

Three Pressures in Porous Media, Updated

Lynn S. Bennethum and Tessa Weinstein *

July 28, 2003

NOTE: This is an updated manuscript from that published in TIPM. All changes are marked in italics. Equations (33) and (37), the constitutive equation governing the rate of swelling, and the resulting consequences have been modified. The reason for making the change is as follows: Consider dry sandstone under compression at equilibrium. In this situation $\bar{p}^l = p^l = 0$ and $\bar{p}^s \neq 0$, but the time rate-of-change of the volume fraction is zero.

Abstract

In a thermodynamic setting for a single phase (usually fluid), the thermodynamically defined pressure, involving the change in energy with respect to volume, is often assumed to be equal to the physically measurable pressure, related to the trace of the stress tensor. This assumption holds under certain conditions such as a small rate of deformation tensor for a fluid. For a two-phase porous medium, an additional thermodynamic pressure has been previously defined for each phase, relating the change in energy with respect to volume fraction. Within the framework of Hybrid Mixture Theory and hence the Coleman and Noll technique of exploiting the entropy inequality, we show how these three macroscopic pressures (the 2 thermodynamically defined pressures and the pressure relating to the trace of the stress tensor) are related and discuss the physical interpretation of each of them. In the process, we show how one can convert directly between different combinations of independent variables without re-exploiting the entropy inequality. The physical interpretation of these three pressures is investigated by examining four media: a single

*University of Colorado at Denver, Center for Computational Mathematics, Campus Box 170, 1250 14th St. Suite 600, P.O. Box 173364, Denver, CO 80217-3364. Lynn.Bennethum@cudenver.edu

solid phase, a porous solid saturated with a fluid which has negligible physico-chemical interaction with the solid phase, a swelling porous medium with a non-interacting solid phase, such as well-layered clay, and a swelling porous medium with an interacting solid phase such as swelling polymers.

Key words: pressure, porous media, mixture theory, swelling, constitutive equations, clay, polymers

1 Introduction

Understanding pressure in porous media is critical for determining flow rate, diffusion, and, for swelling porous media, swelling rate. Here we concentrate on what pressure is, how it may be defined in three different ways, what these pressures represent for different materials, and how the different pressures affect Darcy's law, which governs the rate of flow through the porous media, and the rate of swelling.

For a single phase (e.g. fluid) only one macroscopic pressure is assumed to exist - that which is defined to be the force per unit area in a fluid. Thermodynamically, Gibbs defined pressure as the change of energy with respect to volume keeping the total mass and entropy fixed [16]. Experimentally this can be measured by putting the material in a rigid container, and keeping all other independent variables (e.g., mass, entropy) as fixed as possible (entropy is considered fixed if the deformation occurs so slowly that the action is reversible) applying a force on one side of the container (see Figure 1) and measuring the force per unit area as a function of volume. At equilibrium, this is the pressure at that particular state (set of fixed independent variables). Because energy is assumed to be independent of rate varying variables, the relationship between pressure, volume, and entropy is termed an *equation of state*, i.e. it is assumed to be valid even during non-equilibrium conditions. Of course this particular experiment is really only practical for compressible media such as gases, but this gives the idea of how one relates the thermodynamic definition of pressure with the physical pressure of force per unit area. Through carefully designed thought experiments, it can be proved that for a single phase at equilibrium, the physical pressure is equal to the thermodynamic pressure [16]. At non-equilibrium the physical pres-

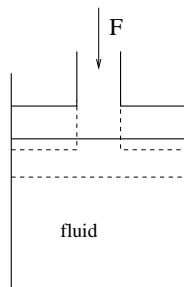


Figure 1: Experiment for classical pressure: $p = - \left. \frac{\partial U}{\partial V} \right|_{M,S,\dots}$

sure (force per unit area) and the thermodynamic pressure of a fluid are generally assumed equal [35].

In porous media however, and especially for swelling porous media, there are many more factors which influence pressure: the physico-chemical forces which dictate the attraction between the fluid and solid, ionic forces, and osmotic effects to name a few. These quantities are microscopic, i.e. they are measured at the pore scale. Our goal here is to try not to capture individual microscopic effects but to capture their effects at the macroscale. The result is that the pressure defined to be the normal force in a fluid and the thermodynamic pressure described by the experiment in Figure 1, are not necessarily equal. The relationship between the pressures are mathematically derived here, where it is shown that without any physical assumptions, the difference between the thermodynamic and physical pressures is the *swelling potential* - which, for the liquid phase, measures the electro-chemical interaction between the liquid and solid phase.

To obtain physical intuition as to the meaning of each of these pressures, constitutive relations must be used, and the derivations of these constitutive relations are accomplished within the framework of hybrid mixture theory (HMT), which is a slight modification of the classical mixture theory of Bowen [14].

Hybrid mixture theory (HMT) is a systematic process for developing governing equations which describe the behavior of porous media. The medium may consist of multiple phases [25, 26, 27], multiple constituents per phase [11, 13, 23, 24], multiple scales [5, 6], and/or include the effects of interfaces and contact lines [2, 21, 22, 29]. The result has been a more concrete foundation for the equations which govern flow through porous media

[10, 21, 28, 31] the adsorption/desorption of constituents [11, 13], the stress in a porous medium [12], heat transfer [7], and capillary pressure [1, 30].

Hybrid mixture theory is a hybridization of classical volume averaging of field equations and the exploitation of the entropy inequality in the sense of Coleman and Noll [17], resulting in restrictions on the form of constitutive equations. The results include governing equations in terms of macroscopic variables, that is, variables which are measured directly at the macroscale (on the order of $10 - 10^4$ pore lengths) as opposed to variables measured at a scale on the order of one pore length or smaller. The results presented here are limited to porous media consisting of two phases (solid and liquid) with negligible interfacial effects, and to porous media which have the same Representative Elementary Volume, REV [3], defined everywhere, i.e. all variables are measurable at one length scale throughout the medium. These results may be extended to more general media by incorporating any of the techniques in [2, 4, 5, 6, 21, 22, 29].

Within the process of exploiting the entropy inequality, one must determine the set of independent variables upon which the constitutive (or dependent) variables depend. Examples of constitutive variables include the stress tensor, heat flux, and energy. It is these independent variables which *define* the medium. For example, if the independent variables for a single-phase medium are the strain tensor and temperature, then the resulting equations are those which describe thermo-elastic solids. If the independent variables for a single-phase medium are the density and rate-of-deformation tensor, then the resulting equations are those which describe viscous fluids. Although the resulting equations for an elastic solid and viscous fluid (namely the Navier-Stokes equation) are well-understood and accepted, those for a two-phase porous medium such as sandstone or polymers are somewhat less well-understood, and those for a swelling porous medium such as clay and swelling polymers, even less.

In the past, HMT as it applies to swelling porous media [5, 6, 7, 11, 13], has been formulated using density, concentration, and volume fraction (volume of fluid phase per volume of porous medium) as independent variables. This has led to two pressures, one defined in terms of change in specific energy with respect to specific volume, and one in terms of change in specific energy with respect to volume fraction. It has not been clear how either of these two pressures relate to the classical definition of pressure: the change in total energy with respect to total volume.

In this paper we show how choosing independent variables which can

be directly related to extensive variables can be used to provide physical interpretations of these pressures. Specifically, we use volume fraction times density, instead of density, as an independent variable. It will be shown that the volume fraction times density has the extensive counterpart of total mass, just as the volume fraction has the extensive counterpart of total volume. The results are shown to be consistent with what has been previously derived, and the physical interpretation of previously defined thermodynamically defined pressures are discovered. In addition we show how different formulations involving different combinations of independent variables may be derived directly rather than going through the entire process of exploiting the entropy inequality.

We begin by introducing the macroscale field equations and associated notation. Next we produce some of the results obtained by exploiting the entropy inequality and define the pressures thermodynamically. In the process we show how to change between different combinations of independent variables and then derive the relationship between the resulting thermodynamically defined variables. In the next section, we discuss four media in which we can compare the physical interpretation of the different pressures. These four media are (1) a single solid phase, (2) a porous solid saturated with a fluid which has negligible physico-chemical interaction with the solid phase, (3) a swelling porous medium with a non-interacting solid phase, such as a well-layered clay sample, and (4) a swelling porous medium with an interacting solid phase so that the solid phase itself can support tension, compression, or both. We conclude with a discussion on the differences between the three pressures.

2 Governing Equations

The governing field equations include the conservation of mass, balance of momentum and energy, and the entropy inequality. The constitutive equations, which differ according to the material being modeled, complete the system of equations necessary to describe the porous medium. The field equations are presented first, and then pertinent restrictions on the constitutive equations based on the Coleman and Noll method [17] as formulated in [2, 13] are then presented. The medium to which these equations apply is a two-phase medium (liquid and solid) with negligible interfacial effects.

The field equations are derived via averaging their microscale counter-

parts, taking into account the movement of interfaces and transfer of mass, momentum, energy, and entropy between phases. The averaging process is explained in [4, 25] so here we only present the resulting macroscale equations. The relationship between these variables and their microscale counterparts are presented in [7], while the relationship between the constituent variables and their bulk-phase counterparts are provided in Appendix A. Throughout, a superscript Greek letter refers to a phase ($\alpha = l, s$, where l refers to the liquid phase and s refers to the solid phase), the subscript on the superscript refers to a constituent within a phase (e.g. l_j is the j th constituent of the liquid phase), and a carrot, $\hat{\cdot}$, indicates a transfer of mass/momentum/energy/entropy between phases or constituents. The complete nomenclature is presented in Appendix C.

Conservation of Mass

The macroscopic mass balance for constituent j in phase α is

$$\frac{D^{\alpha j}(\varepsilon^\alpha \rho^{\alpha j})}{Dt} + \varepsilon^\alpha \rho^{\alpha j} (\nabla \cdot \mathbf{v}^{\alpha j}) = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \hat{e}_\beta^{\alpha j} + \varepsilon^\alpha \rho^{\alpha j} \hat{r}^{\alpha j} \quad (1)$$

where $\frac{D^{\alpha j}}{Dt}$ is the material time derivative given by

$$\frac{D^{\alpha j}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^{\alpha j} \cdot \nabla, \quad (2)$$

and $\varepsilon^\alpha \rho^{\alpha j} \hat{e}_\beta^{\alpha j}$ represents the net rate of mass gained by constituent j in phase α from phase β per unit REV volume.

The bulk phase counterpart is given by

$$\frac{D^\alpha(\varepsilon^\alpha \rho^\alpha)}{Dt} + \varepsilon^\alpha \rho^\alpha (\nabla \cdot \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha \hat{e}_\beta^\alpha. \quad (3)$$

The net rate of mass gained in the α -phase due to chemical reactions in phase α must be zero, implying that:

$$\sum_{j=1}^N \rho^{\alpha j} \hat{r}^{\alpha j} = 0 \quad \forall \alpha. \quad (4)$$

Further, since the interface is assumed to be massless, we have the restriction that the magnitude of the rate of exchange of mass of constituent j from phase β to α must be the same as the rate from α to β :

$$\varepsilon^\alpha \rho^{\alpha j} \hat{e}_\beta^{\alpha j} + \varepsilon^\beta \rho^{\beta j} \hat{e}_\alpha^{\beta j} = 0, \quad j = 1, \dots, N. \quad (5)$$

Linear Momentum Balance

The macroscale linear momentum equation is given by

$$\varepsilon^\alpha \rho^{\alpha j} \frac{D^{\alpha j} \mathbf{v}^{\alpha j}}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \mathbf{g}^{\alpha j} = \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{i}}^{\alpha j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{T}}_\beta^{\alpha j} \quad (6)$$

where we assume the stress tensor is symmetric and $\hat{\mathbf{T}}_\beta^{\alpha j}$ represents the effect constituent j of phase β has on the rate of change of mechanical momentum of the same constituent in phase α . The relation between the macroscale variables and their microscale counterparts are given in [7]. Summing over j yields

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{t}^\alpha) - \varepsilon^\alpha \rho^\alpha \mathbf{g}^\alpha = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha \hat{\mathbf{T}}_\beta^\alpha, \quad (7)$$

with restrictions

$$\sum_{j=1}^N \rho^{\alpha j} (\hat{\mathbf{i}}^{\alpha j} + \hat{\mathbf{r}}^{\alpha j} \mathbf{v}^{\alpha j}) = 0 \quad \forall \alpha \quad (8)$$

$$\varepsilon^\alpha \rho^{\alpha j} (\hat{\mathbf{T}}_\beta^{\alpha j} + \hat{\mathbf{e}}_\beta^{\alpha j} \mathbf{v}^{\alpha j}) + \varepsilon^\beta \rho^{\beta j} (\hat{\mathbf{T}}_\alpha^{\beta j} + \hat{\mathbf{e}}_\alpha^{\beta j} \mathbf{v}^{\beta j}) = 0 \quad j = 1, \dots, N. \quad (9)$$

The first restriction states that there is no net momentum lost or gained due to interactions of species within a phase, and the second that there is no momentum lost at the interface.

Conservation of Energy

The conservation of energy equation is given by

$$\begin{aligned} \varepsilon^\alpha \rho^{\alpha j} \frac{D^{\alpha j} e^{\alpha j}}{Dt} - \varepsilon^\alpha \mathbf{t}^{\alpha j} : \nabla \mathbf{v}^{\alpha j} - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} h^{\alpha j} \\ = \varepsilon^\alpha \rho^{\alpha j} \hat{Q}^{\alpha j} + \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \hat{Q}_\beta^{\alpha j} \end{aligned} \quad (10)$$

where $\hat{Q}_\beta^{\alpha j}$ represents the rate of energy transferred from the β -phase to the j th constituent in the α -phase due to non-mass transfer, non-mechanical means. The relation between the macroscale variables and their microscale counterparts are given in [7]. Summing over constituents yields

$$\begin{aligned} \varepsilon^\alpha \rho^\alpha \frac{D^\alpha e^\alpha}{Dt} - \varepsilon^\alpha \mathbf{t}^\alpha : \nabla \mathbf{v}^\alpha - \nabla \cdot (\varepsilon^\alpha \mathbf{q}^\alpha) - \varepsilon^\alpha \rho^\alpha h^\alpha \\ = \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^\alpha \hat{Q}_\beta^\alpha \end{aligned} \quad (11)$$

with the restrictions

$$\sum_{j=1}^N \left[\rho^{\alpha j} \widehat{Q}^{\alpha j} + \rho^{\alpha j} \widehat{\mathbf{i}}^{\alpha j} \cdot \mathbf{v}^{\alpha j} + \rho^{\alpha j} \widehat{r}^{\alpha j} \left(e^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j})^2 \right) \right] = 0 \quad \forall \alpha \quad (12)$$

$$\begin{aligned} & \left[\varepsilon^{\alpha} \rho^{\alpha j} \widehat{Q}_{\beta}^{\alpha j} + \varepsilon^{\alpha} \rho^{\alpha j} \widehat{\mathbf{T}}_{\beta}^{\alpha j} \cdot \mathbf{v}^{\alpha j} + \varepsilon^{\alpha} \rho^{\alpha j} \widehat{e}_{\beta}^{\alpha j} \left(e^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j})^2 \right) \right] \\ & + \left[\varepsilon^{\beta} \rho^{\beta j} \widehat{Q}_{\alpha}^{\beta j} + \varepsilon^{\beta} \rho^{\beta j} \widehat{\mathbf{T}}_{\alpha}^{\beta j} \cdot \mathbf{v}^{\beta j} + \varepsilon^{\beta} \rho^{\beta j} \widehat{e}_{\alpha}^{\beta j} \left(e^{\beta j} + \frac{1}{2} (\mathbf{v}^{\beta j})^2 \right) \right] = 0 \quad j = 1, \dots, N, \end{aligned} \quad (13)$$

where $(\mathbf{v}^{\alpha j})^2 = \mathbf{v}^{\alpha j} \cdot \mathbf{v}^{\alpha j}$. The first restriction states that energy transfer due to species interacting within a phase must be conserved, and the second states that there is no loss of energy across an interface.

Entropy Balance

The entropy balance for constituent j in phase α is given by

$$\varepsilon^{\alpha} \rho^{\alpha j} \frac{D^{\alpha j} \eta^{\alpha j}}{Dt} - \nabla \cdot \varepsilon^{\alpha} \boldsymbol{\phi}^{\alpha j} - \varepsilon^{\alpha} \rho^{\alpha j} b^{\alpha j} = \sum_{\beta \neq \alpha} \varepsilon^{\alpha} \rho^{\alpha j} \widehat{\Phi}_{\beta}^{\alpha j} + \varepsilon^{\alpha} \rho^{\alpha j} \widehat{\eta}^{\alpha j} + \varepsilon^{\alpha} \rho^{\alpha j} \widehat{\Lambda}^{\alpha j} \quad (14)$$

where $\widehat{\Phi}_{\beta}^{\alpha j}$ represents the rate at which entropy is gained from constituent j in phase β , and $\rho^{\alpha j} \widehat{\Lambda}^{\alpha j}$ is the rate at which entropy is produced (per unit volume of phase α). It is $\widehat{\Lambda}^{\alpha j}$ which allows us to write the entropy balance as an equality, as opposed to an inequality. As a system, the second law of thermodynamics dictates that entropy must not decrease. Taking into account exchanges between phases, entropy fluxes, and entropy sources, this is written as $\sum_{\alpha} \sum_j \varepsilon^{\alpha} \rho^{\alpha j} \widehat{\Lambda}^{\alpha j} \geq 0$. Summing over constituents we get

$$\varepsilon^{\alpha} \rho^{\alpha} \frac{D^{\alpha} \eta^{\alpha}}{Dt} - \nabla \cdot (\varepsilon^{\alpha} \boldsymbol{\phi}^{\alpha}) - \varepsilon^{\alpha} \rho^{\alpha} b^{\alpha} = \sum_{\beta \neq \alpha} \varepsilon^{\alpha} \rho^{\alpha} \widehat{\Phi}_{\beta}^{\alpha} + \varepsilon^{\alpha} \rho^{\alpha} \widehat{\Lambda}^{\alpha}, \quad (15)$$

with restrictions

$$\sum_{j=1}^N \rho^{\alpha j} (\widehat{\eta}^{\alpha j} + \widehat{r}^{\alpha j} \eta^{\alpha j}) = 0 \quad \forall \alpha. \quad (16)$$

$$\varepsilon^{\alpha} \rho^{\alpha j} (\widehat{\Phi}_{\beta}^{\alpha j} + \widehat{e}_{\beta}^{\alpha j} \eta^{\alpha j}) + \varepsilon^{\beta} \rho^{\beta j} (\widehat{\Phi}_{\alpha}^{\beta j} + \widehat{e}_{\alpha}^{\beta j} \eta^{\beta j}) = 0 \quad j = 1, \dots, N. \quad (17)$$

At this point we have made no assumptions regarding the form of the entropy flux or source, or the composition of the medium. This is the topic of the next section.

3 Entropy Inequality and Thermodynamic Definitions of Pressure

The results we obtain are restricted to porous media composed of two phases, multiple constituents per phase, and negligible interfacial effects. We assume local thermal equilibrium so that

$$T^{\alpha_j}(\mathbf{x}, t) = T^{\beta_j}(\mathbf{x}, t) = T(\mathbf{x}, t) \quad j = 1, \dots, N, \quad \alpha, \beta = l, s,$$

and that each constituent of each phase is *simple* in the sense of Eringen, [20], so that the entropy source and entropy flux of each species are proportional to the heat source and heat flux, respectively, i.e.

$$b^{\alpha_j} = \frac{h^{\alpha_j}}{T} \quad \phi^{\alpha_j} = \frac{\mathbf{q}^{\alpha_j}}{T}.$$

We perform a Legendre transformation from energy, e , which depends upon entropy, to the Helmholtz potential, A , which depends on the more easily measurable variable, temperature. We define the internal part of the Helmholtz potential as:

$$A^\alpha = \sum_{j=1}^N C^{\alpha_j} A^{\alpha_j}. \quad (18)$$

With these assumptions and definitions, the entropy inequality within Hybrid Mixture Theory [2, 27] with no constitutive assumptions and with the constituent form of the conservation of mass equations, (1), enforced weakly using Lagrange multipliers λ^{α_j} is:

$$\begin{aligned} \sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha T \hat{\Lambda}^\alpha &= - \sum_{\alpha} \varepsilon^\alpha \rho^\alpha \left[\frac{D^\alpha A^\alpha}{Dt} + \eta^\alpha \frac{D^\alpha T}{Dt} \right] \\ &+ \sum_{\alpha} \sum_j A^{\alpha_j} \left[\frac{D^s(\varepsilon^\alpha \rho^{\alpha_j})}{Dt} + \mathbf{v}^{\alpha,s} \cdot \nabla(\varepsilon^\alpha \rho^{\alpha_j}) \right] \\ &- \sum_{\alpha} \sum_j \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j,\alpha} \cdot \nabla A^{\alpha_j} + \sum_{\alpha} \sum_j \varepsilon^\alpha \rho^{\alpha_j} A^{\alpha_j} \nabla \cdot \mathbf{v}^\alpha - \sum_{\alpha} \sum_j \varepsilon^\alpha \rho^{\alpha_j} A^{\alpha_j} \hat{e}_\beta^\alpha \\ &+ \sum_{\alpha} \mathbf{d}^\alpha : \left[\varepsilon^\alpha \mathbf{t}^\alpha + \sum_j \varepsilon^\alpha \rho^{\alpha_j} \mathbf{v}^{\alpha_j,\alpha} \mathbf{v}^{\alpha_j,\alpha} \right] \end{aligned}$$

$$\begin{aligned}
& + \sum_{\alpha} \sum_j \nabla \mathbf{v}^{\alpha_j, \alpha_j} : \varepsilon^{\alpha} \mathbf{t}^{\alpha_j} \\
& + \sum_{\alpha} \frac{\varepsilon^{\alpha}}{T} \nabla T \cdot \left\{ \mathbf{q}^{\alpha} + \sum_j \left[\rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \left(A^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) - \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} \right] \right\} \\
& - \mathbf{v}^{l, s} \cdot \varepsilon^l \rho^l \widehat{\mathbf{T}}_s^l \\
& + \sum_{\alpha} \sum_j \mathbf{v}^{\alpha_j, \alpha} \cdot \left[-\varepsilon^{\alpha} \rho^{\alpha_j} \widehat{\mathbf{i}}^{\alpha_j} - \sum_{\beta \neq \alpha} \varepsilon^{\alpha} \rho^{\alpha_j} \widehat{\mathbf{T}}_{\beta}^{\alpha_j} \right] \\
& + \sum_{\alpha} \sum_j \sum_{\beta \neq \alpha} \varepsilon^{\alpha} \rho^{\alpha_j} \widehat{e}_{\beta}^{\alpha_j} \left[-A^{\alpha_j} - \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right] \\
& + \sum_{\alpha} \sum_j \varepsilon^{\alpha} \rho^{\alpha_j} \widehat{r}^{\alpha_j} \left[-A^{\alpha_j} - \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right] \\
& - \sum_{\alpha} \sum_{\beta \neq \alpha} \varepsilon^{\alpha} \rho^{\alpha} \widehat{e}_{\beta}^{\alpha} \frac{1}{2} (\mathbf{v}^{\alpha, s})^2 \\
& + \sum_{\alpha} \sum_j \lambda^{\alpha_j} \left[\frac{D^s(\varepsilon^{\alpha} \rho^{\alpha_j})}{Dt} + \mathbf{v}^{\alpha_j, \alpha} \cdot \nabla (\varepsilon^{\alpha} \rho^{\alpha_j}) + \mathbf{v}^{\alpha, s} \cdot \nabla (\varepsilon^{\alpha} \rho^{\alpha_j}) \right. \\
& \left. + \varepsilon^{\alpha} \rho^{\alpha_j} \nabla \cdot \mathbf{v}^{\alpha_j, \alpha} + \varepsilon^{\alpha} \rho^{\alpha_j} \nabla \cdot \mathbf{v}^{\alpha} - \varepsilon^{\alpha} \rho^{\alpha_j} \widehat{e}_{\beta}^{\alpha_j} - \varepsilon^{\alpha} \rho^{\alpha_j} \widehat{r}^{\alpha_j} \right] \geq 0 \tag{19}
\end{aligned}$$

where we have used

$$\begin{aligned}
\sum_{j=1}^N \varepsilon^{\alpha} \rho^{\alpha_j} \frac{D^{\alpha_j} A^{\alpha_j}}{Dt} & = \varepsilon^{\alpha} \rho^{\alpha} \frac{D^{\alpha} A^{\alpha}}{Dt} + \sum_{j=1}^N \left[-A^{\alpha_j} \frac{D^{\alpha}(\varepsilon^{\alpha} \rho^{\alpha_j})}{Dt} \right. \\
& \left. + \varepsilon^{\alpha} \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \nabla A^{\alpha_j} - A^{\alpha_j} \varepsilon^{\alpha} \rho^{\alpha_j} \nabla \cdot \mathbf{v}^{\alpha} + \varepsilon^{\alpha} \rho^{\alpha_j} A^{\alpha_j} \widehat{e}_{\beta}^{\alpha} \right]. \tag{20}
\end{aligned}$$

At this point the unknowns include:

$$\varepsilon^{\alpha}, \varepsilon^{\alpha} \rho^{\alpha_j}, \mathbf{v}^{\alpha_j}, T \tag{21}$$

$$\begin{aligned}
\widehat{e}_{\beta}^{\alpha_j}, \widehat{r}^{\alpha_j}, \mathbf{t}^{\alpha_j}, \widehat{\mathbf{T}}_{\beta}^{\alpha_j}, \widehat{\mathbf{i}}^{\alpha_j}, A^{\alpha_j}, \mathbf{q}^{\alpha_j}, \widehat{Q}_{\beta}^{\alpha_j}, \widehat{Q}^{\alpha_j}, \eta^{\alpha_j}, \widehat{\Phi}_{\beta}^{\alpha_j}, \widehat{\eta}^{\alpha_j}, \widehat{\Lambda}^{\alpha_j} \\
j = 1, \dots, N. \tag{22}
\end{aligned}$$

In order to close the system we need the same number of equations as unknowns. We have the mass conservation equations (which correspond with $\varepsilon^{\alpha} \rho^{\alpha_j}$), the momentum conservation equations (which correspond with $\mathbf{v}^{\alpha_j, \alpha}$), and only one energy equation due to the local thermal equilibrium assumption, which corresponds with the unknown T . To close the system, we assume

that all variables listed in (22) are constitutive variables, i.e. that they are functions of a set of independent variables (the constitutive variables are thus the dependent variables). This still leaves the variable ε^α for which there is no corresponding equation. This is known as the closure issue and is a consequence of upscaling and obscuring the microscale geometry. We choose to follow Bowen [15], and close the system by postulating that the time rate of change of the volume fraction, $\dot{\varepsilon}^l$, is also a constitutive variable.

The most important assumption made in hybrid mixture theory (for near-equilibrium processes) is the choice of independent variables. These are the variables upon which all constitutive (or dependent) variables are a function of. Here we assume the independent variables are:

$$T, \varepsilon^l, \varepsilon^\alpha \rho^{\alpha j}, \mathbf{E}^s, \mathbf{v}^{l,s}, \mathbf{v}^{l,j,l}, \mathbf{d}^l, \nabla \mathbf{v}^{l,j,l}, \nabla T, \nabla \mathbf{E}^s, \nabla(\varepsilon^\alpha \rho^{\alpha j})$$

$$j = 1, \dots, N, \quad \alpha = l, s, \quad (23)$$

where \mathbf{E}^s is the strain of the solid phase. Since the solid phase may be disconnected, the macroscale strain tensor is not the average of the microscale strain, but is defined in terms of the deformation gradient, $\mathbf{F}^s = \nabla_0 \mathbf{x}$, $\mathbf{E}^s = \frac{1}{2}((\mathbf{F}^s)^T \cdot \mathbf{F}^s - \mathbf{I})$, where ∇_0 denotes differentiation with respect to the macroscopic material particle. Because $\varepsilon^l + \varepsilon^s = 1$, one can choose either the volume fraction of the solid phase or liquid phase as an independent variable.

The choice of independent variables is made based on experience and knowledge of the system being modeled. At the microscale the solid is considered elastic, so \mathbf{E}^s is included as an independent variable. The fluid not affected by the solid phase (i.e. bulk phase fluid) is typically a Newtonian fluid, so \mathbf{d}^l is incorporated. The behavior of a swelling mixture as a whole is known to be highly dependent upon the moisture content, so the volume fraction of fluid, ε^l , is also included. Likewise, the composition of the two phases is expected to be important, so $\rho^{\alpha j}$ is incorporated as well. Nonlocal effects are incorporated by including the gradients of these variables, and additional visco-elastic effects may also be obtained by including time rates of change of the independent variables listed above (non-local in time). Here we include just enough non-locality to give us results pertinent to this paper.

This choice of independent variables differs slightly from what has been used previously [6, 11, 13, 24] in that $\varepsilon^\alpha \rho^{\alpha j}$ which has units of [mass α_j / volume REV], is chosen instead of ρ^α , which has units of [mass α / volume α], and mass concentration, $C^{\alpha j}$. This change in the density variables allows a more direct comparison with extensively defined variables, as will be pointed out toward the end of this section.

The independent variables ε^s , ρ^s , \mathbf{E}^s are related through the continuity equation for the solid phase, although the relationship is not obvious. Recall that by geometrical arguments [20] we have the relationship $J^s = V/V_0$ where V is the total volume of the *smearred out* solid phase, V_0 is the initial volume of the (smearred out) solid phase, and $(J^s)^2 = \det((\mathbf{F}^s)^T \cdot \mathbf{F}^s)$. It would appear that we could divide top and bottom by the volume of the REV giving us $J^s = \varepsilon^s/\varepsilon_0^s$. But consider a porous medium composed of incompressible solid and liquid, initially at 50% liquid and drained so that in the end it has no liquid. The final volume is half the initial and $J^s = 1/2$ but $\varepsilon^s/\varepsilon_0^s = 2$. The reason this relationship does not hold is that ε^s is the ratio of the *actual* volume of the solid phase divided by the volume of the REV. To obtain the correct relationship between ρ^s , ε^l , and \mathbf{E}^s we begin with the conservation of mass of the α phase:

$$\int_V \varepsilon^\alpha \rho^\alpha dv = \int_{V_0} \varepsilon^\alpha \rho^\alpha J^s dv_0 = \int_{V_0} \varepsilon_0^s \rho_0^s dv_0 \quad (24)$$

which holds assuming no mass of the α phase leaves the system. This gives

$$J^s = \frac{\varepsilon_0^s \rho_0^s}{\varepsilon^\alpha \rho^\alpha} \quad \text{for total mass of } \alpha \text{ unchanged.} \quad (25)$$

Thus for example if fluid is allowed to leave the system then $J^s = \varepsilon_0^s \rho_0^s / \varepsilon^s \rho^s$ and we have the relationship between the strain, solid-phase density and volume fraction of the solid phase.

One can assume that A^l and A^s are functions of each of the variables listed in (23), but exploiting the entropy inequality shows that the Helmholtz potential is independent of most of the variables [4, 6]. Consequently, we simplify the computations by assuming *a priori*:

$$\begin{aligned} A^l &= A^l(\varepsilon^l, \varepsilon^l \rho^{lj}, T, \mathbf{E}^s) \\ A^s &= A^s(\varepsilon^l, \varepsilon^s \rho^{sj}, T, \mathbf{E}^s). \end{aligned} \quad (26)$$

See [4] for the consequences of assuming these potentials are a function of all independent variables.

Using the independent variables listed in (23) the final form of the entropy inequality is obtained (see Appendix B). The Coleman and Noll method for exploiting the entropy inequality [17] produces results which must always hold, results which hold only at equilibrium, and results which hold near

equilibrium. But before presenting the results we define some thermodynamic variables.

In terms of the Helmholtz potential we define the *thermodynamic pressure* to be:

$$\bar{p}^\alpha = -\varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \Big|_{\varepsilon^\alpha \rho^{\alpha j}, T, \dots} . \quad (27)$$

The reason for this terminology is explained by switching to extensive variables and comparing the result with pressure as defined in Gibbsian thermodynamics as follows: Since $\varepsilon^\alpha \rho^\alpha$ is held fixed in taking the partial derivative, we can bring it inside. The quantity $\varepsilon^\alpha \rho^\alpha A^\alpha$ has units of energy per unit volume REV. Formally multiplying numerator and denominator of the partial by the REV (which is fixed in time and space by assumption) and letting A_T^α denote the total (extensive) Helmholtz energy, we obtain

$$\bar{p}^\alpha = - \frac{\partial A_T^\alpha}{\partial V^\alpha} \Big|_{M^{\alpha j}, T, \dots} \quad (28)$$

i.e. the change in energy of the α -phase with respect to volume of the α -phase keeping the composition and temperature fixed. This is the classical Gibbsian thermodynamic definition of pressure.

Another thermodynamic variable which arises is the following:

$$p^\alpha = \sum_{j=1}^N \rho^\alpha \rho^{\alpha j} \frac{\partial A^\alpha}{\partial \rho^{\alpha j}} \Big|_{\varepsilon^\alpha, T, \dots} . \quad (29)$$

For a single phase composed of one constituent these two definitions coincide, which may be seen by converting to extensive variables where we get:

$$p^\alpha = - \frac{\partial A^\alpha}{\partial v^\alpha} \Big|_{\varepsilon^\alpha, T} = - \frac{\partial A_T^\alpha}{\partial V^\alpha} \Big|_{\varepsilon^\alpha M^\alpha, T} \quad (30)$$

where v^α is the specific volume. For a single phase, $\varepsilon^\alpha = 1$ and the two definitions are identical. As will be seen, for a swelling porous medium these two quantities are distinct. For reasons to be made clear later, we shall refer to p^α as the *classical pressure*.

Using these definitions, we present results obtained by exploiting the entropy inequality using the Coleman and Noll method [17]. There is a wealth

of information which can be obtained by exploiting each term in the entropy inequality, including the form constitutive equations must have to satisfy the second law of thermodynamics, given the assumptions. Here we present only the results pertinent to our discussion. We discuss the physical interpretation of each result in the following section.

Non-Equilibrium Constitutive Restrictions

Among others, the variables $\frac{D^s(\varepsilon^\alpha \rho^{\alpha j})}{Dt}$, \mathbf{d}^s , $\nabla \mathbf{v}^{sj,s}$, $\mathbf{v}^{sj,s}$ are neither constitutive nor independent, so that the coefficients must be zero. Using (B.4) and (29), the coefficient of \mathbf{d}^s gives us:

$$\mathbf{t}^s = -p^s \mathbf{I} + \frac{\varepsilon^l}{\varepsilon^s} \mathbf{t}_s^l + \mathbf{t}_e^s - \sum_{j=1}^N \rho^{sj} \mathbf{v}^{sj,s} \mathbf{v}^{sj,s} \quad (31)$$

where $\mathbf{t}_s^l = \rho^l \mathbf{F}^s \cdot \frac{\partial A^l}{\partial \mathbf{E}^s} \cdot (\mathbf{F}^s)^T$, and $\mathbf{t}_e^s = \rho^s \mathbf{F}^s \cdot \frac{\partial A^s}{\partial \mathbf{E}^s} \cdot (\mathbf{F}^s)^T$. The effective stress tensor \mathbf{t}_e^s , is the stress in the solid phase due to deformation of the solid phase. The other stress tensor, \mathbf{t}_s^l , is termed the hydration stress tensor [12, 36] and is a stress in the liquid phase due to shearing of the solid phase. This latter stress is zero if there is no fluid-solid interaction.

Equilibrium Constitutive Restrictions

We define equilibrium to be when the following set of *functionally independent* variables are zero: \mathbf{d}^l , $\nabla \mathbf{v}^{lj,l}$, $\mathbf{v}^{lj,l}$, $\mathbf{v}^{l,s}$, and $\varepsilon^l \rho^{lj} \hat{\mathbf{e}}_s^l$, where $j = 1, \dots, N-1$ except for $\hat{\mathbf{e}}_s^l$ where $j = 1, \dots, N$ (*omit* $\hat{\mathbf{e}}^l$). Since entropy production is maximum at equilibrium, and these variables are functionally independent (this can be verified by checking the dimensions), the partial of the entropy production with respect to each of these variables must be zero. In particular, taking the partial with respect to \mathbf{d}^l and $\mathbf{v}^{l,s}$ gives the following results:

$$\mathbf{t}^l = -p^l \mathbf{I} \quad (32)$$

$$\text{omit } \bar{p}^l = \bar{p}^s \quad (33)$$

$$\varepsilon^l \rho^l \hat{\mathbf{T}}_s^l = \bar{p}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} : (\nabla \mathbf{E}^s)^T \quad (34)$$

where in indicial notation $\frac{\partial A^l}{\partial \mathbf{E}^s} : (\nabla \mathbf{E}^s)^T = \frac{\partial A^l}{\partial E_{kl}^s} E_{kl,m}^s$. Equation (32) states that at equilibrium the liquid-phase stress tensor is proportional to the classical pressure. Equation (33) states that the classical pressures must be equal

at equilibrium, *but this cannot hold since dry sandstone under pressure can have a zero liquid (gas) thermodynamic pressure, a non-zero solid thermodynamic pressure, and a volume fraction which is constant.* Equation (34) gives the constitutive equation for the exchange of momentum term at equilibrium.

Near-Equilibrium Constitutive Restrictions

By near equilibrium we mean linearized results which produce positive quadratic terms 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

$$f_{\text{neq}} \approx f_{\text{eq}} + Cz \quad (35)$$

where C is the linearization constant. Note that for these results it is not necessary that the coefficients be linearly independent, as the only requirement is that the resulting entropy generation be positive definite.

Linearizing about \mathbf{d}^l , ε^l , and $\mathbf{v}^{l,s}$, we obtain

$$\mathbf{t}^l = -p^l \mathbf{I} + \boldsymbol{\nu}^l : \mathbf{d}^l \quad (36)$$

$$\text{modified } (\bar{p}^l - \bar{p}^s)_{\text{neq}} = (\bar{p}^l - \bar{p}^s)_{\text{eq}} + \eta \varepsilon^l \quad (37)$$

$$\begin{aligned} \varepsilon^l \rho^l \hat{\mathbf{T}}_s^l &= \bar{p}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} : (\nabla \mathbf{E}^s)^T \\ &\quad - \mathbf{R}^l \cdot \mathbf{v}^{l,s} \end{aligned} \quad (38)$$

where $\boldsymbol{\nu}^l$, a fourth-order tensor, η , a scalar, and \mathbf{R}^l , a second-order tensor, are linearization coefficients which are functions of all independent variables which are not necessarily zero at equilibrium, i.e. T , ε^l , $\varepsilon^\alpha \rho^{\alpha j}$.

Darcy's law is the empirically based equation governing the rate of flow through a homogeneous, non-swelling porous medium in thermal equilibrium [19]. To get a generalized version of Darcy's law, use (38) and (36) to eliminate $\varepsilon^l \rho^l \hat{\mathbf{T}}_s^l$ and \mathbf{t}^l , respectively, in the momentum equation, (7). Neglecting the inertial term results in

$$\begin{aligned} \mathbf{R}^l \cdot \mathbf{v}^{l,s} &= -\nabla(\varepsilon^l p^l) + \varepsilon^l \rho^l \mathbf{g} + \bar{p}^l \nabla \varepsilon^l - \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T \\ &\quad - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \mathbf{E}^s} : (\nabla \mathbf{E}^s)^T - \nabla \cdot (\varepsilon^l \boldsymbol{\nu}^l : \mathbf{d}^l). \end{aligned} \quad (39)$$

The last term is known as the Brinkman correction factor, although it is generally not considered to be significant for slow flow of a liquid. The more commonly used correction term is known as the Forchheimer correction factor, and this term is also obtainable within this framework, see [10, 28]. Other terms indicate that flow may be induced by gradients of strain, temperature, and volume fraction, see [7, 12] for further discussion.

We end this section by showing how to change between quantities which use different independent variables. In [2, 7] for example, the independent variables included ε^l , C^{lj} ($j = 1, \dots, N-1$) and ρ^l instead of ε^l and $\varepsilon^l \rho^{lj}$ ($j = 1, \dots, N$). So to make the distinction clear, let $\bar{A}^l = \bar{A}^l(\varepsilon^l, C^{lj}, \rho^l, T, \mathbf{E}^s)$ and $\bar{A}^s = \bar{A}^s(\varepsilon^l, C^{sj}, \rho^s, T, \mathbf{E}^s)$. Now consider the total differential

$$\begin{aligned} DA^l &= \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{lj}} d\varepsilon^l + \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l, C^{lj}} d\rho^l + \sum_{j=1}^{N-1} \left. \frac{\partial \bar{A}^l}{\partial C^{lj}} \right|_{\varepsilon^l, \rho^l} dC^{lj} \\ &= \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^{lj}} d\varepsilon^l + \sum_{j=1}^N \left. \frac{\partial A^l}{\partial (\varepsilon^l \rho^{lj})} \right|_{\varepsilon^l} d(\varepsilon^l \rho^{lj}). \end{aligned} \quad (40)$$

Then for example,

$$\left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{lj}} = \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^{lj}} \left. \frac{\partial \varepsilon^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{lj}} + \sum_{j=1}^N \frac{1}{\varepsilon^l} \left. \frac{\partial A^l}{\partial \rho^{lj}} \right|_{\varepsilon^l} \left. \frac{\partial (\varepsilon^l \rho^{lj})}{\partial \varepsilon^l} \right|_{\rho^l, C^{lj}} \quad (41)$$

$$= \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^{lj}} + \sum_{j=1}^N \frac{\rho^{lj}}{\varepsilon^l} \left. \frac{\partial A^l}{\partial \rho^{lj}} \right|_{\varepsilon^l}, \quad (42)$$

so that by multiplying through by $-\varepsilon^l \rho^l$ we obtain

$$p^l(\varepsilon^l, \rho^l) = \bar{p}^l(\varepsilon^l, \varepsilon^l \rho^l) + \pi^l(\varepsilon^l, \rho^l) \quad (43)$$

where

$$\pi^l = \varepsilon^l \rho^l \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{lj}}. \quad (44)$$

Equation (43) states that the classical pressure is equal to the pressure obtained by changing the volume of the liquid phase while keeping the mass fixed (i.e. changing the density), plus the pressure obtained by changing the

volume fraction while keeping the density fixed. Similarly, one may show that

$$p^l(\varepsilon^l, \varepsilon^l \rho^{lj}) = \sum_{j=1}^N \rho^l \rho^{lj} \left. \frac{\partial A^l}{\partial \rho^{\alpha j}} \right|_{\varepsilon^l} = (\rho^l)^2 \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l, C^{lj}} = p^l(\varepsilon^l, \rho^l, C^{lj}) \quad (45)$$

so that the classical pressures using either set of independent variables coincide. Using these and other similarly obtained relations in the results listed in this section gives us exactly the same results obtained when ε^l and ρ^l are used as independent variables from the outset.

Similar to (44), we can also define π^s so that we have

$$\pi^\alpha = \varepsilon^\alpha \rho^\alpha \left. \frac{\partial \bar{A}^\alpha}{\partial \varepsilon^\alpha} \right|_{\rho^\alpha, C^{\alpha j}}, \quad \alpha = l, s. \quad (46)$$

We refer to π^α as the *swelling potential* for reasons to be made clear in the next section, and we can also derive (43) for the solid phase, so that we have the general relationship

$$p^\alpha = \bar{p}^\alpha + \pi^\alpha, \quad \alpha = l, s. \quad (47)$$

Here we make a small comment on notation. Unlike the different potentials (internal energy, Helmholtz, Gibbs) where the independent variables are truly distinct, the different sets of independent variables (used in A^α and \bar{A}^α) are just different combinations of *the same independent variables*. As such, they are not different potentials, and so we drop the overline for the remainder of the paper. However as a result, the partial derivatives must clearly denote which variables are being held fixed.

4 Four Media

In order to give a physical interpretation to the pressure variables for each phase, p^α , π^α , and \bar{p}^α , we consider four different media. First we consider an isotropic solid phase with no liquid. Next we consider a Biot media, consisting of an elastic solid phase with a non-interacting fluid. Following, a swelling porous media with a non-interacting solid phase such as a well-layered montmorillonite is considered, and lastly, we will consider a swelling porous medium with an interacting solid phase such as a hydrophilic polymer.

Consider first just a **single isotropic solid phase** such as metal. In this case there is no liquid phase and hence no volume fraction. The continuity equation relates \mathbf{E}^s with ρ^s , in the following manner:

$$\sqrt{\det ((\mathbf{F}^s)^T \cdot \mathbf{F}^s)} = \rho_0 / \rho \quad \text{where } 2\mathbf{E}^s = (\mathbf{F}^s)^T \cdot \mathbf{F}^s - \mathbf{I} \quad (48)$$

where ρ_0 is the reference density. Thus not all components of \mathbf{E}^s and ρ^s may be considered as constitutive independent variables. For a compressible solid, the density is typically not used as an independent variable, and all three invariants of the strain tensor may change independently. The result is that the solid-phase stress tensor is the effective solid-phase stress tensor, $\mathbf{t}^s = \mathbf{t}_e^s$. For an incompressible solid, we enforce the continuity equation using a Lagrange multiplier, λ^s , and the resulting expression for the stress tensor is

$$\mathbf{t}^s = -\lambda^s \mathbf{I} + \mathbf{t}_e^s, \quad (49)$$

where now \mathbf{t}_e^s is calculated without any regard to the incompressibility restriction placed on \mathbf{E}^s . The Lagrange multiplier must be obtained directly using the boundary conditions of the problem, and often $1/3\text{tr}(\mathbf{t}_e^s)$ is incorporated into λ^s , which can be done without loss of generality. This simplifies matters as then the effective stress tensor represents only the deviatoric part. In this case, $-\frac{1}{3}\text{tr}(\mathbf{t}^s)$, which represents the physical pressure exerted on the system, is λ^s so that we can associate λ^s with p^s . Thus p^s is the physical (hence *classical*) pressure of the solid phase. In the case of a solid object submerged in water with pressure p^l with negligible acceleration and gravitational effects, the momentum equation gives $\nabla p^s = \mathbf{0}$. Combining this with boundary conditions gives $p^s = p^l$.

Now consider a **two-phase non-swelling porous medium**, such as a sand-water mixture or sandstone under compression. In sandstone, the solid phase is connected and can support a load without any fluid, while in a sand-water mixture the sand can only support compressional forces. If fluid and not solid is allowed to leave the system, then $J^s = \varepsilon_0^s \rho_0^s / \varepsilon^s \rho^s$ and we have the relationship between the strain, solid-phase density and volume fraction of the solid phase. Although these variables are dependent, the derivation used herein enforced the continuity equations using Lagrange multipliers allowing all variables to vary independently. So for example, in evaluating the change in energy with respect to volume fraction in \bar{p}^s , one does not fix the strain

or the density. Instead it is evaluated letting the strain and solid-phase density change naturally and \bar{p}^s is measured as a function of two of the three variables, \mathbf{E}^s , ρ^s , and ε^s . Of course one may choose to not use one of ρ^s , ε^s , or a component of \mathbf{E}^s as an independent variable, in which case one of p^s , \bar{p}^s , and a component of \mathbf{t}_e^s must be eliminated from the governing equations derived. This does not imply that the variable eliminated is necessarily zero. In this case, the remaining thermodynamic variables are evaluated keeping the other independent variables fixed.

For a non-swelling porous medium with no loss of solid mass, we choose to drop one of the components of the strain tensor, that one corresponding to J^s , the determinant of the deformation tensor, \mathbf{F}^s . Thus \mathbf{t}_e^s would be evaluated keeping ε^s and ρ^s fixed, or equivalently, keeping $J^s = \varepsilon_o^s \rho_o^s / \varepsilon^s \rho^s$ fixed. Intuitively, we can think of \mathbf{t}_e^s being evaluated keeping the smeared out solid phase volume (total volume) fixed (see discussion prior to equation (24)), so that it represents the changes primarily due to the deviatoric part of the strain tensor. For the remainder of the paper, we will make the assumption that eliminating this component produces an effective stress tensor with zero trace. This isn't quite mathematically rigorous as the following calculation shows, but this assumption makes the results more physically meaningful. In this calculation $\mathbf{C}^s = (\mathbf{F}^s)^T \cdot \mathbf{F}^s$ is the Green's deformation tensor:

$$\frac{1}{3} \text{tr}(\mathbf{t}_e^s) = \frac{1}{3} \text{tr} \left(\rho^s \mathbf{F}^s \cdot \frac{\partial A^s}{\partial \mathbf{E}^s} \cdot (\mathbf{F}^s)^T \right) \quad (50)$$

$$= \frac{1}{3} \rho^s \frac{\partial A^s}{\partial \mathbf{E}^s} : \mathbf{C}^s = \frac{2}{3} \rho^s \frac{\partial A^s}{\partial \mathbf{C}^s} : \mathbf{C}^s \quad (51)$$

$$\approx \frac{2}{3} \rho^s \frac{\partial A^s}{\partial (J^s)^2} \frac{\partial (J^s)^2}{\partial \mathbf{C}^s} : \mathbf{C}^s \quad (52)$$

$$= 2 \rho^s (J^s)^2 \frac{\partial A^s}{\partial (J^s)^2} = \rho^s J^s \frac{\partial A^s}{\partial J^s} \quad (53)$$

$$= \rho^s J^s \left[\frac{\partial A^s}{\partial \varepsilon^s} \left(-\frac{\varepsilon^s}{J^s} \right) + \frac{\partial A^s}{\partial \rho^s} \left(-\frac{\rho^s}{J^s} \right) \right] \quad (54)$$

$$= -\varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^s} - (\rho^s)^2 \frac{\partial A^s}{\partial \rho^s} \quad (55)$$

$$= -\pi^s - p^s \quad (56)$$

where $\mathbf{A} : \mathbf{B}$ in indicial notation is $A_{ij} B_{ij}$, and for (53), $\frac{\partial (J^s)^2}{\partial \mathbf{C}^s} : \mathbf{C}^s = 3(J^s)^2$ [20]. From this calculation we see that eliminating the component of strain

corresponding to J^s does not eliminate something which cannot be captured by p^s and π^s , and that the trace of the effective stress tensor measures the change in energy with respect to density keeping the volume fraction fixed, p^s , and the change in energy with respect to volume fraction keeping the density fixed, π^s . The assumption that the trace of the effective stress tensor is zero is only as good as the approximation of (52), i.e. that the Green's deformation tensor is primarily a function of the volume of the solid phase ($\varepsilon^s \rho^s$).

We thus assume the effective stress tensor has a zero trace. In addition, the energy of the liquid phase depends negligibly on the strain of the solid phase and the amount of fluid present (i.e. the energy of the liquid does not depend upon its proximity to the solid phase, which is the definition of a non-swelling porous media), so we assume $\mathbf{t}_s^l = \mathbf{0}$ and $\pi^l = 0$. In this case the constitutive equations become:

$$\bar{p}^l = p^l \quad (57)$$

$$\text{modified } (p^l - \bar{p}^s)_{\text{neq}} = (p^l - \bar{p}^s)_{\text{eq}} + \eta \dot{\varepsilon}^l \quad (58)$$

$$\mathbf{t}^s = -p^s \mathbf{I} + \mathbf{t}_e^s = -(\pi^s + \bar{p}^s) \mathbf{I} + \mathbf{t}_e^s \quad (59)$$

$$\mathbf{t}^l = -p^l \mathbf{I}. \quad (60)$$

It should be noted that an equation very similar to (58) has been derived (in a more ad hoc fashion) and used in soil mechanics, see [38, 18, 39], where the form is: $\eta_1 \dot{p}^l - \eta_2 \dot{p}^s = \dot{\varepsilon}^l$. This is a highly unusual form for the constitutive equation for $\dot{\varepsilon}^l$ since, to the authors knowledge, this formulation can not be shown to be thermodynamically consistent and is not found in any other field.

In the case when the liquid and solid phases are compressible, these are the equations to be used. If the liquid and solid phases are incompressible, then the continuity equations are enforced by Lagrange multipliers, and the equations remain the same except that the classical pressures are now unknowns of the problem, just as in the single solid phase case.

We now consider the physical interpretation of the pressures. The classical liquid pressure, p^l , is well-defined, as it is the physical pressure in the liquid phase. The solid phase classical pressure, p^s , is the physically measurable pressure since it is directly related to the stress tensor.

To explore the physical interpretations of π^s and \bar{p}^s , consider first the case of sand surrounded by water. We have a balance of forces and so $p^s = p^l$ and the classical pressures are equal, as they should be. In the case of sandstone

or sand grains not completely surrounded by water, there may not be a balance of forces since the solid may support the entire load with no help from the liquid phase. We have a theoretical framework which now must be converted to something physically measurable. We follow the framework of Terzaghi [40], and define the excess pressure the solid phase supports beyond the fluid pressure $p^s - p^l$, i.e. the total pressure on the solid phase minus the pressure due to the fluid phase. Calculating the total stress we get the Terzaghi stress principal:

$$\mathbf{t} = \varepsilon^s \mathbf{t}^s + \varepsilon^l \mathbf{t}^l \quad (61)$$

$$= -(\varepsilon^l p^l + \varepsilon^s p^s) \mathbf{I} + \varepsilon^s \mathbf{t}_e^s \quad (62)$$

$$= -p \mathbf{I} + (\mathbf{t}_e^s)_{\text{Terzaghi}} \quad (63)$$

where $p = p^l$ and

$$(\mathbf{t}_e^s)_{\text{Terzaghi}} = \varepsilon^s \mathbf{t}_e^s - \varepsilon^s (p^s - p^l) \mathbf{I} \quad (64)$$

which can be measured directly by draining the fluid so that $p^l = 0$. Assuming the same constitutive equations holds for $(\mathbf{t}_e^s)_{\text{Terzaghi}}$ when the media is dry or wet, the constitutive equation for $(\mathbf{t}_e^s)_{\text{Terzaghi}}$ can be determined and used in (63).

Consider an even simpler case in which sandstone is completely dry so that the pressure of the fluid (air) is atmospheric pressure which we define to be zero. In this case, sandstone supports the entire load and the constitutive equation for the stress tensor is

$$\text{modified } \mathbf{t} = \varepsilon^s \mathbf{t}^s = -\varepsilon^s p^s \mathbf{I} + \varepsilon^s \mathbf{t}_e^s = -\varepsilon^s \pi^s - \varepsilon^s \bar{p}_{\text{eq}}^s + \varepsilon^s \eta \varepsilon^l + \varepsilon^s \mathbf{t}_e^s \quad (65)$$

where recall that the trace of \mathbf{t}_e^s is zero. Thus the macroscale stress tensor is, in general, viscoelastic. Note that even if the solid phase (without any voids) is linearly elastic, the presence of voids could produce a viscoelastic media. The larger the coefficient η is, the more resistant to changing the volume fraction, and π^s represents pressure due to configurational changes (since by its thermodynamic definition it is evaluated keeping the density fixed). Thus in this setting it accounts for settling, or re-arrangement of the links making up the solid phase.

An example of a **two-phase swelling porous medium with a non-interacting solid phase** is a well-ordered montmorillonite clay. Montmorillonite clay consists of clay minerals, which are in the shape of very thin

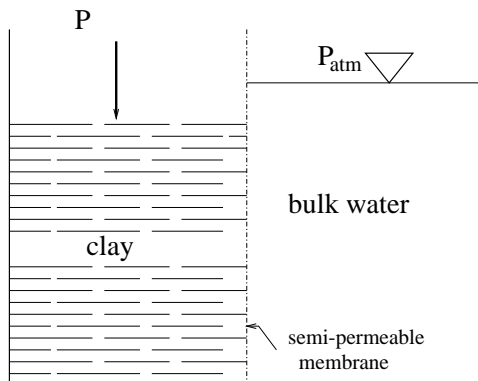


Figure 2: Osmotic swelling pressure experiment.

plates with high surface-area to volume ratios. The swelling of clay is due to electro-chemical forces which cause water to bond with the clay minerals. The water in the near-vicinity of clay minerals, or vicinal water, has thermodynamic properties which may differ significantly from the thermodynamic properties of bulk-phase water. These properties vary depending upon its proximity to the clay minerals. In a well ordered clay sample in which the platelets are parallel, the platelets themselves do not interact. Further, the behavior of the water is highly dependent on the water content, so that the liquid volume fraction is an extremely important variable.

Consider the osmotic swelling experiment in which a well-ordered clay sample is placed in a container in which one side is a semi-permeable membrane which allows water to pass through but not the clay mineral (see Figure 2). The clay sample is loaded on top with pressure P and measurements are taken of the pressure applied and the depression of the clay sample at equilibrium. As in the previous material, because of the interdependence of the solid phase strain, density, and volume fraction, we eliminate one of the components of strain as an independent variable, and assume the effective and hydration stress tensors have zero trace. For the experiment depicted in Figure 2, strain is negligible, so that the effective and hydration stress tensors are zero for this experiment.

The governing equations of interest are

$$\text{omit } \bar{p}^l = \bar{p}^s \quad (66)$$

$$\mathbf{t}^s = -p^s \mathbf{I} \quad (67)$$

$$\mathbf{t}^l = -p^l \mathbf{I} \quad (68)$$

$$p^\alpha = \bar{p}^\alpha + \pi^\alpha \quad \alpha = l, s. \quad (69)$$

The first question of concern is, what is P ? Is it p^l , $\varepsilon^l p^l + \varepsilon^s p^s$, \bar{p}^l or $\varepsilon^l \bar{p}^l + \varepsilon^s \bar{p}^s$? We know that we must have a balance of forces at equilibrium, so the overburden load is balanced by $\mathbf{t} \cdot \mathbf{n}$ where \mathbf{t} is the total stress tensor of the medium and \mathbf{n} is the upward pointing unit normal vector. However, we know from summing the conservation of linear momentum (7) over $\alpha = l, s$, that

$$\mathbf{t} = \varepsilon^l \mathbf{t}^l + \varepsilon^s \mathbf{t}^s = -(\varepsilon^l p^l + \varepsilon^s p^s) \mathbf{I}. \quad (70)$$

Additionally, because the clay is well-layered there is a balance of forces between phases, i.e.

$$\mathbf{t}^l \cdot \mathbf{n} = \mathbf{t}^s \cdot \mathbf{n} \quad \text{or} \quad p^l = p^s, \quad (71)$$

where \mathbf{n} is the unit normal vector from the surface of the clay mineral. We note here that equation (71) does not hold for a porous medium in which the solid phase is connected. In that case the solid matrix can support a pressure independently of the fluid phase because the forces in the solid phase are not necessarily balanced by the forces in the liquid phase. Combining (70) and (71) we have

$$P = p^l = p^s, \quad (72)$$

so that the physical force in the fluid and the solid phase is the *classical pressure*.

In the osmotic experiment, the volume fraction is changed by changing the overburden pressure, P , while keeping the chemical potential of the liquid phase constant. The chemical potential (per unit mass of the liquid phase) is the Gibbs free energy:

$$G^l = \sum_{j=1}^N C^{lj} \mu^{lj} = A^l + \frac{p^l}{\rho^l}, \quad (73)$$

where $\mu^{\alpha j}$ is the chemical potential and is given by

$$\mu^{\alpha j} = \left. \frac{\partial A_T^\alpha}{\partial M^{\alpha j}} \right|_{V^\alpha, T, \dots} = \left. \frac{\partial(\varepsilon^\alpha \rho^\alpha A^\alpha)}{\partial(\varepsilon^\alpha \rho^{\alpha j})} \right|_{\varepsilon^\alpha, T, \dots} = A^\alpha + \rho^\alpha \left. \frac{\partial A^\alpha}{\partial \rho^{\alpha j}} \right|_{\varepsilon^\alpha, T, \dots}. \quad (74)$$

Thus the osmotic experiment measures

$$\left. \frac{\partial p^l}{\partial \varepsilon^l} \right|_{G^l}. \quad (75)$$

We want to take advantage of this commonly performed experiment [33, 34] to gain some insight about the different liquid pressures.

We now show how to perform a transformation from the Helmholtz potential to the Gibbs free energy, with the goal of relating (75) back to one of our thermodynamically defined pressures. Following the argument used to derive (43), (73) yields

$$\begin{aligned}
DG^l &= \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\rho^l} d\varepsilon^l + \left. \frac{\partial A^l}{\partial \rho^l} \right|_{\varepsilon^l} d\rho^l + \frac{dp^l}{\rho^l} - \frac{p^l}{(\rho^l)^2} d\rho^l = \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\rho^l} d\varepsilon^l + \frac{dp^l}{\rho^l} \\
&= \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^l} d\varepsilon^l + \left. \frac{\partial \bar{A}^l}{\partial (\varepsilon^l \rho^l)} \right|_{\varepsilon^l} (\varepsilon^l d\rho^l + \rho^l d\varepsilon^l) + \frac{1}{\rho^l} dp^l - \frac{p^l}{(\rho^l)^2} d\rho^l \\
&= \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^l} d\varepsilon^l + \left. \frac{\rho^l}{\varepsilon^l} \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l} d\varepsilon^l + \frac{1}{\rho^l} dp^l. \tag{76}
\end{aligned}$$

Taking the partial derivative of (76) with respect to ε^l while holding p^l fixed yields

$$\left. \frac{\partial G^l}{\partial \varepsilon^l} \right|_{p^l, T} = \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\rho^l, T} = \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^l, T} + \frac{\rho^l}{\varepsilon^l} \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l, T}. \tag{77}$$

Recalling the thermodynamic definitions of pressures, (27), (29), and (44) we see that (77) yields

$$\left. \frac{\partial G^l}{\partial \varepsilon^l} \right|_{p^l, T} = \frac{1}{\varepsilon^l \rho^l} \pi^l = -\frac{1}{\varepsilon^l \rho^l} \bar{p}^l + \frac{1}{\varepsilon^l \rho^l} p^l, \tag{78}$$

where the second equality is just the fundamental relationship between the three thermodynamically defined pressures, (47). Similarly, if we take the partial of (76) with respect to p^l holding ε^l constant, we find that

$$\left. \frac{\partial G^l}{\partial p^l} \right|_{\varepsilon^l, T} = \frac{1}{\rho^l}, \tag{79}$$

which states that the classical pressure and density are dual variables. Further, we also have

$$\left. \frac{\partial p^l}{\partial \varepsilon^l} \right|_{G^l} = -\frac{\left. \frac{\partial G^l}{\partial \varepsilon^l} \right|_{p^l}}{\left. \frac{\partial G^l}{\partial p^l} \right|_{\varepsilon^l}}, \tag{80}$$

see e.g., [16] Appendix A. Using (77) and (79) in (80) we arrive at

$$\pi^l = -\varepsilon^l \left. \frac{\partial p^l}{\partial \varepsilon^l} \right|_{G^l}, \quad (81)$$

which holds for this experiment. If we plot $p^l = p^l(\varepsilon^l)$ (always at equilibrium) and approximate the partial derivative with a difference quotient, we obtain

$$\pi^l(\varepsilon_{new}^l) \approx -\varepsilon_{new}^l \frac{p^l(\varepsilon_{new}^l) - p^l(\varepsilon_{old}^l)}{\varepsilon_{new}^l - \varepsilon_{old}^l}. \quad (82)$$

If we assume that the swelling potential is not a function of variables which are necessarily zero at equilibrium (e.g. $\mathbf{v}^{l,s}$, ∇T), then this relationship holds at equilibrium and non-equilibrium, i.e. we have an *equation of state*.

Note that the swelling potential is different from what is known as the *swelling pressure*, which is defined to be the difference between the overburden pressure and the atmospheric pressure, $P - p_{atm}$. This latter quantity depends upon the pressure outside the clay mixture system, and therefore cannot (by definition) be an equation of state.

To determine the behavior of the liquid thermodynamic potential, consider the following system of equations for which we would like to solve for P in terms of the volume fraction of the liquid phase, ε^l :

$$P = p^l, \quad p^l = p^s \quad (83)$$

$$p^l = \bar{p}^l + \pi^l, \quad (\text{omit } \bar{p}^l = \bar{p}^s) \quad (84)$$

$$\pi^l = -\varepsilon^l \left. \frac{\partial p^l}{\partial \varepsilon^l} \right|_{G^l}. \quad (85)$$

To close the system we make the additional assumption that

$$|\bar{p}^l| \ll |\pi^l|, \quad (86)$$

i.e. that the volume fraction is changing primarily due to the volume of water changing rather than density (of either the fluid or solid) changing. This assumption can be experimentally checked by using (82). Using this assumption and combining (83) with (84) we have

$$P = p^l \approx \pi^l. \quad (87)$$

Equation (87) implies that the swelling potential is non-negative, $\pi^l \geq 0$, which is why it is defined without the negative sign, (see equation (46)) as

opposed to the definition of the thermodynamic pressure, \bar{p}^l , (see equation (27)). Thus the swelling potential acts as a tensile force, resisting compression.

By combining (83), (85), and (87) we get

$$p^l = -\varepsilon^l \frac{\partial p^l}{\partial \varepsilon^l}. \quad (88)$$

In order to take advantage of the fact that the solid surface area does not change, we change variables from volume fraction to vicinal fluid thickness. Let λ^s and λ^l be the average thicknesses of the clay mineral and vicinal water between two clay platelets, respectively. Then, following [2], we have

$$\varepsilon^l = \frac{\lambda^l}{\lambda^l + \lambda^s}. \quad (89)$$

Assuming that $\lambda^l \gg \lambda^s$, (88) is approximated by

$$\frac{dp^l}{p^l} = -\frac{\lambda^s}{(\lambda^l)^2} d\lambda^l \quad (90)$$

and solving this differential equation yields

$$p^l = C e^{\frac{\lambda^s}{\lambda^l}}, \quad (91)$$

which is exactly the empirical relationship obtained by Low in [32]. The constant C is obtained by using the condition that when λ^l is maximum the overburden pressure, p^l , is equal to the atmospheric pressure, so $C = P_{atm} e^{-\frac{\lambda^s}{\lambda_m^l}}$, where the subscript m denotes the maximum value of that variable. We now want to solve for π^l in terms of λ^s and λ^l , where λ^s is constant. Starting with equation (81) and performing a change of variables from ε^l to λ^l we find that

$$\pi^l = C \frac{\lambda^l + \lambda^s}{\lambda^l} e^{\frac{\lambda^s}{\lambda^l}}, \quad (92)$$

so that we now have explicit expressions for both p^l and π^l in terms of λ^l .

So far we have been operating under the assumption that $\lambda^l \gg \lambda^s$. If instead we choose not to neglect λ^s , solve exactly for p^l and proceed as we have in the above discussion, we recover assumption (87) ($p^l = \pi^l$) so that our system is consistent.

Now consider a second experiment involving swelling porous media, termed the unjacketed test in civil engineering literature. Place a well-ordered clay sample in a container and allow no water to escape. Applying an overburden pressure we can again measure pressure versus depression. In this experiment, the mass remains unchanged, but the volume changes. In thermodynamic language, we are changing the total energy with respect to total volume keeping the total mass fixed:

$$P = - \left. \frac{\partial A_T}{\partial V_T} \right|_M = - \left. \frac{\partial A_T^l}{\partial V_T} \right|_M - \left. \frac{\partial A_T^s}{\partial V_T} \right|_M \quad (93)$$

$$= - \left. \frac{\partial A_T^l}{\partial V_T^l} \right|_{M^l} \frac{\partial V_T^l}{\partial V_T} - \left. \frac{\partial A_T^s}{\partial V_T^s} \right|_{M^s} \frac{\partial V_T^s}{\partial V_T} \quad (94)$$

where $A_T = A_T^l + A_T^s$ and $M_T = M_T^l + M_T^s$, and where the second equality follows from the first if we assume that the energy of each phase is a function of the volume and mass of its phase only. Switching to intensive variables (formally dividing through by the REV) we obtain

$$P = - \left. \frac{\partial(\varepsilon^l \rho^l A^l)}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^l} \varepsilon^l - \left. \frac{\partial(\varepsilon^s \rho^s A^s)}{\partial \varepsilon^s} \right|_{\varepsilon^s \rho^s} \varepsilon^s \quad (95)$$

$$= \varepsilon^l \bar{p}^l + \varepsilon^s \bar{p}^s$$

$$\text{omit} = \bar{p}^l \quad (96)$$

To close the system, assume that $\pi^l = \pi^s$ at equilibrium, i.e. that the affects the amount of liquid has on the solid energy is the same as the amount of solid on the liquid energy. Equivalently, because $p^s = p^l$, this implies that $\varepsilon^l p^l = \varepsilon^s p^s$. Note that this would not be an appropriate assumption at non-equilibrium nor in the case where the solid phase can support its own load. With this assumption we have, contrary to the osmotic experiment, that the change in volume fraction is primarily due to a change in the density instead of the liquid content:

$$P = p^l = \bar{p}^l + \pi^l \quad (97)$$

$$\approx \bar{p}^l, \quad (98)$$

where the approximation comes from the assumption that the energy of each phase is a function of the volume and mass of its phase only, or equivalently, that the change in volume fraction is primarily due to changing the density

instead of the liquid content. Thus we have two experiments, one which measures the swelling potential, π^l , and one which measures the thermodynamic pressure, \bar{p}^l .

We could consider the osmotic experiment in the dynamic case to approximate the coefficient η in (37). However for a swelling porous medium, with no entanglement, the swelling occurs so quickly, that η is essentially zero, and the rate of change of the volume fraction is essentially infinity.

Lastly, consider a **two-phase swelling porous medium with an interacting solid phase** such as a polymer or a non-well-ordered clay system. In this system the solid phase interacts with itself so that it may support compression (in the case of clay) or tension (in the case of polymers). In a swelling polymer, the solid phase is entangled, and as liquid is introduced into the system, the medium transitions from a glassy (elastic) state to a visco-elastic state, capable of significant swelling due to the interaction between the liquid and solid phases. Depending upon the polymer matrix, the solid may swell until it dissipates into the liquid (solute) state, or, if the polymer is crosslinked, the swelling is limited by the polymer matrix.

We consider the same setup as in the previous porous materials, in that we eliminate one of the components of strain as an independent variable, and assume the effective and hydration stress tensors have zero traces. Again we assume experiments have no shear strains involved so that the effective and hydration stress tensors are negligible. The governing equations involving pressures are thus:

$$P = \varepsilon^l p^l + \varepsilon^s p^s \quad (99)$$

$$\mathbf{t}^s = -p^s \mathbf{I} \quad \mathbf{t}^l = -p^l \mathbf{I} \quad (100)$$

$$(\bar{p}^l - \bar{p}^s)_{\text{neq}} = (\bar{p}^l - \bar{p}^s)_{\text{eq}} + \eta \varepsilon^l \quad (101)$$

$$p^\alpha = \bar{p}^\alpha + \pi^\alpha \quad \alpha = l, s \quad (102)$$

$$\bar{p}^s = -\varepsilon^s \rho^s \left. \frac{\partial A^s}{\partial \varepsilon^s} \right|_{\varepsilon^s \rho^{sj}} = - \left. \frac{\partial A_T^s}{\partial V^s} \right|_{M^{sj}} \quad (103)$$

$$\pi^s = \varepsilon^s \rho^s \left. \frac{\partial A^s}{\partial \varepsilon^s} \right|_{\rho^{sj}} \quad (104)$$

where P is the overburden pressure. Note that because of entanglement, we no longer have $p^s = p^l$.

Let's consider π^s . In the non-swelling porous media we saw that π^s captured configurational changes. In the swelling porous medium with a non-

interacting solid phase we *argued that assuming $\pi^s = \pi^l$ is valid*. Thus π^s captures pressure due to configurational changes and due to liquid-solid interactions. The thermodynamic pressure, \bar{p}^s , on the other hand, is the pressure resulting from density changes - a microscopic phenomenon.

To measure π^s we follow the non-swelling porous medium case and measure the overburden pressure at zero liquid pressure ($p^l = p_{\text{atm}} = 0$). In general the constitutive equations for this overburden pressure may be a function of volume fraction. The excess pressure is given by $p_{\text{excess}} = p^s - p^l = \pi^s - \pi^l$ where we have used (101) at equilibrium. Just as in the non-swelling media case, we assume the the excess pressure can be measured when the system has zero liquid pressure and that the constitutive equation remains the same with non-zero liquid pressure. Thus at zero liquid pressure $p_{\text{excess}} = p^s - p^l = p^s$ and the applied pressure, P , is equal to $\varepsilon^s p^s = \varepsilon^s p_{\text{excess}}$. Now assuming that π^l can be measured using the reverse osmosis experiment for the same polymer but where the solid phase has the same pressure as the liquid phase (see discussion for swelling porous medium with a non-interacting solid phase), this gives us a measurement for $\pi^s = p_{\text{excess}} + \pi^l$.

The thermodynamic pressure, \bar{p}^s , is what governs the rate at which swelling occurs (see equation (101)). Thermodynamically it measures the change in energy with respect to the solid-phase volume keeping the mass fixed. Practically, it appears it has to be either backed out from p^s and π^s , or approximated by a microscopic constitutive equation for the single solid phase.

The resistance to swelling is governed by the coefficient η , that is, how difficult is it for the unentangling process to occur. In the polymer literature, see e.g. [41], η is termed the *viscosity coefficient for the polymer*, and is in at least one case, found to be experimentally related to volume fraction as $\eta = \eta_0 e^{[-M\varepsilon^l]}$ [41], where M is a constant. Thus the smaller the volume fraction, the bigger the viscosity coefficient and the more difficult it is for the polymer to swell.

We conclude this section with a short discussion on the equation which governs the rate of flow of fluid in a swelling porous medium, the generalized version of Darcy's law, (39). Neglecting temperature, gravity, and second-order effects, (39) becomes:

$$\mathbf{R}^l \cdot \mathbf{v}^{l,s} = -\nabla(\varepsilon^l p^l) + \bar{p}^l \nabla \varepsilon^l \quad (105)$$

where \mathbf{R}^l is the linearization coefficient which may depend upon density and

volume fraction. Using $\bar{p}^l = p^l - \pi^l$, (105) becomes

$$\mathbf{R}^l \cdot \mathbf{v}^{l,s} = -\varepsilon^l \nabla p^l - \pi^l \nabla \varepsilon^l. \quad (106)$$

The first term on the left-hand side is the standard Darcy's law: flow is directly proportional to the gradient in fluid pressure. The last term denotes the effects of swelling, which is nonzero if there is a swelling potential for the liquid phase. If there is a gradient in the volume fraction, even if the fluid pressure is constant, the liquid will flow from regions of high volume fraction to low volume fraction.

5 Discussion

We have compared different choices of independent variables, and by rewriting the results in terms of macroscopic variables and using total differentials we have mathematically derived the relationships among the pressure variables. The 3 pressures considered are the classical pressure, p^α , the thermodynamic pressure, \bar{p}^α , and the swelling potential, π^α . Assuming the hydration and effective stress tensors have negligible spherical components, the following statements may be made.

- The classical pressure, $p^\alpha = -\frac{\partial A^\alpha}{\partial v^\alpha}|_{\varepsilon^\alpha}$, is the change in Helmholtz potential with respect to the specific volume while keeping the volume fraction fixed. Theoretically, this can be accomplished only if the density can be changed, which is not often practical to experimentally measure. Of more practical use is the relationship between the classical pressure and the stress, (31,36). For the fluid phase we have $\mathbf{t}^l = -p^l \mathbf{I} + \boldsymbol{\nu}^l : \mathbf{d}^l$. Thus we see that when \mathbf{d}^l is small compared to p^l , the classical pressure represents the physical force experienced by the phase - see [35] for a short discussion on this approximation. Thus p^l is the quantity that would be measured, hypothetically, by a force transducer at equilibrium. For negligible rate of deformation tensor, \mathbf{d}^l , the overburden pressure is given by

$$-\frac{1}{3} \text{tr} \mathbf{t} = -\frac{1}{3} \text{tr} (\varepsilon^l \mathbf{t}^l + \varepsilon^s \mathbf{t}^s) = \varepsilon^l p^l + \varepsilon^s p^s.$$

If the force on the fluid is equal to the force on the solid phase, which is the case if the solid phase is disconnected and acts only through the fluid, then $p^l = p^s$.

- The thermodynamic pressure, $\bar{p}^\alpha = -\varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \Big|_{\varepsilon^\alpha \rho^\alpha j} = -\frac{\partial A_T^\alpha}{\partial V^\alpha} \Big|_{M^{\alpha j}, T}$ is the change in energy with respect to volume keeping the mass of both phases fixed. (*omit: At equilibrium it is always true that $\bar{p}^s = \bar{p}^l$.*) We can *approximate* \bar{p}^l in an experiment which has non-interaction solid phase and no change in liquid, such as the sealed container experiment discussed in the previous section. In this case, $\bar{p}^s = \bar{p}^l \approx P$, and thus measuring the overburden pressure, P , gives the thermodynamic pressure, see (96). For the solid phase, \bar{p}^s must be determined indirectly from knowledge of the actual spherical part of the solid phase stress tensor and π^s through (47), or approximated knowing how the single phase solid (with no fluid and zero volume fraction) behaves. It is also the thermodynamic pressure which determines the rate at which the medium swells (37):

$$(\bar{p}^l - \bar{p}^s)_{\text{neq}} = (\bar{p}^l - \bar{p}^s)_{\text{eq}} + \eta \varepsilon^l. \quad (107)$$

Thus it is the relative response of each phase to changes in volume which governs swelling rates. The coefficient η is a measure of how resistant the solid phase is to changes in volume fraction. Since η itself may be a function of density and volume fraction, this coefficient may vary dramatically depending on what the volume fraction is.

- The swelling potential, $\pi^\alpha = \varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \Big|_{\rho^\alpha, C^{\alpha j}}$ is the change in energy with respect to volume fraction keeping the density and composition of each phase fixed. For the liquid phase, assuming the liquid density does not change significantly, this can be measured using a reverse osmotic swelling pressure experiment (see the discussion in the previous section related to a two-phase swelling porous medium with a non-interacting solid phase). For the solid phase, this represents the effects of the void-space amount on the solid phase. For a dry porous material (which has negligible interaction with the gas phase), π^s accounts for re-arrangement (changes in volume fraction where the density remains fixed). In a swelling porous material in which the solid phase does not interact, $\pi^s = \pi^l$. In a swelling porous medium with an interacting solid phase, it captures both the mechanical stress (the part of the solid stress where density remains fixed, such as re-arrangement of the solid phase) and the electro-chemical forces between the liquid and solid phase.

As a final note, we mention the effects of charges and electric fields. The HMT has been laid out in a series of two papers, [8, 9], where it can be shown that the above analysis holds exactly, i.e. the mathematical relations remain unchanged when incorporating charges. The only difference is that now each pressure may now be a function of charge density. Examples of constitutive equations which may be used in this case are given in [37].

In this paper we have discussed three thermodynamic quantities, each of which has units of pressure. The relationship between the three pressures is (43):

$$p^\alpha = \bar{p}^\alpha + \pi^\alpha \quad (108)$$

so that the classical (experimentally measurable) pressure is the sum of the thermodynamic pressure and the swelling potential. In the case of a non-swelling medium, in which there is little change in energy due to moisture content (e.g. sandstone), $\pi^l = 0$ and we have $p^l = \bar{p}^l$ so that classical liquid pressure is the same as the thermodynamic pressure. For a dry porous solid phase, \bar{p}^s represents the viscoelastic response of the porous solid, while π^s is the non-dissipative pressure. In a swelling porous medium, π^l represents the electro-chemical interaction between the phases, and π^s is a combination of mechanical stress and the electro-chemical interaction.

Acknowledgments. Thanks to William G. Gray for suggesting the reformulation in terms of variables which can be directly identified with extensive variables.

References

- [1] S. Achanta and J. H. Cushman. Non-Equilibrium swelling and capillary pressure relations for colloidal systems. *Journal of Colloid and Interface Science*, 168:266–268, 1994.
- [2] S. Achanta, J. H. Cushman, and M. R. Okos. On multicomponent, multiphase thermomechanics with interfaces. *International Journal of Engineering Science*, 32(11):1717–1738, 1994.
- [3] J. Bear. *Dynamics of Fluids in Porous Media*. Dover, New York, 1972.
- [4] L. S. Bennethum. *Multiscale, hybrid mixture theory for swelling systems with interfaces*. PhD thesis, Purdue University, West Lafayette, Indiana, 47907, 1994.

- [5] L. S. Bennethum and J. H. Cushman. Multiscale, hybrid mixture theory for swelling systems - I: Balance laws. *International Journal of Engineering Science*, 34(2):125–145, 1996.
- [6] L. S. Bennethum and J. H. Cushman. Multiscale, hybrid mixture theory for swelling systems - II: Constitutive theory. *International Journal of Engineering Science*, 34(2):147–169, 1996.
- [7] L. S. Bennethum and J. H. Cushman. Coupled solvent and heat transport of a mixture of swelling porous particles and fluids: Single time-scale problem. *Transport in Porous Media*, 36(2):211–244, 1999.
- [8] L. S. Bennethum and J. H. Cushman. Multicomponent, multiphase thermodynamics of swelling porous media with electroquasistatics: I. macroscale field equations. *Transport in Porous Media*, 47(3):309–336, 2002.
- [9] L. S. Bennethum and J. H. Cushman. Multicomponent, multiphase thermodynamics of swelling porous media with electroquasistatics: II. constitutive theory. *Transport in Porous Media*, 47(3):337–362, 2002.
- [10] L. S. Bennethum and T. Giorgi. Generalized forchheimer law for two-phase flow based on hybrid mixture theory. *Transport in Porous Media*, 26(3):261–275, 1997.
- [11] L. S. Bennethum, M. A. Murad, and J. H. Cushman. Clarifying mixture theory and the macroscale chemical potential for porous media. *International Journal of Engineering Science*, 34(14):1611–1621, 1996.
- [12] L. S. Bennethum, M. A. Murad, and J. H. Cushman. Modified darcy’s law, terzaghi’s effective stress principle and fick’s law for swelling clay soils. *Computers and Geotechnics*, 20(3/4):245–266, 1997.
- [13] L. S. Bennethum, M. A. Murad, and J. H. Cushman. Macroscale thermodynamics and the chemical potential for swelling porous media. *Transport in Porous Media*, 39(2):187–225, 2000.
- [14] R. M. Bowen. Theory of mixtures. In A. C. Eringen, editor, *Continuum Physics*. Academic Press, Inc., New York, 1976.

- [15] R. M. Bowen. Compressible porous media models by use of the theory of mixtures. *International Journal of Engineering Science*, 20:697–735, 1982.
- [16] H. B. Callen. *Thermodynamics and an Introduction to Thermostatistics*. John Wiley and Sons, New York, 1985.
- [17] B. D. Coleman and W. Noll. The thermodynamics of elastic materials with heat conduction and viscosity. *Archive for Rational Mechanics and Analysis*, 13:167–178, 1963.
- [18] V. de la Cruz, P. N. Sahay, and T. J. T. Spanos. Thermodynamics of porous media. *Proceedings of the Royal Society of London, A. Math.*, 443:247–255, 1993.
- [19] H. Darcy. *Les Fontaines Publiques de la Ville de Dijon*. Dalmont, Paris, 1856.
- [20] A. C. Eringen. *Mechanics of Continua*. John Wiley and Sons, New York, 1967.
- [21] W. G. Gray. Thermodynamics and constitutive theory for multiphase porous-media flow considering internal geometric constraints. *Advances in Water Resources*, 22(5):521–547, 1999.
- [22] W. G. Gray and S. M. Hassanizadeh. Macroscale continuum mechanics for multiphase porous-media flow including phases, interfaces, common lines, and common points. *Advances in Water Resources*, 21(4):261–281, 1998.
- [23] S. M. Hassanizadeh. Derivation of basic equations of mass transport in porous media, Part 1. Macroscopic balance laws. *Advances in Water Resources*, 9:196–206, 1986.
- [24] S. M. Hassanizadeh. Derivation of basic equations of mass transport in porous media, Part 2. Generalized Darcy’s and Fick’s laws. *Advances in Water Resources*, 9:207–222, 1986.
- [25] S. M. Hassanizadeh and W. G. Gray. General conservation equations for multiphase systems: 1. Averaging procedure. *Advances in Water Resources*, 2:131–144, 1979.

- [26] S. M. Hassanizadeh and W. G. Gray. General conservation equations for multiphase systems: 2. Mass, momenta, energy, and entropy equations. *Advances in Water Resources*, 2:191–208, 1979.
- [27] S. M. Hassanizadeh and W. G. Gray. General conservation equations for multiphase systems: 3. Constitutive theory for porous media. *Advances in Water Resources*, 3:25–40, 1980.
- [28] S. M. Hassanizadeh and W. G. Gray. High velocity flow in porous media. *Transport in Porous Media*, 2:521–531, 1987.
- [29] S. M. Hassanizadeh and W. G. Gray. Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries. *Advances in Water Resources*, 13:169–186, 1990.
- [30] S. M. Hassanizadeh and W. G. Gray. Thermodynamic basis of capillary pressure in porous media. *Water Resources Research*, 29(10):3389–3405, 1993.
- [31] S. M. Hassanizadeh and W. G. Gray. Toward an improved description of the physics of two-phase flow. *Advances in Water Resources*, 16:53–67, 1993.
- [32] P. F. Low. The swelling of clay, II. Montmorillonites-water systems. *Soil Science Society of America Journal*, 44:667–676, 1980.
- [33] P. F. Low. Structural component of the swelling pressure of clays. *Langmuir*, 3:18–25, 1987.
- [34] P. F. Low. The clay/water interface and its role in the environment . In *Progress in Colloid & Polymer Science*, volume 40, pages 500–505, 1994.
- [35] L. E. Malvern. *Introduction to the Mechanics of a Continuous Medium*. Prentice-Hall, Englewood Cliffs, NJ, 1969.
- [36] M. A. Murad, L. S. Bennethum, and J. H. Cushman. A multi-scale theory of swelling porous media: I. Application to one-dimensional consolidation. *Transport in Porous Media*, 19:93–122, 1995.
- [37] S. Nemat-Nasser. Micromechanics of actuation of ionic polymer-metal composites. *Journal of Applied Physics*, 92(5):2899–2915, 2002.

- [38] S. R. Pride, A. F. Gangi, and F. D. Morgan. Deriving the equations of motion for porous isotropic media. *The Journal of the Acoustical Society of America*, 92(6):3278–3290, 1992.
- [39] T. J. T. Spanos. *The Thermodynamics of Porous Media*. Chapman and Hall/CRC Press, New York, 2001.
- [40] K. Terzaghi. *Theoretical soil mechanics*. John Wiley and Sons, New York, 1943.
- [41] N. L. Thomas and A. H. Windle. A theory of Case II diffusion. *Polymer*, 23:529–542, 1982.

Appendix A. Definition of Macroscopic Bulk Variables

The relationships between the macroscopic constituent variables and their bulk counterparts follow:

$$\rho^\alpha = \sum_{j=1}^N \rho^{\alpha j}, \quad (\text{A.1})$$

$$C^{\alpha j} = \frac{\rho^{\alpha j}}{\rho^\alpha}, \quad (\text{A.2})$$

$$\mathbf{v}^\alpha = \sum_{j=1}^N C^{\alpha j} \mathbf{v}^{\alpha j}, \quad (\text{A.3})$$

$$\hat{\mathbf{e}}_\beta^\alpha = \sum_{j=1}^N C^{\alpha j} \hat{\mathbf{e}}_\beta^{\alpha j}, \quad (\text{A.4})$$

$$\mathbf{t}^\alpha = \sum_{j=1}^N [\mathbf{t}^{\alpha j} - \rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha} \mathbf{v}^{\alpha j, \alpha}], \quad (\text{A.5})$$

$$\mathbf{g}^\alpha = \sum_{j=1}^N C^{\alpha j} \mathbf{g}^{\alpha j}, \quad (\text{A.6})$$

$$\hat{\mathbf{T}}_\beta^\alpha = \sum_{j=1}^N C^{\alpha j} \left(\hat{\mathbf{T}}_\beta^{\alpha j} + \hat{\mathbf{e}}_\beta^{\alpha j} \mathbf{v}^{\alpha j, \alpha} \right) \quad (\text{A.7})$$

$$e^\alpha = \sum_{j=1}^N C^{\alpha j} \left(e^{\alpha j} + \frac{1}{2} \mathbf{v}^{\alpha j, \alpha} \cdot \mathbf{v}^{\alpha j, \alpha} \right), \quad (\text{A.8})$$

$$\mathbf{q}^\alpha = \sum_{j=1}^N \left[\mathbf{q}^{\alpha_j} + \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} - \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} \left(e^{\alpha_j} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) \right], \quad (\text{A.9})$$

$$h^\alpha = \sum_{j=1}^N C^{\alpha_j} (h^{\alpha_j} + \mathbf{g}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha}), \quad (\text{A.10})$$

$$\hat{Q}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} \left[\hat{Q}_\beta^{\alpha_j} + \hat{\mathbf{T}}_\beta^{\alpha_j} \cdot \mathbf{v}^{\alpha_j, \alpha} + \hat{e}_\beta^{\alpha_j} \left(e^{\alpha_j, \alpha} + \frac{1}{2} (\mathbf{v}^{\alpha_j, \alpha})^2 \right) \right], \quad (\text{A.11})$$

$$\eta^\alpha = \sum_{j=1}^N C^{\alpha_j} \eta^{\alpha_j}, \quad (\text{A.12})$$

$$\phi^\alpha = \sum_{j=1}^N (\phi^{\alpha_j} - \rho^{\alpha_j} \eta^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha}), \quad (\text{A.13})$$

$$b^\alpha = \sum_{j=1}^N C^{\alpha_j} b^{\alpha_j}, \quad (\text{A.14})$$

$$\hat{\Phi}_\beta^\alpha = \sum_{j=1}^N C^{\alpha_j} \left(\hat{\Phi}_\beta^{\alpha_j} + \hat{e}_\beta^{\alpha_j} \eta^{\alpha_j, \alpha} \right), \quad (\text{A.15})$$

$$\hat{\Lambda}^\alpha = \sum_{j=1}^N C^{\alpha_j} \hat{\Lambda}^{\alpha_j}, \quad (\text{A.16})$$

$$(\text{A.17})$$

Appendix B. Entropy Inequality

The entropy inequality in the final form used for exploitation is given here. The inequality is obtained by taking (19) and using the chain rule assuming the Helmholtz free energy has the functional dependence of 26). Further, we re-write the two terms in the inequality involving $\mathbf{v}^{\alpha_j, \alpha}$ because $\sum_{j=1}^N \rho^{\alpha_j} \mathbf{v}^{\alpha_j, \alpha} = \mathbf{0}$, so that $\mathbf{v}^{\alpha_j, \alpha}$ are not independent for $j = 1, \dots, N$. Thus, in order to exploit the entropy inequality, we re-write these terms using

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

where $\mathbf{G}^{\alpha j}$ is a second order tensor representing the coefficient of $\nabla \mathbf{v}^{\alpha j, \alpha}$ in (B.2), and $\mathbf{F}^{\alpha j}$ represents the vector coefficient of $\mathbf{v}^{\alpha j, \alpha}$. This results in

$$\begin{aligned}
& \sum_{j=1}^N \nabla \mathbf{v}^{\alpha j, \alpha} : [\varepsilon^\alpha \rho^{\alpha j} \mu^{\alpha j} \mathbf{I} - \varepsilon^\alpha \rho^{\alpha j} A^{\alpha j} \mathbf{I} - \varepsilon^\alpha \rho^{\alpha j} A^\alpha \mathbf{I} + \varepsilon^\alpha \mathbf{t}^{\alpha j}] \\
& + \sum_{j=1}^N \mathbf{v}^{\alpha j, \alpha} \cdot [\mu^{\alpha j} \nabla(\varepsilon^\alpha \rho^{\alpha j}) - A^{\alpha j} \nabla(\varepsilon^\alpha \rho^{\alpha j}) - A^\alpha \nabla(\varepsilon^\alpha \rho^{\alpha j}) \\
& \quad - \varepsilon^\alpha \rho^{\alpha j} (\widehat{\mathbf{i}}^{\alpha j} + \widehat{\mathbf{T}}_\beta^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \nabla A^{\alpha j}] \\
& = \sum_{j=1}^{N-1} \nabla \mathbf{v}^{\alpha j, \alpha} : \left[\varepsilon^\alpha \rho^{\alpha j} (\mu^{\alpha j} - \mu^{\alpha N}) \mathbf{I} - \varepsilon^\alpha \rho^{\alpha j} (A^{\alpha j} - A^{\alpha N}) \mathbf{I} + \varepsilon^\alpha (\mathbf{t}^{\alpha j} - \frac{\rho^{\alpha j}}{\rho^{\alpha N}} \mathbf{t}^{\alpha N}) \right] \\
& + \sum_{j=1}^{N-1} \mathbf{v}^{\alpha j, \alpha} \cdot \left[-\varepsilon^\alpha \rho^{\alpha j} (\widehat{\mathbf{i}}^{\alpha j} + \widehat{\mathbf{T}}_\beta^{\alpha j}) + \varepsilon^\alpha \rho^{\alpha j} (\widehat{\mathbf{i}}^{\alpha N} + \widehat{\mathbf{T}}_\beta^{\alpha N}) + (\mu^{\alpha j} - \mu^{\alpha N}) \nabla(\varepsilon^\alpha \rho^{\alpha j}) \right. \\
& \quad \left. - \nabla[\varepsilon^\alpha \rho^{\alpha j} (A^{\alpha j} - A^{\alpha N})] - \varepsilon^\alpha \mathbf{t}^{\alpha N} : \nabla \left(\frac{\rho^{\alpha j}}{\rho^{\alpha N}} \right) \right] \quad (\text{B.1})
\end{aligned}$$

so that the coefficients are indeed independent.

Using the chain rule to expand $\frac{D^\alpha A^\alpha}{Dt}$ in terms of time derivatives of the independent variables and re-arranging variables, we get the entropy inequality in the following form:

$$\begin{aligned}
\sum_{\alpha=l,s} \varepsilon^\alpha \rho^\alpha T \widehat{\Lambda}^\alpha &= \sum_{\alpha=l,s} \sum_{j=1}^N \frac{D^s(\varepsilon^\alpha \rho^{\alpha j})}{Dt} \left[-\varepsilon^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial(\varepsilon^\alpha \rho^{\alpha j})} + A^{\alpha j} + \lambda^{\alpha j} \right] \\
& + \dot{\varepsilon}^l \left[-\varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} - \varepsilon^s \rho^s \frac{\partial A^s}{\partial \varepsilon^l} \right] \\
& - \dot{T} \left[\sum_{\alpha} \varepsilon^\alpha \rho^\alpha \left(\frac{\partial A^\alpha}{\partial T} + \eta^\alpha \right) \right] \\
& + \mathbf{v}^{l,s} \cdot \left[-\varepsilon^l \rho^l \nabla T \left(\frac{\partial A^l}{\partial T} + \eta^l \right) + \sum_{j=1}^N A^{lj} \nabla(\varepsilon^l \rho^{lj}) - \varepsilon^l \rho^l \widehat{\mathbf{T}}_s^l + \sum_{j=1}^N \lambda^{lj} \nabla(\varepsilon^l \rho^{lj}) \right. \\
& \quad \left. - \varepsilon^l \rho^l \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l - \sum_{j=1}^N \varepsilon^l \rho^l \frac{\partial A^l}{\partial(\varepsilon^l \rho^{lj})} \nabla(\varepsilon^l \rho^{lj}) \right] \\
& + \sum_{\alpha=l,s} \frac{\varepsilon^\alpha}{T} \nabla T \cdot \left[\mathbf{q}^\alpha + \sum_{j=1}^N \left(\rho^{\alpha j} \mathbf{v}^{\alpha j, \alpha} (A^{\alpha j} + \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2) - \mathbf{t}^{\alpha j} \cdot \mathbf{v}^{\alpha j, \alpha} \right) \right]
\end{aligned}$$

$$\begin{aligned}
& + \varepsilon^l \mathbf{d}^l : \left[\mathbf{t}^l + \sum_{j=1}^N \rho^{lj} \mathbf{v}^{lj,l} \mathbf{v}^{lj,l} + \sum_{j=1}^N \rho^{lj} (\lambda^{lj} + A^{lj}) \mathbf{I} \right] \\
& + \varepsilon^s \mathbf{d}^s : \left[\mathbf{t}^s + \sum_{j=1}^N \rho^{sj} \mathbf{v}^{sj,s} \mathbf{v}^{sj,s} + \sum_{j=1}^N \rho^{sj} (\lambda^{sj} + A^{sj}) \mathbf{I} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \nabla \mathbf{v}^{\alpha j, \alpha} : \left[\varepsilon^\alpha \rho^{\alpha j} \lambda^{\alpha j} \mathbf{I} + \varepsilon^\alpha \mathbf{t}^{\alpha j} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{v}^{\alpha j, \alpha} \cdot \left[\lambda^{\alpha j} \nabla (\varepsilon^\alpha \rho^{\alpha j}) - \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{i}}^{\alpha j} - \sum_{\beta \neq \alpha} \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{T}}_\beta^{\alpha j} - \varepsilon^\alpha \rho^{\alpha j} \nabla A^{\alpha j} \right] \\
& + \sum_{j=1}^N \varepsilon^l \rho^{lj} \hat{\mathbf{e}}_s^{lj} \left[-A^{lj} + A^{sj} - \lambda^{lj} + \lambda^{sj} - A^l + A^s \right. \\
& \quad \left. - \frac{1}{2} (\mathbf{v}^{lj,l})^2 + \frac{1}{2} (\mathbf{v}^{sj,s})^2 - \frac{1}{2} (\mathbf{v}^{l,s})^2 \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^N \varepsilon^\alpha \rho^{\alpha j} \hat{\mathbf{r}}^{\alpha j} \left[-A^{\alpha j} - \frac{1}{2} (\mathbf{v}^{\alpha j, \alpha})^2 - \lambda^{\alpha j} \right] \geq 0. \tag{B.2}
\end{aligned}$$

The chemical potential is defined to be the change in total Helmholtz potential with respect to mass of the constituent while keeping all other independent variables fixed:

$$\mu^{\alpha j} = \left. \frac{\partial A_T^\alpha}{\partial M^{\alpha j}} \right|_{V^\alpha, T, \dots} = \left. \frac{\partial (\varepsilon^\alpha \rho^\alpha A^\alpha)}{\partial (\varepsilon^\alpha \rho^{\alpha j})} \right|_{\varepsilon^\alpha, T, \dots} \tag{B.3}$$

The coefficient of $\frac{D^s(\varepsilon^\alpha \rho^{\alpha j})}{Dt}$ tells us that near equilibrium:

$$\begin{aligned}
\lambda^{\alpha j} &= \varepsilon^\alpha \rho^\alpha \left. \frac{\partial A^\alpha}{\partial (\varepsilon^\alpha \rho^{\alpha j})} \right|_{\varepsilon^\alpha} - A^{\alpha j} = \rho^\alpha \left. \frac{\partial A^\alpha}{\partial \rho^{\alpha j}} \right|_{\varepsilon^\alpha} - A^{\alpha j} \\
&= \mu^{\alpha j} - A^{\alpha j} - A^\alpha \tag{B.4}
\end{aligned}$$

Equation (B.4) gives us the relationship between the Lagrange multipliers used to enforce the continuity equations, $\lambda^{\alpha j}$, and the chemical potentials and Helmholtz free energies. It is this expression which is used to eliminate the Lagrange multiplier throughout.

Appendix C. Nomenclature

In general, a subscript Greek letter indicates a macroscale quantity from that phase. Superscript minuscules indicate the constituent, so that, e.g. \mathbf{v}_α^j

is the macroscopic velocity of constituent j in the α -phase. A carrot over the symbol, $\hat{}$, is used to emphasize that the quantity represents a transfer from either another phase or from other constituents.

- A^{α_j} Helmholtz free energy density of j th constituent in α -phase
= $e^{\alpha_j} - T\eta^{\alpha_j}$, [energy α_j / mass α_j].
- A^α Helmholtz free energy density of α -phase, [energy α / mass α].
- \overline{A}^α Helmholtz free energy density of α -phase; overline is used in Section 3 only to emphasize a different set of independent variables from those of A^α at the onset. [energy α / mass α].
- A_T^α total (extensive) Helmholtz free energy density of α -phase, [energy of α -phase]
- b^{α_j} external entropy source for j th constituent in α -phase, [entropy α_j /(mass α_j -time)]
- C^{α_j} mass concentration = $\rho^{\alpha_j}/\rho^\alpha$, [-]
- \mathbf{d}^{α_j} symmetric part of $\nabla \mathbf{v}^{\alpha_j}$ [1/time]
- e^{α_j} internal energy, [energy α_j /mass α_j]
- $\hat{e}_\beta^{\alpha_j}$ rate of mass exchange from β -phase to α -phase of j th constituent, [1/time]
- \mathbf{E}^s macroscale strain tensor of solid phase, (23)
- \mathbf{g} gravity, [length/time²]
- G^α Gibbs free energy [energy of α -phase/mass α]
- h^{α_j} external supply of energy, [energy of α_j /(mass α_j -time)]
- $\hat{\mathbf{i}}^{\alpha_j}$ gain of momentum of constituent j of phase α due to mechanical interactions with other species within the same phase, [length/time²]
- p^α classical pressure, [force/length²]
- \bar{p}^α thermodynamic pressure, [force/length²]
- \mathbf{q}^{α_j} heat flux of constituent j in α -phase, [energy α_j /(length²-time)]
- $\hat{Q}_\beta^{\alpha_j}$ gain of energy of constituent j in phase α due to non-chemical, non-mechanical transfer with the other phase, [α_j energy / (mass α_j -time)]
- \hat{Q}^{α_j} energy gained by constituent j in phase α due to non-chemical, non-mechanical interactions with other constituents within phase α [energy of α_j /(mass α_j -time)]
- \hat{r}^{α_j} rate of j th constituent mass gained within phase α , [1/time]

\mathbf{R}^l	resistivity tensor, a linearization coefficient, see (38)
\mathbf{t}^{α_j}	stress tensor of j th constituent in α -phase, [force/length ²]
t	time
T	temperature
$\widehat{\mathbf{T}}_{\beta}^{\alpha_j}$	gain of momentum of phase α due to mechanical interactions with the other phase [length/time ²]
v^{α}	specific volume, [volume α /mass α]
\mathbf{v}^{α_j}	mass averaged velocity of j th constituent in phase α , [length/time]
\mathbf{v}^{α}	velocity of phase $\alpha = \sum_{j=1}^N C^{\alpha_j} \mathbf{v}^{\alpha_j}$, [length/time]
$\mathbf{v}^{\alpha_j, \alpha}$	diffusive velocity, $\mathbf{v}^{\alpha_j} - \mathbf{v}^{\alpha}$
V^{α}	total volume of phase α , [volume α]
V	total volume = $V^s + V^l$, [volume]
$\mathbf{w}_{\alpha\beta}^j$	velocity of j th constituent in the interface [length/time]
\mathbf{x}	Eulerian coordinates
γ_{α}	indicator function for phase α
ε^{α}	volume fraction of α -phase in Representative Elementary Volume (REV) = $ \delta V_{\alpha} / \delta V $
η^{α_j}	entropy density, [α_j entropy/(mass α_j -time)]
$\widehat{\eta}^{\alpha_j}$	entropy gain of j th constituent in α -phase due to non-mass transfer interactions with other constituents within phase α [α_j entropy/(mass α_j -time)]
λ^{α_j}	Lagrange multiplier for continuity equation of j th constituent in phase α
λ^{α}	thickness of layer α in the swelling porous medium with a non-interacting solid phase.
$\widehat{\Lambda}^{\alpha_j}$	entropy production density, [α_j entropy/(mass α_j -time)]
μ^{α_j}	scalar chemical potential of j th constituent in phase α [energy α_j / mass α_j]
π^{α}	swelling potential, [force/area]
ρ^{α_j}	density of j^{th} constituent in phase α , = $C^{\alpha_j} \rho^{\alpha}$, [mass α_j / volume α]
ρ^{α}	averaged mass density of phase α , = $\sum_{j=1}^N \rho^{\alpha_j}$, [mass α / volume α]
ϕ^{α_j}	entropy flux of j^{th} constituent of phase α , [entropy α_j / (length ² -time)]
$\widehat{\Phi}_{\beta}^{\alpha_j}$	entropy gained by j th constituent in α -phase due to non-mass transfer interactions with the other phase [entropy / (mass α_j -time)]