2.67}$$

In order to remove Nth component dependence from Eq. 2.48, we sum from $j = 1$ to N:

$$\frac{\rho^{\alpha_j}}{\rho^{\alpha_N}}\left(\sum_{\beta\neq\alpha}\hat{\mathbf{T}}^{\beta}_{\alpha_N}+\hat{\mathbf{i}}^{\alpha_N}\right)-\sum_{\beta\neq\alpha}\hat{\mathbf{T}}^{\beta}_{\alpha}+\nabla(\epsilon^{\alpha}\rho^{\alpha}A^{\alpha_N})-\epsilon^{\alpha}\rho^{\alpha}(\nabla A^{\alpha})-A^{\alpha}\nabla(\epsilon^{\alpha}\rho^{\alpha})$$
$$+\sum_{j=1}^{N}\tilde{\mu}^{\alpha_j}\nabla(\epsilon^{\alpha}\rho^{\alpha_j})-\epsilon^{\alpha}\mathbf{t}^{\alpha_N}\nabla\left(\frac{\rho^{\alpha}}{\rho^{\alpha_N}}\right)=0,\quad \alpha=l,a \tag{2.68}$$

Expanding ∇A^{α} using Eqs. 2.7–2.9 yields

$$\nabla A^{\mathrm{s}}=\frac{\partial A^{\mathrm{s}}}{\partial\epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}}+\frac{\partial A^{\mathrm{s}}}{\partial T}\nabla T+\frac{\partial A^{\mathrm{s}}}{\partial J^{\mathrm{s}}}\nabla J^{\mathrm{s}}+\sum_{j=1}^{N-1}\tilde{\mu}^{\mathrm{s}_j}\nabla C^{\mathrm{s}_j}$$
$$+\sum_{m=1}^{p}\frac{\partial A^{\mathrm{s}}}{\partial\overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}+\sum_{n=0}^{q}\frac{\partial A^{\mathrm{s}}}{\partial\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}}:\nabla\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} \tag{2.69}$$

$$\nabla A^{\mathrm{l}}=\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}}+\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}}+\frac{\partial A^{\mathrm{l}}}{\partial T}\nabla T+\frac{\partial A^{\mathrm{l}}}{\partial\rho^{\mathrm{l}}}\nabla\rho^{\mathrm{l}}+\sum_{j=1}^{N-1}\tilde{\mu}^{\mathrm{l}_j}\nabla C^{\mathrm{l}_j}$$
$$+\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}+\sum_{n=0}^{q}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}}:\nabla\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} \tag{2.70}$$

$$\nabla A^{\mathrm{a}}=\frac{\partial A^{\mathrm{a}}}{\partial\epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}}+\frac{\partial A^{\mathrm{a}}}{\partial\epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}}+\frac{\partial A^{\mathrm{a}}}{\partial T}\nabla T+\frac{\partial A^{\mathrm{a}}}{\partial\rho^{\mathrm{a}}}\nabla\rho^{\mathrm{a}}+\sum_{j=1}^{N-1}\tilde{\mu}^{\mathrm{a}_j}\nabla C^{\mathrm{a}_j} \tag{2.71}$$

Substituting ∇A^{α} and $\sum_{\beta\neq\alpha}\hat{\mathbf{T}}^{\beta}_{\alpha}$ into Eq. 2.68, for phase l, we get

$$\frac{\rho^{\mathrm{l}}}{\rho^{\mathrm{l}_N}}(\hat{\mathbf{T}}^{\mathrm{s}}_{\mathrm{l}_N}+\hat{\mathbf{T}}^{\mathrm{a}}_{\mathrm{l}_N}+\hat{\mathbf{i}}^{\mathrm{l}_N})-p^{\mathrm{l}}\nabla\epsilon^{\mathrm{l}}+\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}A^{\mathrm{l}_N})-\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\rho^{\mathrm{l}}}\nabla\rho^{\mathrm{l}}-\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{j=1}^{N-1}\tilde{\mu}^{\mathrm{l}_j}\nabla C^{\mathrm{l}_j}$$
$$-A^{\mathrm{l}}\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}})+\sum_{j=1}^{N}\tilde{\mu}^{\mathrm{l}_j}\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}_j})-\epsilon^{\mathrm{l}}\mathbf{t}^{\mathrm{l}_N}\nabla\left(\frac{\rho^{\mathrm{l}}}{\rho^{\mathrm{l}_N}}\right)=0 \tag{2.72}$$

where we have ignored the term involving ∇T since it is zero at equilibrium. If we write out $\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}_j})=\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\nabla C^{\mathrm{l}_j}+C^{\mathrm{l}_j}\nabla\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}$ and simplify, the above equation becomes

$$\frac{\rho^{\mathrm{l}}}{\rho^{\mathrm{l}_N}}(\hat{\mathbf{T}}^{\mathrm{s}}_{\mathrm{l}_N}+\hat{\mathbf{T}}^{\mathrm{a}}_{l_N}+\hat{\mathbf{i}}^{l_N})-\epsilon^{\mathrm{l}}\mathbf{t}^{\mathrm{l}_N}\nabla(\frac{\rho^{\mathrm{l}}}{\rho^{\mathrm{l}_N}})+\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}A^{\mathrm{l}_N})-\mu^{\mathrm{l}_N}\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}})$$
$$=p^{\mathrm{l}}\nabla\epsilon^{\mathrm{l}}+A^{\mathrm{l}}\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}})-\sum_{j=1}^{N}\mu^{\mathrm{l}_j}C^{\mathrm{l}_j}\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}})-\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\rho^{\mathrm{l}}}\nabla\rho^{\mathrm{l}} \tag{2.73}$$

We substitute the third term on the right-hand side using Eq. 2.63 and use the definition that $p^{\mathrm{l}}=(\rho^{\mathrm{l}})^2\frac{\partial A^{\mathrm{l}}}{\partial\rho^{\mathrm{l}}}$ in the above equation to obtain

$$\frac{\rho^{\mathrm{l}}}{\rho^{\mathrm{l}_N}}(\hat{\mathbf{T}}^{\mathrm{s}}_{\mathrm{l}_N}+\hat{\mathbf{T}}^{\mathrm{a}}_{\mathrm{l}_N}+\hat{\mathbf{i}}^{\mathrm{l}_N})-\epsilon^{\mathrm{l}}\mathbf{t}^{\mathrm{l}_N}\nabla\left(\frac{\rho^{\mathrm{l}}}{\rho^{\mathrm{l}_N}}\right)+\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}A^{\mathrm{l}_N})-\mu^{\mathrm{l}_N}\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}})=0 \tag{2.74}$$

Substituting Eq. 2.74 back into Eq. 2.68 and undoing the sum yields

$$\sum_{\beta\neq \mathrm{l}} \hat{\mathbf{T}}^{\beta}_{\mathrm{l}_j} + \hat{\mathbf{i}}^{\mathrm{l}j} = \mu^{\mathrm{l}j}\nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}j}) - \nabla(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}A^{\mathrm{l}j}) \tag{2.75}$$

Following the same procedure, we could find that for phase a we obtain exactly the same form as (2.75). Thus, removing the Nth component dependence from Eq. 2.48, we obtain

$$\sum_{\beta\neq \alpha} \hat{\mathbf{T}}^{\beta}_{\alpha_j} + \hat{\mathbf{i}}^{\alpha j} = \mu^{\alpha j}\nabla(\epsilon^{\alpha}\rho^{\alpha j}) - \nabla(\epsilon^{\alpha}\rho^{\alpha}A^{\alpha j}), \quad \alpha = l, a \tag{2.76}$$

2.5 Near-Equilibrium Results

Other useful information such as Darcy's and Fick's laws could be obtained when we consider the systems to be at a state near equilibrium. Here, we use Taylor's expansion about variables that become zero at equilibrium (2.36) and truncate all second-order and higher-order terms to obtain near-equilibrium results. Taking Taylor's expansion of $\mathbf{t}^{\mathrm{s}}$ about ∇T and $\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}$ (two of the several variables that go to zero at equilibrium) and retaining only linear terms, we perform a two-term linearization (as discussed in Singh et al. (2003a)) and obtain:

$$\epsilon^{\mathrm{s}}\mathbf{t}^{\mathrm{s}} = -\epsilon^{\mathrm{s}}p^{\mathrm{s}}\mathbf{I} + \mathbf{t}^{\mathrm{sh}} + \mathbf{t}^{\mathrm{se}} + \sum_{n=1}^{q} \bar{\mathbf{F}}^{\mathrm{s}}\mathbf{A}^{n} : \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}\,(\bar{\mathbf{F}}^{\mathrm{s}})^{T} + \mathbf{H}^{\mathrm{s}} : \nabla T \tag{2.77}$$

$$\mathbf{t}^{\mathrm{l}} = -p^{\mathrm{l}}\mathbf{I} - \sum_{j=1}^{N} \rho^{\mathrm{l}j}\mathbf{v}^{\mathrm{l}j,\mathrm{l}}\mathbf{v}^{\mathrm{l}j,\mathrm{l}} + \mathbf{B}^{\mathrm{l}} : \mathbf{d}^{\mathrm{l}} + \mathbf{H}^{\mathrm{l}} : \nabla T \tag{2.78}$$

$$\mathbf{t}^{\mathrm{a}} = -p^{\mathrm{a}}\mathbf{I} - \sum_{j=1}^{N} \rho^{\mathrm{a}j}\mathbf{v}^{\mathrm{a}j,\mathrm{a}}\mathbf{v}^{\mathrm{a}j,\mathrm{a}} + \mathbf{B}^{\mathrm{a}} : \mathbf{d}^{\mathrm{a}} + \mathbf{H}^{\mathrm{a}} : \nabla T \tag{2.79}$$

We perform a linearization about $\dot{\epsilon}^{\mathrm{l}}$ and $\dot{\epsilon}^{\mathrm{s}}$ and obtain

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial\epsilon^{\mathrm{l}}} + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}} + \epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial\epsilon^{\mathrm{l}}} - p^{\mathrm{l}} + p^{\mathrm{a}} = -M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}} \tag{2.80}$$

$$\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial\epsilon^{\mathrm{s}}} + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{s}}} + \epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial\epsilon^{\mathrm{s}}} + p^{\mathrm{a}} = -M^{\mathrm{s}}\dot{\epsilon}^{\mathrm{s}} \tag{2.81}$$

The following is obtained by a linearization about $\mathbf{v}^{\mathrm{l,s}}$:

$$\begin{aligned}\sum_{\beta\neq \mathrm{l}} \hat{T}^{\beta}_{\mathrm{l}} &= -\mathbf{R}^{\mathrm{l}}\mathbf{v}^{\mathrm{l,s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}} + p^{\mathrm{l}}\nabla\epsilon^{\mathrm{l}} \\ &\quad -\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}\nabla \overset{(m)\mathrm{l}}{\epsilon}\end{aligned} \tag{2.82}$$

A linearization about $\mathbf{v}^{\mathrm{a,s}}$ gives

$$\sum_{\beta\neq \mathrm{a}} \hat{T}^{\beta}_{\mathrm{a}} = -\mathbf{R}^{\mathrm{a}}\mathbf{v}^{\mathrm{a,s}} - \epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial\epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial\epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}} + p^{\mathrm{a}}\nabla\epsilon^{\mathrm{a}} \tag{2.83}$$

Finally, we perform a linearization about ∇T:

$$\mathbf{q}^{\alpha} = \sum_{j=1}^{N} \left[\mathbf{t}^{\alpha j} \mathbf{v}^{\alpha j,\alpha} - \rho^{j} \mathbf{v}^{\alpha j,\alpha} \left(A^{\alpha j} + \frac{1}{2} \left(\mathbf{v}^{\alpha j,\alpha} \right)^{2} \right) \right] + \mathbf{K}^{\alpha} \cdot \nabla T, \quad \alpha = s,\ l,\ a \tag{2.84}$$

In Eq. 2.77, $\mathbf{A}^{n}$ is a fourth-order positive semi-definite tensor representing dissipation of the viscoelastic solid stress in shear due to relaxation. $\mathbf{H}^{\alpha}, \alpha = s,\ l,\ a$ in Eqs. 2.77, 2.78, and 2.79 are third-rank tensors, and thus, vanish when the material is isotropic. The terms involving $\mathbf{H}^{\alpha}, \alpha = s,\ l,\ a$ vanish when the solid phase is isotropic. $\mathbf{A}^{n}$ and $\mathbf{H}^{\mathrm{s}}$ are not functions of $\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}$ and ∇T, respectively. The quantity $\mathbf{B}^{\alpha}, \alpha = l,\ a$ are fourth-rank positive semi-definite tensors accounting for the viscous dissipation in the liquid and air phase, respectively. M^{s} and M^{l} in Eqs. 2.80 and 2.81 are material coefficients resulting from the Taylor expansion. In Eqs. 2.82 and 2.83, $\mathbf{R}^{\mathrm{l}}$ and $\mathbf{R}^{\mathrm{a}}$ are second rank tensors arising from the Taylor series expansion and represent resistance to the liquid and air flow, respectively. $\mathbf{K}^{\alpha}$ in Eq. 2.84 denotes a second-rank tensor.

2.6 Darcy's Law

We use Eq. 2.82 in the linear momentum balance (A.140) with $\alpha = l$, and we neglect the inertia term. Simplifying, we obtain Darcy's law for the liquid phase as

$$\mathbf{R}^{\mathrm{l}}\mathbf{v}^{\mathrm{l,s}} = -\epsilon^{\mathrm{l}}\nabla p^{\mathrm{l}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}$$

$$-\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}\nabla \overset{(m)\mathrm{l}}{\epsilon} + \nabla\cdot(\epsilon^{\mathrm{l}}\mathbf{B}^{\mathrm{l}} : \mathbf{d}^{\mathrm{l}}) + \nabla\cdot(\epsilon^{\mathrm{l}}\mathbf{H}^{\mathrm{l}} : \nabla T) + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\mathbf{g} \tag{2.85}$$

The first term on the right-hand side is the primary driving force in classical Darcy's law for nonswelling media. This term represents flow due to a negative pressure gradient. The second and third terms denote flow due to the gradient of the volume fraction of the fluid and solid phases, respectively. The fourth term on the right-hand side was presented in Weinstein et al. (2008). The fourth and fifth terms were also first presented in Weinstein and Bennethum (2006). These terms are responsible for flow due to the effect of rate of shear on the free energy of the fluid. At moderate to high moisture content, as the solid phase alters the liquid free energy only through the normal component, these terms could be neglected. As ϵ^{l} is related to the normal component of the strain of the solid phase, the sixth term on the right-hand side represents the effect of the rate of expansion on the free energy of the fluid. The seventh term on the right-hand side is Brinkman's correction and is always neglected at slow velocity flows. The eighth term on the right-hand side was first mentioned in Singh et al. (2003a), and it represents flow due to thermal gradient in anisotropic materials. The last term represents gravity as a driving force.

3 Model Development: Governing Equations

In this section, a two-scale transport model is developed for an unsaturated swelling porous system based on the conservation laws listed in Appendix A and the constitutive relationships developed above. In this model, we assume isothermal conditions. Both the liquid phase and the solid skeleton are assumed to be isotropic and incompressible, while the “smeared-out” solid is compressible due to uptake/release of fluids. The effect of gravity is ignored.

3.1 Solid Phase

After ignoring the inertial terms, linear momentum balance (A.140) for the solid phase is given by

$$\nabla \cdot (\epsilon^{\mathrm{s}} \mathbf{t}^{\mathrm{s}}) = -\sum_{\beta \neq \mathrm{s}} \hat{\mathbf{T}}_{\mathrm{s}}^{\beta} \tag{3.86}$$

Since there is no mass transfer from other phases to the solid phase, summing over all N species, the restriction (A.146) becomes

$$-\sum_{\beta \neq \mathrm{s}} \hat{\mathbf{T}}_{\mathrm{s}}^{\beta} = \sum_{\beta \neq \mathrm{l}} \hat{\mathbf{T}}_{\mathrm{l}}^{\beta} + \sum_{\beta \neq \mathrm{a}} \hat{\mathbf{T}}_{\mathrm{a}}^{\beta} \tag{3.87}$$

We plug Eq. 2.85 into Eq. 2.82 and obtain

$$\sum_{\beta \neq \mathrm{l}} \hat{\mathbf{T}}_{\mathrm{l}}^{\beta} = \nabla(\epsilon^{\mathrm{l}} p^{\mathrm{l}}) \tag{3.88}$$

And similarly, the following is obtained when the air phase is considered:

$$\sum_{\beta \neq \mathrm{a}} \hat{\mathbf{T}}_{\mathrm{a}}^{\beta} = \nabla(\epsilon^{\mathrm{a}} p^{\mathrm{a}}) \tag{3.89}$$

With Eqs. 3.87, 3.88, and 3.89, linear momentum balance of the solid phase is finally given by

$$\nabla \cdot (\epsilon^{\mathrm{s}} \mathbf{t}^{\mathrm{s}}) = \nabla(\epsilon^{\mathrm{l}} p^{\mathrm{l}}) + \nabla(\epsilon^{\mathrm{a}} p^{\mathrm{a}}) \tag{3.90}$$

The right-hand side of the above equation has the linear momentum transported from the liquid and the air phases, to the solid phase, respectively. This indicates that the negative pressure gradient and the negative concentration gradient are the volumetric driving forces of the deformation. Since isotropy is assumed, the last term of Eq. 2.77 vanishes, and the constitutive relationship between the Cauchy stress tensor and the strain becomes

$$\epsilon^{\mathrm{s}} \mathbf{t}^{\mathrm{s}} = -\epsilon^{\mathrm{s}} p^{\mathrm{s}} \mathbf{I} + \mathbf{t}^{\mathrm{sh}} + \mathbf{t}^{\mathrm{se}} + \sum_{n=1}^{q} \bar{\mathbf{F}}^{\mathrm{s}} \mathbf{A}^{n} : \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} (\bar{\mathbf{F}}^{\mathrm{s}})^{T} \tag{3.91}$$

Since the solid phase is assumed to be isotropic, the energy is a function of the strain invariants (Ogden 1984).

$$A(I_1, I_2, I_3) = A(\bar{I}_1, \bar{I}_2, J^{\mathrm{s}}) \tag{3.92}$$

where $I_k, k = 1, 2, 3$ are the principal invariants of $\mathbf{C}^{\mathrm{s}}$, and the ones with bars denote the principal invariants of $\bar{\mathbf{C}}^{\mathrm{s}}$. They are related by

$$\bar{I}_k = (J^{\mathrm{s}})^{-\frac{2}{3}} I_k, \quad k = 1, 2 \tag{3.93}$$

For simplicity, we assume that the material is of the Neo-Hookean type. The modified form of the free energy to account for compressibility is given by Treloar (1943a,b); Holzapfel (2000)

$$\epsilon^{\alpha} \rho^{\alpha} A^{\alpha} = \epsilon_0^{\alpha} \rho^{\alpha} A_0^{\alpha} + \frac{\mu_{\alpha}}{2}(\bar{I}_1 - 3) + \frac{1}{d_{\alpha}}(J^{s} - 1)^2, \quad \alpha = s,\ l \tag{3.94}$$

where we only list terms related to $\bar{\mathbf{C}}^{\mathrm{s}}$. $A_0^\alpha = A^\alpha(\epsilon_0^\alpha)$ is the free energy evaluated at initial volume fraction. μ_α is the initial shear modulus of the α phase, while d_α is related to the initial bulk modulus of the α phase K^α by

$$\frac{2}{d_\alpha} = K^\alpha, \quad \alpha = s,\ l \tag{3.95}$$

In order to express Eq. 3.91 and write out the Cauchy stress, an explicit function of the strain, we take the partial derivative of A^α with respect to $\bar{\mathbf{C}}^{\mathrm{s}}$ using the chain rule:

$$\frac{\partial A^\alpha}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} = \frac{\partial A^\alpha}{\partial \bar{I}_1}\frac{\partial \bar{I}_1}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} + \frac{\partial A^\alpha}{\partial J^{\mathrm{s}}}\frac{\partial J^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} = \frac{\mu_\alpha}{2}\mathbf{I} + \frac{2}{d_\alpha}(J^{\mathrm{s}} - 1)\frac{\partial J^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} \tag{3.96}$$

where

$$\frac{\partial J^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} = \frac{\partial J^{\mathrm{s}}}{\partial \mathbf{C}^{\mathrm{s}}}\frac{\partial \mathbf{C}^{\mathrm{s}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} = \frac{1}{2}J^{\mathrm{s}}(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L} \tag{3.97}$$

where we have used the identity

$$\frac{\partial \det(\cdot)}{\partial(\cdot)} = \det(\cdot)(\cdot)^{-1} \tag{3.98}$$

and the fact that

$$J^{\mathrm{s}} = \sqrt{\det \mathbf{C}^{\mathrm{s}}} \tag{3.99}$$

In Eq. 3.97, $\mathbf{L}$ is a fourth-rank tensor, and its inverse is given by Simo and Hughes (1997)

$$\frac{\partial \bar{\mathbf{C}}^{\mathrm{s}}}{\partial \mathbf{C}^{\mathrm{s}}} = (J^{\mathrm{s}})^{-\frac{2}{3}}\left[\mathbf{I} - \frac{1}{3}\mathbf{C}^{\mathrm{s}} \otimes (\mathbf{C}^{\mathrm{s}})^{-1}\right] \tag{3.100}$$

The Terzaghi and hydration stresses become

$$\begin{aligned}\mathbf{t}^{\mathrm{se}} = 2\Big\{&\frac{\mu_{\mathrm{s}}}{2}\bar{\mathbf{F}}^{\mathrm{s}}(\bar{\mathbf{F}}^{\mathrm{s}})^T + \frac{K^{\mathrm{s}}}{2}J^{\mathrm{s}}(J^{\mathrm{s}} - 1)\bar{\mathbf{F}}^{\mathrm{s}}[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L}](\bar{\mathbf{F}}^{\mathrm{s}})^T \\ &-\frac{1}{3}\frac{\mu_{\mathrm{s}}}{2}tr(\bar{\mathbf{C}}^{\mathrm{s}})\mathbf{I} - \frac{K^{\mathrm{s}}}{6}J^{\mathrm{s}}(J^{\mathrm{s}} - 1)[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L} : \bar{\mathbf{C}}^{\mathrm{s}}]\mathbf{I}\Big\}\end{aligned} \tag{3.101}$$

$$\begin{aligned}\mathbf{t}^{\mathrm{sh}} = 2\Big\{&\frac{\mu_l}{2}\bar{\mathbf{F}}^{\mathrm{s}}(\bar{\mathbf{F}}^{\mathrm{s}})^T + \frac{K^{\mathrm{l}}}{2}J^{\mathrm{s}}(J^{\mathrm{s}} - 1)\bar{\mathbf{F}}^{\mathrm{s}}[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L}](\bar{\mathbf{F}}^{\mathrm{s}})^T \\ &-\frac{1}{3}\frac{\mu_l}{2}tr(\bar{\mathbf{C}}^{\mathrm{s}})\mathbf{I} - \frac{K^{\mathrm{l}}}{6}J^{\mathrm{s}}(J^{\mathrm{s}} - 1)[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L} : \bar{\mathbf{C}}^{\mathrm{s}}]\mathbf{I}\Big\}\end{aligned} \tag{3.102}$$

The pressure p^{s} is given by

$$p^{\mathrm{s}} = -\rho^{\mathrm{s}}J^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial J^{\mathrm{s}}} = -\frac{K^{\mathrm{s}}}{\epsilon_0^{\mathrm{s}}}(J^{\mathrm{s}3} - J^{\mathrm{s}2}) \tag{3.103}$$

Finally, the Cauchy stress tensor is given by

$$\begin{aligned}\epsilon^{\mathrm{s}}\mathbf{t}^{\mathrm{s}} = {} & \frac{K^{\mathrm{s}}}{\epsilon_0^{\mathrm{s}}}(J^{\mathrm{s}3} - J^{\mathrm{s}2})\mathbf{I} \\ & + \mu_{\mathrm{s}}\bar{\mathbf{F}}^{\mathrm{s}}(\bar{\mathbf{F}}^{\mathrm{s}})^T + K^{\mathrm{s}}(J^{\mathrm{s}2} - J^{\mathrm{s}})\bar{\mathbf{F}}^{\mathrm{s}}[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L}](\bar{\mathbf{F}}^{\mathrm{s}})^T \\ & - \frac{\mu_{\mathrm{s}}}{3}tr(\bar{\mathbf{C}}^{\mathrm{s}})\mathbf{I} - \frac{K^{l}}{3}(J^{\mathrm{s}2} - J^{\mathrm{s}})[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L} : \bar{\mathbf{C}}^{\mathrm{s}}]\mathbf{I} \\ & + \mu_{1}\bar{\mathbf{F}}^{\mathrm{s}}(\bar{\mathbf{F}}^{\mathrm{s}})^T + K^{1}(J^{\mathrm{s}2} - J^{\mathrm{s}})\bar{\mathbf{F}}^{\mathrm{s}}[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L}](\bar{\mathbf{F}}^{\mathrm{s}})^T \\ & - \frac{\mu_{1}}{3}tr(\bar{\mathbf{C}}^{\mathrm{s}})\mathbf{I} - \frac{K^{1}}{3}(J^{\mathrm{s}2} - J^{\mathrm{s}})[(\mathbf{C}^{\mathrm{s}})^{-1} : \mathbf{L} : \bar{\mathbf{C}}^{\mathrm{s}}]\mathbf{I} \\ & + \bar{\mathbf{F}}^{\mathrm{s}} \int_0^t \mathbf{G}(t - \tau) : \dot{\bar{\mathbf{C}}}^{\mathrm{s}} d\tau (\bar{\mathbf{F}}^{\mathrm{s}})^T \end{aligned} \tag{3.104}$$

where the last term is obtained by using the Laplace transform technique on the last term in Eq. 3.91. This procedure is explained below.

We first note that the relationship between the Cauchy stress tensor $\mathbf{t}^{\mathrm{s}}$ and the second Piola-Kirchhoff stress tensor $\mathbf{S}^{\mathrm{s}}$ is given by

$$\mathbf{S}^{\mathrm{s}} = J^{\mathrm{s}}\mathbf{F}^{\mathrm{s}-1}\mathbf{t}^{\mathrm{s}}\mathbf{F}^{\mathrm{s}-T} \tag{3.105}$$

Using Eqs. 3.105 and 2.3, we convert the last term in Eq. 3.91, $\sum_{n=1}^{q} \bar{\mathbf{F}}^{\mathrm{s}}\mathbf{A}^n : \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} (\bar{\mathbf{F}}^{\mathrm{s}})^T$, into the corresponding second Piola-Kirchhoff counterpart:

$$J^{\mathrm{s}-1/3}\epsilon^{\mathrm{s}}\mathbf{S}^{\mathrm{vs}} = \sum_{n=1}^{q} \mathbf{A}^n : \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} \tag{3.106}$$

Then, as $\mathbf{A}^n$ is not a function of $\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}$, it is possible that we take the Laplace transform of the above equation:

$$L(J^{\mathrm{s}-1/3}\epsilon^{\mathrm{s}}\mathbf{S}^{\mathrm{vs}}) = \sum_{n=1}^{q} s^{n-1}\mathbf{A}^n : \bar{\mathbf{C}}^{\mathrm{s}} s \tag{3.107}$$

The inverse transform of the above is then given by

$$J^{\mathrm{s}-1/3}\epsilon^{\mathrm{s}}\mathbf{S}^{\mathrm{vs}} = \int_0^t \sum_{n=1}^{q} \frac{d^{n-1}}{dt^{n-1}}\delta(t - \tau)\mathbf{A}^n : \dot{\bar{\mathbf{C}}}^{\mathrm{s}} d\tau \tag{3.108}$$

where $\delta(t)$ is the Dirac's delta function. Let

$$\mathbf{G}(t) \equiv \sum_{n=1}^{q} \mathbf{A}^n \frac{d^{n-1}}{dt^{n-1}}\delta(t) \tag{3.109}$$

where $\mathbf{G}$ is the relaxation function in shear. Equation 3.108 becomes

$$J^{\mathrm{s}-1/3}\epsilon^{\mathrm{s}}\mathbf{S}^{\mathrm{vs}} = \int_0^t \mathbf{G}(t - \tau) : \dot{\bar{\mathbf{C}}}^{\mathrm{s}} d\tau \tag{3.110}$$

The above is then converted back to the Cauchy form, and the last term in Eq. 3.104 is obtained.

3.2 Liquid Phase

Mass conservation of the liquid phase is given by Eq. A.130. We assume that there is no exchange of mass with other phases, so that the right-hand side of this equation vanishes and the equation becomes

$$\frac{D^{\mathrm{l}}(\epsilon^{\mathrm{l}}\rho^{\mathrm{l}})}{Dt} + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}(\nabla \cdot \mathbf{v}^{\mathrm{l}}) = 0 \tag{3.111}$$

Since relative velocity appears in Darcy's law, we rewrite Eq. 3.111 as

$$\dot{\epsilon}^{\mathrm{l}} + \nabla \cdot (\epsilon^{\mathrm{l}}\mathbf{v}^{\mathrm{l,s}}) + \epsilon^{\mathrm{l}}\nabla \cdot \mathbf{v}^{\mathrm{s}} = 0 \tag{3.112}$$

We rewrite Darcy's law (2.85) as

$$\begin{aligned}\mathbf{v}^{\mathrm{l,s}} = (\mathbf{R}^{\mathrm{l}})^{-1}\Bigg[& -\epsilon^{\mathrm{l}}\nabla p^{\mathrm{l}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}}\nabla\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} \\ & -\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}\nabla \overset{(m)\mathrm{l}}{\epsilon}\Bigg]\end{aligned} \tag{3.113}$$

We assume that the term $\epsilon^{\mathrm{s}}\rho^{\mathrm{s}}\frac{\partial A^{\mathrm{s}}}{\partial \epsilon^{\mathrm{l}}}$ and the term $\epsilon^{\mathrm{a}}\rho^{\mathrm{a}}\frac{\partial A^{\mathrm{a}}}{\partial \epsilon^{\mathrm{l}}}$ can be neglected in the capillary pressure result (2.80). The first term is neglected since layers of fluid molecules do not exert stress on molecules of the solid phase when the moisture content is not very low, i.e., when the moisture content is larger than that occupied by 10 fluid monolayers (Bennethum et al. 1997). The second term is ignored when we assume that the free energy of the air phase does not depend on the volume fraction of the liquid phase since the two phases interact only through the boundaries. Then,

$$-\pi^{\mathrm{l}} - p^{\mathrm{l}} + p^{\mathrm{a}} = -M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}} \tag{3.114}$$

where

$$\pi^{\mathrm{l}} = -\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \tag{3.115}$$

is the swelling pressure. This definition is consistent with that in Achanta and Cushman (1994). The negative sign takes into account the fact that fluid flows from regions of high swelling pressure to regions of low swelling pressure. Then Eq. 3.113 can be written as

$$\begin{aligned}\mathbf{v}^{\mathrm{l,s}} = (\mathbf{R}^{\mathrm{l}})^{-1}\Bigg[& -\epsilon^{\mathrm{l}}\nabla(-\pi^{\mathrm{l}} + M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}}) + \pi^{\mathrm{l}}\nabla\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{s}}}\nabla\epsilon^{\mathrm{s}} \\ & -\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial \bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla \overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial \overset{(m)\mathrm{l}}{\epsilon}}\nabla \overset{(m)\mathrm{l}}{\epsilon}\Bigg]\end{aligned} \tag{3.116}$$

where we have assumed that the air pressure is the atmospheric pressure, the gradient of which vanishes. Simplifying Eq. 3.116, we obtain

$$\begin{aligned}\mathbf{v}^{\mathrm{l,s}} = (\mathbf{R}^{\mathrm{l}})^{-1}\Bigg[& -\nabla(-\pi^{\mathrm{l}})\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{l}}\nabla(M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}}) + p^{\mathrm{a}}\nabla\epsilon^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} \\ & -\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}\Bigg]\end{aligned} \tag{3.117}$$

Here, we have used Eq. 2.81. We assumed that M^{s} is zero since it denotes the viscosity. In this case, the swelling pressure reduces to capillary pressure considering the relationship between swelling pressure and capillary pressure in Achanta and Cushman (1994). Substituting Eq. 3.117 into 3.112, we obtain

$$\begin{aligned}\dot{\epsilon}^{\mathrm{l}} + \nabla\cdot\Bigg\{\epsilon^{\mathrm{l}}(\mathbf{R}^{\mathrm{l}})^{-1}\Bigg[& -\nabla(-\pi^{\mathrm{l}})\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{l}}\nabla(M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}}) + p^{\mathrm{a}}\nabla\epsilon^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} \\ & -\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}\Bigg]\Bigg\} + \epsilon^{\mathrm{l}}\nabla\cdot\mathbf{v}^{\mathrm{s}} = 0\end{aligned} \tag{3.118}$$

We assume that the resistivity tensor $\mathbf{R}^{\mathrm{l}}$ is isotropic. The above equation can then be written as

$$\begin{aligned}\dot{\epsilon}^{\mathrm{l}} + \nabla\cdot\Bigg\{\epsilon^{\mathrm{l}}\frac{k^{\mathrm{l}}}{\mu}\mathbf{I}\Bigg[& -E^{\mathrm{l}}\nabla\epsilon^{\mathrm{l}} - \epsilon^{\mathrm{l}}\nabla(M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}}) + p^{\mathrm{a}}\nabla\epsilon^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}} \\ & -\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}\Bigg]\Bigg\} + \epsilon^{\mathrm{l}}\nabla\cdot\mathbf{v}^{\mathrm{s}} = 0\end{aligned} \tag{3.119}$$

where

$$\frac{k^{\mathrm{l}}}{\mu}\mathbf{I} = (\mathbf{R}^{\mathrm{l}})^{-1} \tag{3.120}$$

with k^{l}, the permeability and μ, the viscosity of the liquid phase. We have defined

$$E^{\mathrm{l}} \equiv -\frac{\partial(\pi^{\mathrm{l}}\epsilon^{\mathrm{l}})}{\partial\epsilon^{\mathrm{l}}} \tag{3.121}$$

We also define

$$D \equiv \frac{\epsilon^{\mathrm{l}}k^{\mathrm{l}}}{\mu}E^{\mathrm{l}} \tag{3.122}$$

which is the Darcian diffusion coefficient. Equation 3.119 is further simplified to

$$\dot{\epsilon}^{\mathrm{l}} - \nabla\cdot(D\nabla\epsilon^{\mathrm{l}}) - \nabla\cdot\left\{\epsilon^{\mathrm{l}}\frac{k^{\mathrm{l}}}{\mu}\mathbf{I}\left[\epsilon^{\mathrm{l}}\nabla(M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}}) - p^{\mathrm{a}}\nabla\epsilon^{\mathrm{s}} - \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}}\right.\right.$$

$$\left.\left.+\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{n=1}^{q}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}} : \nabla\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}} + \epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\sum_{m=1}^{p}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}\right]\right\} + \epsilon^{\mathrm{l}}\nabla\cdot\mathbf{v}^{\mathrm{s}} = 0 \qquad (3.123)$$

We assume that the free energy of the liquid phase A^{l} is linear in both $\overset{(m)\mathrm{l}}{\epsilon}, m = 1, \ldots, p$ and $\overset{(n)\mathrm{s}}{\bar{\mathbf{C}}}, n = 1, \ldots, q$, and initially, the material is free of strain and all its material time derivatives. We use the Laplace transform method and merge the term $\nabla(M^{\mathrm{l}}\dot{\epsilon}^{\mathrm{l}})$ with the term $\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\overset{(m)\mathrm{l}}{\epsilon}}\nabla\overset{(m)\mathrm{l}}{\epsilon}$. The details of the discussion can be found in Singh et al. (2003b). Here, we also assume that the air pressure is constant. We thus obtain a differential-integral form of the fluid transport equation:

$$\dot{\epsilon}^{\mathrm{l}} - \nabla\cdot(D\nabla\epsilon^{\mathrm{l}}) - \nabla\cdot\left[-\epsilon^{\mathrm{l}}\frac{k^{\mathrm{l}}}{\mu}p^{\mathrm{a}}\nabla\epsilon^{\mathrm{s}} + \epsilon^{\mathrm{l}}\frac{k^{\mathrm{l}}}{\mu^{\mathrm{l}}}\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\frac{\partial A^{\mathrm{l}}}{\partial\bar{\mathbf{C}}^{\mathrm{s}}} : \nabla\bar{\mathbf{C}}^{\mathrm{s}}\right.$$

$$\left.+\int_{0}^{t}B(t-\tau)(\nabla\dot{\epsilon}^{\mathrm{l}})d\tau + \int_{0}^{t}\mathbf{S}(t-\tau) : \nabla\dot{\bar{\mathbf{C}}}^{\mathrm{s}}d\tau\right] + \epsilon^{\mathrm{l}}\nabla\cdot\mathbf{v}^{\mathrm{s}} = 0 \qquad (3.124)$$

where we follow Singh et al. (2003b) and postulate that $B(t)$ and $\mathbf{S}(t)$ are related to the bulk and shear relaxation functions, respectively. According to Eq. 3.94, we work on the third term and obtain the transport equation:

$$\dot{\epsilon}^{\mathrm{l}} - \nabla\cdot(D\nabla\epsilon^{\mathrm{l}}) - \nabla\cdot\left\{-\epsilon^{\mathrm{l}}\frac{k^{\mathrm{l}}}{\mu}p^{\mathrm{a}}\nabla\epsilon^{\mathrm{s}} + \epsilon^{\mathrm{l}}\frac{k^{\mathrm{l}}}{\mu^{\mathrm{l}}}\left[\frac{\mu_{\mathrm{l}}}{2}\mathbf{I} + \frac{K_{\mathrm{l}}}{2}J^{\mathrm{s}}(J^{\mathrm{s}}-1)\mathbf{C}^{\mathrm{s}-1} : \mathbf{L}\right] : \nabla\bar{\mathbf{C}}^{\mathrm{s}}\right.$$

$$\left.+\int_{0}^{t}B(t-\tau)(\nabla\dot{\epsilon}^{\mathrm{l}})d\tau + \int_{0}^{t}\mathbf{S}(t-\tau) : \nabla\dot{\bar{\mathbf{C}}}^{\mathrm{s}}d\tau\right\} + \epsilon^{\mathrm{l}}\nabla\cdot\mathbf{v}^{\mathrm{s}} = 0 \qquad (3.125)$$

When the moisture content is moderate to high, namely, when the moisture content is larger than that occupied by 10 fluid monolayers (Bennethum et al. 1997), the above is simplified to

$$\dot{\epsilon}^{\mathrm{l}} - \nabla\cdot(D\nabla\epsilon^{\mathrm{l}}) - \nabla\cdot\left[-\epsilon^{\mathrm{l}}\frac{k^{\mathrm{l}}}{\mu}p^{\mathrm{a}}\nabla\epsilon^{\mathrm{s}} + \int_{0}^{t}B(t-\tau)(\nabla\dot{\epsilon}^{\mathrm{l}})d\tau\right] + \epsilon^{\mathrm{l}}\nabla\cdot\mathbf{v}^{\mathrm{s}} = 0 \qquad (3.126)$$

The transport equation is found to be coupled with the other two phases.

3.3 Summary of the Model

The unknowns of the unsaturated problem include ϵ^{l}, ϵ^{s}, and $\mathbf{u}^{\mathrm{s}}(\mathbf{v}^{\mathrm{s}})$, which are the volume fractions of the liquid and solid phase, respectively, and the displacement of the solid phase.

The initial-boundary value problem is composed of the transport equation (3.125) or (3.126) for ϵ^{l}, the mass conservation for the solid phase given by (2.19) for ϵ^{s}, the linear momentum balance of the solid phase given by (3.90) for $\mathbf{t}^{\mathrm{s}}$, and appropriate boundary and initial conditions. We also need the constitutive relationship for the Cauchy stress and the strain given by (3.91) and the strain-displacement relationship:

$$\mathbf{E}^{\mathrm{s}} = \frac{1}{2}(\nabla\mathbf{u}^{\mathrm{s}} + \nabla\mathbf{u}^{\mathrm{s}T} + \nabla\mathbf{u}^{\mathrm{s}}\nabla\mathbf{u}^{\mathrm{s}T}) \tag{3.127}$$

For a saturated system, with $\epsilon^{\mathrm{a}} = 0$, the volume fraction of the solid becomes

$$\epsilon^{\mathrm{s}} = 1 - \epsilon^{\mathrm{l}} \tag{3.128}$$

and J^{s} becomes dependent. Therefore, linear momentum balance for the solid is not needed. For such a case, only ϵ^{l} is independent, and the transport equation (3.125) or (3.126) alone, with the air phase volume fraction ϵ^{a} being zero, is sufficient to describe the behavior of the system. A material that has both saturated and unsaturated regions can potentially be more challenging, as the saturated region and the unsaturated region will have different number of independent unknowns. Possible methods to model such systems are (1) to prevent air phase volume fraction ϵ^{a} from going to zero (i.e., have no-zero residual air fraction); or (2) to track the interface between fully saturated and unsaturated regions, and have two sets of unknowns for the two regions. Both the methods have been successfully implemented to tackle corresponding phase disappearance/appearance issues in rigid porous media (Perre and Moyne 1991; Pruess 1991).

4 Conclusion

Unsaturated flow in porous materials with nonlinear viscoelastic deformation has a wide range of applications in biomedical and agricultural engineering. Previous studies to incorporate both the physics-transport and nonlinear viscoelastic deformation are mostly empirical with “moisture expansion coefficient” or experimentally fitted parameters. In some fundamental theories previously developed, the solid is assumed to be elastic, or only short memories are considered. Complexities and difficulties arise when modeling unsaturated swelling systems in a three-scale hybrid mixture theory. The major contribution of this study is the development of a two-scale mathematical framework to study unsaturated swelling porous systems with coupled effects of moisture transport and nonlinear viscoelastic deformation.

By applying HMT on a two-scale system, a novel model for unsaturated swelling porous systems, with a generalized Kelvin–Voigt viscoelastic solid undergoing large deformation, has been developed in this study. On the basis of the Neo-Hookean model, we have exploited the stress–strain relationship in detail and obtained a new explicit form of the constitutive law for the solid phase. By manipulating the mass conservation equation for the liquid phase and the modified Darcy’s law obtained from HMT, we have developed a differential-integral form of the transport equation. The transport equation for the liquid is coupled with the linear momentum balance for the solid, and the momentum transported from the liquid and the air phases plays the role of the body force for the solid phase. A numerical implementation of the theory presented in this article, for modeling processing of biopolymers, is in progress, and will be published later.

The model developed, thus, can be applied to a whole class of problems where viscoelastic large deformation occurs in a porous medium due to liquid transport. Phenomena such as transport in saturated and unsaturated systems, stresses generated, large deformation due to transport, and effect of viscoelasticity of the solid on fluid transport, for example, drying of gels, stress-crack predictions, soaking of foodstuffs, consolidation of clays, drug delivery, etc., hitherto either studied empirically or studied in detail individually only for simpler systems, can all be brought together under one unified framework.

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Appendices

A Conservation Equations

Here, we list all the conservation equations at the macroscale, including the conservation of mass, linear momentum, energy, and entropy. Details of the upscaling procedure are given in Bennethum and Cushman (1996a).

A.1 Mass Balance

The macroscale mass balance for the jth species in phase α is given as

$$\frac{D^{\alpha_j}(\epsilon^\alpha \rho^{\alpha_j})}{Dt} + \epsilon^\alpha \rho^{\alpha_j}(\nabla \cdot \mathbf{v}^{\alpha_j}) = \sum_{\beta \neq \alpha} \hat{e}^\beta_{\alpha_j} + \hat{r}^{\alpha_j} \tag{A.129}$$

Summing Eq. A.129 for N species gives the conservation of mass for the bulk phase:

$$\frac{D^\alpha(\epsilon^\alpha \rho^\alpha)}{Dt} + \epsilon^\alpha \rho^\alpha(\nabla \cdot \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} \hat{e}^\beta_\alpha \tag{A.130}$$

where the macroscopic species variables and their bulk counterparts are related by

$$\rho^\alpha = \sum_{j=1}^{N} \rho^{\alpha_j} \tag{A.131}$$

$$\mathbf{v}^\alpha = \sum_{j=1}^{N} C^{\alpha_j} \mathbf{v}^{\alpha_j} \tag{A.132}$$

$$C^{\alpha_j} = \frac{\rho^{\alpha_j}}{\rho^\alpha} \tag{A.133}$$

$$\hat{e}^\beta_\alpha = \sum_{\beta \neq \alpha} \hat{e}^\beta_{\alpha_j} \tag{A.134}$$

They are subjected to the following restrictions:

$$\sum_\alpha \epsilon^\alpha = 1 \tag{A.135}$$

$$\sum_{j=1}^{N} C^{\alpha_j} = 1, \quad \alpha = s,\ l,\ a \tag{A.136}$$

$$\sum_{j=1}^{N} \hat{r}^{\alpha_j} = 0, \quad \alpha = s,\ l,\ a \tag{A.137}$$

$$\sum_{\beta \neq \alpha} \hat{e}_{\alpha_j}^{\beta} = 0, \quad j = 1, \ldots, N \tag{A.138}$$

A.2 Linear Momentum Balance

The macroscale linear momentum balance for the jth species in phase α is given as

$$\epsilon^\alpha \rho^{\alpha_j} \frac{D^{\alpha_j} \mathbf{v}^{\alpha_j}}{Dt} - \nabla \cdot (\epsilon^\alpha \mathbf{t}^{\alpha_j}) - \epsilon^\alpha \rho^{\alpha_j} \mathbf{g}^{\alpha_j} = \hat{\mathbf{i}}^{\alpha_j} + \sum_{\beta \neq \alpha} \hat{\mathbf{T}}_{\alpha_j}^{\beta} \tag{A.139}$$

Summing Eq. A.139 for N species yields the conservation of momentum for the bulk phase:

$$\epsilon^\alpha \rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} - \nabla \cdot (\epsilon^\alpha \mathbf{t}^\alpha) - \epsilon^\alpha \rho^\alpha \mathbf{g}^\alpha = \sum_{\beta \neq \alpha} \hat{\mathbf{T}}_{\alpha}^{\beta} \tag{A.140}$$

where the macroscopic species variables and their bulk counterparts are related by

$$\mathbf{t}^\alpha = \sum_{j=1}^{N} (\mathbf{t}^{\alpha_j} - \rho^{\alpha_j} (\mathbf{v}^{\alpha_j,\alpha})^2) \tag{A.141}$$

$$\mathbf{v}^{\alpha_j,\alpha} = \mathbf{v}^{\alpha_j} - \mathbf{v}^\alpha \tag{A.142}$$

$$\mathbf{g}^\alpha = \sum_{j=1}^{N} C^{\alpha_j} \mathbf{g}^{\alpha_j} \tag{A.143}$$

$$\hat{\mathbf{T}}_{\alpha}^{\beta} = \sum_{j=1}^{N} (\hat{\mathbf{T}}_{\alpha_j}^{\beta} + \mathbf{v}^{\alpha_j} \hat{e}_{\alpha_j}^{\beta}) \tag{A.144}$$

The following restrictions apply:

$$\sum_{j=1}^{N} (\hat{\mathbf{i}}^{\alpha_j} + \hat{r}^{\alpha_j} \mathbf{v}^{\alpha_j,\alpha}) = 0, \quad \alpha = s,\ l,\ a \tag{A.145}$$

$$\sum_{\beta \neq \alpha} (\hat{\mathbf{T}}_{\alpha_j}^{\beta} + \mathbf{v}^{\alpha_j} \hat{e}_{\alpha_j}^{\beta}) = 0, \quad j = 1, \ldots, N \tag{A.146}$$

A.3 Energy Balance

The macroscale conservation of energy for the jth species in phase α is given by

$$\epsilon^\alpha \rho^{\alpha_j} \frac{D^{\alpha_j} e^{\alpha_j}}{Dt} - \nabla \cdot (\epsilon^\alpha \mathbf{q}^{\alpha_j}) - \epsilon^\alpha \mathbf{t}^{\alpha_j} : \nabla \mathbf{v}^{\alpha_j} - \epsilon^\alpha \rho^{\alpha_j} h^{\alpha_j} = \hat{Q}^{\alpha_j} + \sum_{\beta \neq \alpha} \hat{Q}_{\alpha_j}^{\beta} \tag{A.147}$$

Summing Eq. A.147 for N species yields the conservation of energy for the bulk phase:

$$\epsilon^\alpha \rho^\alpha \frac{D^\alpha e^\alpha}{Dt} - \nabla \cdot (\epsilon^\alpha \mathbf{q}^\alpha) - \epsilon^\alpha \mathbf{t}^\alpha : \nabla \mathbf{v}^\alpha - \epsilon^\alpha \rho^\alpha h^\alpha = \sum_{\beta \neq \alpha} \hat{Q}_{\alpha_j}^{\beta} \tag{A.148}$$

where the relationships of the macroscopic species variables and their bulk counterparts are

$$e^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} \left(e^{\alpha_j} \frac{1}{2} \mathbf{v}^{\alpha_j,\alpha} \cdot \mathbf{v}^{\alpha_j,\alpha} \right) \tag{A.149}$$

$$\mathbf{q}^{\alpha} = \sum_{j=1}^{N} \left[\mathbf{q}^{\alpha_j} + \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j,\alpha} - \rho^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j,\alpha} \cdot \mathbf{v}^{\alpha_j,\alpha} \right) \mathbf{v}^{\alpha_j,\alpha} \right] \tag{A.150}$$

$$h^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} (h^{\alpha_j} + \mathbf{g}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j,\alpha}) \tag{A.151}$$

$$\hat{Q}_{\alpha}^{\beta} = \sum_{j=1}^{N} \left[\mathbf{v}^{\alpha_j,\alpha} + \hat{\mathbf{T}}_{\alpha_j}^{\beta} \cdot \mathbf{v}^{\alpha_j,\alpha} + \hat{e}_{\alpha_j}^{\beta} \left(e^{\alpha_j,\alpha} \frac{1}{2} \mathbf{v}^{\alpha_j,\alpha} \cdot \mathbf{v}^{\alpha_j,\alpha} \right) \mathbf{v}^{\alpha_j,\alpha} \right] \tag{A.152}$$

They are subjected to the following restrictions:

$$\sum_{j=1}^{N} \left[\hat{Q}^{\alpha_j} + \hat{\mathbf{i}}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j,\alpha} + \hat{r}^{\alpha_j} \left(e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j,\alpha} \cdot \mathbf{v}^{\alpha_j,\alpha} \right) \mathbf{v}^{\alpha_j,\alpha} \right] = 0, \quad \alpha = s,\ l,\ a \tag{A.153}$$

$$\sum_{\beta \neq \alpha} \left[\hat{Q}_{\alpha_j}^{\beta} + \hat{\mathbf{T}}_{\alpha_j}^{\beta} \cdot \mathbf{v}^{\alpha_j,\alpha} + \hat{e}_{\alpha_j}^{\beta} \left(e^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \right) \mathbf{v}^{\alpha_j,\alpha} \right] = 0, \quad j = 1, \ldots, N \tag{A.154}$$

A.4 Entropy Balance

The macroscale conservation of energy for the jth species in phase α is

$$\epsilon^{\alpha} \rho^{\alpha_j} \frac{D^{\alpha_j} \eta^j}{Dt} - \nabla \cdot (\epsilon^{\alpha} \boldsymbol{\phi}^{\alpha_j}) - \epsilon^{\alpha} \rho^{\alpha_j} b^{\alpha_j} = \sum_{\beta \neq \alpha} \hat{\Phi}_{\alpha_j}^{\beta} + \hat{\eta}^{\alpha_j} + \Lambda^{\alpha_j} \tag{A.155}$$

Summing Eq. A.155 for N species yields the entropy balance for the bulk phase:

$$\epsilon^{\alpha} \rho^{\alpha} \frac{D^{\alpha} \eta^j}{Dt} - \nabla \cdot (\epsilon^{\alpha} \boldsymbol{\phi}^{\alpha}) - \epsilon^{\alpha} \rho^{\alpha} b^{\alpha} = \sum_{\beta \neq \alpha} \hat{\Phi}_{\alpha}^{\beta} + \Lambda^{\alpha} \tag{A.156}$$

where the macroscopic species variables are related to their bulk counterparts by

$$\eta^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} \eta^{\alpha_j} \tag{A.157}$$

$$\boldsymbol{\phi}^{\alpha} = \sum_{j=1}^{N} (\boldsymbol{\phi}^{\alpha_j} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j,\alpha} \eta^{\alpha_j}) \tag{A.158}$$

$$b^{\alpha} = \sum_{j=1}^{N} C^{\alpha_j} b^{\alpha_j} \tag{A.159}$$

$$\hat{\Phi}_{\alpha}^{\beta} = \sum_{j=1}^{N} (\hat{\Phi}_{\alpha_j}^{\beta} + \hat{e}_{\alpha_j}^{\beta} \eta^{\alpha_j,\alpha}) \tag{A.160}$$

And, the following restrictions hold

$$\sum_{j=1}^{N} \hat{\eta}^{\alpha_j} + \hat{r}^{\alpha_j} \eta^{\alpha_j} = 0, \quad \alpha = s,\ l,\ a \tag{A.161}$$

$$\sum_{\beta \neq \alpha} (\hat{\Phi}^{\beta}_{\alpha_j} + \hat{e}^{\beta}_{\alpha_j} \eta^{\alpha_j}) = 0, \quad j = 1, \ldots, N \tag{A.162}$$

A.5 Total Entropy Inequality

As we mentioned before, we have assumed that the system is at local thermal equilibrium, resulting in only one temperature for all the phases and their species:

$$T^{\mathrm{s}_j} = T^{\mathrm{l}_j} = T^{\mathrm{a}_j} = T^{\mathrm{s}} = T^{\mathrm{l}} = T^{\mathrm{a}} = T \tag{A.163}$$

Also, we have assumed that the system is thermodynamically simple:

$$\boldsymbol{\phi}^{\alpha_j} = \frac{\alpha_j}{T} \tag{A.164}$$

and

$$b^{\alpha_j} = \frac{h^{\alpha_j}}{T} \tag{A.165}$$

We perform a Legendre transformation to convert the internal energy e^{α_j} into the Helmoltz free energy A^{α_j}:

$$A^{\alpha_j} = e^{\alpha_j} + T\eta^{\alpha_j} \tag{A.166}$$

where

$$A^{\alpha} = \sum_{j}^{N} C^{\alpha_j} A^{\alpha_j} \tag{A.167}$$

We obtain the total entropy inequality by eliminating h^{α_j} from the energy and entropy balance:

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

$$-\frac{1}{T}\sum_{\beta\neq\alpha}\left(A^{\alpha}+\frac{1}{2}\mathbf{v}^{\alpha,s}\cdot\mathbf{v}^{\alpha,s}\right)\Bigg]\geq 0 \tag{A.168}$$

B Complexities with Three-Scale Unsaturated Swelling Systems

We have mentioned before that complexities arise in a three-scale theory when the system is considered as unsaturated. In order to see this, we need to look at the transport equation and linear momentum balance of the solid phase in a three-scale theory. In this section, we present the details of the derivation of the transport equation and linear momentum balance for the solid phase for a three-scale unsaturated swelling porous system. This is based on the study by Singh et al. (2003a,b), in which four phases, solid *sA*, vicinal fluid *wA*, bulk phase *B*, and bulk phase *C*, are considered. Here, we assume isothermal conditions. The solid phase is assumed to be incompressible. The vicinal fluid and the bulk fluid *B* are the same and assumed to be incompressible. The third phase *C* is taken as air.

B.1 Vicinal Fluid

The mass conservation of the vicinal fluid is given by (A.5) in Singh et al. (2003a):

$$\frac{D^{\mathrm{wA}}(\epsilon^{\mathrm{wA}}\rho^{\mathrm{wA}})}{Dt}+\epsilon^{\mathrm{wA}}\rho^{\mathrm{wA}}\nabla\cdot\mathbf{v}^{\mathrm{wA}}=\epsilon^{\mathrm{wA}}\rho^{\mathrm{wA}}\hat{e}_{1}^{\mathrm{wA}} \tag{B.169}$$

where we have replaced ϵ^{A} by ϵ^{wA} as we have mentioned before that the upscaling technique is modified slightly (Cushman et al. 2004). The right-hand side is nonzero as mass could be transferred between the vicinal water and the bulk phase water. We rewrite the above equation as

$$\rho^{\mathrm{wA}}[\dot{\epsilon}^{\mathrm{wA}}+\nabla\cdot(\epsilon^{\mathrm{wA}}\mathbf{v}^{\mathrm{wA,sA}})+\epsilon^{\mathrm{wA}}\nabla\cdot\mathbf{v}^{\mathrm{sA}}]=\epsilon^{\mathrm{wA}}\rho^{\mathrm{wA}}\hat{e}_{1}^{\mathrm{wA}} \tag{B.170}$$

Darcy's law for the vicinal fluid is simplified as

$$\mathbf{v}^{\mathrm{wA,sA}}=\mathbf{R}^{\mathrm{wA}^{-1}}\left[-\epsilon^{\mathrm{wA}}\rho^{\mathrm{wA}}\frac{\partial A^{\mathrm{wA}}}{\partial\epsilon^{\mathrm{wA}}}\nabla\epsilon^{\mathrm{wA}}-\epsilon^{\mathrm{wA}}\rho^{\mathrm{wA}}\sum_{m=0}^{p}\frac{\partial A^{\mathrm{wA}}}{\partial\overset{(m)\mathrm{sA}}{\mathbf{E}}}:\nabla\overset{(m)\mathrm{sA}}{\mathbf{E}}\right] \tag{B.171}$$

The third term on the right side of Eq. 5.30 in Singh et al. (2003a) is neglected because the vicinal fluid interacts with the bulk phase water only through the boundaries, and it is assumed that for such systems the bulk fluid does not affect the free energy of the vicinal fluid. Gravity and higher order effects are also ignored. The second term in the above represents the effect of vicinal water concentration on the flow and the coefficient is known as the swelling potential, while the viscoelastic effect on the flow is accounted for in the third term.

B.2 Bulk Phase Fluid *B*

Mass conservation of the bulk phase *B* is given by (A.7) in Singh et al. (2003a) and is written as

$$\rho^{\mathrm{l}}[\dot{\epsilon}^{\mathrm{l}}+\nabla\cdot(\epsilon^{\mathrm{l}}\mathbf{v}^{\mathrm{l,sA}})+\epsilon^{\mathrm{l}}\nabla\cdot\mathbf{v}^{\mathrm{sA}}]=\epsilon^{\mathrm{l}}\rho^{\mathrm{l}}\hat{e}_{\mathrm{wA}}^{\mathrm{l}} \tag{B.172}$$

Darcy's law is given as

$$\mathbf{v}^{\mathrm{l,sA}} = \mathbf{R}^{\mathrm{l}^{-1}} \left(-\epsilon^{\mathrm{l}} \rho^{\mathrm{l}} \frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \nabla \epsilon^{\mathrm{l}} \right) \tag{B.173}$$

The second term is related to the capillary pressure, and this resembles the classical Darcy's law.

B.3 Transport Equation

As the mass transferred between the vicinal fluid and the bulk fluid adds up to zero $\epsilon^{\mathrm{wA}} \rho^{\mathrm{wA}} \hat{e}_{\mathrm{l}}^{\mathrm{wA}} + \epsilon^{\mathrm{l}} \rho^{\mathrm{l}} \hat{e}_{\mathrm{wA}}^{\mathrm{l}} = 0$, we add (B.169) and (B.172) and use the notation

$$\epsilon^{\mathrm{f}} = \epsilon^{\mathrm{l}} + \epsilon^{\mathrm{wA}} \tag{B.174}$$

where ϵ^{f} is the total volume fraction of the vicinal fluid and the volume fraction of the bulk fluid B; we obtain

$$\begin{aligned} &\dot{\epsilon}^{\mathrm{f}} - \nabla \cdot \Bigg\{ \frac{k^{\mathrm{f}}}{\mu^{\mathrm{f}}} \mathbf{I} \Bigg[K^2 \epsilon^{\mathrm{f}} \left(\epsilon^{\mathrm{wA}} \rho^{\mathrm{wA}} \frac{\partial A^{\mathrm{wA}}}{\partial \epsilon^{\mathrm{wA}}} \right) + (1-K)^2 \epsilon^{\mathrm{f}} \left(\epsilon^{\mathrm{l}} \rho^{\mathrm{l}} \frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) \\ &\quad + \epsilon^{\mathrm{f}} \epsilon^{\mathrm{A}} \frac{\partial p^{\mathrm{wA}}}{\partial \epsilon^{\mathrm{wA}}} \Bigg] \nabla \epsilon^{\mathrm{f}} - K^2 \epsilon^{\mathrm{f}} \left(\epsilon^{\mathrm{f}} \rho^{\mathrm{wA}} \sum_{m=0}^{p} \frac{\partial A^{\mathrm{wA}}}{\partial \overset{(m)\mathrm{sA}}{\mathbf{E}}} : \nabla \overset{(m)\mathrm{sA}}{\mathbf{E}} \right) \Bigg\} + \epsilon^{\mathrm{f}} \nabla \cdot \mathbf{v}^{\mathrm{sA}} = 0 \end{aligned} \tag{B.175}$$

where

$$\mathbf{R}^{\mathrm{wA}^{-1}} = \mathbf{R}^{l^{-1}} = \frac{k^{\mathrm{f}}}{\mu^{\mathrm{f}}} \mathbf{I} \tag{B.176}$$

and we follow Singh et al. (2003b) to assume a linear relationship between ϵ^{wA} and ϵ^{f}:

$$\epsilon^{\mathrm{wA}} = K \epsilon^{\mathrm{f}} \tag{B.177}$$

Then,

$$\epsilon^{\mathrm{l}} = (1-K) \epsilon^{\mathrm{f}} \tag{B.178}$$

We define the Fickian diffusion coefficient as

$$D \equiv \frac{k^{\mathrm{f}}}{\mu^{\mathrm{f}}} \left[K^2 \epsilon^{\mathrm{f}} \left(\epsilon^{\mathrm{wA}} \rho^{\mathrm{wA}} \frac{\partial A^{\mathrm{wA}}}{\partial \epsilon^{\mathrm{wA}}} \right) + (1-K)^2 \epsilon^{\mathrm{f}} \left(\epsilon^{\mathrm{l}} \rho^{\mathrm{l}} \frac{\partial A^{\mathrm{l}}}{\partial \epsilon^{\mathrm{l}}} \right) + \epsilon^{\mathrm{f}} \epsilon^{\mathrm{A}} \frac{\partial p^{\mathrm{wA}}}{\partial \epsilon^{\mathrm{wA}}} K \right] \tag{B.179}$$

The Laplace transform technique is used to convert the fifth term in (B.175) into an integral form and (B.175) then becomes

$$\dot{\epsilon}^{\mathrm{f}} - \nabla \cdot (D \nabla \epsilon^{\mathrm{f}}) - \nabla \cdot \left(\int_0^t \mathbf{B}(t-\tau) : \nabla \dot{\mathbf{E}}^{\mathrm{sA}} d\tau \right) + \epsilon^{\mathrm{f}} \nabla \cdot \mathbf{v}^{\mathrm{sA}} = 0 \tag{B.180}$$

where $\mathbf{B}$ is defined by

$$\mathbf{B}(t) = \frac{k^{\mathrm{f}}}{\mu^{\mathrm{f}}} K^2 \epsilon^{\mathrm{f}^2} \rho^{\mathrm{wA}} \mathbf{M}(t) \tag{B.181}$$

and

$$\mathbf{M}(t) = \sum_{m=0}^{p} \frac{\partial A^{\mathrm{wA}}}{\partial \overset{(m)\mathrm{sA}}{\mathbf{E}}} \frac{\mathrm{d}\delta}{\mathrm{d}t}(t) \tag{B.182}$$

Equation B.180 is the transport equation which needs to be solved simultaneously with the solid phase equations. This is different from Eq. 2.53 in Singh et al. (2003b) because phase C is not immobile anymore, and relation (2.19) in Singh et al. (2003b) is no longer valid.

We have discussed before that the linearity assumption (B.177) is not justified. However, without relating the volume fraction of the vicinal fluid and that of the bulk phase B, it is very difficult to combine the two phases.

B.4 Solid Phase

Linear momentum balance of the solid phase is given below (Here, we ignore gravity and inertial effects):

$$\nabla \cdot (\epsilon^{\mathrm{A}} \mathbf{t}^{\mathrm{sA}}) = - \sum_{\alpha \neq \mathrm{wA,l,a}} \epsilon^{\mathrm{sA}} \rho^{\mathrm{sA}} \hat{\mathbf{T}}_{\alpha}^{\mathrm{sA}} \tag{B.183}$$

The right-hand side is the linear momentum transferred from other phases to the solid phase and could not be obtained directly. We use the restriction

$$\epsilon^{\alpha} \rho^{\alpha} (\hat{\mathbf{T}}_{\alpha}^{\beta} + \hat{e}_{\alpha}^{\beta} \mathbf{v}^{\alpha}) + \epsilon^{\beta} \rho^{\beta} (\hat{\mathbf{T}}_{\beta}^{\alpha} + \hat{e}_{\beta}^{\alpha} \mathbf{v}^{\beta}) = 0, \alpha, \beta = wA, sA, l, a, \alpha \neq \beta \tag{B.184}$$

and Eq. B.183 is equivalent to

$$\nabla \cdot (\epsilon^{\mathrm{A}} \mathbf{t}^{\mathrm{sA}}) = \epsilon^{\mathrm{wA}} \rho^{\mathrm{wA}} \hat{\mathbf{T}}_{\mathrm{sA}}^{\mathrm{wA}} + \epsilon^{\mathrm{l}} \rho^{\mathrm{l}} \hat{\mathbf{T}}_{\mathrm{sA}}^{\mathrm{l}} + \epsilon^{\mathrm{a}} \rho^{\mathrm{a}} \hat{\mathbf{T}}_{\mathrm{sA}}^{\mathrm{a}} \tag{B.185}$$

From the linear momentum balance for phase $\alpha, \alpha = wA, l, a$, the following relationships can be obtained:

$$\epsilon^{\mathrm{wA}} \rho^{\mathrm{wA}} [\hat{\mathbf{T}}_{\mathrm{wA}}^{\mathrm{sA}} + \hat{\mathbf{T}}_{\mathrm{wA}}^{\mathrm{l}} + \hat{\mathbf{T}}_{\mathrm{wA}}^{\mathrm{a}}] = \nabla (p^{\mathrm{wA}} \epsilon^{\mathrm{wA}}) \tag{B.186}$$

$$\epsilon^{\mathrm{l}} \rho^{\mathrm{l}} [\hat{\mathbf{T}}_{\mathrm{l}}^{\mathrm{sA}} + \hat{\mathbf{T}}_{\mathrm{l}}^{\mathrm{wA}} + \hat{\mathbf{T}}_{\mathrm{l}}^{\mathrm{a}}] = \nabla (p^{\mathrm{l}} \epsilon^{\mathrm{l}}) \tag{B.187}$$

$$\epsilon^{\mathrm{a}} \rho^{\mathrm{a}} [\hat{\mathbf{T}}_{\mathrm{a}}^{\mathrm{sA}} + \hat{\mathbf{T}}_{\mathrm{a}}^{\mathrm{wA}} + \hat{\mathbf{T}}_{\mathrm{a}}^{\mathrm{l}}] = \nabla (p^{\mathrm{a}} \epsilon^{\mathrm{a}}) \tag{B.188}$$

Note that the mass transferred between the vicinal fluid and the bulk phase B is nonzero. All the other mass transfers between phases vanish. Thus, if we add the above three equations up, terms cancel on the left-hand side except for those that appear on the right-hand side, as well as $\epsilon^{\mathrm{wA}} \rho^{\mathrm{wA}} \hat{\mathbf{T}}_{\mathrm{wA}}^{\mathrm{l}}$ and $\epsilon^{\mathrm{l}} \rho^{\mathrm{l}} \hat{\mathbf{T}}_{\mathrm{l}}^{\mathrm{wA}}$ on the left-hand side. This is because in (B.184), $\hat{e}_{\mathrm{wA}}^{\mathrm{l}}$ and $\hat{e}_{\mathrm{l}}^{\mathrm{wA}}$ are not zero. However, since no information is available for the momentum transfer between the vicinal fluid and the bulk phase l, we assume that

$$\epsilon^{\mathrm{wA}} \rho^{\mathrm{wA}} \hat{\mathbf{T}}_{\mathrm{wA}}^{\mathrm{l}} + \epsilon^{\mathrm{l}} \rho^{\mathrm{l}} \hat{\mathbf{T}}_{\mathrm{l}}^{\mathrm{wA}} = 0 \tag{B.189}$$

Thus, the linear momentum balance of the solid phase is given as

$$\nabla \cdot (\epsilon^{\mathrm{A}} \mathbf{t}^{\mathrm{sA}}) = \nabla (p^{\mathrm{wA}} \epsilon^{\mathrm{wA}}) + \nabla (p^{\mathrm{l}} \epsilon^{\mathrm{l}}) + \nabla (p^{\mathrm{a}} \epsilon^{\mathrm{a}}) \tag{B.190}$$

The stress–strain relationship is of the form

$$\mathbf{t}^{\mathrm{sA}} = -p^{\mathrm{sA}} \mathbf{I} + \mathbf{t}^{\mathrm{seA}} + \mathbf{t}^{\mathrm{shA}} + \sum_{m=0}^{p} \mathbf{F} (\mathbf{G}^{\mathrm{sA}} \overset{(m)\mathrm{sA}}{\mathbf{E}}) \mathbf{F}^{T} \tag{B.191}$$

The Terzaghi stress $\mathbf{t}^{\mathrm{seA}}$ and the hydration stress $\mathbf{t}^{\mathrm{shA}}$ are given respectively by

$$\mathbf{t}^{\mathrm{seA}} = \rho^{\mathrm{sA}} \mathbf{F} \frac{\partial A^{\mathrm{sA}}}{\partial \mathbf{E}^{\mathrm{sA}}} \mathbf{F}^T \tag{B.192}$$

$$\mathbf{t}^{\mathrm{shA}} = \rho^{\mathrm{wA}} \mathbf{F} \frac{\partial A^{\mathrm{wA}}}{\partial \mathbf{E}^{\mathrm{sA}}} \mathbf{F}^T \tag{B.193}$$

In Eq. B.190, the volume fraction of the particle A composed of the solid phase *sA* and the vicinal fluid *wA* appears. The solid phase linear momentum balance is difficult to implement without separation of the volume fraction ϵ^{sA} from ϵ^{A}. It appears difficult to carry out this separation.

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