

# MOISTURE AND HEAT TRANSPORT IN UNSATURATED SWELLING POROUS MEDIA: A PARALLEL-FLOW, MULTI-SCALE, MIXTURE-THEORETIC APPROACH

Lynn Schreyer Bennethum\*      John H. Cushman†

**Abstract.** A three-scale theory of both moisture and heat transport is presented for an unsaturated swelling porous media. At the microscale the system consists of macromolecules and an adsorbed fluid, both of which are considered as distinct non-overlapping continua. At the mesoscale the macromolecule, and adsorbed fluid are homogenized to form particles. At this scale each phase within the particle is considered as an overlaying continua. The mesoscale particles coexist with a bulk fluid which may be either liquid or vapor; the particles and bulk fluid exist as distinct non-overlapping continua. At the macroscale, the mesoscale particles and bulk fluid are homogenized to form overlaying continua at each point in space. The homogenization procedure is modified mixture theoretic. A single energy equation is used at the macroscale where the constitutive theory is developed. The model has one time scale so it may be thought of as a parallel flow model. The particles are saturated, but the mesoscale and macroscale bulk fluid may be vapor and/or liquid.

**Key Words:** Unsaturated, 3-scale, heat transport, mixture.

## 1 Introduction

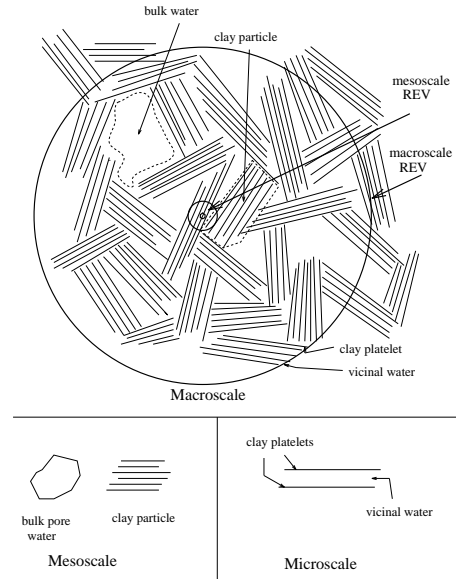
As technology becomes more sophisticated, it is becoming increasingly necessary to model porous materials over a hierarchy of scales. Consider, for example, natural smectitic clays. The macroscopic properties of clay are primarily due to clay particles, which are clusters of clay mineral platelets (a solid phase) and adsorbed water (or vicinal water). The vicinal water is bound to the clay minerals due to electro-chemical effects, and the proximity of the vicinal fluid to the solid strongly affects the thermodynamic properties of the adsorbed water [1, 2, 3]. In naturally occurring clay samples, clay is composed of clay particles with voids which may be filled with a bulk phase liquid (water) and/or air. Thus the clay particles swell or shrink as water transfers between the bulk and vicinal phase. This particular porous medium is an example in which there are 3 distinct scales of observation — a microscale in which clay minerals and adsorbed water are distinguishable, a mesoscale in which the particles and bulk phase fluid are distinguishable, and a macroscale, in which the medium appears to be homogeneous (see Figure 1.1) with saturated particles, but possibly unsaturated large-scale pores.

The derivation of the equations which govern flow and heat transfer in such a medium is accomplished within the framework of Hybrid Mixture Theory (HMT), which is a slight modification of classical mixture theory. In the two-scale approach, HMT involves volume averaging field equations (conservation of mass, momentum balance, energy balance) from the microscale to the mesoscale. This

---

\*Center for Computational Mathematics, University of Colorado at Denver, P.O. Box 173364, Campus Box 170, Denver, CO 80217-3364.

†Center for Applied Math, Math Sciences Building, Purdue University, West Lafayette, IN 47907-1395. To whom correspondence should be addressed.



**Figure 1.1:** Three scales of an idealized smectitic clay.

yields explicit relations between the mesoscopic field variables and their microscopic counterparts. Restrictions on the constitutive equations are obtained within the framework of rational thermodynamics, i.e. the entropy inequality is exploited in the sense of Coleman and Noll [4]. These ideas were first introduced by Hassanizadeh and Gray [5, 6, 7] in 1979 for a multi-phase nonswelling porous medium. They have since been expanded to include multi-constituents [8, 9] and multi-constituent with interfaces for swelling porous media [10]. This work has generated many new insights into the macroscopic behavior of porous media, including non-equilibrium swelling and capillary pressures [11, 12], Darcy and non-Darcy type flow with and without interfacial effects, [13, 14, 15, 16, 17], the macroscale chemical potential [18, 19], and the macroscopic stress tensors for swelling porous media [20, 21, 22]. A three-scale model for swelling porous media by Bennethum and Cushman [23, 24] incorporates multiple phases, multiple species, and interfacial effects. The three scales include a microscale, mesoscale, and macroscale. In this setting hybrid mixture theory was employed by averaging the field equations twice: once going from the microscale to the mesoscale, and then again to upscale from the mesoscale to the macroscale. At the macroscale, the entropy inequality is exploited to obtain constitutive restrictions in terms of macroscopic variables. This work is extremely general, and a wealth of information has yet to be exploited from it. For a summary of these works see Cushman [25]. In this paper, we restrict the model to the specific case in which interfaces do not possess mass and multi-constituent effects are negligible. We concentrate the discussion on moisture transport and heat transfer in combination with solid stresses which result from these processes.

## 2 Two-Scale Model

In this section we discuss the development of the two-scale model. Here we assume the particle is composed of two phases, a liquid phase,  $l$ , and a solid phase,  $s$ . At the microscale, (see Figure 1.1) one can distinguish between the solid and vicinal (adsorbed liquid) phases, while at the mesoscale the particle appears to be continuous. It is assumed the thermodynamic properties of the liquid phase are strongly affected by its proximity to the solid phase, interfacial properties are negligible, the solid and fluid are non-polar so that conservation of angular momentum for each phase implies the stress tensors of each phase are symmetric, and that each phase behaves as a single constituent, i.e. there are no chemical reactions within a phase. We do allow for transfer between phases.

## 2.1 Mesoscale Field Equations and Assumptions

In hybrid mixture theory, the microscale field equations are averaged to obtain mesoscale equations. Constitutive relations are developed using the classical Coleman and Noll method of exploiting the entropy inequality. The averaging of the field equations along with the relationships between the mesoscopic and microscopic variables are presented in several papers [26, 6].

Conservation of mass for the  $\alpha$ -phase is

$$\frac{D^\alpha(\varepsilon^\alpha \rho^\alpha)}{Dt} + \varepsilon^\alpha \rho^\alpha \nabla \cdot \mathbf{v}^\alpha = \widehat{e}_\beta^\alpha, \quad \alpha, \beta = l, s, \quad \alpha \neq \beta, \quad (2.1)$$

where  $\varepsilon^\alpha$  is the volume fraction of phase  $\alpha$ ,  $\rho^\alpha$  and  $\mathbf{v}^\alpha$  denote the averaged density and mass-averaged velocity of the  $\alpha$ -phase, respectively,  $\widehat{e}_\beta^\alpha$  represents the net mass gained by the  $\alpha$ -phase from the other phase, and  $D^\alpha/Dt$  denotes the material time derivative following the  $\alpha$ -phase, i.e.  $D^\alpha/Dt = \partial/\partial t + \mathbf{v}^\alpha \cdot \nabla$ .

Conservation of momentum for each phase is

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^\alpha) - \varepsilon^\alpha \rho^\alpha \mathbf{g} = \widehat{\mathbf{T}}_\beta^\alpha, \quad \alpha, \beta = l, s, \quad \alpha \neq \beta, \quad (2.2)$$

where  $\mathbf{t}^\alpha$  denotes the average symmetric stress tensors for phase  $\alpha$ ,  $\mathbf{g}$  is the body force (i.e. gravity), and  $\widehat{\mathbf{T}}_\beta^\alpha$  denotes the net gain of momentum of the  $\alpha$ -phase due to mechanical interactions with the other phase.

Conservation of energy for phase  $\alpha$  is given by

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha E^\alpha}{Dt} - \varepsilon^\alpha \mathbf{t}^\alpha : \mathbf{d}^\alpha - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^\alpha) + \varepsilon^\alpha \rho^\alpha h^\alpha = \widehat{Q}_\beta^\alpha, \quad \alpha, \beta = l, s, \quad \alpha \neq \beta, \quad (2.3)$$

where  $E^\alpha$  is the average internal energy per unit mass of the  $\alpha$ -phase,  $\mathbf{q}^\alpha$  denotes the heat flux,  $\mathbf{d}^\alpha$  is the symmetric part of  $\nabla \mathbf{v}^\alpha$ ,  $\mathbf{A} : \mathbf{B} = \text{tr}(\mathbf{A}\mathbf{B}^T)$  denotes the classical inner product between tensors,  $h^\alpha$  is the external heat source per unit mass per unit time, and  $\widehat{Q}_\beta^\alpha$  denotes the gain of energy by the  $\alpha$ -phase due to non-mechanical interactions with the other phase. If we sum over all phases, one recovers the familiar form of the energy equation

$$\rho \frac{DE}{Dt} - \mathbf{t} : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} - \rho h = 0, \quad (2.4)$$

where the relationships between the medium and phase thermodynamic variables are

$$\rho = \sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha, \quad (2.5)$$

$$\rho \mathbf{v} = \sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha \mathbf{v}^\alpha, \quad (2.6)$$

$$\mathbf{u}^\alpha = \mathbf{v}^\alpha - \mathbf{v}, \quad (2.7)$$

$$\mathbf{t} = \sum_{\alpha=l,s} [\varepsilon^\alpha \mathbf{t}^\alpha - \varepsilon^\alpha \rho^\alpha \mathbf{u}^\alpha \mathbf{u}^\alpha], \quad (2.8)$$

$$\rho E = \sum_{\alpha=l,s} [\varepsilon^\alpha \rho^\alpha E^\alpha + \varepsilon^\alpha \rho^\alpha \mathbf{u}^\alpha \cdot \mathbf{u}^\alpha], \quad (2.9)$$

$$\mathbf{q} = \sum_{\alpha=l,s} \left[ \varepsilon^\alpha \mathbf{q}^\alpha + \mathbf{t}^\alpha \cdot \mathbf{u}^\alpha - \rho^\alpha \mathbf{u}^\alpha (E^\alpha + \frac{1}{2} \mathbf{u}^\alpha \cdot \mathbf{u}^\alpha) \right], \quad (2.10)$$

$$\rho h = \sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha h^\alpha. \quad (2.11)$$

Note that relative velocities,  $\mathbf{u}^\alpha$ , of the liquid phase over the mass averaged bulk velocity contribute to the net heat flux.

Further, we have restrictions which arise from the fact that the thermodynamic properties of the interface are negligible. This results in the following relations:

$$\widehat{e}_s^l + \widehat{e}_l^s = 0, \quad (2.12)$$

$$\sum_{\alpha=l,s} \left( \widehat{\mathbf{T}}_\beta^\alpha + \widehat{e}_\beta^\alpha \mathbf{v}^\alpha \right) = \mathbf{0}, \quad \beta = l, s \neq \alpha, \quad (2.13)$$

$$\sum_{\alpha=l,s} \left[ \widehat{Q}_\beta^\alpha + \widehat{\mathbf{T}}_\beta^\alpha \cdot \mathbf{v}^\alpha + \widehat{e}_\beta^\alpha \left( E^\alpha + \frac{1}{2} \mathbf{v}^\alpha \cdot \mathbf{v}^\alpha \right) \right] = 0, \quad \beta = l, s \neq \alpha. \quad (2.14)$$

The first equation states that the  $ls$ -interface is massless, and the second and third equations state that no momentum nor energy are lost through the interface. By design, we also have  $\varepsilon^l + \varepsilon^s = 1$ .

After upscaling, the system is now viewed as two co-existing continua, so that at each point in space there exist thermodynamic properties for both the liquid and solid phase. At this point we perform a change of variables using a Legendre transformation to eliminate the energy density,  $E^\alpha$  in favor of the Helmholtz free energy,  $A^\alpha$ ,

$$A^\alpha = E^\alpha - T\eta^\alpha. \quad (2.15)$$

The unknowns in our system are thus:

$$\varepsilon^l, \rho^\alpha, \mathbf{v}^\alpha, T \quad (2.16)$$

$$A^\alpha, \eta^\alpha, \mathbf{t}^\alpha, \widehat{\mathbf{T}}_s^l, \widehat{e}_s^l, \mathbf{q}^\alpha, \widehat{Q}_s^l, \quad \alpha = l, s. \quad (2.17)$$

To arrive at a system which has the same number of equations as unknowns, we consider the second row of variables (2.17) to be dependent, or constitutive. These variables are assumed to be functions of a set of independent variables which we henceforth denote constitutive independent variables. However, even with these constitutive variables a careful count indicates that there is still an additional unknown for which there is no corresponding equation. Making a comparison with classical mixture theory for a single phase, we see that the volume fraction is the variable unaccounted for. Thus there is a problem of closure associated with the loss of information in the upscaling process. To close the system, we follow Bowen [27] and postulate a constitutive relation for the material time derivative of the volume fraction.

We assume the macroscopic fluid is viscous and the fluid and solid phases are compressible. Further, we assume that the temperature of the solid and fluid phases are the same at each point in space, so that the rate at which heat transfers between phases is much faster than the time scale of the problem.

By the Principle of Equipresence (Truesdell [28]), we assume that every constitutive variable is a function of *all* the following macroscopic constitutive independent variables:

$$\varepsilon^l, T, \rho^\alpha, \mathbf{E}^s, \mathbf{v}^{l,s}, \nabla T, \nabla \rho^\alpha, \nabla \mathbf{E}^s, \quad \alpha = l, s, \quad (2.18)$$

where  $\mathbf{E}^s$  is the macroscopic strain tensor of the solid phase defined by

$$\mathbf{E}^s = \frac{1}{2} \left( (\mathbf{F}^s)^T \mathbf{F}^s - \mathbf{I} \right) \quad (2.19)$$

in which  $\mathbf{F}^s = \text{grad } \mathbf{x}^s$  denotes the deformation gradient (with grad denoting the differentiation with respect to a macroscopic material particle). Here we have implicitly assumed the constitutive variables are local functions, i.e. the value of each constitutive variable is determined by the values of the constitutive independent variables at that same material point, so that there is no non-locality in space. With this assumption, the variables and their gradients (2.18) can be considered independent,

since it is possible to have different processes which at a single point can have e.g. the same temperature but varying gradients of the temperature.

The macroscopic strain is a measure of the solid phase geometry, so that by including  $\mathbf{E}^s$  and  $\nabla \mathbf{E}^s$  in the list of constitutive independent variables we are assuming the behavior of the system is partially dictated by the separation and distortion of the solid phase and their spatial variations. It should be noted however, that  $\mathbf{E}^s$ ,  $\varepsilon_l$ , and  $\rho^s$  are closely coupled through the continuity equation, and specifically that they are not independent if there is no exchange of mass between phases. If there is no exchange of mass, then it is necessary to include only two of these variables, and further, if the solid phase is considered incompressible, then it is necessary to choose one of  $\mathbf{E}^s$  and  $\varepsilon^l$  as an independent constitutive variable.

To simplify the quantity of algebra which follows, we deviate slightly from the axiom of equipresence [29], and assume the Helmholtz free energy densities of the phases depend only on a subset of the set of constitutive independent variables. If it is assumed the Helmholtz free energies are a function of all constitutive independent variables listed in (2.18), then exploitation of the entropy inequality requires that both energies are not a function of  $\mathbf{v}^{l,s}$ ,  $\nabla T$ , and  $\nabla \mathbf{E}^s$ . Here we additionally assume that the liquid free energy is not a function of  $\rho^s$  and likewise that the solid free energy is not a function of  $\rho^l$ . Incorporating these additional dependencies still produces the results presented herein if one slightly modifies the thermodynamic definitions of the pressure and chemical potential (see [24, 26] for details). For the system under consideration it is thus postulated that

$$\begin{aligned} A^s &= A^s(\varepsilon^l, T, \rho^s, \mathbf{E}^s), \\ A^l &= A^l(\varepsilon^l, T, \rho^l, \mathbf{E}^s). \end{aligned} \quad (2.20)$$

By assuming the liquid phase energy is a function of the volume fraction, we are allowing the adsorbed liquid structure to be a function of the separation of the solid phase minerals. Recall that the definition of vicinal or adsorbed water is water whose properties vary with the distance from the solid phase. In an ideal case, in which the solid phase is composed of flat parallel platelets, the adsorption of additional water causes the platelets to move further apart, changing the properties (density, viscosity, etc. [3]) of the vicinal fluid. Thus incorporating the volume fraction as an independent variable of  $A^l$  allows for this property — the further apart the solid platelets, the larger the volume fraction of the liquid phase. This allows us to model particles at medium to high moisture content. At low moisture content (5 or fewer layers of water between solid platelets), the liquid phase can also be affected by relative shearing of the solid phase [30, 31, 32]. This is represented in the model by assuming the liquid phase energy is a function of the solid strain tensor which, by definition, is the strain of the “smeared out” solid phase. So as the platelets separate, the solid phase strain tensor is altered. Similarly, if the platelets are sheared relative to each other, this again affects the strain tensor. Using assumption (2.20) gives us a framework to *derive* a constitutive relation for swelling pressure previously obtained only empirically by Low [3] for the first time [10].

To complete the set of definitions, we introduce the thermodynamic pressures ( $p^\alpha$ ), the classical effective stress tensor ( $\mathbf{t}_e^s$ ) in the sense of Terzaghi [33], and the hydration stress tensor ( $\mathbf{t}_s^l$ ) [24, 21]. Within the current framework they are defined as follows:

$$p^\alpha = (\rho^\alpha)^2 \frac{\partial A^\alpha}{\partial \rho^\alpha}, \quad (2.21)$$

$$\mathbf{t}_e^s = \rho^s \mathbf{F}^s \frac{\partial A^s}{\partial \mathbf{E}^s} (\mathbf{F}^s)^T, \quad \mathbf{t}_s^l = \rho^l \mathbf{F}^s \frac{\partial A^l}{\partial \mathbf{E}^s} (\mathbf{F}^s)^T, \quad (2.22)$$

The definition of  $\mathbf{t}_e^s$  is analogous to the Cauchy stress tensor for an elastic medium (see Eringen [29]) although applied to a porous skeleton. In soil mechanics this stress tensor is referred to as the Terzaghi stress tensor. The hydration stress tensor,  $\mathbf{t}_s^l$  is a result of the physico-chemical forces between the fluid and solid phases (see [21] for further discussion). If one of the phases is incompressible, then there is no thermodynamic definition for pressure, but a corresponding term is still obtained by treating

the continuity equation as a restriction enforced weakly using a Lagrange multiplier. In this case, the pressure becomes an unknown in the problem (see [26, 24, 19]).

The entropy inequality can be formulated in the usual manner [10, 26, 7], and in the sense of Coleman and Noll [4] the entropy inequality is exploited to obtain restrictions on the forms of constitutive equations. We present the results in the next section.

## 2.2 Constitutive Restrictions

In this section we present relations resulting from the exploitation of the entropy inequality which are pertinent to the formulation of the flow and heat transfer within the 2-scale model. We present two sets of results which represent a small portion of the results derived in [26, 10] in much greater detail. The first set consists of results which hold at equilibrium and far from equilibrium, and come from the assumption that  $D^s T/Dt$  and  $\mathbf{d}^s$  are not constitutive independent variables:

$$\varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial T} + \eta^l \right) + \varepsilon^s \rho^s \left( \frac{\partial A^s}{\partial T} + \eta^s \right) = 0, \quad (2.23)$$

$$\varepsilon^s \mathbf{t}^s = -\varepsilon^s p^s \mathbf{I} + \varepsilon^s \mathbf{t}_e^s + \varepsilon^l \mathbf{t}_s^l. \quad (2.24)$$

Equation (2.23) is a generalization of the classical result stating that temperature and entropy are dual variables. Equation (2.24) is a constitutive relation for  $\mathbf{t}^s$  and indicates that the solid stress is composed of a thermodynamic pressure, the effective stress tensor, which is a measure of solid-solid interaction, and the hydration stress tensor which incorporates the effects of the fluid-solid interactions.

The second set of results hold near-equilibrium and come from quadratic terms in the entropy inequality so that the entropy generated is always nonnegative. The fact that this comes from a linearization process means that terms of cubic and higher order have been neglected; thus these results hold only near equilibrium. They include

$$\mathbf{t}^l = -p^l \mathbf{I} + \rho^l \boldsymbol{\nu}^l : \mathbf{d}^l, \quad (2.25)$$

$$p^l - p^s = \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^l} + \hat{\mu}^l \frac{D^s \varepsilon^l}{Dt}, \quad (2.26)$$

$$\mathbf{v}^{l,s} = \mathbf{K} \left[ -\hat{\mathbf{T}}_s^l + p^l \nabla \varepsilon^l - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} : (\nabla \mathbf{E}^s) - \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T \right], \quad (2.27)$$

$$\mathbf{v}^{l,s} = \mathbf{K} \left[ -\varepsilon^l \nabla p^l + \varepsilon^l \rho^l \mathbf{g} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} : (\nabla \mathbf{E}^s) - \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T \right], \quad (2.28)$$

$$G^s - G^l = C^l \hat{e}_s^l, \quad (2.29)$$

$$\varepsilon^l \mathbf{q}^l + \varepsilon^s \mathbf{q}^s = K \nabla T. \quad (2.30)$$

The coefficients  $\boldsymbol{\nu}^l$ ,  $\hat{\mu}^l$ ,  $\mathbf{K}$ ,  $C^l$ , and  $K$  are constants which arise from the linearization procedure and may be a function of temperature, densities, volume fraction or solid strain [10, 24].  $G^\alpha$  of equation (2.29) is the Gibbs free energy for phase  $\alpha$  and is given by  $G^\alpha = p^\alpha/\rho^\alpha + A^\alpha$ . Equation (2.25) is the constitutive restriction on  $\mathbf{t}^l$  and when used to eliminate  $\mathbf{t}^l$  in the momentum equation, the Navier-Stokes equation results. At equilibrium  $\mathbf{d}^l$  is zero and we get that the stress tensor in the liquid phase is the hydrostatic pressure.

Equation (2.26) gives an expression for nonequilibrium interfacial pressure jump, and implies that the pressure difference between the liquid and solid phase is a function of the dynamic rate of change of the volume fraction (see [11] for a discussion on this topic and its relation to non-equilibrium interface pressure).

Equation (2.28) is a generalized Darcy-type law and arises when the constitutive equation for  $\hat{\mathbf{T}}_s^l$ , given by (2.27), and the momentum equation are used to eliminate  $\hat{\mathbf{T}}_s^l$ . In this expression, the inertial effects are neglected and the hydrostatic form of the stress tensor is used (see [10, 26] for details). The first two terms on the right-hand-side give what is typically known as Darcy's law, i.e., that the flow

of fluid is directly proportional to the gradient of pressure plus a gravitational effect. In a swelling porous medium in which the free energy of the vicinal phase may be a function of the volume fraction, the third term on the RHS indicates that flow will occur from regions of high volume fraction (high moisture content) to regions of low volume fraction. In a non-swelling medium this term would be negligible, as the energy of the fluid would not be affected by its proximity to the solid phase. Further, flow will also occur in the presence of a temperature gradient. The coefficient of this last term is zero when interfacial effects are negligible, as argued by Hassanizadeh and Gray [7]. However, in clays where the specific surface is large, in general we do not have  $\frac{\partial A_l}{\partial T} = -\eta_l$ .

Equation (2.29) states that the rate of transfer from the solid to liquid phase is directly proportional to the difference of the Gibbs free energies. If the liquid and solid were composed of identical materials (water and ice for example) this statement says that at equilibrium the chemical potential of two phases must be equal.

Finally, equation (2.30) states that the partial heat flux of the system is proportional to the temperature gradient, causing a coupling between this generalized Fourier's law of heat conduction and the generalized Darcy's law (2.28). A further coupling is obtained when the definition of the net heat flux, (2.10), is used, since this relation also involves the stress tensors. Hence, heat flux, fluid flow, and deformation are all coupled within this system of equations.

We end this section by listing the unknowns along with the equations necessary to describe the swelling and heat transfer of a swelling porous media. The unknowns in our final system of equations are:

$$\rho^l, \rho^s, \mathbf{v}^l, \mathbf{U}^s, T, \varepsilon^l, \quad (2.31)$$

$$\mathbf{t}^l, \mathbf{t}^s, \hat{\mathbf{e}}_s^l, \hat{\mathbf{T}}_s^l, \mathbf{q}, A^l, A^s, \eta^l, \eta^s, \quad (2.32)$$

where  $\mathbf{U}^s$  is the displacement of the solid phase. The equations include (roughly corresponding to the above unknowns): The conservation of mass (2.1), generalized Darcy's law for the fluid phase (2.28), conservation of momentum for the solid phase (2.2), the energy equation (2.4), non-equilibrium capillary pressure (or constitutive equation for  $D^s \varepsilon^l / Dt$ ) (2.26), constitutive equations for the stress tensors (2.25, 2.24), constitutive equations for the exchange of mass and momentum terms (2.29, 2.27), and the constitutive equation for the partial heat flux (2.30) combined with (2.10). The remaining 4 variables (Helmholtz energies and entropies) require constitutive equations for which no restrictions on their forms have been obtained. They may be a function of all variables listed in (2.16) and (2.17).

The energy equation (2.4), is not in a practical form and so we make use of the constitutive relations in order to re-write it. We begin with equations (2.3) and eliminate the internal energy in favor of the Helmholtz potential. Making use of constitutive assumptions (2.20) and (2.30), using the chain rule, and summing over the two equations, we obtain

$$\begin{aligned} \gamma_1 \dot{T} + \gamma_2 \dot{\varepsilon}^l + \gamma_3 \cdot \mathbf{v}^{l,s} + \mathbf{\Gamma}_4 : \dot{\mathbf{E}}^s + \mathbf{\Gamma}_5 : \mathbf{d}^l + \gamma_6 \hat{\mathbf{e}}_s^l \\ + \nabla \cdot (\mathbf{K} \nabla T) + \varepsilon^s \rho^s h^s + \varepsilon^l \rho^l h^l = -\hat{Q}_l^s - \hat{Q}_s^l. \end{aligned} \quad (2.33)$$

where  $\gamma_1, \gamma_2, \gamma_6$  are scalar functions,  $\gamma_3$  is a vector valued function, and  $\mathbf{\Gamma}_4$  and  $\mathbf{\Gamma}_5$  are second order tensor valued functions. Using  $\dot{\mathbf{E}}^s = (\mathbf{F}^s)^T \cdot \mathbf{d}^s \cdot \mathbf{F}^s$  it can be shown that these coefficients are related to the Helmholtz potential by

$$\begin{aligned} \gamma_1 &= T \left[ \varepsilon^s \rho^s \frac{\partial^2 A^s}{\partial T^2} + \varepsilon^l \rho^l \frac{\partial^2 A^l}{\partial T^2} \right] \\ &= T \rho \frac{\partial^2 A}{\partial T^2}, \end{aligned} \quad (2.34)$$

$$\begin{aligned} \gamma_2 &= p^l - p^s - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} - \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^l} - T \frac{\partial}{\partial T} \left( p^l - p^s - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} - \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^l} \right) \\ &= \hat{\mu}^l \varepsilon^l - T \frac{\partial}{\partial T} \left( \hat{\mu}^l \varepsilon^l \right) \end{aligned} \quad (2.35)$$

$$= \left( \hat{\mu}^l - T \frac{\partial \hat{\mu}^l}{\partial T} \right) \varepsilon^l, \quad (2.36)$$

$$\begin{aligned} \gamma_3 &= -\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l + p^l \nabla \varepsilon^l - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} : \mathbf{E}^s \nabla + \varepsilon^l \rho^l T \frac{\partial^2 A^l}{\partial T^2} \nabla T \\ &\quad + T \frac{\partial}{\partial T} \left[ \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l - p^l \nabla \varepsilon^l + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} : (\mathbf{E}^s \nabla) \right] \\ &= \mathbf{K}^{-1} \cdot \mathbf{v}^{l,s} + \hat{\mathbf{T}}_s^l + \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial T} + \eta^l - c_p^l \right) \nabla T \\ &\quad - T \frac{\partial}{\partial T} \left( \mathbf{K}^{-1} \cdot \mathbf{v}^{l,s} + \hat{\mathbf{T}}_s^l \right), \end{aligned} \quad (2.37)$$

$$\begin{aligned} \Gamma_4 &= -\varepsilon^s \rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} + \varepsilon^s (\mathbf{F}^s)^{-1} \cdot \mathbf{t}^s \cdot (\mathbf{F}^s)^{-T} + \varepsilon^s p^s (\mathbf{F}^s)^{-1} \cdot (\mathbf{F}^s)^{-T} \\ &\quad + T \frac{\partial}{\partial T} \left( \varepsilon^s \rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} - \varepsilon^s p^s (\mathbf{F}^s)^{-1} \cdot (\mathbf{F}^s)^{-T} \right) \\ &= T \frac{\partial}{\partial T} \left( \varepsilon^s \rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} + \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} - \varepsilon^s p^s \mathbf{I} \right) \\ &= T \frac{\partial \tilde{\mathbf{t}}^s}{\partial T}, \end{aligned} \quad (2.38)$$

$$\Gamma_5 = \varepsilon^l p^l \mathbf{I} + \varepsilon^l \mathbf{t}^l - \varepsilon^l T \frac{\partial p^l}{\partial T} \mathbf{I} = \varepsilon^l \rho^l \boldsymbol{\nu}^l : \mathbf{d}^l - \varepsilon^l T \frac{\partial p^l}{\partial T} \mathbf{I}, \quad (2.39)$$

$$\gamma_6 = \frac{p^s}{\rho^s} - \frac{p^l}{\rho^l} - T \frac{\partial}{\partial T} \left( \frac{p^s}{\rho^s} - \frac{p^l}{\rho^l} \right), \quad (2.40)$$

where  $\rho A = \varepsilon^l \rho^l A^l + \varepsilon^s \rho^s A^s$ ,  $\tilde{\mathbf{t}}^s = (\mathbf{F}^s)^{-1} \mathbf{t}^s (\mathbf{F}^s)^{-1}$  is analogous to the Piola-Kirchhoff stress tensor of the second kind, and the molar heat capacity of the liquid phase,

$$c_p^l = T \left( \frac{\partial \eta^l}{\partial T} \right) \quad (2.41)$$

may be a function of the volume fraction  $\varepsilon^l$ . The second form of equations (2.35)–(2.39) was obtained by incorporating constitutive relations (2.24)–(2.27).

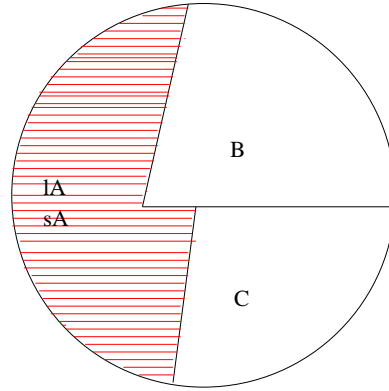
Let us now make some simplifying assumptions. Assume that the material time rate of change of the volume fraction is small, so that  $\gamma_2 \varepsilon^l$  is on the order of  $(\varepsilon^l)^2$  and can be neglected. Similarly, since inertial terms of the momentum equation were neglected in deriving (2.28), all terms of order  $\mathbf{v}^{l,s} \cdot \mathbf{v}^{l,s}$  and  $\mathbf{d}^l : \mathbf{d}^l$  can also be consistently neglected. Further, assume there is no exchange of mass between the liquid and solid phases so that the right-hand-side is  $-\hat{\mathbf{T}}_s^l \cdot \mathbf{v}^{l,s}$  which cancels with the same term on the left-hand-side. If there is no external source of body heat ( $h^l = h^s = 0$ ), then the heat equation is of a more familiar form:

$$\begin{aligned} \left( \rho T \frac{\partial^2 A}{\partial T^2} \right) \dot{T} + \left[ \varepsilon^l \rho^l \left( \frac{\partial A^l}{\partial T} + \eta^l - c_p^l \right) \nabla T - T \frac{\partial \hat{\mathbf{T}}_s^l}{\partial T} \right] \cdot \mathbf{v}^{l,s} + T \frac{\partial \tilde{\mathbf{t}}^s}{\partial T} : \dot{\mathbf{E}}^s - \varepsilon^l T \frac{\partial p^l}{\partial T} \nabla \cdot \mathbf{v}^l \\ + \nabla \cdot (\mathbf{K} \nabla T) = 0. \end{aligned} \quad (2.42)$$

### 3 Three-Scale Model

In this section we consider three-scales, denoted by micro, meso, and macro. As in the two-scale model, the field equations are upscaled via averaging to obtain field equations of Section 2.1. Fig. 3.1





**Figure 3.1:** A colloidal phase which may swell (denoted by  $lA$  and  $sA$ ) and two other phases,  $B$  and  $C$ .

illustrates the setting where we may have some portion of a swelling colloid (denoted by  $lA$  and  $sA$ ) and two other phases. The colloid may swell and shrink due to an overburden load, transfer of fluid, or temperature change.

The averaging of the field equations along with the relationships between the microscopic and macroscopic variables are presented in other papers [26, 23] so here we only present the resulting equations.

### 3.1 Macroscale Field Equations and Assumptions

In this section we discuss the development of the three-scale model. We assume the particle is composed of two phases, a liquid phase  $lA$ , and a solid phase  $sA$ , but now there may be interactions with two other phases. It is assumed that there are 3 distinct scales. At the microscale, (see Figure 1.1) one can distinguish between the solid and adsorbed liquid phase, at the mesoscale the particle can be distinguished from the other bulk phases, and at the macroscale, the medium appears to be continuous. It is assumed that interfacial properties are negligible, and that each phase behaves as a single constituent, i.e. there are no chemical reactions within a phase. We do allow for mass transfer between phases.

### 3.2 Macroscale Field Equations and Assumptions

In this model the field equations are upscaled twice. Averaging of the equations along with the relationships between the macroscopic and microscopic variables are presented in several papers [26, 23], so here again, we only present the resulting equations.

Conservation of mass for the  $\alpha A$ -phase is

$$\frac{D^{\alpha A}(\varepsilon^A \rho^{\alpha A})}{Dt} + \varepsilon^A \rho^{\alpha A} (\nabla \cdot \mathbf{v}^{\alpha A}) = \sum_{K=lA, sA, B, C \neq \alpha A} \widehat{e}_K^{\alpha A}, \quad \alpha A = lA, sA, \quad (3.1)$$

where  $\varepsilon^A$  is the local volume fraction of the colloidal phase,  $\rho^{\alpha A}$  is the mass density of the  $\alpha$ -phase on the macroscale so that  $\varepsilon^A \rho^{\alpha A}$  is the total mass of the  $\alpha$ -phase per unit volume. Further,  $\mathbf{v}^{\alpha A}$  is the mass-averaged macroscale velocity of phase  $\alpha A$ ,  $\widehat{e}_K^{\alpha A}$  represents the net mass gained by the  $\alpha A$ -phase from the  $K$  phase, and  $D^{\alpha A}/Dt$  denotes the material time derivative following the  $\alpha A$ -phase.

Similarly, one can write down the conservation of mass for each bulk phase,  $B$  and  $C$ , as

$$\frac{D^K(\varepsilon^K \rho^K)}{Dt} + \varepsilon^K \rho^K \nabla \cdot \mathbf{v}^K = \sum_{M=lA, sA, B, C \neq K} \widehat{e}_M^K, \quad K = B, C \quad (3.2)$$

where  $\varepsilon^K$  is the volume fraction of phase  $K$ , and  $\widehat{e}_M^K$  represents the rate of mass gained by the  $K$ -phase from phase  $M$ . Since this equation is identical in form to the mesoscale equation of (2.1), we will not explicitly write out the corresponding equations for conservation of momentum and energy, and the entropy inequality for the bulk phases  $B$  and  $C$ . These equations can be deduced from their mesoscale counterpart.

Conservation of momentum for the  $\alpha A$ -phase is

$$\varepsilon^A \rho^{\alpha A} \frac{D^{\alpha A} \mathbf{v}^{\alpha A}}{Dt} - \nabla \cdot (\varepsilon^A \mathbf{t}^{\alpha A}) - \varepsilon^A \rho^{\alpha A} \mathbf{g} = \sum_{K \neq \alpha A} \widehat{\mathbf{T}}_K^{\alpha A} \quad (3.3)$$

where  $\mathbf{t}^{\alpha A}$  denotes the average symmetric stress tensors for phase  $\alpha A$ ,  $\mathbf{g}$  is the body force (i.e. gravity), and  $\widehat{\mathbf{T}}_K^{\alpha A}$  denotes the net gain of momentum of the  $\alpha A$ -phase due to mechanical interactions with phase  $K$ .

Conservation of energy for phase  $\alpha A$  is given by

$$\varepsilon^A \rho^{\alpha A} \frac{D^{\alpha A} E^{\alpha A}}{Dt} - \varepsilon^A \mathbf{t}^{\alpha A} : \nabla \mathbf{v}^{\alpha A} - \nabla \cdot (\varepsilon^A \mathbf{q}^{\alpha A}) - \varepsilon^A \rho^{\alpha A} h^{\alpha A} = \sum_{K \neq \alpha A} \widehat{Q}_K^{\alpha A} \quad (3.4)$$

where  $E^{\alpha A}$  is the average internal energy density per unit mass of the  $\alpha A$ -phase,  $\mathbf{q}^{\alpha A}$  denotes the heat flux, and  $\widehat{Q}_K^{\alpha A}$  denotes the gain of energy by the  $\alpha A$ -phase due to non-mechanical interactions with phase  $K$ . If we sum over all phases, one recovers the familiar form of the energy equation

$$\rho \frac{DE}{Dt} - \mathbf{t} : \nabla \mathbf{v} - \nabla \cdot \mathbf{q} - \rho h = 0, \quad (3.5)$$

where the relationships between the medium and phase thermodynamic variables are

$$\rho = \sum_K \varepsilon^K \rho^K, \quad (3.6)$$

$$\rho \mathbf{v} = \sum_K \varepsilon^K \rho^K \mathbf{v}^K, \quad (3.7)$$

$$\mathbf{u}^K = \mathbf{v}^K - \mathbf{v}, \quad (3.8)$$

$$\mathbf{t} = \sum_K [\varepsilon^K \mathbf{t}^K - \varepsilon^K \rho^K \mathbf{u}^K \mathbf{u}^K], \quad (3.9)$$

$$\rho E = \sum_K [\varepsilon^K \rho^K E^K + \varepsilon^K \rho^K \mathbf{u}^K \cdot \mathbf{u}^K], \quad (3.10)$$

$$\mathbf{q} = \sum_K \left[ \varepsilon^K \mathbf{q}^K + \mathbf{t}^K \cdot \mathbf{u}^K - \rho^K \mathbf{u}^K (E^K + \frac{1}{2} \mathbf{u}^K \cdot \mathbf{u}^K) \right], \quad (3.11)$$

$$\rho h = \sum_K \varepsilon^K \rho^K h^K, \quad (3.12)$$

$$(3.13)$$

where all sums are over  $K = lA, sA, B, C$ . Note that relative velocities of one phase over the mass averaged medium velocity contribute to a macroscopic heat flux.

Further, we have restrictions which arise from the fact that the thermodynamic properties of the interface are negligible. This results in the following relations:

$$\widehat{e}_M^K + \widehat{e}_K^M = 0, \quad (3.14)$$

$$\left( \widehat{\mathbf{T}}_M^K + \widehat{e}_M^K \mathbf{v}^K \right) + \left( \widehat{\mathbf{T}}_K^M + \widehat{e}_K^M \mathbf{v}^M \right) = \mathbf{0}, \quad (3.15)$$

$$\left[ \widehat{Q}_M^K + \widehat{\mathbf{T}}_M^K \cdot \mathbf{v}^K + \widehat{e}_M^K \left( E^K + \frac{1}{2} \mathbf{v}^K \cdot \mathbf{v}^K \right) \right] + \left[ \widehat{Q}_K^M + \widehat{\mathbf{T}}_K^M \cdot \mathbf{v}^M + \widehat{e}_K^M \left( E^M + \frac{1}{2} \mathbf{v}^M \cdot \mathbf{v}^M \right) \right] = 0, \quad (3.16)$$

where  $K, M = lA, sA, B, C$  and  $K \neq M$ . The first equation states that the interfaces are massless, and the second and third equations state that no momentum nor energy are lost through the interfaces. Further we have the relation that

$$\varepsilon^A + \varepsilon^B + \varepsilon^C = 1. \quad (3.17)$$

After upscaling, the system is viewed as 4 co-existing continua, so that at each point in space there exists thermodynamic properties for all phases. At this point we perform a change of variables using a Legendre transformation to eliminate the energy density,  $E^K$ , in favor of the Helmholtz free energy,  $A^K$ ,

$$A^K = E^K - T\eta^K. \quad (3.18)$$

The unknowns in our system are:

$$\varepsilon^A, \varepsilon^B, \rho^K, \mathbf{v}^K, T \quad (3.19)$$

$$A^K, \eta^K, \mathbf{t}^K, \hat{\mathbf{e}}_M^K, \hat{\mathbf{T}}_M^K, \mathbf{q}^K, \hat{Q}_M^K, \quad K = lA, sA, B, C, \quad M = lA, sA, B, C \neq K. \quad (3.20)$$

subject to restrictions (3.14)-(3.17).

To arrive at a system which has the same number of equations as unknowns, we consider the second row of variables (3.20) to be dependent, or constitutive. These variables are assumed to be functions of a set of constitutive independent variables. As in the two-scale case, a careful count indicates that there are 2 additional unknowns for which there is no corresponding equation, namely  $\varepsilon^A$  and  $\varepsilon^B$ . To close the system, we postulate a constitutive relation for the material time derivative of the volume fractions.

We assume the macroscopic vicinal fluid,  $lA$ , and two bulk phase fluids,  $B$  and  $C$ , are viscous and the fluid and solid phases compressible. As before we still assume that the temperature of all phases are the same at each point in space.

By the Principle of Equipresence (Truesdell [28]), we assume that every constitutive variable is a function of *all* the following macroscopic constitutive independent variables:

$$\varepsilon^A, \varepsilon^B, T, \rho^K, \mathbf{E}^{sA}, \mathbf{v}^{K,sA}, \quad (3.21)$$

$$\nabla\varepsilon^A, \nabla\varepsilon^B, \nabla T, \nabla\rho^K, \nabla\mathbf{E}^{sA}, \mathbf{d}^K, \quad K = lA, sA, B, C \quad (3.22)$$

where  $\mathbf{E}^{sA}$  and  $\mathbf{d}^K$  are the macroscopic strain tensor of the solid phase and rate of deformation tensor of phase  $K$ , respectively, defined by

$$\mathbf{E}^{sA} = \frac{1}{2} \left( (\mathbf{F}^{sA})^T \mathbf{F}^{sA} - \mathbf{I} \right), \quad (3.23)$$

$$\mathbf{d}^K = \frac{1}{2} \left( \nabla\mathbf{v}^K + (\nabla\mathbf{v}^K)^T \right), \quad (3.24)$$

in which  $\mathbf{F}^{sA} = \text{grad } \mathbf{x}^{sA}$  denotes the deformation gradient (with grad denoting the differentiation with respect to a macroscopic material particle). As in the two-scale case we assume the constitutive variables are local functions. With this assumption, the variables and their gradients (3.23) can be considered independent.

The macroscopic strain is a measure of the solid phase geometry, so that by including  $\mathbf{E}^{sA}$  and  $\nabla\mathbf{E}^{sA}$  in the list of constitutive independent variables we are still assuming the behavior of the system is partially dictated by the separation, distortion, and entanglement of the solid platelets and their spatial variations. Contrary to the 2-scale case,  $\varepsilon^A$  and  $\mathbf{E}^{sA}$  are not closely coupled in general due to the potentially large amount of fluid which could be transferred between the vicinal,  $lA$ , and bulk phase,  $B$ .

To simplify the quantity of algebra which follows, we deviate slightly from the axiom of equipresence [28], and assume the Helmholtz free energy densities of the phases depend only on a subset of the set of constitutive independent variables. It can be shown that if it is assumed the Helmholtz free energies

are a function of all constitutive independent variables listed in (3.21), that the exploitation of the entropy inequality requires that all energies are not a function of  $\mathbf{v}^{K,sA}$ ,  $\nabla T$ , and  $\nabla \mathbf{E}^{sA}$ . Here we additionally assume that the free energies are not a function of densities of other phases. Incorporating these additional dependencies still produce the results presented herein if one slightly modifies the thermodynamic definitions of the pressure and chemical potential (see [24, 26] for details). For the system under consideration it is thus postulated that

$$A^{lA} = A^{lA}(\varepsilon^A, \varepsilon^B, T, \rho^{lA}, \mathbf{E}^{sA}), \quad (3.25)$$

$$A^{sA} = A^{sA}(\varepsilon^A, \varepsilon^B, T, \rho^{sA}, \mathbf{E}^{sA}), \quad (3.26)$$

$$A^K = A^K(\varepsilon^A, \varepsilon^B, T, \rho^K). \quad (3.27)$$

In this simplification we are still allowing the free energy of the vicinal water to be a function of its proximity to the solid phase by assuming its dependence on the solid phase strain tensor and the volume fraction of the particles. However the bulk phase fluids ( $B$  and  $C$ ) are, by definition, not affected by the proximity to the solid phase, so that their dependence on the solid phase strain tensor is not included. The inclusion of the volume fractions as independent variables in (3.27) provides a weak dependence of the free energies on the interfaces because of the the volume fractions' ability to capture some geometric effects. However, to obtain the full effects of interfaces, interfacial balance laws must be introduced, and additional constitutive independent variables such as interfacial area density must be incorporated [10, 26, 23, 24].

To complete the set of definitions, we introduce macroscale thermodynamic pressures ( $p^K$ ), the macroscale effective stress tensor ( $\mathbf{t}_e^{sA}$ ), and the macroscale hydration stress tensor ( $\mathbf{t}_{sA}^{lA}$ ) [24, 21]. Within the current framework they are defined as follows:

$$p^K = (\rho^K)^2 \frac{\partial A^K}{\partial \rho^K}, \quad K = lA, sA, B, C, \quad (3.28)$$

$$\mathbf{t}_e^{sA} = \rho^{sA} \mathbf{F}^{sA} \frac{\partial A^{sA}}{\partial \mathbf{E}^{sA}} (\mathbf{F}^{sA})^T, \quad \mathbf{t}_{sA}^{lA} = \rho^{lA} \mathbf{F}^{sA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} (\mathbf{F}^{sA})^T. \quad (3.29)$$

The effective stress tensor  $\mathbf{t}_e^{sA}$  captures the effects of entanglement in a porous medium with a disjoint solid phase. Again, the hydration stress tensor,  $\mathbf{t}_{sA}^{lA}$ , captures the physico-chemical forces between the vicinal fluid and the solid phase. Note that the macroscale pressure is not the average of mesoscale pressures, which is the average of a partial derivative, but it is the partial derivative of averaged quantities.

The entropy inequality can be formulated in the usual manner [26, 24], and in the sense of Coleman and Noll [4] exploited to obtain restrictions on the forms of constitutive equations. We present the results in the next section.

### 3.3 Constitutive Restrictions

In this section we present relations resulting from exploiting the entropy inequality. These are pertinent to the formulation of the flow and heat transfer within the 3-scale model. We present two sets of results which are a small portion of the more general results derived in [26, 24]. The first set of results hold at equilibrium and far from equilibrium, and come from the assumption that  $D^{sA}T/Dt$  and  $\mathbf{d}^{sA}$  are not constitutive independent variables:

$$\sum_{K=lA,sA,B,C} \varepsilon^K \rho^K \left( \frac{\partial A^K}{\partial T} + \eta^K \right) = 0, \quad (3.30)$$

$$\mathbf{t}^{sA} = -p^{sA} \mathbf{I} + \mathbf{t}_e^{sA} + \mathbf{t}_{sA}^{lA}. \quad (3.31)$$

As in the 2-scale case, equation (3.30) is a generalization of the classical result stating that temperature and entropy are dual variables. Equation (3.31) is a constitutive relation for  $\mathbf{t}^{sA}$  and indicates that the

solid stress is composed of a thermodynamic pressure, the effective stress tensor, which is a measure of solid-solid interaction, and the hydration stress tensor which incorporates the effects of the fluid-solid interactions.

The second set of results hold near-equilibrium and come from forming quadratic terms in the entropy inequality so that the entropy generated is always positive for any process. The fact that this comes from a linearization process means that terms of cubic and higher order have been neglected; thus these results hold only near equilibrium. Linearizing about the rate of deformation tensor,  $\mathbf{d}^K$ , we obtain

$$\mathbf{t}^K = -p^K \mathbf{I} + \rho^K \boldsymbol{\nu}^K : \mathbf{d}^K, \quad K = lA, B, C. \quad (3.32)$$

As in the two-scale case, at equilibrium  $\mathbf{d}^K = \mathbf{0}$  and the stress tensor of any of the fluid phases is proportional to the hydrostatic pressure.

Linearizing about  $D^{sA} \varepsilon^A / Dt$  and  $D^{sA} \varepsilon^B / Dt$  yields non-equilibrium capillary pressure relations:

$$p^{lA} + p^{sA} - p^C = \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} + \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \varepsilon^A} + \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} + \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^A} + \hat{\mu}^A \frac{D^{sA} \varepsilon^A}{Dt}, \quad (3.33)$$

$$p^B - p^C = \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} + \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \varepsilon^B} + \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^B} + \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^B} + \hat{\mu}^B \frac{D^{sA} \varepsilon^B}{Dt}. \quad (3.34)$$

Note that the natural quantity which appears in regards to the pressure of the particles is the sum of the liquid and solid pressures. This can be interpreted as being the thermodynamic pressure of the particle phase, i.e.  $p^A = p^{lA} + p^{sA}$ .

The constitutive relations for the exchange of momentum terms arise by linearizing about  $\mathbf{v}^{K,sA}$ :

$$\begin{aligned} \mathbf{v}^{lA,sA} &= \mathbf{K}^{lA} \left[ - \sum_{K=sA,B,C} \hat{\mathbf{T}}_K^{lA} + p^{lA} \nabla \varepsilon^A - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B \right. \\ &\quad \left. - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} : (\mathbf{E}^{sA} \nabla) - \varepsilon^A \rho^{lA} \left( \frac{\partial A^{lA}}{\partial T} + \eta^{lA} \right) \nabla T \right], \end{aligned} \quad (3.35)$$

$$\begin{aligned} \mathbf{v}^{K,sA} &= \mathbf{K}^K \left[ - \sum_{M=lA,sA,B,C \neq K} \hat{\mathbf{T}}_M^K + p^K \nabla \varepsilon^K - \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^B} \nabla \varepsilon^B \right. \\ &\quad \left. - \varepsilon^K \rho^K \left( \frac{\partial A^K}{\partial T} + \eta^K \right) \nabla T \right], \quad K = B, C. \end{aligned} \quad (3.36)$$

These relations are then used to eliminate the exchange of momentum terms,  $\hat{\mathbf{T}}_M^K$ , from the momentum equations to obtain generalized Darcy relationships:

$$\begin{aligned} \mathbf{v}^{lA,sA} &= \mathbf{K}^{lA} \left[ - \varepsilon^A \nabla p^{lA} + \varepsilon^A \rho^{lA} \mathbf{g} - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B \right. \\ &\quad \left. - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} : (\nabla \mathbf{E}^{sA}) - \varepsilon^A \rho^{lA} \left( \frac{\partial A^{lA}}{\partial T} + \eta^{lA} \right) \nabla T \right], \end{aligned} \quad (3.37)$$

$$\begin{aligned} \mathbf{v}^{K,sA} &= \mathbf{K}^K \left[ - \varepsilon^K \nabla p^K + \varepsilon^K \rho^K \mathbf{g} - \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^K \rho^K \frac{\partial A^K}{\partial \varepsilon^B} \nabla \varepsilon^B \right. \\ &\quad \left. - \varepsilon^K \rho^K \left( \frac{\partial A^K}{\partial T} + \eta^K \right) \nabla T \right], \quad K = B, C. \end{aligned} \quad (3.38)$$

In these expressions, the inertial effects are neglected and the hydrostatic forms of the stress tensors are used (see [26, 24] for details). Changes in volume fractions, pressure, and temperature all cause the energy of the system to change, and these relations all reflect that fluid flows in such a way as to minimize the energy of the entire system [26, 24].

If  $G^K = p^K/\rho^K + A^K$  is the Gibbs free energy, then the rate at which one phase is transferred to another phase is governed by

$$G^M - G^K = C^K \widehat{e}_M^K, \quad K, M = lA, sA, B, C, \quad K \neq M. \quad (3.39)$$

This equation is especially important for the case when  $M = lA$  and  $K = B$  where  $B$  is the bulk liquid phase. Then  $\widehat{e}_M^K$  is the rate at which mass is transferred from the vicinal water to the bulk water. If the Gibbs free energy is higher in the bulk phase, then particles begin swelling, and if the opposite, the particles shrink.

Finally we have the equation which governs heat transfer, which is similar to the two-scale case, i.e.

$$\varepsilon^A \mathbf{q}^{lA} + \varepsilon^A \mathbf{q}^{sA} + \varepsilon^B \mathbf{q}^B + \varepsilon^C \mathbf{q}^C = K \nabla T. \quad (3.40)$$

The gradient of the temperature couples the heat transfer with the flow of the liquid, which in turn governs the deformation of the porous medium. Note that because of relation (3.11) the left hand side is not the medium-wide heat flux unless there is no relative motion of phases.

All coefficients  $\nu^K$ ,  $\widehat{\mu}^K$ ,  $\mathbf{K}^K$ ,  $C^K$  and  $K$  are constants which arise from the linearization procedure and may be a function of temperature, densities, volume fractions, and solid strain [24].

As in the two-scale case, the energy equation (3.5), can be re-written making use of constitutive relations. We begin with equations (3.4) and eliminate the internal energy in favor of the Helmholtz potential. Making use of constitutive assumptions (3.25-3.27) and (3.40), using the chain rule, and summing over the four equations, we obtain

$$\begin{aligned} \gamma_1 \dot{T} + \gamma_2 \dot{\varepsilon}^A + \gamma_3 \dot{\varepsilon}^B + \gamma_4 \cdot \mathbf{v}^{lA, sA} + \gamma_5 \cdot \mathbf{v}^{B, sA} + \gamma_6 \cdot \mathbf{v}^{C, sA} + \mathbf{\Gamma}_7 : \dot{\mathbf{E}}^{sA} + \mathbf{\Gamma}_8 : \mathbf{d}^{lA} + \mathbf{\Gamma}_9 : \mathbf{d}^B + \mathbf{\Gamma}_{10} : \mathbf{d}^C \\ + \mathbf{\Gamma}_{10} : \mathbf{d}^C + \sum_{K=lA, sA, B, C} \sum_{M \neq K} \gamma_{KM} \widehat{e}_M^K \\ + \nabla \cdot (\mathbf{K} \nabla T) + \rho h = -\widehat{Q}, \end{aligned} \quad (3.41)$$

where  $\widehat{Q} = \sum_{K=lA, sA, B, C} \sum_{M \neq K} \widehat{Q}_M^K$ , scalar coefficient functions are denoted as  $\gamma$ , vector valued functions

are denoted as  $\boldsymbol{\gamma}$ , and  $\mathbf{\Gamma}$  denote second order tensor valued functions. Using  $\dot{\mathbf{E}}^s = (\mathbf{F}^s)^T \cdot \mathbf{d}^s \cdot \mathbf{F}^s$  it can be shown that these coefficients are related to the Helmholtz potential by

$$\gamma_1 = T \rho \frac{\partial^2 A}{\partial T^2}, \quad (3.42)$$

$$\begin{aligned} \gamma_2 &= p^{lA} + p^{sA} - p^C - \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \varepsilon^A} - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^A} \\ &\quad - T \frac{\partial}{\partial T} \left( p^{lA} + p^{sA} - p^C - \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \varepsilon^A} - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^A} \right) \\ &= \left( \widehat{\mu}^A - T \frac{\partial \widehat{\mu}^A}{\partial T} \right) \varepsilon^A, \end{aligned} \quad (3.43)$$

$$\begin{aligned} \gamma_3 &= p^B - p^C - \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \varepsilon^B} - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^B} - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^B} \\ &\quad - T \frac{\partial}{\partial T} \left( p^B - p^C - \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \varepsilon^B} - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^B} - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^B} \right) \\ &= \left( \widehat{\mu}^B - T \frac{\partial \widehat{\mu}^B}{\partial T} \right) \varepsilon^B, \end{aligned} \quad (3.44)$$

$$\gamma_4 = -\varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B + p^{lA} \nabla \varepsilon^A - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} : (\mathbf{E}^{sA} \nabla) + \varepsilon^A \rho^{lA} T \frac{\partial^2 A^{lA}}{\partial T^2} \nabla T$$

$$\begin{aligned}
& +T \frac{\partial}{\partial T} \left[ \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^A} \nabla \varepsilon^A + \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \varepsilon^B} \nabla \varepsilon^B - p^{lA} \nabla \varepsilon^A + \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} : (\mathbf{E}^{sA} \nabla) \right] \quad (3.45) \\
& = (\mathbf{K}^{lA})^{-1} \cdot \mathbf{v}^{lA,sA} + \sum_{K=sA,B,C} \hat{\mathbf{T}}_K^{lA} + \varepsilon^A \rho^{lA} \left( \frac{\partial A^{lA}}{\partial T} + \eta^{lA} - c_p^{lA} \right) \nabla T \\
& \quad - T \frac{\partial}{\partial T} \left( (\mathbf{K}^{lA})^{-1} \cdot \mathbf{v}^{lA,sA} + \sum_{K=sA,B,C} \hat{\mathbf{T}}_K^{lA} \right),
\end{aligned}$$

$$\begin{aligned}
\gamma_5 & = -\varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^B} \nabla \varepsilon^B + p^B \nabla \varepsilon^B + \varepsilon^B \rho^B T \frac{\partial^2 A^B}{\partial T^2} \nabla T \\
& \quad + T \frac{\partial}{\partial T} \left[ \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^A} \nabla \varepsilon^A + \varepsilon^B \rho^B \frac{\partial A^B}{\partial \varepsilon^B} \nabla \varepsilon^B - p^B \nabla \varepsilon^B \right] \quad (3.46) \\
& = (\mathbf{K}^B)^{-1} \cdot \mathbf{v}^{B,sA} + \sum_{K=lA,sA,C} \hat{\mathbf{T}}_K^B + \varepsilon^B \rho^B \left( \frac{\partial A^B}{\partial T} + \eta^B - c_p^B \right) \nabla T \\
& \quad - T \frac{\partial}{\partial T} \left( (\mathbf{K}^B)^{-1} \cdot \mathbf{v}^{B,sA} + \sum_{K=lA,sA,C} \hat{\mathbf{T}}_K^B \right),
\end{aligned}$$

$$\begin{aligned}
\gamma_6 & = -\varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^A} \nabla \varepsilon^A - \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^B} \nabla \varepsilon^B + p^C \nabla \varepsilon^C + \varepsilon^C \rho^C T \frac{\partial^2 A^C}{\partial T^2} \nabla T \\
& \quad + T \frac{\partial}{\partial T} \left[ \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^A} \nabla \varepsilon^A + \varepsilon^C \rho^C \frac{\partial A^C}{\partial \varepsilon^B} \nabla \varepsilon^B - p^C \nabla \varepsilon^C \right] \quad (3.47) \\
& = (\mathbf{K}^C)^{-1} \cdot \mathbf{v}^{C,sA} + \sum_{K=lA,sA,B} \hat{\mathbf{T}}_K^C + \varepsilon^C \rho^C \left( \frac{\partial A^C}{\partial T} + \eta^C - c_p^C \right) \nabla T \\
& \quad - T \frac{\partial}{\partial T} \left( (\mathbf{K}^C)^{-1} \cdot \mathbf{v}^{C,sA} + \sum_{K=lA,sA,B} \hat{\mathbf{T}}_K^C \right),
\end{aligned}$$

$$\begin{aligned}
\Gamma_7 & = -\varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \mathbf{E}^{sA}} - \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} + \varepsilon^A (\mathbf{F}^{sA})^{-1} \cdot \mathbf{t}^{sA} \cdot (\mathbf{F}^{sA})^{-T} + \varepsilon^A p^{sA} (\mathbf{F}^{sA})^{-1} \cdot (\mathbf{F}^{sA})^{-T} \\
& \quad + T \frac{\partial}{\partial T} \left( \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \mathbf{E}^{sA}} + \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} - \varepsilon^A p^{sA} (\mathbf{F}^{sA})^{-1} \cdot (\mathbf{F}^{sA})^{-T} \right) \quad (3.48) \\
& = T \frac{\partial}{\partial T} \left( \varepsilon^A \rho^{sA} \frac{\partial A^{sA}}{\partial \mathbf{E}^{sA}} + \varepsilon^A \rho^{lA} \frac{\partial A^{lA}}{\partial \mathbf{E}^{sA}} - \varepsilon^A p^{sA} (\mathbf{F}^{sA})^{-1} \cdot (\mathbf{F}^{sA})^{-T} \right) \\
& = T \frac{\partial}{\partial T} \left( \varepsilon^A (\mathbf{F}^{sA})^{-1} \cdot \mathbf{t}^{sA} \cdot (\mathbf{F}^{sA})^{-T} \right)
\end{aligned}$$

$$\Gamma_8 = \varepsilon^A p^{lA} \mathbf{I} + \varepsilon^A \mathbf{t}^{lA} - \varepsilon^A T \frac{\partial p^{lA}}{\partial T} \mathbf{I} = \varepsilon^A \rho^{lA} \boldsymbol{\nu}^{lA} : \mathbf{d}^{lA} - \varepsilon^A T \frac{\partial p^{lA}}{\partial T} \mathbf{I}, \quad (3.49)$$

$$\Gamma_9 = \varepsilon^B p^B \mathbf{I} + \varepsilon^B \mathbf{t}^B - \varepsilon^B T \frac{\partial p^B}{\partial T} \mathbf{I} = \varepsilon^B \rho^B \boldsymbol{\nu}^B : \mathbf{d}^B - \varepsilon^B T \frac{\partial p^B}{\partial T} \mathbf{I}, \quad (3.50)$$

$$\Gamma_{10} = \varepsilon^C p^C \mathbf{I} + \varepsilon^C \mathbf{t}^C - \varepsilon^C T \frac{\partial p^C}{\partial T} \mathbf{I} = \varepsilon^C \rho^C \boldsymbol{\nu}^C : \mathbf{d}^C - \varepsilon^C T \frac{\partial p^C}{\partial T} \mathbf{I}, \quad (3.51)$$

$$\gamma_{KM} = \frac{p^M}{\rho^M} - \frac{p^K}{\rho^K} - T \frac{\partial}{\partial T} \left( \frac{p^M}{\rho^M} - \frac{p^K}{\rho^K} \right), \quad (3.52)$$

where  $\rho A = \varepsilon^l \rho^l A^l + \varepsilon^s \rho^s A^s$ , and the molar heat capacities for each fluid phase is

$$c_p^K = T \left( \frac{\partial \eta^K}{\partial T} \right) \quad K = lA, B, C, \quad (3.53)$$

where  $c_p^K$  may be a function of the volume fractions. The second form of equations (3.43) - (3.51) were obtained by incorporating constitutive relations (3.31) - (3.36).

As in the two-scale case, let us now consider some simplifying assumptions. Assume that the material time rates of change of the volume fractions are small, so that the terms involving  $\gamma_2$  and  $\gamma_3$  can be neglected. Similarly, since inertial terms of the momentum equation were neglected in deriving (2.28), all terms of order  $\mathbf{v}^{lA, sA} \cdot \mathbf{v}^{lA, sA}$ ,  $\mathbf{v}^{lA, sA} \cdot \mathbf{v}^{B, sA}$ ,  $\mathbf{v}^{B, sA} \cdot \mathbf{v}^{B, sA}$ ,  $\mathbf{v}^{C, sA} \cdot \mathbf{v}^{C, sA}$ ,  $\mathbf{d}^{lA} : \mathbf{d}^{lA}$ ,  $\mathbf{d}^B : \mathbf{d}^B$ ,  $\mathbf{d}^C : \mathbf{d}^C$ , can also be consistently neglected. Further, assume there is no exchange of mass involving the solid phase so that  $\widehat{e}_{sA}^{lA} = \widehat{e}_{lA}^{sA} = \widehat{e}_B^{sA} = \widehat{e}_{sA}^B = \widehat{e}_C^{sA} = \widehat{e}_{sA}^C = 0$ . Then, using (3.16), the right-hand-side can be simplified and the terms involving  $\widehat{\mathbf{T}}$  and  $\widehat{e}$  combined with the corresponding terms on the left-hand-side. If there is no external source of body heat ( $h = 0$ ), then the heat equation is of the form:

$$\begin{aligned} & \left( \rho T \frac{\partial^2 A}{\partial T^2} \right) \dot{T} + \left[ \varepsilon^A \rho^{lA} \left( \frac{\partial A^{lA}}{\partial T} + \eta^{lA} - c_p^{lA} \right) \nabla T - \sum_{K=sA, B, C} T \frac{\partial \widehat{\mathbf{T}}_K^{lA}}{\partial T} \right] \cdot \mathbf{v}^{lA, sA} \\ & + \left[ \varepsilon^B \rho^B \left( \frac{\partial A^B}{\partial T} + \eta^B - c_p^B \right) \nabla T - \sum_{K=lA, sA, C} T \frac{\partial \widehat{\mathbf{T}}_K^B}{\partial T} \right] \cdot \mathbf{v}^{B, sA} \\ & + \left[ \varepsilon^C \rho^C \left( \frac{\partial A^C}{\partial T} + \eta^C - c_p^C \right) \nabla T - \sum_{K=lA, sA, B} T \frac{\partial \widehat{\mathbf{T}}_K^C}{\partial T} \right] \cdot \mathbf{v}^{C, sA} \\ & + T \frac{\partial}{\partial T} \left( \varepsilon^A (\mathbf{F}^{sA})^{-1} \cdot \mathbf{t}^{sA} \cdot (\mathbf{F}^{sA})^{-T} \right) : \dot{\mathbf{E}}^{sA} \\ & - \varepsilon^A T \frac{\partial p^{lA}}{\partial T} \nabla \cdot \mathbf{v}^{lA} - \varepsilon^B T \frac{\partial p^B}{\partial T} \nabla \cdot \mathbf{v}^B - \varepsilon^C T \frac{\partial p^C}{\partial T} \nabla \cdot \mathbf{v}^C \\ & + \sum_{K=lA, B, C} \sum_{M \neq (K, sA)} \widehat{e}_M^K \left[ G^M - G^K + T(\eta^M - \eta^K) - T \frac{\partial}{\partial T} \left( \frac{p^M}{\rho^M} - \frac{p^K}{\rho^K} \right) \right] \\ & + \nabla \cdot (\mathbf{K} \nabla T) = 0. \end{aligned} \quad (3.54)$$

Thus rate of flow of a fluid phase is driven by (1) the gradient of the temperature, which is strongly affected by the interaction of the phases; (2) how temperature affects momentum transfer between phases; (3) the rate at which the solid phase is deforming; (4) the effect of temperature on the pressure of each phase individually - note that if there is no exchange of mass between phases and the fluid phases are considered incompressible, these terms would vanish; and (5) the rate of mass exchanged between phases.

#### 4 Discussion

Consider the following system. Let colloidal sized molecules (polymers, clay platelets) be in a solvent bath such that all the solvent is adsorbed to the molecules. The solvent plus the colloid sized molecules considered as a single body can be thought of as a swelling particle. Now place a large number of the swelling particles in a bulk solvent bath. If the bath is suitably small, then the particles and solvent bath will form a partially saturated porous medium consisting of swelling porous particles. The solvent continues to saturate the particles, but the spaces between particles may contain vapor and/or liquid solvent. The net result is a swelling unsaturated porous medium with three distinct scales.



The microscale consists of two phases, the macromolecule and the adsorbed solvent. The mesoscale consists of a homogenization of the macromolecules with the adsorbed solvent. The mesoscale particles when homogenized with the bulk liquid and vapor phase solvent form the macroscale. Such a model is consistent with many natural soils, foods, drug delivery substrates, wood and many other systems. The model proposed herein allows one to simulate flows of mass and energy in such systems.

Classical irreversible thermodynamics suggests moisture flow in a porous medium can be driven by temperature gradients [34, 35, 36]. In addition, early experiments [37]–[38] also suggest flows may be driven by thermal gradients. We believe the analysis presented here provides a rational framework for this phenomenon. Of specific note in this regard is that the coefficients multiplying  $\nabla T$  in (2.37), (2.42), (3.45–3.47), (3.54) are non-zero and strongly affected by the phase-interactions due to the heat capacity terms and the fact that the entropy inequality does not mandate that  $\frac{\partial A^i}{\partial T} = -\eta^i$  on the mesoscale, nor does it mandate  $\frac{\partial A^*}{\partial T} = -\eta^*$  on the macroscale. In both unsaturated media where there is a liquid/vapor interface, and in colloids where the solvent energy is strongly perturbed by the surface, the interfaces liquid-vapor and solid-liquid play a predominant role.

**Acknowledgements:** Partial support for this work arises from NSF Grant #9510066-BES.

## REFERENCES

- [1] R. E. Grim. *Clay mineralogy*. McGraw-Hill, New York, 1968.
- [2] P. F. Low. Nature and properties of water in montmorillonite-water systems. *J. Soil Sci. Soc. Am.*, 43:651–658, 1979.
- [3] P. F. Low. The swelling of clay, II. Montmorillonites-water systems. *J. Soil Sci. Soc. Am.*, 44:667–676, 1980.
- [4] B. D. Coleman and W. Noll. The thermodynamics of elastic materials with heat conduction and viscosity. *Arch. Rat. Mech. Anal.*, 13:167–178, 1963.
- [5] S. M. Hassanizadeh and W. G. Gray. General conservation equations for multiphase systems: 1. Averaging procedure. *Adv. Water Resour.*, 2:131–144, 1979.
- [6] S. M. Hassanizadeh and W. G. Gray. General conservation equations for multiphase systems: 2. Mass, momenta, energy, and entropy equations. *Adv. Water Resour.*, 2:191–208, 1979.
- [7] S. M. Hassanizadeh and W. G. Gray. General conservation equations for multiphase systems: 3. Constitutive theory for porous media. *Adv. Water Resour.*, 3:25–40, 1980.
- [8] S. M. Hassanizadeh. Derivation of basic equations of mass transport in porous media, Part 1. Macroscopic balance laws. *Adv. Water Resour.*, 9:196–206, 1986.
- [9] S. M. Hassanizadeh. Derivation of basic equations of mass transport in porous media, Part 2. Generalized Darcy’s and Fick’s laws. *Adv. Water Resour.*, 9:207–222, 1986.
- [10] S. Achanta, J. H. Cushman, and M. R. Okos. On multicomponent, multiphase thermomechanics with interfaces. *Int. J. Eng. Sci.*, 32(11):1717–1738, 1994.
- [11] S. Achanta and J. H. Cushman. Non-Equilibrium swelling and capillary pressure relations for colloidal systems. *J. Col. Int. Sci.*, 168:266–268, 1994.
- [12] S. M. Hassanizadeh and W. G. Gray. Thermodynamic basis of capillary pressure in porous media. *Water Resources Research*, 29(10):3389–3405, 1993.
- [13] L. S. Bennethum and T. Giorgi. Generalized forchheimer law for two-phase flow based on hybrid mixture theory. *Transport in Porous Media*, 26(3):261–275, 1997.

- [14] W. G. Gray and S. M. Hassanizadeh. Paradoxes and realities in unsaturated flow theory. *Water Resour. Res.*, 27:1847–1854, 1991.
- [15] W. G. Gray and S. M. Hassanizadeh. Unsaturated flow theory including interfacial phenomena. *Water Resour. Res.*, 27:1855–1863, 1991.
- [16] S. M. Hassanizadeh and W. G. Gray. High velocity flow in porous media. *Transport in Porous Media*, 2:521–531, 1987.
- [17] S. M. Hassanizadeh and W. G. Gray. Toward an improved description of the physics of two-phase flow. *Advances in Water Resources*, 16:53–67, 1993.
- [18] L. S. Bennethum, M. A. Murad, and J. H. Cushman. Clarifying mixture theory and the macroscale chemical potential for porous media. *International Journal of Engineering Science*, 34(14):1611–1621, 1996.
- [19] L. S. Bennethum, M. M. Murad, and J. H. Cushman. Macroscale thermodynamics and the chemical potential for swelling porous media. submitted, 1997.
- [20] M. Murad, L. S. Bennethum, and J. H. Cushman. A multi-scale theory of swelling porous media: I. Application to one-dimensional consolidation. *Transport in Porous Media*, 19:93–122, 1995.
- [21] M. A. Murad and J. H. Cushman. Multiscale flow and deformation in hydrophilic swelling porous media. *International Journal of Engineering Science*, 34(3):313–336, 1996.
- [22] L. S. Bennethum, M. M. Murad, and J. H. Cushman. Modified darcy’s law, terzaghi’s effective stress principle and fick’s law for swelling clay soils. *Computers and Geotechnics*, 20(3/4):245–266, 1997.
- [23] L. S. Bennethum and J. H. Cushman. Multiscale, hybrid mixture theory for swelling systems - I: Balance laws. *Int. J. Engrg. Sci.*, 34(2):125–145, 1996.
- [24] L. S. Bennethum and J. H. Cushman. Multiscale, hybrid mixture theory for swelling systems - II: Constitutive theory. *Int. J. Engrg. Sci.*, 34(2):147–169, 1996.
- [25] J. H. Cushman. *The Physics of Fluids in Heirarchical Porous Media: Angstroms to Miles*. Kluwer Academic, N.Y., 1997.
- [26] L. S. Bennethum. *Multiscale, hybrid mixture theory for swelling systems with interfaces*. PhD thesis, Purdue University, West Lafayette, Indiana, 47907, 1994.
- [27] R. M. Bowen. Compressible porous media models by use of the theory of mixtures. *Int. J. Engrg. Sci.*, 20:697–735, 1982.
- [28] C. Truesdell and R. A. Toupin. The classical field theories. In S. Flügge, editor, *Handbuch der Physik*. Springer-Verlag, New York, 1960.
- [29] A. C. Eringen. *Mechanics of Continua*. John Wiley and Sons, New York, 1967.
- [30] J. H. Cushman. Molecular-scale lubrication. *Nature*, 347(6290):227–228, 1990.
- [31] M. Schoen, D. J. Diestler, and J. H. Cushman. Fluids in micropores. I. Structure of a simple classical fluid in a slit-pore. *The Journal of Chemical Physics*, 87(9):5464–5476, 1987.
- [32] J. Israelachvili. *Intermolecular and Surface Forces*. Academic Press, New York, 1992.
- [33] K. Terzaghi. *Theoretical soil mechanics*. John Wiley and Sons, New York, 1943.

- [34] J. W. Carey. Onsager's relation and nonisothermal diffusion of water vapor. *J. Phys. Chem.*, 67:126–129, 1963.
- [35] J. W. Carey. An evaporation experiment and its irreversible thermodynamics. *Int. J. Heat and Mass Trans.*, 7:531–538, 1964.
- [36] S. A. Taylor and J. W. Carey. Analysis of simultaneous flow of water and heat or electricity with the thermodynamics of irreversible processes. In *7th Int. Congr. of Soil Sci. Trans.*, volume 1, pages 80–90, 1960.
- [37] B. V. Deryaguin and M. K. Melnikova. Experimental study of the migration of water through the soil under the influence of salt concentration, temperature, and moisture gradients. In *Int. Congr. Soil Sci., Trans. 6th (Paris)*, pages 305–314, 1956.
- [38] R. L. Rollins, M. G. Spangler and D. Kirkham. Movement of soil moisture under a thermal gradient. *Highway Research Board Proc.*, 33:492–508, 1954.