Total stress tensors and heat fluxes of single flow through a porous viscoelastic medium

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Abstract: Using the second law of thermodynamics, we examine the macroscopic equations for mass, momentum, energy and entropy for a biphasic system whose interface has thermodynamic properties. This system is made up of mesoscopic particles and a fluid, including mass exchange and different phase temperatures. By exploiting the entropy inequality in terms of Coleman and Noll's method we obtain nonequilibrium and equilibrium results. We show how the solid phase stress tensor depends on the solid phase pressure, the Terzaghi stress, the hydration stress and the stress contributed by the interface properties, which is similar to the Terzaghi stress. We determine the heat fluxes. We further linearize the non-equilibrium parts of their constitutive forms in terms of heat conduction, fluid viscosity and viscoelasticity about the equilibrium. Finally we obtain expressions of the total stress and the total heat flux for a particle.

Keywords: Cauchy stress tensors; heat fluxes; Hybrid mixture Theory method; viscoelaticity.

1 Introduction

The description of physical processes which occur in multi-phase systems has been a topic of practical as well as theoretical interest for many years in subsurface hydrology, waste containment, enhanced recovery of petroleum, aquifer remediation, agriculture and seismic phenomena in geological formation. Porous materials consisting of a swelling solid matrix with fluid-filled pores are ubiquitous. Some examples are food stuffs, drugs, cartilage, plant seeds, carbohydrates, proteins, clay soils and biotissue (see Almeida and Spilker (1998), Singh (2002), Singh et al. (2003), (2004) and Weinstein (2006)).

Swelling clays (see Loret et al. (2002)), especially Montmorillonites, play a prominent role in several natural and industrial domains, such as soil science, hydrogeology and catalysis, engineering barrier systems for nuclear waste repository and municipal waste disposals sites.

During the past few decades, significant progress has been made in developing general theories describing thermodynamic processes in general multi-phase systems and in porous media (see Bennethum and Cushman (1996b), Gray and Hassanizadeh (1998) and Gray (2002)). Examples of these, are the swelling (see Almeida and Spilker (1998), Bennethum and Cushman (1996a)) and non-swelling systems (see Hassanizadeh and Gray (1980), (1990), Hassanizadeh (1987a, b)).

The modeling framework which we use is the hybrid mixture theory (HMT). This theory consists of averaging (see Hassanizadeh and Gray (1979a, b)) the microscopic field equations (conservation of mass, conservation of momentum, conservation of energy and balance of entropy) for each phase in order to obtain macroscopic field equation. At this point the medium is viewed as mixture of phases, that is, each phase has clearly defined properties (densities, stress, etc.) at every point in space and time. The HMT approach was pioneered by Gray and Hassanizadeh, in a series of papers (1979a, b), (1980), (1990) and (1993). From 1979 to the present, HMT has been successfully used to model swelling and shrinking behaviour of gels, food stuffs, and collodial systems where phase interactions play an important role in the mesoscopic and macroscopic behaviour (see Bennethum and Cushman (1996) and Bennethum (2007)). In Singh (2002), Singh et al. (2003), Singh et al. (2004a, b), Weinstein (2006) and Weinstein and Bennethum (2006), models were developed in which the solid itself was assumed to be viscoelastic but the interface was not assumed to have thermodynamic properties. Gray and Miller (2005a, b) and (2006) use a different modeling approach, namely the thermodynamically constrained averaging theory, where they thermodynamically constrain the microscale entropy inequality before averaging to macroscale.

The purpose of the present research is to develop a constitutive theory, for the total Cauchy stress tensor and the total heat flux in a system under the following assumptions:

(i) the system is biphasic, has mass exchange and different temperature.

(ii) the solid matrix is viscoelastic and the fluid is viscous.

(iii) the interface has full thermodynamic properties,

2 Macroscale equations

Conservation of mass

We consider a viscoelastic solid matrix s, a viscous fluid f, an interface, denoted by a superscript or subscript sf or fs, which has thermodynamic properties and a system which has mass exchange. The macroscopic balanced equations on which this study is based result from an averaging process of the mesoscale equations of mass, momentum, energy and entropy, on a representative elementary volume, for each phase and the interface. Details of this averaging process are not included here, but can be obtained from several works of Gray and Hassanizadeh (1989), Hassanizadeh and Gray (1979) and other authors. From Gray and Hassanizadeh (1998), we recall the following macroscale balance equations for both the bulk phases and the interfaces.

The bulk phase equations

$$\frac{D^\alpha(\varepsilon_\alpha \rho^\alpha)}{Dt} + \varepsilon_\alpha \rho^\alpha (\bigtriangledown \cdot \mathbf{v}^\alpha) = \hat{e}^\alpha_{sf}, \quad \alpha = f, s, \tag{1}$$

where ε_α is the volume fraction of the α-phase, ρ^α is the intrinsic mass density, $\mathbf{v}^\alpha$ is the velocity of the α-phase and $\hat{e}^\alpha_{sf}$ is the exchange of mass from the only sf-interface to the α-phase. Furthermore, we observe that the two volume fractions satisfy the identity $\varepsilon_s + \varepsilon_f = 1$.

The interface equation

$$\frac{D^{fs}(\varepsilon_{fs}\rho^{fs})}{Dt} + \varepsilon_{fs}\rho^{fs}(\bigtriangledown \cdot \mathbf{v}^{fs}) = -\hat{e}^{s}_{fs} - \hat{e}^{f}_{fs}, \qquad (2)$$

where ε_{sf} is the specific interfacial area of the sf-interface, ρ^{sf} is the mass per unit area of the sf-interface and $\mathbf{v}^{sf}$ is the velocity of the sf-interface. Note that since there is only one interface, the superscripts or subscripts sf, fs, refer to the same object.

Conservation of linear momentum

The bulk phase equations

$$\varepsilon_{\alpha}\rho^{\alpha}\frac{D^{\alpha}\mathbf{v}^{\alpha}}{Dt} - \bigtriangledown \cdot (\varepsilon_{\alpha}\mathbf{t}^{\alpha}) - \varepsilon_{\alpha}\rho^{\alpha}\mathbf{g}^{\alpha} = \hat{\mathbf{T}}^{\alpha}_{sf} \quad \alpha = f, s. \qquad (3)$$

Here $\mathbf{t}^{\alpha}$ is the α-phase Cauchy stress tensor, $\mathbf{g}^{\alpha}$ is the α-phase external supply of momentum and $\hat{\mathbf{T}}^{\alpha}_{sf}$ is the exchange of momentum from the interface to the α-phase.

The interface equation

$$\varepsilon_{fs}\rho^{fs}\frac{D^{fs}\mathbf{v}^{fs}}{Dt} - \bigtriangledown \cdot (\varepsilon_{fs}\mathbf{t}^{fs}) - \varepsilon_{fs}\rho^{fs}\mathbf{g}^{fs} = -\sum_{\alpha=s,f}(\hat{\mathbf{T}}^{\alpha}_{sf} + \hat{e}^{\alpha}_{sf}\mathbf{v}^{\alpha,sf}), \qquad (4)$$

where $\mathbf{t}^{sf}$ is the interface stress tensor, $\mathbf{g}^{sf}$ is the interface external supply of momentum, the product $\hat{e}^{\alpha}_{sf}\mathbf{v}^{\alpha,sf}$ is the exchange of momentum between the α-phase and the interface due to the exchange of mass and $\mathbf{v}^{\alpha,sf} = \mathbf{v}^{\alpha} - \mathbf{v}^{sf}$ is velocity of the α-phase relative to that of the interface.

Angular Momentum

Due to the nonpolarity assumption which we adopt in this study, we have the following symmetric stress tensors.

For the *bulk phase*, we have

$$\mathbf{t}^{\alpha} = (\mathbf{t}^{\alpha})^{T} \qquad (5)$$

and for the *interface*, we have

$$\mathbf{t}^{\alpha\beta} = (\mathbf{t}^{\alpha\beta})^{T}. \qquad (6)$$

where the superscript T, refers to the transpose.

Conservation of energy

The bulk phase equations

$$\varepsilon_{\alpha}\rho^{\alpha}\frac{D^{\alpha}E^{\alpha}}{Dt} - \varepsilon_{\alpha}\mathbf{t}^{\alpha} : \bigtriangledown\mathbf{v}^{\alpha} - \bigtriangledown \cdot (\varepsilon_{\alpha}\mathbf{q}^{\alpha}) - \varepsilon_{\alpha}\rho^{\alpha}h^{\alpha} = \hat{Q}^{\alpha}_{sf}, \qquad (7)$$

where E^{α} is the α-phase macroscopic internal energy density function, $\mathbf{q}^{\alpha}$ is the α-phase heat flux, h^{α} is the α-phase external supply of energy and $\hat{Q}^{\alpha}_{sf}$ is the exchange of internal energy between the α-phase and the interface due to mechanical interactions.

The interface equation

$$\varepsilon_{fs}\rho^{fs}\frac{D^{fs}E^{fs}}{Dt} - \varepsilon_{fs}\mathbf{t}^{fs} : \bigtriangledown\mathbf{v}^{fs} - \bigtriangledown \cdot(\varepsilon_{fs}\mathbf{q}^{fs}) - \varepsilon_{fs}\rho^{fs}h^{fs} = -\sum_{\alpha=s,f}\Big[\hat{Q}^{\alpha}_{sf} + \hat{\mathbf{T}}^{\alpha}_{sf} \cdot \mathbf{v}^{\alpha,sf} + \hat{e}^{\alpha}_{sf}(E^{\alpha,sf} + \frac{1}{2}(v^{\alpha,sf})^{2})\Big] \qquad (8)$$

where the product $\hat{e}^{\alpha}_{sf}(E^{\alpha,sf} + \frac{1}{2}(v^{\alpha,sf})^{2})$ is the exchange of energy between the α-phase and the interface due to exchange of mass, $\mathbf{q}^{sf}$ is the interface heat flux and h^{sf} is the interface external supply of energy. Note that $E^{\alpha,sf} = E^{\alpha} - E^{sf}$ is the internal energy of α-phase relative to that of the interface.

Balance of entropy

The bulk phase equations

$$\varepsilon_{\alpha}\rho^{\alpha}\frac{D^{\alpha}\eta^{\alpha}}{Dt} - \bigtriangledown \cdot \left(\varepsilon_{\alpha}\frac{\mathbf{q}^{\alpha}}{\theta^{\alpha}}\right) - \varepsilon_{\alpha}\rho^{\alpha}\left(\frac{h^{\alpha}}{\theta^{\alpha}}\right) = \hat{\Phi}^{\alpha}_{sf} + \Lambda^{\alpha}, \quad \alpha = f, s, \qquad (9)$$

where η^α is the α-phase entropy density function, $\varphi^\alpha = \mathbf{q}^\alpha/\theta^\alpha$ is the α-phase entropy flux, $\hat{\Phi}^\alpha_{sf}$ is the exchange of entropy between the α-phase and the interface due to the mechanical interactions and Λ^α is the α-phase net production of entropy.

The interface equation

$$\varepsilon_{fs}\rho^{fs}\frac{D^{fs}\eta^{fs}}{Dt} - \nabla\cdot\left(\varepsilon_{fs}\frac{\mathbf{q}^{sf}}{\theta^{sf}}\right) - \varepsilon_{fs}\rho^{fs}\left(\frac{h^{sf}}{\theta^{sf}}\right) = -\sum_{\alpha=s,f}(\hat{\Phi}^\alpha_{fs} + \hat{e}^\alpha_{fs}\eta^{s,sf}) + \Lambda^{sf}, \quad (10)$$

where η^{sf} is the interface internal entropy density function, $\varphi^{sf} = \mathbf{q}^{sf}/\theta^{sf}$ is the interface entropy flux, the product $\hat{e}^\alpha_{fs}\eta^{s,sf}$ is the exchange of entropy between the α-phase and the interface due to exchange of mass, $\eta^{s,sf} = \eta^s - \eta^{sf}$ is the entropy of the solid phase relative to that of the interface and Λ^{sf} is the interface net production of entropy.

3 Kinematics and the second law of thermodynamics

Let $\mathbf{X} = (X_1, X_2, X_3)$ be the Lagrangian coordinates of a typical particle at time $t = 0$ and let this particle be carried to a point with Eulerian coordinates $\mathbf{x}^s = (x_1, x_2, x_3)$ at time t. This motion is defined by the function

$$x_k = F^s_k(X_K, t), \quad k = 1,2,3 \quad \text{and} \quad K = 1,2,3.$$

We assume that $\mathbf{x}^s = \mathbf{x}(\mathbf{X}, t)$ possesses continuous partial derivative with respect to their arguments to whatever order needed. Let $\mathbf{F}^s$ denote the deformation gradient; i.e

$$F^s_{kK} = \frac{\partial x_k}{\partial X_K} \quad \text{or} \quad \mathbf{F}^s = GRAD(\mathbf{x}^s)$$

where $GRAD$ is the gradient with respect to Lagrangian coordinates. The Jacobian is given by

$$J^s = \det(\mathbf{F}^s).$$

Since the motion is invertible, then the Jacobian $J^s \neq 0$. We also have the following expression for the Jacobian, Hassanizadeh and Gray (1980) and Gray (1983)

$$J^s = \frac{(\varepsilon_s\rho^s)_0}{(\varepsilon_s\rho^s)}. \quad (11)$$

The factor $(\varepsilon_s\rho^s)_0$ in equation (11), is independent of time and space. Using this equation and the continuity equation (1) for the solid phase, we obtain (see Gray (1983))

$$\frac{1}{J^s}\frac{D^sJ^s}{Dt} = \mathbf{I} : \left[\mathbf{d}^s - \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}\right], \quad (12)$$

where

$$\mathbf{d}^\alpha = \frac{1}{2}(\nabla\mathbf{v}^\alpha + (\nabla\mathbf{v}^\alpha)^T) \quad \alpha = s, f$$

is the α-phase rate of deformation tensor. From Eringen (1980) and Holzapfel (2000), we obtain this identity relating the Jacobian and the deformation tensor

$$\frac{\partial J^s}{\partial \mathbf{F}^s} = J^s(\mathbf{F}^s)^{-1}.$$

By using the chain rule, we have the following material time derivative of the Jacobian

$$\frac{D^sJ^s}{Dt} = \frac{\partial J^s}{\partial \mathbf{F}^s} : \frac{D^s\mathbf{F}^s}{Dt} = J^s(\mathbf{F}^s)^{-1} : \frac{D^s\mathbf{F}^s}{Dt} \quad . \quad (13)$$

Substitution of equation (13) into (12), yields

$$\frac{D^s\mathbf{F}^s}{Dt} = \frac{\mathbf{F}^s}{J^s}\frac{D^sJ^s}{Dt} = \mathbf{F}^s : \left[\mathbf{d}^s - \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}\right] \quad (14)$$

The transpose of (14) is

$$\left(\frac{D^s\mathbf{F}^s}{Dt}\right)^T = \left[\mathbf{d}^s - \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}\right]\cdot(\mathbf{F}^s)^T \quad (15)$$

Since the Lagrangian strain tensor is defined by

$$\mathbf{E}^s = \frac{1}{2}[(\mathbf{F}^s)^T\cdot\mathbf{F}^s - \mathbf{I}],$$

then its time derivative is

$$\begin{aligned}\frac{D^s\mathbf{E}^s}{Dt} &= \frac{1}{2}\left[\frac{D^s(\mathbf{F}^s)^T}{Dt}\cdot\mathbf{F}^s + (\mathbf{F}^s)^T\cdot\frac{D^s\mathbf{F}^s}{Dt}\right]\\ &= \frac{1}{2}\left[\left(\frac{D^s\mathbf{F}^s}{Dt}\right)^T\cdot\mathbf{F}^s + (\mathbf{F}^s)^T\cdot\frac{D^s\mathbf{F}^s}{Dt}\right]\\ &\quad . \qquad (16)\end{aligned}$$

Furthermore, equations (14), (15) and (16) yield this time derivative of the strain tensor

$$\frac{D^s\mathbf{E}^s}{Dt} = (\mathbf{F}^s)^T\cdot\left(\mathbf{d}^s - \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}\right)\cdot\mathbf{F}^s$$

or the rate of deformation tensor has an extra term involving the mass exchange and is given by (see Weinstein (2006))

$$\begin{aligned}\mathbf{d}^s &= (\mathbf{F}^s)^{-T}\cdot\dot{\mathbf{E}}^s\cdot(\mathbf{F}^s)^{-1} + \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}\\ &\quad . \qquad (17)\end{aligned}$$

We define the right Cauchy-Green tensor as

$$\mathbf{C}^s = (\mathbf{F}^s)^T\cdot\mathbf{F}^s$$

and hence the strain tensor is

$$\mathbf{E}^s = \frac{1}{2}(\mathbf{C}^s - \mathbf{I}).$$

Following Holzapfel (2000), we now consider a multiplicative decomposition of the deformation tensor $\mathbf{F}^s$ and $\mathbf{C}^s$ as follows:

$$\mathbf{F}^s = (J^s)^{1/3}\bar{\mathbf{F}}^s$$

and

$$\mathbf{C}^s = (J^s)^{2/3}\bar{\mathbf{C}}^s,$$

where $(J^s)^{1/3}\mathbf{I}$ and $(J^s)^{2/3}\mathbf{I}$ represent the volumetric deformation, and $\bar{\mathbf{F}}^s$ and $\bar{\mathbf{C}}^s$ are the modified deformation gradient and the modified right Cauchy-Green tensor respectively. These two modified tensors account for distortional deformation and are related by

$$\bar{\mathbf{C}}^s = (\bar{\mathbf{F}}^s)^T\cdot\bar{\mathbf{F}}^s.$$

The equation (17) is now expressed in terms of the modified deformation gradient, the modified Cauchy-Green tensor and the Jacobian as follows:

$$\begin{aligned}\mathbf{d}^s &= (\mathbf{F}^s)^{-T}\cdot\dot{\mathbf{E}}^s\cdot(\mathbf{F}^s)^{-1} + \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}\\ &= \frac{1}{2}(\mathbf{F}^s)^{-T}\cdot\dot{\mathbf{C}}^s\cdot(\mathbf{F}^s)^{-1} + \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}\\ &= \frac{1}{3}(J^s)^{-1}J^s\mathbf{I} + \frac{1}{2}(\bar{\mathbf{F}}^s)^{-T}\cdot\dot{\bar{\mathbf{C}}}^s\cdot(\bar{\mathbf{F}}^s)^{-1}\\ &\quad + \frac{\hat{e}^s_{sf}}{3\varepsilon_s\rho^s}\mathbf{I}. \qquad (18)\end{aligned}$$

The inner product of $\mathbf{d}^s$ with $\mathbf{I}$, yields

$$\begin{aligned}\mathbf{I}:\mathbf{d}^s &= \frac{\dot{J}^s}{J^s} + \frac{1}{2}((\bar{\mathbf{F}}^s)^{-1}\cdot(\bar{\mathbf{F}}^s)^{-T}):\dot{\bar{\mathbf{C}}}^s\\ &\quad + \frac{\hat{e}^s_{sf}}{\varepsilon_s\rho^s}. \qquad (19)\end{aligned}$$

Weinstein (2006), has a similar identity without the last term.

Second law of thermodynamics

The conservation laws are supplemented with the second law of thermodynamics which states that, the rate of net production of entropy of a system must be non-negative. Using the macroscopic equations of the phases and the interface, we then develop the entropy inequalities to express this law. We start with the old entropy inequality which is expressed as follows:

$$\Lambda_{old} = -\sum_{\alpha=s,f}\frac{\varepsilon_\alpha\rho^\alpha}{\theta^\alpha}\left(\frac{D^\alpha A^\alpha}{Dt} + \eta^\alpha\frac{D^\alpha\theta^\alpha}{Dt}\right)$$

$$
\begin{aligned}
&+\sum_{\alpha=s,f}\frac{\varepsilon_\alpha \mathbf{t}^\alpha}{\theta^\alpha}:\mathbf{d}^\alpha+\sum_{\alpha=s,f}\frac{\varepsilon_\alpha \mathbf{q}^\alpha}{(\theta^\alpha)^2}\cdot\triangledown\theta^\alpha \\
&-\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\left(\frac{D^{sf}A^{sf}}{Dt}+\eta^{sf}\frac{D^{sf}\theta^{sf}}{Dt}\right) \\
&+\frac{\varepsilon_{sf}\mathbf{t}^{sf}}{\theta^{sf}}:\mathbf{d}^{sf}+\frac{\varepsilon_{sf}\mathbf{q}^{sf}}{(\theta^{sf})^2}\cdot\triangledown\theta^{sf} \\
&-\frac{1}{\theta^{sf}}\sum_{\alpha=s,f}\left\{\frac{\hat{Q}^\alpha_{sf}\theta^{sf,\alpha}}{\theta^\alpha}+[\hat{\mathbf{T}}^\alpha_{sf}\mathbf{v}^{\alpha,sf}\right. \\
&\left.+\hat{e}^\alpha_{sf}\left(A^{\alpha,sf}-\eta^\alpha\theta^{sf,\alpha}\;+\frac{1}{2}(v^{\alpha,sf})^2\right)\Bigr]\right\} \\
&\geq 0. \qquad (20)
\end{aligned}
$$

where A^α and A^{sf} are the Helmholtz free energies of the α-phase and the sf-interface respectively and are defined as follows:

$$
\begin{aligned}
A^\alpha &= E^\alpha-\eta^\alpha\theta^\alpha \quad \alpha=s,f \\
A^{sf} &= E^{sf}-\eta^{sf}\theta^{sf}.
\end{aligned}
$$

4 Choice of variables

Since we have more variables than the number of equations and our system has particular assumptions, we need to choose independent and dependent variables. The independent variables will have to capture our assumptions.

Independent variables

We assume the following indenedent variables: ε_f, $\nabla\varepsilon_f$, $\dot{\varepsilon}_f$, $\overset{(m)}{\varepsilon}_f$, $\nabla\overset{(m)}{\varepsilon}_f$, θ^s, θ^f, θ^{sf}, ε_{sf}, ρ^f, ρ^{sf}, $\mathbf{d}^f$, $\mathbf{d}^{sf}$, $\mathbf{v}^{f,s}$, $\mathbf{v}^{sf,s}$, J^s, $\bar{C}^s$, $\bar{\mathbf{C}}^s$, $\overset{(n)}{\bar{\mathbf{C}}^s}$, for $m=1,...,p$ and $n=1,...,q$.

where ε_f is the porosity which accounts for local volume changes; $\nabla\varepsilon_f$, the porosity gradient accounts for buoyancy effects; ε_{sf} is the amount of sf-interface per unit volume; $\overset{(m)}{\varepsilon}_f$ is the m-th order material derivatives of ε_f in the direction of the solid phase velocity. These derivatives from orders 1 to p, i.e. $(m=1,...,p)$, capture the viscoelasticity of the solid (see Weinstein (2006)). The higher order gradients of porosity $\nabla\overset{(m)}{\varepsilon}_f$, account for flow due to moisture content. ε_{sf} is the areal density or specific surface of the sf-interface. The temperature gradients, $\nabla\theta^s, \nabla\theta^f$ and $\nabla\theta^{sf}$ account for the conduction of thermal energy at intermediate rates of heat transfer. The inclusion of fluid density gives rise to pressure, p^f; ρ^{sf} is the surface excess mass density of sf-interface. The rate of deformation tensor $\mathbf{d}^f$, incorporates the viscous nature of the fluid. The relative velocities are $\mathbf{v}^{f,s}$, the velocity of the fluid phase relative to that of solid phase and $\mathbf{v}^{sf,s}$, velocity of the interface relative to that of solid. The Jacobian J^s, captures the volumetric changes of the solid phase. The modified right Cauchy-Green tensor, $\bar{C}^s$, incorporates changes due to shear and the n-th time rates of change of the modified Cauchy-Green tensor $\overset{(n)}{\bar{\mathbf{C}}^s}$, $n=1,...,q$ accounts for the viscoelastic nature of the material Weinstein (2006).

Dependent variables

The following variables A^s, A^f, A^{sf}, $\mathbf{t}^s$, $\mathbf{t}^f$, $\mathbf{t}^{sf}$, $\mathbf{q}^s$, $\mathbf{q}^f$, $\mathbf{q}^{sf}$, η^s, η^f, η^{sf}, $\hat{e}^s_{sf}$, $\hat{e}^f_{sf}$, $\hat{\mathbf{T}}^s_{sf}$, $\hat{\mathbf{T}}^f_{sf}$ $\hat{Q}^s_{sf}$, $\hat{Q}^f_{sf}$, are not directly measurable but are determined as functions of directly measurable (independent) variables, where A^s, A^f, A^{sf} are the Helmholtz free energies, $\mathbf{t}^s$, $\mathbf{t}^f$, $\mathbf{t}^{sf}$ are the Cauchy stress tensors, $\mathbf{q}^s$, $\mathbf{q}^f$, $\mathbf{q}^{sf}$ are heat vectors, η^s, η^f, η^{sf} are entropy densities, $\hat{e}^s_{sf}$, $\hat{e}^f_{sf}$ are the mass exchange terms, $\hat{\mathbf{T}}^s_{sf}$, $\hat{\mathbf{T}}^f_{sf}$ are the momentum exchange terms, $\hat{Q}^s_{sf}$, $\hat{Q}^f_{sf}$ are the internal energy exchange terms.

Postulate

As a departure from the principle of equipresence, we hypothesize that the Helmholtz free energies A^s, A^f and A^{sf} of the solid phase, fluid phase and interface respectively, have the following independent variables (see Weinstein (2006)):

$$\begin{aligned} A^s &= A^s(\varepsilon_f, \overset{(m)}{\varepsilon}_f, \theta^s, J^s, \bar{\mathbf{C}}^s, \overset{(n)}{\bar{\mathbf{C}}^s}) && (21)\\ A^f &= A^f(\varepsilon_f, \overset{(m)}{\varepsilon}_f, \theta^f, \rho^f, \mathbf{d}^f, \bar{\mathbf{C}}^s, \overset{(n)}{\bar{\mathbf{C}}^s}) && (22)\\ A^{sf} &= A^{sf}(\varepsilon_f, \overset{(m)}{\varepsilon}_f, \theta^{sf}, \varepsilon_{sf}, \rho^{sf}, \bar{\mathbf{C}}^s, \overset{(n)}{\bar{\mathbf{C}}^s}) &&\\ & \quad m = 1, \ldots, p, \quad n = 1, \ldots, q. && (23)\end{aligned}$$

Extended entropy inequality

Liu (1972) proposed the extension of the entropy inequality by adding the products of Lagrange multipliers with conservation equations. In the present work we only use the conservation of mass equation as demonstrated in Bennethum and Cushman (1996),Singh (2002), Cushman and Bennethum (2004) and Weintein (2006),

$$\begin{aligned} \Lambda_{new} &= \Lambda_{old} + \sum_{\alpha=s,f} \lambda^{\alpha}_{\mathcal{M}} \mathcal{M}^{\alpha} + \lambda^{sf}_{\mathcal{M}} \mathcal{M}^{sf} \\ & \geq 0. && (24)\end{aligned}$$

where

$$\begin{aligned} \mathcal{M}^{\alpha} &= \frac{1}{\theta^{\alpha}} \left\{ \frac{D^{\alpha}(\varepsilon_{\alpha}\rho^{\alpha})}{Dt} + \varepsilon_{\alpha}\rho^{\alpha}\mathbf{I} : \mathbf{d}^{\alpha} \right. \\ & \left. -\hat{e}^{\alpha}_{sf} \right\} = 0, \\ \mathcal{M}^{sf} &= \frac{1}{\theta^{sf}} \left\{ \frac{D^{sf}(\varepsilon_{sf}\rho^{sf})}{Dt} + \varepsilon_{sf}\rho^{sf}\mathbf{I} : \mathbf{d}^{sf} \right. \\ & \left. +\hat{e}^{s}_{sf} + \hat{e}^{f}_{sf} \right\} = 0. \end{aligned}$$

The full expansion of the extended entropy inequality is presented in the appendix. We then use Coleman and Noll (1963) method to exploit this inequality, which leads to non-equilibrium results.

5 Stress tensor and heat flux results

Non-equilibrium results

Considering the extended entropy inequality from the appendix, the coefficients of the following variables, which are neither independent nor dependent

$$\dot{J}^s, \quad \dot{\rho}^f, \quad \dot{\rho}^{sf}, \quad \mathbf{d}^{sf},$$

must be zero. This results in the following non-equilibrium results:

$$\begin{aligned} \frac{1}{3} tr(\mathbf{t}^s) &= \rho^s J^s \frac{\partial A^s}{\partial J^s} = -p^s && (25)\\ \lambda^{sf} &= \rho^{sf} \frac{\partial A^{sf}}{\partial \rho^{sf}} = \frac{p^{sf}}{\rho^{sf}} && (26)\\ \mathbf{t}^{sf} &= -\rho^{sf}\lambda^{sf} = -p^{sf}\mathbf{I} && (27)\end{aligned}$$

Equation (25) tells us that physical pressure is equal to thermodynamic pressure. Equation (27) tells us that the interface Cauchy stress tensor is given by interfacial surface tension.

Equilibrium results

By letting all the coefficients variables that are neither independent nor dependent be zero, we obtain the dissipative or residual entropy inequality. Results from this dissipative entropy inequality at equilibrium are:

the fluid stress tensor is

$$\mathbf{t}^f = -(\rho^f)^2 \frac{\partial A^f}{\partial \rho^f} \mathbf{I} = -p^f \mathbf{I}. \qquad (28)$$

the solid stress tensor is

$$\begin{aligned} \mathbf{t}^s &= -p^s\mathbf{I} + 2\rho^s(\bar{\mathbf{F}^s}) \cdot \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}^s})^T \\ & +2\frac{\varepsilon_{sf}\rho^{sf}}{\varepsilon_s}(\bar{\mathbf{F}^s}) \cdot \frac{\partial A^{sf}}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}^s})^T \end{aligned}$$

$$
\begin{aligned}
&+\frac{2}{3}\rho^s \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s + \frac{2}{3}\frac{\varepsilon_f \rho^f}{\varepsilon_s}\frac{\partial A^f}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s \\
&+\frac{2}{3}\frac{\varepsilon_{sf}\rho^{sf}}{\varepsilon_s}\frac{\partial A^{sf}}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s .
\end{aligned}
$$

or

$$
\mathbf{t}^s = -p^s\mathbf{I} + \bar{\mathbf{t}}^{se} + \frac{\varepsilon_f}{\varepsilon_s}\bar{\mathbf{t}}^{sh} + \frac{\varepsilon_{sf}}{\varepsilon_s}\bar{\mathbf{t}}^{si} \tag{29}
$$

where

$$
\begin{aligned}
\bar{\mathbf{t}}^{se} &= 2\rho^s \left(\bar{\mathbf{F}}^s \cdot \frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}}^s)^T - \frac{1}{3}\frac{\partial A^s}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s \right) \\
\bar{\mathbf{t}}^{sh} &= 2\rho^f \left(\bar{\mathbf{F}}^s \cdot \frac{\partial A^f}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}}^s)^T - \frac{1}{3}\frac{\partial A^f}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s \right) \\
\bar{\mathbf{t}}^{si} &= 2\rho^{sf} \left(\bar{\mathbf{F}}^s \cdot \frac{\partial A^{sf}}{\partial \bar{\mathbf{C}}^s} \cdot (\bar{\mathbf{F}}^s)^T \right. \\
&\quad \left. - \frac{1}{3}\frac{\partial A^{sf}}{\partial \bar{\mathbf{C}}^s} : \bar{\mathbf{C}}^s \right) .
\end{aligned}
$$

The term $\bar{\mathbf{t}}^{se}$ is the effective stress and also referred to as Terzhagi's stress in Weinstein (2006). Hydration stress is given by $\bar{\mathbf{t}}^{sh}$. The last term of equation (29) is new and brought about by the inclusion of the thermodynamic properties of the interface. We notice that $\bar{\mathbf{t}}^{si}$ is directly proportional to the areal density function of the interface and also depends on the change in interface free energy with respect to shear. Furthermore,

$$
\bar{\mathbf{t}}^{se} + \frac{\varepsilon_f}{\varepsilon_s}\bar{\mathbf{t}}^{sh} + \frac{\varepsilon_{sf}}{\varepsilon_s}\bar{\mathbf{t}}^{si}
$$

forms the deviatoric part of the solid phase stress tensor.

There is no heat flux at equilibrium and thus we have

$$
\mathbf{q}^\alpha = \mathbf{q}^{sf} = \mathbf{0} \quad \alpha = s, f.
$$

Constitutive forms

If at equilibrium, we have a result $A|_e = B$, then away from equilibrium we will have $A = B + C$, where $C|_e = 0$. Note that C will depend on all the chosen independent variables. We will refer to $A = B + C$ as a constitutive form. From equation (28), away from equilibrium the fluid stress tensor becomes

$$
\mathbf{t}^f = -p^f\mathbf{I} + \tau^f, \tag{30}
$$

the solid stress tensor becomes

$$
\mathbf{t}^s = -p^s\mathbf{I} + \bar{\mathbf{t}}^{se} + \frac{\varepsilon_f}{\varepsilon_s}\bar{\mathbf{t}}^{sh} + \frac{\varepsilon_{sf}}{\varepsilon_s}\bar{\mathbf{t}}^{si} + \tau^s, \tag{31}
$$

the heat fluxes for the phases become

$$
\mathbf{q}^\alpha = \bar{\mathbf{q}}^\alpha, \quad \alpha = s, f \tag{32}
$$

and for the interface, we have

$$
\mathbf{q}^{sf} = \bar{\mathbf{q}}^{sf}. \tag{33}
$$

The additional non-equilibrium terms in the constitutive forms (30) and (31) are highly nonlinear.

6 Near equilibrium

We use Taylor's theorem to linearize nonequilibrium terms of constitutive forms about the equilibrium. The linearization is done with respect to heat conduction, fluid viscosity and viscoelasticity of the solid.

For the fluid phase stress tensor the nonequilibrium term becomes

$$
\tau^f = \mathbf{H}^f \cdot \nabla\theta + \mathbf{D}^f : \mathbf{d}^f \tag{34}
$$

For the solid phase stress tensor the nonequilibrium term becomes

$$
\begin{aligned}
\tau^s &= \mathbf{H}^s \cdot \nabla\theta + \sum_{r=1}^{p} \mathbf{E}^{sr} \overset{(r)}{\varepsilon_f} \\
&\quad + \sum_{n=1}^{q} \mathbf{F}^s \mathbf{K}^{sn} : \overset{(n)}{\bar{\mathbf{C}}^s} (\mathbf{F}^s)^{-1}
\end{aligned} \tag{35}
$$

The heat fluxes for the fluid and the solid are given respectively by

$$\bar{\mathbf{q}}^f \quad = \quad -\mathbf{M}^f : \nabla\theta + \mathbf{N}^f : \mathbf{d}^f. \qquad (36)$$

$$\begin{aligned} \bar{\mathbf{q}}^s \quad &= \quad -\mathbf{M}^s : \nabla\theta + \mathbf{N}^s : \mathbf{d}^f + \sum_{l=1}^{p} \mathbf{S}^{sl} \overset{(l)}{\varepsilon}_f \\ &\quad + \sum_{n=1}^{q} \mathbf{F}^s \cdot \mathbf{W}^{sn} \overset{(n)}{\overline{\mathbf{C}}}^{s} \cdot (\mathbf{F}^s)^{-1}. \qquad (37) \end{aligned}$$

We note that the material coefficients in these expressions, viz. $\mathbf{S}^{sl}$ is a first order tensor, $\mathbf{M}^\alpha$ is a second order tensor, $\mathbf{N}^\alpha$ and $\mathbf{W}^{sn}$ are third order tensors.

$$\bar{\mathbf{q}}^{sf} \quad = \quad -\mathbf{M}^{sf}\nabla\theta + \mathbf{N}^{sf} : \mathbf{d}^f. \qquad (38)$$

In this expression, the material coefficient $\mathbf{M}^{sf}$ is a second order tensor and $\mathbf{N}^{sf}$ is a third order tensor.

In order to determine the exact nature of all these material coefficients, we need to perform experiments.

Remark: All the heat fluxes generalize Fourier's law of heat conduction.

Constitutive form near equilibrium

The expression of the fluid phase stress tensor near equilibrium is

$$\mathbf{t}^f \quad = \quad -p\mathbf{I} + \mathbf{H}^f \cdot \nabla\theta + \mathbf{D}^f : \mathbf{d}^f. \qquad (39)$$

The expression of the solid phase stress tensor near equilibrium is

$$\begin{aligned} \mathbf{t}^s \quad &= \quad -p^s\mathbf{I} + \bar{\mathbf{t}}^{se} + \frac{\varepsilon_f}{(1-\varepsilon_f)}\bar{\mathbf{t}}^{sh} \\ &\quad + \frac{\varepsilon_{sf}}{(1-\varepsilon_f)}\mathbf{t}^{si} + \mathbf{H}^s \cdot \nabla\theta + \sum_{r=1}^{p} \mathbf{E}^{sr} \overset{(r)}{\varepsilon}_f \\ &\quad + \sum_{n=1}^{q} \mathbf{F}^s . \mathbf{K}^{sn} : \overset{(n)}{\overline{\mathbf{C}}}^{s} . (\mathbf{F}^s)^{-1} \qquad (40) \end{aligned}$$

The expressions of the fluid and solid phase heat fluxes near equilibrium are

$$\mathbf{q}^f \quad = \quad -\mathbf{M}^f : \nabla\theta + \mathbf{N}^f : \mathbf{d}^f \qquad (41)$$

and

$$\begin{aligned} \mathbf{q}^s \quad &= \quad -\mathbf{M}^s : \nabla\theta + \mathbf{N}^s : \mathbf{d}^f + \sum_{l=1}^{p} \mathbf{S}^{sl} \overset{(l)}{\varepsilon}_f \\ &\quad + \sum_{n=1}^{q} \mathbf{F}^s \cdot \mathbf{W}^{sn} \overset{(n)}{\overline{\mathbf{C}}}^{s} \cdot (\mathbf{F}^s)^{-1}. \qquad (42) \end{aligned}$$

respectively.

Total stress and heat fluxes

First we have the total pressure given by

$$p = (1-\varepsilon_f)p^s + \varepsilon_f p^f.$$

We then have the total stress tensor as

$$\mathbf{t} = (1-\varepsilon_f)\mathbf{t}^s + \varepsilon_f \mathbf{t}^f$$

or

$$\begin{aligned} \mathbf{t} \quad &= \quad -p\mathbf{I} + \mathbf{t}^{se} + \frac{\varepsilon_f}{(1-\varepsilon_f)}\mathbf{t}^{sh} \\ &\quad + \frac{\varepsilon_{sf}}{(1-\varepsilon_f)}\mathbf{t}^{si} + \mathbf{D}^f : \mathbf{d}^f \\ &\quad + [(1-\varepsilon_f)\mathbf{H}^s + \varepsilon_f \mathbf{H}^f] \cdot \nabla\theta \\ &\quad + \sum_{r=1}^{p} \mathbf{E}^{sr} \overset{(r)}{\varepsilon}_f + \sum_{n=1}^{q} \mathbf{F}^s \cdot \mathbf{K}^{sn} : \overset{(n)}{\overline{\mathbf{C}}}^{s} \cdot (\mathbf{F}^s)^{-1}. \\ &\qquad (43) \end{aligned}$$

The total heat flux is

$$\mathbf{q} = (1-\varepsilon_f)\mathbf{q}^s + \varepsilon_f \mathbf{q}^f$$

or

$$\begin{aligned} \mathbf{q} \quad &= \quad -[(1-\varepsilon_f)\mathbf{M}^s + \varepsilon_f \mathbf{M}^f] \cdot \nabla\theta \\ &\quad + [(1-\varepsilon_f)\mathbf{N}^s + \varepsilon_f \mathbf{N}^f] : \mathbf{d}^f + \sum_{l=1}^{p} \mathbf{S}^{sl} \overset{(l)}{\varepsilon}_f \\ &\quad + \sum_{n=1}^{q} \mathbf{F}^s \cdot \mathbf{W}^{sn} : \overset{(n)}{\overline{\mathbf{C}}}^{s} \cdot (\mathbf{F}^s)^{-1}. \qquad (44) \end{aligned}$$

Conclusion

Using macroscopic balance equation (averaged from mesoscale to macroscale), the hybrid mixture theory method, Coleman and Noll method and Liu's Lagrange multiplier's, we obtained the interfacial tension as the only result which is valid everywhere. All other results were determined near equilibrium by applying linear Taylor expansion about equilibrium. These all have the following dependencies

- From equation (27) the interfacial tension $\mathbf{t}^{sf}$, depends on the interface thermodynamic pressure only.
- From equation (43) the total particle stress tensor $\mathbf{t}$, depends on the porosity, the total thermodynamic pressure, hydration forces, effective stresses due to the solid phase and the interphase, heat conduction, fluid viscosity and the solid matrix viscoelasticity.
- From equation (44) the total particle heat flux $\mathbf{q}$ depends on the porosity, fluid viscosity, heat conductio and the solid matrix viscoelasticity.

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Appendix

After appropriate substitutions of the old entropy inequality, the Lagrange multipliers, the conservation of mass equations and simplification, we obtain the following expression of the extended entropy inequality (24):

$$\begin{aligned}\Lambda_{new} &= \Lambda_{old} + \lambda^s \mathcal{M}^s + \lambda^f \mathcal{M}^f + \lambda^{sf} \mathcal{M}^{sf} \geq 0 \\ &= -\left(\frac{\varepsilon_s \rho^s}{\theta^s} \frac{\partial A^s}{\partial \varepsilon_f} + \frac{\varepsilon_f \rho^f}{\theta^f} \frac{\partial A^f}{\partial \varepsilon_f} \right. \\ &\quad \left. + \frac{\varepsilon_{sf} \rho^{sf}}{\theta^{sf}} \frac{\partial A^{sf}}{\partial \varepsilon_f} - \frac{\rho^f}{\theta^f} \lambda^f \right) \frac{D^s \varepsilon_f}{Dt}\end{aligned}$$

$$-\sum_{m=1}^{p-1}\Bigg(\frac{\varepsilon_s\rho^s}{\theta^s}\frac{\partial A^s}{\partial\overset{(m)}{\varepsilon}_f}+\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\overset{(m)}{\varepsilon}_f}$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\overset{(m)}{\varepsilon}_f}\Bigg)\overset{(m+1)}{\varepsilon}_f$$

$$-\Bigg[\frac{\varepsilon_s\rho^s}{\theta^s}\frac{\partial A^s}{\partial\varepsilon_f^{(p)}}+\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\varepsilon_f^{(p)}}$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\varepsilon_f^{(p)}}\Bigg]\varepsilon_f^{(p+1)}$$

$$-\left[\frac{\varepsilon_s\rho^s}{\theta^s}\frac{\partial A^s}{\partial J^s}-\frac{1}{3}\frac{\varepsilon_s}{\theta^s J^s}tr(\mathbf{t}^s)\right]\frac{D^s J^s}{Dt}$$

$$-\Bigg(\frac{\varepsilon_s\rho^s}{\theta^s}\frac{\partial A^s}{\partial\overline{\mathbf{C}}^s}+\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\bar{C}^s}+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\overline{\mathbf{C}}^s}$$

$$-\frac{1}{2}(\bar{\mathbf{F}}^s)^{-1}\cdot\frac{\varepsilon_s\mathbf{t}^s}{\theta^s}\cdot(\bar{\mathbf{F}}^s)^{-T}$$

$$-\frac{1}{2}\frac{\varepsilon_s\rho^s}{\theta^s}\lambda^s\cdot(\bar{\mathbf{F}}^s)^{-1}.(\bar{\mathbf{F}}^s)^{-T}\Bigg):\frac{D^s\bar{\mathbf{C}}^s}{Dt}$$

$$-\left[\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\rho^f}-\frac{\varepsilon_f\lambda^f}{\theta^f}\right]\frac{D^s\rho^f}{Dt}$$

$$-\left[\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\varepsilon_{sf}}-\frac{\rho^{sf}\lambda^{sf}}{\theta^{sf}}\right]\frac{D^s\varepsilon_{sf}}{Dt}$$

$$-\left[\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\rho^{sf}}-\frac{\varepsilon_{sf}\lambda^{sf}}{\theta^{sf}}\right]\frac{D^s\rho^{sf}}{Dt}$$

$$-\sum_{n=1}^{q-1}\Bigg(\frac{\varepsilon_s\rho^s}{\theta^s}\frac{\partial A^s}{\partial\overset{(n)}{\bar{\mathbf{C}}^s}}+\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\overset{(n)}{\bar{\mathbf{C}}^s}}$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\overset{(n)}{\bar{\mathbf{C}}^s}}\Bigg):\frac{D^s\overset{(n+1)}{\bar{\mathbf{C}}^s}}{Dt}$$

$$-\Bigg[\frac{\varepsilon_s\rho^s}{\theta^s}\frac{\partial A^s}{\partial\overset{(q)}{\bar{\mathbf{C}}^s}}+\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\overset{(q)}{\bar{\mathbf{C}}^s}}$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\overset{(q)}{\bar{\mathbf{C}}^s}}\Bigg]:\frac{D^s\overset{(q)}{\bar{\mathbf{C}}^s}}{Dt}$$

$$-\left[\frac{\varepsilon_s\rho^s}{\theta^s}\left(\frac{\partial A^s}{\partial\theta^s}+\eta^s\right)\right]\frac{D^s\theta^s}{Dt}$$

$$-\left[\frac{\varepsilon_f\rho^f}{\theta^f}(\frac{\partial A^f}{\partial\theta^f}+\eta^f)\right]\frac{D^s\theta^f}{Dt}$$

$$-\left[\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\left(\frac{\partial A^{sf}}{\partial\theta^{sf}}+\eta^{sf}\right)\right]\frac{D^s\theta^{sf}}{Dt}$$

$$-\left[\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\mathbf{d}^f}\right]:\frac{D^f\mathbf{d}^f}{D^t}$$

$$-\Bigg[\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\varepsilon_f}\nabla\varepsilon_f+\frac{\varepsilon_f\rho^f}{\theta^f}\sum_{m=1}^{p}\frac{\partial A^f}{\partial\overset{(m)}{\varepsilon_f}}\nabla\overset{(m)}{\varepsilon}_f$$

$$+\frac{\varepsilon_f\rho^f}{\theta^f}\left(\frac{\partial A^f}{\partial\theta^f}+\eta^f\right)\nabla\theta^f+\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\bar{C}^s}:\nabla\bar{C}^s$$

$$+\frac{\varepsilon_f\rho^f}{\theta^f}\sum_{n=1}^{q}\frac{\partial A^f}{\partial\overset{(n)}{\overline{\mathbf{C}}^s}}:\nabla\overset{(n)}{\overline{\mathbf{C}}^s}+\frac{\varepsilon_f\rho^f}{\theta^f}\frac{\partial A^f}{\partial\rho^f}\nabla\rho^f$$

$$-\frac{\varepsilon_f\lambda^f}{\theta^f}\nabla\rho^f-\frac{\rho^f\lambda^f}{\theta^f}\nabla\varepsilon_f+\frac{\hat{\mathbf{T}}_{sf}^f}{\theta^f}\Bigg]\mathbf{v}^{f,s}$$

$$-\Bigg(\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\varepsilon_f}\nabla\varepsilon_f+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\sum_{m=1}^{p}\frac{\partial A^{sf}}{\partial\overset{(m)}{\varepsilon_f}}\nabla\overset{(m)}{\varepsilon}_f$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\varepsilon_{sf}}\nabla\varepsilon_{sf}-\frac{\rho^{sf}\lambda^{sf}}{\theta^{sf}}\nabla\varepsilon_{sf}$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\rho^{sf}}\nabla\rho^{sf}-\frac{\varepsilon_{sf}\lambda^{sf}}{\theta^{sf}}\nabla\rho^{sf}$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\left(\frac{\partial A^{sf}}{\partial\theta^{sf}}+\eta^{sf}\right)\nabla\theta^{sf}$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\frac{\partial A^{sf}}{\partial\bar{\mathbf{C}}^s}:\nabla\bar{\mathbf{C}}^s$$

$$+\frac{\varepsilon_{sf}\rho^{sf}}{\theta^{sf}}\sum_{n=0}^{q}\frac{\partial A^{sf}}{\partial\overset{(n)}{\bar{\mathbf{C}}^s}}:\nabla\overset{(n)}{\bar{\mathbf{C}}^s}$$

$$-\frac{1}{\theta^{sf}}\left(\hat{\mathbf{T}}_{sf}^s+\hat{\mathbf{T}}_{sf}^f\right)\Bigg)\mathbf{v}^{sf,s}$$

$$+\frac{1}{(\theta^s)^2}\varepsilon_s\mathbf{q}^s\cdot\nabla\theta^s+\left(\frac{\varepsilon_f\mathbf{t}^f}{\theta^f}+\frac{\varepsilon_f\rho^f\lambda^f}{\theta^f}\mathbf{I}\right):\mathbf{d}^f$$

$$+\frac{1}{(\theta^f)^2}\varepsilon_f\mathbf{q}^f\cdot\nabla\theta^f+\left[\frac{\varepsilon_{sf}\mathbf{t}^{sf}}{\theta^{sf}}+\frac{\varepsilon_{sf}\rho^{sf}\lambda^{sf}}{\theta^{sf}}\mathbf{I}\right]:\mathbf{d}^{sf}$$

$$+\frac{1}{(\theta^{sf})^2}\varepsilon_{sf}\mathbf{q}^{sf}\cdot\nabla\theta^{sf}$$

$$-\frac{1}{\theta^{sf}}\sum_{\alpha=s,f}\left(\frac{\hat{Q}_{sf}^\alpha}{\theta^\alpha}-\hat{e}_{sf}^\alpha\eta^\alpha\right)\theta^{sf,\alpha}$$

$$-\frac{\hat{e}_{sf}^s}{\theta^{sf}}\left(A^{s,sf}-\frac{1}{3}\frac{\theta^{sf}}{\theta^s\rho^s}tr(\mathbf{t}^s)+\lambda^{sf}+\frac{1}{2}(v^{s,sf})^2\right)$$

$$-\frac{\hat{e}_{sf}^f}{\theta^{sf}}\left(A^{f,sf}+\frac{\lambda^f\theta^{sf}}{\theta^f}+\lambda^{sf}+\frac{1}{2}(v^{f,sf})^2\right)\geq 0.$$

Nomenclature

A^α	Helmholtz free energy function for the α-phase.
A^{sf}	Helmholtz free energy function for the sf-interface.
b^α	external supply of entropy to the α-phase.
$b^{\alpha\beta}$	external supply of entropy to the $\alpha\beta$-interface.
$\mathbf{C}^s$	Right Cauchy-Green tensor.
$\bar{\mathbf{C}}^s$	modified right Cauchy-Green tensor.
$\mathbf{d}^\alpha$	strain rate tensor for the α-phase.
$\mathbf{E}^s$	Lagrangian strain tensor.
E^α	internal energy of the α-phase per mass of α phase.
$E^{\alpha\beta}$	internal energy of the $\alpha\beta$-interface per mass of $\alpha\beta$-interface.
$\hat{e}^\alpha_{\alpha\beta}$	rate of transfer of mass from $\alpha\beta$- interface to the α phase.
$\mathbf{F}^s$	deformation gradient of the solid phase.
$\bar{\mathbf{F}}^s$	modified deformation gradient of the solid phase.
G^α	Gibbs free energy function.
$\mathbf{g}^\alpha$	external supply of momentum to the α-phase.
$\mathbf{g}^{\alpha\beta}$	external supply of momentum to the $\alpha\beta$-interface.
h^α	external supply of energy to the α-phase .
$h^{\alpha\beta}$	external supply of energy to the $\alpha\beta$-interface.
J^s	Jacobian of the solid phase.
$\hat{Q}^\alpha_{\alpha\beta}$	energy transferred to the α-phase from the $\alpha\beta$ interface.
$\mathbf{q}^\alpha$	heat conduction vector for the α-phase.
$\mathbf{q}^{\alpha\beta}$	heat conduction vector for the $\alpha\beta$-interface.
$\hat{\mathbf{T}}^\alpha_{\alpha\beta}$	force exerted on the α phase by the $\alpha\beta$-interface.
$\mathbf{t}^\alpha$	stress tensor for the α phase.
$\mathbf{t}^{\alpha\beta}$	stress tensor for the $\alpha\beta$-interface.
$\mathbf{v}^\alpha$	velocity of the α-phase.
$\mathbf{v}^{\alpha\beta}$	velocity of the $\alpha\beta$-interface.
$\mathbf{v}^{\alpha,\alpha\beta}$	velocity of the α-phase relative to the velocity of the $\alpha\beta$-interface, $\mathbf{v}^\alpha - \mathbf{v}^{\alpha\beta}$.
$\mathbf{x}$	position vector of a solid phase particle in the deformed configuration.
$\mathbf{X}$	position vector of a solid phase particle in the undeformed configuration.
η^α	entropy of the α-phase.
$\eta^{\alpha\beta}$	entropy of the $\alpha\beta$ interface.
ε^α	volume fraction of the α-phase.
$\varepsilon^{\alpha\beta}$	specific interfacial area of $\alpha\beta$-interface (area per unit of system volume).
ρ^α	density of α-phase, mass of α-phase per volume of α-phase.
$\rho^{\alpha\beta}$	density of $\alpha\beta$-interface, mass of $\alpha\beta$-interface per area of $\alpha\beta$ interface.
φ^α	entropy conduction vector of the α-phase.
$\varphi^{\alpha\beta}$	entropy conduction vector of the $\alpha\beta$-interface.
ρ^α	volumetric mass density of the α-phase.
ρ^α	volumetric mass density of the interface.

Φ^{α}_{sf}	body supply of of entropy to the α-phase from the sf-interface.
Λ^{α}	rate of net production of entropy to the α-phase.
Λ^{sf}	rate of net production of entropy to the interface.
$\mathcal{M}^{\alpha}$	The α-phase continuity equation.
$\mathcal{P}^{\alpha}$	The α-phase momentum equation.
$\mathcal{E}^{\alpha}$	The α-phase energy equation.
$\mathcal{M}^{sf}$	The interface continuity equation.
$\mathcal{P}^{sf}$	The interface momentum equation.
$\mathcal{E}^{sf}$	The interface energy equation.
$\overset{(m)}{\varepsilon_f}$	m^{th} order material derivative of the ε_f with respect to the macroscale solid phase velocity.
$\overset{(n)}{\bar{\mathbf{C}}^s}$	n^{th} order material derivative of the $\bar{\mathbf{C}}^s$ with respect to the macroscale solid phase velocity.

Differential operators used

D^{α}/Dt	material derivative following the motion in the α-phase, $\partial/\partial t + \mathbf{v}^{\alpha} \cdot \bigtriangledown$.
$D^{\alpha\beta}/Dt$	material derivative following the motion in the $\alpha\beta$-interface, $\partial/\partial t + \mathbf{v}^{\alpha\beta} \cdot \bigtriangledown$.
$\bigtriangledown$	gradient operator with respect to spatial coordinates.

Superscripts and subscripts

s	solid phase.
f	fluid phase.
sf	solid-fluid interface.
T	transpose of a tensor.