

# Clarifying Mixture Theory and the Macroscale Chemical Potential

Lynn Schreyer Bennethum\*    Márcio A. Murad†    John H. Cushman ‡

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## Abstract

Hybrid mixture theory, HMT, consists of classical mixture theory applied to a multiphase system with volume averaged field equations. HMT is applicable to a multi-phase mixture in which the characteristic length of each phase is "small" relative to the extent of the mixture. A porous body is the canonical model of a system to which HMT is applicable. When a phase contains  $N$  constituents, the linearized fluxes derived through HMT are historically expressed relative to the  $N$ th constituent, e.g. Fick's law for the  $j$ th species is expressed in terms of a gradient of the  $j$ th chemical potential relative to the  $N$ th. This is in contrast to classical Gibbsian thermodynamics, which gives rise to results of similar form, but with absolute (non-relative) driving forces. Here we modify HMT to construct results which are completely analogous to Gibbsian thermodynamics. This is accomplished by modifying the way the entropy inequality is exploited and by re-examining the definition of the averaged chemical potential of a constituent and the averaged Gibbs energy of a phase. Particular emphasis is placed on the relations between the scalar chemical potential of Gibbs and the tensorial chemical potential of Bowen. Previous HMT results gave rise to an averaged chemical potential that may experience a jump between the solid and fluid phases at equilibrium; a result in clear contrast to Gibbsian theories. This discontinuity in the potential is due to an "effective" external field (e.g. the effective stress induced by a load in the solid phase). A notable consequence of the approach proposed herein is a HMT chemical potential in complete analogy with the Gibbsian chemical potential.

## 1 Introduction

In classical mixture theory a single phase medium composed of  $N$  constituents is viewed as  $N$  overlaying continua. Bowen [1, 2, 3] extended this idea to model a porous medium so that at the macroscale a two-phase medium is viewed as two overlaying continua. In his work, macroscale forms of the field equations (conservation of mass, momentum balance, and conservation of energy), which incorporate exchange terms between the overlaying continua, are postulated. Hassanizadeh and Gray [4, 5, 6] showed that if the microscale field equations are averaged then the terms in Bowen's macroscale field equations can be identified precisely with microscale counterparts. The combination of averaging and mixture theory is referred to as *hybrid mixture theory* (HMT). In both of these formulations, the constitutive restrictions are determined at the macroscale by exploiting the entropy inequality using the Coleman and Noll method [7].

Despite the growing use of HMT, we believe that the conventional treatment of obtaining constitutive restrictions which hold near equilibrium are not as concise as they could be. In particular, we

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

†Laboratório Nacional de Computação Científica, LNCC/CNPq, Rua Lauro Muller 455, 22290 - Rio de Janeiro, Brazil 47907.

‡Center for Applied Math, Math Sciences Building, Purdue University, W. Lafayette, IN 47907.

are interested in deriving results about the chemical potential which are analogous to classical results. The classical Gibbrian chemical potential,  $\mu_j$ , which is defined to be the derivative of the extensive Helmholtz energy with respect to the number of molecules of constituent  $j$  [8], has the following characteristics: (1) it is a scalar and measures the energy required to insert a particle into the system (see e.g. [9]), (2) its gradient is the driving force for diffusive flow (Fick's law) [10, 8], and (3) it is constant for a single constituent coexisting in two phases at equilibrium, i.e. for the solid,  $s$ , and liquid phase,  $l$ ,  $\mu_s^j = \mu_l^j$ ,  $j = 1, \dots, N$  where  $N$  is the number of miscible components in each phase (see e.g. [8]). However, in applying HMT or mixture theory to a two phase system, results are obtained only for a *relative* chemical potential,  $\widetilde{\mu}_\alpha^j$ :

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

Here  $A_\alpha$  is the intensive Helmholtz potential of phase  $\alpha$ , and  $\mu_\alpha^j$  and  $C_\alpha^j$  denote the chemical potential and the mass concentration of the  $j$ th constituent in the  $\alpha$  phase, respectively. So for example, instead of obtaining the result corresponding to characteristic (3), the result historically derived is the equality of the relative chemical potentials at equilibrium, i.e.  $\widetilde{\mu}_s^j = \widetilde{\mu}_l^j$  (see e.g. [11]).

But even more disturbing is that standard exploitation of the entropy inequality near equilibrium yields expressions which depend upon the *labeling of the constituents*. For example, in [12] and [11] the following generalized form of Fick's law is derived:

$$R_\alpha^j \mathbf{u}_\alpha^j = \nabla \widetilde{\mu}_\alpha^j \quad j = 1, \dots, N-1 \quad (2)$$

where  $\mathbf{u}_\alpha^j$  is the diffusive velocity of constituent  $j$  in phase  $\alpha$  ( $\alpha = l, s$ ), and  $R_\alpha^j$  is a material coefficient arising from a linearization procedure. After appropriate simplifications (see [12]) equation (2) reduces to the classical Fick's law which states that the diffusive velocity is proportional to the concentration gradient. We are interested in reproducing the more general form of Fick's law, which according to classical irreversible thermodynamics, states that flow is driven by an absolute chemical potential gradient (i.e.  $\nabla \mu_\alpha^j$ ) [8]. This is in contrast to equation (2) which states that flow is driven by a chemical potential gradient *relative* to the  $N$ th component, implying that the diffusive velocity is a function of how the constituents are labeled.

The primary reason for obtaining results in terms of the relative chemical potential is the interdependence of the concentrations ( $\sum_{j=1}^N C_\alpha^j = 1$ ). In classical thermodynamics this is avoided because extensive variables representing the number of molecules of each constituent are used as independent variables, instead of intensive variables (concentrations). Using extensive variables such as the number of molecules of each constituent is not possible in HMT as the upscaling process and the exploitation of the entropy inequality can not be performed on extensive variables, at least not in a physically meaningful manner. Thus all results standardly derived [11, 12] are in terms of the relative chemical potential.

Some of the results involving the relative chemical potential can be sharpened by choosing  $\mu_\alpha^N$  appropriately and subsequently deriving results for the absolute (non-relative) chemical potentials. Bowen [1] and Bowen and Wiese [13] proposed the following tensorial definition for the chemical potential which has been used in most of the hybrid mixture theory derivations [12, 11]:

$$\boldsymbol{\mu}_\alpha^j \equiv A_\alpha^j \mathbf{I} - \frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j \quad (3)$$

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

$$\sum_{j=1}^N C_\alpha^j \boldsymbol{\mu}_\alpha^j = A_\alpha \mathbf{I} - \frac{1}{\rho_\alpha} \mathbf{t}_\alpha, \quad (4)$$

where  $\mathbf{t}_\alpha$  and  $\rho_\alpha$  are the stress tensor and the density for phase  $\alpha$ , respectively. For the case of a perfect fluid,  $\mathbf{t}_\alpha = -p_\alpha \mathbf{I}$  ( $p_\alpha$  denotes pressure of phase  $\alpha$ ), the right hand side of (4) reduces to the classical

thermodynamics concept of Gibbs energy (see e.g. [8]). This definition for the  $N$ th chemical potential seems to be motivated by convenience and is not easily reconciled with the classical definition, which is a scalar. In fact, as we shall show, if the  $N$ th chemical potential in the solid phase is chosen to be Bowen's chemical potential (3) and the solid matrix is strained, then Bowen's tensorial chemical potential does not satisfy characteristics 2 or 3.

The purpose of this note is to illustrate how sharper results such as Fick's law (2) can be obtained in terms of a non-relative chemical potential and to define a chemical potential which is a scalar and has the classical properties which Bowen's chemical potential does not.

## 2 Constitutive Relations

We begin with a medium composed of two phases, a liquid and a solid, in which each phase is composed of the same  $N$  constituents (it may be that the concentrations of some of these constituents in a phase are zero). The medium is viewed at the macroscale as  $2N$  overlaying continua. We assume that at the macroscale the solid phase is elastic and is saturated with a compressible, non-viscous fluid. Furthermore, we assume the medium is non-heat conducting and that interfacial effects are negligible. These assumptions are made purely for ease of exposition, and the results which follow can be extended to more general cases (see e.g [14, 11]). Thus, the behavior of this medium is postulated to be dictated by the following list of variables, which we henceforth refer to as "independent variables":

$$T, \rho_\alpha, \mathbf{E}_s, \mathbf{v}_{l,s}, \mathbf{u}_\alpha^j, C_\alpha^j, \nabla C_\alpha^j, \nabla \rho_\alpha, \quad j = 1, \dots, N-1, \quad \alpha = l, s \quad (5)$$

where  $T$  is temperature,  $\rho_l$  the density of the liquid phase,  $\mathbf{v}_{l,s}$  the velocity of the mass averaged bulk phase liquid relative to the solid phase,  $\mathbf{u}_\alpha^j$  the diffusive velocity of constituent  $j$  ( $\mathbf{u}_\alpha^j = \mathbf{v}_\alpha^j - \mathbf{v}_\alpha$ ),  $C_\alpha^j$  the mass concentration, and  $\mathbf{E}_s$  the macroscale solid-phase strain tensor which is defined in terms of the macroscale solid phase deformation gradient,  $\mathbf{F}_s$ , through the relation  $\mathbf{E}_s = 1/2(\mathbf{F}_s^T \mathbf{F}_s - \mathbf{I})$ .

It is normally assumed that the Helmholtz free energy of each phase  $A_\alpha$ , which is a dependent (or constitutive) variable, is a function of a subset of the independent variables. The choice of these subsets are based on the behavior of the system, observed experiments, and otherwise. For this formulation the following dependence is usually postulated:

$$\begin{aligned} A_s &= A_s(T, \mathbf{E}_s, \rho_s, C_s^j) \\ A_l &= A_l(T, \rho_l, C_l^j), \quad j = 1, \dots, N-1. \end{aligned} \quad (6)$$

The assumptions and details of the derivation of the entropy inequality in a form necessary for its exploitation are given in several papers [12, 11, 15]. Here we give the portion of the entropy inequality necessary for the following discussion. If  $\Lambda$  represents the total rate at which entropy is generated, and the thermodynamic pressures ( $p_l, p_s$ ) and the effective stress tensor ( $\mathbf{t}_s^e$ ) in the sense of Terzaghi [16] are given by

$$p_s = \rho_s^2 \frac{\partial A_s}{\partial \rho_s}, \quad p_l = \rho_l^2 \frac{\partial A_l}{\partial \rho_l}, \quad \mathbf{t}_s^e = \rho_s \mathbf{F}_s \frac{\partial A_s}{\partial \mathbf{E}_s} \mathbf{F}_s^T, \quad (7)$$

then we have:

$$\begin{aligned} T\Lambda &= \dots + \varepsilon_l \mathbf{d}_l : \left[ \mathbf{t}_l + p_l \mathbf{I} + \sum_{j=1}^N \rho_l^j \mathbf{u}_l^j \otimes \mathbf{u}_l^j \right] \\ &+ \varepsilon_s \mathbf{d}_s : \left[ \mathbf{t}_s + p_s \mathbf{I} - \mathbf{t}_s^e + \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \right] + \mathbf{v}_{l,s} \cdot \left[ p_l \nabla \varepsilon_l - \widehat{\mathbf{T}}_l \right] \\ &+ \sum_{\alpha=l,s} \sum_{j=1}^N \nabla \mathbf{u}_\alpha^j : \left[ \varepsilon_\alpha \mathbf{t}_\alpha^j - \varepsilon_\alpha \rho_\alpha^j A_\alpha^j \mathbf{I} + \varepsilon_\alpha \rho_\alpha^j \widetilde{\Pi}_\alpha^j \mathbf{I} \right] \end{aligned}$$

$$\begin{aligned}
& + \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \left[ \tilde{\mu}_\alpha^j \nabla(\varepsilon_\alpha \rho_\alpha^j) - \nabla(\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) - (\tilde{\mathbf{i}}_\alpha^j + \widehat{\mathbf{T}}_\alpha^j) \right] \\
& - \sum_{j=1}^N \left[ \widehat{e}_l^j \left( \tilde{\mu}_l^j + \frac{1}{2} \mathbf{u}_l^j \cdot \mathbf{u}_l^j + \frac{1}{2} \mathbf{v}_{l,s} \cdot \mathbf{v}_{l,s} \right) + \widehat{e}_s^j \left( \tilde{\mu}_s^j + \frac{1}{2} \mathbf{u}_s^j \cdot \mathbf{u}_s^j \right) \right] \\
& - \widehat{e}_l \left[ \frac{p_l}{\rho_l} - \sum_{j=1}^{N-1} C_l^j \tilde{\mu}_l^j + A_l \right] - \widehat{e}_s \left[ \frac{p_s}{\rho_s} - \sum_{j=1}^{N-1} C_s^j \tilde{\mu}_s^j + A_s \right] \geq 0, \tag{8}
\end{aligned}$$

where  $\tilde{\mu}_\alpha^N$  is defined to be zero,  $\varepsilon_\alpha$  is the volume fraction of phase  $\alpha$ ,  $\mathbf{d}_\alpha$  is the deformation rate tensor for phase  $\alpha$  given by  $\mathbf{d}_\alpha = \frac{1}{2}(\nabla \mathbf{v}_\alpha + (\nabla \mathbf{v}_\alpha)^T)$ ,  $\widehat{\mathbf{T}}_\alpha^j$  and  $\widehat{\mathbf{T}}_\alpha$  denote respectively the net gain of momentum for the  $j$ th component of the  $\alpha$ -phase and gain of momentum of the  $\alpha$ -phase due to interactions with the other phase,  $\tilde{\mathbf{i}}_\alpha^j$  measures the gain of momentum of the  $j$ th component through interactions with other species in the same phase, and  $\tilde{e}_\alpha^j$  and  $\widehat{e}_\alpha$  represent the net gain of mass of the  $j$ th component in the  $\alpha$ -phase and the net mass gained by the  $\alpha$ -phase from the other phase, respectively (these latter two quantities are related via  $\sum_{j=1}^N \tilde{e}_\alpha^j = \widehat{e}_\alpha$ ).

Within the Coleman and Noll framework of exploiting the entropy inequality pursued in [12],  $\mathbf{u}_\alpha^N$  and  $\nabla \mathbf{u}_\alpha^N$  are eliminated in terms of  $\mathbf{u}_\alpha^j$  and  $\nabla \mathbf{u}_\alpha^j$  using the interdependence of the concentrations and the diffusive velocities,  $\mathbf{u}_\alpha^j$ , through the constraint

$$\sum_{j=1}^N C_\alpha^j \mathbf{u}_\alpha^j = 0. \tag{9}$$

Using this with the fact that  $\tilde{e}_l^j = -\widehat{e}_s^j$  and  $\widehat{e}_l = -\widehat{e}_s$  allows us to rewrite (8) as

$$\begin{aligned}
T\mathbf{\Lambda} & = \dots + \varepsilon_l \mathbf{d}_l : \left[ \mathbf{t}_l + p_l \mathbf{I} + \sum_{j=1}^N \rho_l^j \mathbf{u}_l^j \otimes \mathbf{u}_l^j \right] \\
& + \varepsilon_s \mathbf{d}_s : \left[ \mathbf{t}_s + p_s \mathbf{I} - \mathbf{t}_s^e + \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \right] + \mathbf{v}_{l,s} \cdot \left[ p_l \nabla \varepsilon_l - \widehat{\mathbf{T}}_l \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \varepsilon_\alpha \nabla \mathbf{u}_\alpha^j : \left[ \mathbf{t}_\alpha^j - \frac{C_\alpha^j}{C_\alpha^N} \mathbf{t}_\alpha^N - \rho_\alpha^j (A_\alpha^j - A_\alpha^N - \tilde{\mu}_\alpha^j) \mathbf{I} \right] \\
& + \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left[ \tilde{\mu}_\alpha^j \nabla(\varepsilon_\alpha \rho_\alpha^j) - \nabla \left( \varepsilon_\alpha \rho_\alpha^j (A_\alpha^j - A_\alpha^N) \right) - (\tilde{\mathbf{i}}_\alpha^j + \widehat{\mathbf{T}}_\alpha^j) \right. \\
& \quad \left. + \frac{C_\alpha^j}{C_\alpha^N} (\widehat{\mathbf{i}}_\alpha^N + \widehat{\mathbf{T}}_\alpha^N) - \varepsilon_\alpha \mathbf{t}_\alpha^N \nabla \left( \frac{C_\alpha^j}{C_\alpha^N} \right) \right] \\
& - \sum_{j=1}^N \widehat{e}_l^j \left( \tilde{\mu}_l^j - \tilde{\mu}_s^j + \Delta^2 \right) \\
& - \widehat{e}_l \left( \frac{p_l}{\rho_l} - \frac{p_s}{\rho_s} + \sum_{j=1}^{N-1} (C_s^j \tilde{\mu}_s^j - C_l^j \tilde{\mu}_l^j) + A_l - A_s \right) \geq 0, \tag{10}
\end{aligned}$$

where  $\Delta^2 = (1/2)(\mathbf{u}_l^j \cdot \mathbf{u}_l^j + \mathbf{v}_{l,s} \cdot \mathbf{v}_{l,s} - \mathbf{u}_s^j \cdot \mathbf{u}_s^j)$ .

Here we present the pertinent results obtained after exploiting the entropy inequality using the Coleman and Noll method. Results which hold for all processes (including non-equilibrium) include

(see [12, 11]):

$$\mathbf{t}_l = -p_l \mathbf{I} - \sum_{j=1}^N \rho_l^j \mathbf{u}_l^j \otimes \mathbf{u}_l^j \quad \mathbf{t}_s = -p_s \mathbf{I} + \mathbf{t}_s^e - \sum_{j=1}^N \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j \quad (11)$$

$$\mathbf{t}_\alpha^j - \frac{C_\alpha^j}{C_\alpha^N} \mathbf{t}_\alpha^N = \rho_\alpha^j (A_\alpha^j - A_\alpha^N - \widetilde{\mu}_\alpha^j) \mathbf{I}. \quad (12)$$

Equation (11) gives the constitutive expressions for the bulk phase stress tensors given the assumed set of independent variables. Equation (12) gives the relationship between the chemical potential and stress tensor for the  $j$ th-component. Note in particular that Bowen's definition of chemical potential, (3), naturally arises from this expression.

For the system under consideration, equilibrium is defined when  $\{\mathbf{v}_{l,s}, \mathbf{u}_\alpha^j, \hat{\mathbf{e}}_l^j, \hat{\mathbf{e}}_l\}$  vanish. It is postulated that at equilibrium entropy is maximum and entropy generation is minimum. Therefore we must have  $(\partial\Lambda/\partial z_a)_e = 0$  and  $(\partial^2\Lambda/\partial z_a \partial z_b)_e$  positive definite where  $z_a$  and  $z_b$  denote any of the above set of variables. Application of these conditions to the entropy inequality (10) yields the following equilibrium results

$$p_l \nabla \varepsilon_l = \widehat{\mathbf{T}}_l \quad (13)$$

$$\operatorname{div} \left[ \varepsilon_\alpha \rho_\alpha^j \left( \widetilde{\mu}_\alpha^j \mathbf{I} - (A_\alpha^j - A_\alpha^N) \mathbf{I} + \left( \frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j - \frac{1}{\rho_\alpha^N} \mathbf{t}_\alpha^N \right) \right) \right] = \varepsilon_\alpha \rho_\alpha^j \nabla \widetilde{\mu}_\alpha^j \quad (14)$$

$$\widetilde{\mu}_l^j = \widetilde{\mu}_s^j \quad (15)$$

$$\frac{p_l}{\rho_l} + A_l - \sum_{j=1}^N C_l^j \widetilde{\mu}_l^j = \frac{p_s}{\rho_s} + A_s - \sum_{j=1}^N C_s^j \widetilde{\mu}_s^j \quad (16)$$

where in the derivation of (14) the momentum equation for species  $\varepsilon_\alpha \rho_\alpha^j \partial \mathbf{v}_\alpha^j / \partial t + \varepsilon_\alpha \rho_\alpha^j \mathbf{v}_\alpha^j \cdot \nabla \mathbf{v}_\alpha^j - \operatorname{div}(\varepsilon_\alpha \mathbf{t}_\alpha^j) - \varepsilon_\alpha \rho_\alpha^j \mathbf{g} = \widehat{\mathbf{T}}_\alpha^j + \widehat{\mathbf{i}}_\alpha^j$  was used to eliminate  $\widehat{\mathbf{i}}_\alpha^j + \widehat{\mathbf{T}}_\alpha^j$ .

Note that combining (12) and (14) yields

$$\nabla \widetilde{\mu}_\alpha^j = 0, \quad j = 1, \dots, N \quad \alpha = l, s. \quad (17)$$

The above result only implies that the relative chemical potential  $\widetilde{\mu}_\alpha^j = \mu_\alpha^j - \mu_\alpha^N$  is constant at equilibrium which clearly is not the sharpest result.

The results which hold near equilibrium are obtained by linearizing the equilibrium results in such a fashion as to retain positivity in the entropy inequality. In a general theory the coefficients can be linearized about all variables which are zero at equilibrium ( $z_a$  in the aforementioned set) (see e.g. [11, 12]). However here we pursue the approach of Bennethum and Cushman [17] and choose to linearize only about the one variable which gives a positive quadratic form in the entropy inequality. So for example, if  $z$  is a variable which vanishes at equilibrium and  $f$  is the coefficient of  $z$  within the entropy inequality, the linearization procedure gives an approximation for the near-equilibrium value of  $f$  as,

$$f_{neq} \approx f_{eq} + Cz \quad (18)$$

where  $C$  is the linearization constant. Using this procedure we then have

$$\operatorname{div} \left[ \varepsilon_\alpha \rho_\alpha^j \left( \widetilde{\mu}_\alpha^j \mathbf{I} - (A_\alpha^j - A_\alpha^N) \mathbf{I} + \frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j - \frac{1}{\rho_\alpha^N} \mathbf{t}_\alpha^N \right) \right] - \varepsilon_\alpha \rho_\alpha^j \nabla \widetilde{\mu}_\alpha^j = R_\alpha^j \mathbf{u}_\alpha^j. \quad (19)$$

$$\tilde{\mu}_l^j - \tilde{\mu}_s^j = K^j \tilde{e}_\alpha^j \quad j = 1, \dots, N-1 \quad (20)$$

where  $R_\alpha^j$  and  $K^j$  are material coefficients. Equation (20) is a form of an adsorption law, indicating that the rate of transfer of constituent  $j$  between phases is proportional to the difference in the relative chemical potentials with the coefficient  $K^j$  being identified with the kinetic constant of linear chemical adsorption (see e.g. [18]). As in (17) this consists of a sub-optimal result since the classical form of this law is identical except that the absolute chemical potentials replace the relative chemical potentials.

To get a generalized form of Fick's law, which states that the driving force for diffusive flow is the gradient of the relative chemical potential, we combine equations (19) and (12) to obtain

$$R_\alpha^j \mathbf{u}_\alpha^j = -\varepsilon_\alpha \rho_\alpha^j \nabla \tilde{\mu}_\alpha^j, \quad j = 1, \dots, N-1, \quad \alpha = l, s. \quad (21)$$

As mentioned in the introduction these results are in terms of the relative chemical potential, i.e. relative to the  $N$ th constituent. Obviously the choice of definition for the  $N$ th chemical potential affects the physical interpretation of any results derived from the above relations. But more than this, we note that equation (21) is particularly disturbing. It states that the diffusive flow is a function of *the labeling of the constituents* - clearly an undesirable result.

### 3 The Macroscale Chemical Potential and Sharper Results

Here we define two chemical potentials, one tensorial and one scalar, and compare the results of the Coleman and Noll method using both of these definitions. Subsequently, we sharpen the results of the previous section by using these two definitions of the chemical potential and by manipulating further those results to eliminate the relative chemical potentials.

#### 3.1 Two Definitions of the Macroscale Chemical Potential

We first define the  $N$ th chemical potential as in [12] and [11] to be Bowen's tensorial chemical potential [1, 13], i.e.

$$\boldsymbol{\mu}_\alpha^N \equiv A_\alpha^N \mathbf{I} - \frac{1}{\rho_\alpha^N} \mathbf{t}_\alpha^N. \quad (22)$$

By using (12), we then get a macroscale definition for all constituents:

$$\boldsymbol{\mu}_\alpha^j = A_\alpha^j \mathbf{I} - \frac{1}{\rho_\alpha^j} \mathbf{t}_\alpha^j \quad j = 1, \dots, N. \quad (23)$$

Multiplying through by  $C_\alpha^j$  and summing on  $j$  from 1 to  $N$ , we find that near equilibrium,

$$\sum_{j=1}^N C_\alpha^j \boldsymbol{\mu}_\alpha^j = A_\alpha \mathbf{I} - \frac{1}{\rho_\alpha} \mathbf{t}_\alpha \quad (24)$$

where we have neglected second order terms involving the diffusive velocity and used the following relationship between  $\mathbf{t}_\alpha$  and  $\mathbf{t}_\alpha^j$  (see [12, 11])

$$\mathbf{t}_\alpha = \sum_{j=1}^N (\mathbf{t}_\alpha^j - \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j). \quad (25)$$

Recall that as pointed out in the introduction, in the case of a perfect fluid in which  $\mathbf{t}_\alpha = -p_\alpha \mathbf{I}$  the right hand side of (24) reduces to the classical Gibbs energy. Eliminating the stress tensors in (24)

using equations (11) at equilibrium, and then combining this result with equilibrium conditions (15) and (16) gives

$$\boldsymbol{\mu}_l^j - \boldsymbol{\mu}_s^j = \frac{p_s}{\rho_s} \mathbf{I} + \frac{1}{\rho_s} \mathbf{t}_s = \frac{1}{\rho_s} \mathbf{t}_s^e \quad j = 1, \dots, N. \quad (26)$$

This tells us that when the solid phase is stressed at equilibrium the macroscale tensorial chemical potential of a single constituent co-existing in two phases is not constant. This is in direct contrast to classical microscopic results, which state that the scalar chemical potential of a single species in two phases is constant at equilibrium. This result is due to the definition of the *macroscale* tensorial chemical potential, (22), and in no way should this be applied at the microscale. We may interpret the right hand side of (26), the effective stress tensor of the solid phase, as being an external source. It is nonzero, for example, when an external load is applied to the medium. Also note that if the solid phase is replaced by, e.g., another immiscible perfect fluid, we would get, by following the same procedure, equality between the two tensorial chemical potentials.

By choosing the definition of the  $N$ th chemical potential slightly differently we can reproduce classical Gibbsian results in form, namely the equality of chemical potentials at equilibrium. So alternatively, let

$$\boldsymbol{\mu}_l^N \equiv A_l^N \mathbf{I} - \frac{1}{\rho_l^N} \mathbf{t}_l^N \quad (27)$$

$$\boldsymbol{\mu}_s^N \equiv A_s^N \mathbf{I} - \frac{1}{\rho_s^N} \mathbf{t}_s^N + \frac{1}{\rho_s} \mathbf{t}_s^e \quad (28)$$

which, by using (12), gives

$$\boldsymbol{\mu}_l^j = A_l^j \mathbf{I} - \frac{1}{\rho_l^j} \mathbf{t}_l^j, \quad (29)$$

$$\boldsymbol{\mu}_s^j = A_s^j \mathbf{I} - \frac{1}{\rho_s^j} \mathbf{t}_s^j + \frac{1}{\rho_s} \mathbf{t}_s^e, \quad j = 1, \dots, N. \quad (30)$$

We next show that these definitions of chemical potentials are scalar multiples of the identity. Beginning with the relationship between the stress tensors of the components and phases (25) and eliminating  $\sum_{j=1}^N \mathbf{t}_\alpha^j$  using (12) gives

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

where we have also used (11) to eliminate  $\mathbf{t}_\alpha$ . This tells us that  $\mathbf{t}_l^N$  and  $(\rho_s)^{-1} \mathbf{t}_s^e - (\rho_s^N)^{-1} \mathbf{t}_s^N$  are scalar multiples of the identity and hence  $\boldsymbol{\mu}_\alpha^N$  are as well. Since  $\tilde{\mu}_\alpha^j$  are scalar quantities, we can conclude that this second definition for chemical potentials, which we label  $\mu_\alpha^j$ , are *scalar chemical potentials*, and consequently we define  $\mu_\alpha^j \mathbf{I} \equiv \boldsymbol{\mu}_\alpha^j$  to distinguish it from Bowen's tensorial chemical potential which we continue to write in bold face. Multiplying (29, 30) by  $C_\alpha^j$  and then summing on  $j$  gives us the near-equilibrium relationship analogous to (24)

$$\sum_{j=1}^N C_\alpha^j \mu_\alpha^j = A_\alpha + \frac{1}{\rho_\alpha} p_\alpha = G_\alpha, \quad \alpha = l, s, \quad (31)$$

where  $G_\alpha$  is the Gibbs energy for phase  $\alpha$ . Moreover, if we define the pressure of the  $j$ th component,  $p_\alpha^j$ , as

$$\begin{aligned} -p_l^j \mathbf{I} &\equiv \mathbf{t}_l^j \\ -p_s^j \mathbf{I} &\equiv \mathbf{t}_s^j - C_s^j \mathbf{t}_s^e, \quad j = 1, \dots, N, \end{aligned}$$

then (29) and (30) can be expressed as

$$A_\alpha^j + \frac{1}{\rho_\alpha^j} p_\alpha^j = \mu_\alpha^j \quad \alpha = l, s \quad (32)$$

which shows consistency with (31). Summing (32) over all components and comparing with (31) implies  $p_\alpha = \sum_{j=1}^N p_\alpha^j$  so that in particular, this gives us an alternative way of interpreting  $p_s$ .

Using (31) in equilibrium condition (16) gives  $\mu_l^N = \mu_s^N$ . This together with (15) gives

$$\mu_l^j = \mu_s^j \quad (33)$$

which is consistent in form with classical Gibbsian results. Comparing the two definitions of the tensorial and scalar chemical potentials (23), (29, 30), we arrive at the following relationships:

$$\mu_l^j \mathbf{I} = \boldsymbol{\mu}_l^j \quad (34)$$

$$\mu_s^j \mathbf{I} = \boldsymbol{\mu}_s^j + \frac{1}{\rho_s} \mathbf{t}_s^e, \quad j = 1, \dots, N. \quad (35)$$

As an aside, by combining this result with definition (1) we recover the definition of  $\tilde{\mu}_\alpha^j$  in terms of the scalar chemical potential,

$$\tilde{\mu}_\alpha^j \mathbf{I} \equiv \frac{\partial A_\alpha}{\partial C_\alpha^j} \mathbf{I} \equiv \mu_\alpha^j - \mu_\alpha^N = (\mu_\alpha^j - \mu_\alpha^N) \mathbf{I}. \quad (36)$$

By incorporating the effective stress tensor into the definition of the scalar chemical potential, we have in some sense incorporated an “external” source. Physically, both  $\mu_\alpha^j$  and  $1/3\text{tr}(\boldsymbol{\mu}_\alpha^j)$  may be interpreted as a measure of the amount of energy required to place a particle into the system. But we must keep in mind the slight difference between them, i.e. that the scalar definition incorporates the amount of energy associated with  $\text{tr}(\mathbf{t}_s^e)$ . When viewing the effective stress tensor as a source term, we see that the scalar chemical potential is analogous to the well-known “gravi-chemical potential” of classical thermodynamics whose definition incorporates the energy due to gravity.

### 3.2 Sharper Results

Using the above definitions for the  $N$ th chemical potential we derive the “absolute” (non-relative) form of non-equilibrium result (12), equilibrium results (15), (16), (17), and near-equilibrium result (21). To obtain the non-relative form of the nonequilibrium result (12) and equilibrium results (15) and (16) requires only that the appropriate definition of the chemical potential be substituted into the relative form of these equations. These results were presented in Section 3.1 (see (23, 27, 30), (26, 33), and (24, 31) respectively). However, the derivation of the absolute form of equilibrium result (17) requires further manipulation. First note that combining (36) with (17) implies only the relative equilibrium result

$$\text{div}(\boldsymbol{\mu}_\alpha^j - \boldsymbol{\mu}_\alpha^N) = \nabla(\mu_\alpha^j - \mu_\alpha^N) = \mathbf{0}. \quad (37)$$

To derive the absolute form of the above equation for the scalar chemical potentials, begin by taking the gradient of the constitutive relation for  $A_l$  (6). Using the chain rule and the constraint  $\sum_{j=1}^N C_\alpha^j = 1$  we get

$$\nabla A_l = \frac{p_l}{(\rho_l)^2} \nabla \rho_l + \sum_{j=1}^{N-1} \tilde{\mu}_l^j \nabla C_l^j = \frac{p_l}{(\rho_l)^2} \nabla \rho_l + \sum_{j=1}^N \mu_l^j \nabla C_l^j. \quad (38)$$

By taking the gradient of (31) and setting  $\alpha = l$  we also have

$$\nabla A_l = \frac{p_l}{(\rho_l)^2} \nabla \rho_l - \frac{1}{\rho_l} \nabla p_l + \sum_{j=1}^N (C_l^j \nabla \mu_l^j + \mu_l^j \nabla C_l^j). \quad (39)$$



Eliminating  $\nabla A_l$  via (38) and (39) yields

$$\sum_{j=1}^N C_l^j \nabla \mu_l^j = \frac{1}{\rho_l} \nabla p_l, \quad (40)$$

which is the Gibbs-Duhem relation for the liquid phase. By eliminating  $\widehat{\mathbf{T}}_l$  from (13) using the momentum equation for the liquid phase at equilibrium,  $-\text{div}(\varepsilon_l \mathbf{t}_l) - \varepsilon_l \rho_l \mathbf{g} = \widehat{\mathbf{T}}_l$ , and then eliminating  $\mathbf{t}_l$  using (11) gives the classical hydrostatic relation  $\nabla p_l = \rho_l \mathbf{g}$  so that (40) can be re-written as

$$\sum_{j=1}^N C_l^j \nabla \mu_l^j = \mathbf{g}.$$

If the scalar version of (37) is multiplied by  $C_l^j$  and summed over all constituents, we find, by using the above result, that  $\nabla \mu_l^N = \mathbf{g}$ . Combining this with (33) and (37) gives

$$\nabla \mu_l^j = \nabla \mu_s^j = \mathbf{g}, \quad j = 1, \dots, N. \quad (41)$$

The above result provides a sharper description of equilibrium condition (17) and shows consistency with the classical result of Gibbsian thermodynamics which states that in the absence of gravity, the chemical potential is constant at equilibrium. The corresponding result for the tensorial chemical potential can be easily obtained by combining the above equation with (34, 35)

$$\text{div} \boldsymbol{\mu}_l^j = \mathbf{g} \quad \text{div} \boldsymbol{\mu}_s^j = \mathbf{g} - \frac{1}{\rho_s} \text{div} \mathbf{t}_s^e \quad (42)$$

which confirms the interpretation of the effective stress tensor as being a source at equilibrium for Bowen's chemical potential.

Next we turn to the task of sharpening the near equilibrium results for constituent adsorption, (20), and for Fick's laws, (21). To derive an improved form of the former, we begin by rewriting the exchange of mass term  $\widehat{e}_l^j$  of the entropy inequality. Neglecting terms involving products of relative velocities in (10) we have

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

Note that by using (15) and (33), we can show that each coefficient (given in square brackets) is zero at equilibrium. The last coefficient is independent of  $j$ , so it will contribute to the coefficient of  $\widehat{e}_l$  in entropy inequality (10) (recall that  $\sum_{j=1}^N \widehat{e}_l^j = \widehat{e}_l$ ). Linearizing the remaining coefficient using equation (18) yields

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

The above result is an improved description of near equilibrium adsorption given in Section 2, (20). Again using (34, 35) to express the adsorption law in terms of the tensorial chemical potential we obtain

$$K_l^j \widehat{e}_l^j \mathbf{I} = \boldsymbol{\mu}_s^j - \boldsymbol{\mu}_l^j + \frac{1}{\rho_s} \mathbf{t}_s^e \quad j = 1, \dots, N$$

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

We now derive an improved form of Fick's law. Begin with the form of the entropy inequality given by equation (8). Using relationship (9) we can rewrite the two terms involving  $\mathbf{u}_\alpha^j$  and  $\nabla \mathbf{u}_\alpha^j$  as

$$\begin{aligned} T\mathbf{\Lambda} = & \dots + \sum_{\alpha=l,s} \sum_{j=1}^N \nabla \mathbf{u}_\alpha^j : \left[ \varepsilon_\alpha \mathbf{t}_\alpha^j - \varepsilon_\alpha \rho_\alpha^j A_\alpha^j \mathbf{I} + \varepsilon_\alpha \rho_\alpha^j \mu_\alpha^j \mathbf{I} \right] \\ & + \sum_{\alpha=l,s} \sum_{j=1}^N \mathbf{u}_\alpha^j \cdot \left[ \mu_\alpha^j \nabla (\varepsilon_\alpha \rho_\alpha^j) - \nabla (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) - (\tilde{\mathbf{i}}_\alpha^j + \hat{\mathbf{T}}_\alpha^j) \right] + \dots \end{aligned} \quad (43)$$

Note that we cannot obtain equilibrium results from the above form of the entropy inequality because  $\nabla \mathbf{u}_\alpha^j$  and  $\mathbf{u}_\alpha^j$  are not independent (recall equation (9)). Thus the equilibrium results obtained by applying standard Coleman and Noll arguments cannot be read off directly from this form of the entropy inequality.

Next we use (18) to linearize the coefficient of  $\mathbf{u}_\alpha^j$  about equilibrium. As before, the exchange of momentum terms,  $\tilde{\mathbf{i}}_\alpha^j + \hat{\mathbf{T}}_\alpha^j$ , are eliminated using the momentum equation. If we neglect inertial effects we have

$$\begin{aligned} & \left[ -\varepsilon_\alpha \rho_\alpha^j \nabla \mu_\alpha^j + \operatorname{div} \left( \varepsilon_\alpha \rho_\alpha^j (\mu_\alpha^j - A_\alpha^j) \mathbf{I} + \varepsilon_\alpha \mathbf{t}_\alpha^j \right) + \varepsilon_\alpha \rho_\alpha^j \mathbf{g} \right]_{neq} \\ & = \left[ -\varepsilon_\alpha \rho_\alpha^j \nabla \mu_\alpha^j + \operatorname{div} \left( \varepsilon_\alpha \rho_\alpha^j (\mu_\alpha^j - A_\alpha^j) \mathbf{I} + \varepsilon_\alpha \mathbf{t}_\alpha^j \right) + \varepsilon_\alpha \rho_\alpha^j \mathbf{g} \right]_{eq} + R_\alpha^j \mathbf{u}_\alpha^j, \quad j = 1, \dots, N. \end{aligned}$$

Using the definition of the scalar chemical potential (29, 30), equilibrium condition (41), and the fact that  $\mathbf{t}_s^e|_{neq} = \mathbf{t}_s^e|_{eq}$  we find

$$R_\alpha^j \mathbf{u}_\alpha^j = -\varepsilon_\alpha \rho_\alpha^j (\nabla \mu_\alpha^j - \mathbf{g}) \quad j = 1, \dots, N, \quad (44)$$

i.e. a form of Fick's law which is identical in form to the classical result. Using relations (34, 35) the above form of Fick's law can be written in terms of the tensorial chemical potential as

$$R_l^j \mathbf{u}_l^j = -\varepsilon_l \rho_l^j (\operatorname{div} \boldsymbol{\mu}_l^j - \mathbf{g}), \quad (45)$$

$$R_s^j \mathbf{u}_s^j = -\varepsilon_s \rho_s^j (\operatorname{div} \boldsymbol{\mu}_s^j - \mathbf{g}) - \varepsilon_s C_s^j \operatorname{div} \mathbf{t}_s^e \quad j = 1, \dots, N. \quad (46)$$

The above result is consistent with equilibrium relation (42) and in particular, indicates that stressing the solid phase affects the diffusive velocity of solid constituents.

## 4 Conclusions

Within the framework of hybrid mixture theory for multicomponent single phase flow in an elastic porous medium, we derived macroscale results which reproduce classical Gibbsian thermodynamics. In particular, we obtained results involving the chemical potential, such as Fick's law and the adsorption/desorption relationship between phases, which are not dependent upon the labeling of the constituents. This was accomplished by re-examining the definition of the macroscale chemical potential, using the Gibbs-Duhem relation with additional equilibrium results, and modifying the linearization procedure.

The definition of the macroscale chemical potential significantly affects the form of the macroscale results. We discussed the consequences of two alternative definitions: a scalar which mimics in form classical Gibbsian thermodynamics, and a tensorial quantity originally introduced by Bowen. We showed that the difference between the two chemical potentials for the solid phase involves the macroscale effective stress tensor, which can be viewed as external sources when using the tensorial definition for the chemical potential.

Finally, we note that the modification of the linearization procedure involved linearizing about variables which are not necessarily independent. This is an extension to what has been done traditionally [14, 19, 20] where coefficients of constitutive variables such as  $D_s \varepsilon_l / Dt$  (material time derivative of the volume fraction following the solid phase) and  $\hat{e}^l$  are linearized about equilibrium. Here we have linearized about variables which are not constitutive, but are explicitly related to other independent variables, e.g.,  $\mathbf{u}_\alpha^N$ . In fact, one can linearize the coefficient of any variable (independent, constitutive, or directly dependent), using equation (18), however it may not be trivial to determine the coefficient at equilibrium. It should be noted that this philosophy cannot be applied when deriving nonequilibrium or equilibrium results, as the argument requires the entropy inequality to be expressed as linear combinations of variables which are independent.

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