Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries

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The main purpose of this work is to develop a macroscale thermodynamic theory to describe two-phase flow in porous media. Full thermodynamic properties are assigned to the boundary surfaces separating the phases at the microscale. Macroscopic equations of balance for mass, momentum, and energy for each phase and interface along with the averaged entropy inequality are employed as the starting point. A constitutive theory is developed resulting in balance equations and thermodynamics appropriate for modeling multiphase flow in porous media. Volume fractions of phases and areal fractions of interfaces are explicitly included in the theory. Incorporation of the interface equations into the theory allows for a complete description of the problem. The manipulations provide explicit functional dependence of the capillary pressure. An extended form of Darcy's law for multiphase flow is obtained from the macroscopic equations of momentum balance. An additional term which accounts for non-uniform fluid saturation at equilibrium appears in the result.

INTRODUCTION

In the past few decades, a wealth of theoretical work on various aspects of thermomechanics of multiphase systems has appeared in the literature. This has been due, at least partly, to the fact that multiphase flows are encountered in numerous practical engineering problems. The majority of these studies are aimed at developing a macroscopic description of multiphase systems.

An important issue in modeling multiphase systems is the correct mathematical description of boundary surfaces separating the phases. In describing even the simplest thermomechanical problem for a medium consisting of two or more phases, one must take into account the thermodynamic properties of the interfaces. For example, the distribution of two immiscible fluids in a porous medium is strongly influenced by the presence of interfaces and their properties such as surface tension.

These considerations apply to the macroscopic as well as the microscopic description of multiphase systems. The conceptual transformation of the microscopic description of a multiphase system to a macroscopic one apparently removes microscopically identifiable interfaces. However, the interfacial properties may not be discarded and one must properly incorporate the attributes of interfaces into the full macroscopic description. For example, the capillary pressure, the difference in the average pressure of two fluids in a porous medium, must be appropriately related to the interfacial tension of the two fluids.

Because the theoretical description of multiphase flow is such a difficult problem, efforts to obtain appropriate balance laws have proceeded in more than one direction. The various approaches used in developing macroscopic theories for multiphase systems can be classified into three main groups: macroscopicization, mixture theory, and a combination of the two. The identifying characteristics—contributions and stumbling blocks—of these approaches are discussed next.

Macroscopicization or averaging

The development starts with a microscopic description. Conservation laws are introduced at the microscopic scale. Assumptions are made about the microscopic behaviour of phases and interfaces, and accordingly, constitutive equations are also introduced at the microscopic scale (e.g. Newtonian fluid, rigid or elastic solid, Fickian diffusion, etc.). Resulting field equations are then averaged to obtain macroscopic field equations. Often in order to make the averaging procedure tractable and to obtain desirable results, many assumptions are made before, during and after averaging. These assumptions typically relate to the spatial and/or temporal distribution of properties, expected order of magnitude of various terms, and existence of certain relations among various properties; all based on intuitive and somewhat heuristic arguments. For example, sometimes microscopic quantities such as temperature, velocity, and mass density are required to vary monotonously within a representative elementary volume (REV), while other quantities — such as heat capacity and viscosity — are assumed to remain constant or vary linearly (see, e.g., Bachmat and Bear5). Alternatively, a unique mapping may be assumed to exist between the


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microscopic and macroscopic velocity field at a point (see, e.g., Whitaker\textsuperscript{46}). The advantage of the averaging approach is that information available at the microscale is passed on to the macroscale; the interfaces and their thermodynamic properties are explicitly taken into account; and the microstructure is more appropriately modeled. Often, useful closed-form relations are obtained for macroscopic material coefficients. The disadvantage of this approach is that the types of restrictions imposed, especially those justifying neglect of various microscopic and macroscopic terms, may seriously limit the generality of the results and the opportunity to systematically explore fundamental behavior of complex phenomena. Also, construction of a full thermodynamic theory at the macroscale becomes intractable. That is, basic thermodynamic relations among macroscopic free energy, pressure, temperature, entropy, chemical potential, mass density and solute concentrations cannot be obtained. The second law of thermodynamics is typically not studied in this group of theories. Works of Whitaker\textsuperscript{41}, Bear and Bachmat\textsuperscript{6}, and Slattery\textsuperscript{38} are examples within this group.

Mixture theory

The development starts with a macroscopic description of the system. Conservation laws are introduced at the macroscale in analogy with the balance laws of single-phase bodies. Additional terms are introduced to account for the exchange of properties among the phases. Assumptions are made about the expected behavior of the phases at the macroscale. Constitutive equations are then introduced either by direct postulation of desirable relations or by following a systematic procedure based on the exploitation of the second law of thermodynamics known as the Coleman and Noll method. These theories are advanced largely by researchers from continuum mechanics and are generally referred to as ‘mixture theories’. A review of these works is contained in Ref. 7. The advantages of this approach are that assumptions are kept to a minimum and are all introduced at the level of observations (i.e. the macroscopic level). Therefore, identification of practical situations where the assumptions apply is more feasible.

The disadvantage of the mixture theory approach is that no connection is made with the microscopic reality. As a result, certain essential features of multiphase systems are easily overlooked; and sometimes unnecessary assumptions are imposed on macroscopic quantities. For example, in some works, volume fractions of individual phases are not considered at all (e.g. Bowen\textsuperscript{4} and Dobran\textsuperscript{19}). Also, virtually no immiscible mixture theory includes the interfacial area per volume (areal density). Indeed, a serious deficiency of these theories, especially when applied to porous media, is the absence of interfacial properties from both conservation laws and constitutive equations. Thus, for example, interfacial tension and its relation to capillary pressure is not accounted for. Such effects must be present in the macroscopic conservation laws for the system\textsuperscript{10,19,28}. However, mixture theories for multiphase flow in porous media exist\textsuperscript{10,39} where the difference in fluid pressure is identified as capillary pressure even though interfacial effects are totally absent from the theory. Exceptions may be found in the works of Williams\textsuperscript{42} and Sampaio and Williams\textsuperscript{36} where a term is introduced and called ‘interaction stress’ which resembles interfacial stress in the theory to be developed here.

Combination

These are theories which basically combine the best aspects of the previous two groups. The development starts at the microscale. Conservation laws for phases and interfaces are introduced at the microscopic scale. These equations are then averaged to obtain macroscopic conservation laws. No assumptions are made about the constitution of the phases at the microscale. Instead, these constitutive assumptions are introduced at the macroscale either by direct postulation of desirable relations or by following the Coleman and Noll method. Although this method is more general than other approaches, the ultimate quality of the results obtained is related to the appropriateness of the constitutive assumptions postulated. Furthermore, functional dependence of some variables is obtained, but the explicit functional form must be subjected to experimental investigation.

This constitutive approach has proved to be very powerful in obtaining fundamentally sound theories for multiphase media. It is attractive because it provides both physical and thermodynamic descriptions of multiphase processes. This approach has been employed by Drew\textsuperscript{15}, Ishii\textsuperscript{24}, Nigmatulin\textsuperscript{52}, Hassanizadeh and Gray\textsuperscript{22}, Marle\textsuperscript{28}, Ahmadi and Farshad\textsuperscript{3}, Hassanizadeh\textsuperscript{20}, and Kalaydjian\textsuperscript{25}.

Two recent advances in the description of multiphase flow in porous media are particularly notable:

(1) A physical basis for describing thermomechanics of multiphase systems has been obtained. In particular, a general set of macroscopic conservation laws has been derived which incorporates the effects of thermodynamic properties of interfacial boundaries. Equations for these boundaries, as they evidence themselves at the macroscale, have also been developed. The most complete set of conservation equations are obtained by Marle\textsuperscript{28} and Gray and Hassanizadeh\textsuperscript{19}. They assign mass, momentum, stress, energy, and entropy to the interfaces and systematically average microscopic interfacial balance laws to arrive at macroscopic conservation equations for the system. Accounting for the important interfacial properties such as surface tension is essential in developing a coherent thermodynamics of multiphase systems, as will be demonstrated in the current manuscript.

(2) The physical bases of such phenomenological relations as Darcy’s law and Fourier’s law in the form modified for application to multiphase flow can be explored and elucidated. In particular, a more general formulation of Darcy’s law has been obtained which allows for an intrinsic coupling between the motion of various fluids in the medium\textsuperscript{10,25,39,41}. The potential significance of such a coupling to the correct description of multiphase flow has been discussed in a series of articles by Rose\textsuperscript{35}.

Despite these advances, a number of outstanding issues remain. Among these are the following:

(1) How does the capillary pressure, the difference between two fluid pressures, relate to other macroscopic properties? In existing models of porous media multiphase flow, capillary pressure is empirically expressed as a function of saturation of the
wetting phase. What is the thermodynamic basis for this relation?

(2) Experimental evidence indicates that microscopic interfacial tension, interfacial curvature, fluid pressure, and other microscopic quantities have a determining effect on the thermodynamics of individual phases. How do these effects manifest themselves at the macroscopic scale?

(3) At the microscale, a set of thermodynamic relationships exists among variables such as Gibbs and Helmholtz free energies, temperature, pressure, density, entropy, etc. Do corresponding thermodynamic relationships exist among the macroscopic properties? How does fluid saturation, a quantity which is not defined at the microscale, enter the thermodynamic relations?

(4) According to the Darcy-Buckingham equation, the necessary condition for no horizontal flow in an unsaturated soil is to have zero horizontal suction gradient. On the other hand, in an unsaturated, uniform soil a saturation gradient (and thus a suction gradient) may exist under no flow conditions. How is this contradiction explained? Is Darcy's law inadequate for description of multiphase flow?

The main purpose of the present work is to develop a macroscopic thermodynamic theory to describe two-phase flow in porous media. This theory will show the way to find answers to at least some of the questions raised above. The theory is systematic in the sense that simplifying assumptions made in the course of the development may be relaxed if more general results are desired. Also, extension of the theory to more than two fluid phases is rather straightforward, although not explicitly considered here. Equilibrium and non-equilibrium relationships are obtained for capillary pressure. These relationships allow for physical interpretation of capillary pressure more insightful than merely recognizing it as the difference between two fluid pressures. The macroscopic counterpart of interfacial tension comes out of the results naturally and is meaningfully related to other thermodynamic properties. An extended form of Darcy's law is obtained which allows for a gradient in fluid pressures even under no flow conditions.

The paper is organized to provide a short description of microscopic and macroscopic pictures. Then kinematics and some auxiliary relations are given. Macroscopic conservation laws for phases and interfaces are introduced. A general formulation of the second law of thermodynamics for a multiphase system is given and utilized to obtain an expanded form of the entropy inequality. Constitutive equations are discussed in general, and then an appropriate set is postulated. The reduced forms of constitutive relations which arise from the Coleman and Noll method are obtained. Based on the definition of thermodynamic equilibrium, further information concerning the form of the constitutive relations is obtained. Linearization of these constitutive expressions provides a generalized form of Darcy's law. Finally, a discussion of the results and a set of conclusions is provided.

**KINEMATICS, AUXILIARY RELATIONS AND NOTATION**

Consider a porous medium composed of a deformable rock skeleton saturated with two compressible fluids. It is known that of two fluids filling the pore space of a porous medium, one will always have a higher potential to form interfaces with the solid phase, or in other words, to 'wet' the solid phase boundaries. Thus, the two fluid phases are commonly termed as 'wetting' and 'nonwetting' fluids. In this work, superscripts (and/or subscripts) \( w \), \( n \), and \( s \) are employed to designate the wetting fluid phase, the nonwetting fluid phase, and the solid phase, respectively. Greek letters are employed to designate a general phase. They range over all phases \( w \), \( n \), and \( s \) unless otherwise specified.

The two fluids and the solid phases are separated at the microscale by sharp interfaces. The interfaces mass and other thermodynamic properties are supposed to have their own independent motions. Superscripts (and/or subscripts) \( w_n \), \( w_s \), and \( n_s \) are employed to designate the interfaces between wetting and nonwetting fluids, wetting fluid and solid, and nonwetting fluid and solid, respectively. A combination of two Greek letters, e.g., \( \alpha \beta \), is employed to designate a general interface. They range over all three interfaces unless otherwise specified. Note that \( \alpha \beta \) and \( \beta \alpha \) would refer to the same interface.

A final characteristic of a multiphase system which is of importance at the microscale is a contact line; a line where three interfaces intersect (see Fig. 1). In this manuscript, contact lines will be assumed to possess no thermodynamic properties but to allow for exchange of properties among interfaces. The subscript sequence \( \alpha \beta \gamma \) is used to designate a contact line where the interfaces \( \alpha \beta \), \( \beta \gamma \), and \( \gamma \alpha \) intersect. For the three phase system studied here, \( w_n s \) (in any order) is the only type of contact line.

The concept of microscopic surface excess mass (as well as other surface excess properties) is used to account for the transition in density from one phase to another over a finite region. This transition is represented as an abrupt change over an interface of zero thickness but with an

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**Fig. 1. Schematic of a subregion of an REV depicting portions of the three bulk phases: \( \alpha \), \( \beta \), \( \gamma \); portions of the three interfaces \( \delta A_{\alpha \beta} \), \( \delta A_{\alpha \gamma} \), \( \delta A_{\beta \gamma} \); and a portion of the contact curve \( \delta C_{\alpha \beta \gamma} \).**

excess mass per unit area. Miller and Neogi discuss surface excess properties based on Gibbs’ description. Denote the abrupt surface of discontinuity between α and β phases as δA_{αβ}. Let l^α and l^β be the distances in the α and β phases, respectively, normal to an infinitesimal part of δA_{αβ}, δA_{αβ}, over which the density undergoes a transition. If the density did not undergo this transition, the mass one would expect to find in the region would be

$$dM_{αβ} = (ρ_1 l^α + ρ_2 l^β) \deltaA_{αβ}$$

(1a)

where $ρ_1$ and $ρ_2$ are the expected microscopic densities of the α and β phases, respectively. The difference between the mass actually present, dM, and the expected mass is the surface excess mass. This mass per area of δA_{αβ} is the microscopic interfacial mass density or

$$Γ_{αβ} = \frac{dM}{dδA_{αβ}} - ρ_1 l^α - ρ_2 l^β$$

(1b)

Note that depending on where the sharp interface is arbitrarily located between two phases, Γ_{αβ} may be positive, negative, or zero. At the macroscale, the actual position of the interface need not be considered but is implicitly accounted for by macroscopic variables such as porosity, saturation, and interfacial surface area per unit volume.

A macroscopic model can also be defined at which one can model the system as a superposition of six continua: three phases and three interfaces. At every spatial point and at any instance, average or macroscopic properties are defined for each and every continuum. These continua interact and exchange properties. Throughout this work, any reference to a phase or an interface is actually made to a phase continuum or an interface continuum. A full macroscopic description of a multiphase system has been developed by Hassanizadeh and Gray and Gray and Hassanizadeh. Here we simply employ the macroscopic quantities and balance laws which were defined and/or derived in those works.

Macroscopic quantities are defined at the scale of a representative elementary volume (REV), δV. All quantities introduced subsequently are macroscopic unless a vertical bar with a subscript (e.g. v_(l)) is used to designate a macroscopic quantity. For example, the macroscopic mass density function $ρ^α$ of an α-phase continuum is the mass of α-phase fluid present within an REV divided by the volume of α-phase. Similarly, the macroscopic mass density function $Γ_{αβ}^α$ of an αβ-interface continuum is defined as the mass of αβ-interface present within an REV divided by the total area of that interface in the REV. For convenience reference, a full list of definitions of macroscopic quantities in terms of microscopic quantities is provided in Appendix A.

In order to account partially for the microstructure of the system, the volume fraction $ε^α$ of an α-phase continuum and the areal density $a_{αβ}$ of each αβ-interface are defined. Basically, $a_{αβ}$ is the area of all αβ-interfaces per unit volume of the REV, or $δA_{αβ}/δV$; and $ε^α$ is the fraction of the REV occupied by the α-phase, $δV^α/δV$. Porosity of the medium, $ε$, is equal to the sum of the volume fractions of the two fluid phases.

$$ε = ε^α + ε^β$$

(2a)

Thus, the volume fraction of the solid phase $ε^s$ will be:

$$ε^s = 1 - ε$$

(2b)

In addition to these, volume saturation functions $s^α$ are defined for the fluid phases:

$$S^α = ε^α/ε \quad α = w, n$$

(3)

such that

$$s^α + s^w = 1$$

(4)

The three phase continua and the three interface continua may each undergo independent motion as a result of thermodynamic processes. The solid phase motion is defined as a transformation $F(X, t)$ which changes the reference configuration $X$ of the object at time $t=0$ to a new configuration $x$ at time $t$, such that

$$x = F(X, t)$$

(5)

A measure of deformation of the solid phase is the Lagrangian strain tensor $E^s$, defined by

$$E^s = 1/2((GRAD F^s) \cdot (GRAD F^s)^T - I)$$

(6)

where GRAD denotes differentiation with respect to the reference frame $X$ and the superscript $T$ denotes the transpose of a tensor. The velocity of the solid phase is then defined to be

$$v^s = \left( \frac{∂F^s}{∂t} \right)_{X} = v(X, t)$$

(7)

In writing $v^s$ as a function of $x$ rather than $X$, it is assumed that transformation (5) is reversible. This will be true if, and only if, the jacobian of the transformation, defined by $J = det (GRAD F^s)$, is nonzero. This is commonly assumed to hold in local theories of continuum mechanics (see, e.g., Bowen).

The motion of a fluid phase α and that of an interface αβ are characterized at the macroscale by their velocities $v^α$ and $w^αβ$, respectively. Note that $Γ_{αβ}^α w^αβ$ is actually a macroscopic measure of the average momentum of the excess mass associated with an αβ-interface.

In multiphase mechanics, the absolute velocities of phases are not representative of any mechanical changes. For example, all components of the system could undergo a rigid body motion with equal velocities. However, for this case, the relative velocities are zero and no mechanical changes actually occur. Therefore, for the porous media flow, relative velocities of phases and interfaces with respect to the solid phase are employed. These are defined as

$$v^α = v^α - v^s$$

(8a)

$$w^αβ = w^αβ - v^s$$

(8b)

From these definitions, additional relative velocities can be defined such as

$$v^αβ = v^αβ - v^β$$

(8c)

$$w^αβγ = w^αβγ - v^γ$$

(8d)

Throughout the text, a comma in the superscripts will be used to indicate relative values of functions such as those defined in equation (8) and also

$$E^αβ = E^αβ - E^α$$

(9a)

and

$$θ^α = θ^α - θ^s$$

(9b)
In formulating the balance laws and the second law of thermodynamics, it is more convenient to work with total material derivatives instead of partial derivatives. The material derivative of a function, \( \psi \), following the motion of phase \( \alpha \) is introduced:

\[
\frac{D^a \psi}{Dt} = \frac{\partial \psi(x, t)}{\partial t} + v^a \cdot \nabla \psi(x, t)
\]  
(10a)

where \( \nabla \) denotes differentiation with respect to \( x \). Similarly, one may define \( D^a_{\alpha \beta} \psi / Dt \) by

\[
\frac{D^a_{\alpha \beta} \psi}{Dt} = \frac{\partial \psi}{\partial t} + w^a_{\alpha \beta} \cdot \nabla \psi
\]  
(10b)

From equations (8) and (9), the following identities can be established:

\[
\frac{D^a \psi}{Dt} = \frac{D^a \psi}{Dt} + (v^a, - v^a' \cdot \nabla \psi)
\]  
(11a)

\[
\frac{D^a_{\alpha \beta} \psi}{Dt} = \frac{D^a \psi}{Dt} + (w^a_{\alpha \beta}, - w^a_{\alpha \beta} \cdot \nabla \psi)
\]  
(11b)

Finally, the deformation rate tensors \( d^a \) and \( d^a_{\alpha \beta} \) for \( \alpha \)-phase and \( \alpha \beta \)-interfaces, respectively, are defined

\[
d^a = \frac{1}{2} \left[ \nabla v^a + (\nabla v^a)^T \right]
\]  
(12a)

\[
d^a_{\alpha \beta} = \frac{1}{2} \left[ \nabla w^a_{\alpha \beta} + (\nabla w^a_{\alpha \beta})^T \right]
\]  
(12b)

Then, the following relation can be established for the material derivative of \( E^a \) (See Ref. 17).

\[
\frac{D^a E^a}{Dt} = (\text{GRAD } F^a) \cdot d^a \cdot (\text{GRAD } F^a)^T
\]  
(13)

**GENERAL BALANCE LAWS**

For describing thermodynamic processes in multiphase systems, two sets of macroscopic conservation equations are necessary: one set in terms of average phase properties and one set in terms of average interfacial properties. The two sets of equations are coupled via terms accounting for exchange of thermodynamic properties between phase and interface continua. Equations of conservation of mass, momentum, energy and entropy can be cast in the following general forms:

For a typical phase \( \alpha \):

\[
\frac{\partial}{\partial t} \left( \varepsilon^a \rho^a \psi^a \right) + \nabla \cdot (\varepsilon^a \rho^a v^a \psi^a) - \nabla \cdot (\varepsilon^a F^a) = \sum_{\beta \neq \alpha} \left( \hat{I}_{\alpha \beta}^a + \hat{e}_{\alpha \beta}^a \psi^a \right) - \varepsilon^a \rho^a f^a
\]

\[
= \sum_{\gamma \neq \alpha} \left( \hat{I}_{\alpha \gamma}^a + \hat{e}_{\alpha \gamma}^a \psi^a \right) + \Psi^a
\]

\( \alpha, \beta = n, w, s \)

which upon incorporation of the mass balance equation becomes

\[
\varepsilon^a \rho^a \frac{D^a \psi^a}{Dt} - \nabla \cdot (\varepsilon^a \mathbf{v}^a) - \varepsilon^a \rho^a f^a = \sum_{\beta \neq \alpha} \hat{I}_{\alpha \beta}^a + \Psi^a
\]  
(14b)

where

\[
\hat{I}_{\alpha \beta}^a = \frac{1}{\delta V} \int_{\partial \mathbf{c}_{\alpha \beta}} \left[ \mathbf{l}_\beta + \rho \mathbf{l}_\alpha (\psi^\alpha - \psi^\beta) \right] (\mathbf{w}_\alpha - \mathbf{v}_\alpha) \cdot \mathbf{n}^a \ \text{da}
\]  
(14c)

and

\[
\hat{e}_{\alpha \beta}^a = \frac{1}{\delta V} \int_{\partial \mathbf{c}_{\alpha \beta}} \rho \mathbf{l}_\alpha \cdot (\mathbf{w}_\alpha - \mathbf{v}_\alpha) \cdot \mathbf{n}^a \ \text{da}
\]  
(14d)

In equation (14a), the left hand side accounts for storage, influx, and external supply of \( \psi \) within the \( \alpha \)-phase. The quantity \( \hat{e}_{\alpha \beta}^a \) is the rate of mass transfer from the \( \alpha \beta \)-interface to the phase \( \alpha \), and \( \hat{I}_{\alpha \beta}^a \) accounts for the transfer of property \( \psi \) to the \( \alpha \)-phase in addition to \( \hat{e}_{\alpha \beta}^a \psi^a \).

Throughout this work, the combination of superscript \( \alpha \) and subscript \( \alpha \beta \) are applied to terms accounting for transfer of properties from the \( \alpha \beta \)-interface to the \( \alpha \)-phase. For additional emphasis, exchange terms are indicated by a cat. Note that \( \mathbf{l}_\gamma, \rho, \mathbf{v}_\gamma, \psi^\gamma \) and \( \mathbf{v}_\alpha \) in equations (14c) and (14d) are microscopic values in the \( \alpha \)-phase, \( \mathbf{w}_\alpha \) is the microscopic velocity of an \( \alpha \beta \) interface and \( \mathbf{n}^a \) is normal to \( \delta \mathbf{c}_{\alpha \beta} \) pointing out of the \( \alpha \)-phase. The term \( \Psi^a \) is the rate of production of \( \psi^a \) in the \( \alpha \)-phase.

For a typical interface \( \alpha \beta \):

\[
\frac{\partial}{\partial t} \left( a^a \Gamma_{\alpha \beta} \psi^a \right) + \nabla \cdot (a^a \Gamma_{\alpha \beta} \mathbf{w}_\alpha \psi^a) - \nabla \cdot (a^a \Gamma_{\alpha \beta} \mathbf{v}^a) = a^a \Gamma_{\alpha \beta} f^a - (\hat{I}_{\alpha \beta}^a + \hat{e}_{\alpha \beta}^a \psi^a) - (\hat{I}_{\alpha \beta}^a + \hat{e}_{\alpha \beta}^a \psi^a)
\]

\[
+ \sum_{\gamma \neq \alpha \beta} \left( \hat{I}_{\alpha \gamma}^a + \hat{e}_{\alpha \gamma}^a \psi^a \right) + \Psi^a
\]

where

\( \alpha \beta = ns, wn, ws \)

or, after simplification making use of the mass balance equation,

\[
a^a \Gamma_{\alpha \beta} \frac{D^a \psi^a}{Dt} = - \nabla \cdot (a^a \mathbf{v}^a) - a^a \Gamma_{\alpha \beta} f^a
\]

\[
= - \left( \hat{I}_{\alpha \beta}^a + \hat{e}_{\alpha \beta}^a (\psi^a - \psi^\beta) \right)
\]

\[
- \left( \hat{I}_{\alpha \beta}^a + \hat{e}_{\alpha \beta}^a (\psi^\beta - \psi^\alpha) \right) + \sum_{\gamma \neq \alpha \beta} \hat{I}_{\alpha \gamma}^a + \Psi^a
\]  
(15a)

where

\[
\hat{I}_{\alpha \gamma}^a = \frac{1}{\delta V} \int_{\partial \mathbf{c}_{\alpha \gamma}} \left[ \mathbf{l}_\gamma + \Gamma_{\alpha \gamma}(\psi^\alpha - \psi^\gamma) \right] (\mathbf{u}_\alpha - \mathbf{w}_\alpha) \cdot \mathbf{n}^a \ \text{dc}
\]  
(15c)

and

\[
\hat{e}_{\alpha \gamma}^a = \frac{1}{\delta V} \int_{\partial \mathbf{c}_{\alpha \gamma}} \Gamma_{\alpha \gamma} (\mathbf{u}_\alpha - \mathbf{w}_\alpha) \cdot \mathbf{n}^a \ \text{dc}
\]  
(15d)

In equation (15a), the left side accounts for macroscopic storage, influx, and external supply of \( \psi \) within the \( \alpha \beta \) interface. The first two groups of terms in parentheses.
on the right side of equation (15a) have been discussed following equations (14) and describe the interaction of the $\alpha\beta$ interface with the phases on each side. The terms defined in equations (15c) and (15d) account for interaction between the $\alpha\beta$ interface and the bounding curve of its interface, the contact line among the phases $\alpha$, $\beta$ and $\gamma$, denoted by $\delta C_{\alpha\beta\gamma}$. While $\dot{e}_{\alpha\beta\gamma}^{a}$ is the rate of mass transfer due to phase change from the curve $\delta C_{\alpha\beta\gamma}$ to surface $\delta A_{\alpha\beta}$, the integral $\int_{\beta\alpha}^{a}$ provides the transfer of $\Psi$ from the curve $\delta C_{\alpha\beta\gamma}$ to the interface $\delta A_{\alpha\beta}$ in addition to $\dot{e}_{\alpha\beta\gamma}^{a}$.

Again, a carat is used to identify quantities accounting for exchange; and the paired combination of superscript $\alpha\beta$ and subscript $\alpha\beta\gamma$ indicates transfer from the contact curve $\alpha\beta\gamma$ to the $\alpha\beta$ interface. The last term, $\Psi^{a}\Psi^{b}$ accounts for production of $\Psi^{a\beta}$ within the interface. For local theories, such as presented here, $\Psi^{a}$ and $\Psi^{b}$ are assumed to be zero for mass, momentum and energy and nonzero only for entropy.

In addition to the preceding equations, the following restriction on interaction among interfaces and contact lines is enforced:

$$\sum_{\alpha \beta} \sum_{\gamma \neq \alpha} \left( \dot{e}_{\alpha\beta\gamma}^{a} + \dot{e}_{\alpha\beta\gamma}^{a} \Psi^{a\beta}\right) = 0$$

This restriction follows from the stipulation that a contact line possesses no mass or any other thermodynamic property such that the net transfer of a thermodynamic property among the three interfaces meeting at a contact line must be zero.

Specific balance laws

Specific balance laws for each phase and interface can be obtained by substituting appropriate properties for $\Psi$, $I$, $I_{p}$, $I_{a}$, and $\Psi$ (see Hassanizadeh and Gray (22) and Gray and Hassanizadeh (23)). We assume that the phases of the system are microscopically nonpolar. Then, following a derivation similar to that of Hassanizadeh and Grey (22), the angular momentum balance can be used to show that the phase stress tensors $T^{a}$ and interface stress tensors $S^{a\beta}$ are symmetric.

$$T^{a} = (T^{a})^{T}$$

$$S^{a\beta} = (S^{a\beta})^{T}$$

Incorporating equations (17) and (18) and relationships (1)–(10) into general equations (14)–(15), one obtains, after some manipulations, the following specific conservation laws:

Conservation of mass

For the solid phase

$$\frac{D'(1 - e')}{D} + (1 - e') \rho'(\nabla \cdot v') = \dot{\epsilon}_{\alpha}^{a} + \dot{\epsilon}_{ws}^{a}$$

For a fluid phase

$$D'(\varepsilon_{p}^{a}\rho^{a}) + \varepsilon_{p}^{a}\rho^{a}(\nabla \cdot v^{a}) = \sum_{\beta \neq a} \dot{\epsilon}_{\alpha\beta}^{a} \quad \alpha = n, w$$

For an interface

$$\frac{D^{a\beta}a^{\alpha\beta}G_{\alpha\beta}}{D} + a^{\alpha\beta}G_{\alpha\beta}(\nabla \cdot w^{a\beta}) = - \dot{\epsilon}_{\alpha}^{a} - \dot{\epsilon}_{\alpha\beta}^{a} + \dot{\epsilon}_{\alpha\beta\gamma}^{a}$$

$$\alpha\beta = wn, ws, ns$$

$$\alpha\beta\gamma = wns$$

Conservation of momentum

For a bulk phase

$$\frac{D_{w}^{\alpha\beta}}{D} - \nabla \cdot (e^{a\beta\gamma}) - e^{a\beta\gamma}g^{a\beta\gamma} = \sum_{\beta \neq a} \dot{\hat{T}}_{\alpha\beta}^{a}$$

$$\alpha = n, w, s$$

For an interface

$$\frac{D_{f}^{\alpha\beta}}{D} - \nabla \cdot (a^{\alpha\beta}S^{a\beta}) - a^{\alpha\beta}G_{\alpha\beta}^{a\beta}$$

$$= - (\dot{\hat{T}}_{\alpha\beta}^{a} + \dot{\hat{\epsilon}}_{\alpha\beta}^{a} v^{a\beta\gamma}) - (\dot{\hat{G}}_{\alpha\beta}^{a} + \dot{\hat{\epsilon}}_{\alpha\beta}^{a} w^{a\beta\gamma})$$

$$+ (\dot{\hat{\epsilon}}_{\alpha\beta}^{a} + \dot{\epsilon}_{\alpha\beta}^{a}) w^{a\beta\gamma} + \dot{\hat{S}}_{\alpha\beta}^{a\beta\gamma}$$

$$\alpha\beta = wn, ws, ns$$

Conservation of energy

For a bulk phase

$$\frac{D_{w}^{\alpha\beta}}{D} - \varepsilon^{a\beta\gamma}v^{a\beta\gamma} - e^{a\beta\gamma}(\varepsilon^{a\beta\gamma})$$

$$\varepsilon^{a\beta\gamma}h^{a\beta\gamma} = \sum_{\beta \neq a} \dot{\hat{Q}}_{\alpha\beta}^{a} \quad \alpha = n, w, s$$

For an interface

$$\frac{D_{f}^{\alpha\beta}}{D} - a^{\alpha\beta}S^{a\beta}(\nabla w^{a\beta}) - (\nabla \cdot (a^{\alpha\beta}q^{a\beta}))$$

$$- a^{\alpha\beta}G_{\alpha\beta}^{a\beta}$$

$$= \frac{1}{2}(v^{a\beta\gamma})^{2} - \sum_{\beta \neq a} (\dot{Q}_{\alpha\beta}^{a} + \dot{\hat{G}}_{\alpha\beta}^{a} + \dot{\hat{\epsilon}}_{\alpha\beta}^{a} (E_{\alpha\beta}^{a\beta}))$$

$$\alpha\beta = wn, ws, ns$$

$$\alpha\beta\gamma = wns$$

Mass and momentum conservation equations (19)–(23) are used in obtaining the preceding energy equations. The colon sign between two tensors denotes a double inner product operation. For example $t: v$ in indicial notation may be written as $t_{ij}v_{ij}$. Also recall that a comma in the superscript denotes relative values of functions as defined in equations (8)–(9).

Balance of Entropy

For a bulk phase

$$e^{a\beta\gamma} \frac{D_{w}^{\alpha\beta}}{D} - \varepsilon^{a\beta\gamma}(\varepsilon^{a\beta\gamma}) - e^{a\beta\gamma}b^{a\beta\gamma} = \sum_{\beta \neq a} \dot{\Phi}_{\alpha\beta}^{a} + \Lambda^{a}$$

$$\alpha = n, w, s$$
For an interface
\[
\alpha \beta^\alpha \Gamma_{\alpha \beta} \frac{D^n \eta_{\alpha \beta}}{Dt} - \nabla \cdot (\alpha \beta^\alpha \varphi_{\alpha \beta}) - \alpha \beta^\alpha \Gamma_{\alpha \beta}^\beta \varphi_{\alpha \beta}^\beta \\
= -(\hat{\Phi}_{\alpha \beta}^\alpha + \hat{\epsilon}_{\alpha \beta}^\alpha \eta_{\alpha \beta}) - (\hat{\Phi}_{\alpha \beta}^\beta + \hat{\epsilon}_{\alpha \beta}^\beta \eta_{\alpha \beta}) \\
+ \hat{\Phi}_{\alpha \beta \gamma}^\alpha + \Lambda_{\alpha \beta} \eta_{\alpha \beta} \\
\alpha \beta \gamma = \omega, \eta, \sigma \\
\alpha \beta \gamma = \omega \sigma (27)
\]
The terms accounting for exchange of mass, momentum, energy and entropy among interfaces via the contact lines are subject to the following restrictions
\[
\sum_{\alpha \beta} \sum_{\gamma \neq \alpha \beta} \tilde{\epsilon}_{\alpha \beta \gamma}^\alpha = 0 (28)
\]
\[
\sum_{\alpha \beta} \sum_{\gamma \neq \alpha \beta} \left( \tilde{S}_{\alpha \beta \gamma}^\alpha + \tilde{\epsilon}_{\alpha \beta \gamma}^\alpha \omega_{\alpha \beta}^\gamma \right) = 0 (29)
\]
\[
\sum_{\alpha \beta} \sum_{\gamma \neq \alpha \beta} \left( \tilde{Q}_{\alpha \beta \gamma}^\alpha + \tilde{S}_{\alpha \beta \gamma}^\alpha \cdot \omega_{\alpha \beta}^\gamma \\
+ \tilde{\epsilon}_{\alpha \beta \gamma}^\alpha \left[ E_{\alpha \beta}^\alpha + \frac{1}{2} \omega_{\alpha \beta}^\gamma \right] \right) = 0 (30)
\]
\[
\sum_{\alpha \beta} \sum_{\gamma \neq \alpha \beta} \left( \tilde{\phi}_{\alpha \beta \gamma}^\alpha + \tilde{\epsilon}_{\alpha \beta \gamma}^\alpha \eta_{\alpha \beta}^\gamma \right) = 0 (31)
\]
These restrictions are based on the contact lines not being allowed to possess any thermodynamic properties and are the particular forms of equation (16). Note that in the current work where only three phases are considered, the summation over \( \gamma \) in equations (28)–(31) is superfluous because \( \alpha \beta \gamma \) is unique, the curve where the three phases come together at a contact curve. Thus, in this case, summation over \( \gamma (\neq \alpha, \beta) \) may be eliminated with \( \alpha \beta \gamma \) set equal to \( \omega \gamma n \) to obtain, for example, from equation (28)
\[
\sum_{\alpha \beta} \tilde{\epsilon}_{\alpha \beta \gamma}^\alpha = 0 (32)
\]

SECOND LAW OF THERMODYNAMICS

The conservation laws must be supplemented with the second law of thermodynamics. According to this law, regardless of the process a system undergoes, the rate of net production of entropy of the system must be non-negative. The correct form of the second law for multiphase systems reads 19:
\[
\Lambda = \sum_{\alpha} \Lambda^\alpha + \sum_{\alpha \beta} \Lambda_{\alpha \beta} \geq 0 (33)
\]
where \( \Lambda^\alpha \) and \( \Lambda_{\alpha \beta} \) may be substituted for from equations (26) and (27). However, before doing so, certain assumptions are introduced.

The entropy fluxes are assumed to be due solely to heat input, and the entropy external source terms are assumed to be due only to external energy sources. Thus the following relations hold:
\[
\varphi^\alpha = q_{\alpha}^\alpha / \theta^\alpha \\
\varphi_{\alpha \beta}^\alpha = q_{\alpha \beta}^\alpha / \theta_{\alpha \beta} \\
h^\alpha = h^\alpha / \theta^\alpha \\
h_{\alpha \beta}^\alpha = h_{\alpha \beta}^\alpha / \theta_{\alpha \beta} (34)
\]
where \( 1 / \theta^\alpha \) and \( 1 / \theta_{\alpha \beta} \) may be considered as positive multipliers. Using the method of Lagrange multipliers, Liu 19 has shown that \( \theta^\alpha \) is equivalent to the macroscopic experimental temperature function of the \( \alpha \)-phase. Relations (34) and (35) are widely accepted in continuum mechanics (see e.g., Eringen 17 and Bowen 11) and serve as special constitutive relations. Alternatively, \( \varphi^\alpha \) and \( \varphi_{\alpha \beta}^\alpha \) may be left unspecified such that a general constitutive form will have to be postulated. That alternative is not considered here.

In developing constitutive equations, it is convenient to employ the Helmholtz free energy function instead of the internal energy. The Helmholtz free energies \( A^\alpha \) and \( A_{\alpha \beta} \) are defined by
\[
A^\alpha = E^\alpha - \theta^\alpha \eta^\alpha (36)
\]
\[
A_{\alpha \beta} = E_{\alpha \beta} - \theta_{\alpha \beta} \eta_{\alpha \beta} (37)
\]
Substitution of relations (34)–(35) into (26) and (27) and elimination of \( h^\alpha \) and \( h_{\alpha \beta}^\alpha \) by means of energy equations (24) and (25) yield the following equations for \( \Lambda^\alpha \) and \( \Lambda_{\alpha \beta} \):
\[
\Lambda^\alpha = -\frac{\epsilon_{\alpha}^\alpha}{\theta^\alpha} \left[ \frac{D^\alpha A^\alpha}{Dt} + \eta_{\alpha}^\alpha \frac{D^\alpha \theta^\alpha}{Dt} \right] + \frac{\epsilon_{\alpha}^\alpha}{\theta^\alpha} q_{\alpha}^\alpha \cdot \nabla \theta^\alpha \\
+ \frac{\epsilon_{\alpha}^\alpha}{\theta^\alpha} t^\alpha \cdot \nabla \eta^\alpha - \sum_{\beta \neq \alpha} \left( \hat{\Phi}_{\alpha \beta}^\alpha - \hat{\Phi}^\alpha_{\alpha \beta} \right) \\
\alpha = n, w, s (38)
\]
\[
\Lambda_{\alpha \beta} = -\frac{\epsilon_{\alpha \beta}^\alpha}{\theta_{\alpha \beta}^\alpha} \left[ \frac{D_{\alpha \beta}^\alpha A_{\alpha \beta}}{Dt} + \eta_{\alpha \beta} \frac{D_{\alpha \beta} \theta_{\alpha \beta}}{Dt} \right] + \frac{\epsilon_{\alpha \beta}^\alpha}{\theta_{\alpha \beta}^\alpha} q_{\alpha \beta} \cdot \nabla \theta_{\alpha \beta} \\
+ \frac{\epsilon_{\alpha \beta}^\beta}{\theta_{\alpha \beta}^\beta} \left( \hat{\Phi}_{\alpha \beta}^\beta - \hat{\Phi}^\beta_{\alpha \beta} \right) \cdot \nabla \omega_{\alpha \beta}^\beta \\
+ \frac{\epsilon_{\alpha \beta}^\alpha}{\theta_{\alpha \beta}^\alpha} A_{\alpha \beta} - \eta_{\alpha \beta} \theta_{\alpha \beta} \delta_{\alpha \beta} + \frac{1}{2} \omega_{\alpha \beta}^\gamma \left( \omega_{\alpha \beta}^\gamma \right) (39)
\]
\[
\alpha \beta = \omega, \eta, \sigma \\
\alpha \beta \gamma = \omega \sigma (39)
\]
Substitute from (38) and (39) into (33) to obtain:
\[
\sum_{\alpha} \Lambda^{\alpha} + \sum_{\alpha\beta} \Lambda_{\alpha\beta}^{\alpha\beta} = -\sum_{\alpha} \epsilon^{\alpha\beta} \rho^{\alpha} \left( \frac{D^{\alpha} A^{\alpha}}{\theta^{\alpha}} + \eta^{\alpha} \frac{D^{\alpha} \theta^{\alpha}}{\theta^{\alpha}} \right) + \sum_{\alpha} \epsilon^{\alpha\beta} \left( A^{\alpha} \mathbf{q}^{\alpha} \right) \cdot \nabla \theta^{\alpha} + \sum_{\alpha} \epsilon^{\alpha\beta} \left( \mathbf{q}^{\alpha} \right) : \mathbf{d}^{\alpha} - \sum_{\alpha\beta} a^{\alpha\beta} \left( \frac{D^{\alpha} A^{\alpha}}{\theta^{\alpha}} + \eta^{\alpha} \frac{D^{\alpha} \theta^{\alpha}}{\theta^{\alpha}} \right) + \sum_{\alpha\beta} a^{\alpha\beta} \left( \frac{D^{\alpha} \mathbf{q}^{\alpha}}{\theta^{\alpha}} \right) \cdot \nabla \theta^{\alpha} + \sum_{\alpha\beta} a^{\alpha\beta} \left( \frac{D^{\alpha} \mathbf{s}^{\alpha \beta}}{\theta^{\alpha}} \right) \cdot \mathbf{d}^{\alpha} + \frac{1}{\theta^{\alpha}} \sum_{\alpha\beta} \left[ Q_{\alpha\beta}^{\alpha\beta} \frac{\mathbf{q}^{\alpha \beta}}{\theta^{\alpha \beta}} - \dot{S}_{\alpha\beta\gamma}^{\alpha \beta \gamma} + w^{\alpha \beta} \right]
\]

\[
+ \epsilon^{\alpha\beta} \left( A^{\alpha \beta} + \frac{1}{2} (w^{\alpha \beta})^2 + \eta^{\alpha \beta} \frac{\theta^{\alpha \beta}}{w^{\alpha \beta}} \right)
\]

\[
+ \sum_{\alpha} \sum_{\beta\alpha\alpha} \left[ \frac{1}{\theta^{\alpha \beta}} \left( \frac{\dot{Q}_{\alpha\beta \gamma}^{\alpha \beta \gamma} \theta^{\alpha \beta}}{\theta^{\alpha \beta}} + \dot{T}_{\alpha\beta \gamma}^{\alpha \beta \gamma} \right) + w^{\alpha \beta} \right] + \epsilon^{\alpha \beta} \left( \frac{A^{\alpha \beta} + \frac{1}{2} (w^{\alpha \beta})^2 + \eta^{\alpha \beta} \theta^{\alpha \beta}}{w^{\alpha \beta}} \right) \geq 0
\]

where restrictions (28) through (31) have been used to eliminate \( \Phi_{\alpha\beta}^{\alpha \beta} \) and \( \Phi_{\alpha\beta}^{\alpha \beta} \) and further rearrange the terms which account for interactions of the phase interfaces with the contact curves. Relation (40) is the macroscopic form of the second law of thermodynamics which serves to restrict the behaviour of a multiphase system.

**CONSTITUTIVE EQUATIONS**

Balance equations presented in the previous section are not sufficient to fully characterize a multiphase system. These must be supplemented with equations which describe the constitutive behavior of individual phases. If we consider a multiphase porous media flow consisting of a single solid phase and \( N - 1 \) fluid phases, then \( N \) different bulk phases exist and \( N(N - 1)/2 \) different interfaces exist. For the bulk phases, separate balance equations may be written for each phase such that we obtain \( N \) mass balances, \( N \) energy balances, and \( 3N \) momentum balances (because the momentum equation is a vector equation with three components). Thus a total of \( 5N \) bulk phase equations are obtained. Anlogously, \( 5N(N - 1)/2 \) interface equations are obtained making the total number of equations \( 5N(N + 1)/2 \). The primary unknowns may be selected to be the \( 5N(N + 1)/2 \) quantities \( (\epsilon^{\alpha \beta} \rho^{\alpha}), (a^{\alpha \beta} \Gamma^{\alpha \beta}), (v^{\alpha} (\alpha \neq s)), F^{\alpha}, w^{\alpha \beta}, \theta^{\alpha} \) and \( \theta^{\alpha \beta} \).

(41)

To obtain a complete description of the system, the remaining variables must be expressible in terms of the primary unknowns and their derivatives. Therefore constitutive equations must be provided for the following dependent variables:

\[
A^{\alpha}, A^{\alpha \beta}, (\epsilon^{\alpha \beta} \mathbf{r}^{\alpha}), (a^{\alpha \beta} S^{\alpha \beta}), \hat{T}_{\alpha \beta}, S_{\alpha \beta \gamma}^{\alpha \beta \gamma}, (\epsilon^{\alpha \beta} \mathbf{q}^{\alpha}), \hat{Q}_{\alpha \beta \gamma}^{\alpha \beta \gamma}.
\]

These may be hypothesized to depend on the independent variables:

\[
(\epsilon^{\alpha \beta} \rho^{\alpha}), (a^{\alpha \beta} \Gamma^{\alpha \beta}), v^{\alpha}, w^{\alpha \beta}, \mathbf{F}^{\alpha}, \theta^{\alpha}, \nabla \theta^{\alpha}, \theta^{\alpha \beta}.
\]

(43)

Note that the dependent variables are functions only of the independent variables while the independent variables are functions of time and space.

The choice of independent variables is based on the expected behavior of the phases and interfaces, and on our knowledge of the internal state variables of the system. For example, temperature gradients are included because they are expected to cause heat conduction within the system. Also, relative velocities contribute to exchange among the phases and interfaces. Absence of velocity gradients in the list of independent variables stems from the fact that the phases and interfaces are considered to behave as nonviscous materials at the macroscale. Note that instead of \( v^{\alpha} \) and \( w^{\alpha \beta} \), relative velocities are selected as the independent variables because the former variables are not objective whereas the latter variables are. The same argument applies to the choice of \( \mathbf{F}^{\alpha} \) instead of \( \mathbf{F}^{\alpha} \). All constitutive variables must be objective, that is: independent of the frame of reference.

Although the above listing of variables along with the balance equations forms a complete set of equations, these are inadequate for describing a system with microstructure. This is due to the lumping of volume fractions and areal densities with other variables. As a result, the microstructure is not properly accounted for, and the model does not provide information on 'true' mass densities and 'true' stress and heat flux terms. Therefore, \( \epsilon^{\alpha \beta} \) and \( a^{\alpha \beta} \) and their spatial gradients must be introduced as additional independent variables. This, however, causes the system of equations to become indeterminate. By this approach, \( N \) volume fractions and \( N(N - 1)/2 \) areal fractions are introduced as primary unknowns creating a need for \( N(N + 1)/2 \) additional equations. One of these equations is provided by the restriction \( \Sigma_{\alpha} \epsilon^{\alpha \beta} = 1 \), but a deficit of \( (N + 2)(N + 1)/2 \) equations remains. This is a so-called 'closure problem' which is discussed in detail by Bouré and see also Bedford and Drumheller, among others, who give balance laws involving the time derivative of volume fractions, \( \dot{\epsilon}^{\alpha} \) (they do not introduce any areal densities). However, the relation of these equations to microscopic continuum theories needs to be explored. The second alternative has been employed by authors who introduce \( \epsilon^{\alpha} \) (e.g. Morland) or \( \dot{\epsilon}^{\alpha} \) (e.g. Bowen) as dependent variables and then postulate constitutive equations. Bouré refers to such equations as 'topological laws'. Although additional balance laws related to the microstructure of a multiphase system would ideally be available, in the absence of appropriate laws we choose to set up a con-
sistent constitutive theory to provide a determinate set of equations.

In the description of multiphase flow in porous media, fluid saturations, \( s^\alpha (\alpha \neq s) \), and the medium porosity, \( \epsilon \), are typically selected as primary unknowns. Because the saturations sum to unity, a net total of \( N - 1 \) primary unknowns are added to those listed in (41). Therefore, \( N - 1 \) dependent variables, along with appropriate constitutive postulates, must be introduced to close the system. These are selected to be

\[
\dot{\epsilon} \quad \text{and} \quad s^\alpha \quad (\text{for} \quad N - 2 \quad \text{of the fluid phases}) \quad (44)
\]

where the overdot indicates material derivative with respect to a reference frame fixed to the solid:

\[
\dot{\epsilon} = \frac{D\epsilon}{Dt} \quad (45)
\]

Furthermore, in the list of independent variables in (43), the product \( \epsilon^\alpha \rho^\alpha \) is split such that \( (\epsilon^\alpha \rho^\alpha) \) and \( \nabla (\epsilon^\alpha \rho^\alpha) \) are replaced by:

\[
\rho^\alpha, \quad \nabla \epsilon, \quad s^\alpha \quad \text{and} \quad \nabla s^\alpha \quad (\text{for} \quad N - 1 \quad \text{for the fluid phases}) \quad (46)
\]

Next, to account macroscopically for the microstructure due to interphase boundaries, \( MN - 1 \) or areal densities, \( a^\alpha \) \( \alpha \neq s \), are added to list (41) of primary unknowns. Therefore, \( MN - 1 \) additional dependent variables must be introduced and added to (42). These may be selected to be either \( a^\alpha \) or \( T^\alpha \). The procedure will be demonstrated here with \( a^\alpha \) so that the additional dependent variables are:

\[
a^\alpha \quad (\text{for the} \quad MN - 1 \quad / 2 \quad \text{interfaces}) \quad (47)
\]

The following set is then added to the list of independent variables in (43) in place of \( a^\alpha T^\alpha \) and \( \nabla (a^\alpha T^\alpha) \):

\[
a^\alpha \quad \Gamma^\alpha \quad \nabla a^\alpha \quad (\text{for the} \quad MN - 1 \quad / 2 \quad \text{interfaces}) \quad (48)
\]

With these considerations in mind, constitutive functions are sought for the following dependent variables:

\[
A^\alpha, \quad T^\alpha, \quad S^\alpha, \quad T^\alpha_a, \quad \dot{S}^\alpha_a, \quad q^\alpha, \quad \dot{Q}^\alpha_a, \quad Q^\alpha_a, \quad q^\alpha_a, \quad \eta^\alpha, \quad \eta^\alpha_a, \quad \dot{\epsilon}^\alpha, \quad \dot{\epsilon}^\alpha_a, \quad \epsilon, \quad s^\alpha \quad (\text{or} \quad s^\alpha), \quad a^\alpha
\]

\[
\alpha = n, w, s \quad (49a)
\]

in terms of the following independent variables:

\[
\rho^\alpha, \quad \Gamma^\alpha, \quad \nabla \rho^\alpha, \quad \nabla (\rho^\alpha), \quad \nabla \theta^\alpha, \quad \nabla \theta^\alpha, \quad \dot{s}^\alpha \quad (\text{or} \quad s^\alpha), \quad \nabla \dot{s}^\alpha \quad (\text{or} \quad \nabla s^\alpha), \quad a^\alpha, \quad \nabla a^\alpha
\]

\[
\alpha = n, w, s \quad (49b)
\]

In general, each dependent variable would be postulated to depend on all independent variables. However, dependence of free energies on velocities and gradients of saturation and temperature is often ruled out as violating the second law of thermodynamics or excluded based on intuitive understanding of the system under consideration. Here, as a departure from the principle of equipresence, a simpler functional dependence of free energies is hypothesized such that

\[
A^\alpha = A^\alpha (\rho^\alpha, \theta^\alpha, s^\alpha) \quad \alpha = n, w \quad (50a)
\]

\[
A^\alpha = A^\alpha (\rho^\alpha, \theta^\alpha, E^\alpha, s^\alpha) \quad (50b)
\]

and

\[
A^\alpha = A^\alpha (\Gamma^\alpha, \theta^\alpha, a^\alpha, s^\alpha) \quad \alpha = m, ns, ws \quad (51)
\]

The retention of saturation as an independent variable in these expressions is a direct consequence of the experimental observation that fluid pressures depend on saturation. The incorporation of this dependence into the macroscopic thermodynamics is an important feature of the present work. All dependent variables other than the free energies are allowed to depend on the complete set of independent variables listed in (49b).

According to the principle of admissibility, the general constitutive postulates relating dependent to independent variables must not violate the conservation laws and/or the second law of thermodynamics formulated as inequality (40). Restrictions imposed by this requirement are explored by the Coleman and Noll \cite{13} method. Details of the manipulations are provided in Appendix B and lead to the following simplifications of the constitutive relations:

\[
\eta^\alpha = - \frac{\partial A^\alpha}{\partial \theta^\alpha} \quad \alpha = n, w, s \quad (52a)
\]

\[
\eta^\alpha = - \frac{\partial A^\alpha}{\partial \theta^\alpha} \quad \alpha = m, ns, ws \quad (52b)
\]

\[
t^\alpha = - p^a I \quad \alpha = n, w \quad (53a)
\]

\[
t^\alpha = - p^a I + t^\alpha \quad (53b)
\]

\[
S^\alpha = \gamma^\alpha I \quad \alpha = m, ns, ws \quad (54)
\]

where

\[
p^\alpha (\rho^\alpha, \theta^\alpha, s^\alpha) = (\rho^\alpha)^\gamma \frac{\partial A^\alpha}{\partial \rho^\alpha} \quad \alpha = n, w \quad (55a)
\]

\[
p^\alpha (\rho^\alpha, \theta^\alpha, E^\alpha, s^\alpha) = (\rho^\alpha)^\gamma \frac{\partial A^\alpha}{\partial \rho^\alpha} \quad (55b)
\]

are the thermodynamic pressures of the fluid and solid phases respectively; and

\[
\gamma^\alpha (\Gamma^\alpha, \theta^\alpha, a^\alpha, s^\alpha) = -(\Gamma^\alpha)^\gamma \frac{\partial A^\alpha}{\partial \Gamma^\alpha} \quad (56)
\]

\[
\gamma^\alpha (\Gamma^\alpha, \theta^\alpha, a^\alpha, s^\alpha) = -a^\alpha \Gamma^\alpha \frac{\partial A^\alpha}{\partial a^\alpha} \quad (56)
\]

is the macroscopic interfacial tension of the \( \alpha \beta \)-interface. Additionally,

\[
t^\alpha = \rho^a (\text{GRAD} \ F^a)^T \cdot \frac{\partial A^\alpha}{\partial E^a} \cdot (\text{GRAD} \ F^a) \quad (57)
\]

is the effective stress tensor of the solid phase.
With these results incorporated into equation (B.3), the residual entropy inequality becomes:

\[
\sum_{\alpha} \Lambda^\alpha + \sum_{\alpha \neq \beta} \Lambda^{\alpha \beta} = \Lambda = \sum_{\alpha} \left( s''^\alpha p_\alpha + s''^\alpha p_\alpha - p' \right)
\]

\[
+ \sum_{\alpha \neq \beta} \frac{1}{\beta} \varepsilon^{\alpha \beta} \left( p'' \nabla (\varepsilon^\alpha) - \varepsilon^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \nabla s^\alpha \right)
\]

\[
- \sum_{\beta \neq \alpha} \hat{\varepsilon}_{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \nabla s^\alpha
\]

\[
+ \sum_{\alpha \neq \beta} \frac{1}{\beta} \nabla \theta^{\alpha \beta} \left( -a^{\alpha \beta} \Gamma^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \nabla s^\alpha \right)
\]

\[
+ \hat{T}_{\alpha \beta} - \hat{T}_{\alpha \beta} - \frac{S_{\alpha \beta \gamma}}{\theta^\alpha} \frac{\partial A^{\alpha \beta \gamma}}{\partial s^\alpha}
\]

\[
+ \frac{1}{\beta} \left( s''^\alpha - s''^\alpha p' \right)
\]

\[
+ \sum_{\alpha \neq \beta} \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \nabla s^\alpha
\]

Equilibrium restrictions

For the system under consideration, the state of thermodynamic equilibrium is defined to be the state at which the following variables are all zero

\[
\{ z_\alpha, \mu = 1.46 \} = \{ v_\alpha, w_\alpha, \theta^\alpha, \theta^{\alpha \beta}, \nabla \theta^\alpha, \nabla \theta^{\alpha \beta}, \varepsilon, \varepsilon^\alpha, \varepsilon^{\alpha \beta} \}
\]

These restrictions imply that at equilibrium, there will be no relative movement of phases and interfaces; the rate of change of saturations, areal fractions, and porosity will be zero; and the rate of mass exchange between phases, interfaces, and contact lines will be zero. These restrictions also imply that at equilibrium all phases and interfaces will have the same uniform temperature such that \( \theta^\alpha = \theta^{\alpha \beta} = \theta \). One can readily verify that at equilibrium \( \Lambda \) will be zero which means, by equation (58), that it attains its minimum value. The necessary and sufficient conditions for \( \Lambda \) to be a minimum at equilibrium are

\[
\left[ \frac{\partial \Lambda}{\partial z_\alpha} \right] = 0 \quad \mu = 1.46 \quad (60a)
\]

and

\[
\left[ \frac{\partial^2 \Lambda}{\partial z_\alpha \partial z_\beta} \right] \text{ be positive semi-definite} \quad \mu, \kappa = 1.46 \quad (60b)
\]

Application of restriction (60a) to the residual entropy inequality (58) requires the terms inside each and every set of braces to go to zero at equilibrium. As a result, the following restrictions are obtained after some rearrangements:

\[
(p'')_\alpha = s''^\alpha p'' + s''^\alpha p'' \quad (61a)
\]

\[
(p'''' - p'')_\alpha = p' \quad (61b)
\]

\[
(\mathbf{T}'^\alpha)_\alpha = \left( \sum_{\beta \neq \alpha} \hat{T}_{\alpha \beta} \right)_\alpha = p'' \nabla (\varepsilon^\alpha) + \varepsilon^\alpha \nabla s^\alpha \quad \alpha = w, n \quad (62a)
\]

\[
\left( S_{\alpha \beta \gamma} - \hat{T}_{\alpha \beta} - \hat{T}_{\alpha \beta} \right)_\alpha = -a^{\alpha \beta} \nabla a^{\alpha \beta}
\]

\[
- a^{\alpha \beta} \Gamma^{\alpha \beta} \left( \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \right) \nabla s^\alpha
\]

\[
\alpha \beta = wn, ws, ns \quad (62b)
\]

\[
(q''''_\alpha)_\alpha = 0 \quad a = w, n, s \quad (63a)
\]

\[
(q''''^{(\alpha \beta)})_\alpha = 0 \quad a \beta = wn, ws, ns \quad a \beta \gamma = wns \quad (63b)
\]

\[
(\hat{Q}^{(\alpha \beta)}_{\alpha \beta})_\alpha = 0 \quad a \beta = wn, ws, ns \quad (64)
\]

\[
(\hat{Q}^{(\alpha \beta)}_{\alpha \beta})_\alpha = 0 \quad a \beta = wn, ws, ns \quad (65)
\]

\[
(a^{(\alpha \beta)})_\alpha = 0 \quad a \beta = wn, ws, ns \quad \alpha \beta \gamma = wns \quad (66)
\]

\[
(a^{(\alpha \beta)})_\alpha = 0 \quad a \beta = wn, ws, ns \quad (67)
\]

where \( ( \ ) \alpha \) indicates evaluation at equilibrium. In equa-

Additional information can be extracted from the residual entropy inequality when examined at equilibrium.
tion (62a) \( \Omega^\alpha \), herein named `wettability potential', is defined by
\[
\frac{\Omega^\alpha}{s^\alpha p^\alpha} = \frac{\partial A^\alpha}{\partial s^\alpha}
\]
(68)

Equations (62) suggest that the momentum exchange terms have an equilibrium part and a non-equilibrium part which vanishes at equilibrium. Accordingly, one may write
\[
\hat{\tau}^\alpha = \sum_{\beta \neq \alpha} \hat{\tau}_{\alpha \beta}^\alpha = \hat{\tau}^\alpha + \left( \sum_{\beta \neq \alpha} \hat{\tau}_{\alpha \beta}^\alpha \right)
\]
(69)

and
\[
\hat{S}_{\alpha \beta}^\alpha - \hat{\tau}_{\alpha \beta}^\alpha = \hat{\tau}_{\alpha \beta}^\alpha = \sum_{\beta \neq \alpha} \hat{\tau}_{\alpha \beta}^\alpha = \hat{\tau}_{\alpha \beta}^\alpha
\]
(70)

where \( \hat{\tau}^\alpha \) and \( \hat{\tau}_{\alpha \beta}^\alpha \) are the non-equilibrium parts and are allowed to be general functions of the full set of independent variables listed in (49b). Equations (63) and (64) indicate that at equilibrium no heat transfer within and/or among the phases and interfaces will occur.

For subsequent discussion here, attention is restricted more to the mechanical aspects and less to the thermal aspects of the problem. For a large class of problems, temperature differences between phases at a macroscopic point is negligible. For these cases, a state of `local thermal equilibrium' prevails such that all phases and interfaces will have the same temperature, \( \theta \), at a point although \( \theta \) may still vary in space. Therefore, \( \theta_{\alpha \beta} \) is zero and all terms in equation (58) multiplied by \( \theta_{\alpha \beta} \) drop out. Additionally, when \( \hat{e} \), \( \hat{e}_{\alpha \beta} \), and \( \hat{e}_{\alpha \beta} \) are small, the contribution of the solid phase pressure, and the mass exchange terms to the entropy inequality will be negligible.

These simplifications are not essential for the development which follows but merely specify the types of systems which will be studied further here. It is always possible to relax these restrictions and examine their effects on the mechanical equations. With these restrictions, and utilizing (61)–(70), the residual entropy inequality multiplied by \( \theta \) becomes
\[
\theta \dot{\Lambda} = -\sum_{\alpha \neq \beta} \mathbf{v}_{\alpha \beta}^\alpha \cdot \hat{s}^\alpha - \sum_{\alpha \beta} \mathbf{w}_{\alpha \beta}^\alpha \cdot \hat{\tau}_{\alpha \beta}^\alpha
\]
\[
- \frac{\nabla \theta}{\theta} \left( \sum_{\alpha} \epsilon^\alpha q^\alpha - \sum_{\alpha \beta} a_{\alpha \beta} q^{\alpha \beta} \right) \geq 0
\]
(71)

**LINEAR THEORY AND EQUATIONS OF MOTION**

To this point, the equations developed are rather general, and with that generality comes the need to determine the functional forms of the constitutive functions prior to application. For some problems, additional simplification may be obtained by considering the dynamics of the system `near' equilibrium such that linear dependence of the constitutive functions on independent variables which go to zero at equilibrium may be postulated. Of course, such postulations require experimental study for verification and to determine acceptable `nearness' to equilibrium.

In this section, equations of motion of the two fluid phases and the three interfaces applicable to commonly encountered porous media problems are obtained. The fluid motion will be obtained relative to \( \mathbf{r} \) with the solution of the solid phase equations considered as decoupled from the movement of other phases and interfaces.

Substitution of equations (53a), (62a), and (69), into the momentum equation (22), substitution of (54), (62b), and (70) into (23), neglect of the advective term for slow flow, and neglect of the phase change terms yield:
\[
\nabla p^\alpha - \rho^\alpha \mathbf{g} = -\frac{\Omega^\alpha}{s^\alpha} \nabla s^\alpha + \frac{\hat{\tau}^\alpha}{\epsilon s^\alpha}
\]
(72)

\[
\alpha = n, w
\]

\[
\nabla (a^{\alpha \beta} \hat{\tau}_{\alpha \beta}^\alpha) + \Gamma^{\alpha \beta} a_{\alpha \beta}^\alpha g = a^{\alpha \beta} \Gamma^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \nabla s^\alpha - \hat{\tau}^{\alpha \beta}
\]
(73)

In these equations, gravity is assumed to be the only external supply of momentum to the system.

The dissipative drag forces, \( \hat{\tau}^\alpha \) and \( \hat{\tau}_{\alpha \beta}^\alpha \) in equations (72) and (73) are general functions of the independent variables. If the deviation from equilibrium is small such that these forces may be assumed to be linear functions of the independent variables \( \mathbf{v}^\alpha, w^{\alpha \beta} \), and \( \nabla \theta \); and if the effect of temperature gradient is assumed to be small in comparison to that of flow velocities (or for isothermal processes), then
\[
\hat{\tau}^\alpha = -R_{\alpha}^\alpha \cdot \mathbf{v}^\alpha - R_{\alpha}^\beta \cdot \mathbf{w}^{\alpha \beta} - \sum_{\alpha \beta} R_{\alpha \beta}^{\alpha \beta} \cdot \mathbf{w}^{\alpha \beta}
\]
(74)

and
\[
\hat{\tau}_{\alpha \beta}^\alpha = -R_{\alpha \beta}^\alpha \cdot \mathbf{v}^\alpha - R_{\alpha \beta}^\alpha \cdot \mathbf{w}^{\alpha \beta} - \sum_{\alpha \beta} R_{\alpha \beta}^{\alpha \beta} \cdot \mathbf{w}^{\alpha \beta}
\]
(75)

where the tensors \( R \) are material coefficient and functions of the independent variables listed in (49b) except for the velocities and the temperature gradient. Note that a linear dependence of \( \hat{\tau}^\alpha \) and \( \hat{\tau}_{\alpha \beta}^\alpha \) on \( E^\alpha \), \( \nabla \epsilon \), and \( \nabla s^\alpha \) is not allowed because these variables are not necessarily zero at equilibrium whereas \( \hat{\tau}^\alpha \) and \( \hat{\tau}_{\alpha \beta}^\alpha \) do vanish at equilibrium according to equations (70).

Next consider \( s^\alpha \). For the linear case under consideration here, with reference to residual entropy inequality (71), the following relationship is proposed:
\[
\dot{s}^\alpha = -\Pi^\alpha (p^\alpha - p^\alpha - p^\alpha)
\]
(76)

where \( \Pi^\alpha \) is a general material coefficient which must be determined experimentally. In general, it may be a function of \( \rho^\alpha, \epsilon, s^\alpha, a^{\alpha \beta}, \Gamma^{\alpha \beta}, \) and \( \theta \).

The heat flux is the final grouping in the entropy inequality which will be linearized. With the temperatures of all phases and interfaces equal due to the `local equilibrium' assumption, the heat flux is parameterized by
\[
\sum_{\alpha} \epsilon^\alpha q^\alpha + \sum_{\alpha \beta} a_{\alpha \beta} q^{\alpha \beta} = K \cdot \nabla \theta
\]
(77)

where \( K \) is, again, a material property.
Substitution of equations (74) through (77) back into the residual entropy inequality (71) provides

\[ \theta \Lambda = \sum_{\alpha \neq \tau} \sum_{\beta \neq s} \mathbf{v}^{\alpha \beta} \cdot \mathbf{R}^{\alpha}_{\beta} + \sum_{\alpha \neq s} \sum_{\beta \neq} \mathbf{v}^{\alpha \beta} \cdot \mathbf{R}^{\alpha}_{\beta} + \sum_{\alpha \neq} \sum_{\beta \neq} \mathbf{w}^{\alpha \beta} \cdot \mathbf{R}^{\alpha}_{\beta} \cdot \mathbf{w}^{\alpha \beta} \cdot \mathbf{w}^{\alpha \beta} = \epsilon (\Pi^n)^{-1} (s^n)^{\frac{2}{\theta}} \cdot \nabla \theta \cdot \mathbf{K} \cdot \nabla \theta \geq 0 \]  

(78)

Imposition of the second condition of equilibrium, equation (60b) on this expression provides restrictions on the material coefficients such that

\[ \mathbf{K} \text{ is positive semi-definite} \]  

(79a)

\[ \Pi^n \geq 0 \text{ (79b)} \]

\[ R^{\alpha}_{\beta} + (R^{\alpha}_{\beta})^T \text{ is positive semi-definite } \alpha, \beta \neq s \]  

(79c)

\[ R^{\alpha}_{\beta} + (R^{\beta}_{\alpha})^T \text{ is positive semi-definite } \alpha, \beta \neq s \]  

(79d)

\[ R^{\alpha\beta}_{\gamma\delta} + (R^{\alpha\beta}_{\gamma\delta})^T \text{ is positive semi-definite} \]  

(79e)

Substitution of linearized relations (74) and (75) into the momentum equation (72) yields, for the fluid phases

\[ \frac{1}{s^n} \left[ \sum_{\beta \neq s} R^{\alpha}_{\beta} \cdot \mathbf{v}^{\alpha \beta} + \sum_{\beta \neq} R^{\alpha}_{\beta} \cdot \mathbf{w}^{\alpha \beta} \right] = -(\nabla p^n - \rho^n \mathbf{g}) + \frac{\Omega^n}{s^n} \nabla s^n \quad \alpha = n, w \]  

(80)

and for the interfaces

\[ \left[ \sum_{\gamma \neq s} R^{\alpha\beta}_{\gamma\delta} \cdot \mathbf{v}^{\alpha \beta} + \sum_{\gamma \neq} R^{\alpha\beta}_{\gamma\delta} \cdot \mathbf{w}^{\alpha \beta} \right] = \nabla (a^{\alpha\beta} \gamma^{\alpha\beta}) + a^{\alpha\beta} \Gamma^{\alpha\beta} - \Gamma^{\alpha\beta} a^{\alpha\beta} \left( \frac{\partial A^{ad}}{\partial s^n} \right) \nabla s^n \
\alpha \beta = wn, ws, ns \]  

(81)

Equation (80) is a generalized form of the momentum equation suitable for multiphase media including the case where the motion of interfaces affects the motion of phases. When this effect is small, the second term in brackets involving the relative interfacial velocity will be negligible. Coupling effects of motion of phases is accounted for by the first term in brackets in equation (80) where \( \beta \neq \alpha \). This coupling has also been obtained by other investigators (e.g., Thigpen and Berryman99, Whitaker91 and Kalaydjian25). Whereas the coupling effects may be negligible under certain conditions, the term involving \( \Omega^n \) seems to have some potential significance. That term can be neglected only if the following restriction holds

\[ \epsilon [\Omega^n \nabla s^n] \leq |R^{\alpha}_{\beta} \cdot \mathbf{v}^{\alpha \beta}| \]  

(82)

This condition may not hold under equilibrium conditions or in low permeable media where \( \mathbf{v}^{\alpha \beta} \) is either zero or very small. Restriction (82) would imply that the wettability potential, \( \Omega^n \), is unimportant. However, the known dependence of capillary pressure on saturation indicates that this is not the case. Thus when the coupling between velocities is not considered, equation (80) reduces to

\[ \frac{1}{s^n} R^{\alpha}_{\beta} \cdot \mathbf{v}^{\alpha \beta} = -(\nabla p^n - \rho^n \mathbf{g}) + \frac{\Omega^n}{s^n} \nabla s^n \quad \alpha = n, w \]  

(83)

The actual significance of the last term in this equation is an important issue requiring experimental study. Note that (83) directly reduces to the classical Darcy’s law for single-phase fluid flow or for multiphase flow if restriction (82) holds.

**DISCUSSION AND CONCLUSIONS**

The main purpose of this work has been to develop, based on fundamental laws of physics, a macroscopic thermodynamic theory for the description of multiphase flow in porous media. The Helmholtz free energy of fluid phases have been taken to be functions of their mass density, saturation and temperature such that for fluid phase \( \alpha \):

\[ \frac{\partial A^{\alpha}}{\partial p^{\alpha}} \rho^{\alpha} = p^{\alpha}/(\rho^{\alpha})^2 \]  

(84a)

\[ \frac{\partial A^{\alpha}}{\partial \theta^{\alpha}} \rho^{\alpha} = -\eta^{\alpha} \]  

(84b)

\[ \frac{\partial A^{\alpha}}{\partial s^{\alpha}} \rho^{\alpha} = \Omega^{\alpha} \]  

(84c)

Therefore, one can write

\[ dA^{\alpha} = \frac{p^{\alpha}}{\rho^{\alpha}} dp^{\alpha} - \eta^{\alpha} d\theta^{\alpha} + \frac{\Omega^{\alpha}}{s^{\alpha} \rho^{\alpha}} ds^{\alpha} \quad \alpha = n, w \]  

(85)

In water resources and petroleum literature, equations similar to (84a) and (84b) have been employed based on ad hoc extension of analogous relationships valid at the microscale. The current study proves that these equations indeed hold at the macroscale for multiphase flow. The wettability potential, \( \Omega^n \), is a new quantity which accounts for the dependence of free energy on saturation. Thermodynamics of multiphase flow in porous media is incomplete without introduction of the wettability potential.

The interfaces in a multiphase system have been considered to have thermodynamic properties of their own. The Helmholtz free energy of the interface per unit excess mass, \( A^{ad} \), is taken to depend on \( \Gamma^{ad}, a^{ad}, \theta, \) and \( s^n \). In particular, the macroscopic interfacial tension, \( \gamma^{ad} \), is shown to be

\[ \gamma^{ad}(\Gamma^{ad}, \theta, a^{ad}, s^n) = -\left( \frac{\partial A^{ad}}{\partial \Gamma^{ad}} \right)_{\theta,a^{ad}} \]  

(86)
This term accounts for the change in the free energy of interfaces as they are formed or disappear. It is the macroscopic counterpart of microscopic surface tension. In practice, one works with and measures capillary pressure instead of the macroscopic interfacial tension. However, this term serves the purpose of linking capillary pressure to other thermodynamic properties as illustrated by (59). Furthermore, if one is interested in solving (81) to obtain the motion of interfaces, \( \gamma^{ad} \) will be an important variable analogous to pressure in (80). If macroscopic area per unit mass of the interface is denoted by \( A^{ad} (= \Gamma^{ad} / \rho) \), then (86) may alternatively be written as

\[
\gamma^{ad} = \left( \frac{\partial A^{ad}}{\partial s^{ad}} \right)_{\theta, s^{ad}} \tag{87}
\]

This equation resembles the definition of interfacial tension of surfaces at the macroscale (see e.g. Adamson\(^1\)). Until now, it was employed on an \textit{ad hoc} basis at the macroscale but, it is shown to indeed be valid. Note that dependence on volumetric saturations is specific to the macroscale only.

Another interesting result obtained in this work is the relationship (59) for \( p^* \). For the case that all phases have the same temperature, \( p^* \) is defined to be:

\[
p^* = -\Omega^* + \Omega^* \frac{(1 - \epsilon)}{\epsilon} p^* + \frac{1}{\epsilon} \frac{\partial A^*}{\partial s^*} - \sum_{a,b} \frac{a^{a,b} \Omega^b}{\epsilon} \frac{\partial A^{a,b}}{\partial s^*} \tag{88}
\]

This equation actually relates the capillary pressure to the net release of energy by the phases and interfaces in the system. Previously, the relationship \( p^* = 2 \gamma / r \) for a microscopic interface, has been simply extended to give the macroscopic capillary pressure. Kalaydjian\(^25\) obtained only one of the terms on the right side of (88) when he derived

\[
p^* = \gamma^{mn} \frac{\partial a^{mn}}{\partial (s^*)} \tag{89a}
\]

This term is obtained for \( \partial A^{mn}/\partial s^* \) by noting that

\[
\frac{a^{mn} \Gamma^{mn}}{\epsilon} \frac{\partial A^{mn}}{\partial s^*} = -\gamma^{mn} \left( \frac{\partial a^{mn}}{\partial s^*} \right)_{A^{mn}, \theta, \Gamma^{mn}} \tag{89b}
\]

Kalaydjian does not have all the terms which appear in (88) because his theory does not include a dependence of free energies on saturation. On the other hand, in works based on mixture theories where no explicit accounting for interfaces is attempted, terms related to \( \partial A^{mn}/\partial s^* \) are absent. For example, Allen\(^6\) obtains (in our notation):

\[
p^* = \epsilon s^* p^* \frac{\partial A^*}{\partial (s^*)} - \epsilon s^* p^* \frac{\partial A^*}{\partial (s^*)} \tag{89b}
\]

while Bowen\(^11\) obtained

\[
p^* = -\frac{\partial}{\partial (s^*)} \sum_{a} \epsilon^a \rho^a A^a \tag{89c}
\]

The current formulation leading to equation (88) accounts for all relevant mechanisms, and the full significance of this expression deserves further study. Note that in this approach \( p^* \) is not simply defined to be \( p^* = p^* - p^* \). Rather, it is defined based on thermodynamic considerations, and it is only at equilibrium that it would be equal to \( p^* - p^* \). In other cases, relation (76) will be applicable.

According to (88), capillary pressure is a function of \( \rho^a, \Gamma^{ad}, \epsilon, s^a, a^{ad}, \theta, \) and \( E^a \). This is a much more general statement than \( p^* = p^*(s^a, \theta) \) normally used in the literature. A dependence on \( \rho^a, \Gamma^{ad}, \epsilon \) and \( E^a \) simply means that saturation–capillary pressure curves are specific to a particular set of fluids and solids, are dependent on the interface condition, and may vary if the medium deforms. These are probably implicit assumptions behind the relation \( p^* = p^*(s^a, \theta) \) as well. However, the dependence of \( p^* \) on \( a^{ad} \) also suggests a dependence of capillary pressure on the curvature of interfaces at a given saturation. This property may be used to provide a quantitative description of hysteresis.

Finally, among the important results, are the linearized equations of motion (80) and (81) and their simplification in certain circumstances to (83). In principle, these equations, together with equations of state for \( p^*(\alpha \neq s), \gamma^{ad}(\Omega^a, \text{ and } a^{ad}), \) the nonequilibrium relation (76), and the mass conservation equations (20) and (21), neglecting the solid phase motion and assuming that \( \epsilon \) and \( a^{a} \) are known), provide 28 equations to be solved for the 28 unknowns; \( v^*, w^{ad}, \rho^a, p^*, \Gamma^{ad}, \gamma^{ad}, s^a, \) and \( a^{ad} \). Consequences of these relations and the extended equations of motion will be studied in future works.

The systematic procedure of exploiting the second law of thermodynamics has resulted in a coherent thermodynamic theory of two phase flow in a porous medium. Relationships among internal energy, Helmholtz free energy, Gibbs free energy, entropy, thermodynamic pressure, temperature, interfacial tension and saturation of phases are obtained at the macroscopic level. It appears that some formulæ which are simply ‘borrowed’ from microscopic thermodynamics are indeed valid at the macroscopic. Whereas, some other macroscopic formulæs are incorrect and deficient at the macroscale.

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**APPENDIX**

**Definition of macroscopic quantities**

Most macroscopic quantities are obtained in terms of the average of microscopic quantities using the averaging procedure. The definitions can be found in Hassanizadeh and Gray and in Gray and Hassanizadeh. However, for the sake of completeness, definition of basic macroscopic quantities in terms of microscopic variables are given below.

Mass densities are defined by:

$$\rho^\alpha = \frac{1}{\epsilon} \delta V \int_{\partial V} \rho \mid_{\alpha} dV$$

(A.1)

$$\Gamma^\alpha = \frac{1}{\epsilon} \delta V \int_{\partial V} \Gamma \mid_{\alpha} dV$$

(A.2)

Velocities, external supplies of momentum and energy, internal entropy, and rate of net production entropy, each typically denoted by $\psi$, are defined

$$\psi^\alpha = \frac{1}{\epsilon} \rho^\alpha \delta V \int_{\partial V} (\rho \psi) \mid_{\alpha} dV$$

(A.3)

$$\psi^a = \frac{1}{\epsilon} \rho^a \delta V \int_{\partial V} (\rho \psi^a) \mid_{a} da$$

(A.4)

Macroscopic internal energy and external supply of energy are given by:

$$E^\alpha = \int \frac{1}{\epsilon} \rho \delta V \int_{\partial V} (\rho \psi) \mid_{\alpha} (E \mid a) + \frac{1}{2} \psi^a \cdot \psi^a) dV$$

(A.5)

where

$$\psi^a = v_{\alpha} - v^a$$

(A.6)

$$E^a = \frac{1}{\epsilon} \rho^a \delta V \int_{\partial V} (\Gamma \mid_{a} (E \mid a) + \frac{1}{2} \w^a \cdot \w^a) dV$$

(A.7)

where

$$\w^a = \w_{\alpha} - \w^a$$

(A.7)

$$h^\alpha = \frac{1}{\epsilon} \rho^\alpha \delta V \int_{\partial V} (\rho \psi) \mid_{\alpha} (h \mid a) + g \mid a \cdot \psi^a) dV$$

(A.8)
\( h^{ad} = \frac{1}{a^{ad}} \int_{\text{A}_{ad}} \left( \Gamma_{\text{ad}} + g_{\text{ad}} \cdot \tilde{w}^{ad} \right) \, dv \) \hfill (A.9)

Macroscopic stress tensors are defined by:

\[
\tau^{\alpha} \cdot \mathbf{N} = \frac{1}{\epsilon^{\alpha \delta}} \int_{\text{A}_{ad}} n \cdot \left( t^{\alpha} - \rho l^{\alpha} \tilde{\varsigma}^{\nu} \tilde{\varsigma}^{\nu} \right) \, dv \hfill (A.10)
\]

\[
S^{ad} \cdot \mathbf{N} = \frac{1}{a^{ad}} \sum_{\gamma \in \text{A}_{ad}} \int_{\text{B}_{\gamma \text{A}_{ad}}} \rho^{\alpha \beta} \cdot \left( S^{\alpha \gamma} - \Gamma l^{\alpha}_{\gamma \text{A}_{ad}} \tilde{w}^{\alpha \gamma} \tilde{w}^{\alpha \gamma} \right) \, dc \hfill (A.11)
\]

Macroscopic heat vectors are:

\[
q^{\alpha} \cdot \mathbf{N} = \frac{1}{\epsilon^{\alpha \delta}} \int_{\text{A}_{ad}} \left[ q l^{\alpha} + t l^{\alpha} \cdot \tilde{\varsigma}^{\nu} \cdot \rho l^{\alpha} (E l^{\alpha} - \nu^{\alpha}) + \frac{1}{2} \tilde{\varsigma}^{\nu} \cdot \nu^{\alpha} \right] \, dv \hfill (A.12)
\]

\[
q^{\alpha \beta} \cdot \mathbf{N} = \frac{1}{a^{ad}} \sum_{\gamma \in \text{A}_{ad}} \int_{\text{B}_{\gamma \text{A}_{ad}}} \left[ q l^{\alpha \beta} + S l^{\alpha \beta} \cdot \tilde{w}^{\alpha \beta} \cdot (E l^{\alpha \beta} + \frac{1}{2} \tilde{w}^{\alpha \beta} \cdot \tilde{w}^{\alpha \beta}) \right] \cdot \nu^{\alpha \beta} \, dc \hfill (A.13)
\]

Macroscopic entropy flux vector

\[
\varphi^{\alpha} \cdot \mathbf{N} = \frac{1}{\epsilon^{\alpha \delta}} \int_{\text{A}_{ad}} \left[ \varphi l^{\alpha} - \rho l^{\alpha} \eta l^{\alpha} \tilde{\varsigma}^{\nu} \cdot \nu^{\alpha} \right] \, dv \hfill (A.14)
\]

\[
\varphi^{\alpha \beta} \cdot \mathbf{N} = \frac{1}{a^{ad}} \sum_{\gamma \in \text{A}_{ad}} \int_{\text{B}_{\gamma \text{A}_{ad}}} \left[ \varphi l^{\alpha \beta} - \rho l^{\alpha \beta} \eta l^{\alpha \beta} \tilde{\varsigma}^{\nu} \cdot \nu^{\alpha \beta} \right] \, dc \hfill (A.15)
\]

Finally, momentum, energy and entropy exchange terms are defined as follows:

\[
\dot{T}^{\alpha} = \frac{1}{\delta V} \int_{\text{A}_{ad}} n^{\alpha} \cdot \left[ t^{\alpha} + \rho l^{\alpha} \tilde{\varsigma}^{\nu} (w l^{\alpha} - \nu l^{\alpha}) \right] \, da \hfill (A.16)
\]

\[
\dot{S}^{\alpha \beta} = \frac{1}{\delta V} \int_{\text{B}_{\gamma \text{A}_{ad}}} \rho^{\alpha \beta} \cdot \left[ S l^{\alpha \beta} + \Gamma l^{\alpha \beta} \tilde{w}^{\alpha \beta} (u l^{\alpha \beta} - w l^{\alpha \beta}) \right] \, dc \hfill (A.17)
\]

\[
\dot{Q}^{\alpha} = \frac{1}{\delta V} \int_{\text{A}_{ad}} \left[ q l^{\alpha} + t^{\alpha} \cdot \tilde{\varsigma}^{\nu} \cdot \rho l^{\alpha} (E l^{\alpha} - \nu^{\alpha}) + \frac{1}{2} \tilde{\varsigma}^{\nu} \cdot \nu^{\alpha} (w l^{\alpha} - \nu l^{\alpha}) \right] \cdot n^{\alpha} \, da \hfill (A.18)
\]

\[
\dot{Q}^{\alpha \beta} = \frac{1}{\delta V} \int_{\text{B}_{\gamma \text{A}_{ad}}} \left[ q l^{\alpha \beta} + S l^{\alpha \beta} \cdot \tilde{w}^{\alpha \beta} \cdot (E l^{\alpha \beta} - \nu^{\alpha \beta}) + \Gamma l^{\alpha \beta} (w l^{\alpha \beta} - \nu l^{\alpha \beta}) \right] \cdot \nu^{\alpha \beta} \, dc \hfill (A.19)
\]

\[
\dot{\phi}^{\alpha} = \frac{1}{\delta V} \int_{\text{A}_{ad}} \left[ \varphi l^{\alpha} + \rho l^{\alpha} (\eta l^{\alpha} - \eta^{\alpha}) (w l^{\alpha} - \nu l^{\alpha}) + \Gamma l^{\alpha} (w l^{\alpha} - \nu l^{\alpha}) \right] \cdot n^{\alpha} \, da \hfill (A.20)
\]

\[
\dot{\phi}^{\alpha \beta} = \frac{1}{\delta V} \int_{\text{B}_{\gamma \text{A}_{ad}}} \left[ \varphi l^{\alpha \beta} + \Gamma l^{\alpha \beta} (\eta l^{\alpha \beta} - \eta^{\alpha \beta}) \right] \cdot \nu^{\alpha \beta} \, dc \hfill (A.21)
\]

The mass exchange terms are defined by (14d) and (15d):

**APPENDIX B**

**Exploitation of the entropy inequality**

The set of constitutive equations for dependent variables (49a) must not be in contradiction with the second law of thermodynamics or balance laws; this is called the principle of admissibility. As was shown, the entropy inequality (40) is obtained by combining the equations of balance of mass, momentum, energy and entropy with the second law of thermodynamics. Therefore, when constitutive assumptions are substituted into (40), the inequality must remain valid for all possible thermodynamic states. This requirement places certain restrictions on the constitutive assumptions. The restrictions are explored by the method originally developed by Coleman and Noll.

When equations (50) are substituted into inequality (40), the derivatives of \( A^v, A^v_x, A^v_t, A^n, A^n_x, A^n_t \) and \( A^n \) have to be evaluated by means of the chain rule of differentiation. For example, for \( A^v \) and \( A^n \) one obtains

\[
\frac{DA^v}{Dt} = \frac{\partial A^v}{\partial \rho^v} \frac{D\rho^v}{Dt} + \frac{\partial A^v}{\partial s^v} \frac{Ds^v}{Dt} + \frac{\partial A^v}{\partial \theta^v} \frac{D\theta^v}{Dt}
\]

\[
\frac{D^n A^n}{Dt} = \frac{\partial A^n}{\partial \Gamma^n} \frac{D\Gamma^n}{Dt} + \frac{\partial A^n}{\partial s^n} \frac{Ds^n}{Dt} + \frac{\partial A^n}{\partial \theta^n} \frac{D\theta^n}{Dt}
\]  

Similar relations will be obtained for $A^a$, $A^r$, $A^{ws}$, and $A^{ns}$. To evaluate equations such as (B.1) and (B.2), substitutions for $D^a p^{a}/Dt$ and $D^{ad} T^{ad}/Dt$ from equations of mass balance (19)–(21) must be made. Also, use should be made of relationships (2)–(13). After much manipulation and algebra, the inequality (40) becomes:

$$\Lambda = - \sum \frac{e^{\alpha}p^{\alpha}}{\theta^{\alpha}} \frac{D^{\alpha}a^{\alpha}}{D^{t}} \left\{ \frac{\partial A_{\alpha}}{\partial \theta^{\alpha}} + \eta^{\alpha} \right\}$$

$$- \sum_{\alpha \beta} a^{\alpha \beta} \Gamma_{\alpha \beta} \frac{D^{\alpha \beta}p^{\beta}}{D^{t}} \left\{ \frac{\partial A_{\alpha \beta}}{\partial \theta^{\alpha \beta}} + \eta^{\alpha \beta} \right\}$$

$$+ \sum_{\alpha \neq \alpha} d^{\alpha} \quad \left\{ \epsilon^{\alpha}(p^{\alpha}I + t^{\alpha}) \right\}$$

$$+ \left( 1 - \epsilon \right) \frac{d^{t}}{\theta^{t}} \left\{ - \rho'(GRAD F')^T \right\}$$

$$- \sum_{\alpha \neq \alpha} \frac{\partial A_{\alpha}}{\partial \theta^{\alpha}} \cdot (GRAD F') + p^{\alpha} I + t^{\alpha} \right\}$$

$$+ \epsilon \left[ \frac{s^{\alpha}p^{\alpha}}{\theta^{\alpha}} + \frac{s^{\alpha}p^{\alpha}}{\theta^{\alpha}} - p^{\alpha} \right] + \sum v_{\alpha \beta}$$

$$- \frac{1}{\theta^{\alpha}} \left\{ p^{\alpha} \nabla (\epsilon^{\alpha}) - \epsilon^{\alpha} \frac{\partial A_{\alpha}}{\partial s^{\alpha}} \nabla s^{\alpha} \right\}$$

$$- \sum_{\alpha \neq \alpha} \frac{\hat{T}^{\alpha}_{\alpha \beta}}{\theta^{\alpha}} + \sum_{\alpha \neq \alpha} \frac{\hat{T}^{\alpha}_{\alpha \beta}}{\theta^{\alpha \beta}}$$

$$+ \sum_{\alpha \neq \alpha} \frac{\hat{T}^{\alpha}_{\alpha \beta}}{\theta^{\alpha \beta}} \left[ \frac{\partial A_{\alpha \beta}}{\partial s^{\alpha \beta}} \nabla s^{\alpha \beta} \right]$$

$$- \left( a^{\alpha \beta} \Gamma^{\alpha \beta} \frac{\partial A_{\alpha \beta}}{\partial s^{\alpha \beta}} + \gamma^{\alpha \beta} \right)$$

$$+ \hat{T}^{\alpha}_{\alpha \beta} + \hat{T}^{\alpha}_{\alpha \beta} - \hat{S}^{\alpha}_{\alpha \beta \gamma} - \frac{\hat{S}^{\alpha}_{\alpha \beta \gamma}}{\theta^{t}} \right\}$$

$$+ s^{\alpha} \left[ \frac{\epsilon}{\theta^{\alpha}} p^{\alpha} - \frac{\epsilon}{\theta^{\alpha}} p^{\alpha} \right] + \sum_{\alpha \neq \alpha} \frac{\Gamma^{\alpha \beta}}{\theta^{\alpha \beta}} \left( \frac{\partial A_{\alpha \beta}}{\partial s^{\alpha \beta}} \right)$$

$$+ \sum_{\alpha \neq \alpha} \frac{1}{\theta^{\alpha \beta}} a^{\alpha \beta} : \left\{ a^{\alpha \beta} \left( S_{\alpha \beta} - \gamma^{\alpha \beta} I \right) \right\}$$

$$- \sum_{\alpha \neq \alpha} a^{\alpha \beta} \Gamma^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial s^{\alpha \beta}} + \gamma^{\alpha \beta}$$

$$+ \sum v_{\alpha \beta}$$

$$+ \nabla \theta^{\alpha} \quad \left\{ \epsilon^{\alpha} q^{\alpha} / (\theta^{\alpha})^2 + \sum_{\alpha \neq \alpha} \nabla \theta^{\alpha \beta} \right\}$$

$$\frac{c^{\alpha \beta} q^{\alpha \beta}}{(\theta^{\alpha \beta})^2} - \frac{1}{\theta^{t}} \sum_{\alpha \neq \alpha} \frac{\hat{Q}^{\alpha \beta} q^{\alpha \beta \gamma}}{\theta^{\alpha \beta \gamma}}$$

$$- \frac{1}{\theta^{t}} \sum_{\alpha \neq \alpha} \frac{\hat{Q}^{\alpha \beta} q^{\alpha \beta \gamma}}{\theta^{\alpha \beta \gamma}} \left( G^{\alpha \beta \gamma} + \frac{1}{2} (w^{\alpha \beta \gamma})^2 \right)$$

$$+ \eta^{\alpha \beta} \theta^{\alpha \beta \gamma} \left( \frac{\gamma^{\alpha \beta \gamma} \theta^{\alpha \beta \gamma}}{\Gamma^{\alpha \beta \gamma}} \right)$$

$$+ \sum_{\alpha \neq \alpha} \frac{\hat{Q}^{\alpha \beta} q^{\alpha \beta \gamma}}{\theta^{\alpha \beta \gamma}} - \frac{1}{\theta^{t}} \frac{1}{2} (w^{\alpha \beta \gamma})^2$$

$$+ \sum_{\alpha \neq \alpha} \frac{\hat{Q}^{\alpha \beta} q^{\alpha \beta \gamma}}{\theta^{\alpha \beta \gamma}} \left( \eta^{\alpha \beta} \theta^{\alpha \beta \gamma} - \frac{p^{\alpha}}{\rho^{\alpha}} \right) \theta^{\alpha \beta \gamma} \geq 0$$

(B.3)

where

$$p^{\alpha} = \left( \rho^{\alpha} \right)^2 \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} = a = w, n, s$$

(B.4a)

and

$$\gamma^{\alpha \beta} = - \left( \Gamma^{\alpha \beta} \right)^2 \frac{\partial A^{\alpha \beta}}{\partial \Gamma^{\alpha \beta}} = \alpha \beta = wn, ws, ns$$

(B.4b)

If $\Gamma^{\alpha \beta}$ is used as a dependent variable in place of $a^{\alpha \beta}$, the relation is developed that

$$\gamma^{\alpha \beta} = - a^{\alpha \beta} \Gamma^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial \Gamma^{\alpha \beta}}$$

(B.4c)

Thus (B.4b) and (B.4c) are equivalent definitions of $\gamma^{\alpha \beta}$ which may be used alternatively in the equation development. The Gibbs free energy also appears in equation (B.3) and is defined by

$$G^{\alpha} = A^{\alpha} + p^{\alpha} / \rho^{\alpha}$$

(B.5a)

and

$$G^{\alpha \beta} = A^{\alpha \beta} - \gamma^{\alpha \beta} \Gamma^{\alpha \beta}$$

(B.5b)

In the left hand side of (B.3), variables $D^{\alpha \beta} q^{\alpha \beta}/Dt$, $D^{\alpha \beta} a^{\alpha \beta}/Dt$, $d^{\alpha}$, and $d^{\alpha \beta} \Gamma^{\alpha \beta}$ appear linearly, because none of the constitutive functions were assumed to depend on these variables (see list in (49b)). Therefore, for the inequality to remain valid for all thermodynamic states, terms inside the braces (i.e. the coefficients of the variables just listed) must be zero. This results in the following relationships:

$$\eta^{\alpha \beta} = - \frac{\partial A^{\alpha \beta}}{\partial \theta^{\alpha \beta}} = \alpha \beta = wn, ws, ns$$

(B.6a)

$$\eta^{\alpha \beta} = - \frac{\partial A^{\alpha \beta}}{\partial \theta^{\alpha \beta}} = \alpha \beta = wn, ws, ns$$

(B.6b)

$$t^{\alpha} = - p^{\alpha} I$$

(B.7)

$$t^{\alpha} = - p^{\alpha} I$$

(B.8)
\[ t^i = t^i_v - p^i \] (B.9)
\[ t^i_v = \rho (\text{GRAD} F)^v \cdot \frac{\partial A_v}{\partial E_v} \cdot (\text{GRAD} F^v) \] (B.10)
\[ S^{\text{ad}} = \gamma^{\text{ad}} I \] (B.11)

The residual entropy inequality becomes the form given as equation (58).

**NOMENCLATURE**

**Latin symbols**

- \( A \): Helmholtz free energy function defined by (36) and (37), \( [L^2/T^2] \)
- \( \alpha^i \): specific surface of the porous medium, \( [L^{-1}] \)
- \( \rho \alpha \): area density, or specific surface, of \( \alpha\beta \)-interface, \( [L^{-1}] \)
- \( b \): macroscopic external supply of entropy, \( [L^2/T^2] \)
- \( d \): deformation rate tensor defined in (12), \( [T^{-1}] \)
- \( da \): infinitesimal element of area
- \( dc \): infinitesimal element of length
- \( dM \): expected mass, defined in (1a), \( [M] \)
- \( d\delta A_{\alpha\beta} \): infinitesimal element of area of an interface (at the microscale), \( [L^2] \)
- \( E \): macroscopic internal energy per unit mass, \( [L^2/T^2] \)
- \( E^i_v \): solid phase stress tensor defined by (6), \( [-] \)
- \( \dot{E}_{\alpha\beta}^{\text{ex}} \): exchange term defined in (14d), \( [M/LT] \)
- \( \dot{E}_{\alpha\beta}^{\text{ex}} \): exchange term defined in (15d), \( [M/LT] \)
- \( F^i \): motion of the solid phase defined by (5)
- \( f \): general external supply of \( \psi \)
- \( G \): Gibbs free energy function defined by (B.5), \( [L^2/T^2] \)
- \( g \): external supply of momentum; gravity vector if without superscript, \( [L^2/T^3] \)
- \( h \): external supply of energy, \( [L^2/T^3] \)
- \( I \): unit tensor
- \( I_{\alpha\beta} \): exchange term defined in (14c)
- \( I_{\alpha\beta}^{\text{ex}} \): exchange term defined in (15c)
- \( i \): general flux vector of \( \psi \)
- \( K \): effective heat conductivity tensor of the porous medium, \( [M/LT^3] \)
- \( l^\alpha, l^\beta \): a characteristic length in a direction normal to an interface over which transition in properties of two adjacent phases occurs, \( [L] \)
- \( M^{\alpha\beta} \): material coefficient in (77), \( [T/M] \)
- \( N \): number of phases of a multiphase system
- \( n^{\alpha} \): unit vector normal to \( \delta A_{\alpha\beta} \) and pointing out of the \( \alpha \)-phase
- \( p^c \): capillary pressure defined by (67), \( [M/LT^2] \)
- \( p_p^{\alpha} \): spreading pressure defined by (69), \( [M/LT^2] \)
- \( P^{\alpha} \): thermodynamic pressure of \( \alpha \)-phase, \( [M/LT^2] \)
- \( Q_{\alpha\beta} \): body supply of heat to the \( \alpha \)-phase from \( \alpha\beta \)-interface, \( [M/LT^3] \)
- \( Q_{\alpha\beta}^{\text{ad}} \): body supply of heat to the \( \alpha\beta \)-interface from the \( \alpha\beta \gamma \)-contact line, \( [M/LT^3] \)
- \( q \): heat vector, \( [M/LT^3] \)
- \( R^{\alpha} \): macroscopic stress tensor of \( \alpha\beta \)-interface, \( [M/LT^2] \)

**Greek symbols**

- \( \Gamma \): surface excess mass density, \( [M/L^3] \)
- \( \gamma^{\alpha\beta} \): macroscopic interfacial tension of the \( \alpha\beta \)-interface, \( [-] \)
- \( \delta A_{\alpha\beta} \): the union of interfacial areas between \( \alpha \)- and \( \beta \)-phases present within an REV, \( [L^2] \)
- \( \delta S_{\alpha\beta} \): the union of \( \alpha\beta \gamma \) contact lines within an REV, \( [L] \)
- \( \delta V \): the representative elementary volume, \( [L^3] \)
- \( \epsilon \): porosity, \( [-] \)
- \( \epsilon^{\alpha} \): volume fraction of \( \alpha \)-phase, \( [-] \)
- \( \eta \): macroscopic internal entropy per unit mass, \( [L^2/T^2] \)
- \( \theta \): temperature
- \( \Delta \): rate of net production of entropy
- \( \rho^{\alpha\beta} \): unit vector tangent to and pointing away from \( \alpha\beta \)-interface and normal to the \( \alpha\beta \gamma \) contact line
- \( \Pi^{\alpha} \): material coefficient in (76), \( [L^2/TM] \)
- \( \rho \): (volumetric) mass density, \( [M/L^3] \)
- \( \dot{z}^{\alpha} \): non-equilibrium part body supply of momentum to \( \alpha \)-phase; see (69), \( [M/LT^2] \)
- \( \dot{z}^{\alpha\beta} \): non-equilibrium part body supply of momentum to the \( \alpha\beta \)-interface; see (70), \( [M/LT^2] \)
- \( \dot{\Phi}_{\alpha\beta} \): body supply of entropy to the \( \alpha \)-phase from the \( \alpha\beta \)-interface
- \( \dot{\Phi}_{\alpha\beta}^{\text{ad}} \): body supply of entropy to the \( \alpha\beta \)-interface from the \( \alpha\beta \gamma \)-contact line
- \( \varphi \): macroscopic entropy flux vector, \( [M/LT^2] \)
- \( \Psi \): rate of net production of \( \psi \)
- \( \Psi^{\alpha\beta} \): typical thermodynamic property
- \( \Omega^{\alpha\beta} \): wettability potential defined by (68), \( [M/LT^2] \)

**Superscripts and subscripts**

- \( n \): nonwetting fluid phase
- \( nS \): interface boundary between nonwetting fluid and solid phases
- \( s \): solid phase
- \( T \): transpose of a tensor
- \( w \): wetting fluid phase
- \( wn \): interface boundary between wetting and nonwetting fluid phases
**Mechanics and thermodynamics of multiphase flow:** Majid Hassanizadeh and W. G. Gray

\[ \frac{D_{\alpha\beta}}{Dt} \]
material derivative following the motion of \( \alpha\beta \)-interface defined by (10b)  
\[ \nabla \]
gradient operator, \([L^{-1}]\)  
\[ \sum_{\alpha\beta} \]
summation over all interfaces  
\[ \sum_{\alpha \neq \beta} \]
summation over all phases except \( \beta \)-phase  

**Special notations**

\( l_{a} \)
microscopic value of the quantity given in front of the vertical line  
\[ D^{\alpha} \]
material derivative following the motion of \( \alpha \)-phase, defined by (10a)  

between two tensors, indicates a double inner product e.g. \( t:s \) becomes \( t_{ij}s_{ij} \) in indicial notation  

an overdot indicates a material derivative with respect to a reference frame fixed to the solid in the superscripts denotes a relative quantity; see (9)  

terms inside parentheses evaluated at equilibrium