

Three Pressures in Swelling Porous Media

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Abstract

For a two-phase swelling porous medium, two pressures have been previously defined thermodynamically in terms of intensive variables for each phase: one relating the change in energy with respect to specific volume, and the other 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 that a different choice of independent variables allows the comparison of these pressures with the extensive (and hence more classically defined) pressure. In the process we show how one can convert directly between different combinations of independent variables without re-exploiting the entropy inequality and discover the relationship between three thermodynamically defined pressures. The physical interpretation of these three pressures is investigated by examining two media: 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.

1 Introduction

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 [20, 21, 22], multiple constituents per phase [9, 11, 18, 19], multiple scales [5, 6], and/or include the effects of interfaces

and contact lines [2, 16, 17, 24]. The result has been a more concrete foundation for the equations which govern flow through porous media [8, 16, 23, 26] the adsorption/desorption of constituents [9, 11], the stress in a porous medium [10], heat transfer [7], and capillary pressure [1, 25].

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 [13], 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 oppose 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, 16, 17, 24].

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, hybrid mixture theory (HMT) as it applies to swelling porous media [5, 6, 7, 9, 11], 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 thermodynamic pressures. 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 two media in which we can compare the physical interpretation of the different pressures. These two media are a swelling porous medium in which the solid phase does not interact directly, and a swelling porous medium in which the solid phase is entangled and hence interacts. We conclude with a discussion on the differences between the 3 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 [13] as formulated in [2, 11] are then presented. We restrict the medium to which these equations apply to a two-phase medium (liquid and solid) with negligible interfacial effects.

The field equations are derived via averaging their microscale counter-

part, taking into account the movement of interfaces and transfer of mass, momentum, energy, and entropy between phases. The averaging process is explained in [4, 20] so here we only present the resulting macroscale equations. The relationship between these variables and their microscale counterparts are presented in Appendix A, while the relationship between the constituent variables and their bulk-phase counterparts are provided in Appendix B. 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 D.

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 $\hat{e}_\beta^{\alpha_j}$ represents the net rate of mass gained by constituent j in phase α from phase β .

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 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 other macroscale variables and their microscale counterparts are given in Appendix A. Summing over j yields

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

with restrictions

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

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

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 Appendix A. Summing over constituents yields

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

with the restrictions

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

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

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

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

where $\widehat{\Phi}_\beta^{\alpha j}$ represents the rate at which entropy is gained from constituent j in phase β . Summing over constituents we get

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

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, [15], 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, 22] 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:

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

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

where we have used

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

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 [12], and close the system by postulating that the time rate of change of the volume fraction, $\dot{\varepsilon}^l$, is also a constitutive variable. Thus we assume that all constitutive variables are a function of the following variables:

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

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

This choice of independent variables differs slightly from what has been done previously [6, 9, 11, 19] in that the solid-phase strain tensor is not included, and $\varepsilon^\alpha \rho^{\alpha_j}$ 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^{α_j} . This change in the density variables allows a more direct comparison with extensively defined variables, as will be pointed out towards the end of this section. We do not assume dependence on the solid-phase strain tensor since the solid-phase strain tensor, volume fraction, $\varepsilon^s = 1 - \varepsilon^l$, and density, are coupled through the solid-phase continuity equation. Since the focus of our discussion is on pressure, there is no loss of information as long as shearing does not occur.

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

$$A^l = A^l(\varepsilon^l, \varepsilon^l \rho^{l_j}, T)$$

$$A^s = A^s(\varepsilon^l, \varepsilon^s \rho^{s_j}, T). \quad (24)$$

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

At this point we define some thermodynamic variables. In terms of the Helmholtz potential we define the *classical pressure* to be:

$$p^\alpha = -\varepsilon^\alpha \rho^\alpha \left. \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \right|_{\varepsilon^\alpha \rho^{\alpha_j}, T, \dots}. \quad (25)$$

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

$$p^\alpha = - \left. \frac{\partial A_T^\alpha}{\partial V^\alpha} \right|_{M^{\alpha_j}, T, \dots} \quad (26)$$

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 frequently is the following:

$$\pi^\alpha = \sum_{j=1}^N \rho^\alpha \rho^{\alpha_j} \left. \frac{\partial A^\alpha}{\partial \rho^{\alpha_j}} \right|_{\varepsilon^\alpha, T, \dots} . \quad (27)$$

For a single phase composed of one constituent, $\pi^\alpha = p^\alpha$ and these two definitions coincide, which may be seen by converting to extensive variables where we get:

$$p^\alpha = - \left. \frac{\partial A_T^\alpha}{\partial V^\alpha} \right|_{M^{\alpha_j}, T} \quad (28)$$

$$\pi^\alpha = - \left. \frac{\partial A^\alpha}{\partial v^\alpha} \right|_{\varepsilon^\alpha, T} = - \left. \frac{\partial A_T^\alpha}{\partial V^\alpha} \right|_{\varepsilon^\alpha M^\alpha, T} \quad (29)$$

where v^α is the specific volume, and the subscript T on A denotes total energy, as oppose to energy per unit REV. For a swelling porous medium, these two quantities are distinct. In keeping with tradition, [15], we shall refer to π^α as the *thermodynamic pressure*.

Using these definitions, we obtain the final form of the entropy inequality (see Appendix C). From this we obtain results which must always hold, results which hold only at equilibrium, and results which hold near equilibrium. Here we present only the results pertinent to our discussion.

Non-Equilibrium Constitutive Restrictions

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

$$\mathbf{t}^s = -\pi^s \mathbf{I} - \sum_{j=1}^N \rho^{s_j} \mathbf{v}^{s_j, s} \mathbf{v}^{s_j, s} \quad (30)$$

which tells us the macroscale solid-phase stress tensor is proportional to the thermodynamic pressure if the magnitude of diffusion is small.

Equilibrium Constitutive Restrictions

We define equilibrium to be when the following set of variables are zero: \mathbf{d}^l , ε^l , $\nabla \mathbf{v}^{l_j, l}$, $\mathbf{v}^{l_j, l}$, $\mathbf{v}^{l, s}$, and $\varepsilon^l \rho^{l_j} \hat{\mathbf{e}}_s^{l_j}$, where $j = 1, \dots, N-1$ except for $\hat{\mathbf{e}}_s^{l_j}$ where $j = 1, \dots, N$. 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 , ε^l , and $\mathbf{v}^{l, s}$ gives the following results:

$$\mathbf{t}^l = -\pi^l \mathbf{I} \quad (31)$$

$$p^l = p^s \quad (32)$$

$$\varepsilon^l \rho^l \hat{\mathbf{T}}_s^l = p^l \frac{\partial A^l}{\partial \varepsilon^l} \nabla \varepsilon^l - \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T \quad (33)$$

Equation (31) states that at equilibrium the liquid-phase stress tensor is proportional to the thermodynamic pressure. Equation (32) states that the classical pressures must be equal at equilibrium. Equation (33) 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

$$f_{\text{neq}} \approx f_{\text{eq}} + Cz \quad (34)$$

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

$$\mathbf{t}^l = -\pi^l \mathbf{I} + \boldsymbol{\nu}^l : \mathbf{d}^l \quad (35)$$

$$p^l - p^s = \eta \dot{\varepsilon}^l \quad (36)$$

$$\varepsilon^l \rho^l \widehat{\mathbf{T}}_s^l = p^l \nabla \varepsilon^l - \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T - \mathbf{K}^l \cdot \mathbf{v}^{l,s} \quad (37)$$

where $\boldsymbol{\nu}^l$, a fourth-order tensor, η , a scalar, and \mathbf{K}^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 [14]. To get a generalized version of Darcy's law, use (37) and (35) to eliminate $\varepsilon^l \rho^l \widehat{\mathbf{T}}_s^l$ and \mathbf{t}^l , respectively, in the momentum equation, (7). Neglecting the inertial term results in

$$\begin{aligned} \mathbf{K}^{l,s} \cdot \mathbf{v}^{l,s} = & -\nabla \cdot (\varepsilon^l \pi^l) + \varepsilon^l \rho^l \mathbf{g} + p^l \nabla \varepsilon^l - \varepsilon^l \rho^l \left(\frac{\partial A^l}{\partial T} + \eta^l \right) \nabla T \\ & - \nabla \cdot (\varepsilon^l \boldsymbol{\nu}^l : \mathbf{d}^l). \end{aligned} \quad (38)$$

The last term is known as the Brinkman correction factor, although it is generally not considered to be significant. The more commonly used correction factor is known as the Forchheimer correction factor, and this term is also obtainable within this framework, see [8, 23].

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^{l_j} ($j = 1, \dots, N-1$) and ρ^l instead of ε^l and $\varepsilon^l \rho^{l_j}$ ($j = 1, \dots, N$). First consider the total differential

$$DA^l = \left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^l} d\varepsilon^l + \left. \frac{\partial A^l}{\partial (\varepsilon^l \rho^l)} \right|_{\varepsilon^l} d(\varepsilon^l \rho^l) = \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l} d\varepsilon^l + \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l} d\rho^l, \quad (39)$$

where we have used an overline to emphasize the difference in independent variables. Then for example,

$$\left. \frac{\partial A^l}{\partial \varepsilon^l} \right|_{\varepsilon^l, \rho^l} = \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l} \left. \frac{\partial \varepsilon^l}{\partial \varepsilon^l} \right|_{\varepsilon^l, \rho^l} + \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l} \left. \frac{\partial \rho^l}{\partial \varepsilon^l} \right|_{\varepsilon^l, \rho^l} \quad (40)$$

$$= \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l} - \frac{\rho^l}{\varepsilon^l} \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l} \quad (41)$$

so that we obtain

$$\pi^l(\varepsilon^l, \rho^l) = p^l(\varepsilon^l, \varepsilon^l \rho^l) - \bar{p}^l(\varepsilon^l, \rho^l) \quad (42)$$

where

$$\bar{p}^l = -\varepsilon^l \rho^l \left. \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \right|_{\rho^l, C^{l_j}}. \quad (43)$$

Equation (42) states that the thermodynamic pressure is equal to the pressure obtained by changing the volume fraction while keeping the total mass fixed, minus the pressure obtained by changing the volume fraction while keeping the density fixed. Similarly, one may show that

$$\pi^l(\varepsilon^l, \varepsilon^l \rho^{l_j}) = \sum_{j=1}^N \rho^l \rho^{l_j} \left. \frac{\partial A^l}{\partial \rho^{\alpha_j}} \right|_{\varepsilon^l} = (\rho^l)^2 \left. \frac{\partial \bar{A}^l}{\partial \rho^l} \right|_{\varepsilon^l, C^{l_j}} = \pi^l(\varepsilon^l, \rho^l, C^{l_j}) \quad (44)$$

so that the thermodynamic pressures in both formulations 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.

We refer to \bar{p}^α as the *swelling pressure* for reasons to be made clear in the next section.

4 Swelling Media

In order to give a physical interpretation to the pressure variables for each phase, π^α , \bar{p}^α , and p^α , we first consider a swelling porous media with a non-interacting solid phase such as a well-layered montmorillonite. Following, we

will consider a swelling porous medium with an interacting solid phase such as a hydrophilic polymer.

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 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 first 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 1). The clay sample is loaded on top with pressure P and measurements are taken between the pressure applied and the depression of the clay sample at equilibrium. The governing equations of interest are then

$$p^l = p^s \quad (45)$$

$$\mathbf{t}^s = -\pi^s \quad (46)$$

$$\mathbf{t}^l = -\pi^l. \quad (47)$$

The first question we concern ourselves with is, what is P ? Is it π^l , $\varepsilon^l \pi^l + \varepsilon^s \pi^s$, p^l or $\varepsilon^l p^l + \varepsilon^s p^s$? To begin, we must have a balance of forces at equilibrium (we have assumed that the measurements are always taken at equilibrium), so that the overburden load must be 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 vector. Summing the conservation of momentum equations (7) for $\alpha = l$ and s , we find that the total stress of the clay mixture is given by

$$\mathbf{t} = \varepsilon^l \mathbf{t}^l + \varepsilon^s \mathbf{t}^s = -(\varepsilon^l \pi^l + \varepsilon^s \pi^s) \mathbf{I}. \quad (48)$$

Further, because of the layering of the clay minerals we have a balance of forces between phases, i.e.

$$\mathbf{t}^l \cdot \mathbf{n} = \mathbf{t}^s \cdot \mathbf{n} \quad \text{or} \quad \pi^l = \pi^s, \quad (49)$$

Figure 1: Osmotic swelling pressure experiment.

where \mathbf{n} is the unit outward normal vector from the surface of the clay mineral. Note that (49) would not hold for a porous medium with a connected solid phase which can support a pressure independently of a fluid phase as the forces in the solid phase are not necessarily balanced by the forces in the liquid phase. Combining (49) and (48) we have

$$P = \pi^l = \pi^s \quad (50)$$

so that the physical force in the fluid and solid phase is the *thermodynamic pressure*. We now recall (42) which we repeat here:

$$\pi^l = p^l(\varepsilon^l, \varepsilon^l \rho^l) - \bar{p}^l(\varepsilon^l, \rho^l)$$

i.e. the physical pressure has two components, p^l , which is the pressure obtained by changing ε^l while keeping the mass fixed, and \bar{p}^l which is the pressure obtained by changing ε^l while keeping the density fixed (by e.g. letting fluid out of the system).

In the osmotic experiment, the volume fraction is changed 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:

$$G^l = \sum_{j=1}^N C^{lj} \mu^{lj} = A^l + \frac{\pi^l}{\rho^l}, \quad (51)$$

where μ^{α_j} is the chemical potential and is given by

$$\mu^{\alpha_j} = \left. \frac{\partial A_T^\alpha}{\partial M^{\alpha_j}} \right|_{V^\alpha, T, \dots} = \left. \frac{\partial(\varepsilon^\alpha \rho^\alpha A^\alpha)}{\partial(\varepsilon^\alpha \rho^{\alpha_j})} \right|_{\varepsilon^\alpha, T, \dots} = A^\alpha + \rho^\alpha \left. \frac{\partial A^\alpha}{\partial \rho^{\alpha_j}} \right|_{\varepsilon^\alpha, T, \dots}. \quad (52)$$

We want to use the fact that G^l is constant to obtain relationships between the different pressures. In particular following the argument used in going from (39) to (44), (51) yields

$$DG^l = \frac{\partial A^l}{\partial \varepsilon^l} \Big|_{\varepsilon^l \rho^l} d\varepsilon^l + \frac{\partial A^l}{\partial (\varepsilon^l \rho^l)} \Big|_{\varepsilon^l} d(\varepsilon^l \rho^l) + \frac{1}{\rho^l} \left[\frac{\partial \pi^l}{\partial \varepsilon^l} \Big|_{\varepsilon^l \rho^l} d\varepsilon^l + \frac{\partial \pi^l}{\partial (\varepsilon^l \rho^l)} \Big|_{\varepsilon^l} d(\varepsilon^l \rho^l) \right] - \frac{\pi^l}{(\rho^l)^2} d\rho^l \quad (53)$$

$$D\bar{G}^l = \frac{\partial \bar{A}^l}{\partial \varepsilon^l} \Big|_{\rho^l} d\varepsilon^l + \frac{\partial \bar{A}^l}{\partial \rho^l} \Big|_{\varepsilon^l} d\rho^l + \frac{1}{\rho^l} \left[\frac{\partial \pi^l}{\partial \varepsilon^l} \Big|_{\rho^l} d\varepsilon^l + \frac{\partial \pi^l}{\partial \rho^l} \Big|_{\varepsilon^l} d\rho^l \right] - \frac{\pi^l}{(\rho^l)^2} d\rho^l \quad (54)$$

where the overline implies that we are using ε^l and ρ^l as independent variables as oppose to ε^l and $\varepsilon^l \rho^l$. The thermodynamic pressure is defined the same regardless of which set of independent variables are used, see (44). Beginning with (54), taking the partial derivative with respect to ε^l keeping ρ^l fixed, and setting it equal to zero (since the chemical potential of the liquid phase is constant) we have, *for this experiment*:

$$\bar{p}^l = \varepsilon^l \frac{\partial \pi^l}{\partial \varepsilon^l} \Big|_{\rho^l}. \quad (55)$$

Expression (55) can also be obtained from (53) by calculating $(\partial G^l)/(\partial \varepsilon^l)$ keeping ρ^l fixed, using (42) and

$$\begin{aligned} \frac{\partial \pi^l}{\partial \varepsilon^l} \Big|_{\varepsilon^l \rho^l} &= \frac{\partial \pi^l}{\partial \varepsilon^l} \Big|_{\rho^l} - \frac{\rho^l}{\varepsilon^l} \frac{\partial \pi^l}{\partial \rho^l} \Big|_{\varepsilon^l} \\ \frac{\partial \pi^l(\varepsilon^l, \varepsilon^l \rho^l)}{\partial \rho^l} \Big|_{\varepsilon^l} &= \frac{\partial \pi^l(\varepsilon^l, \rho^l)}{\partial \rho^l} \Big|_{\varepsilon^l} \end{aligned}$$

to switch between the different variables.

We now have the following system of equations for which we would like to solve for P in terms of volume fraction, ε^l :

$$P = \pi^l \quad \pi^l = \pi^s \quad (56)$$

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

$$\bar{p}^l = \varepsilon^l \frac{\partial \pi^l}{\partial \varepsilon^l} \Big|_{\rho^l}. \quad (58)$$

Figure 2: Experiment needed to test hypothesis (59) and measure p^l .

In order to close the system, we make the additional assumption that

$$|p^l| \ll |\bar{p}^l|, \quad (59)$$

or the volume fraction is changing primarily due to the volume of water changing, as oppose to density changing (see (28) and (43)). This assumption can be tested in an experiment. Begin with the swelling experiment as depicted in Figure 1. After depressing the clay with a fixed load P_0 , replace the semi-permeable membrane by an impermeable membrane so that the mass of the fluid is fixed (see Figure 2). Because the vicinal fluid is no longer interacting with the bulk water, the pressure required to keep the medium at the same height, or same volume fraction, is less, say P_1 . The assumption is valid if P_1 is much smaller than P_0 . This experiment may also be done in reverse order: Beginning with a sample with an impermeable membrane separating the sample from the bulk water, depress the sample by applying a load P_1 . Now replace the impermeable membrane with a permeable membrane, and measure the new pressure, P_0 required to keep the sample at the same height. This also gives an experiment which measures p^l and hence, \bar{p}^l through (42).

Assumption (59) simplifies equation (42) to

$$P = \pi^l \approx -\bar{p}^l \quad (60)$$

i.e. we're assuming that most of the overburden load P_0 is due to hydration effects and not due to changing the density. Equation (60) also implies that $\bar{p}^l < 0$, or that the force acting to change the volume fraction (while keeping the density fixed) is actually a tensile stress. This makes sense if one compares the system with a geometrically similar system in which the liquid and solid phase do not interact. In the non-interacting system, the liquid can hold only compressional forces, and in fact, by (42), $\bar{p}^l = 0$ and $\pi^l = p^l$

which agrees with (28) and (29). If one attempted the osmosis experiment in a non-interacting system, applying any pressure at all would cause the system to collapse, so that compressional forces themselves are not capable of withstanding an overburden pressure in such an experiment.

By combining (56), (58), and (60) we get

$$P = -\varepsilon^l \frac{\partial P}{\partial \varepsilon^l}. \quad (61)$$

Let λ^s be the thickness of the clay mineral, while λ^l represents the thickness of the vicinal water between two clay platelets. Then, following [2], we have

$$\varepsilon^l = \frac{\lambda^l}{\lambda^l + \lambda^s}. \quad (62)$$

Assuming that $\lambda^l \gg \lambda^s$, (61) is approximated by

$$\frac{dP}{P} = -\frac{\lambda^s}{(\lambda^l)^2} d\lambda^l \quad (63)$$

and solving yields

$$P = C e^{\frac{\lambda^s}{\lambda^l}} \quad (64)$$

which is exactly the empirical relationship which Low obtained in [27]. The constant C may be obtained by using the condition that when λ^l is maximum, the overburden pressure, P , is equal to the atmospheric pressure.

Now consider a second experiment involving swelling porous media, termed the undrained 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:

$$P = -\left. \frac{\partial A_T}{\partial V_T} \right|_M = -\left. \frac{\partial A_T^l}{\partial V_T} \right|_M - \left. \frac{\partial A_T^s}{\partial V_T} \right|_M \quad (65)$$

$$= -\left. \frac{\partial A_T^l}{\partial V_T^l} \right|_{M^l} \frac{\partial V_T^l}{\partial V_T} - \left. \frac{\partial A_T^s}{\partial V_T^s} \right|_{M^s} \frac{\partial V_T^s}{\partial V_T} \quad (66)$$

where $A_T = A_T^l + A_T^s$ and $M_T = M_T^l + M_T^s$, and where the last equality implies the first since 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

$$P = - \left. \frac{\partial(\varepsilon^l \rho^l A^l)}{\partial \varepsilon^l} \right|_{\varepsilon^l \rho^l} \varepsilon^l - \left. \frac{\partial(\varepsilon^s \rho^s A^s)}{\partial \varepsilon^s} \right|_{\varepsilon^s \rho^s} \varepsilon^s \quad (67)$$

$$= \varepsilon^l p^l + \varepsilon^s p^s = p^l \quad (68)$$

where the last equality holds at equilibrium by (36).

This result may also be obtained consistently with the approach taken in the osmotic experiment, where we have the total overburden pressure given by $P = \pi^l = \pi^s$ (see (50)). In this experiment however, we have that the change in volume fraction is primarily due to changing the density instead of the liquid content, so that

$$P = \pi^l = p^l - \bar{p}^l \quad (69)$$

$$\approx p^l. \quad (70)$$

Thus we have two experiments, one which measures the swelling pressure, \bar{p}^l , and one which measures p^l .

Now consider the osmotic experiment and the undrained experiment in the dynamic case. Here we measure the *rate* at which the volume fraction is changing. We now must consider the viscosity relationship (36):

$$p^l - p^s = \eta \dot{\varepsilon}^l,$$

which states that the rate at which the medium swells/shrinks is governed by the difference in the classical pressures, p^l and p^s . The coefficient η may be a function of density (or $\varepsilon^\alpha \rho^\alpha$) and volume fraction, ε^l , as well as temperature, concentrations, etc. If we assume the solid phase reaches equilibrium much more quickly than the liquid phase due to the re-arrangement of the liquid molecules, then p^s reaches its equilibrium state much more quickly than p^l . Thus we consider $p^s = p_0^s$, a constant, which is the pressure in the undrained test at equilibrium. If this assumption is valid, we have a way of measuring the coefficient η using the undrained test. In the polymer literature, Thomas and Windle [29] empirically obtained this coefficient, and refer to it as the viscosity coefficient. They obtained the functional relationship $\eta = \eta_0 e^{[-M\varepsilon^l/\varepsilon_m^l]}$ where, for polymers, η_0 is the viscosity of the solid in the

limiting case of $\varepsilon^l = 0$, M is a coefficient, and ε_m^l is the maximum volume fraction. This may be used as a first approximation for this coefficient. See also [1]. Using these relationships we may use them in the dynamic osmosis experiment and check to see that our system is consistent.

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.

Because the solid phase is connected, we need to consider the physical interpretations of the solid-phase pressures. Because $\mathbf{t}^s = -\pi^s \mathbf{I}$, (30), the thermodynamic pressure always represents the physical stress of the solid phase. Recall also that $p^s = - \left. \frac{\partial A_T^s}{\partial V^s} \right|_{M^s, j, T}$, which is a measure of pressure required to change the volume keeping the composition fixed. If the solid itself (not the porous medium) is unaffected by the presence of the liquid, then it seems reasonable to approximate p^s using the results of tensile and compression tests on the solid material with no pores. If the solid is considered to be incompressible, then p^s should be considered a primary unknown, just as incompressible materials are treated in solid mechanics [15]. At equilibrium, it is always true that $p^s = p^l$.

Recall also that the swelling pressure is given by $\bar{p}^s = -\varepsilon^s \rho^s \left. \frac{\partial A^s}{\partial \varepsilon^s} \right|_{\rho^s, C^s, j}$.

This is the thermodynamic quantity which tells us how the porosity affects the behavior of the solid. As such, it will be strongly affected by the geometry. So for example, a solid which looks like swiss cheese will behave one way as the number of holes are increased (ε^l increased), while a porous medium with a non-connected solid, such as the well-layered montmorillonite clay just discussed, will have a function for \bar{p}^s which would not strongly depend upon the volume fraction. The swelling pressure is also what puts the polymer in tension ($\pi^s = p^s - \bar{p}^s < 0$) as the polymer expands, even though the density remains constant (it is just the geometry which changes). In this case the

swelling pressure of the solid phase is positive, i.e., the solid phase would prefer to not have so much liquid in the system.

Now consider the case in which a solid polymer is placed in solution. The solution seeps into the polymer until a critical moisture content is reached, at which point the polymer swells. It is the swelling we would like to model. Consider the viscosity relationship (36):

$$p^l - p^s = \eta \dot{\varepsilon}^l.$$

As mentioned in the discussion on well-ordered clay, the pressure p^l is governed by how quickly the particles in the liquid phase can re-order. Unlike the well-ordered clay however, the solid phase may now restrict the rate at which the polymer swells due to solid-phase entanglement, $p^s = \pi^s + \bar{p}^s$. As \bar{p}^s increases due to entanglement, the swelling rate will decrease. Because the coefficient η does not depend upon any dynamically changing variable (it depends upon variables such as volume fraction, density, temperature, but not upon any variable which is necessarily zero at equilibrium, such as velocity, time-rate of change of volume fraction, etc.), the functional dependence of η on volume fraction and density obtained from the experiments proposed in the well-layered swelling porous medium are still valid for this system if we assume $\pi^l = \pi^s$. Similarly, the same argument holds for p^l , since the exploitation of the entropy inequality requires that the Helmholtz free energy not depend on variables which are necessarily zero at equilibrium (see equations (24) and (25)). Thus, if we know the density and volume fraction, ε^l , we have a way of obtaining $p^s(\varepsilon^l, \varepsilon^s, \rho^s)$.

Now consider the generalized version of Darcy's law, (38). Neglecting temperature, gravity, and second-order effects, (38) becomes:

$$\mathbf{K}^{l,s} \cdot \mathbf{v}^{l,s} = -\nabla(\varepsilon^l \pi^l) + p^l \nabla \varepsilon^l \quad (71)$$

where $\mathbf{K}^{l,s}$ is the linearization coefficient which may depend upon density and volume fraction. We now make some assumptions to re-write (71) so that it is specific to the experiment of placing a dry polymer in solution.

In this experiment, the overburden pressure, $\varepsilon^l \pi^l + \varepsilon^s \pi^s$, remains unchanged so that we have $\nabla(\varepsilon^l \pi^l + \varepsilon^s \pi^s) = \mathbf{0}$. Using this and adding and subtracting $p^s \nabla \varepsilon^l$ yields

$$\begin{aligned} \mathbf{K}^{l,s} \cdot \mathbf{v}^{l,s} &= \nabla(\varepsilon^s \pi^s) - p^s \nabla \varepsilon^s + (p^l - p^s) \nabla \varepsilon^l \\ &= \varepsilon^s \nabla \pi^s + (\pi^s - p^s) \nabla \varepsilon^s + (p^l - p^s) \nabla \varepsilon^l \\ &= \varepsilon^s \nabla \pi^s - \bar{p}^s \nabla \varepsilon^s + (p^l - p^s) \nabla \varepsilon^l \end{aligned}$$

where in the last equality we used $\pi^s = p^s - \bar{p}^s$. We assume that the change in volume fraction is primarily due to changes in the amount of liquid, as oppose to density changes. Thus we assume that $p^s \ll \bar{p}^s$ which allows us to write

$$\begin{aligned} \mathbf{K}^{l,s} \cdot \mathbf{v}^{l,s} &\approx \varepsilon^s \nabla \pi^s + (p^s - \bar{p}^s) \nabla \varepsilon^s + (p^l - p^s) \nabla \varepsilon^l \\ &= \nabla(\varepsilon^s \pi^s) + \eta \dot{\varepsilon}^l \nabla \varepsilon^l \\ &= -\nabla(\varepsilon^l \pi^l) + \eta \dot{\varepsilon}^l \nabla \varepsilon^l \end{aligned} \quad (72)$$

where in the last equality we again used the assumption that in this experiment the overburden pressure is constant. Assuming the physical pressure, π^l , and the volume fraction are measurable, we have a modified Darcy's law which indicates the polymer has a visco-elastic behavior. We remark that the solid phase contributes directly through the coefficient η and the rate of swelling, $\dot{\varepsilon}^l$.

As in [1], we may make additional simplifying assumptions. If we assume that $\varepsilon^l \pi^l$ is only a function of volume fraction (i.e. the effects of density changes in the liquid phase is small compared to the effects of volume fraction), then we may assume that

$$\nabla(\varepsilon^l \pi^l) \approx \frac{d(\varepsilon^l \pi^l)}{d\varepsilon^l} \nabla \varepsilon^l. \quad (73)$$

Further as a first approximation, we may assume the coefficient of $\nabla \varepsilon^l$ in (73) is a constant, $-E$, so that (72) becomes

$$\mathbf{K}^{l,s} \cdot \mathbf{v}^{l,s} \approx (E + \eta \dot{\varepsilon}^l) \nabla \varepsilon^l. \quad (74)$$

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 been able to concretely determine what the relationships among the pressure variables are. The 3 pressures considered are the classical pressure p^α , the thermodynamic pressure π^α , and the hydration or swelling pressure \bar{p}^α . Assuming negligible shear strain, the following statements may be made.

- The thermodynamic pressure, $\pi^\alpha = -\frac{\partial A^\alpha}{\partial v^\alpha}|_{\varepsilon^\alpha}$, 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. Of more practical use is the relationship between the thermodynamic pressure and the stress: $\mathbf{t}^\alpha = -\pi^\alpha \mathbf{I} + \boldsymbol{\nu}^\alpha : \mathbf{d}^\alpha$ (30,35). Thus we see that when \mathbf{d}^α is small compared to π^α , the thermodynamic pressure represents the physical force experienced by the phase - see [28] for a short discussion on this approximation. The overburden pressure is then given by

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

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 $\pi^l = \pi^s$.

- The classical pressure, $p^\alpha = -\varepsilon^\alpha \rho^\alpha \left. \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \right|_{\varepsilon^\alpha, \rho^\alpha, C^\alpha} = -\left. \frac{\partial A_T^\alpha}{\partial V^\alpha} \right|_{M^\alpha, T}$ is the change in energy with respect to volume keeping the composition fixed. At equilibrium it is always true that $p^s = p^l$. We can measure 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, $\pi^s = \pi^l \approx p^l$, and thus measuring the overburden pressure gives the classical pressure, see (68). As for the solid-phase classical pressure, if the solid phase (not the porous medium) is unaffected by the presence of the liquid phase, it seems reasonable to approximate p^s by the properties of the solid material with no pores. It is also the classical pressure which determines the rate at which the medium swells (36):

$$p^l - p^s = \eta \varepsilon^l. \quad (75)$$

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

- The swelling pressure, $\bar{p}^\alpha = -\varepsilon^\alpha \rho^\alpha \left. \frac{\partial A^\alpha}{\partial \varepsilon^\alpha} \right|_{\rho^\alpha, C^\alpha}$ is the change in energy with respect to volume fraction keeping the density and composition of the 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 noninteracting solid phase). For the solid phase, this represents the affects of the void-space amount on the solid phase. In materials with a non-interacting solid phase, this quantity may not change much with volume fraction. In a porous medium with an interacting solid phase, it captures the tensile stress and may become quite large, inhibiting swelling.

In this paper we have discussed three thermodynamic quantities, each of which has units of pressure. The relationship between the three pressures is (42):

$$\pi^\alpha = p^\alpha - \bar{p}^\alpha \quad (76)$$

so that the thermodynamic pressure is the difference between the classical pressure and the swelling pressure. In the case of a non-swelling medium, in which there is little change in energy due to moisture content (e.g. sandstone), $\bar{p}^\alpha = 0$ and we have $\pi^\alpha = p^\alpha$ so that thermodynamic pressure is the same as the classical pressure. In a swelling porous medium, \bar{p}^l is negative, i.e., it is a tensile force - see the discussion in the previous section under a two-phase swelling porous medium with a non-interacting solid phase.

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Appendix A. Definition of Macroscopic Bulk Variables

The following formulas are the relationships between the microscale and macroscale (continuum scale) variables. In previous papers [4, 20], the relationships are derived assuming small perturbations so that $\overline{\overline{\psi^{\alpha\alpha}}} = \overline{\psi^{\alpha}}$ and $\overline{\psi} - \overline{\overline{\psi^{\alpha\alpha}}} = 0$. Here we have made no such assumptions.

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

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

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

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

$$\rho^{\alpha_j} \equiv \overline{\rho^j}^{\alpha} \tag{A.77}$$

$$C^{\alpha_j} \equiv \frac{\rho^{\alpha_j}}{\rho^{\alpha}} \tag{A.78}$$

$$\varepsilon^{\alpha} \equiv \frac{|\delta V_{\alpha}|}{|\delta V|} \tag{A.79}$$

$$\mathbf{v}^{\alpha_j} \equiv \overline{\mathbf{v}^j}^\alpha \quad (\text{A.80})$$

$$\widehat{\mathbf{e}}_\beta^{\alpha_j} \equiv \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \quad (\text{A.81})$$

$$\widehat{\mathbf{r}}^{\alpha_j} \equiv \varepsilon^\alpha \rho^{\alpha_j} \overline{\widehat{\mathbf{r}}^j}^\alpha \quad (\text{A.82})$$

$$\mathbf{t}^{\alpha_j} \equiv \langle \mathbf{t}^j \rangle^\alpha + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \mathbf{v}^{\alpha_j} - \rho^{\alpha_j} \overline{\mathbf{v}^j \mathbf{v}^j}^\alpha \quad (\text{A.83})$$

$$\mathbf{g} \equiv \overline{\mathbf{g}}^\alpha \quad (\text{A.84})$$

$$\begin{aligned} \widehat{\mathbf{T}}_\beta^{\alpha_j} &\equiv \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}_\alpha da \\ &\quad - \frac{\mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \end{aligned} \quad (\text{A.85})$$

$$\widehat{\mathbf{i}}^{\alpha_j} \equiv \varepsilon^\alpha \rho^{\alpha_j} \left(\widehat{\mathbf{i}}^j{}^\alpha + \overline{\widehat{\mathbf{r}}^j \mathbf{v}^j}^\alpha - \widehat{\mathbf{r}}^{\alpha_j} \mathbf{v}^{\alpha_j} \right) \quad (\text{A.86})$$

$$E^{\alpha_j} \equiv \overline{E^j}^\alpha + \frac{1}{2} \overline{\mathbf{v}^j \cdot \mathbf{v}^j}^\alpha - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \quad (\text{A.87})$$

$$\begin{aligned} \mathbf{q}^{\alpha_j} &\equiv \langle \mathbf{q}^j \rangle^\alpha + \langle \mathbf{t}^j \cdot \mathbf{v}^j \rangle^\alpha - \mathbf{t}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} (E^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}) \\ &\quad - \overline{\rho^{\alpha_j} \mathbf{v}^j (E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j)}^\alpha \end{aligned} \quad (\text{A.88})$$

$$h^{\alpha_j} \equiv \overline{h^j}^\alpha + \overline{\mathbf{g}^j \cdot \mathbf{v}^j}^\alpha - \mathbf{g}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} \quad (\text{A.89})$$

$$\begin{aligned} \widehat{\mathbf{Q}}_\beta^{\alpha_j} &\equiv \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[\mathbf{q}^j + \mathbf{t}^j \cdot \mathbf{v}^j + \rho^j (E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}_\alpha da \\ &\quad - \frac{\mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[\mathbf{t}^j + \rho^j \mathbf{v}^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}_\alpha da \\ &\quad - \left(\frac{E^{\alpha_j} - \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}}{\rho^{\alpha_j} |\delta V_\alpha|} \right) \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \end{aligned} \quad (\text{A.90})$$

$$\begin{aligned} \widehat{E}^{\alpha_j} &\equiv \varepsilon^\alpha \rho^{\alpha_j} \left(\widehat{E}^j{}^\alpha + \widehat{\mathbf{i}}^j \cdot \mathbf{v}^j - \widehat{\mathbf{i}}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j} + \overline{(E^j + \frac{1}{2} \mathbf{v}^j \cdot \mathbf{v}^j) \widehat{\mathbf{r}}^j}^\alpha \right. \\ &\quad \left. - (E^{\alpha_j} + \frac{1}{2} \mathbf{v}^{\alpha_j} \cdot \mathbf{v}^{\alpha_j}) \widehat{\mathbf{r}}^{\alpha_j} \right) \end{aligned} \quad (\text{A.91})$$

$$\eta^{\alpha_j} \equiv \overline{\eta^j}^\alpha \quad (\text{A.92})$$

$$\phi^{\alpha_j} \equiv \langle \phi^j \rangle^\alpha + \rho^{\alpha_j} \mathbf{v}^{\alpha_j} \eta^{\alpha_j} - \rho^{\alpha_j} \overline{\mathbf{v}^j \eta^j}^\alpha \quad (\text{A.93})$$

$$b^{\alpha_j} \equiv \overline{b^j}^\alpha \quad (\text{A.94})$$

$$\widehat{\Phi}_\beta^{\alpha_j} \equiv \frac{1}{\rho^{\alpha_j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \left[\phi^j + \rho^j \eta^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \right] \cdot \mathbf{n}_\alpha da$$

$$-\frac{\eta^{\alpha j}}{\rho^{\alpha j} |\delta V_\alpha|} \int_{\delta A_{\alpha\beta}} \rho^j (\mathbf{w}_{\alpha\beta}^j - \mathbf{v}^j) \cdot \mathbf{n}_\alpha da \quad (\text{A.95})$$

$$\widehat{\eta}^{\alpha j} \equiv \varepsilon^\alpha \rho^{\alpha j} \left(\widehat{\eta}^{j\alpha} + \widehat{r}^j \overline{\eta}^{j\alpha} - \widehat{r}^{\alpha j} \eta^{\alpha j} \right) \quad (\text{A.96})$$

$$\widehat{\Lambda}^{\alpha j} \equiv \overline{\Lambda}^{j\alpha} \quad (\text{A.97})$$

Appendix B. Definition of Macroscopic Bulk Variables

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Appendix C. 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 24). 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}^{α_j} is a second order tensor representing the coefficient of $\nabla \mathbf{v}^{\alpha_j, \alpha}$ in (C.2), and \mathbf{F}^{α_j} represents the vector coefficient of $\mathbf{v}^{\alpha_j, \alpha}$. This results in

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

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

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 \hat{\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] \\
&+ \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^{l_j} \nabla (\varepsilon^l \rho^{l_j}) - \varepsilon^l \rho^l \hat{\mathbf{T}}_s^l + \sum_{j=1}^N \lambda^{l_j} \nabla (\varepsilon^l \rho^{l_j}) \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^{l_j})} \nabla (\varepsilon^l \rho^{l_j}) \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] \\
&+ \varepsilon^l \mathbf{d}^l : \left[\mathbf{t}^l + \sum_{j=1}^N \rho^{l_j} \mathbf{v}^{l_j, l} \mathbf{v}^{l_j, l} + \sum_{j=1}^N \rho^{l_j} (\lambda^{l_j} + A^{l_j}) \mathbf{I} \right] \\
&+ \varepsilon^s \mathbf{d}^s : \left[\mathbf{t}^s + \sum_{j=1}^N \rho^{s_j} \mathbf{v}^{s_j, s} \mathbf{v}^{s_j, s} + \sum_{j=1}^N \rho^{s_j} (\lambda^{s_j} + A^{s_j}) \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]
\end{aligned}$$

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

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:

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

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

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

Equation (C.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 D. 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, $\widehat{}$, 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_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]
\hat{E}^{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)]
\mathbf{g}	gravity, [length/time ²]
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/time ²]
\mathbf{n}_{α}	unit outward normal to phase α
p^{α}	classical pressure, [force/length ²]
\mathbf{q}^{α_j}	heat flux of constituent j in α -phase, [energy α_j /(length ² -time)]
$\hat{Q}_{\beta}^{\alpha_j}$	gain of energy of constituent j in phase α due to non-mass transfer non-mechanical interactions with the other phase, [α_j energy / (mass α_j -time)]
\hat{Q}^{α_j}	gain of energy of constituent j in phase α due to non-mass transfer non-mechanical interactions with other species within phase α , [α_j energy / (mass α_j -time)]
\hat{r}^{α_j}	rate of j th constituent mass gained within phase α , [1/time]
\mathbf{t}^{α_j}	stress tensor of j th constituent in α -phase, [force/length ²]
t	time
T	temperature
$\hat{\mathbf{T}}_{\beta}^{\alpha_j}$	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]
δV	Representative Elementary Volume (REV)

δV_α	portion of α -phase within REV
$\mathbf{w}_{\alpha\beta}^j$	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)]
$\hat{\eta}^{\alpha_j}$	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
$\hat{\Lambda}^{\alpha_j}$	entropy production density, [α_j entropy/(mass α_j -time)]
μ^{α_j}	scalar chemical potential of j th constituent in phase α
π^α	thermodynamic pressure, [force/area] [mass α_j / volume α]
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)]
$\hat{\Phi}_\beta^{\alpha_j}$	entropy gained by j th constituent in α -phase due to non-mass transfer interactions with the other phase [entropy / (mass α_j -time)]