Multi-component Multiphase Flow

Brian Seguin · Noel J. Walkington

Abstract An axiomatic foundation for models of multi-component multiphase porous flow appearing ubiquitously in the engineering literature is developed. This unifies and extends various disparate and empirical formulations appearing in the literature. Constitutive restrictions are derived from an appropriate statement of the second law of thermodynamics, and the corresponding dissipation inequalities establish stability of solutions. The convexity properties and variational structure of these models are elucidated.

1 Introduction

A thermodynamically consistent system of balance laws and constitutive hypotheses are developed which realize the equations used to model geophysical flows involving multi-component, mulitphase, flows in a porous media. These equations model the gross properties of these flows since a precise description of the physical system involved is neither available nor tractable. Specifically:

Brian Seguin
Department of Mathematics and Statistics, Loyola University Chicago,
Chicago , IL 60660
Tel.: +1-773-508-3558
E-mail: bseguin@luc.edu

Noel J. Walkington
Department of Mathematics, Carnegie
Mellon University,
Pittsburgh, PA 15213
Tel.: +1412-268-6291
E-mail: noelw@andrew.cmu.edu

- Even in the case of only a few components forming a small number of phases, precise balances of mass, force, and energy, for each component and phase would result in an enormous system of coupled partial differential equations (PDE's). Three dimensional numerical simulation involving even one of these difficulties would greatly exceed the capability of today's computers.

  To mitigate this issue it is postulated that thermodynamic equilibrium occurs on a time scale much shorter than the pore-to-pore transport. Classical thermodynamics can then be used to determine the composition and volume fraction of each phase within the pores. With this approximation, precise statements of the balance laws at the pore scale are approximated using constitutive relations derived from classical thermodynamics; this tacitly neglects pore scale transfer of momentum due to phase changes.

- Geophysical flows can take place over many kilometers and a precise description of the pore structure is not available. The porous medium contains features which span multiple length scales, and only gross properties, such as the pore ratio and permeability, can be estimated by interpolating and extrapolating available geological data.

  In the absence of a precise description of the medium, macroscopic transport of mass, momentum, and energy, are modeled using phenomenological laws motivated by homogenization theory. Gross properties of the porous medium are then used to estimate the coefficients in the corresponding Fick, Darcy, and Fourier laws.

Using Darcy's law to model momentum balances replaces vector-valued partial differential equations with algebraic relations. This results in a substantial reduction in the computational resources needed to simulate these flows, and results in coarse grained models where (i) a scalar transport equation is used to represent the balance of mass for each conserved component (species or molecule), and (ii) a single scalar equation is used to represent the balance of energy if the system is not isothermal. Currently it is accepted that these models are computationally tractable and provide acceptable predictive capability [9,11]. These considerations motivated the continuum theory below which utilizes ideas found ubiquitously in the engineering literature to yield macroscopic approximations of these problems.

1.1 Background

The literature on the modeling and simulation of multiphase porous flow is vast. See, for example, the monographs [9,11]. The ideas introduced above to develop macroscopic continuum descriptions appear ubiquitously. However, frequently these are developed within a specific context where the delineation between kinematic assumptions, constitutive assumptions, and balance laws, is blurred. In this work care is taken to provide precise statements that distinguish between balance and constitutive laws, and to develop constitutive laws which are consistent with the second law of thermodynamics. By doing so, we are able to expose essential variational and other mathematical structures that assist in the formulation of effective numerical schemes. This provides a formulation which encompass essentially all of the models for porous flow in a rigid medium that appear in the engineering literature.

Continuum descriptions of porous flow formulate the problem in the context of mixture theory where the properties of each constituent are described by functions taking values at every point. Classical mixture theory [6,12,22] treats each component as a separate continuum with its own motion and balance laws. This results in a large system of coupled PDE's which model many of the fine scale interactions among the phases. Numerical solution of these systems for geological problems is not tractable, so in the engineering literature coarse scale models are formulated by assuming that local thermodynamic equilibrium is attained at the microscopic pore level. This assumption results in a substantial simplification (balance laws/PDE's are replaced by constitutive assumptions/algebraic relations) and can be viewed as a separation of time scales whereby equilibrium at the microlevel is achieved at a much faster rate than at the macrolevel. In this context constitutive descriptions of the mixture are derived using the laws of classical thermodynamics. Below care is taken to elucidate how classical thermodynamical models for the microstructure can be integrated into a consistent formulation of the second law for deformable continua given by the Coleman–Noll procedure [10].

1.2 Classical Thermodynamics

Since there is a substantial schism between the classical and continuum notation, formulation, and statement of thermodynamic principles, in this section the essential elements of classical thermodynamics entering our continuum theory are reviewed. A fundamental outcome of the theory is that the components (constituents) combine to form phases which constitute a classical *homogeneous* thermodynamic system. Identities guaranteed by the structure theorem for homogeneous functions will be used in an essential fashion to integrate the classical and continuum statements of the second law.

Classical thermodynamics postulates that for a mixture with mass (or moles) $\tilde{M}_c$ of a component c, in a volume $\tilde{V}$, with (internal) energy $\tilde{E}$, there exists a concave function, the entropy, $S = \hat{S}(\tilde{E}, \tilde{V}, \{\tilde{M}_c\}_{c=1}^{N_c})$ for which $\partial S/\partial \tilde{E} > 0$ [21]. In isolation, it is postulated that the system evolves to an equilibrium state for which the entropy is maximized subject to the constraints that the energy, volume, and mass of each component are fixed. In this context there exist Lagrange multipliers $\left(1/\theta, p/\theta, \{\mu_c/\theta\}_{c=1}^{N_c}\right)$ dual to the constraints for which

$$\theta \frac{\partial S}{\partial \tilde{E}} = 1, \qquad \theta \frac{\partial S}{\partial \tilde{V}} = p, \qquad \theta \frac{\partial S}{\partial \tilde{M}_c} = -\mu_c,$$

and have the physical interpretation of temperature θ, pressure p, and chemical potentials μ_c. When the mixture takes the form of a *homogeneous* phase the entropy satisfies

$$\hat{S}(\lambda \tilde{E}, \lambda \tilde{V}, \{\lambda \tilde{M}_c\}_{c=1}^{N_c}) = \lambda \hat{S}(\tilde{E}, \tilde{V}, \{\tilde{M}_c\}_{c=1}^{N_c}), \qquad \lambda \geq 0,$$

and Euler's representation theorem for homogeneous functions gives,

$$\theta S = \tilde{E} + p\tilde{V} - \sum_{c=1}^{N_c} \mu_c \tilde{M}_c.$$

In a continuum description of a porous flow, if $V \subset \Omega$ is a subset of the porous medium and $\tilde{V} \subset V$ denotes the volume occupied by this phase, then scaling with $\lambda = 1/|V|$ and localizing gives $\eta = \hat{S}\big(e, s, \{M_c\}_{c=1}^{N_c}\big)$, where

$$(\eta, e, s, M_c) = \lim_{|V| \to 0} (1/|V|)\big(S, \tilde{E}, \tilde{V}, \tilde{M}_c\big).$$

Here (η, e, M_c) are the entropy, internal energy, and mass of component c in this phase *per unit volume of Ω*, and $s \in [0, 1]$ is the saturation (volume fraction) of this phase. If e, s, and $M_c : \Omega \to \mathbb{R}$ are defined on Ω, and $\eta = \hat{S}\big(e, s, \{M_c\}_{c=1}^{N_c}\big)$, then the identity

$$\eta \nabla \theta - s \nabla p + \sum_{c=1}^{N_c} M_c \nabla \mu_c = \mathbf{0}, \tag{1}$$

follows from the homogeneity of $\hat{S}$.

Frequently the dominant heat capacity is that of the medium and the fluids in the pores rapidly take on its temperature. In this "isothermal" setting it is convenient to introduce the Helmholtz free energy $\psi = e - \theta \eta$. Writing the free energy as $\psi = \hat{\Psi}(\theta, s, \{M_c\}_{c=1}^{N_c})$, then $\hat{\Psi}$ is convex and homogeneous in the last variables, and takes the form

$$\hat{\Psi}(\theta, s, \{M_c\}_{c=1}^{N_c}) = -p\, s + \sum_{c=1}^{N_c} \mu_c M_c, \quad \text{with} \quad \frac{\partial \Psi}{\partial s} = -p, \quad \frac{\partial \Psi}{\partial M_c} = \mu_c, \tag{2}$$

and $\partial \psi / \partial \theta = -\eta$. The formulae in this section may be viewed as instances of the statements $dE = T\, dS - p\, dV + \mu\, dN$ and $dA = S\, dT - p\, dV + \mu\, dN$ which appear ubiquitously in classical thermodynamics texts.

1.3 Scaling, Homogenization, and Darcy Laws

Motivated by homogenization theory [1,2,3,19], porous flow models utilize Darcy laws as proxies for momentum equations of the fluids. The Darcy law postulates that the macroscopic velocity of a fluid is a linear function of the pressure gradient. Scaling the velocity by the density gives the mass flux vector appearing in the balance(s) of mass. In addition, the Darcy velocity also determines the viscous dissipation which appears as a source term in the energy equation. For the geological problems under consideration the porosity may vary substantially and the porous flow equations may degenerate in regions where the strata is impervious or one fluid is displaced by another. In this section a simple example is presented to explicitly illustrate how the mass flux and viscous dissipation scale with the saturation (volume available to a fluid).

If $Y^\epsilon = [-\epsilon, \epsilon]^3$ and $Y_f^\epsilon = \{|z| \le \epsilon s\}$ as in Figure 1, then Poiseuille's solution of the Stokes' equations,

$$-\operatorname{div}(2\mu D(\mathbf{v}) - pI) = \mathbf{0}, \qquad \operatorname{div}(\mathbf{v}) = 0,$$

in Y_f^ϵ with $p = \bar{p} + p_1' x + p_2' y$ affine is

$$\mathbf{v}_\epsilon(x, y, z) = \left(\frac{z^2 - (\epsilon s)^2}{2\mu} \right) \nabla p, \qquad |z| \le \epsilon s.$$
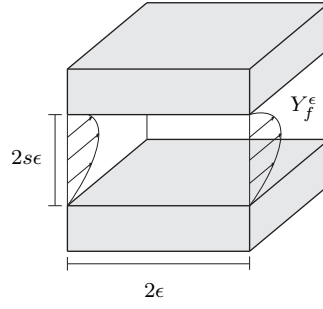
Fig. 1 Poiseuille flow in a pore Y^ϵ.

Consider then a porous medium $\Omega \subset \mathbb{R}^3$ containing a periodic array of these cells with one of the fluids occupying the pores Y_f^ϵ. When the complement $Y^\epsilon \setminus Y_f^\epsilon$ is essentially immobile (medium and/or other fluids bound to the medium) the fluid in Y_f^ϵ will exhibit a Poiseuille flow. If the fluid has mass density ρ then the mass per unit volume of Ω is $M = \rho s$, and the macroscopic mass flux per unit area in Ω is

$$\mathbf{q} = \frac{1}{2\epsilon} \int_{-\epsilon s}^{s\epsilon} \rho \mathbf{v}_\epsilon \, dz = \left(\frac{-\rho \epsilon^2 s^3}{3\mu} \right) \nabla p = M \left(\frac{-\epsilon^2 s^2}{3\mu} \right) \nabla p \equiv M\mathbf{v},$$

so that the corresponding Darcy law is $\mathbf{v} = -(s^2 k/\mu)\nabla p$ with permeability $k = \epsilon^2/3$. For geological flows the small parameter $\epsilon \ll 1$ gives rise to small Darcy velocities. In this situation inertia is frequently negligible, and this is assumed in the force balance postulated in Section 2.1.

The dissipation per unit volume of Ω is

$$\mathcal{D} = \frac{1}{|Y^\epsilon|} \int_{Y_f^\epsilon} 2\mu |D(\mathbf{v}_\epsilon)|^2 \, dv = \left(\frac{\epsilon^2 s^3}{3\mu} \right) |\nabla p|^2 \equiv s\mathbf{f} \cdot \mathbf{v},$$

where $\mathbf{f} = -s\nabla p$ represents the force the medium exerts on the fluid due to the no-slip condition which, in turn, gives rise to the velocity gradients responsible for dissipation. Eliminating the pressure gives $\mathbf{f} = (sk/\mu)^{-1}\mathbf{v}$; this scaling motivated the constitutive laws appearing below in Section 3.3. In particular, that the force scales with the inverse of the saturation.

2 Balance Laws

The porous medium is assumed to be rigid and to reside in a domain $\Omega \subset \mathbb{R}^d$. At each point the fraction of volume occupied by the medium, $s_0 : \Omega \to [0,1]$, is specified. Unless explicitly stated otherwise, all densities are taken per unit volume of Ω. The presence of multiple components and phases necessitates the introduction of a large number of variables which are collected here for ease of reference.

It is assumed that the volume and motion of each phase are characterized by the following.

- $s_\pi : \Omega \to [0,1]$ represents the volume fraction of phase $1 \leq \pi \leq N_p$. With s_0 denoting the volume fraction of the porous medium it is immediate that $\sum_{\pi=0}^{N_p} s_\pi = 1$. Writing $\mathbf{s} = (s_1, \ldots, s_{N_p}) \in [0,1]^{N_p}$, this relation becomes $\mathbf{s} \cdot \mathbf{1} = 1 - s_0$, where $\mathbf{1} = (1, \ldots, 1) \in \mathbb{R}^{N_p}$.
- $\mathbf{v}_\pi : \Omega \to \mathbb{R}^d$ represents the velocity field which transports the mass and internal energy of each phase, $1 \leq \pi \leq N_p$.

Laws will be postulated for the balance of the mass of each component, force balance, energy balance, and an entropy imbalance. Mass balance involves the following quantities.

- $M_{c\pi} : \Omega \to [0,\infty)$ represents the mass of component c in phase π per unit volume; the matrix of pore mass densities is denoted as $M = [M_{c\pi}] \in [0,\infty)^{N_c \times N_p}$.
- $m_c : \Omega \to [0,\infty)$ is the mass per unit volume of component $1 \leq c \leq N_c$; the vector of mass densities is denoted as $\mathbf{m} = (m_1, \ldots, m_{N_c}) \in [0,\infty)^{N_c}$. Clearly $\mathbf{m} = M\mathbf{1}$. The mass per unit volume of phase π is $\rho_\pi = \sum_{c=1}^{N_c} M_{c\pi}$.
- $\mathbf{h}_c : \Omega \to \mathbb{R}^d$ represents the mass flux due to diffusion, $1 \leq c \leq N_c$.
- $q_c : \Omega \to \mathbb{R}$ is the supply (sinks and sources) of component c.

Next we list the quantities appearing in the balance of forces. A fundamental assumption in our formulation is that the phases are viscous fluids, so rather than postulating a stress tensor, pressures and viscous forces are stipulated for each phase, as well as forces describing the interactions between the phases.

- $p_\pi : \Omega \to \mathbb{R}$ represents the pressure (force per unit area in phase π) of phase $1 \leq \pi \leq N_p$.
- $\mathbf{f}_\pi : \Omega \to \mathbb{R}^d$ represents the viscous force per unit volume of Ω the medium exerts upon phase π, $1 \leq \pi \leq N_p$.
- $\mathbf{f}_{\pi\pi'} : \Omega \to \mathbb{R}^d$ represents the viscous forces per unit volume of Ω that phase π exerts upon phase π', $1 \leq \pi, \pi' \leq N_p$.
- $\mathbf{b}_\pi : \Omega \to \mathbb{R}^d$ is the body force acting on phase π per unit volume of phase π.

Quantities such as energy and heat appear in the balance of energy.

- $e : \Omega \to \mathbb{R}$ is the internal energy per unit volume of Ω.
- $e_\pi : \Omega \to \mathbb{R}$ with $1 \leq \pi \leq N_p$ represents the internal energy of phase π per unit volume of Ω, and e_0 denotes the internal energy of the medium. The vector of internal energy densities is denoted as $\mathbf{e} = (e_0, e_1, \ldots, e_{N_p}) \in \mathbb{R}^{N_p+1}$.
- $\mathbf{q} : \Omega \to \mathbb{R}^d$ represents the flux of thermal energy due to heat conduction.
- $\mu_c : \Omega \to \mathbb{R}$ represents the chemical potential of each component $1 \leq c \leq N_c$.
- $r : \Omega \to \mathbb{R}$ is supply of energy (radiation absorbed or emitted).

Finally, we list the quantities appearing in the entropy imbalance.

- $\eta : \Omega \to \mathbb{R}$ is entropy per unit volume of Ω.
- $\eta_\pi : \Omega \to \mathbb{R}$ represents the entropy of phase π per unit volume of Ω.
- $\theta : \Omega \to (0,\infty)$ represents the (absolute) temperature. The inverse temperature will be denoted by $\beta = 1/\theta$.

2.1 Balances for inertialess continua

Under the assumption that effects due to inertia are negligible and that the medium is a rigid, chemically inert heat conductor, we postulate the following balance laws.

1. *Mass Balances:* For each control volume $V \subset \Omega$

$$\frac{d}{dt} \int_V m_c \, dv = \int_V q_c \, dv - \int_{\partial V} \Big(\mathbf{h}_c + \sum_{\pi=1}^{N_p} M_{c\pi} \mathbf{v}_\pi \Big) \cdot \mathbf{n} \, da \qquad 1 \leq c \leq N_c,$$

where $\mathbf{n}$ is the unit outward normal to the boundary of V. The local form of these balance laws are

$$(m_c)_t + \text{div}\Big(\sum_{\pi=1}^{N_p} M_{c\pi} \mathbf{v}_\pi + \mathbf{h}_c \Big) = q_c. \tag{3}$$

2. *Force Balances:* For each control volume $V \subset \Omega$, let V_π be the volume occupied by phase π in V. Assume for each $P \subset \{1, \ldots, N_p\}$ that

$$\mathbf{0} = \sum_{\pi \in P} \Big[\int_V \Big(-\mathbf{f}_\pi - \sum_{\pi' \in P^c} \mathbf{f}_{\pi\pi'} \Big) dv + \int_{V_\pi} \mathbf{b}_\pi \, dv_\pi - \int_{\partial V_\pi} p_\pi \mathbf{n} \, da_\pi \Big]$$

where dv_π and da_π are the volume and area elements associated with the volume occupied by phase π and P^c is the complement of P. The local form of this law written per unit volume of Ω is

$$\sum_{\pi \in P} \Big(s_\pi \nabla p_\pi + \mathbf{f}_\pi + \sum_{\pi' \in P^c} \mathbf{f}_{\pi\pi'} \Big) = \sum_{\pi \in P} s_\pi \mathbf{b}_\pi. \tag{4}$$

3. *Energy Balance:* For each control volume $V \subset \Omega$

$$\frac{d}{dt} \int_V e \, dv = \int_V \Big(r + \sum_{c=1}^{N_c} \mu_c q_c + \sum_{\pi=1}^{N_p} s_\pi \mathbf{b}_\pi \cdot \mathbf{v}_\pi \Big) dv$$

$$- \int_{\partial V} \Big(\mathbf{q} + \sum_{c=1}^{N_c} \mu_c \mathbf{h}_c + \sum_{\pi=1}^{N_p} (e_\pi + s_\pi p_\pi) \mathbf{v}_\pi \Big) \cdot \mathbf{n} \, da. \tag{5}$$

The local form of this balance is

$$e_t + \text{div}\Big(\mathbf{q} + \sum_{c=1}^{N_c} \mu_c \mathbf{h}_c + \sum_{\pi=1}^{N_p} (e_\pi + s_\pi p_\pi) \mathbf{v}_\pi \Big) = r + \sum_{c=1}^{N_c} \mu_c q_c + \sum_{\pi=1}^{N_p} s_\pi \mathbf{b}_\pi \cdot \mathbf{v}_\pi.$$

4. *Entropy imbalance:* For each control volume $V \subset \Omega$

$$\frac{d}{dt} \int_V \eta \, dv \geq \int_V \frac{r}{\theta} \, dv - \int_{\partial V} \Big(\frac{1}{\theta} \mathbf{q} \cdot \mathbf{n} + \sum_{\pi=1}^{N_p} \eta_\pi \mathbf{v}_\pi \cdot \mathbf{n} \Big) da.$$

The local form of this law is

$$\eta_t + \text{div}\Big(\frac{\mathbf{q}}{\theta} + \sum_{\pi=1}^{N_p} \eta_\pi \mathbf{v}_\pi \Big) \geq \frac{r}{\theta}. \tag{6}$$

Remark 1 The presence of the saturations s_π in several places of the above balances deserves some comment. First, our mass, energy, and entropy, densities are taken per unit volume of the domain Ω. Taking these quantities to be per unit mass in their respective phases, as is often done in the literature, causes difficulties when the Coleman–Noll procedure is applied (see Proposition 1). Thus, these densities can be integrated over a volume without reference to the saturation of the phases. The one exception to this is the body force $\mathbf{b}_\pi$ acting on phase π, which is taken per unit volume in the phase π. This term is scaled by the saturation s_π in both the force balance and the energy balance to give equations identical in form to those appearing in the engineering literature.

The presence of the saturation in relation to the pressure p_π is more subtle. In the global form of the force balance, the saturation does not appear. Rather, the pressure is integrated over the boundary of the volume V_π, which is the portion of V occupied by phase π, to obtain the total traction force acting on phase π in V. The saturation appears in the local form of this balance law since the measures dv and dv_π are related through the identity $dv = s_\pi dv_\pi$. The saturations directly appear in the global form of the energy balance since, as can be seen in (2), saturation times pressure is a form of energy density. Thus, the term $s_\pi p_\pi$ appears with e_π in the boundary term in (5).

2.2 Basic consequences of the balances

Force balance can be used to obtain a law of mutual action for the forces $\mathbf{f}_{\pi\pi'}$. Choosing $P = \{1, \ldots, N_p\}$ in (4) yields

$$\sum_{\pi \in P} \left(s_\pi \nabla p_\pi + \mathbf{f}_\pi \right) = \sum_{\pi \in P} s_\pi \mathbf{b}_\pi. \tag{7}$$

Consider (4) for the choices P equals $Q \subset \{1, \ldots, N_p\}$ and Q^c, add the results, and utilize (7) to find that

$$\sum_{\pi \in Q} \sum_{\pi' \in Q^c} \mathbf{f}_{\pi\pi'} = - \sum_{\pi' \in Q^c} \sum_{\pi \in Q} \mathbf{f}_{\pi'\pi}.$$

Since this holds for any Q, one can deduce that

$$\mathbf{f}_{\pi\pi'} = -\mathbf{f}_{\pi'\pi} \quad \text{for all } \pi, \pi' \in \{1, \ldots, N_p\}$$

using standard arguments in the theory of additive interactions. See, for example, [16].

It is possible to rewrite the energy balance in several ways that are useful in different contexts. Using the force balance to eliminate the power expended by the external body forces gives the alternative statement of energy balance

$$e_t + \text{div}\Big(\mathbf{q} + \sum_{c=1}^{N_c} \mu_c \mathbf{h}_c + \sum_{\pi=1}^{N_p} e_\pi \mathbf{v}_\pi \Big) + \sum_{\pi=1}^{N_p} p_\pi \, \text{div}(s_\pi \mathbf{v}_\pi)$$

$$= r + \sum_{c=1}^{N_c} \mu_c q_c + \sum_{\pi=1}^{N_p} \Big(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p} \mathbf{f}_{\pi\pi'} \Big) \cdot \mathbf{v}_\pi. \tag{8}$$

Moreover, the mass balances (3) can be used to eliminate the mass supplies q_c to obtain

$$
e_t - \mathbf{m}_t \cdot \boldsymbol{\mu} + \sum_{\pi=1}^{N_p} \mathrm{div}\left(\left(e_\pi + s_\pi p_\pi - \sum_{c=1}^{N_c} M_{c\pi}\mu_c\right)\mathbf{v}_\pi \right)
$$

$$
+ \sum_{\pi=1}^{N_p} \mathbf{v}_\pi \cdot \left(-s_\pi \nabla p_\pi + \sum_{c=1}^{N_c} M_{c\pi}\nabla\mu_c\right) = r - \mathrm{div}(\mathbf{q}) - \sum_{c=1}^{N_c} \mathbf{h}_c \cdot \nabla\mu_c + \sum_{\pi=1}^{N_c} \left(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p} f_{\pi\pi'}\right) \cdot \mathbf{v}_\pi.
$$

$$(9)$$

Finally, this equation can be used to eliminate the radiation term from the local form of the entropy inequality to find that

$$
\theta\eta_t - e_t + \boldsymbol{\mu}\cdot\mathbf{m}_t + \sum_{\pi=1}^{N_p}\left(\theta\eta_\pi - e_\pi - s_\pi p_\pi + \sum_{c=1}^{N_c} M_{c\pi}\mu_c\right)\mathrm{div}(\mathbf{v}_\pi)
$$

$$
+ \sum_{\pi=1}^{N_p}\left(\theta\nabla\eta_\pi - \nabla e_\pi - p_\pi\nabla s_\pi + \sum_{c=1}^{N_c}\mu_c\nabla M_{c\pi}\right)\cdot\mathbf{v}_\pi
$$

$$
\geq \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta + \sum_{c=1}^{N_c}\mathbf{h}_c\cdot\nabla\mu_c - \sum_{\pi=1}^{N_p}\left(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p}\mathbf{f}_{\pi\pi'}\right)\cdot\mathbf{v}_\pi. \quad (10)
$$

This last relation is sometimes referred to as the reduced entropy inequality and does not involve any external influences.

3 Constitutive Relations

3.1 Local thermodynamic equilibrium

At each point it is postulated that the energy, volume, and mass $(e, s_0, \mathbf{m})$ corresponds to the macroscopic state of a classical thermodynamic system in equilibrium. Specifically, we assume that there is a constitutive law

$$
\hat{\eta}_\pi : \mathbb{R} \times [0,1] \times [0,\infty)^{N_c} \to \mathbb{R}, \tag{11}
$$

such that $\hat{\eta}_\pi(e_\pi, s_\pi, \{M_{c\pi}\}_{c=1}^{N_c})$ gives the entropy in phase π when this phase has energy e_π, volume fraction s_π, and consists of the mass densities $\{M_{c\pi}\}_{c=1}^{N_c}$, and that there is a function

$$
\hat{e}_I : \mathbb{R}^{N_p+1} \times [0,1]^{N_p} \times [0,\infty)^{N_c \times N_p} \to \mathbb{R} \tag{12}
$$

such that $e_I = \hat{e}_I(\mathbf{e}, \mathbf{s}, M)$ is the interfacial energy within the pores when the energy of the medium and phases is given by $\mathbf{e}$, the volume fractions are specified by $\mathbf{s}$, and the distribution of the masses of the components in the different phases is described by M. Set

$$
\hat{S}(\mathbf{e}, \mathbf{s}, M) = \hat{\eta}_0(e_0) + \sum_{\pi=1}^{N_p} \hat{\eta}_\pi(e_\pi, s_\pi, \{M_{c\pi}\}_{c=1}^{N_c}),
$$

where $\hat{\eta}_0 : \mathbb{R} \to \mathbb{R}$ is the entropy of the medium per unit volume of Ω. Since the medium is assumed to be rigid and chemically inert its entropy depends only upon its internal energy. The following local equilibrium assumption is made.

Assumption 1 (Local equilibrium) *The macroscopic entropy η is specified by*

$$\hat{\eta}(e, s_0, \mathbf{m}) = \max_{(\mathbf{e},\mathbf{s},M)} \left\{ \hat{S}(\mathbf{e}, \mathbf{s}, M) \mid \mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{e}, \mathbf{s}, M) = e, \right.$$

$$\left. \mathbf{s} \cdot \mathbf{1} = 1 - s_0, \ M\mathbf{1} = \mathbf{m} \right\}, \quad (13)$$

where $(1, \mathbf{1}) \equiv (1, 1, \ldots, 1) \in \mathbb{R}^{N_p+1}$. Moreover, for each argument $(e, s_0, \mathbf{m})$ the maximum is attained at a unique value

$$(\mathbf{e}, \mathbf{s}, M) = \arg\max_{(\mathbf{e},\mathbf{s},M)} \left\{ \hat{S}(\mathbf{e}, \mathbf{s}, M) \mid \mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{e}, \mathbf{s}, M) = e, \right.$$

$$\left. \mathbf{s} \cdot \mathbf{1} = 1 - s_0, \ M\mathbf{1} = \mathbf{m} \right\}. \quad (14)$$

Because of uniqueness, the local equilibrium assumption yields constitutive laws for the energy, volume fraction, and mass densities:

$$(\mathbf{e}, \mathbf{s}, M) = (\hat{\mathbf{e}}(e, s_0, \mathbf{m}), \hat{\mathbf{s}}(e, s_0, \mathbf{m}), \hat{M}(e, s_0, \mathbf{m})). \quad (15)$$

Under the assumption that the phase entropy functions η_π are smooth and that $\partial \eta_\pi / \partial e_\pi > 0$, the local equilibrium assumption implies there exist Lagrange multipliers $(\tilde{\theta}, p, \tilde{\boldsymbol{\mu}})^1$ and KKT multipliers $\{(\lambda_\pi^0, \lambda_\pi^1, \{\Lambda_{c\pi}\}_{c=1}^{N_c})\}_{\pi=1}^{N_p}$, all non-negative, such that

$$\tilde{\theta} \frac{\partial \eta_\pi}{\partial e_\pi} = 1 + \frac{\partial e_I}{\partial e_\pi}, \qquad 0 \le \pi \le N_p,$$

$$\tilde{\theta} \left(\frac{\partial \eta_\pi}{\partial s_\pi} + \lambda_\pi^0 - \lambda_\pi^1 \right) = p + \frac{\partial e_I}{\partial s_\pi}, \qquad \tilde{\theta} \left(\frac{\partial \eta_\pi}{\partial M_{c\pi}} + \Lambda_{c\pi} \right) = -\tilde{\mu}_c + \frac{\partial e_I}{\partial M_{c\pi}}, \quad (16)$$

$$s_\pi \lambda_\pi^0 = 0, \qquad (1 - s_\pi) \lambda_\pi^1 = 0, \qquad M_{c\pi} \Lambda_{c\pi} = 0.$$

Moreover, since the value of $(\mathbf{e}, \mathbf{s}, M)$ is assumed to be unique, we also have the constitutive relations $(\hat{\theta}(e, s_0, \mathbf{m}), \hat{p}(e, s_0, \mathbf{m}), \hat{\boldsymbol{\mu}}(e, s_0, \mathbf{m}))$ for the intrinsic variables.

The above assumption allows the entropy to be viewed as both a function of a macroscopic state $(e, s_0, \mathbf{m})$ and a microscopic state $(\mathbf{e}, \mathbf{s}, M)$ so that

$$\hat{\eta}(e, s_0, \mathbf{m}) = \hat{S}(\mathbf{e}, \mathbf{s}, M), \quad (17)$$

and a calculation involving the chain rule shows that

$$\tilde{\theta} \frac{\partial \eta}{\partial e} = 1, \quad \tilde{\theta} \frac{\partial \eta}{\partial s_0} = p, \quad \text{and} \quad \tilde{\theta} \frac{\partial \eta}{\partial m_c} = -\tilde{\mu}_c. \quad (18)$$

In Section 4.1 below it is shown that, in the prototypical situation where the entropy functions are concave, these expressions for the partial derivatives of η are valid even if $\hat{S}$ is not smooth provided the partial derivatives and KKT multipliers on the left of equation (16) are interpreted as sub-gradients.

---

[1] This choice of notation is justified by Proposition 1.

3.2 Restrictions due to the Second Law (Coleman–Noll procedure)

The Second Law of Thermodynamics, as interpreted by Coleman and Noll [10], says that the entropy imbalance (6) must hold for any thermodynamic process that is compatible with the balances of mass, force, and energy. This places restrictions on the constitutive laws for the various thermodynamics quantities that appear in the balances. Rather than explicitly state constitutive laws for all of the quantities introduced at the beginning of Section 2, here we take the approach of finding sufficient conditions to guarantee that the second law holds and these conditions will motivate additional constitutive laws that are consistent with the Second Law of Thermodynamics.

Proposition 1 *Assume that local equilibrium, Assumption 1, holds so that the macroscopic entropy η, is determined by (13) and that the macroscopic energies, saturations, and densities are determined by (14). Under these constitutive assumptions, the entropy imbalance holds for all thermodynamic processes if*

1. The entropy of phase π is

$$\eta_\pi = \frac{1}{\theta}\Big(e_\pi + s_\pi p_\pi - \sum_{c=1}^{N_c} M_{c\pi}\mu_c\Big). \tag{19}$$

2. The interfacial energy only depends upon the saturations; that is, $e_I = \hat{e}_I(\mathbf{s})$.
3. The temperature, phase pressures, and the chemical potential of the components are related to the Lagrange multipliers in (16) through

$$\theta = \tilde{\theta}, \qquad p_\pi = p + \frac{\partial e_I}{\partial s_\pi}, \qquad \mu_c = \tilde{\mu}_c. \tag{20}$$

4. The diffusive mass fluxes, viscous forces, and heat flux satisfy

$$\sum_{c=1}^{N_c} \mathbf{h}_c \cdot \nabla\mu_c \le 0, \qquad \sum_{\pi=1}^{N_p}\Big(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p} \mathbf{f}_{\pi\pi'}\Big) \cdot \mathbf{v}_\pi \ge 0, \qquad \mathbf{q}\cdot\nabla\theta \le 0. \tag{21}$$

Proof First notice that $(20)_{1,3}$ together with $(18)_{1,3}$ imply that

$$\theta\frac{\partial\eta}{\partial e} = 1 \qquad \text{and} \qquad \theta\frac{\partial\eta}{\partial \mathbf{m}} = -\boldsymbol{\mu}. \tag{22}$$

Moreover, taking the gradient of (19), utilizing (16), Item 2 of the proposition, and $(20)_2$ yields

$$\theta\nabla\eta_\pi = \nabla e_\pi + p_\pi\nabla s_\pi - \sum_{c=1}^{N_c}\mu_c\nabla M_{c\pi}. \tag{23}$$

Using the previous two equations as well as Items 1 and 4, we see that

$$(\theta\frac{\partial\eta}{\partial e} - 1)e_t + (\theta\frac{\partial\eta}{\partial\mathbf{m}} + \boldsymbol{\mu})\cdot\mathbf{m}_t + \sum_{\pi=1}^{N_p}\Big(\theta\eta_\pi - e_\pi - s_\pi p_\pi + \sum_{c=1}^{N_c} M_{c\pi}\mu_c\Big)\,\mathrm{div}(\mathbf{v}_\pi)$$

$$+ \sum_{\pi=1}^{N_p}\Big(\theta\nabla\eta_\pi - \nabla e_\pi - p_\pi\nabla s_\pi + \sum_{c=1}^{N_c}\mu_c\nabla M_{c\pi}\Big)\cdot\mathbf{v}_\pi$$

$$\ge \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta + \sum_{c=1}^{N_c}\mathbf{h}_c\cdot\nabla\mu_c - \sum_{\pi=1}^{N_p}\Big(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p}\mathbf{f}_{\pi\pi'}\Big)\cdot\mathbf{v}_\pi.$$

holds for all thermodynamic processes. From the chain rule

$$\eta_t = \frac{\partial \eta}{\partial e} e_t + \frac{\partial \eta}{\partial \mathbf{m}} \cdot \mathbf{m}_t, \tag{24}$$

it follows that the previous inequality is equivalent to the reduced dissipation inequality (10).   □

Notice that Item 1 in the previous proposition implies that the entropy η_π is a positive homogeneous function of $(e_\pi, s_\pi, M_{c\pi})$, which is a common assumption in classical thermodynamics; see, for example, [21]. While the previous result only yields sufficient conditions for the Second Law to hold, it can be shown that Item 1 is also a necessary condition under the assumption that the energy, pressure, and chemical potential of each phase is independent of the velocity of that phase. Thus, the homogeneity of η_π is necessary for the Second Law of Thermodynamics to hold in this context.

The relation (19), along with (1) applied to each phase, allows the balance of energy (9) to be written in a simplified form using the entropy η_π:

$$e_t - \mathbf{m}_t \cdot \boldsymbol{\mu} + \sum_{\pi=1}^{N_p} \theta \,\mathrm{div}(\eta_\pi \mathbf{v}_\pi) = r - \mathrm{div}(\mathbf{q}) - \sum_{c=1}^{N_c} \mathbf{h}_c \cdot \nabla \mu_c + \sum_{\pi=1}^{N_c} \left(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p} \mathbf{f}_{\pi\pi'} \right) \cdot \mathbf{v}_\pi. \tag{25}$$

This form of the energy balance can be used to obtain a dissipation relation. In particular, by (24), (18), (20), and (25) we obtain the identity $\theta \eta_t = e_t + \mathbf{m}_t \cdot \boldsymbol{\mu}$ so that

$$-\frac{d}{dt} \int_\Omega \eta \, dv + \int_\Omega \frac{1}{\theta} \Big\{ -(1/\theta)\mathbf{q} \cdot \nabla \theta + \sum_{\pi=1}^{N_c} \left(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p} \mathbf{f}_{\pi\pi'} \right) \cdot \mathbf{v}_\pi - \sum_{c=1}^{N_c} \mathbf{h}_c \cdot \nabla \mu_c \Big\} dv$$

$$= \int_\Omega -r/\theta + \int_{\partial\Omega} \left((1/\theta)\mathbf{q} + \sum_{\pi=1}^{N_p} \eta_\pi \mathbf{v}_\pi \right) \cdot \mathbf{n} \, da.$$

This equality can be used to obtain lower bounds for the entropy and upper bounds for the dissipation, which are an essential ingredient for any theory for existence of solutions to PDE's and stability of numerical schemes.

To ensure the Second Law of Thermodynamics is not violated, henceforth we shall assume that Items 1–4 of the previous proposition hold. It follows from (20) that we now have constitutive laws for θ, p_π, and μ_c. However, the conditions in (21) do not fully determine $\mathbf{h}_c$, $\mathbf{f}_\pi$, $\mathbf{f}_{\pi\pi'}$, and $\mathbf{q}$. These will be discussed in the next subsection.

3.3 Fluxes and Darcy's law

The requirement that mass and heat diffuse from high to low values of their potentials is classical. Fick and Fourier laws are prototypical constitutive relations which realize this,

$$\mathbf{h}_c = -\hat{K}_c(\mathbf{e}, \mathbf{s}, M) \nabla \mu_c, \qquad \text{and} \qquad \mathbf{q} = -\hat{K}_\theta(\mathbf{e}, \mathbf{s}, M) \nabla \theta, \tag{26}$$

where $\hat{K}_c(\mathbf{e}, \mathbf{s}, M)$ and $\hat{K}_\theta(\mathbf{e}, \mathbf{s}, M)$ are positive semidefinite symmetric tensors. More general statements of Fick's law admit coupling between the chemical potentials [13].

One systematic way to formulate constitutive laws for viscous forces that satisfy the relations (4) is to first introduce a dissipation function (a Raleighian in the physics literature) of the form $\mathcal{R}_\mathbf{s}(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \{\mathbf{v}_\pi - \mathbf{v}_{\pi'}\}_{\pi'<\pi})$ and, with D_π and $D_{(\pi\pi')}$ denoting derivatives with respect to the corresponding arguments, to define

$$\mathbf{f}_\pi = D_\pi \mathcal{R}_\mathbf{s}, \qquad \text{and} \qquad \mathbf{f}_{\pi\pi'} = \frac{1}{2} D_{(\pi\pi')}\mathcal{R}_\mathbf{s}, \quad \pi' < \pi,$$

and $\mathbf{f}_{\pi'\pi} = -\mathbf{f}_{\pi\pi'}$ when $\pi' > \pi$. If $\mathcal{R}_\mathbf{s}$ is a non-negative convex function of its arguments taking values in $[0, \infty]$ which vanishes when $\mathbf{v}_\pi = \mathbf{v}_\pi - \mathbf{v}_{\pi'} = \mathbf{0}$, then (omitting the arguments of $\mathcal{R}_\mathbf{s}$)

$$\sum_{\pi=1}^{N_p} \left(\mathbf{f}_\pi \cdot \mathbf{v}_\pi + \sum_{\pi'=1}^{N_p} \mathbf{f}_{\pi\pi'} \cdot \mathbf{v}_\pi \right) = \sum_{\pi=1}^{N_p} \left(D_\pi \mathcal{R}_\mathbf{s} \cdot \mathbf{v}_\pi + \sum_{\pi'<\pi} D_{(\pi\pi')}\mathcal{R}_\mathbf{s} \cdot (\mathbf{v}_\pi - \mathbf{v}_{\pi'}) \right) \geq \mathcal{R}_\mathbf{s}.$$

In this context Darcy's law for the velocities is realized as the Euler–Lagrange relation for the convex function

$$I_\mathbf{s}(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}) = \mathcal{R}_\mathbf{s}\left(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \{\mathbf{v}_\pi - \mathbf{v}_{\pi'}\}_{\pi'<\pi} \right) + \sum_{\pi=1}^{N_p} s_\pi (\mathbf{b}_\pi - \nabla p_\pi) \cdot \mathbf{v}_\pi.$$

Prototypically dissipation functions are formulated using an inner product on the set of velocities which, as in Section 1.3, take the form

$$\left(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \{\mathbf{w}_\pi\}_{\pi=1}^{N_p} \right)_\mathbf{s}$$
$$= \sum_{\pi=1}^{N_p} \left(\frac{1}{s_\pi}(\mathbf{v}_\pi, \mathbf{w}_\pi)_{A_\pi} + \sum_{\pi'<\pi} \frac{2}{\sqrt{s_\pi s_{\pi'}}}(\mathbf{v}_\pi - \mathbf{v}_{\pi'}, \mathbf{w}_\pi - \mathbf{w}_{\pi'})_{A_{\pi\pi'}} \right), \quad (27)$$

where the tensors A_π and $A_{\pi\pi'} = A_{\pi'\pi}$ are symmetric and positive definite and for a symmetric, positive definition tensor A, $(\mathbf{v}, \mathbf{w})_A = \mathbf{v} \cdot A\mathbf{w}$ denotes the induced inner product on vectors. These tensors correspond to the (pseudo) inverses of the permeability tensors that appear in the engineering and experimental literature. Letting the velocities be determined by

$$\left(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \{\mathbf{w}_\pi\}_{\pi=1}^{N_p} \right)_\mathbf{s} = \sum_{\pi=1}^{N_p} s_\pi (\mathbf{b}_\pi - \nabla p_\pi) \cdot \mathbf{w}_\pi, \qquad \text{for all } \{\mathbf{w}_\pi\}_{\pi=1}^{N_p} \quad (28)$$

gives the force system

$$\mathbf{f}_\pi = \frac{1}{s_\pi} A_\pi \mathbf{v}_\pi \quad \text{and} \quad \mathbf{f}_{\pi\pi'} = \frac{1}{\sqrt{s_\pi s_{\pi'}}} A_{\pi\pi'}(\mathbf{v}_\pi - \mathbf{v}_{\pi'}),$$

which satisfies the force balance (4) with (viscous) dissipation

$$\sum_{\pi=1}^{N_p} \left(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p} \mathbf{f}_{\pi\pi'} \right) \cdot \mathbf{v}_\pi = |\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}|_\mathbf{s}^2,$$

where $|.|_\mathbf{s} = (.,.)_\mathbf{s}^{1/2}$ denotes the norm corresponding to the $\mathbf{s}$-weighted inner product. In the case of a single phase, substituting (28) into the right-hand side of the previous equation results in the traditional form of Darcy's law.

3.4 Mechanical & isothermal case

Frequently it is assumed that the temperature is either constant or that the transport of energy by the flow is negligible. The later may happen when the thermal energy stored in the medium dominates that of the fluid(s) in the pores and thermal equilibrium is quickly attained whereby the fluid(s) take on the temperature of the medium. In this situation the temperature will satisfy a classical heat equation of the form

$$(c\theta)_t + \mathrm{div}\,(K\nabla\theta) = r, \tag{29}$$

where c and K are the specific heat and conductivity of the medium respectively. Thus, the temperature can be solved for independently of the other thermodynamic quantities. In this case, it is preferable to formulate constitutive laws so that temperature is an independent variable. This is accomplished by introducing the Helmholtz free-energy density of the system:

$$\hat{\Psi}(\theta,\mathbf{s},M) = \hat{\psi}_0(\theta) + \sum_{\pi=1}^{N_p} \hat{\psi}_\pi\left(\theta, s_\pi, \{M_{c\pi}\}_{c=1}^{N_c}\right) + \hat{e}_I(\theta,\mathbf{s},M), \tag{30}$$

where $\psi_\pi = e_\pi - \theta\eta_\pi$ is the Helmholtz free-energy density for phase π.

The local equilibrium assumption, Assumption 1, requires $\hat{\Psi}(\theta,\mathbf{s},M)$ to be at a minimum,

$$\hat{\psi}(\theta, s_0, \mathbf{m}) = \inf_{(\mathbf{s},M)} \{\hat{\Psi}(\theta,\mathbf{s},M) \mid \mathbf{s}\cdot\mathbf{1} = 1 - s_0,\ M\mathbf{1} = \mathbf{m}\}, \tag{31}$$

and that for each argument $(\theta, s_0, \mathbf{m})$ the minimum is attained at a unique value

$$(\mathbf{s},M) = \operatorname*{arg\,min}_{(\mathbf{s},M)}\left\{\hat{\Psi}(\theta,\mathbf{s},M) \mid \mathbf{s}\cdot\mathbf{1} = 1 - s_0,\ M\mathbf{1} = \mathbf{m}\right\}. \tag{32}$$

As in Section 3.1, this gives rise to Lagrange multipliers $\tilde{\boldsymbol{\mu}}$ and p and KKT multipliers $\boldsymbol{\lambda}^0$, $\boldsymbol{\lambda}^1$, and Λ for which

$$\frac{\partial\psi_\pi}{\partial s_\pi} + \lambda_\pi^0 - \lambda_\pi^1 = -p - \frac{\partial e_I}{\partial s_\pi}, \qquad \text{and} \qquad \frac{\partial\psi_\pi}{\partial M_{c\pi}} + \Lambda_{c\pi} = \tilde{\mu}_c.$$

The analog of equations $(18)_{2,3}$ are

$$\frac{\partial\psi}{\partial s_0} = -p, \quad \text{and} \quad \frac{\partial\psi}{\partial m_c} = \tilde{\mu}_c. \tag{33}$$

Replacing the entropy with the Helmholtz free energy in the reduced entropy inequality (10) results in

$$-\psi_t - \eta\theta_t + \boldsymbol{\mu}\cdot\mathbf{m}_t - \sum_{\pi=1}^{N_p}\left(\psi_\pi + s_\pi p_\pi - \sum_{c=1}^{N_c} M_{c\pi}\mu_c\right)\mathrm{div}(\mathbf{v}_\pi)$$

$$-\sum_{\pi=1}^{N_p}\left(\nabla\psi_\pi + \eta_\pi\nabla\theta + p_\pi\nabla s_\pi - \sum_{c=1}^{N_c}\mu_c\nabla M_{c\pi}\right)\cdot\mathbf{v}_\pi$$

$$-\mathbf{q}\cdot\nabla\theta - \sum_{c=1}^{N_c}\mathbf{h}_c\cdot\nabla\mu_c + \sum_{\pi=1}^{N_p}\left(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p}\mathbf{f}_{\pi\pi'}\right)\cdot\mathbf{v}_\pi \geq 0, \tag{34}$$

which is referred to as the free energy imbalance.

The analog of Proposition 1 in this case is the following, which is presented without proof.

Proposition 2 *Assume that local equilibrium holds so that the macroscopic Helmholtz free energy ψ is determined by (31) and that the macroscopic saturations and densities are determined by (32). Under these constitutive assumptions, the free energy imbalance holds for all thermodynamic processes if*

1. *The microscopic entropy is given by $\eta_\pi = -\frac{\partial \psi_\pi}{\partial \theta}$ for $0 \leq \pi \leq N_p$.*
2. *The Helmholtz free energy of phase π, for $1 \leq \pi \leq N_p$, is given by*

$$\psi_\pi = -s_\pi p_\pi + \sum_{c=1}^{N_c} M_{c\pi} \mu_c. \tag{35}$$

3. *The interfacial energy only depends upon the saturations; that is, $e_I = \hat{e}_I(\mathbf{s})$.*
4. *The pressures in the phases π, for $1 \leq \pi \leq N_p$, and the chemical potential of the components are related to the Lagrange multipliers through*

$$p_\pi = p + \frac{\partial e_I}{\partial s_\pi} \quad and \quad \mu_c = \tilde{\mu}_c. \tag{36}$$

5. *The diffusive mass fluxes, viscous forces, and heat conductivity satisfy*

$$\sum_{c=1}^{N_c} \mathbf{h}_c \cdot \nabla \mu_c \leq 0, \qquad \sum_{\pi=1}^{N_p} \left(\mathbf{f}_\pi + \mathbf{f}_{\pi\pi'} \right) \cdot \mathbf{v}_\pi \geq 0, \qquad \mathbf{q} \cdot \nabla \theta \leq 0. \tag{37}$$

Notice that Item 2 says that ψ_π is a homogeneous function of s_π and $\{M_{c\pi}\}_{c=1}^{N_c}$ for $1 \leq \pi \leq N_p$. Then upon assuming that Assumptions 1–4 of the previous proposition hold, and using equation (1) to simplify the time derivative of $\psi = \hat{\psi}(\theta, s_0, \mathbf{m})$ shows that the total Helmholtz free energy evolves according to

$$\frac{d}{dt} \int_\Omega \psi \, dv = \int_\Omega \left(\sum_{\pi=1}^{N_p} s_\pi \nabla p_\pi \cdot \mathbf{v}_\pi + \sum_{c=1}^{N_c} (q_c \mu_c + \mathbf{h}_c \cdot \nabla \mu_c) \right) dv$$

$$- \int_\Omega \left(\eta \theta_t + \sum_{\pi=1}^{N_p} \eta_\pi \mathbf{v}_\pi \cdot \nabla \theta \right) dv - \int_{\partial\Omega} \sum_{c=1}^{N_c} \mu_c \left(\sum_{\pi=1}^{N_p} M_{c\pi} \mathbf{v}_\pi + \mathbf{h}_c \right) \cdot \mathbf{n} \, da.$$

Using force balance to eliminate the pressures and assuming isothermal conditions (θ_t and $\nabla\theta$ are negligible) gives the dissipation relation

$$\frac{d}{dt} \int_\Omega \psi \, dv + \int_\Omega \left\{ \sum_{\pi=1}^{N_p} \left(\mathbf{f}_\pi + \sum_{\pi'=1}^{N_p} \mathbf{f}_{\pi\pi'} \right) \cdot \mathbf{v}_\pi - \sum_{c=1}^{N_c} \mathbf{h}_c \cdot \nabla \mu_c \right\} dv$$

$$= \int_\Omega \left\{ \sum_{\pi=1}^{N_p} s_\pi \mathbf{b}_\pi \cdot \mathbf{v}_\pi + \sum_{c=1}^{N_c} q_c \mu_c \right\} dv - \int_{\partial\Omega} \sum_{c=1}^{N_c} \mu_c \left(\sum_{\pi=1}^{N_p} M_{c\pi} \mathbf{v}_\pi + \mathbf{h}_c \right) \cdot \mathbf{n} \, da.$$

3.5 Summary

Substituting the constitutive postulates into the local forms of the balances of mass and energy gives the following system of partial differential equations for the mass densities and internal energy, $(\mathbf{m}, e)$, which model multiphase flow in a porous medium:

$$\frac{\partial m_c}{\partial t} + \text{div}\left(\sum_{\pi=1}^{N_p} M_{c\pi}\mathbf{v}_\pi - K_c\nabla\mu_c\right) = q_c, \qquad c = 1, 2, \ldots, N_c,$$

and

$$e_t - \mathbf{m}_t \cdot \boldsymbol{\mu} + \sum_{\pi=1}^{N_p} \theta\, div(\eta_\pi\mathbf{v}_\pi) = r + \text{div}(K_\theta\nabla\theta) + \sum_{c=1}^{N_c} |\nabla\mu_c|_{K_c}^2 + |\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}|_\mathbf{s}^2.$$

In these equations q_c and r model the source of each components and heat supply respectively, and the body force $\mathbf{b}_\pi$ on each phase is specified in the Darcy law for the phase velocities $\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}$. The constitutive input consists of:

- Entropy functions (11) for each phase or, equivalently, the free energy functions.
- The interfacial surface and wetting energy (12).
- Mass diffusion tensors for each component and heat conduction tensor (26).
- Diffusion tensors for the phases appearing in the Darcy law (28).

The dependence of microvariables $(\mathbf{e}, \mathbf{s}, M)$ and Lagrange multipliers $(\theta, p, \boldsymbol{\mu})$ upon $(e, s_0, \mathbf{m})$ is then determined by $\mathbf{m} = M\mathbf{1}$ and Assumption 1, and the phase pressures in the Darcy law for the velocities are $p_\pi = p + \partial e_I/\partial s_\pi$.

4 Structural Properties

4.1 Entropy maximization

Here we justify the formal calculations done in Section 3. We begin by showing that if the entropy functions $\hat{\eta}_\pi$ for each phase are concave, then the entropy of the mixture $\hat{\eta}(e, s_0, \mathbf{m})$ is also a concave function and can be realized as the maximum value of a concave function on a convex set.

Proposition 3 *For each $1 \leq \pi \leq N_p$ let $\hat{\eta}_\pi : \mathbb{R} \times [0, 1] \times [0, \infty)^{N_c} \to \mathbb{R}$ and $\hat{\eta}_0 : \mathbb{R} \to \mathbb{R}$ be concave functions. Suppose that $\partial\eta_\pi/\partial e_\pi \geq 0$ and that the inequality is strict for at least one phase. Let $\hat{e}_I : [0, 1]^{N_p} \to \mathbb{R}$ be convex and set*

$$\hat{S}(\mathbf{e}, \mathbf{s}, M) = \hat{\eta}_0(e_0) + \sum_{\pi=1}^{N_p} \hat{\eta}_\pi(e_\pi, s_\pi, \{M_{c\pi}\}_{c=1}^{N_c}),$$
$$(\mathbf{e}, \mathbf{s}, M) \in \mathbb{S} \equiv \mathbb{R}^{N_p+1} \times [0, 1]^{N_p} \times [0, \infty)^{N_c \times N_p}.$$

For each $(e, s_0, \mathbf{m}) \in \mathbb{R} \times [0, 1] \times [0, \infty)^{N_c}$ assume that the maximum in the definition

$$\hat{\eta}(e, s_0, \mathbf{m}) \equiv \max_{(\mathbf{e}, \mathbf{s}, M) \in \mathbb{S}} \{\hat{S}(\mathbf{e}, \mathbf{s}, M) \mid \mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{s}) = e,\ \mathbf{s} \cdot \mathbf{1} = 1 - s_0,\ M\mathbf{1} = \mathbf{m}\}$$

is achieved. Then

$$\hat{\eta}(e, s_0, \mathbf{m}) = \max_{(\mathbf{e}, \mathbf{s}, M) \in \mathbb{S}} \{\hat{S}(\mathbf{e}, \mathbf{s}, M) \mid \mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{s}) \le e, \ \mathbf{s} \cdot \mathbf{1} = 1 - s_0, \ M\mathbf{1} = \mathbf{m}\},$$
$$(38)$$

in particular, $\hat{\eta}$ is a concave function.

Proof If the maximum of $\hat{S}(\mathbf{e}, \mathbf{s}, M)$ was achieved at a point in $\mathbb{S}$ where $\mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{s}) < e$ then there exists $\epsilon > 0$ for which $(\mathbf{e} + \epsilon(1, \mathbf{1})) \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{s}) = e$ and the hypothesis that $\partial \eta_\pi / \partial e_\pi > 0$ gives the contradiction $\hat{S}(\mathbf{e} + \epsilon(1, \mathbf{1}), \mathbf{s}, M) > \hat{S}(\mathbf{e}, \mathbf{s}, M)$. It follows that the formula (38) for $\hat{\eta}$ holds.

Since $\hat{e}_I$ is convex (and the other constraints are linear) it is immediate that

$$\mathbb{K} = \mathbb{K}(e, s_0, \mathbf{m}) \equiv \{(\mathbf{e}, \mathbf{s}, M) \in \mathbb{S} \mid \mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{s}) \le e, \ \mathbf{s} \cdot \mathbf{1} = 1 - s_0, \ M\mathbf{1} = \mathbf{m}\}$$

is a convex set. Concavity of $\hat{\eta}$ then follows from the concavity of $\hat{S}$ and the fact that η is the maximum over all convex combinations of elements of the set in $\mathbb{S}$. □

In this context results from convex analysis can be used to elucidate the relationship between $\hat{\eta}$ and $\hat{S}$. The extension of the domain of $\hat{S}$ to $\mathbb{V} = \mathbb{R}^{N_p+1} \times \mathbb{R}^{N_p} \times \mathbb{R}^{N_c \times N_p}$ by

$$\hat{S}(\mathbf{e}, \mathbf{s}, M) = \begin{cases} \hat{S}(\mathbf{e}, \mathbf{s}, M) \text{ if } (\mathbf{e}, \mathbf{s}, M) \in \mathbb{S}, \\ -\infty \qquad \text{otherwise,} \end{cases}$$

defines a proper, upper semi-continuous, concave function $\hat{S} : \mathbb{V} \to \mathbb{R} \cup \{-\infty\}$. For $(e, s_0, \mathbf{m}) \in \mathbb{R} \times [0, 1] \times [0, \infty)^{N_c}$ set

$$\hat{I}_{\mathbb{K}}(\mathbf{e}, \mathbf{s}, M) \equiv \hat{I}(\mathbf{e}, \mathbf{s}, M; e, s_0, \mathbf{m}) = \begin{cases} 0 \quad \text{if } (\mathbf{e}, \mathbf{s}, M) \in \mathbb{K}, \\ -\infty \quad \text{otherwise} \end{cases}$$

to be the concave indicator of the (closed and convex) set $\mathbb{K} \subset \mathbb{V}$ over which the extreme value of $\hat{S}$ is to be taken. With these definitions

$$\hat{\eta}(e, s_0, \mathbf{m}) = \max_{(\mathbf{e}, \mathbf{s}, M) \in \mathbb{V}} \left(\hat{S}(\mathbf{e}, \mathbf{s}, M) + \hat{I}_{\mathbb{K}}(\mathbf{e}, \mathbf{s}, M)\right).$$

Since the intersections of the domains of these functions is non-empty, at an extremim $0 \in \partial \hat{S}(\mathbf{e}, \mathbf{s}, M) + \partial \hat{I}_{\mathbb{K}}(\mathbf{e}, \mathbf{s}, M)$. Here $\partial \hat{S} \subset \mathbb{V}$ and $\partial \hat{I}_{\mathbb{K}} \subset \mathbb{V}$ are the super gradients of $\hat{S}$ and $\hat{I}_{\mathbb{K}}$, respectively:

$$\partial \hat{S}(\mathbf{e}, \mathbf{s}, M) = \Big\{ (\mathbf{f}, \mathbf{t}, N) \in \mathbb{V} \mid \big((\mathbf{f}, \mathbf{t}, N), (\tilde{\mathbf{e}}, \tilde{\mathbf{s}}, \tilde{M}) - (\mathbf{e}, \mathbf{s}, M)\big)_{\mathbb{V}}$$
$$\ge \hat{S}(\tilde{\mathbf{e}}, \tilde{\mathbf{s}}, \tilde{M}) - \hat{S}(\mathbf{e}, \mathbf{s}, M), \quad \forall (\tilde{\mathbf{e}}, \tilde{\mathbf{s}}, \tilde{M}) \in \mathbb{V} \Big\},$$

and $\partial \hat{I}_{\mathbb{K}}$ is defined similarly. In this expression the pairing $(. , .)_{\mathbb{V}}$ is the usual inner product on $\mathbb{V}$.

Upon assuming that the entropy functions $\hat{\eta}_\pi$ are differentiable, classical results from optimization show

$$\partial \hat{S}(\mathbf{e}, \mathbf{s}, M) = \Big\{ (D_{\mathbf{e}} S, D_{\mathbf{s}} S + \boldsymbol{\lambda}^0 - \boldsymbol{\lambda}^1, D_M S + \boldsymbol{\Lambda}) \mid$$
$$\boldsymbol{\lambda}^0, \boldsymbol{\lambda}^1 \in [0, \infty)^{N_p}, \ \boldsymbol{\Lambda} \in [0, \infty)^{N_c \times N_p}, \boldsymbol{\lambda}^0 \cdot \mathbf{s} = 0, \ \boldsymbol{\lambda}^1 \cdot (\mathbf{1} - \mathbf{s}) = 0, \ \boldsymbol{\Lambda} : M = 0 \Big\},$$

where $\boldsymbol{\lambda}^0$, $\boldsymbol{\lambda}^1$, and $\boldsymbol{\Lambda}$ are the KKT multipliers dual to the constraints $0 \leq s_\pi \leq 1$ and $0 \leq M_{c\pi}$ respectively. When $\hat{e}_I$ is differentiable and $\mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{s}) = e$; that is, $(\mathbf{e}, \mathbf{s}, M) \in \partial\mathbb{K}$, a similar calculation shows

$$\partial \hat{I}_\mathbb{K}(\mathbf{e}, \mathbf{s}, M) = \left\{ \beta\big(-(1, \mathbf{1}), -p\mathbf{1} + D_\mathbf{s}e_I, \boldsymbol{\mu} \otimes \mathbf{1} \big) \mid \beta \in [0, \infty), \ p \in \mathbb{R}, \ \boldsymbol{\mu} \in \mathbb{R}^{N_c} \right\},$$

where β is the KKT multiplier for the inequality constraint and p and $\boldsymbol{\mu}$ are the Lagrange multipliers for the equality constraints scaled by β. The following lemma is useful in this context.

Lemma 1 ([20, IV.4.3]) *Let $\phi : H \to \mathbb{R} \cup \{\infty\}$ be a proper, convex, and lower semi-continuous function on a Hilbert space H. If $\frac{d}{d\tau}u \in L^2[0, T; H]$ and if there exists a $g \in L^2[0, T; H]$ with $g(\tau) \in \partial\phi(u(\tau))$ a.e. on $[0, T]$, then $\phi \circ u$ is absolutely continuous on $[0, T]$ and*

$$\frac{d}{d\tau}\phi(u(\tau)) = \big(h(\tau), \tfrac{d}{d\tau}u(\tau)\big)_H, \qquad a.e. \ \tau \in (0, T).$$

for any function h with $h \in \partial\phi(u)$ a.e. on $[0, T]$.

We abuse the notation by writing $\frac{d}{d\tau}\phi(u) = \big(\partial\phi(u), \frac{du}{d\tau}\big)_H$. Combining the above then shows that if

$$(\mathbf{e}, \mathbf{s}, M)(\tau) = \underset{(\mathbf{e}, \mathbf{s}, M) \in \mathbb{S}}{\arg\max} \left\{ \hat{S}(\mathbf{e}, \mathbf{s}, M) \mid \mathbf{e} \cdot (1, \mathbf{1}) + \hat{e}_I(\mathbf{s}) \leq e(\tau), \right.$$

$$\left. \mathbf{s} \cdot \mathbf{1} = 1 - s_0, \ M\mathbf{1} = \mathbf{m}(\tau) \right\} \quad (39)$$

is sufficiently regular in time and $\tau \mapsto (e(\tau), s_0(\tau), \mathbf{m}(\tau))$ is a smooth function from $[0, T]$ to $\mathbb{R} \times \mathbb{R}_+ \times \mathbb{R}_+^{N_c}$, then the derivative of the entropy function in Proposition 3 with respect to τ can be computed as

$$\frac{d}{d\tau}\hat{\eta}(e, s_0, \mathbf{m}) = \frac{d}{d\tau}\hat{S}(\mathbf{e}, \mathbf{s}, M) = \Big(\partial\hat{S}(\mathbf{e}, \mathbf{s}, M), \tfrac{d}{d\tau}(\mathbf{e}, \mathbf{s}, M)\Big)_\mathbb{V}$$

$$= \Big(-\partial\hat{I}_{\mathbb{K}(\tau)}(\mathbf{e}, \mathbf{s}, M), \tfrac{d}{d\tau}(\mathbf{e}, \mathbf{s}, M)\Big)_\mathbb{V}.$$

Substituting in the formula for $\partial\hat{I}_{\mathbb{K}(\tau)}$ then shows

$$\frac{1}{\beta}\frac{d}{d\tau}\hat{\eta}(e, s_0, \mathbf{m}) = \mathbf{1} \cdot \mathbf{e}_\tau + D_\mathbf{s}e_I \cdot \mathbf{s}_\tau + p\mathbf{1} \cdot \mathbf{s}_\tau - (\boldsymbol{\mu} \otimes \mathbf{1}) : M_\tau = e_\tau + p\, s_{0\tau} - \boldsymbol{\mu} \cdot \mathbf{m}_\tau.$$

Substituting τ with position shows that the same formula holds if the time derivatives are replaced by spatial gradients. Also, the hypotheses of Proposition 3 guarantee that $\beta > 0$, so upon defining $\theta = 1/\beta$, we see that

$$\theta\frac{d}{d\tau}\hat{\eta}(e, s_0, \mathbf{m}) = e_\tau + p\, s_{0\tau} - \boldsymbol{\mu} \cdot \mathbf{m}_\tau.$$

This result is used to deduce (18) from (17).

4.2 Variational structure: (I) Isothermal setting

The equations for the balance of mass in the isothermal setting with Darcy laws as in Proposition 2 may be viewed as a maximally dissipative system [4,5,7,8,14, 17]. Specifically, in the absence of mass supplies and diffusion, an implicit Euler approximation of these equations with time step τ may be constructed as a sequence of "minimizing movements"; that is as the Euler–Lagrange equations for minimizers of

$$\hat{I}\big(\mathbf{s}, M, \{\mathbf{v}_\pi\}_{\pi=1}^{N_p}\big) = \int_\Omega \left\{ \frac{\tau}{2} |\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}|_{\mathbf{s}^{n-1}}^2 - \tau \sum_{\pi=1}^{N_p} s_\pi \mathbf{b}_\pi \cdot \mathbf{v}_\pi + \hat{\Psi}(\mathbf{s}, M) \right\} dv,$$

subject to the constraints: $0 \le s_\pi \le 1$, $0 \le M_{c\pi}$,

$$m_c + \tau \operatorname{div}\Big(\sum_{\pi=1}^{N_p} M_{c\pi}^{n-1} \mathbf{v}_\pi \Big) = m_c^{n-1}, \qquad \mathbf{s} \cdot \mathbf{1} = 1 - s_0,$$

and $\mathbf{v}_\pi \cdot \mathbf{n}|_{\partial\Omega} = 0$, with $\mathbf{m} \equiv M\mathbf{1}$ and $|\cdot|_\mathbf{s} = (.,.)_\mathbf{s}^{1/2}$ denoting the (semi) norm characterizing the Darcy law (28). To verify this, introduce Lagrange multipliers $\boldsymbol{\mu}$ and p and formulate the Lagrangian[2]

$$\hat{L}\left(\mathbf{s}, M, \{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \boldsymbol{\mu}, p \right) = \int_\Omega \left\{ \frac{\tau}{2} |\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}|_{\mathbf{s}^{n-1}}^2 - (\mathbf{m} - \mathbf{m}^{n-1}) \cdot \boldsymbol{\mu} \right.$$

$$\left. + \tau \sum_{\pi=1}^{N_p} \Big(\sum_{c=1}^{N_c} M_{c\pi}^{n-1} \nabla \mu_c - s_\pi^{n-1} \mathbf{b}_\pi \Big) \cdot \mathbf{v}_\pi + \hat{\Psi}(\mathbf{s}, M) + (s_0 + \mathbf{s} \cdot \mathbf{1} - 1)p \right\} dv.$$

Formally computing the variations gives

$$\delta \hat{L}_{\mathbf{v}_\pi} \qquad 0 = \left(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \{\delta\mathbf{v}_\pi\}_{\pi=1}^{N_p} \right)_{\mathbf{s}^{n-1}} + \sum_{\pi=1}^{N_p} \Big(\sum_{c=1}^{N_c} M_{c\pi}^{n-1} \nabla \mu_c - s_\pi^{n-1} \mathbf{b}_\pi \Big) \cdot \delta\mathbf{v}_\pi,$$

$$\delta \hat{L}_{M_{c\pi}} \qquad 0 = \frac{\partial \Psi}{\partial M_{c\pi}} + \Lambda_{c\pi} - \mu_c$$

$$\delta \hat{L}_{s_\pi} \qquad 0 = \frac{\partial \Psi}{\partial s_\pi} + \lambda_\pi^0 - \lambda_\pi^1 + p,$$

where the KKT multipliers λ_π^0, λ_π^1, and $\Lambda_{c\pi}$ are non-negative and satisfy

$$\Lambda_{c\pi} M_{c\pi} = 0, \qquad \lambda_\pi^0 s_\pi = 0, \qquad \lambda_\pi^1 (1 - s_\pi) = 0,$$

and the variations with respect to $\boldsymbol{\mu}$ and p trivially give the mass balance and the constraint on the saturations. When $\hat{\Psi}$ takes the form shown in equations (30), an

---

[2] A priori it is not known that the Lagrange multipliers associated with the mass and volume fraction constraints are the chemical potential $\boldsymbol{\mu}$ and pressure p. However, due to how these multipliers appear in the equations, it can be shown that indeed these Lagrange multipliers have the expected physical interpretation.

approximation of the Darcy law (28) is recovered,

$$
\left(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \{\delta\mathbf{v}_\pi\}_{\pi=1}^{N_p}\right)_{\mathbf{s}^{n-1}} = \sum_{\pi=1}^{N_p} \left(s_\pi^{n-1}\mathbf{b}_\pi - \sum_{c=1}^{N_c} M_{c\pi}^{n-1}\nabla\mu_c\right) \cdot \delta\mathbf{v}_\pi,
$$

$$
\simeq \sum_{\pi=1}^{N_p} s_\pi\left(\mathbf{b}_\pi - \nabla p_\pi\right) \cdot \delta\mathbf{v}_\pi,
$$

which, for isothermal conditions, follows from equation (1).

4.3 Variational structure: (II) General case

Very few variational characterizations of the thermo-mechanical laws of continuum mechanics are available; this section presents one extension of the isothermal case to include thermal effects. In the absence of heat conduction ($\mathbf{q} = \mathbf{0}$), it is possible to proceed as in the previous section and construct an implicit Euler scheme for the porous flow equations which takes the form of a constrained minimization problem. The associated saddle point problem involves the temperature θ as the Lagrange multiplier for the energy equation. The temperature gradient is required to model heat conduction and is not available for the minimization problem; for this reason the saddle point problem is presented directly. The formulation presented in this section was not derived from fundamental variational principles such as Hamilton's principles or those in [15, 18]. Instead an extension of the isothermal principle was "reverse engineered" give the desired equations.

Upon assuming a Darcy law of the form (28), the energy equation may be written as

$$
\frac{\partial\eta}{\partial t} + \mathrm{div}\left(\sum_{\pi=1}^{N_\pi}\eta_\pi\mathbf{v}_\pi\right) = \frac{1}{\theta}\left(r - \mathrm{div}(\mathbf{q}) + |\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}|_{\mathbf{s}}^2\right),
$$

where $\eta = \eta_0 + \sum_{\pi=1}^{N_p}\eta_\pi \equiv \boldsymbol{\eta} \cdot (1, \mathbf{1})$. Since $\partial\eta_\pi/\partial e_\pi = 1/\theta > 0$ it is possible to express the internal energy of each phase as $e_\pi = \hat{e}_\pi(\eta_\pi, s_\pi, \{M_{c\pi}\}_{c=1}^{N_c})$ where $\hat{e}_\pi$ is homogeneous. Write the total energy as

$$
\hat{E}(\boldsymbol{\eta}, \mathbf{s}, M) = \hat{e}_0(\eta_0) + \sum_{\pi=1}^{N_p}\hat{e}_\pi(\eta_\pi, s_\pi, \{M_{c\pi}\}_{c=1}^{N_c}) + \hat{e}_I(\mathbf{s}),
$$

and let τ denote a time step. Given $(\boldsymbol{\eta}^{n-1}, \mathbf{s}^{n-1}, M^{n-1})$, set $\theta^{n-1} = \partial e_\pi/\eta_\pi$, and let

$$
\hat{L}\left(\boldsymbol{\eta}, \mathbf{s}, M, \{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \theta, p, \boldsymbol{\mu}\right) = \int_\Omega \left\{\frac{\tau}{2}(\theta/\theta^{n-1})^2|\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}|_{\mathbf{s}^{n-1}}^2\right.
$$

$$
+\tau\sum_{\pi=1}^{N_p}\left(\eta_\pi^{n-1}\nabla\theta + \sum_{c=1}^{N_c}M_{c\pi}^{n-1}\nabla\mu_c - s_\pi^{n-1}\mathbf{b}_\pi\right)\cdot\mathbf{v}_\pi + (1/2)|\nabla(1/\theta)|_{K_\theta^{n-1}}^2 + (\theta/\theta^{n-1})r
$$

$$
\left. + \hat{E}(\boldsymbol{\eta}, \mathbf{s}, M) - \theta(\boldsymbol{\eta} - \boldsymbol{\eta}^{n-1})\cdot(1, \mathbf{1}) + (s_0 + \mathbf{s}\cdot\mathbf{1} - 1)p - (\mathbf{m} - \mathbf{m}^{n-1})\cdot\boldsymbol{\mu}\right\}dv,
$$

where $K_\theta^{n-1} = (\theta^{n-1})^2 K_\theta$ with K_θ denoting the usual heat conductivity tensor appearing in Fourier's law. Formally computing the variations gives

$$\delta\hat{L}_{\mathbf{v}_\pi} \qquad 0 = (\theta/\theta^{n-1})^2 \left(\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}, \{\delta\mathbf{v}_\pi\}_{\pi=1}^{N_p}\right)_{\mathbf{s}^{n-1}}$$
$$+ \sum_{\pi=1}^{N_p} \left(\eta_\pi^{n-1}\nabla\theta + \sum_{c=1}^{N_c} M_{c\pi}^{n-1}\nabla\mu_c - s_\pi^{n-1}\mathbf{b}_\pi\right)\cdot\delta\mathbf{v}_\pi,$$

$$\delta\hat{L}_\theta \qquad \eta + \tau\operatorname{div}\left(\sum_{\pi=1}^{N_\pi}\eta_\pi^{n-1}\mathbf{v}_\pi\right) = \eta^{n-1} + \frac{\tau}{\theta^{n-1}}\Big(r$$
$$- (\theta^{n-1}/\theta)^2\operatorname{div}((\theta^{n-1}/\theta)^2 K_\theta\nabla\theta) + (\theta/\theta^{n-1})|\{\mathbf{v}_\pi\}_{\pi=1}^{N_p}|_{\mathbf{s}^{n-1}}^2\Big),$$

$$\delta\hat{L}_{\eta_\pi} \qquad 0 = \frac{\partial E}{\partial\eta_\pi} - \theta,$$

$$\delta\hat{L}_{s_\pi} \qquad 0 = \frac{\partial E}{\partial s_\pi} + \lambda_\pi^0 - \lambda_\pi^1 + p,$$

$$\delta\hat{L}_{M_{c\pi}} \qquad 0 = \frac{\partial E}{\partial M_{c\pi}} + \Lambda_{c\pi} - \mu_c,$$

where λ_π^0, λ_π^1, and $\Lambda_{c\pi}$ are KKT multipliers. Equation (1) shows that the variations with respect to $\mathbf{v}_\pi$ gives (an approximation of) the Darcy law (28), and variations with respect to p and $\boldsymbol{\mu}$ yield the constraints on the saturation and the discrete balances of mass.

Conflict of Interest: The authors declare that they have no conflict of interest.

References

1. Allaire, G.: Homogenization of the Stokes flow in a connected porous medium. Asymptotic Anal. **2**(3), 203–222 (1989)
2. Allaire, G.: Continuity of the Darcy's law in the low-volume fraction limit. Ann. Scuola Norm. Sup. Pisa Cl. Sci. (4) **18**(4), 475–499 (1991). URL http://www.numdam.org/item?id=ASNSP_1991_4_18_4_475_0
3. Allaire, G.: Homogenization and two-scale convergence. SIAM J. Math. Anal. **23**(6), 1482–1518 (1992). DOI 10.1137/0523084. URL http://dx.doi.org/10.1137/0523084
4. Ambrosio, L.: Minimizing movements. Rend. Accad. Naz. Sci. XL Mem. Mat. Appl. (5) **19**, 191–246 (1995)
5. Ambrosio, L., Mainini, E.: Infinite-dimensional porous media equations and optimal transportation. J. Evol. Equ. **10**(1), 217–246 (2010). DOI 10.1007/s00028-009-0047-1. URL http://dx.doi.org/10.1007/s00028-009-0047-1
6. Bedford, A.: Theories of immiscible and structured mixtures. Int. J. Engng. Sci. **2**(8), 863–960 (1983)
7. Benamou, J.D., Brenier, Y.: A computational fluid mechanics solution to the monge-kantorovich mass transfer problem. Numerische Mathematik **84**(3), 375–393 (2000). DOI 10.1007/s002110050002. URL http://dx.doi.org/10.1007/s002110050002
8. Brenier, Y.: Polar factorization and monotone rearrangement of vector–valued functions. Comm. Pure Appl. Math. **44**, 375–417 (1991)
9. Chen, Z., Huan, G., Ma, Y.: Computational methods for multiphase flows in porous media. Computational Science & Engineering. Society for Industrial and Applied Mathematics (SIAM), Philadelphia, PA (2006). DOI 10.1137/1.9780898718942. URL http://dx.doi.org/10.1137/1.9780898718942
10. Coleman, B.D., Noll, W.: The thermodynamics of elastic materials with heat conduction and viscosity. Arch. Rational Mech. Anal. **13**, 167–178 (1963)

11. Ewing, R.: The Mathematics of Reservoir Simulation. Frontiers in Applied Mathematics. Society for Industrial and Applied Mathematics (SIAM, 3600 Market Street, Floor 6, Philadelphia, PA 19104) (1983). URL `https://books.google.com/books?id=k_4Y-RBOK9oC`

12. Flügge, S.: Principles of Classical Mechanics and Field Theory / Prinzipien der Klassischen Mechanik und Feldtheorie. Prinzipien der theoretischen Physik / Principles of Theoretical Physics. Springer-Verlag Berlin Heidelberg (1960)

13. Gurtin, M.E., Fried, E., Anand, L.: The mechanics and thermodynamics of continua. Cambridge University Press, Cambridge (2010). DOI 10.1017/CBO9780511762956. URL `http://dx.doi.org/10.1017/CBO9780511762956`

14. Jordan, R., Kinderlehrer, D., Otto, F.: The variational formulation of the Fokker–Planck equation. SIAM J. Math. Anal., **29**(1), 1–17 (1998)

15. Mielke, A.: Deriving effective models for multiscale systems via evolutionary Γ-convergence. In: Control of self-organizing nonlinear systems, Underst. Complex Syst., pp. 235–251. Springer, [Cham] (2016)

16. Noll, W.: Lectures on the foundations of continuum mechanics and thermodynamics. Archive for Rational Mechanics and Analysis **52**, 62–92 (1973)

17. Otto, F.: The geometry of dissipative evolution equations: the porous medium equation. Comm. Partial Differential Equations **26**(1-2), 101–174 (2001)

18. Otto, F., E, W.: Thermodynamically driven incompressible fluid mixtures. J. Chemical Physics **107**(23), 10,177–10,184 (1997)

19. Sanchez-Palencia, E.: Nonhomogeneous media and vibration theory. No. 127 in Lecture Notes in Physics. Springer-Verlag (1980)

20. Showalter, R.E.: Monotone operators in Banach space and nonlinear partial differential equations. Available online at `http://www.ams.org/online_bks/surv49/`. American Mathematical Society, Providence, RI (1997)

21. Swendsen, R.: An Introduction to Statistical Mechanics and Thermodynamics. Oxford Graduate Texts. OUP Oxford (2012). URL `https://books.google.com/books?id=hbW6O9uEobsC`

22. Truesdell, C.: Rational Thermodyanics, second edn. Springer-Verlag New York (1984)