

# MACROSCALE THERMODYNAMICS AND THE CHEMICAL POTENTIAL FOR SWELLING POROUS MEDIA

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## Abstract.

The thermodynamical relations for a two-phase, N-constituent, swelling porous medium are derived using a hybridization of averaging and the mixture-theoretic approach of Bowen. Examples of such media include 2-1 lattice clays and lyophilic polymers. The homogenized field equations are obtained by volume averaging microscale field equations so that explicit relationships between the macroscale field variables and their microscale counterparts are obtained. The system of equations is closed by assuming the rate of change of the volume fraction is a dependent constitutive variable, resulting in viscoelastic behavior of the porous medium. A novel, scalar definition for the macroscale chemical potential for porous media is introduced, and it is shown how the properties of this chemical potential can be derived by slightly expanding the usual Coleman and Noll approach for exploiting the entropy inequality to obtain near-equilibrium results. Within this approach, we use Lagrange multipliers to weakly enforce the continuity equations as well as the relationship between the gradients of the diffusive velocities. The relationship between this novel scalar chemical potential and the tensorial chemical potential of Bowen is discussed. The tensorial chemical potential may be discontinuous between the solid and fluid phases at equilibrium; a result in clear contrast to Gibbsian theories. This discontinuity in the potential is due to an "effective" external field (e.g. the effective stress induced by a load in the solid phase). It is shown that the macroscopic scalar chemical potential is completely analogous with the Gibbsian chemical potential. The relation between the two potentials is illustrated in three examples.

## Nomenclature

In general, a subscript greek letter indicates a macroscale quantity from that phase. Superscript minuscules indicate the constituent, so that, e.g.  $v_{\alpha}^j$  is the macroscopic velocity of constituent  $j$  in the  $\alpha$ -phase. A carrot over the symbol,  $\hat{\phantom{x}}$ , is used to emphasize that the quantity represents a transfer from either another phase or from other constituents.

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$A_\alpha^j$	Helmholtz free energy density of $j$ th constituent in $\alpha$ -phase
$b_\alpha^j$	external entropy source for $j$ th constituent in $\alpha$ -phase
$C_\alpha^j$	mass concentration
$\mathbf{d}_\alpha^j$	Symmetric part of $\nabla \mathbf{v}_\alpha^j$
$\widehat{e}_\alpha^j$	rate of mass exchange from other phase to $\alpha$ -phase of $j$ th constituent
$E_\alpha^j$	energy density
$\mathbf{E}_s$	macroscale strain tensor of solid phase
$\widehat{E}_\alpha^j$	energy gained by constituent $j$ in phase $\alpha$ due to non-chemical, non-mechanical interactions with other constituents within phase $\alpha$
$\mathbf{F}_s$	deformation gradient, $\text{grad} \mathbf{x}_s$ , of the solid phase
$\mathbf{g}$	gravity
$G_\alpha$	Gibbs free energy
$\mathbf{G}_\alpha$	generalized tensorial Gibbs free energy
$h_\alpha^j$	external supply of energy
$\widehat{\mathbf{i}}_\alpha^j$	gain of momentum of constituent $i$ of phase $\alpha$ due to mechanical interactions with other species within the same phase
$\mathbf{n}_\alpha$	unit outward normal to phase $\alpha$
$p_\alpha$	thermodynamic pressure
$\mathbf{q}_\alpha^j$	heat flux of constituent $j$ in $\alpha$ -phase.
$\widehat{Q}_\alpha^j$	gain of energy of constituent $j$ in phase $\alpha$ due to non-mass transfer interactions with the other phase
$\widehat{r}_\alpha^j$	rate of $j$ th constituent mass gained within phase $\alpha$
$\mathbf{t}_\alpha^j$	stress tensor of $j$ th constituent in $\alpha$ -phase
$T$	temperature
$\widehat{\mathbf{T}}_\alpha^j$	gain of momentum of phase $\alpha$ due to mechanical interactions with the other phase
$\mathbf{u}_\alpha^j$	diffusive velocity, $\mathbf{v}_\alpha^j - \mathbf{v}_\alpha$
$\mathbf{v}_\alpha$	velocity of phase $\alpha$
$\mathbf{v}_\alpha^j$	mass averaged velocity of $j$ th constituent in phase $\alpha$
$\delta V$	Representative Elementary Volume (REV)
$\delta V_\alpha$	portion of REV within $\alpha$ -phase
$\mathbf{w}_{\alpha\beta}^j$	velocity of $j$ th constituent in the interface
$\varepsilon^\alpha$	volume fraction of $\alpha$ -phase in Representative Elementary Volume (REV)
$\gamma_\alpha$	indicator function for phase $\alpha$
$\lambda_\alpha$	Lagrange multiplier for continuity equation of phase $\alpha$
$\lambda_\alpha^j$	Lagrange multiplier for continuity equation of $j$ th constituent in phase $\alpha$
$\mathbf{\Gamma}_\alpha^N$	Lagrange multiplier for restrictions on sum of gradients of diffusive velocities
$\Lambda_\alpha^j$	entropy production density
$\mu_\alpha^j$	scalar chemical potential
$\boldsymbol{\mu}_\alpha^j$	tensorial chemical potential
$\eta_\alpha^j$	entropy density
$\widehat{\eta}_\alpha^j$	entropy gain of $j$ th constituent in $\alpha$ -phase due to non-mass transfer interactions with other constituents within phase $\alpha$
$\phi_\alpha^j$	entropy flux
$\widehat{\Phi}_\alpha^j$	entropy gained by $j$ th constituent in $\alpha$ -phase due to non-mass transfer interactions with the other phase
$\rho_\alpha^j$	averaged mass density of $j$ th constituent in $\alpha$ -phase = $C_\alpha^j \rho_\alpha$
$\rho_\alpha$	averaged mass density of $\alpha$ -phase = $\sum_{j=1}^N \rho_\alpha^j$

## 1 Introduction

The purpose of this paper is three-fold: to introduce a novel definition of the macroscale chemical potential for a porous medium, to show how one can derive the properties of this chemical potential by slightly expanding the usual Coleman and Noll approach for exploiting the entropy inequality to obtain near-equilibrium results, and to discuss the application of mixture theory to swelling porous media. By our modified approach and by using an appropriate definition of the chemical potential, we have been able to *derive* properties of the chemical potential which corresponds exactly with the properties of the classical Gibbsian chemical potential. We illustrate these techniques and the motivation for a new definition of the chemical potential within the context of swelling porous media.

Due to the chemical and physical forces between phases, many porous media can swell or shrink resulting in macroscopic behavior which may differ significantly from granular media. Examples of such media include lyophilic polymers and clay soils. The understanding of the constitutive behavior of these materials is crucial in applications involving almost all aspects of life. Swelling polymers have numerous technological applications in drug delivery, contact lenses, semiconductor manufacturing and food stuffs, and clay soils are widely distributed in the earth's crust. Hence they play a critical role in the transport of nutrients and pesticides in agriculture, in various high level nuclear waste isolation scenarios, in barriers for commercial land fills, and in consolidation and failure of foundations, highways and runways. Although everything derived in this paper can be applied to a wide variety of swelling systems, for ease of exposition we restrict our discussion to swelling clay soils.

The complex mechanisms underlying the constitutive behavior of a hydrophilic clay soil are a consequence of its complicated microstructure. Clay minerals consist of hydrous aluminum and magnesium silicates with an expanding layer lattice. Their tremendous specific surface area and their charged character cause hydrated clay platelets to form "particles". These particles swell under hydration and shrink under desiccation. The platelet-water bonding forces are usually referred to as "hydration forces" and cause the macroscopic behavior of clays to differ significantly from the behavior of granular non-swelling media. In the case of hydrophilic colloidal particles (e.g. smectites), the hydration forces are believed to arise from the hydrophilic character of the mineral surfaces. These interactions modify the thermodynamical properties of the water in the interlamellar spaces and consequently its properties vary with the proximity to the solid surface (Low [1],[2],[3], Grim [4]). Hence, the interlamellar water is termed *vicinal* water to distinguish it from its bulk or free-phase counterpart (i.e. water free of any adsorptive force). It has been advocated by Low and co-workers [5],[6], Derjaguin and co-workers [7],[8],[9] and Israelachvili and co-workers [10],[11],[12] that surface hydration forces are the dominant mechanism causing the swelling of clays, and it is these forces which we account for when developing this theory.

In this paper we combine techniques developed in earlier papers [13, 14, 15, 16, 17, 18] and apply them to a multicomponent swelling porous media with particular emphasis on the definition of the chemical potential. This is accomplished by adopting a proper theory of constitution which includes appropriate internal variables needed to capture the swelling character of the system. In particular, the approach developed herein provides a thermodynamical basis for the role hydration forces play in the adsorption and diffusion of contaminants in a swelling medium, as well as their affect on the consolidation of the matrix under an applied load.

In classical mixture theory a single-phase medium composed of  $N$  constituents is viewed as  $N$  co-existing continua. Bowen [19, 20, 21] extended this idea to model a porous medium so that at the macroscale a two-phase medium is viewed as two co-existing continua. In his work, macroscopic forms of the field equations (conservation of mass, momentum balance, and conservation of energy), which incorporate exchange terms between the co-existing continua, are postulated. Hassanizadeh and Gray [22, 23] showed that if the microscopic field equations are averaged then the terms in Bowen's macroscopic field equations can be identified precisely with microscopic counterparts. The combination of averaging and mixture theory is referred to as *hybrid mixture theory* (HMT). In both of these formulations, the constitutive restrictions are determined at the macroscale by exploiting the entropy inequality using the method of Coleman and Noll [24].

Although HMT has been used in several fields (e.g. alloy solidification [25]), a porous body is the canonical model of a system to which HMT is applied (see [26, 27, 28, 29, 30, 31, 32, 13, 14, 33, 15, 16, 17, 18]). In fact, the first application of HMT was to model single-phase flow through a deformable, elastic porous medium in which Darcy's law, which governs the flow of the liquid phase, as well as Biot's classical model for consolidation [34] were recovered [26]. Later the theory was extended to describe multicomponent fluid flow in porous media, in which the derivation of Fick's law and a generalized Darcy's law were the primary objectives [27]. Soon after, the theory was again extended to include multiphase flow in porous media with interfacial effects [31, 32]. Among other results, Hassanizadeh and Gray [29, 32, 28] extended the thermodynamical groundwork for the physics of two-phase flow of e.g. Bowen [21], Marle [35], Fremond and Nicolas [36]. In particular, a near-equilibrium capillary pressure relation and a generalized macroscopic form of Darcy's law were derived in which the generalized Darcy's law includes an additional interaction potential involving a saturation gradient. This generalized form of Darcy's law circumvents the usual heuristic extension of the single-fluid Darcy's law to that for multiple-fluid phases with relative permeability.

We discuss in detail the consequence of postulating the existence of a constitutive relation for the time rate of change of the volume fraction as a means of closing the system of equations (after Bowen [21]). As in all upscaling approaches, there exists an additional variable, the volume fraction in this case, for which there is no additional equation. The appearance of the additional variable is a consequence of losing information about the microscopic geometry, and is known as the closure issue (for a detailed discussion on this issue, see [37]). The means of closing the system is crucial in our formulation since, as a result, the macroscopic system has some viscoelastic constitutive behavior. As we shall see, the results are in agreement with some empirically based constitutive theories.

The macroscale chemical potential has been defined in a variety of ways, and here we concentrate on the definitions relating the change of the intensive Helmholtz potential with respect to the concentration, i.e. if  $\widetilde{\mu}_\alpha^j$  is the chemical potential of the  $j$ th constituent relative to the  $N$ th constituent, then

$$\widetilde{\mu}_\alpha^j \equiv \frac{\partial A_\alpha}{\partial C_\alpha^j} \quad j = 1, \dots, N-1,$$

in which  $A_\alpha$  is the intensive Helmholtz potential of phase  $\alpha$ , and  $C_\alpha^j$  is the mass concentration of the  $j$ th constituent in the  $\alpha$  phase. We employ a modification of the traditional linearization procedure for the dissipative entropy inequality to obtain near-equilibrium relations. The traditional procedure involves linearizing coefficients which are zero at equilibrium. For a system composed of  $N$  miscible components, this traditional approach yields a generalized form of Fick's law which has not been as sharp as needed for practical applications. In [27] and [13] the following form of Fick's law is derived:

$$\mathbf{R}_\alpha^j \mathbf{u}_\alpha^j = \nabla \widetilde{\mu}_\alpha^j = \nabla (\mu_\alpha^j - \mu_\alpha^N) \quad j = 1, \dots, N-1 \quad \alpha = l, s \quad (1.1)$$

where  $\mathbf{u}_\alpha^j$  is the diffusive velocity of constituent  $j$  in phase  $\alpha$  relative to the velocity of phase  $\alpha$  ( $\alpha = l, s$  denotes the liquid and solid phase, respectively),  $\mathbf{R}_\alpha^j$  is a material tensor arising from a linearization procedure, and  $\mu_\alpha^j$  is the chemical potential of the  $j$ th constituent. After appropriate simplifications (see [38, 27]) equation (1.1) reduces to the classical Fick's law which states that the diffusive velocity is proportional to the concentration gradient (see [39]). We are interested, however, in reproducing the more general form of Fick's law, which according to statistical thermodynamics, states that flow is driven by an absolute chemical potential gradient (i.e.  $\nabla \mu_\alpha^j$ ) [40]. This is in contrast to equation (1.1) which states that flow is driven by a chemical potential gradient *relative* to the  $N$ th component, implying that the diffusive velocity is a function of how the constituents are labeled.

This lack of clarity is similarly manifest in equilibrium relations obtained from the entropy principle. For example, classical Gibbsian thermodynamics tells us that at equilibrium, the chemical potential of a single constituent coexisting in two phases is constant, i.e.  $\mu_s^j = \mu_l^j$ ,  $j = 1, \dots, N$  (see e.g. [41]). Yet historically the only derivable comparable result obtained by exploiting the entropy inequality in mixture theory is [13]

$$\widetilde{\mu}_s^j = \widetilde{\mu}_l^j \quad j = 1, \dots, N-1. \quad (1.2)$$

As we shall see, there is no single method for extending the above relative result to the absolute form at the macroscale. The primary reason for obtaining results in terms of the relative chemical potential is the interdependence of the concentrations ( $\sum_{j=1}^N C_\alpha^j = 1$ ) and the interdependence of  $\mathbf{u}_\alpha^j$ ,  $j = 1, \dots, N$ , through the constraint

$$\sum_{j=1}^N C_\alpha^j \mathbf{u}_\alpha^j = 0. \quad (1.3)$$

In classical Gibbsian thermodynamics, this interdependence is avoided because extensive variables representing the number of molecules of each constituent are used as independent variables, instead of intensive variables (concentrations). Using extensive variables, such as the number of molecules of each constituent, is not possible in HMT as the upscaling process can not be performed on extensive variables, at least not in a physically meaningful manner. Thus, all results standardly derived [13, 27] are in terms of the relative chemical potential.

Some of the results involving the relative chemical potential can be sharpened by choosing  $\mu_\alpha^N$  appropriately and subsequently deriving results for the absolute (non-relative) chemical potentials. For example, Bowen [19] and Bowen and Wiese [42] proposed the following tensorial definition for the chemical potential which has been used in most hybrid mixture theory derivations [27, 13]:

$$\boldsymbol{\mu}_\alpha^j \equiv A_\alpha^j \mathbf{I} - \frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j \quad (1.4)$$

where  $\rho_\alpha^j \equiv C_\alpha^j \rho_\alpha$ ,  $\rho_\alpha$  denotes the density of the  $\alpha$ -phase, and  $A_\alpha^j$ ,  $\mathbf{t}_\alpha^j$  are the Helmholtz free energy and stress tensor of the  $j$ th component in the  $\alpha$ -phase, respectively. This definition has the nice property that

$$\sum_{j=1}^N C_\alpha^j \boldsymbol{\mu}_\alpha^j = A_\alpha \mathbf{I} - \frac{1}{\rho_\alpha} \mathbf{t}_\alpha, \quad (1.5)$$

where  $\mathbf{t}_\alpha$  and  $A_\alpha$  are the stress tensor and the internal Helmholtz free energy density [19] of phase  $\alpha$ , respectively. For the case of a perfect fluid,  $\mathbf{t}_\alpha = -p_\alpha \mathbf{I}$  ( $p_\alpha$  denotes pressure of phase  $\alpha$ ), the right hand side of (1.5) reduces to the classical thermostatics concept of Gibbs energy (see e.g. [41]). This definition for the chemical potential seems to be motivated by convenience and is not easily reconciled with the classical definition, which is a scalar. The classical Gibbsian chemical potential,  $\mu_\alpha^j$ , which is defined as the derivative of the extensive Helmholtz energy with respect to the number of molecules of constituent  $j$  [41], has the following characteristics: (1) it is a scalar and measures the energy required to insert a particle into the system (see e.g. [43]), (2) its gradient is the driving force for diffusive flow (Fick's law) [40], and (3) it is constant for a single constituent coexisting in two phases at equilibrium, i.e. for the solid,  $s$ , and liquid phase,  $l$ ,  $\mu_s^j = \mu_l^j$ ,  $j = 1, \dots, N$  where  $N$  is the number of miscible components in each phase (see e.g. [41]). The fact that the tensorial definition is not a scalar has led to some difficulty in evaluating all its components, especially the off-diagonal terms [44, 45]. Furthermore, Bowen's tensorial chemical potential (1.4) also does not satisfy characteristics 2 or 3.

The above issues on the chemical potential were addressed by Bennethum et al. [46] within the context of HMT applied to diffusion and adsorption of contaminants in a granular, or non-swelling, porous media. In this work, two definitions for the  $N$ th chemical potential were introduced, and their effects on the relative form of Fick's law (1.1) and equilibrium result (1.2) were discussed. Sharper forms of these results were derived by using relative result (1.1), modifying the linearization procedure used in the exploitation of the entropy inequality, and using a form of the Gibbs-Duhem relation. Here the sharper results of Bennethum et al. [46] are extended to accurately describe diffusion and adsorption of multicomponents in a swelling porous media. This shall be accomplished by adopting the Lagrange multiplier technique of Liu [47] to enforce the constraint on the gradient of diffusive

velocities (1.3) weakly. Liu proved that exploiting the entropy inequality subject to constraints is equivalent to exploiting a modified entropy inequality formed by adding linear combinations of the constraints premultiplied by Lagrange factors. Müller and Ruggeri have made extensive use of this theorem in their work, extended thermodynamics, [48], which has been successfully used to model the non-equilibrium phenomenon associated with the propagation of shock waves through a gaseous medium [49]. The technique we use to derive our results is a modification of the Lagrange multiplier technique developed by Liu. In contrast to Liu and Muller [47, 48, 49], who view the field equations as constraints, we show how the Lagrange multiplier technique can be extended to enforce other relationships between various variables, such as the relationship given by equation (1.3).

In the next section we state the governing balance laws and entropy inequality as derived by averaging, along with notation and major assumptions. In the following section, constitutive assumptions in the form of the choice of constitutive independent variables are made, and the entropy inequality is formulated in terms of Lagrange multipliers. In section 4 we derive general non-equilibrium results (i.e. results which always hold) obtained by exploiting the entropy inequality in the sense of Coleman and Noll and present two definitions for the macroscale chemical potential. In sections 5 and 6 results which hold at equilibrium and which are obtained by linearizing about equilibrium, are derived, respectively. In section 8 we compare several definitions of the chemical potential by studying three hypothetical experiments. In the final section we provide a few salient concluding remarks.

## 2 Macroscale Balance Laws and Entropy Inequality

In this section we briefly review the derivation of the macroscale balance laws and entropy inequality. In the process it is shown how macroscale variables in the field equations can be precisely defined in terms of their microscopic counterparts.

Consider a multi-constituent single-phase flow (denoted by  $l$  for liquid) through a deformable porous medium (denoted by  $s$  for solid). For simplicity we consider the range of moderate moisture content which allows us to assume that interfaces contain no thermodynamic properties. Consequently it is assumed no amount of mass, momentum, energy, or entropy are lost when being transferred between phases. Interfacial effects can easily be included by pursuing any of the approaches of [50, 31, 32], however, since this issue is not our primary purpose, we shall omit these terms to keep the level of algebra at a minimum.

In addition, it is assumed that there exists the same  $N$  constituents in each phase. This assumption is necessary to derive the correct equilibrium results for the chemical potential [13]. For the more practical case where there are less than  $N$  constituents per phase, the corresponding results can be obtained after exploiting the entropy inequality by setting the concentrations of the appropriate constituents to zero. Because of this restriction, it is necessary to consider the governing equations for each constituent in each bulk phase. We first present the governing microscopic equations, then the averaging procedure, and finally we present the averaged equations for the bulk phase as derived by Hassanizadeh and Gray in [22, 23] and extended and clarified by Achanta et al. in [13].

At the microscale we assume the governing equations used in mixture theory hold for each phase. Consequently, thermodynamic properties exist for each constituent at each point *within* each phase, and each constituent must satisfy the governing field equations: conservation of mass, balance of linear and angular momentum, conservation of energy, and entropy production. Assuming no surface discontinuities, the constituent, microscopic, field equations can be expressed for a given phase,  $\alpha$ , as (following the notation of Eringen [51]):

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

where  $\psi^j$  is the mass-average (over the phase) thermodynamic property of constituent  $j$ ,  $\mathbf{v}^j$  is the mass-average velocity vector,  $\rho^j$  is the mass density,  $\mathbf{i}^j$  is the flux vector,  $f^j$  is the external supply,  $G^j$  is the net production, and  $\hat{\psi}^j$  represents the influx of  $\psi$  from all other constituents (i.e. due to

chemical reactions). If there is only one constituent,  $\widehat{\psi}^j$  is zero. For each of the respective equations, the quantities given in Table 1 are used. In Table 1,  $\mathbf{t}$  is the stress tensor,  $\mathbf{g}$  is the external supply of momentum (gravity),  $\mathbf{r}$  is the position vector,  $E$  is the internal energy density function,  $\mathbf{q}$  is the heat flux,  $h$  is the external supply of energy,  $\eta$  is the entropy density,  $\phi$  is the entropy flux,  $b$  is the external supply of entropy, and  $\Lambda$  is the entropy production.

Table 1: Quantities for Equation (2.1)

Quantity	$\psi$	$\mathbf{i}$	$f$	$\widehat{\psi}$	$G$
Mass	1	$\mathbf{0}$	0	$\widehat{r}$	0
Linear Momentum	$\mathbf{v}$	$\mathbf{t}$	$\mathbf{g}$	$\widehat{\mathbf{i}} + \widehat{r}\mathbf{v}$	0
Angular Momentum	$\mathbf{r} \times \mathbf{v}$	$\mathbf{r} \times \mathbf{t}$	$\mathbf{r} \times \mathbf{g}$	$\mathbf{r} \times (\widehat{\mathbf{i}} + \widehat{r}\mathbf{v})$	0
Energy	$E + \frac{1}{2}v^2$	$\mathbf{t}\mathbf{v} + \mathbf{q}$	$\mathbf{g} \cdot \mathbf{v} + h$	$\widehat{E} + \widehat{\mathbf{i}} \cdot \mathbf{v} + \widehat{r}(E + \frac{1}{2}v^2)$	0
Entropy	$\eta$	$\phi$	$b$	$\widehat{\eta} + \widehat{r}\mathbf{v}$	$\Lambda$

The averaging procedure is based on ideas laid down by Eringen and Suhubi [52], Whitaker [53, 54] and Slattery [55]. Several methods are available, but to illustrate the procedure we choose the computationally simplest. Equations are averaged over a representative elementary volume, REV, by weighted integration using the indicator function of the  $\alpha$ -phase, denoted by  $\gamma_\alpha$ . To avoid the mathematical difficulties of, for example, defining a derivative of the averaged quantities resulting from using such a weighting function, one must treat the averaged quantity as a distribution (Schwartz [56], Richards and Youn [57]).

It should be noted that using this simple weight function may mean that the averaged value may not represent the actual values being measured. To account for the measuring technique, one needs to choose a weight function which represents the instrument used to measure the physical properties (Cushman [58]). Extensions of the presented theory to such cases are straight forward.

Let  $\delta V$  denote the REV,  $\delta V_\alpha$  the portion of the REV in the  $\alpha$ -phase, and  $\delta A_{ts}$  the portion of the interface within the REV. It is assumed that  $\delta V_\alpha$  and  $\delta A_{ts}$  are isolated simply connected regions. If the magnitude of the REV is denoted by  $|\delta V|$  then the volume fraction can be expressed as

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

so that

$$\sum_{\alpha=t,s} \varepsilon_\alpha = 1. \quad (2.3)$$

The indicator function is

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

To obtain the macroscale equations formally, one multiplies equation 2.1 by  $\gamma_\alpha$ , integrates over the REV,  $\delta V$ , and divides by  $|\delta V|$ . Then in order to obtain equations of the forms which mirror the microscale equations, the following theorem is applied to interchange the order of differentiation and integration.

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

$$\frac{1}{|\delta V|} \int_{\delta V} \frac{\partial f}{\partial t} \gamma_\alpha dv = \frac{\partial}{\partial t} \left[ \frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha dv \right] - \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} f \mathbf{w}_{\alpha\beta} \cdot \mathbf{n}_\alpha da \quad (2.4)$$

$$\frac{1}{|\delta V|} \int_{\delta V} \nabla f \gamma_\alpha dv = \nabla \left[ \frac{1}{|\delta V|} \int_{\delta V} f \gamma_\alpha dv \right] + \sum_{\beta \neq \alpha} \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} f \mathbf{n}_\alpha da. \quad (2.5)$$

After averaging equation (2.1), the system is considered to be a mixture so that each component in each phase and each phase now have thermodynamic properties existing at each point within the macroscopic body. The macroscopic definition of each field variable in terms of its microscopic counterpart is given in Appendix A.

Here we make the additional assumptions that all external sources except for body forces (gravity), are negligible and that the solid and fluid are at local thermal equilibrium so that a common temperature  $T$  can be assigned for both phases, i.e.  $T_l = T_s = T$ . Furthermore, we assume 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. For ease of exposition we assume no exchange of mass exists between constituents within a phase (i.e. no chemical reactions:  $\widehat{\rho}_\alpha^j = 0$ ), although extending the theory to such cases is straight forward [13, 27]. We do allow exchange of mass between phases. If the macroscopic variables are defined as in Appendix A, then the form of the macroscopic field equations have the following form:

### Conservation of Mass

For the  $j$ th component in the  $\alpha$ -phase, conservation of mass can be expressed as

$$\frac{D_\alpha^j(\varepsilon_\alpha \rho_\alpha^j)}{Dt} + \varepsilon_\alpha \rho_\alpha^j \nabla \cdot \mathbf{v}_\alpha^j = \widehat{e}_\alpha^j \quad \alpha = l, s \quad j = 1, \dots, N \quad (2.6)$$

where  $\rho_\alpha^j$  and  $\mathbf{v}_\alpha^j$  denote the volume-averaged density and mass-averaged velocity of the  $j$ th component in the  $\alpha$ -phase,  $\widehat{e}_\alpha^j$  represents the net gain of mass of the  $j$ th component in the  $\alpha$ -phase from the other phase (not due to chemical reactions), and  $D_\alpha^j/Dt$  denotes the material time derivative following the  $j$ th component in the  $\alpha$ -phase, i.e.

$$\frac{D_\alpha^j}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}_\alpha^j \cdot \nabla, \quad j = 1, \dots, N, \quad \alpha = l, s \quad .$$

Summing over all constituents, and defining the bulk phase variables appropriately, we obtain conservation of mass for the  $\alpha$ -phase,

$$\frac{D_\alpha(\varepsilon_\alpha \rho_\alpha)}{Dt} + \varepsilon_\alpha \rho_\alpha \nabla \cdot \mathbf{v}_\alpha = \widehat{e}_\alpha \quad \alpha = l, s \quad (2.7)$$

where  $\rho_\alpha$  and  $\mathbf{v}_\alpha$  denote the volume averaged density and mass-averaged velocity of the  $\alpha$ -phase, respectively,  $\widehat{e}_\alpha$  represents the net mass gained by the  $\alpha$ -phase from the other phase, and  $D_\alpha/Dt$  denote the material time derivative following the  $\alpha$ -phase. Subtracting  $C_\alpha^j$  times equation (2.7) from (2.6) yields a more useful form of the continuity equation for constituents:

$$\varepsilon_\alpha \rho_\alpha \frac{D_\alpha C_\alpha^j}{Dt} + \nabla \cdot (\varepsilon_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j) = (\widehat{e}_\alpha^j - C_\alpha^j \widehat{e}_\alpha) \quad \alpha = l, s \quad j = 1, \dots, N, \quad (2.8)$$

where  $C_\alpha^j = \rho_\alpha^j / \rho_\alpha$  is the mass fraction of the  $j$ th component in the  $\alpha$ -phase, and  $\mathbf{u}_\alpha^j = \mathbf{v}_\alpha^j - \mathbf{v}_\alpha$  denotes the diffusion velocity of the  $j$ th component relative to the  $\alpha$ -phase.

### Conservation of Momentum

Momentum balance for the  $j$ th component of the  $\alpha$ -phase can be expressed as

$$\varepsilon_\alpha \rho_\alpha^j \frac{D_\alpha^j \mathbf{v}_\alpha^j}{Dt} - \nabla \cdot (\varepsilon_\alpha \mathbf{t}_\alpha^j) - \varepsilon_\alpha \rho_\alpha^j \mathbf{g} = \widehat{\mathbf{T}}_\alpha^j + \widehat{\mathbf{i}}_\alpha^j \quad \alpha = l, s \quad j = 1, \dots, N \quad (2.9)$$

and for the  $\alpha$ -phase we have



$$\varepsilon_\alpha \rho_\alpha \frac{D_\alpha \mathbf{v}_\alpha}{Dt} - \nabla \cdot (\varepsilon_\alpha \mathbf{t}_\alpha) - \varepsilon_\alpha \rho_\alpha \mathbf{g} = \widehat{\mathbf{T}}_\alpha \quad \alpha = l, s, \quad (2.10)$$

where  $\mathbf{t}_\alpha^j$  and  $\mathbf{t}_\alpha$  denote the average symmetric stress tensors for the  $j$ th component and phase  $\alpha$  respectively,  $\mathbf{g}$  is the body force (i.e. gravity),  $\widehat{\mathbf{T}}_\alpha^j$  and  $\widehat{\mathbf{T}}_\alpha$  denote the net gain of momentum for the  $j$ th component of the  $\alpha$ -phase and gain of momentum of the  $\alpha$ -phase due to interactions with the other phase, respectively, and  $\widehat{\mathbf{t}}_\alpha^j$  measures the gain of momentum of the  $j$ th component through interactions with other species in the same phase. This form of the momentum equation differs from Bowen's [21] or Atkin and Craine's [59] in that their definition for the partial stress tensor and density incorporate the volume fraction.

### Conservation of Energy

For the  $j$ th component of the  $\alpha$ -phase, conservation of energy is given by

$$\varepsilon_\alpha \rho_\alpha^j \frac{D_\alpha^j E_\alpha^j}{Dt} - \varepsilon_\alpha \mathbf{t}_\alpha^j : \mathbf{d}_\alpha^j - \nabla \cdot (\varepsilon_\alpha \mathbf{q}_\alpha^j) = \widehat{Q}_\alpha^j + \widehat{E}_\alpha^j \quad \alpha = l, s \quad j = 1, \dots, N$$

and for the  $\alpha$ -phase by

$$\varepsilon_\alpha \rho_\alpha \frac{D_\alpha E_\alpha}{Dt} - \varepsilon_\alpha \mathbf{t}_\alpha : \mathbf{d}_\alpha - \nabla \cdot (\varepsilon_\alpha \mathbf{q}_\alpha) = \widehat{Q}_\alpha \quad \alpha = l, s \quad (2.11)$$

where  $E_\alpha^j$  and  $E_\alpha$  are the average internal energy densities, per unit mass, of the  $j$ th component and  $\alpha$ -phase, respectively,  $\mathbf{q}_\alpha^j$  and  $\mathbf{q}_\alpha$  denote the corresponding heat fluxes,  $\mathbf{d}_\alpha^j$  and  $\mathbf{d}_\alpha$  are the symmetric parts of  $\nabla \mathbf{v}_\alpha^j$  and  $\nabla \mathbf{v}_\alpha$  respectively,  $\mathbf{A} : \mathbf{B} = \text{tr}(\mathbf{A}\mathbf{B}^T)$  denotes the classical inner product between tensors,  $\widehat{Q}_\alpha^j$  and  $\widehat{Q}_\alpha$  denote the gain of energy by the  $j$ th component in the  $\alpha$ -phase and  $\alpha$ -phase, respectively, due to the interaction with the other phase, and  $\widehat{E}_\alpha^j$  denotes the exchange of energy between the  $j$ th component and other species in the same phase.

### Entropy Inequality

The entropy inequality for the entire mixture is

$$\Lambda = \sum_{\alpha=l,s} \sum_{j=1}^N \left[ \varepsilon_\alpha \rho_\alpha^j \frac{D_\alpha^j \eta_\alpha^j}{Dt} - \nabla \cdot \left( \frac{\varepsilon_\alpha \mathbf{q}_\alpha^j}{T} \right) - \widehat{\phi}_\alpha^j - \widehat{\eta}_\alpha^j \right] \geq 0$$

where  $\eta_\alpha^j$  is the entropy of the  $j$ th component in phase  $\alpha$  per unit mass,  $T$  is the temperature,  $\widehat{\phi}_\alpha^j$  denotes the gain of entropy of the  $j$ th component of the  $\alpha$ -phase due to interactions with the other phase,  $\widehat{\eta}_\alpha^j$  is the net entropy gained by the  $j$ th constituent due to interactions with other constituents within phase  $\alpha$ , and  $\Lambda$  is the net rate of entropy production. Here we have assumed that each constituent in each phase undergoes only simple thermodynamical processes, i.e. the entropy flux is proportional to the heat flux. As a result, using (2.11), the entropy inequality can be rewritten as

$$\begin{aligned} \Lambda = \sum_{\alpha=l,s} \sum_{j=1}^N \left[ -\frac{\varepsilon_\alpha \rho_\alpha^j}{T} \left( \frac{D_\alpha^j A_\alpha^j}{Dt} + \eta_\alpha^j \frac{D_\alpha^j T}{Dt} \right) + \frac{\varepsilon_\alpha}{T} \mathbf{t}_\alpha^j : \mathbf{d}_\alpha^j + \frac{\varepsilon_\alpha}{T^2} \mathbf{q}_\alpha^j \cdot \nabla T \right. \\ \left. + \frac{1}{T} (\widehat{E}_\alpha^j + \widehat{Q}_\alpha^j) - \widehat{\phi}_\alpha^j - \widehat{\eta}_\alpha^j \right] \geq 0 \end{aligned}$$

where  $A_\alpha^j = E_\alpha^j - T\eta_\alpha^j$  is the Helmholtz free energy of the  $j$ th component.

Recall that the bulk phase variables are defined so as to obtain bulk phase field equations which resemble the traditional form of the field equations. The various relations between the phase and species properties are (see [13, 27])

$$\rho_\alpha = \sum_{j=1}^N \rho_\alpha^j, \quad \widehat{e}_\alpha = \sum_{j=1}^N \widehat{e}_\alpha^j, \quad \rho_\alpha \mathbf{v}_\alpha = \sum_{j=1}^N \rho_\alpha^j \mathbf{v}_\alpha^j = \rho_\alpha \sum_{j=1}^N C_\alpha^j \mathbf{v}_\alpha^j, \quad (2.12)$$

$$\mathbf{t}_\alpha = \sum_{j=1}^N (\mathbf{t}_\alpha^j - \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j), \quad \widehat{\mathbf{T}}_\alpha = \sum_{j=1}^N (\widehat{\mathbf{T}}_\alpha^j + \widehat{\mathbf{e}}_\alpha^j \mathbf{u}_\alpha^j), \quad (2.13)$$

$$\eta_\alpha = \sum_{j=1}^n C_\alpha^j \eta_\alpha^j, \quad A_\alpha = \sum_{j=1}^n C_\alpha^j A_\alpha^j, \quad (2.14)$$

$$E_\alpha = \sum_{j=1}^N C_\alpha^j \left( E_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right), \quad \mathbf{q}_\alpha = \sum_{j=1}^N \left[ \mathbf{q}_\alpha^j + \mathbf{t}_\alpha^j \mathbf{u}_\alpha^j - \rho_\alpha^j \left( E_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) \mathbf{u}_\alpha^j \right] \quad (2.15)$$

$$\widehat{\mathbf{Q}}_\alpha = \sum_{j=1}^N \left[ \widehat{\mathbf{Q}}_\alpha^j + \widehat{\mathbf{T}}_\alpha^j \cdot \mathbf{u}_\alpha^j + \widehat{\mathbf{e}}_\alpha^j \left( E_\alpha^j - E_\alpha + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) \right] \quad (2.16)$$

where  $\eta_\alpha$  and  $A_\alpha$  denote the entropy and free energy of phase  $\alpha$ , respectively, and  $\otimes$  denotes the tensorial product between vectors.

In addition we have the following constraints (see [13, 27])

$$\sum_{\alpha=l,s} \varepsilon_\alpha = 1, \quad \sum_{j=1}^N C_\alpha^j = 1, \quad \sum_{j=1}^N \rho_\alpha^j \mathbf{u}_\alpha^j = 0, \quad (2.17)$$

$$\sum_{j=1}^N \widehat{\mathbf{i}}_\alpha^j = 0, \quad \sum_{j=1}^N \widehat{\eta}_\alpha^j = 0, \quad \sum_{j=1}^N \left( \widehat{\mathbf{E}}_\alpha^j + \widehat{\mathbf{i}}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) = 0, \quad (2.18)$$

$$\sum_{\alpha=l,s} \widehat{\mathbf{e}}_\alpha = 0, \quad \sum_{\alpha=l,s} \widehat{\mathbf{e}}_\alpha^j = 0, \quad j = 1, \dots, N \quad (2.19)$$

$$\sum_{\alpha=l,s} \left[ \widehat{\mathbf{Q}}_\alpha^j + \widehat{\mathbf{T}}_\alpha^j \cdot \mathbf{v}_\alpha^j + \widehat{\mathbf{e}}_\alpha^j \left( E_\alpha^j + \frac{1}{2} \mathbf{v}_\alpha^j \cdot \mathbf{v}_\alpha^j \right) \right] = 0, \quad j = 1, \dots, N \quad (2.20)$$

$$\sum_{\alpha=l,s} \left( \widehat{\mathbf{T}}_\alpha^j + \widehat{\mathbf{e}}_\alpha^j \mathbf{v}_\alpha^j \right) = 0, \quad \sum_{\alpha=l,s} \left( \widehat{\phi}_\alpha^j + \widehat{\mathbf{e}}_\alpha^j \eta_\alpha^j \right) = 0, \quad j = 1, \dots, N. \quad (2.21)$$

Relations (2.17) are a consequence of the definition of the variables. Restrictions (2.18) are a result of summing the balance laws over each constituent and requiring the bulk phase to satisfy the balance laws (for more details, see e.g. Bowen [19]). Restrictions (2.19)-(2.21) are a consequence of assuming that the interfaces have no thermodynamical properties, e.g. the momentum transfer from the liquid phase to the solid phase is the same magnitude as that from the solid to the liquid phase.

Expressing the entropy inequality in terms of phase properties and using (2.12)-(2.21) we have

$$\begin{aligned} T\Lambda &= \sum_{\alpha=l,s} -\varepsilon_\alpha \rho_\alpha \left[ \frac{D_\alpha A_\alpha}{Dt} + \eta_\alpha \frac{D_\alpha T}{Dt} \right] + \sum_{\alpha=l,s} \varepsilon_\alpha \mathbf{d}_\alpha : \left[ \mathbf{t}_\alpha + \sum_{j=1}^N \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j \right] \\ &+ \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon_\alpha \nabla \mathbf{u}_\alpha^j : \left[ \mathbf{t}_\alpha^j - \rho_\alpha^j A_\alpha^j \mathbf{I} \right] - \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \left[ \nabla (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) + \widehat{\mathbf{i}}_\alpha^j + \widehat{\mathbf{T}}_\alpha^j \right] \end{aligned}$$

$$\begin{aligned}
 & + \sum_{\alpha=l,s} \frac{\varepsilon_\alpha}{T} \nabla T \cdot \left[ \mathbf{q}_\alpha + \sum_{j=1}^N \left( \rho_\alpha^j \mathbf{u}_\alpha^j \left( A_\alpha^j + \frac{1}{2} \mathbf{u}_\alpha^j \cdot \mathbf{u}_\alpha^j \right) - \mathbf{t}_\alpha^j \mathbf{u}_\alpha^j \right) \right] - \mathbf{v}_{l,s} \cdot \hat{\mathbf{T}}_l \\
 & - \sum_{\alpha=l,s} \sum_{j=1}^N \hat{c}_l^j \left[ \frac{1}{2} \mathbf{u}_l^j \cdot \mathbf{u}_l^j - \frac{1}{2} \mathbf{u}_s^j \cdot \mathbf{u}_s^j \right] - \hat{e}_l \left[ A^l - A^s + \frac{1}{2} \mathbf{v}_{l,s} \cdot \mathbf{v}_{l,s} \right] \geq 0
 \end{aligned} \tag{2.22}$$

where  $\mathbf{v}_{l,s} = \mathbf{v}_l - \mathbf{v}_s$  denotes the relative velocity,  $\mathbf{I}$  denotes the identity matrix, and the following relation has been employed

$$\sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon_\alpha \rho_\alpha^j \frac{D_\alpha^j A_\alpha^j}{Dt} = \sum_{\alpha=l,s} \varepsilon_\alpha \rho_\alpha \frac{D_\alpha A_\alpha}{Dt} + \sum_{\alpha=l,s} \sum_{j=1}^N \left[ \hat{c}_\alpha^j (A_\alpha - A_\alpha^j) + \nabla \cdot (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j \mathbf{u}_\alpha^j) \right].$$

### 3 Constitution

In this section we assume the material is a swelling colloid. We focus our discussion on clay, but the results can be applied to other swelling systems, such as lyophilic polymers. The clay systems we have in mind are smectic clays such as montmorillonite. We assume the clay systems can be described as an assemblage of mineral platelets, forming the solid phase, and vicinal water, forming the fluid phase. This system may swell under hydration and shrink under desiccation.

The unknowns in our system are:

$$\varepsilon_l, \rho_\alpha, C_\alpha^j, \mathbf{v}_a, \mathbf{v}_\alpha^j, T \tag{3.1}$$

$$\begin{aligned}
 A_\alpha, A_\alpha^j, \eta_\alpha, \eta_\alpha^j, \mathbf{t}_\alpha, \mathbf{t}_\alpha^j, \hat{\mathbf{T}}_l, \hat{\mathbf{T}}_l^j, \hat{e}_l, \hat{e}_l^j, \mathbf{q}_\alpha, \mathbf{q}_\alpha^j, \hat{\mathbf{i}}_\alpha^j, \hat{\mathbf{Q}}_l, \hat{\mathbf{Q}}_l^j, \hat{\mathbf{E}}_\alpha, \\
 j = 1, \dots, N-1 \quad \alpha = l, s.
 \end{aligned} \tag{3.2}$$

Note that since we only consider  $N-1$  constituents, the above variables are indeed independent. To arrive at a system which has the same number of equations as unknowns, we consider the last row of variables (3.2) to be dependent, or constitutive. These variables are assumed to be functions of a set of independent variables which we henceforth denote as the 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. One way of closing the system is to assume the solid phase is incompressible (e.g.  $D_s \rho_s / Dt = 0$ ) [26]. However we are interested in more general results so that these ideas can be extended to more complicated systems, such as systems with more than 2 bulk phases, or a system for which interfacial effects cannot be neglected. One popular method, introduced first for granular media by Goodman and Cowin [60] and generalized by Passman et al. [61] is to postulate another balance law, called the ‘‘balance of equilibrated forces’’. As stated in Passman et al. [61], this law, which does not differentiate species in different phases, can be stated in our notation as:

$$\rho^j \frac{D^j}{Dt} \left( K_\alpha^j \frac{D^j \nu^j}{Dt} \right) - \nabla \cdot \mathbf{h}^j - \rho^j \iota^j + l^j = \hat{v}^j - \sum_{\alpha=l,s} \hat{c}_\alpha^j K^j \frac{D^j \nu^j}{Dt}$$

where  $\rho^j = \sum_{\alpha=l,s} \varepsilon_\alpha \rho_\alpha^j$ ,  $K^j$  is the equilibrated inertia,  $\nu^j$  is the constituent volume fraction such that  $\nu^j \rho^j$  is the mass of the  $j$ th constituent per unit volume of REV,  $\mathbf{h}^j$  is the equilibrated stress,  $l^j$  is the external equilibrated body force,  $\iota^j$  is the equilibrated force supply, and  $\hat{v}^j$  is the equilibrated force interaction subject to the constraint that  $\sum_{j=1}^N \hat{v}^j = 0$ . It also involves additional terms in the energy equation which corresponds to work done by the respective terms in the balance of equilibrated forces. Eventually constitutive relations must be postulated for these additional terms. In a fashion similar to this approach, Aifantis and co-workers have suggested that there should be additional

balance equations for *all* internal variables [62, 63]. Again the system must be closed by introducing additional constitutive variables.

Although some nice results have been obtained using this approach, we have not chosen to close our system of equations in this manner for several reasons. First, the additional balance equation has no microstructural origin. Within HMT all balance equations are upscaled from the microscale. Not relating each additional variable to a microscale counterpart has resulted in confusion as to the physical interpretation of these variables [64]. Further, many of the physical interpretations attributed to the variables in the additional balance equation correspond to terms within the original macroscale balance laws, especially if one includes the interfacial balance equations as well. Lastly, we feel the system should be closed by a constitutive relation. The change in the volume fraction is a consequence of the constitution of each phase of the porous media, as well as the state of each phase.

Although we feel this issue needs to be examined more closely, the closure method we feel most comfortable with is that of postulating a constitutive relation for the material time derivative of the volume fraction, which was first introduced by Bowen [21]. One particular question which should be addressed is: Why should the material time derivative of the volume fraction be the constitutive variable instead of, e.g., the gradient of the volume fraction? We have no answer for this, but it is of interest to note that this method of closure can be viewed as a simplified version of adding an additional balance equation; within the additional balance law for the volume fraction, if it is assumed there is no external supply of the volume fraction, all variables except for the time rate of change of the volume fraction are considered constitutive. Thus there is a relation between the aforementioned closure method and this one. Additionally this closure approach allows the derivation of results which had previously only been heuristically derived (see e.g. [13]).

We assume the macroscopic medium is non-heat conducting, the macroscopic fluid is non-viscous, and the fluid and solid phases are compressible. By the Principle of Equipresence (Truesdell [65]), we assume that every constitutive variable is a function of *all* the following macroscopic constitutive independent variables:

$$T, \rho_\alpha, \mathbf{E}_s, \mathbf{v}_{l,s}, \mathbf{u}_\alpha^j, C_\alpha^j, \nabla C_\alpha^j, \nabla \rho_\alpha, \nabla \mathbf{E}_s, \quad j = 1, \dots, N-1, \quad \alpha = l, s. \quad (3.3)$$

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

$$\mathbf{E}_s = \frac{1}{2} \left( \mathbf{F}_s^T \mathbf{F}_s - \mathbf{I} \right) \quad (3.4)$$

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 (3.3) can be considered independent, since it is possible to have different processes which at a single point can have e.g. the same strain but varying gradients of the strain. As we shall see in the next section, including the gradient of the strain tensor in the list of constitutive independent variables is crucial for deriving a proper form of Darcy's law for the vicinal fluid.

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 platelets and their spatial variations. Moreover, although both  $\varepsilon_l$  and  $\mathbf{E}_s$  could be considered as independent variables (see, e.g. [66, 17]),  $\mathbf{E}_s$  is closely related to  $\varepsilon_l$  through the continuity equation, especially if the mass transfer of constituents between phases is negligible (see section 8), so that we choose to include only  $\mathbf{E}_s$  as an independent constitutive variable. In addition,  $\mathbf{u}_\alpha^N$  and  $C_\alpha^N$  are not considered independent variables since they are coupled with other independent variables through (2.17).

To simplify manipulations of the entropy inequality, we use Liu's [47] Lagrange multiplier technique. We first choose to view conservation of mass equations as constraints which are weakly enforced

in the entropy inequality using scalar Lagrange multipliers,  $\lambda_\alpha$  and  $\lambda_\alpha^j$ . We further use Lagrange multipliers to enforce the relationship between  $\nabla \mathbf{u}_\alpha^j$ ,  $j = 1, \dots, N$  obtained by differentiating (1.3). This approach differs from the more commonly used method which involves eliminating  $\nabla \mathbf{u}_\alpha^N$  directly via (1.3) (see [27, 13], or for a more direct comparison with this formulation see [46]). The two techniques give identical results, but this procedure provides a more systematic method, simplifying the manipulations required to exploit the entropy inequality. Let  $\mathbf{\Gamma}_\alpha^N$  denote the second order tensorial Lagrange multiplier corresponding to the constraint on  $\nabla \mathbf{u}_\alpha^j$ . The superscript  $N$  is carried to remind us that we view the constraints as restrictions on  $\mathbf{u}_\alpha^N$ , i.e. they depend on the labeling of the constituents.

Let  $\Lambda_{old} \equiv \Lambda$  of (2.22). Modifying the entropy inequality we get

$$\begin{aligned} T\Lambda_{new} = & T\Lambda_{old} + \sum_{\alpha=l,s} \lambda_\alpha \left[ \frac{D_\alpha(\varepsilon_\alpha \rho_\alpha)}{Dt} + \varepsilon_\alpha \rho_\alpha \nabla \cdot \mathbf{v}_\alpha - \widehat{e}_\alpha \right] \\ & + \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \lambda_\alpha^j \left[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha C_\alpha^j}{Dt} + \nabla \cdot (\varepsilon_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j) - (\widetilde{e}_\alpha^j - C_\alpha^j \widehat{e}_\alpha) \right] \\ & + \sum_{\alpha=l,s} \varepsilon_\alpha \mathbf{\Gamma}_\alpha^N : \left[ \sum_{j=1}^N \nabla(\rho_\alpha^j \mathbf{u}_\alpha^j) \right] \geq 0. \end{aligned}$$

Next we invoke the theorem of Liu, [47], which states equivalence between the entropy inequality with restrictions and the modified entropy inequality above.

To simplify the quantity of algebra which follows, we deviate slightly from the axiom of equipresence [51], 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 (3.3), that the exploitation of the entropy inequality requires that both energies are not a function of  $\mathbf{v}_{l,s}$ ,  $\mathbf{u}_\alpha^j$ ,  $\nabla \rho_\alpha^j$ ,  $\nabla C_\alpha^j$ , and  $\nabla \mathbf{E}_s$ . Here we additionally assume that the liquid free energy is not a function of  $\rho_s$  and  $C_s^j$ , and likewise that the solid free energy is not a function of  $\rho_l$  and  $C_l^j$ . Incorporating these additional dependencies still produces the results presented herein if one slightly modifies the thermodynamic definitions of the pressure and chemical potential (see [67, 66] for details). For the system under consideration it is thus postulated that

$$\begin{aligned} A_s &= A_s(T, \rho_s, C_s^j, \mathbf{E}_s) \\ A_l &= A_l(T, \rho_l, C_l^j, \mathbf{E}_s), \quad j = 1, \dots, N-1. \end{aligned} \quad (3.5)$$

By assuming the liquid phase energy is a function of the solid phase strain tensor, we are adopting the framework of [17, 18] in order to allow the adsorbed liquid structure to be a function of the separation and shear strain of the macroscopic solid phase. 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. This change is represented by the 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. This is a generalization of the work of Achanta et al. [13] where it was assumed that the liquid phase energy is a function of  $\varepsilon_l$  instead of  $\mathbf{E}_s$ . In Achanta’s work, an empirical result for the swelling pressure obtained by Low [3] was derived for the first time using this constitutive assumption and the exploitation of the entropy inequality. The derivation of this result in our formulation is presented in Section 7. In the more general theory considered here, we are assuming that the Helmholtz free energy of the adsorbed liquid is not only a function of the separation of clay platelets, but also of the shear strain of the macroscopic solid phase. By including shear strains, we are attempting to capture the behavior of clay soils at low moisture content (interlayer spacings less than 10 molecular diameters

of water or  $25\text{\AA}$ ) where the behavior of the microscopic vicinal water may be neither liquid-like nor solid-like, but glassy (see Schoen et al. [68], Cushman [69], Israelachvili [10]). In this state the fluid molecules are more ordered and are layered parallel to the surface so that the fluid, on the microscale, is structured, inhomogeneous, and anisotropic. The interlamellar fluid is relatively immobile due to the higher viscosity, allowing the fluid to support a shear stress.

To complete the set of definitions, we introduce the thermodynamic pressures ( $p_\alpha$ ), the generalized tensorial Gibbs energy density of the  $\alpha$ -phase as in Bowen [19] or Bowen and Wiese [42] ( $\mathbf{G}_\alpha$ ), the chemical potentials of the  $j$ th component relative to the  $N$ th component in the  $\alpha$ -phase ( $\tilde{\mu}_\alpha^j$ ) [27], the classical effective stress tensor ( $\mathbf{t}_s^e$ ) in the sense of Terzaghi [70], and the hydration stress tensor ( $\mathbf{t}_s^l$ ) [17, 18]. Within the current framework they are defined as follows:

$$p_\alpha = \rho_\alpha^2 \frac{\partial A_\alpha}{\partial \rho_\alpha}, \quad \mathbf{G}_\alpha = A_\alpha \mathbf{I} - \rho_\alpha^{-1} \mathbf{t}_\alpha, \quad (3.6)$$

$$\mathbf{t}_s^e = \rho_s \mathbf{F}_s \frac{\partial A_s}{\partial \mathbf{E}_s} \mathbf{F}_s^T, \quad \mathbf{t}_s^l = \rho_l \mathbf{F}_s \frac{\partial A_l}{\partial \mathbf{E}_s} \mathbf{F}_s^T, \quad (3.7)$$

$$\tilde{\mu}_\alpha^j = \frac{\partial A_\alpha}{\partial C_\alpha^j}, \quad \alpha = l, s \quad j = 1, \dots, N-1. \quad (3.8)$$

The definition of  $\mathbf{t}_s^e$  is analogous to the Cauchy stress tensor for an elastic medium (see Eringen [51]) 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 novel, and is a result of the physico-chemical forces between the vicinal fluid and the clay minerals (see [18] and Section 4 for further discussion). Also note that the Gibbs energies of phases,  $\mathbf{G}_\alpha$ , are in the most general setting, tensors. The tensorial definitions for the Gibbs free energy densities reduce to the classical Gibbsian thermodynamical definitions (Callen [41]) by setting  $\mathbf{t}_\alpha = -p_\alpha \mathbf{I}$  and  $\mathbf{G}_\alpha = G_\alpha \mathbf{I}$ , i.e.

$$G_\alpha \equiv A_\alpha + \rho_\alpha^{-1} p_\alpha, \quad \alpha = l, s. \quad (3.9)$$

The Coleman and Noll method [24] is now used to exploit the restrictions placed by the entropy inequality on the constitutive theory. Within this framework the total derivatives of the free energies are rewritten in terms of partial derivatives using the chain rule and the functional forms postulated in (3.5). Using the relations  $D_s \mathbf{E}_s / Dt = \mathbf{F}_s^T \mathbf{d}_s \mathbf{F}_s$  and  $D_l / Dt = D_s / Dt + \mathbf{v}_{l,s} \cdot \nabla$  (Eringen [51]) and the above definitions we then have

$$\frac{D_l A_l}{Dt} = \frac{\partial A_l}{\partial T} \frac{D_l T}{Dt} + \frac{p_l}{\rho_l^2} \frac{D_l \rho_l}{Dt} + \sum_{j=1}^{N-1} \tilde{\mu}_l^j \frac{D_l C_l^j}{Dt} + \frac{1}{\rho_l} \mathbf{t}_s^l : \mathbf{d}_s + \mathbf{v}_{l,s} \cdot \left( \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s \right)$$

and

$$\frac{D_s A_s}{Dt} = \frac{\partial A_s}{\partial T} \frac{D_s T}{Dt} + \frac{p_s}{\rho_s^2} \frac{D_s \rho_s}{Dt} + \sum_{j=1}^{N-1} \tilde{\mu}_s^j \frac{D_s C_s^j}{Dt} + \frac{1}{\rho_s} \mathbf{t}_s^e : \mathbf{d}_s,$$

where the term in parenthesis in indicial notation is  $(\partial A / \partial E_{ij}) E_{ij,k}$  in which repeated indices imply summation and a comma denotes a partial derivative.

To minimize the required algebra, we restrict our analysis to the case where temperature gradients and heat fluxes are absent. Using the above expansions entropy inequality (2.22) can be rewritten as

$$\begin{aligned} T\Lambda &= \sum_{\alpha=l,s} \frac{D_s \rho_\alpha}{Dt} \left[ \varepsilon_\alpha \lambda_\alpha - \varepsilon_\alpha \frac{p_\alpha}{\rho_\alpha} \right] + \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \frac{D_s C_\alpha^j}{Dt} \left[ \varepsilon_\alpha \rho_\alpha \lambda_\alpha^j - \varepsilon_\alpha \rho_\alpha \tilde{\mu}_\alpha^j \right] \\ &- \sum_{\alpha=l,s} \varepsilon_\alpha \rho_\alpha \frac{D_s T}{Dt} \left[ \frac{\partial A_\alpha}{\partial T} + \eta_\alpha \right] + \varepsilon_l \mathbf{d}_l : \left[ \mathbf{t}_l + \rho_l \lambda_l \mathbf{I} + \sum_{j=1}^N \rho_l^j \mathbf{u}_l^j \otimes \mathbf{u}_l^j \right] \end{aligned}$$

$$\begin{aligned}
 & + \varepsilon_s \mathbf{d}_s : \left[ \mathbf{t}_s + \rho_s \lambda_s \mathbf{I} - \mathbf{t}_s^e - \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l + \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \right] \\
 & + \mathbf{v}_{l,s} \cdot \left[ -\varepsilon_l \frac{p_l}{\rho_l} \nabla \rho_l - \sum_{j=1}^{N-1} \varepsilon_l \rho_l \tilde{\mu}_l^j \nabla C_l^j - \varepsilon_l \rho_l \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s + \varepsilon_l \lambda_l \nabla \rho_l \right. \\
 & \quad \left. + \sum_{j=1}^{N-1} \varepsilon_l \rho_l \lambda_l^j \nabla C_l^j + \rho_l \lambda_l \nabla \varepsilon_l - \hat{\mathbf{T}}_l \right] \\
 & + \frac{D_s \varepsilon_l}{Dt} \left[ \rho_l \lambda_l - \rho_s \lambda_s \right] + \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon_\alpha \nabla \mathbf{u}_\alpha^j : \left[ \mathbf{t}_\alpha^j + \rho_\alpha^j (\lambda_\alpha^j - A_\alpha^j) \mathbf{I} + \rho_\alpha^j \mathbf{\Gamma}_\alpha^N \right] \\
 & + \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \left[ \lambda_\alpha^j \nabla (\varepsilon_\alpha \rho_\alpha^j) - \nabla (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) - (\tilde{\mathbf{t}}_\alpha^j + \hat{\mathbf{T}}_\alpha^j) + \varepsilon_\alpha \mathbf{\Gamma}_\alpha^N \nabla \rho_\alpha^j \right] \\
 & - \sum_{j=1}^N \hat{e}_l^j \left[ \lambda_l^j - \lambda_s^j + \Delta^2 \right] \\
 & - \hat{e}_l \left[ \lambda_l - \lambda_s + \sum_{j=1}^{N-1} (C_s^j \lambda_s^j - C_l^j \lambda_l^j) + A_l - A_s \right] \geq 0, \tag{3.10}
 \end{aligned}$$

where  $\tilde{\mu}_\alpha^N$  and  $\lambda_\alpha^N$  are defined to be zero for notational convenience, and where  $\Delta^2 = (1/2)(\mathbf{u}_l^j \cdot \mathbf{u}_l^j + \mathbf{v}_{l,s} \cdot \mathbf{v}_{l,s} - \mathbf{u}_s^j \cdot \mathbf{u}_s^j)$ . Note that because the restriction associated with the Lagrange multiplier  $\mathbf{\Gamma}_\alpha^N$ ,  $\nabla \mathbf{u}_\alpha^j$ ,  $j = 1, \dots, N$ , can be considered independent when exploiting the entropy inequality. However  $\mathbf{u}_\alpha^j$ ,  $j = 1, \dots, N$ , may not be considered independent.

#### 4 General Non-Equilibrium Results and Two Definitions for the $N$ th Chemical Potential

As usual,  $\Lambda$  is a linear function of the following set of variables which are neither independent (set (3.3)) nor constitutive (set (3.2)) and thus are arbitrary,

$$\frac{D_s \rho_\alpha}{Dt}, \quad \frac{D_s C_\alpha^j}{Dt}, \quad \frac{D_s T}{Dt}, \quad \mathbf{d}_\alpha, \quad \nabla \mathbf{u}_\alpha^j, \quad \alpha = l, s,$$

where  $j = 1, \dots, N-1$  for  $\frac{D_s C_\alpha^j}{Dt}$  and  $j = 1, \dots, N$  for  $\nabla \mathbf{u}_\alpha^j$ . Note that the index on  $\nabla \mathbf{u}_\alpha^j$  ranges from 1 to  $N$  because we have used a Lagrange multiplier to enforce the relation between these variables so that we can consider them to be independent. In order to satisfy the entropy inequality for all possible processes, the coefficients of these variables must be identically zero. This yields

$$\lambda_\alpha = \frac{p_\alpha}{\rho_\alpha} \tag{4.1}$$

$$\lambda_\alpha^j = \tilde{\mu}_\alpha^j \quad j = 1, \dots, N-1 \tag{4.2}$$

$$\sum_{\alpha=l,s} \varepsilon_\alpha \rho_\alpha \left( \frac{\partial A_\alpha}{\partial T} + \eta_\alpha \right) = 0 \tag{4.3}$$

$$\mathbf{t}_l = -p_l \mathbf{I} - \sum_{j=1}^N \rho_l^j \mathbf{u}_l^j \otimes \mathbf{u}_l^j \tag{4.4}$$

$$\mathbf{t}_s = -p_s \mathbf{I} + \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l - \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \tag{4.5}$$

$$\mathbf{t}_\alpha^j = \rho_\alpha^j A_\alpha^j \mathbf{I} - \rho_\alpha^j \tilde{\mu}_\alpha^j \mathbf{I} - \rho_\alpha^j \mathbf{\Gamma}_\alpha^N \quad j = 1, \dots, N. \tag{4.6}$$

Equations (4.1) and (4.2) determine the Lagrange multipliers. If any phase or constituent is incompressible, then there is no equation for the corresponding Lagrange multiplier, and it becomes an unknown of the problem. *For the remainder of this paper, we will replace the Lagrange multipliers by their corresponding definitions given in (4.1) and (4.2).* Equation (4.3) is a classical result stating that entropy and temperature are dual variables [41]. The macroscopic stress tensor for the vicinal liquid (4.4) is, in a first order theory, a scalar multiple of the identity. Note that if  $\nabla \mathbf{E}_s$  had not been included in the list of independent variables, then it would have been included in the above list of variables which are neither independent nor constitutive. This would have resulted in the conclusion that  $A_l$  is not a function of  $\mathbf{E}_s$ , and the above results could only be used to model non-swelling porous media.

Equation (4.5) gives important insight into the behavior of the stress tensor for the swelling particles. If we introduce the total stress tensor  $\mathbf{t} = \varepsilon_s \mathbf{t}_s + \varepsilon_l \mathbf{t}_l$  and total thermodynamic pressure  $p = \varepsilon_l p_l + \varepsilon_s p_s$ , then by using (4.4) and (4.5) we obtain

$$\mathbf{t} + p\mathbf{I} = \varepsilon_l \mathbf{t}_s^l + \varepsilon_s \mathbf{t}_s^e - \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j. \quad (4.7)$$

Equation (4.7) is a modified Terzaghi's effective stress principle for swelling clays which incorporates the effect of hydration stresses. It states that the equilibrium part of the stress tensor for a swelling medium is composed of both the classical effective stress tensor in the sense of Terzaghi [70],  $\mathbf{t}_s^e$ , and an additional stress,  $\mathbf{t}_s^l$ , which accounts for the stress in the adsorbed water due to hydration forces. The effective stress tensor,  $\mathbf{t}_s^e$ , measures stresses induced by solid-solid interaction and hence is the dominant factor when considering non-swelling systems such as sands, silts and low and medium plastic clays such as kaolinite or illite. On the other hand,  $\mathbf{t}_s^l$  dominates when there is a significant amount of solid-fluid interaction, such as swelling particles. Clearly this additional stress component is due to the presence of physico-chemical forces arising from surface hydration. Whence, as in [18, 17] we term the coupling tensor  $\mathbf{t}_s^l$  the "hydration stress tensor". An important consequence of (4.7) is that it overcomes some limitations involved in the works of Lambe [71] and Ma and Hueckel [72] where the clay particles are treated as a single phase so that it is assumed the pressures in the liquid and solid phases are equal. Other attempts to obtain the hydration stress tensor have been primarily heuristic (see [73],[71],[74],[75]).

Equation (4.6) relates the chemical potential to the stress tensor of the components within each phase,  $\mathbf{t}_\alpha^j$ . One consequence of (4.6) is that by letting  $j = N$  we obtain the definition of the Lagrange multiplier,  $\Gamma_\alpha^N$ :

$$\Gamma_\alpha^N = A_\alpha^N \mathbf{I} - \frac{1}{\rho_\alpha^N} \mathbf{t}_\alpha^N. \quad (4.8)$$

But more importantly, equation (4.6) illustrates that applying the Coleman and Noll method only yields results relative to the  $N$ th constituent. This is due to the interdependence of the concentrations (2.17). In order to derive more specific results, a definition for the absolute chemical potential must be postulated, and this strongly affects the form of the final results. This procedure is mostly avoided in classical and statistical thermodynamics because extensive variables, namely the number of molecules of each constituent, are used as independent variables instead of intensive variables (concentrations). Using extensive variables such as the number of molecules of each constituent, is not possible since the upscaling process involves averaging over an open system.

We believe the appropriate definition of the absolute chemical potential within mixture theory needs to be carefully examined. Indeed, one can find a variety of definitions in the literature. Here we mention a few. In terms of our notation, Kremer et al. [76] define the chemical potential at equilibrium to be  $\frac{\partial(\rho_\alpha A_\alpha)}{\partial \rho_\alpha^j}$  for fixed vibrational energy. Adams and Brown [64] define the chemical potential to



be  $\frac{\partial(C_\alpha^j A_\alpha^j)}{\partial C_\alpha^j}$ . Probably the most popularly used definition is the tensorial definition of Bowen [19, 42]

$$\boldsymbol{\mu}_\alpha^j \equiv A_\alpha^j \mathbf{I} - \frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j \quad j = 1, \dots, N, \quad (4.9)$$

see e.g. [27, 13]. To determine the most appropriate definition, a criteria must be established, and we believe the criteria should be that *the macroscale chemical potential should have the same properties as that of the classical Gibbsian chemical potential*. Further, these properties should be consistent with the entropy inequality.

In classical Gibbsian thermodynamics, the chemical potential is defined to be the change of the total extensive Helmholtz potential,  $A$ , with respect to the number of molecules of constituent  $j$ ,  $n^j$ , keeping temperature, volume, and the number of molecules of all other constituents fixed, i.e.  $\left. \frac{\partial A}{\partial n^j} \right|_{T, V, n_i}$  [77]. In this setting, the chemical potential has the following properties [77]:

1. It is a scalar quantity representing the amount of chemical energy required to insert/remove a molecule of constituent  $j$  (by definition).
2. At equilibrium, the chemical potential of a single constituent in different phases is the same.
3. The chemical potential is the driving force for diffusive flow. In particular, at equilibrium the gradient of the chemical potential is zero.

Note that the above properties do not imply that at equilibrium the chemical potentials of two different constituents are the same, an error commonly found in the literature. It is especially important that property 3 holds, as it is the property used to indirectly measure the chemical potential [77].

Of the definitions given above, only Bowen's arises naturally within our framework. In fact, using Bowen's definition (4.9) we get from (4.8) and (4.6)

$$\boldsymbol{\mu}_\alpha^N \equiv \boldsymbol{\Gamma}_\alpha^N \quad (4.10)$$

$$\tilde{\boldsymbol{\mu}}_\alpha^j \mathbf{I} = \boldsymbol{\mu}_\alpha^j - \boldsymbol{\mu}_\alpha^N, \quad (4.11)$$

respectively. By multiplying (4.9) through by  $C_\alpha^j$  and summing on  $j$  from 1 to  $N$ , we find that  $\boldsymbol{\mu}_\alpha^j$  is related to the generalized Gibbs free energy tensor,  $\mathbf{G}_\alpha$  defined in (3.6), as follows

$$\sum_{j=1}^N C_\alpha^j \boldsymbol{\mu}_\alpha^j = A_\alpha \mathbf{I} - \frac{1}{\rho_\alpha} \mathbf{t}_\alpha = \mathbf{G}_\alpha, \quad (4.12)$$

where we have used the relationship between the phase stress tensor and partial stress tensors in (2.13) and neglected second order terms involving diffusive velocities. This definition for the chemical potential seems to be motivated by convenience and is not easily reconciled with the classical definition, which is a scalar. Although for a single constituent liquid, the classical scalar and Bowen's tensorial definitions agree, i.e.  $\boldsymbol{\mu}_l = \mu_l \mathbf{I} = (p_l/\rho_l + A_l) \mathbf{I}$ , the question remains as to how to interpret this tensorial quantity in the solid phase, which, according to classical statistical theory, is physically interpreted as a measure of the amount of chemical energy required to place a particle in the system (property 1, see also McQuarrie [43]). Indeed, we will show that Bowen's tensorial chemical potential definition is not reconciled with classical properties 1, 2, and 3 when considering a stressed solid phase. This has caused some problems with measuring the tensorial stress tensor [44, 45].

Alternatively, by defining the chemical potential slightly differently, we can reproduce in form classical Gibbsian results. To this end, note that beginning with the relationship between the stress tensors of the components and phases, (2.13), and eliminating  $\sum_{j=1}^N \mathbf{t}_\alpha^j$ ,  $\mathbf{t}_\alpha$ , and  $\boldsymbol{\Gamma}_\alpha^N$  using (4.6), (4.4,

4.5), and (4.8), respectively, gives

$$\begin{aligned} -\frac{1}{\rho_l^N} \mathbf{t}_l^N &= \left( \frac{1}{\rho_l} p_l + A_l - \sum_{j=1}^N C_l^j \tilde{\mu}_l^j - A_l^N \right) \mathbf{I} \\ -\frac{1}{\rho_s^N} \mathbf{t}_s^N + \frac{1}{\rho_s} \left( \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right) &= \left( \frac{1}{\rho_s} p_s + A_s - \sum_{j=1}^N C_s^j \tilde{\mu}_s^j - A_s^N \right) \mathbf{I}. \end{aligned}$$

This tells us that the left-hand-sides of the above equations are scalar multiples of the identity. By using (4.6) we can show that the above quantities on the left-hand-side are scalars for all  $j$ ,  $j = 1, \dots, N$ . With this as a motivation, define the scalar chemical potentials

$$\mu_l^j \mathbf{I} \equiv A_l^j \mathbf{I} - \frac{1}{\rho_l^j} \mathbf{t}_l^j, \quad (4.13)$$

$$\mu_s^j \mathbf{I} \equiv A_s^j \mathbf{I} - \frac{1}{\rho_s^j} \mathbf{t}_s^j + \frac{1}{\rho_s} \left( \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right), \quad j = 1, \dots, N, \quad (4.14)$$

where we have used the non-bold symbol,  $\mu_\alpha^j$ , to distinguish it from Bowen's tensorial chemical potential which we continue to write in bold face. Multiplying (4.13, 4.14) by  $C_\alpha^j$  and then summing on  $j$  gives us the relationship analogous to (4.12)

$$\sum_{j=1}^N C_\alpha^j \mu_\alpha^j = A_\alpha + \frac{1}{\rho_\alpha} p_\alpha = G_\alpha, \quad \alpha = l, s, \quad (4.15)$$

where definition (3.9) for  $G_\alpha$  has been used. Moreover, if we define the pressure of the  $j$ th component,  $p_\alpha^j$ , as

$$\begin{aligned} -p_l^j \mathbf{I} &\equiv \mathbf{t}_l^j \\ -p_s^j \mathbf{I} &\equiv \mathbf{t}_s^j - C_s^j \left( \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right), \quad j = 1, \dots, N, \end{aligned}$$

then (4.13) and (4.14) can be expressed as

$$A_\alpha^j + \frac{1}{\rho_\alpha^j} p_\alpha^j = \mu_\alpha^j \quad \alpha = l, s \quad (4.16)$$

which shows consistency with (4.15). Summing (4.16) over all components and comparing with (4.15) implies  $p_\alpha = \sum_{j=1}^N p_\alpha^j$  so that in particular, this gives us an alternative way of interpreting  $p_s$ .

Comparing the two definitions of the tensorial and scalar chemical potentials (4.9), (4.13, 4.14), we arrive at the following relationships:

$$\mu_l^j \mathbf{I} = \boldsymbol{\mu}_l^j \quad (4.17)$$

$$\mu_s^j \mathbf{I} - \boldsymbol{\mu}_s^j = \frac{1}{\rho_s} \left( \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right), \quad j = 1, \dots, N. \quad (4.18)$$

For future reference, if definition (3.8) is combined with the above result and (4.11), we obtain the relation:

$$\tilde{\mu}_\alpha^j \mathbf{I} \equiv \frac{\partial A_\alpha}{\partial C_\alpha^j} \mathbf{I} \equiv \boldsymbol{\mu}_\alpha^j - \boldsymbol{\mu}_\alpha^N = (\mu_\alpha^j - \mu_\alpha^N) \mathbf{I}, \quad (4.19)$$

which is also obtained by using the interdependence of  $C_\alpha^j$ ,  $j = 1, \dots, N$  and the chain rule (e.g. Groot and Mazur, [38]). If one assumes a priori that the absolute chemical potential satisfies (4.19), then

it is only necessary to define the  $N$ th chemical potential, which is a much weaker postulate than the assumptions presented in this section. Furthermore, note that the difference between the tensorial and scalar chemical potentials (4.18) is due to the effective and hydration stresses. If, for example, the solid phase is replaced by, e.g., another immiscible fluid, we would get equality between the two definitions. As we shall illustrate in next section, the right hand side of (4.18) plays a crucial role in the deviation of the tensorial chemical potential from classical Gibbsian results. Also note that constitutive theory for a granular media falls out naturally by setting  $\mathbf{t}_s^l = \mathbf{0}$ . In this case the difference between the tensorial and scalar definitions are only due to the effective stresses,  $\mathbf{t}_s^e$ .

## 5 Equilibrium Restrictions

For the system under consideration, equilibrium is defined when  $D_s \varepsilon_l / Dt$ ,  $\mathbf{v}_{l,s}$ ,  $\mathbf{u}_\alpha^j$ ,  $\hat{\mathbf{e}}_l^j$ ,  $\hat{\mathbf{e}}_l$  vanish for  $j = 1, \dots, N-1$ . It is postulated that at equilibrium entropy is maximum and entropy generation is minimum. Therefore we must have  $(\partial \Lambda / \partial z_a)_e = 0$  and  $(\partial^2 \Lambda / \partial z_a \partial z_b)_e$  positive definite where  $z_a$  and  $z_b$  denote any of the above set of variables. Before applying these conditions, it is necessary to re-write the term in entropy inequality (3.10) associated with  $\mathbf{u}_\alpha^j$ ,  $j = 1, \dots, N$  in terms of independent variables  $\mathbf{u}_\alpha^j$ ,  $j = 1, \dots, N-1$ . To do so, we use the following result obtained by using restriction (1.3):

$$\sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \mathbf{w}_\alpha^j = \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left[ \mathbf{w}_\alpha^j - \frac{C_\alpha^j}{C_\alpha^N} \mathbf{w}_\alpha^N \right]$$

where  $\mathbf{w}_\alpha^j$  is the vector representing the coefficient of  $\mathbf{u}_\alpha^j$  in (3.10). Using (4.8) and (4.2) we can now express this term as

$$\sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left[ \tilde{\boldsymbol{\mu}}_\alpha^j \nabla (\varepsilon_\alpha \rho_\alpha^j) - \nabla [\varepsilon_\alpha \rho_\alpha^j (A_\alpha^j - A_\alpha^N)] - (\hat{\mathbf{i}}_\alpha^j + \hat{\mathbf{T}}_\alpha^j) + \frac{C_\alpha^j}{C_\alpha^N} (\hat{\mathbf{i}}_\alpha^N + \hat{\mathbf{T}}_\alpha^N) - \varepsilon_\alpha \mathbf{t}_\alpha^N \nabla \left( \frac{C_\alpha^j}{C_\alpha^N} \right) \right].$$

We thus obtain the following results which hold at equilibrium

$$p_l = p_s \tag{5.1}$$

$$\hat{\mathbf{T}}_l = p_l \nabla \varepsilon_l - \varepsilon_l \rho_l \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s \tag{5.2}$$

$$\nabla \cdot \varepsilon_\alpha \rho_\alpha^j \left[ \tilde{\boldsymbol{\mu}}_\alpha^j \mathbf{I} - (A_\alpha^j - A_\alpha^N) \mathbf{I} + \left( \frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j - \frac{1}{\rho_\alpha^N} \mathbf{t}_\alpha^N \right) \right] = \varepsilon_\alpha \rho_\alpha^j \nabla \tilde{\boldsymbol{\mu}}_\alpha^j \tag{5.3}$$

$$\tilde{\boldsymbol{\mu}}_l^j = \tilde{\boldsymbol{\mu}}_s^j \tag{5.4}$$

$$\left( \frac{p_l}{\rho_l} + A_l \right) \mathbf{I} - \sum_{j=1}^N C_l^j \boldsymbol{\mu}_l^j + \boldsymbol{\mu}_l^N = \left( \frac{p_s}{\rho_s} + A_s \right) \mathbf{I} - \sum_{j=1}^N C_s^j \boldsymbol{\mu}_s^j + \boldsymbol{\mu}_s^N \tag{5.5}$$

where we have used the definition of the Lagrange multipliers given in (4.1) and (4.2). Further, we used the momentum equation for species, (2.9), at equilibrium in the derivation of (5.3), and equation (4.11) was used in the derivation of (5.5). Relation (5.1) states that at equilibrium, the thermodynamic pressures of the two phases are equal. Relation (5.4) resembles in form the classical Gibbsian result stating that at equilibrium, the chemical potentials of a single constituent in two phases are equal, although it is not yet in the sharpest form since it is expressed only in terms of the relative chemical potential. Expression (5.5) gives a relationship between the Gibbs energy and the weighted sum of the chemical potentials. To obtain a more physically intuitive interpretation for (5.2), begin by eliminating

$\widehat{\mathbf{T}}_l$  by using the momentum equation for the liquid phase (2.10), and then eliminate  $\mathbf{t}_l$  using (4.4) to get

$$\nabla p_l - \rho_l \mathbf{g} = -\rho_l \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s. \quad (5.6)$$

This shows that in contrast with a bulk liquid, the vicinal fluid does not satisfy the classical hydrostatic relation  $\nabla p_l = \rho_l \mathbf{g}$ . This result will be exploited in the next section to obtain a modified form of Darcy's law for the vicinal fluid.

Using (4.6) to eliminate  $\mathbf{t}_\alpha^j$  in (5.3) yields:

$$\nabla \tilde{\mu}_\alpha^j = \nabla (\mu_\alpha^j - \mu_\alpha^N) = \nabla \cdot (\boldsymbol{\mu}_\alpha^j - \boldsymbol{\mu}_\alpha^N) = 0, \quad (5.7)$$

where (4.19) is used for  $\tilde{\mu}_\alpha^j$ . This resembles the classical Gibbsian result stating that at equilibrium, the chemical potential is constant, but, similar to (5.4), it is expressed only in terms of the relative chemical potential.

We now use the two definitions of the chemical potential to obtain non-relative results corresponding to (5.4) and (5.7). The non-relative results corresponding to (5.5) are given by equations (4.12) and (4.15) for the tensorial and scalar definitions, respectively.

Eliminating the stress tensors in (4.12) using equations (4.4, 4.5) at equilibrium, and then eliminating  $\sum_{j=1}^N C_\alpha^j \boldsymbol{\mu}_\alpha^j$  and  $\boldsymbol{\mu}_l^N - \boldsymbol{\mu}_s^N$  using (5.5) and (5.4), respectively, gives, in terms of the tensorial chemical potential,

$$\boldsymbol{\mu}_l^j - \boldsymbol{\mu}_s^j = \frac{1}{\rho_s} \left( \mathbf{t}_e^s + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right) \quad j = 1, \dots, N. \quad (5.8)$$

To get the equivalent expression in terms of the scalar chemical potential subtract (4.18) from (4.17) and combine this result with (5.8). This yields

$$\mu_l^j = \mu_s^j, \quad j = 1, \dots, N, \quad (5.9)$$

which tells us that the scalar chemical potential satisfies the classical Gibbsian result stating that the chemical potentials of a single species in two phases are equal at equilibrium. In contrast, when the solid phase is stressed, (5.8) indicates the macroscale tensorial chemical potential does not recover the classical result. This is due to the definition of the *macroscale* tensorial chemical potential, (4.9), and in no way should this be applied at the microscale. We may interpret the right hand side of (5.8), the effective and hydration stress tensors, as being an external source. It is nonzero, for example, when an external load is applied to the medium. Also note that if the solid phase is replaced by, e.g., another immiscible fluid we would get, by following the same procedure, equality between the two tensorial chemical potentials.

We now turn to the derivation of the absolute form of (5.7). This requires the derivation of an extended form of the Gibbs-Duhem relation for the vicinal fluid. To this end, begin by taking the gradient of the constitutive assumption for  $A_l$  (3.5). Using the chain rule and the constraint  $\sum_{j=1}^N C_\alpha^j = 1$  we get

$$\nabla A_l = \frac{p_l}{(\rho_l)^2} \nabla \rho_l + \sum_{j=1}^{N-1} \tilde{\mu}_l^j \nabla C_l^j + \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s = \frac{p_l}{(\rho_l)^2} \nabla \rho_l + \sum_{j=1}^N \mu_l^j \nabla C_l^j + \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s. \quad (5.10)$$

By taking the gradient of (4.15) and setting  $\alpha = l$  we also have

$$\nabla A_l = \frac{p_l}{(\rho_l)^2} \nabla \rho_l - \frac{1}{\rho_l} \nabla p_l + \sum_{j=1}^N (C_l^j \nabla \mu_l^j + \mu_l^j \nabla C_l^j). \quad (5.11)$$

Eliminating  $\nabla A_l$  via (5.10) and (5.11) and using equilibrium result (5.6) yields

$$\sum_{j=1}^N C_l^j \nabla \mu_l^j = \frac{1}{\rho_l} \nabla p_l + \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s = \mathbf{g}, \quad (5.12)$$

which is the Gibbs-Duhem relation for the vicinal liquid. This relation can be used to obtain a sharper form of the relative result (5.7). By multiplying the scalar version of (5.7) by  $C_l^j$  and summing over all constituents, we find, by using the above result, that  $\nabla \mu_l^N = \mathbf{g}$ . Combining this with (5.9) and (5.7) gives

$$\nabla \mu_l^j = \nabla \mu_s^j = \mathbf{g}, \quad j = 1, \dots, N. \quad (5.13)$$

The above result provides a sharper description of equilibrium condition (5.7) and shows consistency with the classical result of Gibbsian thermodynamics which states that in the absence of gravity, the scalar chemical potential is constant at equilibrium. The corresponding result for the tensorial chemical potential can be easily obtained by combining the above expression, (5.13), with (4.17, 4.18):

$$\nabla \cdot \boldsymbol{\mu}_l^j = \mathbf{g} \quad \nabla \cdot \boldsymbol{\mu}_s^j = \mathbf{g} - \nabla \cdot \left[ \frac{1}{\rho_s} \left( \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right) \right], \quad (5.14)$$

which confirms that in the absence of gravity, Bowen's tensorial chemical potential for the solid phase is not constant at equilibrium.

By incorporating the effective and hydration stress tensors into the definition of the scalar chemical potential in the solid phase (4.14), we have in some sense incorporated an "external" source. Physically, both  $\mu_\alpha^j$  and  $(1/3)\text{tr}(\boldsymbol{\mu}_\alpha^j)$  may be interpreted as the amount of chemical energy required to place a particle into the system. But we must keep in mind the slight difference between them, i.e. that the scalar definition incorporates the amount of energy associated with  $\text{tr}(\mathbf{t}_s^e) + (\varepsilon_l/\varepsilon_s)\text{tr}(\mathbf{t}_s^l)$ . When viewing the hydration and effective stresses as a source term, we see that the scalar chemical potential is analogous to the well-known "gravi-chemical potential" of classical thermodynamics whose definition incorporates the energy due to gravity. In Section 8 we shall illustrate this analogy with some examples.

## 6 Near-Equilibrium Theory

To derive near-equilibrium results, the coefficients of  $D_s \varepsilon_l / Dt$ ,  $\mathbf{u}_\alpha^j$ ,  $\mathbf{v}_{l,s}$ ,  $\hat{c}_\alpha^j$ ,  $\hat{e}_\alpha$  in entropy inequality (3.10) are linearized about the above variables since they vanish at equilibrium. Strictly speaking the coefficients should be linearized about all variables of the above set (see e.g. [13, 27]). However here we pursue the approach of Bennethum et al. [46] and choose to linearize only about the one variable which gives a positive quadratic form in the entropy inequality. So for example, if  $z$  is a variable which vanishes at equilibrium and  $f$  is the coefficient of  $z$  within the entropy inequality, the linearization procedure gives an approximation for the near-equilibrium value of  $f$  as,

$$f_{neq} \approx f_{eq} + Cz \quad (6.1)$$

where  $C$  is the linearization constant. Using this procedure for the coefficients of  $D_s \varepsilon_l / Dt$ ,  $\mathbf{v}_{l,s}$ , and  $\hat{c}_\alpha^j$ , we have

$$p_l - p_s = \mu_* \frac{D_s \varepsilon_l}{Dt} \quad (6.2)$$

$$p_l \nabla \varepsilon_l - \varepsilon_l \rho_l \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s - \hat{\mathbf{T}}_l = R_l \mathbf{v}_{l,s} \quad (6.3)$$

$$\tilde{\mu}_l^j - \tilde{\mu}_s^j = K^j \hat{c}_\alpha^j \quad j = 1, \dots, N-1 \quad (6.4)$$

where  $\mu_*$ ,  $R_l$ ,  $R_\alpha^j$  and  $K^j$  are material coefficients which may be a function of the independent variables which are not necessarily zero at equilibrium.

The above relations are nice in some sense because the term  $f_{eq}$  is zero. This is not true of the coefficient for  $\mathbf{u}_\alpha^j$ , so for this case it is necessary to do some further manipulations. Consider the term involving  $\mathbf{u}_\alpha^j$  in entropy inequality (3.10). Eliminating the Lagrange multipliers using (4.2) and (4.10), and adding  $\sum_{j=1}^N \mathbf{u}_\alpha^j [\rho_\alpha^j \mu_\alpha^N \nabla \varepsilon_\alpha]$ , which is zero by constraint (1.3), we have

$$\begin{aligned} & \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \left[ \mu_\alpha^j \nabla (\varepsilon_\alpha \rho_\alpha^j) - \mu_\alpha^N \nabla (\varepsilon_\alpha \rho_\alpha^j) - \nabla (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) - (\hat{\mathbf{i}}_\alpha^j + \hat{\mathbf{T}}_\alpha^j) + \varepsilon_\alpha \mu_\alpha^N \nabla \rho_\alpha^j + \rho_\alpha^j \mu_\alpha^N \cdot \nabla \varepsilon_\alpha \right] \\ &= \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \left[ \mu_\alpha^j \nabla (\varepsilon_\alpha \rho_\alpha^j) - \nabla (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) - (\hat{\mathbf{i}}_\alpha^j + \hat{\mathbf{T}}_\alpha^j) \right]. \end{aligned}$$

Linearizing this term about equilibrium using (6.1) and eliminating  $\hat{\mathbf{i}}_\alpha^j + \hat{\mathbf{T}}_\alpha^j$  using momentum equation (2.9) we have

$$\begin{aligned} & \left[ \mu_\alpha^j \nabla (\varepsilon_\alpha \rho_\alpha^j) - \nabla (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) + \nabla \cdot (\varepsilon_\alpha \mathbf{t}_\alpha^j) + \varepsilon_\alpha \rho_\alpha^j \mathbf{g} \right]_{neq} \\ &= \left[ \mu_\alpha^j \nabla (\varepsilon_\alpha \rho_\alpha^j) - \nabla (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) + \nabla \cdot (\varepsilon_\alpha \mathbf{t}_\alpha^j) + \varepsilon_\alpha \rho_\alpha^j \mathbf{g} \right]_{eq} + \mathbf{R}_\alpha^j \mathbf{u}_\alpha^j, \end{aligned}$$

where  $\mathbf{R}_\alpha^j$  is the linearization constant which in general is a second order tensor and where we have assumed the inertial term in the momentum equation is negligible near equilibrium. Using (4.9) to rewrite this expression in terms of the tensorial chemical potential yields

$$\left[ -\varepsilon_\alpha \rho_\alpha^j \nabla \cdot \mu_\alpha^j + \varepsilon_\alpha \rho_\alpha^j \mathbf{g} \right]_{neq} = \left[ -\varepsilon_\alpha \rho_\alpha^j \nabla \cdot \mu_\alpha^j + \varepsilon_\alpha \rho_\alpha^j \mathbf{g} \right]_{eq} + \mathbf{R}_\alpha^j \mathbf{u}_\alpha^j.$$

At equilibrium we can use (5.14) so that we obtain generalized Fick's laws,

$$\begin{aligned} R_l^j \mathbf{u}_l^j &= -\varepsilon_l \rho_l^j (\nabla \cdot \mu_l^j - \mathbf{g}) \\ R_s^j \mathbf{u}_s^j &= -\varepsilon_s \rho_s^j (\nabla \cdot \mu_s^j - \mathbf{g}) - \varepsilon_s C_s^j \nabla \cdot \left( \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right) \quad j = 1, \dots, N. \end{aligned}$$

$$R_\alpha^j \mathbf{u}_\alpha^j = -\varepsilon_\alpha \rho_\alpha^j (\nabla \cdot \mu_\alpha^j - \mathbf{g}), \quad j = 1, \dots, N, \quad \alpha = l, s$$

i.e. a form of Fick's law which is identical in form to the statistical thermodynamical result [40]. Note that this is a much sharper result than what has been previously obtained, (1.1). The coefficients  $R_\alpha^j$  must be such that the constraint on the diffusive velocities, (2.17), is satisfied. This extends to swelling media the results of Bennethum et al. [46] where a macroscopic form of Fick's law involving the absolute chemical potential gradient was derived for granular media. The above results are consistent with equilibrium relations (5.13, 5.14) and in particular, indicate that stressing the solid phase affects the diffusive velocity of solid constituents.

Equation (6.2) tells us that near equilibrium, the thermodynamic pressure of the vicinal fluid and solid phases are not necessarily equal, especially for colloidal systems. The coefficient  $\mu_*$  may be thought of as a retardation factor which among other effects, accounts for the re-ordering of the water molecules as they are disturbed, i.e. an entropic effect. If this is the only source of retardation, then it follows that for a granular media,  $\mu_* \approx 0$ , since there is very little ordering of the liquid phase in such a medium. We remark that an equation identical to (6.2) with  $p_s = 0$  was heuristically derived and used in polymer physics [78] and in the mechanics of thin films [79]. In this latter reference the authors

discuss the appearance of a viscous disjoining pressure component due to the excess in viscosity of the thin liquid film relative to the bulk phase (see also Murad and Cushman [80] for details). Furthermore, using (6.2) in expressions (4.5) and (4.7) for  $\mathbf{t}_s$  and  $\mathbf{t}$ , respectively, we obtain the near-equilibrium relations,

$$\begin{aligned}\mathbf{t}_s &= \left(-p_l + \mu_* \frac{D_s \varepsilon_l}{Dt}\right) \mathbf{I} + \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l - \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \\ \mathbf{t} &= \left(-p_l + \varepsilon_s \mu_* \frac{D_s \varepsilon_l}{Dt}\right) \mathbf{I} + \varepsilon_s \mathbf{t}_s^e + \varepsilon_l \mathbf{t}_s^l - \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j.\end{aligned}$$

The above result can be viewed as a near-equilibrium modified Terzaghi principle, which in our notation can be stated as  $\mathbf{t} = -p_l \mathbf{I} + \varepsilon_s \mathbf{t}_s^e$ . Note that though the solid is considered elastic, the appearance of the retardation factor in (6.2) leads to a viscoelastic behavior for the volumetric stresses.

By neglecting inertial effects and using analogous arguments to those which gave rise to the vicinal fluid hydrostatic relation (5.6), equation (6.3) leads to the modified Darcy's law

$$\frac{1}{\varepsilon_l} R_l \mathbf{v}_{l,s} = -\nabla p_l - \rho_l \frac{\partial A_l}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s + \rho_l \mathbf{g},$$

In addition to a pressure gradient, the above form of Darcy's law contains a gradient of a generalized interaction potential which accounts for flow of vicinal water induced by the deformation of the clay particle. The appearance of this additional term indicates that strain gradients provide a potential for vicinal water flow in a swelling medium. If vicinal water flow due to particle shearing is neglected, then this interaction potential reduces to  $\rho_l \partial A_l / \partial \varepsilon_l \nabla \varepsilon_l$ , as was shown in [13] and [15] by positing  $A_l = A_l(T, \rho_l, \varepsilon_l, C_l^j)$  rather than the constitutive dependency of (3.5). We also remark that an extended form of Darcy's law for multiphase flows which incorporates an interaction potential was first derived within the current framework for nonswelling, granular systems by Hassanizadeh and Gray [29], [32].

Equation (6.4) governs the near-equilibrium adsorption/desorption of the  $j$ th component by the solid phase. The coefficient  $K^j$  may be identified with the kinetic constant of linear chemical adsorption (see e.g. [81]). Since it is expressed in terms of the relative chemical potentials, we turn to the task of sharpening it. To this end, we begin by rewriting the  $\hat{e}_l^j$  term of entropy inequality (3.10). Neglecting higher order terms near equilibrium (i.e.  $\Delta^2$ ) we have

$$\sum_{j=1}^N \hat{e}_l^j \left[ -\tilde{\mu}_l^j + \tilde{\mu}_s^j \right] = \sum_{j=1}^N \hat{e}_l^j \left[ -\mu_l^j + \mu_s^j \right] - \sum_{j=1}^N \hat{e}_l^j \left[ -\mu_l^N + \mu_s^N \right].$$

Note that by using (5.9), we can show that each coefficient (given in square brackets) is zero at equilibrium. The last coefficient is independent of  $j$ , so it will contribute to the coefficient of  $\hat{e}_l$  in the entropy inequality (recall that  $\sum_{j=1}^N \hat{e}_l^j = \hat{e}_l$ ). Linearizing the remaining coefficient using equation (6.1) yields

$$K^j \hat{e}_l^j = \mu_s^j - \mu_l^j \quad j = 1, \dots, N,$$

which is the absolute form of the near-equilibrium adsorption/desorption relation in terms of the scalar chemical potential. Again using (4.17, 4.18) to express the adsorption law in terms of the tensorial chemical potential we obtain

$$K_l^j \hat{e}_l^j \mathbf{I} = \boldsymbol{\mu}_s^j - \boldsymbol{\mu}_l^j + \frac{1}{\rho_s} \left( \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l \right) \quad j = 1, \dots, N,$$

which again emphasizes the recurring theme that replacing the scalar chemical potential by the tensorial chemical potential yields an additional source term due to  $\mathbf{t}_s^e$  and  $\mathbf{t}_s^l$ . This result indicates a stressed solid matrix affects the adsorption rate of the constituents.

## 7 Comparing the Chemical Potentials for Selected Examples

Our goal in this section is to compare the scalar and tensorial chemical potentials in selected one-dimensional examples. In so doing we provide a better physical feel for the two potentials. In this section we assume there is no net exchange of mass between the liquid and solid phases, and that the solid phase is incompressible so that  $D_s \rho_s / Dt = 0$ .

We begin with equation (4.18) which relates the solid phase scalar and tensorial chemical potentials:

$$\mu_s^j \mathbf{I} = \boldsymbol{\mu}_s^j + \frac{1}{\rho_s} (\mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l). \quad (7.1)$$

To compare the two quantities at equilibrium, we define their scalar difference

$$\Delta \mu_s^j \equiv \frac{1}{3} \text{tr} \boldsymbol{\mu}_s^j - \mu_s^j. \quad (7.2)$$

Using (7.1) in (7.2) gives

$$\Delta \mu_s^j = -\frac{1}{3} \frac{1}{\rho_s} \left( \text{tr} \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s} \text{tr} \mathbf{t}_s^l \right)$$

which, when using the definitions of  $\mathbf{t}_s^e$  (3.7),  $\mathbf{t}_s^l$  (3.7), and  $\mathbf{E}_s$  (3.4) yields

$$\begin{aligned} \Delta \mu_s^j &= -\frac{1}{3} \frac{\partial A_s}{\partial \mathbf{E}_s} : \mathbf{C}_s - \frac{1}{3} \frac{\varepsilon_l \rho_l}{\varepsilon_s \rho_s} \frac{\partial A_l}{\partial \mathbf{E}_s} : \mathbf{C}_s \\ &= -\frac{2}{3} \frac{\partial A_s}{\partial \mathbf{C}_s} : \mathbf{C}_s - \frac{2}{3} \frac{\varepsilon_l \rho_l}{\varepsilon_s \rho_s} \frac{\partial A_l}{\partial \mathbf{C}_s} : \mathbf{C}_s \end{aligned} \quad (7.3)$$

where  $\mathbf{C}_s = \mathbf{F}_s^T \mathbf{F}_s$ .

Next we rewrite the above expression for the case in which we assume the free energies are independent of the shearing components (or deviatoric part) of  $\mathbf{E}_s$ , i.e. for the one dimensional problem in which the free energy,  $A_\alpha$ , depends on the volume change of the solid phase. Let  $J_s = \det \mathbf{F}_s$  be the Jacobian of the solid phase motion, which represents the volumetric change in the solid phase (Eringen [51]). For an incompressible solid, the macroscopic volumetric deformation of the matrix is governed by changes in the volume fraction. Therefore, if we denote the volume fraction of the reference configuration by  $\bar{\varepsilon}_s = \bar{\varepsilon}_s(\mathbf{X}_s)$ , we have (see [26])

$$J_s \varepsilon_s = \bar{\varepsilon}_s. \quad (7.4)$$

Using the identity  $(\partial J_s^2 / \partial \mathbf{C}_s) : \mathbf{C}_s = 3J_s^2$  (Eringen [51]), and using (7.4) leads to

$$\begin{aligned} \frac{2}{3} \frac{\partial A_\alpha}{\partial \mathbf{C}_s} : \mathbf{C}_s &= \frac{2}{3} \frac{\partial A_\alpha}{\partial J_s^2} \frac{\partial J_s^2}{\partial \mathbf{C}_s} : \mathbf{C}_s = 2J_s^2 \frac{\partial A_\alpha}{\partial J_s^2} = 2J_s^2 \frac{\partial A_\alpha}{\partial \varepsilon_s} \frac{\partial \varepsilon_s}{\partial J_s^2} \\ &= -\frac{\bar{\varepsilon}_s}{J_s} \frac{\partial A_\alpha}{\partial \varepsilon_s} = \varepsilon_s \frac{\partial A_\alpha}{\partial \varepsilon_l}. \end{aligned}$$

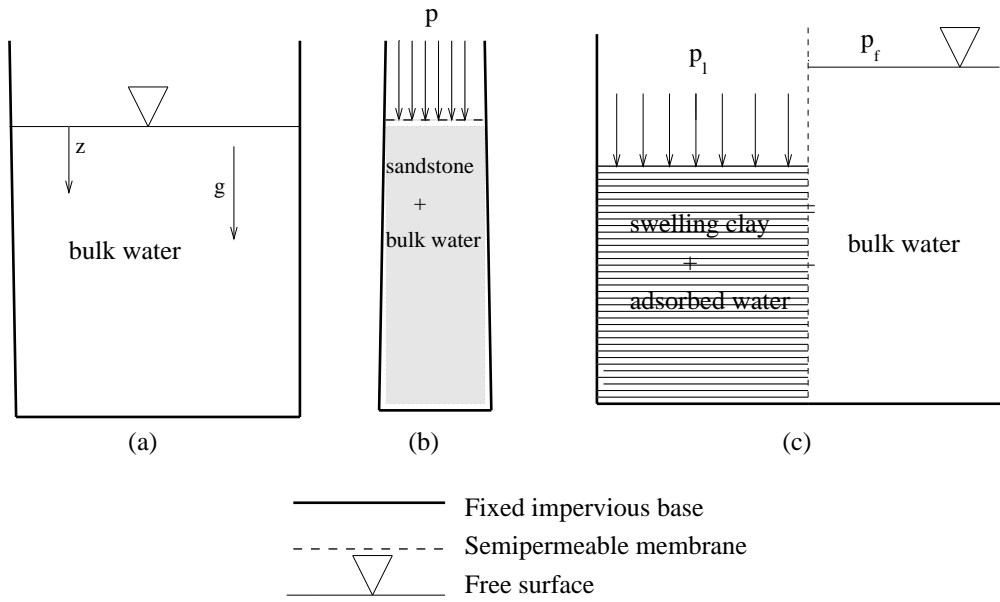
Combining the above result with (7.3) gives

$$\Delta \mu_s^j = -\varepsilon_s \frac{\partial A_s}{\partial \varepsilon_l} - \frac{\varepsilon_l \rho_l}{\rho_s} \frac{\partial A_l}{\partial \varepsilon_l}, \quad (7.5)$$

which is of a simplified one-dimensional relationship between the tensorial and scalar chemical potentials. The terms on the right hand side of (7.5) represent the one-dimensional version of the effective stress tensor and the hydration stress tensor, respectively.

To illustrate the effects of the effective and hydration stress components on  $\Delta \mu_s^j$ , we consider the consolidation of non-swelling and swelling media in two one-dimensional examples. But before





**Figure 7.1:** One Dimensional Examples: (a) Classical Static Fluid Column, (b) Terzaghi's consolidation column example with components, (c) Low's Swelling pressure experiment with components.

proceeding to these examples, we consider a classical static fluids example with the purpose of setting up an analogy between our scalar-tensorial chemical potentials and the gravitational-classical chemical potentials.

*Example 1: Classical Static Fluid Column Problem.* Consider a static column filled with an incompressible fluid (see Figure 7.1(a)). In this example, we assume the fluid is composed of a single constituent so that its classical (scalar) chemical potential is equal to the Gibbs free energy of the fluid,  $G_l$ . We denote the gravi-chemical potential by  $G_l^g$  and define it in terms of  $G_l$  to be

$$G_l^g \equiv G_l - \psi, \quad (7.6)$$

where  $\psi$  is the gravitational potential, i.e.  $\nabla\psi = \mathbf{g}$ . The gravitational potential in (7.6) plays the same role as the effective and hydration stresses in (7.5). Orienting the coordinate system as depicted in Figure 7.1(a), we set  $\mathbf{g} = g\mathbf{i}_z$  where  $\mathbf{i}_z$  is the unit vector along the  $z$ -axis. Hence

$$\psi = gz$$

where we have set  $\psi = 0$  at  $z = 0$  (i.e. the gravi-chemical and chemical potentials are identical at the top of the column). Thus

$$G_l - G_l^g = gz. \quad (7.7)$$

Also, since the single constituent fluid is incompressible, (5.10) reduces to  $\nabla A_l = \mathbf{0}$ . Thus, taking the gradient in (4.15) and using equilibrium expression (5.12) yields

$$\nabla G_l = \frac{1}{\rho_l} \nabla p_l = g$$

so that when combined with (7.7) we obtain

$$\nabla G_l^g = \mathbf{0}. \quad (7.8)$$

Results (7.7) and (7.8) show that  $G_l^g$  is constant throughout the length of the column while  $G_l$  must increase linearly as  $z$  increases. Consequently the chemical energy required to place a particle in the bottom of the column is greater than the chemical energy required at the top due to the gravitational potential.

We have thus illustrated an analogy between gravity, which acts as an external source when using the classical Gibbs free energy,  $G_l$ , and the effective and hydration stresses which act as an external source when using the tensorial chemical potentials. Keeping these results in mind, we consider the role of effective and hydration stress tensors on  $\Delta\mu_s^j$ .

*Example 2: Terzaghi's Consolidation Problem.* To illustrate the influence of the effective stress tensor on  $\Delta\mu_s^j$ , we consider Terzaghi's one-dimensional consolidation problem for a non-swelling elastic medium as described in [70]. In our formulation, these results can be easily reproduced by setting  $\mathbf{t}_s^l = \mathbf{0}$ . As depicted in Figure 7.1(b), a porous elastic column is bounded on the sides and bottom by a rigid, adiabatic, impermeable wall. At the top, a load is applied and the bulk water is free to drain. We consider the equilibrium configuration and assume each phase contains  $N$  miscible components. By neglecting the dependency of  $A_l$  on  $\varepsilon_l$  in (7.5) we have

$$\Delta\mu_s^j = -\varepsilon_s \frac{\partial A_s}{\partial \varepsilon_l}. \quad (7.9)$$

We assume the porous medium is linearly elastic and neglect gravitational effects. If the system under consideration is initially free of stress with a constant volume fraction  $\bar{\varepsilon}_l$ , then we can assume the following quadratic form for  $A_s$  [51]:

$$A_s = \frac{C}{2} (\varepsilon_l - \bar{\varepsilon}_l)^2$$

where  $C$  is a constant representing the compressibility of the solid matrix. Using (7.9) we then have

$$\Delta\mu_s^j \equiv \frac{1}{3} \text{tr} \boldsymbol{\mu}_s^j - \mu_s^j = -C \varepsilon_s (\varepsilon_l - \bar{\varepsilon}_l) \approx -\bar{C} (\varepsilon_l - \bar{\varepsilon}_l) \quad (7.10)$$

where we have linearized the above expression about equilibrium ( $\varepsilon_l = \bar{\varepsilon}_l$ ) so that  $\bar{C} = \bar{\varepsilon}_s C$ . In addition, we can derive the linear relationship between the effective pressure ( $p_s^e$ ) and volume fraction

$$p_s^e \equiv -\frac{1}{3} \text{tr} \mathbf{t}_s^e = -\varepsilon_s \rho_s \frac{\partial A_s}{\partial \varepsilon_l} = -\bar{C} \rho_s (\varepsilon_l - \bar{\varepsilon}_l)$$

which is similar in form to the one heuristically proposed by Terzaghi. Equation (7.10) can be interpreted physically in a manner similar to the previous example. As the overburden pressure is increased,  $\varepsilon_l$  decreases, and since  $\mu_s^j$  is constant at equilibrium (see equation (5.13)), then  $\text{tr} \boldsymbol{\mu}_s^j$  increases. Hence, the chemical energy required to insert a solid particle into the compressed system is greater than at the unstressed (initial) state.

*Example 3: Swelling Pressure Experiment.* To illustrate the influence of the hydration stress tensor,  $\mathbf{t}_s^j$ , on  $\Delta\mu_s^j$  we consider the classical reverse osmosis swelling pressure experiment of Low [3] or Achanta et al. [13]. As depicted in Figure 7.1(c), a saturated mixture of montmorillonite clay and adsorbed (incompressible) fluid is separated from a bulk (non-adsorbed) fluid by a semi-permeable membrane which only allows fluid to pass. An overburden pressure is applied to the clay mixture and the shrinkage due to the loss of fluid is recorded. As in the previous example, gravity is assumed

negligible and each phase is assumed to be composed of the same  $N$  miscible components where the concentrations of some of these components within a phase may be zero. It is assumed the clay mineral consists of flat plates and the clay medium is such that the flat plates are parallel so that the effective stress tensor,  $\mathbf{t}_s^e$ , is negligible. Consequently, equation (7.5) reduces to

$$\Delta\mu_s^j = -\frac{\varepsilon_l \rho_l}{\rho_s} \frac{\partial A_l}{\partial \varepsilon_l}. \quad (7.11)$$

Next, following Achanta et al. [13], we will show that, in contrast with the previous example,  $\Delta\mu_s^j$  appears inversely proportional to the volume fraction,  $\varepsilon_l$ . Begin by assuming the macroscopic solid phase stress tensor in the clay mixture is negligible ( $\mathbf{t}_s = \mathbf{0}$ ) so that all the overburden pressure is supported by the adsorbed liquid (recall that the total stress is given by  $\varepsilon_s \mathbf{t}_s + \varepsilon_l \mathbf{t}_l$ ). Since we have already assumed  $\mathbf{t}_s^e$  is negligible, the equation for the solid phase stress tensor (4.5) reduces to

$$p_l \mathbf{I} = \frac{\varepsilon_l}{\varepsilon_s} \mathbf{t}_s^l, \quad (7.12)$$

where we have used the equilibrium condition  $p_s = p_l$  (equation (5.1)). This tells us that the pressure in the adsorbed fluid is balanced by the hydration forces (otherwise all the fluid would pass through the membrane with minimal applied pressure). Taking the trace of (7.12), using definition (3.7) and using the same reasoning as from equation (7.3) to (7.5), we have for the one-dimensional case,

$$p_l = \frac{1}{3} \frac{\varepsilon_l}{\varepsilon_s} \text{tr}(\mathbf{t}_s^l) = \varepsilon_l \rho_l \frac{\partial A_l}{\partial \varepsilon_l}. \quad (7.13)$$

Moreover, by design we have that the concentrations of all constituents are constant. Since the scalar chemical potentials of the liquid phase are constant at equilibrium (equation (5.13)) we have that the Gibb's free energy is also constant by (4.15), i.e.

$$G_l = A_l + \frac{1}{\rho_l} p_l = \text{const.}$$

Hence, since adsorbed water was assumed incompressible

$$\frac{\partial A_l}{\partial \varepsilon_l} = -\frac{1}{\rho_l} \frac{\partial p_l}{\partial \varepsilon_l}$$

or when combining with (7.13)

$$p_l = -\varepsilon_l \frac{\partial p_l}{\partial \varepsilon_l}. \quad (7.14)$$

Upon integrating and using the condition that when  $\varepsilon_l = 1$ , the pressure in the adsorbed fluid,  $p_l$ , is equal to the the bulk fluid pressure,  $p_f$ , we get

$$p_l = \frac{p_f}{\varepsilon_l}. \quad (7.15)$$

Combining (7.13) and (7.11) and eliminating  $p_l$  using (7.15) gives

$$\frac{1}{3} \text{tr} \boldsymbol{\mu}_s^j - \mu_s^j = \Delta\mu_s^j = -\frac{p_l}{\rho_s} = -\frac{p_f}{\varepsilon_l \rho_s}. \quad (7.16)$$

We note that  $\Delta\mu_s^j$  is never zero due to the assumption that there is always some hydration force between the adsorbed liquid and solid phase. We conclude, contrary to the Terzaghi problem, that increasing the overburden pressure, which causes  $\varepsilon_l$  to decrease, results in a *decrease* in the magnitude of the  $\text{tr} \boldsymbol{\mu}_s^j$ . Hence it is easier to insert a solid particle into a compressed swelling media. This can

be physically attributed to the stronger adsorption forces in the compressed system due to the closer proximity of the liquid and solid phases.

As was done in [13] we can rewrite the above result in terms of the separation of platelets,  $\lambda$ . Denote the thickness of a clay platelet by  $\lambda_s$ , so that the volume fraction can be expressed as

$$\varepsilon_l = \frac{\lambda}{\lambda + \lambda_s}. \quad (7.17)$$

Using (7.17), we can express (7.14) in terms of the separation between platelets as

$$\left(\frac{\lambda^2}{\lambda_s} + \lambda\right) \frac{\partial p_l}{\partial \lambda} = -p_l.$$

At high moisture contents,  $\lambda \ll \lambda^2/\lambda_s$  and hence after integrating we obtain

$$p_l = p_f \exp(\lambda_s/\lambda),$$

where the thickness of the solid platelets,  $\lambda_s$ , is assumed constant. This result is identical to the swelling pressure result obtained empirically by Low [3]. Thus, by rewriting the dependency of  $\Delta\mu_s^j$  in (7.16) in terms of  $\lambda$  gives the alternative expression

$$\Delta\mu_s^j = -\frac{p_f}{\rho_s} \exp(\lambda_s/\lambda).$$

## 8 Conclusions

Within the framework of hybrid mixture theory for multicomponent single-phase flow in a colloidal porous medium, we have introduced a novel definition of the macroscale chemical potential. Unlike Bowen's tensorial chemical potential, this new chemical potential is a scalar which satisfies three properties consistent with the classical Gibbsian chemical potential for a single phase medium: (1) it is a scalar, (2) at equilibrium, the chemical potential of a single constituent in different phases is the same, and (3) the chemical potential is the driving force for diffusive flow (generalized Fick's law). After defining this chemical potential, the aforementioned properties were derived by exploiting the entropy inequality and using a generalized Gibbs-Duhem relation. Of particular note is that we used a Lagrange multiplier to enforce the gradient of the relationship between the diffusive velocities (1.3). Further, near-equilibrium results were obtained by linearizing coefficients which were not necessarily zero at equilibrium. This is an extension to what has been traditionally done [14, 32] where coefficients of constitutive variables such as  $D_s \varepsilon_l / Dt$  and  $\hat{e}^l$  are linearized about equilibrium. Here we have linearized about variables which are not constitutive, but are explicitly related to other independent variables, e.g.,  $\mathbf{u}_\alpha^N$ . In fact, one can linearize the coefficient of any variable (independent, constitutive, or directly dependent), using equation (6.1), however it may not be trivial to determine the coefficient at equilibrium. It should be noted that this philosophy cannot be applied when deriving nonequilibrium or equilibrium results, as the argument requires the entropy inequality to be expressed as linear combinations of variables which are independent.

From the entropy inequality, we rederived in a unified manner macroscopic constitutive results which captured the physics of swelling particles. Principle results include: (1) A modified effective stress principle for swelling porous media which incorporates an additional stress component ( $\mathbf{t}_s^l$ ) accounting for hydration stresses of physico-chemical nature. (2) A modified form of Darcy's law governing the flow of vicinal water which involves an additional interaction potential gradient accounting for the adsorptive character of the clay platelets. (3) The appearance of a retardation viscosity coefficient ( $\mu_*$ ) as a natural consequence of the topological law (Boure [37]) used to close the system. Among other effects this coefficient led to a viscoelastic behavior for the volumetric stresses even though the solid is considered a priori to be elastic. The coefficient may provide an important rational basis for the rheology of polymers and thin films as it may account for the re-ordering of the vicinal

water molecules as they are disturbed. In contrast, for a granular media there is very little ordering of the bulk liquid phase and consequently we may expect very little viscous behavior in such a medium due to this mechanism. (4) Improved forms of Fick's law and the adsorption/desorption relationship between phases, which are not dependent upon the labeling of the constituents.

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### Appendix A. Definition of Macroscopic Bulk Variables

The following formulas are the relationships between the microscale and macroscale (continuum scale) variables. In previous papers [66, 82, 22, 83], the relationships are derived assuming such approximations as  $\overline{\psi^{\alpha\alpha}} = \overline{\psi}^\alpha$  and  $\overline{\psi - \psi^{\alpha\alpha}} = 0$ . Here we have not made such assumptions. Following [22], the notation needed in macroscale field variable definitions include:

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

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

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

A few notes regarding the notation follow. In surface integrals, the unit normal outward vector  $\mathbf{n}_\alpha$  indicates the surface integral should be evaluated in the limit as the  $\alpha\beta$ -interface is approached from the  $\alpha$ -side. A  $\widehat{\phantom{x}}$  above the variable is used to emphasize that the quantity represents a transfer from the other phase or from other constituents.

$$\rho_\alpha^j \equiv \overline{\rho^j}^\alpha \tag{A.1}$$

$$C_\alpha^j \equiv \frac{\rho_\alpha^j}{\rho_\alpha} \tag{A.2}$$

$$\varepsilon_\alpha \equiv \frac{|\delta V_\alpha|}{|\delta V|} \tag{A.3}$$

$$\mathbf{v}_\alpha^j \equiv \overline{\mathbf{v}^j}^\alpha \tag{A.4}$$

$$\widehat{\mathbf{c}}_\alpha^j \equiv \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \tag{A.5}$$

$$\widehat{\mathbf{r}}_\alpha^j \equiv \varepsilon_\alpha \rho_\alpha^j \widehat{\mathbf{r}^j}^\alpha \tag{A.6}$$

$$\mathbf{t}_\alpha^j \equiv \langle \mathbf{t}^j \rangle^\alpha + \rho_\alpha^j \mathbf{v}_\alpha^j \mathbf{v}_\alpha^j - \rho_\alpha^j \overline{\mathbf{v}^j \mathbf{v}^j}^\alpha \tag{A.7}$$

$$\mathbf{g} \equiv \overline{\mathbf{g}}^\alpha \tag{A.8}$$

$$\widehat{\mathbf{T}}_\alpha^j \equiv \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} \left[ \mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}_\alpha da - \frac{\mathbf{v}_\alpha^j}{|\delta V|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \tag{A.9}$$

$$\widehat{\mathbf{i}}_\alpha^j \equiv \varepsilon_\alpha \rho_\alpha^j \left( \widehat{\mathbf{i}^j}^\alpha + \widehat{\mathbf{r}^j}^\alpha \mathbf{v}_\alpha^j - \widehat{\mathbf{r}}_\alpha^j \mathbf{v}_\alpha^j \right) \tag{A.10}$$

$$E_\alpha^j \equiv \overline{E^j}^\alpha + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha - \frac{1}{2} \mathbf{v}_\alpha^j \cdot \mathbf{v}_\alpha^j \tag{A.11}$$

$$\mathbf{q}_\alpha^j \equiv \langle \mathbf{q}^j \rangle^\alpha + \langle \mathbf{t}^j \mathbf{v}^j \rangle^\alpha - \mathbf{t}_\alpha^j \mathbf{v}_\alpha^j + \rho_\alpha^j \overline{\mathbf{v}_\alpha^j (E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j)}^\alpha - \rho_\alpha^j \mathbf{v}^j (E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j)^\alpha \quad (\text{A.12})$$

$$h_\alpha^j \equiv \overline{h^j}^\alpha + \overline{\mathbf{g}^j \cdot \mathbf{v}^j}^\alpha - \mathbf{g}_\alpha^j \cdot \mathbf{v}_\alpha^j \quad (\text{A.13})$$

$$\begin{aligned} \widehat{Q}_\alpha^j &\equiv \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} \left[ \mathbf{q}^j + \mathbf{t}^j \mathbf{v}^j + (E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \rho_\alpha^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}_\alpha da \\ &\quad - \frac{\mathbf{v}_\alpha^j}{|\delta V|} \int_{\delta A_{\alpha\beta}} \mathbf{t}^j \cdot \mathbf{n}_\alpha da - \left( \frac{\overline{E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j}^\alpha - \mathbf{v}_\alpha^j \cdot \mathbf{v}_\alpha^j}{|\delta V|} \right) \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \\ &\quad - \frac{\mathbf{v}_\alpha^j}{|\delta V|} \int_{\delta A_{\alpha\beta}} \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \end{aligned} \quad (\text{A.14})$$

$$\widehat{E}_\alpha^j \equiv \varepsilon_\alpha \rho_\alpha^j \left( \overline{\widehat{E}^j}^\alpha + \overline{\widehat{\mathbf{i}}^j \cdot \mathbf{v}^j}^\alpha - \widehat{\mathbf{i}}_\alpha^j \cdot \mathbf{v}_\alpha^j + (E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \widehat{r}^j - (E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \widehat{r}_\alpha^j \right) \quad (\text{A.15})$$

$$\eta_\alpha^j \equiv \overline{\eta^j}^\alpha \quad (\text{A.16})$$

$$\phi_\alpha^j \equiv \langle \phi^j \rangle^\alpha + \rho_\alpha^j \mathbf{v}_\alpha^j \eta_\alpha^j - \rho_\alpha^j \overline{\mathbf{v}^j \eta^j}^\alpha \quad (\text{A.17})$$

$$b_\alpha^j \equiv \overline{b^j}^\alpha \quad (\text{A.18})$$

$$\widehat{\Phi}_\alpha^j \equiv \frac{1}{|\delta V|} \int_{\delta A_{\alpha\beta}} \left[ \phi^j + \rho^j \eta^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}_\alpha da - \frac{\eta_\alpha^j}{|\delta V|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \quad (\text{A.19})$$

$$\widehat{\eta}_\alpha^j \equiv \varepsilon_\alpha \rho_\alpha^j \left( \overline{\widehat{\eta}^j}^\alpha + \overline{\widehat{r}^j \eta^j}^\alpha - \widehat{r}_\alpha^j \eta_\alpha^j \right) \quad (\text{A.20})$$

$$\widehat{\Lambda}_\alpha^j \equiv \overline{\Lambda^j}^\alpha \quad (\text{A.21})$$