Transport in Porous Media **47:** 29–65, 2002.

Closure Conditions for Two-Fluid Flow in Porous Media

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(Received: 8 August 2000; in final form: 31 May 2001)

Abstract. Modeling of multiphase flow in porous media requires that the physics of the phases present be well described. Additionally, the behavior of interfaces between those phases and of the common lines where the interfaces come together must be accounted for. One factor complicating this description is the fact that geometric variables such as the volume fractions, interfacial areas per volume, and common line length per volume enter the conservation equations formulated at the macroscale or core scale. These geometric densities, although important physical quantities, are responsible for a deficit in the number of dynamic equations needed to model the system. Thus, to obtain closure of the multiphase flow equations, one must supplement the conservation equations with additional evolutionary equations that account for the interactions among these geometric variables. Here, the second law of thermodynamics, the constraint that the energy of the system must be at a minimum at equilibrium, is used to motivate and generate linearized evolutionary equations for these geometric variables and interactions. The constitutive forms, along with the analysis of the mass, momentum, and energy conservation equations, provide a necessary complete set of equations for multiphase flow modeling in the subsurface.

Key words: multiphase flow, porous media, closure, unsaturated flow, interfacial area, entropy inequality, thermodynamics.

Nomenclature

Latin

A	measure of disequilibrium between changes in solid surface area and porosity.
a	interfacial area per unit volume.
B	measure of disequilibrium between changes in wn interfacial area and other geometric properties.
b	entropy source term per unit mass.
C	measure of disequilibrium between changes in common line length and other geometric properties.
C_{wns}	common line wns within an averaging volume.
D^i/Dt	material time derivative following the motion of the i component, $\partial/\partial t + \mathbf{v}^i \bullet \nabla$.
$\mathbf{d}$	rate of strain tensor, $(\nabla\mathbf{v} + \nabla\mathbf{v}^T)/2$.
$\hat{E}^i$	internal energy of component i per unit volume.

$\mathbf{E}^s$	Lagrangian strain tensor of the solid phase.
$\hat{e}^i_{\ j}$	rate of mass exchange from component j to component i.
$\mathbf{F}^s$	location of macroscale solid that was initially at $\mathbf{X}^s$.
$\mathbf{G}^{\alpha\beta}$	macroscale orientation tensor for $\alpha\beta$ interface.
$\mathbf{G}^{wns}$	macroscale orientation tensor for wns common line.
h	external supply of energy per unit mass.
$\mathbf{I}$	unit tensor.
J^s	macroscopic curvature of s interface based on unit normal outward from s phase.
$J^\alpha_{\alpha\beta}$	macroscopic curvature of $\alpha\beta$ interface based on unit normal outward from α phase.
$\mathbf{K}_\theta$	heat conduction tensor.
$K^i_{\alpha\beta}$	mass transfer exchange coefficient between phase i and interface $\alpha\beta$.
$K^{\alpha\beta}_{wns}$	mass transfer exchange coefficient between interface $\alpha\beta$ and common line wns.
L_s	coefficient in dynamic capillary pressure equation.
L_{ws}	coefficient in dynamic spreading pressure equation.
L_ϵ	coefficient in dynamic total pressure equation.
l^{wns}	length of common line wns per unit volume.
M^i	mass conservation equation for phase, interface, or common line i.
$\mathcal{M}^i$	mass of component i.
$\mathbf{n}^s$	unit vector normal to the surface of and pointing outward from the s phase.
$\mathbf{n}^\alpha_{\alpha\beta}$	unit vector normal to the $\alpha\beta$ interface pointing outward from the α phase.
P^s	grand canonical potential (GCP) of solid phase per unit volume of solid phase.
p	pressure.
$\hat{Q}^i_{\ j}$	rate of energy exchange from component j to component i.
$\mathbf{q}$	non-advective heat flux vector.
$\mathbf{R}^i_{\ j}$	flow resistance coefficient between components i and j.
$S_{\alpha\beta}$	interfacial area between α and β phases.
$\hat{\mathbf{T}}^i_{\ j}$	momentum exchange between components i and j.
$\mathbf{t}^i$	stress tensor for component i.
$\mathcal{V}$	total volume of system.
V	macroscale, representative averaging volume.
$\mathbf{v}^i$	macroscale velocity of component i.
$\mathbf{X}^s$	initial location of solid phase.
$x^{\alpha s}_s$	fraction of the s surface that is in contact with the α phase.

Greek

$\Gamma^{\alpha\beta}$	grand canonical potential (GCP) of $\alpha\beta$ interface per unit area of $\alpha\beta$ interface.
Γ^{wns}	grand canonical potential (GCP) of wns common line per unit length of wns common line.
γ	interfacial or lineal tension.
δ	variation.
$\overline{\delta}$	fixed point variation.
ϵ	porosity.
ϵ^α	volume fraction of phase α.
$\hat{\eta}$	entropy per unit volume.
θ	temperature.
κ^{wns}_G	macroscale geodesic curvature of the wns common line.
κ^{wns}_g	microscale geodesic curvature of the wns common line.
κ^{wns}_N	macroscale normal curvature of the wns common line.
κ^{wns}_n	microscale normal curvature of the wns common line.

Λ rate of entropy generation.
λ_{E}^{i} Lagrange multiplier for incorporation of energy conservation constraint for component i into the entropy inequality.
λ_{M}^{i} Lagrange multiplier for incorporation of mass conservation constraint for component i into entropy inequality.
$\boldsymbol{\lambda}_{\mathrm{P}}^{i}$ Lagrange multiplier for incorporation of momentum conservation equation for component i into the entropy inequality.
$\boldsymbol{\lambda}^{wns}$ microscale unit vector tangent to the wns common line.
μ chemical potential.
$\boldsymbol{\nu}_{wns}^{\alpha\beta}$ unit vector normal to the wns common line, tangent to the $\alpha\beta$ interface, positive outward from the $\alpha\beta$ interface.
$\boldsymbol{\xi}$ microscale spatial coordinate.
ρ density, mass per unit volume.
$\sum_{\alpha}$ summation over all phases (w, n, and s).
$\sum_{\beta\neq\alpha}$ summation over all phases except α-phase.
$\sum_{\alpha\beta}$ summation over all interfaces (wn, ws, and ns).
$\boldsymbol{\sigma}^{s}$ solid phase stress.
$\boldsymbol{\tau}^{i}$ dynamic momentum exchange term for component i.
Φ macroscale effective contact angle between the wetting phase and the solid.
Φ^{i} gravitational potential for component i.
φ microscale contact angle between the wetting phase and the solid.
$\boldsymbol{\varphi}$ non-advective entropy flux vector.
$\hat{\Omega}$ grand canonical potential (GCP) per unit volume.

Superscripts/Subscripts

i generic reference to either the w, n, or s phase; the ns, wn, or wn interface; or the wns common line.
n relating to the non-wetting phase.
ns relating to the interface between the non-wetting and solid phases.
s relating to the solid phase.
w relating to the wetting phase.
wn relating to the interface between the wetting and non-wetting phases.
wns relating to the common line.
ws relating to the interface between the wetting and solid phases.
, a relative quantity (e.g. $\theta^{w,wn} = \theta^{w} - \theta^{wn}$).

1. Introduction

Although multiphase flow in porous media has been germane to the fields of petroleum engineering and hydrology for decades, its proper physical and mathematical representation is still a subject of considerable study. The traditional conceptualization of a two-fluid system, for example, begins at the microscale at which the porous medium is composed of a solid phase and a connected void space in which the fluids may move and interact (Figure 1). The phases are considered to be immiscible and to have distinct thermodynamic properties. They are separated by very thin transition regions which are typically modeled as two-dimensional interfacial surfaces. In principle, an interface between a particular pair of phases has its own thermodynamic properties that are distinct from those of the phases and

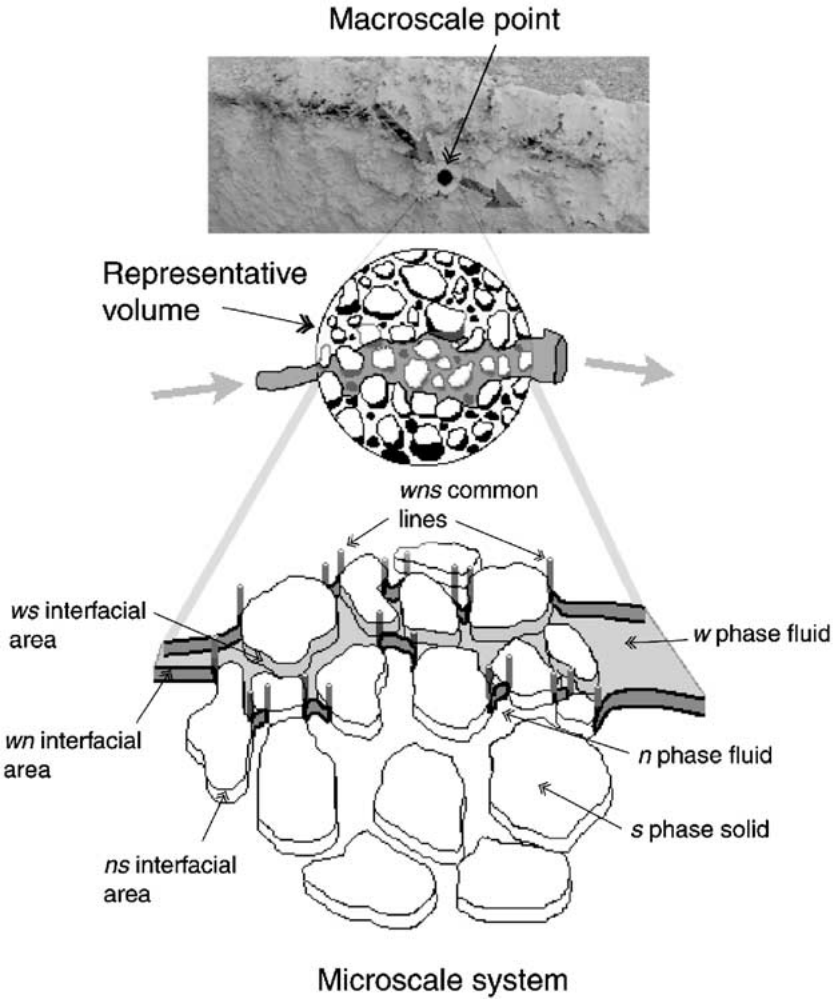

Figure 1. Microscale perspective of a three phase (*wns*) system (below) showing the particular phases, interfaces, and common lines employed in the analysis and the averaging pathway to a macroscale point (top) using a representative volume approach.

from other interfaces. In a three phase system, transition regions at the junction of all three phases may also exist. These may be assigned thermodynamic properties of their own and are typically represented as one-dimensional common lines. The phases are bounded by interfaces and the interfaces are bounded by common lines. Thus, the microscopic picture of a porous medium system is a space occupied by phases, interfaces, and common lines that exist in mutually exclusive domains.

Although microscale conservation equations may be formulated for this system, their solution is complicated by the fact that the evolving geometry of each phase throughout the domain must be known so that boundary conditions can be specified. Interfaces and common lines are moving boundaries. For natural systems,

such geometric detail is unavailable, even for an immobile solid phase, except for very small samples, and the solution of practical problems over realistic length scales is infeasible. Therefore the equations describing the physics of the flow are typically formulated at a larger scale encompassing tens to thousands of pores within a representative volume centered on a macroscopic 'point' in the system (Figure 1). At such a point, the phases are considered to coexist yet are understood to occupy only a fraction of the region in the representative volume itself. Thus, at the macroscale the phases are overlapping continua.

The mass, momentum, and energy conservation equations for interfaces and common lines can also be integrated from the microscale to the macroscale. Although these equations are neglected in traditional analyses (e.g. Whitaker, 1967, 1969; Bachmat, 1972; Slattery, 1972; Hassanizadeh and Gray, 1979), their inclusion is needed to realistically and systematically account for the thermodynamic effects of interfaces and common lines in multiphase flow problems. As a by-product of changing from the microscale to the macroscale, several new primary 'geometric' variables enter the formulation that have no counterparts at the microscale. These include the familiar phase volume fractions (often expressed in terms of saturations and porosity) as well as the interfacial areas per volume and common line length per volume. Unfortunately, the change of scale also introduces an equation deficit into the formulation, as evolutionary equations for the geometric variables are not directly available. In addition, constitutive postulates must be made for quantities such as the macroscale stress tensor, the expressions for mass, momentum, and energy exchanges between phases, and the heat conduction vector. Systematic processes for obtaining the needed constitutive relations have been presented elsewhere, as described subsequently.

The problem of formulating a comprehensive constitutive theory has led to several different approaches. Whitaker (e.g. 1998) uses an approach that maps a microscale quantity into a macroscale quantity such that a differential equation arises whose solution completes the closure problem. This approach has been most often applied for the case of a rigid solid matrix. Interface dynamics and macroscale thermodynamics are not considered. Kalaydjian (1987) has developed a formulation that employs the entropy inequality and also has some equations for interface dynamics. However, the common line is not included and the development makes some significant assumptions along the way rather than looking at the complete entropy inequality. Allen (1984) has developed the multiphase flow equations using a mixture theory approach, but the closure conditions obtained are incomplete because the interfaces have not been incorporated. A paper by Hilfer (1998) indicates further the difficulties in closing the complex system of multiphase flow equations obtained if one uses the mixture theory approach. His heuristic assumptions are not able to properly account for interfacial area or the energy of the interfaces and erroneously lead to an equation that indicates flow can be driven by gradients in volume fraction. Gray and Hassanizadeh (1991) presented an unsaturated flow theory that included interface dynamics that employed the averaged entropy

inequality to obtain the needed constitutive relations. Bennethum and Giorgi (1997) and Bennethum (1994) have also used the entropy inequality in obtaining porous media flow equations. The postulation of the thermodynamic dependence of internal energy was improved in Gray (1999) by making the postulations in terms of extensive variables. This change also clarified the need for closure conditions involving the dynamics of the geometric variables. The closure conditions developed there are based on approximations to averaging theorems and do not account for the average orientation of the interfaces within the averaging volume and thus are somewhat limited in their applicability. Presentation of a systematic process based on exploitation of the second law of thermodynamics for overcoming the equation deficit and obtaining geometric evolutionary equations is the thrust of this paper. These equations are essential to specification of a complete model.

2. Macroscale Conservation Equations

The multiphase system to be considered is composed of three phases (Figure 1): a wetting phase, w, a non-wetting phase, n, and a solid phase, s. Therefore, three different types of interfaces will exist denoted as: wn between the wetting and non-wetting phases, ws between the wetting and solid phases, and ns between the non-wetting and solid phases. The only type of common line is formed where the three phases (or more precisely, the three interfaces) intersect. The common line is designated as wns. Note that interfaces are adjacent to phases, phases and common lines are adjacent to interfaces, and interfaces are adjacent to common lines.

The derivation of general macroscale equations by averaging or localization is well-understood and will not be repeated here (see e.g. Gray and Hassanizadeh, 1998). However, the equations themselves are necessary precursors to the constitutive approach. Therefore the balance equations are provided here in tabular form.

The mass balance equations appear in Table I with the notation given previously. Observe that the entries in the third column have units of mass per macroscale volume; the entries in the fourth column account for exchanges of mass between a region and the adjacent regions.

When the interfaces and common line are treated as massless, only the source/sink terms survive. This simplified form of the interface mass conservation equation is equivalent to the standard jump condition for the exchange of mass between two phases of different densities with no accumulation of mass within the interface.

The component terms of the momentum balance per unit macroscale volume are provided in Table II. The source and sink terms for momentum are each composed of two parts, one associated with mass exchange and a second due to surface stress effects between adjacent regions due to pressures, tensions, and the macroscale accounting for microscale viscous effects. The sum of the source terms over all regions of the macroscale volume is equal to the sum of the sink terms over all

Table I. Conservation of mass

$$M^i = \frac{D^i \mathcal{M}^i}{Dt} + \mathcal{M}^i \mathbf{d}^i : \mathbf{I} + \mathcal{M}^i_{\text{sink}} - \mathcal{M}^i_{\text{source}} = 0$$

Region	i	$\mathcal{M}^i$	$\mathcal{M}^i_{\text{sink}} - \mathcal{M}^i_{\text{source}} = 0$
w-phase	w	$\varepsilon^w \rho^w$	$-\hat{e}^w_{wn} - \hat{e}^w_{ws}$
n-phase	n	$\varepsilon^n \rho^n$	$-\hat{e}^n_{wn} - \hat{e}^n_{ns}$
s-phase	s	$\varepsilon^s \rho^s$	$-\hat{e}^s_{ws} - \hat{e}^s_{ns}$
wn-interface	wn	$a^{wn} \rho^{wn}$	$\hat{e}^w_{wn} + \hat{e}^n_{wn} - \hat{e}^{wn}_{wns}$
ws-interface	ws	$a^{ws} \rho^{ws}$	$\hat{e}^w_{ws} + \hat{e}^s_{ws} - \hat{e}^{ws}_{wns}$
ns-interface	ns	$a^{ns} \rho^{ns}$	$\hat{e}^n_{ns} + \hat{e}^s_{ns} - \hat{e}^{ns}_{wns}$
wns-line	wns	$l^{wns} \rho^{wns}$	$\hat{e}^{wn}_{wns} + \hat{e}^{ws}_{wns} + \hat{e}^{ns}_{wns}$

regions as momentum is not created within the volume. When the interfaces and common lines are massless, the surviving terms in the interface momentum equation express the macroscale forms of the standard jump conditions for momentum exchange between phases. If microscale interfacial and lineal tensions are zero, it can be shown that the stress tensors $\mathcal{J}^i$ for the interfaces and common lines will be zero.

The energy balance terms appear in Table III. The equations provide the balances of total energy (internal plus kinetic plus potential) for each region per macroscale volume. The source and sink terms appearing in the last column sum over all regions to zero. Because of the possibility of considering massless interfaces and common lines, the internal energy is expressed directly on a per volume basis. If the interface is massless, the kinetic and potential energy terms will be zero. Also, for the case of a massless interface, the interface momentum equations reduce to the standard jump conditions between phases. The massless common line energy equation expresses the jump condition for energy among the interfaces that meet at the common line.

The entropy inequalities for the phase, interface, and common line regions are given in Table IV. The entropy is expressed per unit of system volume in each equation. Note that although the source and sink terms, accounting for exchanges among the regions, cancel when summed over all phases and interfaces, the sum of the generation term survives. This sum must be non-negative for the entropy inequality to be satisfied. This condition serves to help guide the development of the constitutive forms needed to close the problem.

Tables I through 3 provide five macroscale conservation equations for each of the seven phase 'regions' that may be solved for 35 primary dependent variables: density, velocity (displacement for the solid phase), and temperature. These variables may be listed as:

Table II. Conservation of momentum

$$\mathbf{P}^i = \frac{D^i(\mathcal{M}^i\mathbf{v}^i)}{Dt} + \mathcal{M}^i\mathbf{v}^i\mathbf{d}^i : \mathbf{I} - \nabla \bullet \mathcal{J}^i + \mathcal{M}^i\nabla\Phi^i + \mathbf{P}^i_{\text{sink}} - \mathbf{P}^i_{\text{source}} = 0$$

Region	i	$\mathcal{M}^i$	$\mathcal{J}^1$	$\mathbf{P}^i_{\text{sink}} - \mathbf{P}^i_{\text{source}}$
w-phase	w	$\varepsilon^w\rho^w$	$\varepsilon^w\mathbf{t}^w$	$-\hat{e}^w_{wn}\mathbf{v}^w - \hat{\mathbf{T}}^w_{wn}$ $-\hat{e}^w_{ws}\mathbf{v}^w - \hat{\mathbf{T}}^w_{ws}$
n-phase	n	$\varepsilon^n\rho^n$	$\varepsilon^n\mathbf{t}^n$	$-\hat{e}^n_{wn}\mathbf{v}^n - \hat{T}^n_{wn}$ $-\hat{e}^n_{ns}\mathbf{v}^n - \hat{\mathbf{T}}^n_{ns}$
s-phase	s	$\varepsilon^s\rho^s$	$\varepsilon^s\mathbf{t}^s$	$-\hat{e}^s_{ws}\mathbf{v}^s - \hat{\mathbf{T}}^s_{ws}$ $-\hat{e}^s_{ns}\mathbf{v}^s - \hat{\mathbf{T}}^s_{ns}$
wn-interface	wn	$a^{wn}\rho^{wn}$	$a^{wn}\mathbf{t}^{wn}$	$\hat{e}^w_{wn}\mathbf{v}^w + \hat{\mathbf{T}}^w_{wn} + \hat{e}^n_{wn}\mathbf{v}^n + \hat{\mathbf{T}}^n_{wn}$ $-\hat{e}^{wn}_{wns}\mathbf{v}^{wn} - \hat{\mathbf{T}}^{wn}_{wns}$
ws-interface	ws	$a^{ws}\rho^{ws}$	$a^{ws}\mathbf{t}^{ws}$	$\hat{e}^w_{ws}\mathbf{v}^w + \hat{\mathbf{T}}^w_{ws} + \hat{e}^s_{ws}\mathbf{v}^s + \hat{\mathbf{T}}^s_{ws}$ $-\hat{e}^{ws}_{wns}\mathbf{v}^{ws} - \hat{\mathbf{T}}^{ws}_{wns}$
ns-interface	ns	$a^{ns}\rho^{ns}$	$a^{ns}\mathbf{t}^{ns}$	$\hat{e}^n_{ns}\mathbf{v}^n + \hat{\mathbf{T}}^n_{ns} + \hat{e}^s_{ns}\mathbf{v}^s + \hat{\mathbf{T}}^s_{ns}$ $-\hat{e}^{ns}_{wns}\mathbf{v}^{ns} - \hat{\mathbf{T}}^{ns}_{wns}$
wns-line	wns	$l^{wns}\rho^{wns}$	$l^{wns}\mathbf{t}^{wns}$	$\hat{e}^{wn}_{wns}\mathbf{v}^{wn} + \hat{\mathbf{T}}^{wn}_{wns} + \hat{e}^{ws}_{wns}\mathbf{v}^{ws} + \hat{\mathbf{T}}^{ws}_{wns}$ $+\hat{e}^{ns}_{wns}\mathbf{v}^{ns} + \hat{\mathbf{T}}^{ns}_{wns}$

$$\rho^i, \mathbf{v}^i, \theta^i, \rho^s, \mathbf{F}^s, \theta^s \quad \text{where } i = w, n, wn, ws, ns, wns. \tag{1}$$

In addition, the macroscale equations also contain seven primary geometric variables that do not occur in the corresponding microscale problem. These variables are geometric in nature and include the volume fraction of each phase, the specific areas per unit bulk volume of the interfaces, and the specific length per unit bulk volume of the common lines. These variables are listed as:

$$\epsilon^w, \epsilon^n, \epsilon^s, a^{wn}, a^{ws}, a^{ns}, l^{wns}. \tag{2}$$

They should be recognized as spatially and temporally variable quantities that evolve with changing system conditions. To solve the conservation equations, additional information is needed concerning the inter-relation of these seven variables and their relation to changes of the primary variables. Ideally, seven dynamic geometric evolutionary equations for these quantities would be specified which would

Table III. Conservation of energy

$$E^i = \frac{D^i \left\{ \hat{E}^i + \mathcal{M}^i \left[\frac{(v^i)^2}{2} + \Phi^i \right] \right\}}{Dt} + \left\{ \hat{E}^i + \mathcal{M}^i \left[\frac{(v^i)^2}{2} + \Phi^i \right] \right\} \mathbf{d}^i : \mathbf{I} - \nabla \bullet \mathcal{F}^i - \mathcal{M}^i \mathcal{H}^i + E^i_{\text{sink}} - E^i_{\text{source}} = 0$$

Region	i	$\mathcal{M}^i$	$\mathcal{F}^i$	$\mathcal{H}^i$	$E^i_{\text{sink}} - E^i_{\text{source}}$
w-phase	w	$\varepsilon^w \rho^w$	$\varepsilon^w (\mathbf{t}^w \bullet \mathbf{v}^w + \mathbf{q}^w)$	$h^w + \dfrac{\partial \Phi^w}{\partial t}$	$-\dfrac{(\hat{e}^w_{wn} + \hat{e}^w_{ws}) E^w_T}{\varepsilon^w \rho^w} - (\hat{\mathbf{T}}^w_{wn} + \hat{\mathbf{T}}^w_{ws}) \bullet \mathbf{v}^w - \hat{Q}^w_{wn} - \hat{Q}^w_{ws}$
n-phase	n	$\varepsilon^n \rho^n$	$\varepsilon^n (\mathbf{t}^n \bullet \mathbf{v}^n + \mathbf{q}^n)$	$h^n + \dfrac{\partial \Phi^n}{\partial t}$	$-\dfrac{(\hat{e}^n_{wn} + \hat{e}^n_{ns}) E^n_T}{\varepsilon^n \rho^n} - (\hat{\mathbf{T}}^n_{wn} + \hat{\mathbf{T}}^n_{ns}) \bullet \mathbf{v}^n - \hat{Q}^n_{wn} - \hat{Q}^n_{ns}$
s-phase	s	$\varepsilon^s \rho^s$	$\varepsilon^s (\mathbf{t}^s \bullet \mathbf{v}^s + \mathbf{q}^s)$	$h^s + \dfrac{\partial \Phi^s}{\partial t}$	$-\dfrac{(\hat{e}^s_{ws} + \hat{e}^s_{ns}) E^s_T}{\varepsilon^s \rho^s} - (\hat{\mathbf{T}}^s_{ws} + \hat{\mathbf{T}}^s_{ns}) \bullet \mathbf{v}^s - \hat{Q}^s_{ws} - \hat{Q}^s_{ns}$
wn-interface	wn	$a^{wn} \rho^{wn}$	$a^{wn} (\mathbf{t}^{wn} \bullet \mathbf{v}^{wn} + \mathbf{q}^{wn})$	$h^{wn} + \dfrac{\partial \Phi^{wn}}{\partial t}$	$\dfrac{\hat{e}^w_{wn} E^w_T}{\varepsilon^w \rho^w} + \dfrac{\hat{e}^n_{wn} E^n_T}{\varepsilon^n \rho^n} + \hat{\mathbf{T}}^w_{wn} \bullet \mathbf{v}^w + \hat{\mathbf{T}}^n_{wn} \bullet \mathbf{v}^n +$ $+ \hat{Q}^w_{wn} + \hat{Q}^n_{wn} - \dfrac{\hat{e}^{wn}_{wns} E^{wn}_T}{a^{wn} \rho^{wn}} - \hat{\mathbf{T}}^{wn}_{wns} \bullet \mathbf{v}^{wn} - \hat{Q}^{wn}_{wns}$
ws-interface	ws	$a^{ws} \rho^{ws}$	$a^{ws} (\mathbf{t}^{ws} \bullet \mathbf{v}^{ws} + \mathbf{q}^{ws})$	$h^{ws} + \dfrac{\partial \Phi^{ws}}{\partial t}$	$\dfrac{\hat{e}^w_{ws} E^w_T}{\varepsilon^w \rho^w} + \dfrac{\hat{e}^s_{ws} E^s_T}{\varepsilon^s \rho^s} + \hat{\mathbf{T}}^w_{ws} \bullet \mathbf{v}^w + \hat{\mathbf{T}}^s_{ws} \bullet \mathbf{v}^s +$ $+ \hat{Q}^w_{ws} + \hat{Q}^s_{ws} - \dfrac{\hat{e}^{ws}_{wns} E^{ws}_T}{a^{ws} \rho^{ws}} - \hat{\mathbf{T}}^{ws}_{wns} \bullet \mathbf{v}^{ws} - \hat{Q}^{ws}_{wns}$

Table III. (*continued*)

Region	i	$\mathcal{M}^i$	$\mathcal{F}^i$	$\mathcal{H}^i$	$E^i_{\text{sink}} - E^i_{\text{source}}$
ns-interface	ns	$a^{ns}\rho^{ns}$	$a^{ns}(\mathbf{t}^{ns}\bullet\mathbf{v}^{ns}+\mathbf{q}^{ns})$	$h^{ns}+\dfrac{\partial\Phi^{ns}}{\partial t}$	$\dfrac{\hat{e}^n_{ns}E^n_T}{\varepsilon^n\rho^n}+\dfrac{\hat{e}^s_{ns}E^s_T}{\varepsilon^s\rho^s}+\hat{\mathbf{T}}^n_{ns}\bullet\mathbf{v}^n+\hat{\mathbf{T}}^s_{ns}\bullet\mathbf{v}^s+\hat{Q}^n_{ns}+$
					$+\hat{Q}^s_{ns}-\dfrac{\hat{e}^{ns}_{wns}E^{ns}_T}{a^{ns}\rho^{ns}}-\hat{\mathbf{T}}^{ns}_{wns}\bullet\mathbf{v}^{ns}-\hat{Q}^{ns}_{wns}$
wns-line	wns	$l^{wns}\rho^{wns}$	$l^{wns}(\mathbf{t}^{wns}\bullet\mathbf{v}^{wns}+\mathbf{q}^{wns})$	$h^{wns}+\dfrac{\partial\Phi^{wns}}{\partial t}$	$\dfrac{\hat{e}^{wn}_{wns}E^{wn}_T}{a^{wn}\rho^{wn}}+\dfrac{\hat{e}^{ws}_{wns}E^{ws}_T}{a^{ws}\rho^{ws}}+\dfrac{\hat{e}^{ns}_{wns}E^{ns}_T}{a^{ns}\rho^{ns}}+\hat{\mathbf{T}}^{wn}_{wns}\bullet\mathbf{v}^{wn}$
					$+\hat{\mathbf{T}}^{ws}_{wns}\bullet\mathbf{v}^{ws}+\hat{\mathbf{T}}^{ns}_{wns}\bullet\mathbf{v}^{ns}+\hat{Q}^{wn}_{wns}+\hat{Q}^{ws}_{wns}+\hat{Q}^{ns}_{wns}$

$$E^i_T=\hat{E}^i+\mathcal{M}^i\left[\frac{(v^i)^2}{2}+\Phi^i\right].$$

Table IV. Entropy inequality

$$R^i_{\text{generation}} = \frac{D^i \hat{\eta}^i}{Dt} + \hat{\eta}^i \mathbf{d}^i : \mathbf{I} - \nabla \bullet \mathcal{B}^i - \mathcal{M}^i b^i + \eta^i_{\text{sink}} - \eta^i_{\text{source}} \geqslant 0$$

Region	i	$\mathcal{M}^i$	$\mathcal{B}^i$	$\eta^i_{\text{sink}} - \eta^i_{\text{source}}$	$R^i_{\text{generation}}$
w-phase	w	$\varepsilon^w \rho^w$	$\varepsilon^w \varphi^w$	$-\hat{e}^w_{wn}\hat{\eta}^w/\mathcal{M}^w - \hat{\Phi}^w_{wn}$ $-\hat{e}^w_{ws}\hat{\eta}^w/\mathcal{M}^w - \hat{\Phi}^w_{ws}$	$\varepsilon^w \Lambda^w$
n-phase	n	$\varepsilon^n \rho^n$	$\varepsilon^n \varphi^n$	$-\hat{e}^n_{wn}\hat{\eta}^n/\mathcal{M}^n - \hat{\Phi}^w_{wn}$ $-\hat{e}^n_{ns}\hat{\eta}^n/\mathcal{M}^n - \hat{\Phi}^n_{ns}$	$\varepsilon^n \Lambda^n$
s-phase	s	$\varepsilon^s \rho^s$	$\varepsilon^s \varphi^s$	$-\hat{e}^s_{ws}\hat{\eta}^s/\mathcal{M}^s - \hat{\Phi}^s_{ws}$ $-\hat{e}^s_{ns}\hat{\eta}^s/\mathcal{M}^s - \hat{\Phi}^s_{ns}$	$\varepsilon^s \Lambda^s$
wn-interface	wn	$a^{wn}\rho^{wn}$	$a^{wn}\varphi^{wn}$	$\hat{e}^w_{wn}\hat{\eta}^w/\mathcal{M}^w + \hat{\Phi}^w_{wn} + \hat{e}^n_{wn}\hat{\eta}^n/\mathcal{M}^n$ $+\hat{\Phi}^n_{wn} - \dfrac{\hat{e}^{wn}_{wns}\hat{\eta}^{wn}}{\mathcal{M}^{wn}} - \hat{\Phi}^{wn}_{wns}$	$a^{wn}\Lambda^{wn}$
ws-interface	ws	$a^{ws}\rho^{ws}$	$a^{ws}\varphi^{ws}$	$\hat{e}^w_{ws}\hat{\eta}^w/\mathcal{M}^w + \hat{\Phi}^w_{ws} + \hat{e}^s_{ws}\hat{\eta}^s/\mathcal{M}^s$ $+\hat{\Phi}^s_{ws} - \dfrac{\hat{e}^{ws}_{wns}\hat{\eta}^{ws}}{\mathcal{M}^{ws}} - \hat{\Phi}^{ws}_{wns}$	$a^{ws}\Lambda^{ws}$
ns-interface	ns	$a^{ns}\rho^{ns}$	$a^{ns}\varphi^{ns}$	$\hat{e}^n_{ns}\hat{\eta}^n/\mathcal{M}^n + \hat{\Phi}^s_{ns} + \hat{e}^s_{ns}\hat{\eta}^s/\mathcal{M}^s$ $+\hat{\Phi}^s_{ns} - \dfrac{\hat{e}^{ns}_{wns}\hat{\eta}^{ns}}{\mathcal{M}^{ns}} - \hat{\Phi}^{ns}_{wns}$	$a^{ns}\Lambda^{ns}$
wns-line	wns	$l^{wns}\rho^{wns}$	$l^{wns}\varphi^{wns}$	$\dfrac{\hat{e}^{wn}_{wns}\hat{\eta}^{wn}}{\mathcal{M}^{wn}} + \hat{\Phi}^{wn}_{wns} + \dfrac{\hat{e}^{ws}_{wns}\hat{\eta}^{ws}}{\mathcal{M}^{ws}}$ $+\Phi^{ws}_{wns} + \dfrac{\hat{e}^{ns}_{wns}\hat{\eta}^{ns}}{\mathcal{M}^{ns}} + \hat{\Phi}^{ns}_{wns}$	$l^{wns}\Lambda^{wns}$

allow the system to be closed. Unfortunately, only one such equation is available, the requirement that the sum of the volume fractions be 1:

$$\epsilon^w + \epsilon^n + \epsilon^s = 1. \tag{3}$$

The six additional equations needed are much more elusive. Gray (1999) has proposed some forms based on an examination of the averaging theorems in conjunction with the entropy inequality. Here, more less restrictive forms are obtained by considering the conditions of mechanical equilibrium at the macroscale in conjunction with the entropy inequality. However, it must be stressed that these six relationships are evolutionary approximations and are not conservation laws. They are subject to further improvement based on insights derived from numerical and experimental studies in the future.

For application to a particular system, the macroscale conservation equations must be augmented or closed by a series of approximate constitutive equations for the 115 additional variables (such as mass exchange terms, stress tensor, internal energy, etc.) that appear in the equations. These functions must ideally be expressed in terms of the primary dependent and geometric variables and their derivatives in such a way that the forms obtained do not violate the second law of thermodynamics and are consistent with observed physical systems. For example, the stress tensor has been previously shown to be symmetric based on the form of the macroscale angular momentum equation (Hassanizadeh and Gray, 1979) reducing the number of unknown stress components from nine to six for each phase. Note also that although, for example, the heat conduction in an interface will be a two-dimensional vector at the microscale, the fact that an interface does not necessarily have a single orientation within the macroscale region means that interfacial heat conduction is a spatial process viewed from the macroscale. Indeed, all the tensors and vectors that are two-dimensional at the microscale will be three-dimensional at the macroscale. The procedures for obtaining constitutive forms based on the entropy inequality may be found, for example, in Gray and Hassanizadeh (1998).

To obtain the additional expressions needed for evolution of the geometric variables, it is necessary to first set up the second law of thermodynamics for the full system. This is obtained from the entropy inequalities for each of the system regions subject to the constraints of the conservation equations. The development of this constrained entropy inequality is not new to this work, however its exploitation to obtain the closure conditions as a deviation from the thermomechanical equilibrium state is new.

3. The Second Law of Thermodynamics

The second law of thermodynamics is a powerful tool that can be used to guide the development of closure and constitutive relationships for the macroscopic equations of multiphase flow (Hassanizadeh and Gray, 1980; Gray, 1999). It is especially useful in complicated multiphase systems such as that considered here. The starting point is the general statement of the second law, which prescribes that the net rate of production of entropy of a system inside a large system volume $\mathcal{V}$ must be non-negative:

$$\int_{\mathcal{V}} \Lambda \mathrm{d}\mathcal{V} \geqslant 0. \tag{4}$$

The macroscale entropy production per unit volume, Λ, must be non-negative for this inequality to hold for any volume. In terms of the macroscopic quantities employed in our three phase system, this may be written as:

$$\begin{aligned} \Lambda &= \epsilon^w \Lambda^w + \epsilon^n \Lambda^n + \epsilon^s \Lambda^s + a^{wn} \Lambda^{wn} + a^{ws} \Lambda^{ws} + a^{ns} \Lambda^{ns} + l^{wns} \Lambda^{wns} \\ &= \sum_i R^i_{\text{generation}} \geqslant 0. \end{aligned} \tag{5}$$

Every solution to the generally-posed field equations in Tables I–III must be such that inequality (5) is satisfied. Hence, these equations serve as constraints on inequality (5) and need to be imposed or incorporated within it in order to extract useful system insights. This may be accomplished through a rather long substitution process, such as that pursued by Hassanizadeh and Gray (1980) and Gray (1999), or via a conceptually simpler approach first suggested by Liu (1972). In Liu's technique, Equation (5) is modified through the addition of a linear combination of the balance equations appearing in Tables I–III,

$$\Lambda = \sum_i R^i_{\text{generation}} + \lambda^i_{\text{M}} M^i + \boldsymbol{\lambda}^i_{\text{P}} \bullet \mathbf{P}^i + \lambda^i_{\text{E}} E^i \geqslant 0, \tag{6}$$

where λ^i_{M}, $\boldsymbol{\lambda}^i_{\text{P}}$, and λ^i_{E} are arbitrary parameters. Since all the terms added to the entropy inequality are zero, the calculated rate of entropy generation is unchanged by this modification. However, the new version can be rearranged in terms of like quantities that appear throughout the balance equations and used to identify particular non-zero values of λ^i_{M}, $\boldsymbol{\lambda}^i_{\text{P}}$, and λ^i_{E} that strategically simplify the resulting relationship.

The uniform extensive (or integrated) energy for each phase, interface, and common line lying within a macroscopic volume $\mathcal{V}$ is postulated to be a function of the extensive variables of the system, namely its integrated entropy, mass, volume, interfacial area, common line length, etc. To allow for gradients in the energy that may exist, energy density is obtained as a function of the densities of the independent variables. Additionally, the first order homogeneous property of the thermodynamic functions (Callen, 1985; Bailyn, 1994) is exploited to obtain the explicit form of the energy density. The energy of each system component is written as depending explicitly on, at least, the entropy of that component, the mass of the component, and the geometric extent (volume, area, or length) of that component as:

$$\hat{E}^\alpha(\hat{\eta}^\alpha, \epsilon^\alpha \rho^\alpha, \epsilon^\alpha, \ldots) = \hat{\eta}^\alpha \theta^\alpha + \epsilon^\alpha \rho^\alpha \mu^\alpha - \epsilon^\alpha p^\alpha + \ldots, \qquad \alpha = w, n, \tag{7a}$$

$$\hat{E}^s(\hat{\eta}^s, \epsilon^s \rho^s, \epsilon^s_0 \mathbf{E}^s, \ldots) = \hat{\eta}^s \theta^s + \epsilon^s \rho^s \mu^s - \epsilon^s \boldsymbol{\sigma}^s : \mathbf{E}^s + \ldots, \tag{7b}$$

$$\hat{E}^{\alpha\beta}(\hat{\eta}^{\alpha\beta}, a^{\alpha\beta} \rho^{\alpha\beta}, a^{\alpha\beta}, \ldots) = \hat{\eta}^{\alpha\beta} \theta^{\alpha\beta} + a^{\alpha\beta} \rho^{\alpha\beta} \mu^{\alpha\beta} + a^{\alpha\beta} \gamma^{\alpha\beta} + \ldots, \quad \alpha\beta = wn, ws, ns, \tag{7c}$$

$$\hat{E}^{wns}(\hat{\eta}^{wns}, l^{wns} \rho^{wns}, l^{wns}, \ldots) = \hat{\eta}^{wns} \theta^{wns} + l^{wns} \rho^{wns} \mu^{wns} - l^{wns} \gamma^{wns} + \ldots. \tag{7d}$$

The inclusion of interfacial areas and common line lengths as independent variables in these expressions are critically important for the thermodynamic description of the macroscale state (Gray, 1999). As indicated by the ellipses, additional

independent variables could be included at this stage (as in Gray (1999)) that would allow for other particular effects to be considered. To treat film flow, for example, this might entail allowing the interfacial or contact line energies ($\hat{E}^{\alpha\beta}$ or $\hat{E}^{wns}$) to be functions of the neighboring phase volumes (ϵ^{α} and ϵ^{β}). However, in the development that follows, only the explicit dependences shown in Equations (7a) through (7d) will be retained and incorporated.

Before proceeding further, it is useful to recast the internal energy densities that appear in Equation (6) into grand canonical potential (GCP) functions using the Lagrange transformation (Callen, 1985). In essence, this transformation provides an energy potential (the GCP) that depends on chemical potentials and temperature in place of an energy potential (the internal energy) that depends on mass and entropy per volume. This change of independent variables is not required for this analysis but is convenient in anticipation the form of the final set of equations. A Lagrange transformation on the entropy per unit volume and the mass per unit volume can be made to obtain the GCP functions per unit volume for each phase, designated here as $\hat{\Omega}^{i}$. The results of the transformation are:

$$-\epsilon^{\alpha} P^{\alpha} = \hat{\Omega}^{\alpha}(\theta^{\alpha}, \mu^{\alpha}, \epsilon^{\alpha}, \ldots) = \hat{E}^{\alpha} - \hat{\eta}^{\alpha}\theta^{\alpha} - \epsilon^{\alpha}\rho^{\alpha}\mu^{\alpha}, \quad \alpha = w, n \tag{8a}$$

$$-\epsilon^{s}\mathbf{\Sigma}^{s}{:}\mathbf{E}^{s} = -\epsilon^{s} P^{s} = \hat{\Omega}^{s}(\hat{\theta}^{s}, \mu^{s}, \epsilon_{0}^{s}\mathbf{E}^{s}, \ldots) = \hat{E}^{s} - \hat{\eta}^{s}\theta^{s} - \epsilon^{s}\rho^{s}\mu^{s}, \tag{8b}$$

$$a^{\alpha\beta}\Gamma^{\alpha\beta} = \hat{\Omega}^{\alpha\beta}(\theta^{\alpha\beta}, \mu^{\alpha\beta}, a^{\alpha\beta}, \ldots) = \hat{E}^{\alpha\beta} - \hat{\eta}^{\alpha\beta}\theta^{\alpha\beta} - a^{\alpha\beta}\rho^{\alpha\beta}\mu^{\alpha\beta}, \quad \alpha\beta = wn, ws, ns \tag{8c}$$

$$\begin{aligned} -l^{wns}\Gamma^{wns} &= \hat{\Omega}^{wns}(\theta^{wns}, \mu^{wns}, l^{wns}, \ldots) \\ &= \hat{E}^{wns} - \hat{\eta}^{wns}\theta^{wns} - l^{wns}\rho^{wns}\mu^{wns}. \end{aligned} \tag{8d}$$

The GCPs have units of energy per volume (or force per unit area) and allow the various phase pressure variables to be formally introduced. The capitalized terms on the left side of these equations are used to represent the intrinsic GCPs. For example, P^{α} in Equation (8a) is the GCP of the α phase per unit volume of α phase, while $\Gamma^{\alpha\beta}$ in Equation (8c) is the GCP of the $\alpha\beta$ interface per unit area of $\alpha\beta$ interface. The use of a capitalized letters for these terms refers to their most general functional representation. They are equivalent to their lower case counterparts (e.g. p^{α}, $\gamma^{\alpha\beta}$, or γ^{wns}), appearing on the right sides of (7a) through (7d) when the energy specifically, and only, depends on the particular variables listed.

The macroscopic balance laws shown in Tables I–III are now substituted into the pointwise entropy inequality (6). The GCP functions ($\hat{\Omega}^{i}$) are used in place of the internal energies ($\hat{E}^{i}$). As a shorthand notation to help reveal the structure of the full entropy inequality, the geometric densities are given a general notation such that

$$\chi^{\alpha} = \epsilon^{\alpha}, \quad \chi^{\alpha\beta} = a^{\alpha\beta} \quad \text{and} \quad \chi^{wns} = l^{wns}. \tag{9}$$

We also utilize the Gibbs–Duhem equation

$$0 = -\chi^i \, \mathrm{d}p^i + \hat{\eta}^i \, \mathrm{d}\theta^i + \chi^i \rho^i \, \mathrm{d}\mu^i, \tag{10}$$

for further simplification, yielding

$$\begin{aligned}
\Lambda \;=\; \sum_i \Bigg\{ & \left[\frac{D^i \hat{\eta}^i}{Dt} + \hat{\eta}^i \mathbf{d}^i : \mathbf{I} \right] \times \\
& \times (1 + \lambda_{\mathrm{E}}^i \theta^i) - \nabla \bullet (\chi^i \boldsymbol{\varphi}^i) - \chi^i \rho^i b^i - (\hat{\eta}^i_{\mathrm{source}} - \hat{\eta}^i_{\mathrm{sink}}) + \\
& + \left[\frac{D^i (\chi^i \rho^i)}{Dt} + \chi^i \rho^i \mathbf{d}^i : \mathbf{I} \right] \left[\lambda_{\mathrm{M}}^i + \boldsymbol{\lambda}_{\mathrm{P}}^i \bullet \mathbf{v}^i + \lambda_{\mathrm{E}}^i \left(\mu^i \frac{(v^i)^2}{2} + \Phi^i \right) \right] - \\
& - (\mathcal{M}^i_{\mathrm{source}} - \mathcal{M}^i_{\mathrm{sink}}) \lambda_{\mathrm{M}}^i + \\
& + \left[\chi^i \rho^i \left(\frac{D^i \mathbf{v}^i}{Dt} + \nabla \Phi^i \right) - \nabla \bullet (\chi^i \mathbf{t}^i) \right] \bullet (\boldsymbol{\lambda}_{\mathrm{P}}^i + \lambda_{\mathrm{E}}^i \mathbf{v}^i) - \\
& - (\mathbf{P}^i_{\mathrm{source}} - \mathbf{P}^i_{\mathrm{sink}}) \bullet \boldsymbol{\lambda}_{\mathrm{P}}^i + \\
& + \left[\frac{D^i \hat{\Omega}^i}{Dt} \bigg|_{\theta^i, \mu^i} + (\hat{\Omega}^i \mathbf{I} - \chi^i \mathbf{t}^i) : \mathbf{d}^i - \nabla \bullet (\chi^i \mathbf{q}^i) - \chi^i \rho^i h^i - \right. \\
& \left. - (E^i_{\mathrm{source}} - E^i_{\mathrm{sink}}) \right] \lambda_{\mathrm{E}}^i \Bigg\} \geqslant 0,
\end{aligned} \tag{11}$$

where the sum over the index i is such that $i = w, n, s, wn, ws, ns$ and wns. The values of λ_{M}^i, $\boldsymbol{\lambda}_{\mathrm{P}}^i$, and λ_{E}^i are now chosen such that the factors multiplying the time derivatives of entropy, mass density, and velocity in Equation (11) are zero. In the sense of Liu (1972), this step can be motivated by the need for the inequality to be independent of the derivative quantities appearing in these particular terms. Thus,

$$\lambda_{\mathrm{E}}^i = -\frac{1}{\theta^i}, \tag{12a}$$

$$\boldsymbol{\lambda}_{\mathrm{P}}^i = \frac{\mathbf{v}^i}{\theta^i} \tag{12b}$$

and

$$\lambda_{\mathrm{M}}^i = \frac{1}{\theta^i} \left[\mu^i + \Phi^i - \frac{(v^i)^2}{2} \right]. \tag{12c}$$

This results in a modified entropy inequality that is reflective of the balance law constraints. Two additional assumptions are now invoked to provide a simplification that is consistent with many systems found in nature, namely

- The system is considered to be thermodynamically simple (Eringen, 1980) such that, for corresponding superscripts, $h^i = b^i \theta^i$ and $\theta^i \boldsymbol{\varphi}^i = \mathbf{q}^i$; and

- Temperatures in phases, interfaces, and the common line at a point are considered to be equal and will be designated as $\theta = \theta^i$.

In addition, it will be convenient to express all the material derivatives with respect to the solid phase velocity, as the reference velocity, using the equation

$$\frac{D^i}{Dt} = \frac{D^s}{Dt} + \mathbf{v}^{i,s} \bullet \nabla, \tag{13}$$

where $\mathbf{v}^{i,s} = \mathbf{v}^i - \mathbf{v}^s$. With these changes, and upon multiplication by θ, Equation (11) takes the form

$$\begin{aligned}\theta\Lambda \;=\; \sum_i \Bigg\{ & -\left[\frac{D^s\hat{\Omega}^i}{Dt}\bigg|_{\theta,\mu^i} + (\hat{\Omega}^i\mathbf{I} - \chi^i\mathbf{t}^i)\colon \mathbf{d}^i + \mathbf{v}^{i,s} \bullet \nabla\hat{\Omega}^i\Big|_{\theta,\mu^i} \right] + \\ & + \frac{\chi^i\mathbf{q}^i}{\theta} \bullet \nabla\theta + \\ & + \left(\mu^i + \frac{(v^i)^2}{2} + \Phi^i \right) (\mathcal{M}^i_{\text{source}} - \mathcal{M}^i_{\text{sink}}) - \mathbf{v}^i \bullet (\mathbf{P}^i_{\text{source}} - \mathbf{P}^i_{\text{sink}}) \; + \\ & + (E^i_{\text{source}} - E^i_{\text{sink}}) - \theta(\hat{\eta}^i_{\text{source}} - \hat{\eta}^i_{\text{sink}}) \Bigg\} \geqslant 0, \end{aligned} \tag{14}$$

where it is understood that the sum over i represents a sum over the w, n, and s phases, the wn, ws, and ns interfaces, and the wns contact lines.

In general, the solid phase GCP requires additional, special consideration. This is because the deformation of a solid is described differently from the deformation of a fluid, as accounted for by the presence of the mechanical Lagrangian strain tensor in the list of independent variables in Equation (8b). Callen (1985) has noted, however, that the conventional thermodynamic theory, in which the volume is the single mechanical parameter, fully applies to solids. When this approach is followed, a solid phase 'pressure' is obtained. The inclusion of elastic strain then serves to provide additional information about the mechanics of the solid phase pressure. Here, the prime objective is not to obtain information about solid phase mechanics so that, in the interest of simplicity, the solid phase pressure, designated as P^s in Equation (8b) will appear rather than the details of its dependence on strain. Therefore expansion of Equation (14) (where we revert back to the explicit forms of the geometric densities ϵ^α, $a^{\alpha\beta}$, and l^{wns} instead of χ^i) provides:

$$\begin{aligned}\theta\Lambda \;=\; & -\sum_\alpha \left\{ \frac{D^s\hat{\Omega}^\alpha}{Dt}\bigg|_{\theta,\mu^\alpha} + (\hat{\Omega}^\alpha\mathbf{I} - \epsilon^\alpha\mathbf{t}^\alpha)\colon \mathbf{d}^\alpha \right\} - \\ & - \sum_{\alpha\beta} \left\{ \frac{D^s\hat{\Omega}^{\alpha\beta}}{Dt}\bigg|_{\theta,\mu^{\alpha\beta}} + (\hat{\Omega}^{\alpha\beta}\mathbf{I} - a^{\alpha\beta}\mathbf{t}^{\alpha\beta})\colon \mathbf{d}^{\alpha\beta} \right\} - \end{aligned}$$

$$
\begin{aligned}
&- \left\{ \left. \frac{D^s \hat{\Omega}^{wns}}{Dt} \right|_{\theta,\mu^{wns}} + (\hat{\Omega}^{wns}\mathbf{I} - l^{wns}\mathbf{t}^{wns}) : \mathbf{d}^{wns} \right\} + \\
&+ \left\{ \sum_{\alpha} \frac{\epsilon^{\alpha}\mathbf{q}^{\alpha}}{\theta} + \sum_{\alpha\beta} \frac{a^{\alpha\beta}\mathbf{q}^{\alpha\beta}}{\theta} + \frac{l^{wns}\mathbf{q}^{wns}}{\theta} \right\} \bullet \nabla\theta + \\
&+ \sum_{\alpha\beta} \sum_{i=\alpha,\beta} (\mu^{\alpha\beta} - \mu^{i})\hat{e}^{i}_{\alpha\beta} + \sum_{\alpha\beta=wn,ws,ns} (\mu^{wns} - \mu^{\alpha\beta})\hat{e}^{\alpha\beta}_{wns} - \\
&- \sum_{\alpha=w,n} \mathbf{v}^{\alpha,s} \bullet \left\{ \nabla \left. \hat{\Omega}^{\alpha} \right|_{\theta,\mu^{\alpha}} + \sum_{\beta\neq\alpha} \left(\hat{\mathbf{T}}^{\alpha}_{\alpha\beta} + \frac{\mathbf{v}^{\alpha,\alpha\beta}}{2}\hat{e}^{\alpha}_{\alpha\beta} \right) \right\} - \\
&- \sum_{\alpha\beta} \mathbf{v}^{\alpha\beta,s} \bullet \left\{ \nabla \left. \hat{\Omega}^{\alpha\beta} \right|_{\theta,\mu^{\alpha\beta}} + \hat{\mathbf{T}}^{\alpha\beta}_{wns} + \frac{\mathbf{v}^{\alpha\beta,wns}}{2}\hat{e}^{\alpha\beta}_{wns} - \right. \\
&\left. - \sum_{i=\alpha,\beta} \left(\hat{\mathbf{T}}^{i}_{\alpha\beta} + \frac{\mathbf{v}^{i,\alpha\beta}}{2}\hat{e}^{i}_{\alpha\beta} \right) \right\} - \\
&- \mathbf{v}^{wns,s} \bullet \left\{ \nabla \left. \hat{\Omega}^{wns} \right|_{\theta,\mu^{wns}} - \sum_{ij=wn,ws,ns} \left(\hat{\mathbf{T}}^{ij}_{wns} + \frac{\mathbf{v}^{ij,wns}}{2}\hat{e}^{ij}_{wns} \right) \right\} \geqslant 0, \quad (15)
\end{aligned}
$$

where the source terms from Tables I–III have been substituted. This form of the entropy inequality, will be used to study two aspects of the problem of multiphase flow. First, mechanical equilibrium conditions that must exist among some of the constitutive variables may be established. The approach to developing these conditions at the macroscale has been provided in Gray (2000) and the results will be collected in Appendix A. Second, 'near' equilibrium conditions are examined to provide the evolutionary closure conditions useful for modeling dynamic problems. This part of the analysis is new and will be accomplished following a review of the mechanical equilibrium situation.

4. Mechanical Equilibrium Conditions

Continued analysis of the entropy inequality will be aided by insights derived from the conditions of mechanical equilibrium for this system. These conditions represent how infinitesimal changes in geometric variables affect one another when the system is otherwise at thermal and chemical equilibrium. As shown in the next section, they will ultimately be useful in determining thermodynamic equilibrium and dynamic relations between changes in the geometric variables and thermodynamic state of the system.

The mechanical equilibrium conditions are obtained using a variational approach outlined in Appendix A similar to that of Boruvka and Neumann (1977) for microscale constraints and Gray (2000) for macroscale constraints. A principal

result of this analysis is the fact that the following three conditions must hold at equilibrium:

$$p^w - p^n - J^w_{wn}\gamma^{wn} = 0, \tag{16a}$$

$$p^w x^{ws}_s + p^n x^{ns}_s - P^s + \gamma^{ws} J^s_{ws} x^{ws}_s + \gamma^{ns} J^s_{ns} x^{ns}_s + \\ + \frac{l^{wns}}{a^s}(\gamma^{wns}\kappa^{wns}_N - \gamma^{wn}\sin\Phi) = 0, \tag{16b}$$

$$\gamma^{ws} - \gamma^{ns} + \gamma^{wn}\cos\Phi + \gamma^{wns}\kappa^{wns}_G = 0, \tag{16c}$$

where $x^{\alpha s}_s = a^{\alpha s}/a^s$ is the fractional solid phase area and $\overline{\delta}\epsilon$, $\overline{\delta}\epsilon^w$, and $\overline{\delta}x^{ws}_s$ are infinitesimal variations of ϵ, ϵ^w, and x^{ws}_s about otherwise fixed macroscale coordinates. The macroscale curvatures of the interfaces ($J^\alpha_{\alpha\beta}$, J^s) and of the common line (κ^{wns}_G, κ^{wns}_N) as well as the macroscopic measures contact angles (Φ) are defined in Appendix A.

These variables can be considered as secondary, or derivative geometric variables since they are inherently dependent on the geometric configuration of phases and interfaces that is represented by the primary geometric variables (ϵ^w, ϵ^n, a^{wn}, a^{ws}, a^{ns}, and l^{wns}). Thus, in general, relations for the secondary geometric variables must be obtained as state functions of some or all of the primary geometric variables, as necessary and appropriate (e.g. $J^\alpha_{\alpha\beta} = J^\alpha_{\alpha\beta}(\epsilon^\alpha, a^{\alpha\beta}, l^{wns})$). Recall that in the traditional multiphase modeling approach, this same philosophy is followed when the capillary pressure, which is the product of the interfacial tension multiplied by the interfacial curvature, is postulated to be a function of saturation.

5. Expansion of the Entropy Inequality in terms of Independent Variables

Since the GCP depends on time only through its dependence on the independent variables, the time derivatives of the GCP functions in Equation (15) are expanded in terms of the independent variables listed in Equations (8a) through (8d). In this process, several of the resultant terms are purposely collected into forms that are consistent with the structure of the equilibrium conditions of Equations (16a) through (16c). To complete this rearrangement, the curvature and contact angle terms have to be added in and subtracted out, as they do not otherwise appear in the expanded version of Equation (15). This process yields:

$$\theta\Lambda = -\gamma^{wn}\left\{\frac{D^s a^{wn}}{Dt} - J^w_{wn}\frac{D^s\epsilon^w}{Dt} - (\cos\Phi)a^s\frac{D^s x^{ws}_s}{Dt} + \right. \\ \left. + \left[x^{ws}_s J^w_{wn} - (\sin\Phi)\frac{l^{wns}}{a^s} - x^{ws}_s(J^s_{ws} - J^s)(\cos\Phi)\right]\frac{D^s\epsilon}{Dt}\right\} - \\ - (\gamma^{ws}x^{ws}_s + \gamma^{ns}x^{ns}_s)\left[\frac{D^s a^s}{Dt} + J^s\frac{D^s\epsilon}{Dt}\right] +$$

$$
\begin{aligned}
&+\gamma^{wns}\left\{\frac{D^s l^{wns}}{Dt}+\kappa_G^{wns}a^s\frac{D^s x_s^{ws}}{Dt}+\right.\\
&\left.+\left[\kappa_G^{wns}x_s^{ws}(J_{ws}^s-J^s)-\kappa_N^{wns}\frac{l^{wns}}{a^s}\right]\frac{D^s\epsilon}{Dt}\right\}+\\
&+\left[\frac{D^s\epsilon^w}{Dt}-x_s^{ws}\frac{D^s\epsilon}{Dt}\right][p^w-p^n-\gamma^{wn}J_{wn}^w]-\\
&-\frac{D^s\epsilon}{Dt}\left\{-p^w x_s^{ws}-p^n x_s^{ns}+P^s-\gamma^{ws}J_{ws}^s x_s^{ws}-\gamma^{ns}J_{ns}^s x_s^{ns}+\right.\\
&\left.+\frac{l^{wns}}{a^s}[\gamma^{wn}\sin\Phi-\gamma^{wns}\kappa_N^{wns}]\right\}+\\
&+\left[a^s\frac{D^s x_s^{ws}}{Dt}+x_s^{ws}(J_{ws}^s-J^s)\frac{D^s\epsilon}{Dt}\right]\times\\
&\times[-\gamma^{wn}\cos\Phi-\gamma^{ws}+\gamma^{ns}-\gamma^{wns}\kappa_G^{wns}]-\\
&-\sum_\alpha(\hat{\Omega}^\alpha\mathbf{I}-\epsilon^\alpha\mathbf{t}^\alpha):\mathbf{d}^\alpha-\sum_{\alpha\beta}[\hat{\Omega}^{\alpha\beta}\mathbf{I}-a^{\alpha\beta}\mathbf{t}^{\alpha\beta}]:\mathbf{d}^{\alpha\beta}-\\
&-[\hat{\Omega}^{wns}\mathbf{I}-l^{wns}\mathbf{t}^{wns}]:\mathbf{d}^{wns}+\\
&+\left\{\sum_\alpha\frac{\epsilon^\alpha\mathbf{q}^\alpha}{\theta}+\sum_{\alpha\beta}\frac{a^{\alpha\beta}\mathbf{q}^{\alpha\beta}}{\theta}+\frac{l^{wns}\mathbf{q}^{wns}}{\theta}\right\}\bullet\nabla\theta+\\
&+\sum_{\alpha\beta}\sum_{i=\alpha,\beta}[\mu^{\alpha\beta}-\mu^i]\hat{e}_{\alpha\beta}^i+\sum_{\alpha\beta=wn,ws,ns}[\mu^{wns}-\mu^{\alpha\beta}]\hat{e}_{wns}^{\alpha\beta}-\\
&-\sum_{\alpha=w,n}\mathbf{v}^{a,s}\bullet\left\{\nabla\hat{\Omega}^\alpha\big|_{\theta,\mu^\alpha}+\sum_{\beta\neq\alpha}\left(\hat{\mathbf{T}}_{\alpha\beta}^\alpha+\frac{\mathbf{v}^{\alpha,\alpha\beta}}{2}\hat{e}_{\alpha\beta}^\alpha\right)\right\}-\\
&-\sum_{\alpha\beta}\mathbf{v}^{\alpha\beta,s}\bullet\left\{\nabla\hat{\Omega}^{\alpha\beta}\big|_{\theta,\mu^{\alpha\beta}}+\hat{\mathbf{T}}_{wns}^{\alpha\beta}+\frac{\mathbf{v}^{\alpha\beta,wns}}{2}\hat{e}_{wns}^{\alpha\beta}-\right.\\
&\left.-\sum_{i=\alpha,\beta}\left(\hat{\mathbf{T}}_{\alpha\beta}^i+\frac{\mathbf{v}^{i,\alpha\beta}}{2}\hat{e}_{\alpha\beta}^i\right)\right\}-\\
&-\mathbf{v}^{wns,s}\bullet\left\{\nabla\hat{\Omega}^{wns}\big|_{\theta,\mu^{wns-}}\sum_{ij=wn,ws,ns}\left(\hat{\mathbf{T}}_{wns}^{ij}+\frac{\mathbf{v}^{ij,wns}}{2}\hat{e}_{wns}^{ij}\right)\right\}\geqslant 0. \quad (17)
\end{aligned}
$$

Ultimately, the idea in this manipulation is to develop a form appropriate for exploitation. Restrictions and constraints on the form and value of the various constitutive variables, dictated by this expression of the second law, should become apparent.

Since the entropy production rate must be zero at equilibrium, each of the product terms added together in Equation (17) must be zero at equilibrium. To properly exploit the inequality, it is also desirable for each of the individual factors

comprising each product to also be zero at equilibrium. Unfortunately, this is not the case with the current form of (17), as the first factor in each of the first three products do not meet this criterion. To obtain a more manageable form, three approximate evolutionary equations, (52), (60), and (62), have been developed in Appendix B to re-express the second factors in each of these products in terms of other variables that appear elsewhere in the entropy inequality. The evolutionary equations are determined using averaging theory, an examination of the mechanical equilibrium state reviewed in Appendix A, and a linearization around this state for near equilibrium conditions. These particular approximations comprise three of the six dynamic constraint equations needed to close the system as discussed previously in Section 2. They describe changes in geometric variables as the phases, interfaces, and common lines deform. When the approximations in Equations (52), (60), and (62) are substituted into Equation (17), it becomes:

$$
\begin{aligned}
\theta\Lambda \;=\; & \left[\frac{D^s\epsilon^w}{Dt} - x_s^{ws}\frac{D^s\epsilon}{Dt}\right][p^w - p^n - \gamma^{wn}J_{wn}^w] - \\
& - \frac{D^s\epsilon}{Dt}\Bigg\{ - p^w x_s^{ws} - p^n x_s^{ns} + P^s - \gamma^{ws}J_{ws}^s x_s^{ws} - \gamma^{ns}J_{ns}^s x_s^{ns} + \\
& + \frac{l^{wns}}{a^s}[\gamma^{wn}(\sin\Phi) - \gamma^{wns}\kappa_N^{wns}]\Bigg\} + \\
& + \left[a^s\frac{D^s x_s^{ws}}{Dt} + x_s^{ws}(J_{ws}^s - J^s)\frac{D^s\epsilon}{Dt}\right]\times \\
& \times[-\gamma^{wn}(\cos\Phi) - \gamma^{ws} + \gamma^{ns} - \gamma^{wns}\kappa_G^{wns}] - \\
& - \sum_\alpha\{(\hat{\Omega}^\alpha\mathbf{I} - \epsilon^\alpha\mathbf{t}^\alpha)\colon \mathbf{d}^\alpha\} - \\
& - [\hat{\Omega}^{wn}\mathbf{I} - \gamma^{wn}a^{wn}\mathbf{G}^{wn} - a^{wn}\mathbf{t}^{wn}]\colon \mathbf{d}^{wn} - \\
& - \{\hat{\Omega}^{ws}\mathbf{I} - [\gamma^{ws} - x_s^{ns}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \\
& + \gamma^{wns}\kappa_G^{wns})]a^{ws}\mathbf{G}^{ws} - a^{ws}\mathbf{t}^{ws}\}\colon \mathbf{d}^{ws} - \\
& - \{\hat{\Omega}^{ns}\mathbf{I} - [\gamma^{ns} + x_s^{ws}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \\
& + \gamma^{wns}\kappa_G^{wns})]a^{ns}\mathbf{G}^{ns} - a^{ns}\mathbf{t}^{ns}\}\colon \mathbf{d}^{ns} - \\
& - \{[\hat{\Omega}^{wns}\mathbf{I} + \gamma^{wns}l^{wns}\mathbf{G}^{wns} - l^{wns}\mathbf{t}^{wns}]\colon \mathbf{d}^{wns}\} + \\
& + \left\{\sum_\alpha\frac{\epsilon^\alpha\mathbf{q}^\alpha}{\theta} + \sum_{\alpha\beta}\frac{a^{\alpha\beta}\mathbf{q}^{\alpha\beta}}{\theta} + \frac{l^{wns}\mathbf{q}^{wns}}{\theta}\right\}\bullet\nabla\theta + \\
& + \sum_{\alpha\beta}\left\{\sum_{i=\alpha,\beta}[\mu^{\alpha\beta} - \mu^i]\hat{e}_{\alpha\beta}^i\right\} + \sum_{\alpha\beta=wn,ws,ns}[\mu^{wns} - \mu^{\alpha\beta}]\hat{e}_{wns}^{\alpha\beta} - \\
& - \sum_{\alpha=w,n}\mathbf{v}^{\alpha,s}\bullet\left\{\nabla\hat{\Omega}^\alpha\big|_{\theta,\mu^\alpha} + \sum_{\beta\neq\alpha}\left(\hat{\mathbf{T}}_{\alpha\beta}^\alpha + \frac{\mathbf{v}^{\alpha,\alpha\beta}}{2}\hat{e}_{\alpha\beta}^\alpha\right)\right\} -
\end{aligned}
$$

$$
\begin{aligned}
&- \mathbf{v}^{wn,s} \bullet \left\{ \nabla \hat{\Omega}^{wn} \big|_{\theta,\mu^{wn}} - \gamma^{wn} \nabla \bullet (\mathbf{G}^{wn} a^{wn}) + \hat{\mathbf{T}}^{wn}_{wns} + \right. \\
&+ \frac{\mathbf{v}^{wn,wns}}{2} \hat{e}^{wn}_{wns} - \left. \sum_{i=w,n} \left(\hat{\mathbf{T}}^{i}_{wn} + \frac{\mathbf{v}^{i,wn}}{2} \hat{e}^{i}_{wn} \right) \right\} - \\
&- \mathbf{v}^{ws,s} \bullet \left\{ \nabla \hat{\Omega}^{ws} \big|_{\theta,\mu^{ws}} - [\gamma^{ws} - x^{ns}_{s} (\gamma^{wn} \cos\Phi - \gamma^{ns} + \gamma^{ws} + \right. \\
&+ \gamma^{wns} \kappa^{wns}_{G})] \nabla \bullet (a^{ws} \mathbf{G}^{ws}) + \\
&+ \hat{\mathbf{T}}^{ws}_{wns} + \frac{\mathbf{v}^{ws,wns}}{2} \hat{e}^{ws}_{wns} - \left. \sum_{i=w,s} \left(\hat{\mathbf{T}}^{i}_{ws} + \frac{\mathbf{v}^{i,ws}}{2} \hat{e}^{i}_{ws} \right) \right\} - \\
&- \mathbf{v}^{ns,s} \bullet \left\{ \nabla \hat{\Omega}^{ns} \big|_{\theta,\mu^{ns}} - [\gamma^{ns} + x^{ws}_{s} (\gamma^{wn} \cos\Phi - \gamma^{ns} + \gamma^{ws} + \right. \\
&+ \gamma^{wns} \kappa^{wns}_{G})] \nabla \bullet (a^{ns} \mathbf{G}^{ns}) + \\
&+ \hat{\mathbf{T}}^{ns}_{wns} + \frac{\mathbf{v}^{ns,wns}}{2} \hat{e}^{ns}_{wns} - \left. \left[\sum_{i=n,s} \left(\hat{\mathbf{T}}^{i}_{ns} + \frac{\mathbf{v}^{i,ns}}{2} \hat{e}^{i}_{ns} \right) \right] \right\} - \\
&- \mathbf{v}^{wns,s} \bullet \left\{ \nabla \hat{\Omega}^{wns} \big|_{\theta,\mu^{wns}} + \gamma^{wns} \nabla \bullet [\mathbf{G}^{wns} l^{wns}] - \right. \\
&- \left. \left[\sum_{ij=wn,ws,ns} \left(\hat{\mathbf{T}}^{ij}_{wns} + \frac{\mathbf{v}^{ij,wns}}{2} \hat{e}^{ij}_{wns} \right) \right] \right\} \geqslant 0. \qquad (18)
\end{aligned}
$$

In this new, approximate form, the individual factors comprising each product term of the inequality are now all zero at equilibrium making it possible to obtain additional constitutive information. The independent terms in this inequality must be non-negative to ensure that the entropy inequality is satisfied.

6. Constitutive Equation Insights from the Entropy Inequality

In this section, the form of the inequality in Equation (18) will be exploited to suggest functional forms of several of the constitutive variables introduced in Section 2. By definition, these forms will be consistent with the second law of thermodynamics and the current choice of independent variables. In particular, attention will be focused on the stress tensors $\mathbf{t}^i$ and momentum exchange vectors, $\hat{\mathbf{T}}^{i}_{j}$, that appear in the momentum balance equations, the heat conduction vectors, $\mathbf{q}^i$, that appear in the energy balance equations, and the mass exchange terms, $\hat{e}^{i}_{j}$, that appear in the mass and momentum balance equations.

Consider, first, the various stress tensors $\mathbf{t}^i$ that appear in this analysis. Since the entropy production rate has been assumed independent of the rate of strain tensor (that is, $\mathbf{d}^i$ is not an independent variable), the multipliers appearing in front of $\mathbf{d}^i$ in (18) must always be zero, even when the system is not at equilibrium. Using elements of Equations (8a) through (8d), this suggests that the stress tensors take the following forms:

$$\epsilon^{\alpha}\mathbf{t}^{\alpha} = \hat{\Omega}^{\alpha}\mathbf{I} = -\epsilon^{\alpha} p^{\alpha}\mathbf{I}, \qquad \alpha = w, n, \tag{19a}$$

$$\epsilon^{s}\mathbf{t}^{s} = \hat{\Omega}^{s}\mathbf{I} = -\epsilon^{s} P^{s}\mathbf{I}, \tag{19b}$$

$$a^{wn}\mathbf{t}^{wn} = \hat{\Omega}^{wn}\mathbf{I} - \gamma^{wn} a^{wn}\mathbf{G}^{wn} = \gamma^{wn} a^{wn}(\mathbf{I} - \mathbf{G}^{wn}), \tag{19c}$$

$$\begin{aligned} a^{ws}\mathbf{t}^{ws} &= \hat{\Omega}^{ws}\mathbf{I} - [\gamma^{ws} - x_s^{ns}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \\ &\quad + \gamma^{wns}\kappa_G^{wns})] a^{ws}\mathbf{G}^{ws} \\ &= \gamma^{ws} a^{ws}(\mathbf{I} - \mathbf{G}^{ws}) + [x_s^{ns}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \\ &\quad + \gamma^{wns}\kappa_G^{wns})] a^{ws}\mathbf{G}^{ws} \end{aligned} \tag{19d}$$

$$\begin{aligned} a^{ns}\mathbf{t}^{ns} &= \hat{\Omega}^{ns}\mathbf{I} - [\gamma^{ns} + x_s^{ws}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \gamma^{wns}\kappa_G^{wns})] a^{ns}\mathbf{G}^{ns} \\ &= \gamma^{ns} a^{ns}(\mathbf{I} - \mathbf{G}^{ns}) - [x_s^{ws}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \\ &\quad + \gamma^{wns}\kappa_G^{wns})] a^{ns}\mathbf{G}^{ns}, \end{aligned} \tag{19e}$$

$$l^{wns}\mathbf{t}^{wns} = \hat{\Omega}^{wns}\mathbf{I} + \gamma^{wns} l^{wns}\mathbf{G}^{wns} = -\gamma^{wns} l^{wns}(\mathbf{I} - \mathbf{G}^{wns}). \tag{19f}$$

Now consider the multipliers of the relative velocities that appear in the entropy inequality (18). These terms specifically involve the momentum exchange vectors, $\hat{\mathbf{T}}_j^i$, and mass exchange terms, $\hat{e}_j^i$. As with the velocities, each of these terms is individually zero at equilibrium, but not necessarily zero away from equilibrium. For convenience, these terms have been denoted by the vectors $\boldsymbol{\tau}^i$ which can be reexpressed, for simplicity, using elements of Equations (8a) through (8d):

$$\begin{aligned} \boldsymbol{\tau}^{\alpha} = p^{\alpha}\nabla\epsilon^{\alpha} &- \left(\hat{\mathbf{T}}_{wn}^{\alpha} + \frac{\mathbf{v}^{\alpha,wn}}{2}\hat{e}_{wn}^{\alpha}\right) - \\ &- \left(\hat{\mathbf{T}}_{\alpha s}^{\alpha} + \frac{\mathbf{v}^{\alpha,\alpha s}}{2}\hat{e}_{\alpha s}^{\alpha}\right), \qquad \alpha = w, n \end{aligned} \tag{20a}$$

$$\begin{aligned} \boldsymbol{\tau}^{wn} &= -\gamma^{wn}\nabla \bullet [(\mathbf{I} - \mathbf{G}^{wn}) a^{wn}] - \left(\hat{\mathbf{T}}_{wns}^{wn} + \frac{\mathbf{v}^{wn,wns}}{2}\hat{e}_{wns}^{wn}\right) + \\ &\quad + \sum_{i=w,n}\left(\hat{\mathbf{T}}_{wn}^{i} + \frac{\mathbf{v}^{i,wn}}{2}\hat{e}_{wn}^{i}\right), \end{aligned} \tag{20b}$$

$$\begin{aligned} \boldsymbol{\tau}^{ws} &= -\gamma^{ws}\nabla \bullet [(\mathbf{I} - \mathbf{G}^{ws}) a^{ws}] - \left(\hat{\mathbf{T}}_{wns}^{ws} + \frac{\mathbf{v}^{ws,wns}}{2}\hat{e}_{wns}^{ws}\right) + \\ &\quad + \sum_{i=w,s}\left(\hat{\mathbf{T}}_{ws}^{i} + \frac{\mathbf{v}^{i,ws}}{2}\hat{e}_{ws}^{i}\right) - \\ &\quad - x_s^{ns}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \gamma^{wns}\kappa_G^{wns})\nabla \bullet (a^{ws}\mathbf{G}^{ws}), \end{aligned} \tag{20c}$$

$$\boldsymbol{\tau}^{ns} = -\gamma^{ns}\nabla \bullet [(\mathbf{I} - \mathbf{G}^{ns})a^{ns}] - \left(\hat{\mathbf{T}}^{ns}_{wns} + \frac{\mathbf{v}^{ns,wns}}{2}\hat{e}^{ns}_{wns}\right) + \\ + \sum_{i=n,s}\left(\hat{\mathbf{T}}^{i}_{ns} + \frac{\mathbf{v}^{i,ns}}{2}\hat{e}^{i}_{ns}\right) + \\ + x_s^{ws}(\gamma^{wn}\cos\Phi - \gamma^{ns} + \gamma^{ws} + \gamma^{wns}\kappa_G^{wns})\nabla \bullet (a^{ns}\mathbf{G}^{ns}), \tag{20d}$$

$$\boldsymbol{\tau}^{wns} = \gamma^{wns}\nabla \bullet [(\mathbf{I} - \mathbf{G}^{wns})l^{wns}] + \\ + \sum_{ij=wn,ws,ns}\left(\hat{\mathbf{T}}^{ij}_{wns} + \frac{\mathbf{v}^{ij,wns}}{2}\hat{e}^{ij}_{wns}\right). \tag{20e}$$

In general, these vectors can be considered functions of independent variables that are zero at equilibrium and approximated by a linearization around the equilibrium state. These linearizations may be performed in terms of all equilibrium variables or over a subset considered to be the most dominant. Such a linearization for $\boldsymbol{\tau}^i = \boldsymbol{\tau}^i(\mathbf{v}^{i,s}, \ldots)$ will be considered in the next section.

As a more specific example, consider how the heat conduction vector appearing in inequality (18) can be approximated using this linearization approach. At equilibrium, each element of the term

$$\mathbf{q} = \left[\sum_{\alpha}\epsilon^{\alpha}\mathbf{q}^{\alpha} + \sum_{\alpha\beta}a^{\alpha\beta}\mathbf{q}^{\alpha\beta} + l^{wns}\mathbf{q}^{wns}\right] \bullet \nabla\theta \tag{21}$$

must be zero. Thus, if the simple linearization is employed such that the heat flux $\mathbf{q}$ depends only on $\nabla\theta$, a simple linearization yields

$$\mathbf{q} = \mathbf{K}_{\theta} \bullet \nabla\theta, \tag{22}$$

where $\mathbf{K}_{\theta}$ is a positive definite coefficient tensor and the negative sign is required to maintain a positive contribution to the entropy production away from equilibrium.

A similar approximation of the mass exchange terms assumes $\hat{e}^i_{\alpha\beta} = \hat{e}^i_{\alpha\beta}(\mu^{\alpha\beta} - \mu^i)$ and $\hat{e}^{\alpha\beta}_{wns} = \hat{e}^{\alpha\beta}_{wns}(\mu^{wns} - \mu^{\alpha\beta})$ to obtain

$$\hat{e}^i_{\alpha\beta} = K^i_{\alpha\beta}(\mu^{\alpha\beta} - \mu^i), \qquad \alpha\beta = wn, ws, ns, \qquad i = \alpha, \beta \tag{23a}$$

and

$$\hat{e}^{\alpha\beta}_{wns} = K^{\alpha\beta}_{wns}(\mu^{wns} - \mu^{\alpha\beta}), \qquad \alpha\beta = wn, ws, ns \tag{23b}$$

where $K^i_{\alpha\beta}$ and $K^{\alpha\beta}_{wns}$ are positive coefficients. We note that these terms apply for systems where there is an exchange of phase mass between pure phases (e.g. melting ice), as opposed to the transfer of species mass between phases which is not considered here. Although no mechanism has been included for following the properties of individual species within a phase, addition of the appropriate

equations to the formulation can be made directly, albeit with increased algebraic complexity.

Interestingly, this linearization approach can also be utilized to identify an approximation to the geometric variable terms appearing in the first three terms of the inequality (18). Here, the simplest linearizations approach is used in which the effects if cross-coupling among the different dependent variables is neglected. Thus, linearization of the first term in the inequality provides

$$\frac{D^s\epsilon^w}{Dt} - x_s^{ws}\frac{D^s\epsilon}{Dt} = L_s[p^w - p^n - \gamma^{wn}J_{wn}^w], \tag{24}$$

where L_s is a positive coefficient. Similarly, the second and third terms in Equation (18) linearize to

$$\begin{aligned}\frac{D^s\epsilon}{Dt} \;=\; -L_\epsilon\Bigg\{ &- p^w x_s^{ws} - p^n x_s^{ns} + P^s - \gamma^{ws}J_{ws}^s x_s^{ws} - \gamma^{ns}J_{ns}^s x_s^{ns} + \\ &+ \frac{l^{wns}}{a^s}[\gamma^{wn}\sin\Phi - \gamma^{wns}\kappa_N^{wns}]\Bigg\}\end{aligned} \tag{25}$$

and

$$\begin{aligned}a^s\frac{D^s x_s^{ws}}{Dt} \;+\; x_s^{ws}(J_{ws}^s - J^s)\frac{D^s\epsilon}{Dt} = L_{ws}[&-\gamma^{wn}\cos\Phi - \gamma^{ws} + \\ &+\; \gamma^{ns} - \gamma^{wns}\kappa_G^{wns}],\end{aligned} \tag{26}$$

where L_ϵ and L_{ws} are positive coefficients. Equations (24) through (26) provide three approximate closure equations for the geometric variables that, along with Equations (52), (60), and (62), comprise the six extra conditions needed to fully close the system, as discussed previously in Section 2. Although the results here are similar to previous closure relations developed by Gray (1999), they have been developed here in the context of deviations from thermodynamic equilibrium rather than simply as approximations to mathematical averaging theorems. They are more complete and give rise to the improved approximations to be employed in the mometum equations indicated in constitutive expressions (20a) through (20e).

Notice that Equations (24) through (26) are dynamic equations that independently reproduce the equilibrium relationships suggested by the mechanical equilibrium analysis of Appendix A (and shown as Eqs. (16a)–(16c)). There are two apparent and important implications of Equation (24):

- If the product of the mean macroscale curvature J_{wn}^w and the interfacial tension, γ^{wn} is identified as the capillary pressure, Equation (24) provides the standard equilibrium condition that the capillary pressure is equal to the pressure difference between the fluid phases. Since, from previous discussions and Gray (1999), it is reasonable to postulate that $J_{wn}^w = J_{wn}^w(\epsilon^w, a^{wn})$, then the usual assumption that capillary pressure at equilibrium is only dependent on saturation is not necessarily complete. The actual dependence will have to be determined or verified experimentally.

- Away from equilibrium, under transient, flowing conditions, the capillary pressure is a dynamic function that is not necessarily equal to the phase pressure difference. This has also been suggested by Kalaydjian (1992), who was able to measure a coefficient of proportionality in a simple experiment. Thus, even if J^w_{wn} is a function only of saturation, the difference between its equilibrium and non equilibrium values needs to be carefully distinguished.

Similarly, Equation (25) relates to the dynamic relation among the solid pressure and the fluid pressures and tensions while transients in Equation (26) are indicative of a disequilibrium in the force balance at the common line, commonly referred to as spreading pressure.

7. Closure and Simplification of the Mass and Momentum Equations

As an example, let us consider the closure of the mass and momentum balance equations using the above constitutive relationships. For simplicity, mass exchange processes due to phase change will be ignored such that $\hat{e}^i_{\alpha\beta} = \hat{e}^{\alpha\beta}_{wns} = 0$. This is a reasonable approximation in many instances where the exchange terms are small and also do not influence the momentum transport significantly. Therefore, mass conservation equations for the phases, interfacial areas, and common line follow directly from Table I with no further simplification.

The momentum equations for the fluid phases may be obtained from Table II, Equation (19a) for the stress tensor, Equation (20a) for the momentum exchange between phases, and linearization of $\boldsymbol{\tau}^\alpha$ around the zero-velocity equilibrium state. The form obtained is

$$\frac{D^\alpha(\epsilon^\alpha \rho^\alpha \mathbf{v}^\alpha)}{Dt} + \epsilon^\alpha \rho^\alpha \mathbf{d}^\alpha : \mathbf{I} + \epsilon^\alpha \nabla p^\alpha + \epsilon^\alpha \rho^\alpha \nabla \Phi^\alpha = -\mathbf{R}^\alpha_\alpha \bullet \mathbf{v}^{\alpha,s} - - \mathbf{R}^\alpha_{\alpha s} \bullet \mathbf{v}^{\alpha s,s} - \mathbf{R}^\alpha_{wn} \bullet \mathbf{v}^{wn,s}, \qquad \alpha = w, n. \tag{27}$$

In contrast to the previous linearizations, here some coupling between the α phase and the bounding interfaces is allowed through the tensors $\mathbf{R}^\alpha_{\alpha s}$ and $\mathbf{R}^\alpha_{wn}$. Coupling between the α phase velocity and all other system component velocities could be allowed by including resistance tensors multiplying the other relative velocities on the right side of Equation (27). For simplicity, this is not done here. The tensor $\mathbf{R}^\alpha_\alpha$ is representative of an inverse permeability. It should be noted that the coefficients that arise in the linearization step (as well as in preceding and following linearizations) are functions of the independent variables around which linearizations are not performed. For example, the resistance tensors in Equation (27), are reasonably assumed to be functions of θ, ϵ^α, and $a^{\alpha\beta}$.

Similar manipulations and assumptions can be used to close the momentum equations for the interfaces when linearizations around the equilibrium state for the momentum exchange terms are employed. When interactions of the interfaces with the adjacent phases and common lines are included, the three closed interface

momentum equations are:

$$\begin{aligned}\frac{D^{wn}(a^{wn}\rho^{wn}\mathbf{v}^{wn})}{Dt} &+ a^{wn}\rho^{wn}\mathbf{d}^{wn}:\mathbf{I}-a^{wn}(\mathbf{I}-\mathbf{G}^{wn})\bullet\nabla\gamma^{wn}+\\ &+ a^{wn}\rho^{wn}\nabla\Phi^{wn}=\\ &- \mathbf{R}_{w}^{wn}\bullet\mathbf{v}^{w,s}-\mathbf{R}_{n}^{wn}\bullet\mathbf{v}^{n,s}-\\ &- \mathbf{R}_{wn}^{wn}\bullet\mathbf{v}^{wn,s}-\mathbf{R}_{wns}^{wn}\bullet\mathbf{v}^{wns,s},\end{aligned}\tag{28a}$$

$$\begin{aligned}\frac{D^{ws}(a^{ws}\rho^{ws}\mathbf{v}^{ws})}{Dt} &+ a^{ws}\rho^{ws}\,\mathbf{d}^{ws}:\mathbf{I}-a^{ws}(\mathbf{I}-\mathbf{G}^{ws})\bullet\nabla\gamma^{ws}-\\ &- a^{ws}\mathbf{G}^{ws}\bullet\nabla[x_{s}^{ns}(\gamma^{wn}\cos\Phi-\gamma^{ns}+\\ &+ \gamma^{ws}+\gamma^{wns}\kappa_{G}^{wns})]+a^{ws}\rho^{ws}\nabla\Phi^{ws}\\ &= -\mathbf{R}_{w}^{ws}\bullet\mathbf{v}^{w,s}-\mathbf{R}_{ws}^{ws}\bullet\mathbf{v}^{ws,s}-\mathbf{R}_{wns}^{ws}\bullet\mathbf{v}^{wns,s}\end{aligned}\tag{28b}$$

and

$$\begin{aligned}\frac{D^{ns}(a^{ns}\rho^{ns}\mathbf{v}^{ns})}{Dt} &+ a^{ns}\rho^{ns}\mathbf{d}^{ns}:\,\mathbf{I}-a^{ns}(\mathbf{I}-\mathbf{G}^{ns})\bullet\nabla\gamma^{ns}+\\ &+ a^{ns}\mathbf{G}^{ns}\bullet\nabla[x_{s}^{ws}(\gamma^{wn}\cos\Phi-\gamma^{ns}+\\ &+ \gamma^{ws}+\gamma^{wns}\kappa_{G}^{wns})]+a^{ns}\rho^{ns}\nabla\Phi^{ns}\\ &= -\mathbf{R}_{n}^{ns}\bullet\mathbf{v}^{n,s}-\mathbf{R}_{ns}^{ns}\bullet\mathbf{v}^{ns,s}-\mathbf{R}_{wns}^{ns}\bullet\mathbf{v}^{wns,s}.\end{aligned}\tag{28c}$$

Similar manipulations involving the momentum equation for the common line in Table II yield:

$$\begin{aligned}\frac{D^{wns}(l^{wns}\rho^{wns})}{Dt} &+ l^{wns}\rho^{wns}\mathbf{d}^{wns}:\,\mathbf{I}+l^{wns}(\mathbf{I}-\mathbf{G}^{wns})\bullet\nabla\gamma^{wns}+\\ &+ l^{wns}\rho^{wns}\nabla\Phi^{wns}=\\ &- \mathbf{R}_{wn}^{wns}\bullet\mathbf{v}^{wn,s}-\mathbf{R}_{ws}^{wns}\bullet\mathbf{v}^{ws,s}-\\ &- \mathbf{R}_{ns}^{wns}\bullet\mathbf{v}^{ns,s}-\mathbf{R}_{wns}^{wns}\bullet\mathbf{v}^{wns,s}.\end{aligned}\tag{29}$$

In the momentum equations, the factors $\mathbf{I}-\mathbf{G}^{\alpha\beta}$ and $\mathbf{I}-\mathbf{G}^{wns}$ that are dotted with the gradients of the surface tensions account at the macroscale for the particular orientations that the interfaces and common line have at the microscale. In particular, microscopic gradients in surface tension will drive the flow only in directions tangent to the surface. The orientation factor $\mathbf{G}^{\alpha\beta}$ is equal to $1/3\mathbf{I}$ if there is no preferred orientation of an interface within the averaging volume. It accounts for the fact that flow of interface mass cannot be driven in directions normal to the surface by gradients in the surface tension. Similarly, the orientation factor $\mathbf{G}^{wns}$ is equal to $2/3\mathbf{I}$ if the common line orientation within the averaging volume is random. It accounts for the fact that gradients in the common line tension can only drive flow along the common line and not in directions orthogonal to the line.

For most problems involving multiphase flow in porous, geologic media, additional assumptions may be applied to the momentum equations such as negligible advective terms or negligible coupling of momentum between phases. Under such assumptions, the momentum equations reduce to Darcian forms.

8. Conclusion

A systematic procedure has been presented for obtaining and analyzing the equations describing two-phase flow in a porous medium. The analysis makes use of the conservation equations of mass, momentum, and energy for the phases, interfaces, and common line, averaged so that they are expressed at the macroscale or core scale. As a result of the averaging procedure, a deficit of six equations is created that involves the principal geometric properties or variables of the macroscopic system (i.e. the volume fractions of the phases, area per volume of the interfaces, and the common line length per volume). To overcome this deficit, six new evolutionary equations (or supplementary conditions) were developed to relate these variables and their rates of change to the primary system variables. Three of these Equations, (52), (60), and (62), were obtained by noting the need to eliminate a product from the entropy inequality that contained a non-zero factor and then making use of averaging equations. Three more Equations, (24), (25), and (26), were obtained, in linearized form, from analysis of the equilibrium relations that must exist among the independent thermodynamic variables and from analysis of the dynamic entropy inequality. It must be emphasized that these six supplementary conditions are closure approximations subject to improvement as future insights might allow.

In addition, the current analysis has also introduced a series of secondary geometric factors, such as interfacial curvature and macroscale contact angle, into the equations that must be parameterized in terms of a series of state equations to complete the formulation. These factors are related to the macroscale representation of the microscale curvatures and orientations of the interfaces and common lines. In particular, the orientation tensors appearing in the momentum equations enforce the condition at the macroscale that microscale gradients in surface (lineal) tension can only produce interfacial (lineal) flow in directions tangent to the interface (common line). Thus, at the macroscale where the orientation of individual interfaces must be replaced by information about their average orientation within a core scale volume, this particular geometric factor provides this information.

Within the analysis, it is possible to identify the relative importance of a number of parameters and sequentially simplify the form and dependence the various state equations. This reduces the new equation set to the more traditional set that is currently employed in two-phase flow modeling. Thus, at the very least, the current work provides explicit information about what assumptions are being employed in using the traditional equations of two-phase flow. If those assumptions are deemed to be overly restrictive, the expanded set of equations provided here

provides information on what supporting experimental data is needed to provide a consistent and useful set of equations. Indeed, the current theoretical approach requires continuing experimental support from network modeling efforts (e.g. Lowry and Miller, 1995; Reeves and Celia, 1996), measurements of interfacial area (e.g. Montemagno and Gray, 1995; Schaefer *et al.*, 2000), and lattice Boltzmann simulations (e.g. Hou *et al.*, 1997, Hazlett *et al.*, 1998) so that the mechanisms that influence two phase flow can be properly accounted for.

Appendix A: Derivation of Mechanical Equilibrium Conditions

The mechanical equilibrium conditions are derived from constraining or relating small (or variational) changes in geometric variables to one another. This analysis is performed by examining the variation of the GCP around the equilibrium state, a state for which this potential will be at a minimum. To complete the study, the functional dependence of these potentials must be fully postulated. It has been shown previously (Gray, 2000) that the conditions for macroscale thermodynamic equilibrium are equality of temperature and of chemical potential at a macroscale point. If films are not included in the analysis, the postulated forms of the GCPs will be complete as indicated in Equations (8a) through (8d) with no additional independent variables. To obtain the mechanical equilibrium relations of importance, the variational for the entire system should be examined. The procedure followed is the same as in (Gray, 2000) and will only be outlined here.

The variational expression for mechanical equilibrium is given by

$$-\delta \int_{\mathcal{V}} \hat{\Omega}\big|_{\theta,\mu}\, \mathrm{d}\mathcal{V} =$$
$$-\int_{\mathcal{V}} [\overline{\delta}(\hat{\Omega}^{w} + \hat{\Omega}^{n} + \hat{\Omega}^{s} + \hat{\Omega}^{wn} + \hat{\Omega}^{ws} + \hat{\Omega}^{ns} + \hat{\Omega}^{wns})_{\theta,\mu}]\, \mathrm{d}\mathcal{V} = 0, \quad (30)$$

where $\overline{\delta}$ is a fixed point variation with the macroscale coordinates being held fixed. Postulates (7a) through (7d) are substituted into this expression and the variations in the right side are of the geometric densities. The variations are applied so that the microscopic changes in the positions of interfaces and common lines are around the equilibrium state. Thus, for example, the macroscale variation of a volume fraction is expanded such that it is related to the microscale variation of the position of the surface bounding the phase

$$\overline{\delta}\epsilon^{\alpha} = \sum_{\alpha\beta} \frac{1}{V} \int_{S_{\alpha\beta}} \mathbf{n}^{\alpha}_{\alpha\beta} \bullet \delta\xi\, \mathrm{d}S. \quad (31)$$

Similarly, for example, the variation of the interfacial area between the wetting and non-wetting phases is

$$\overline{\delta}a^{wn} = \frac{1}{V} \int_{S_{wn}} [(\nabla \bullet \mathbf{n}^{w}_{wn})(\mathbf{n}^{w}_{wn} \bullet \delta\xi)]\, \mathrm{d}S + \frac{1}{V} \int_{C_{wns}} \boldsymbol{\nu}^{wn}_{wns} \bullet \delta\xi\, \mathrm{d}C. \quad (32)$$

The geometric relations at the common line among the unit vectors normal to the interfaces, tangent to the interfaces and normal to the common line, and tangent to the common line may be written where the contact angle, the geodesic curvature, and the normal curvature at the common line also appear. These equations allow elimination of some of the unit vectors that appear in variational relations such as Equations (31) and (32).

When the manipulations outlined are employed, Equation (30) can be rearranged to the expression:

$$\begin{aligned}
&\int_{\mathcal{V}} \left\{ (p^w - p^n - J^w_{wn}) \int_{S_{wn}} \mathbf{n}^w_{wn} \bullet \delta\xi \, \mathrm{d}S \right\} \mathrm{d}\mathcal{V} - \\
&- \int_{\mathcal{V}} \left\{ \left[p^w x^{ws}_s + p^n x^{ns}_s - P^s + \gamma^{ws} J^s_{ws} x^{ws}_s + \gamma^{ns} J^s_{ns} x^{ns}_s + \right. \right. \\
&\left. \left. + \frac{l^{wns}}{a^s} (\gamma^{wns} \kappa^{wns}_N - \gamma^{wn} \sin\Phi) \right] \int_{S_s} \mathbf{n}^s \bullet \delta\xi \, \mathrm{d}S \right\} \mathrm{d}\mathcal{V} - \\
&- \int_{\mathcal{V}} \left\{ [\gamma^{ws} - \gamma^{ns} + \gamma^{wn} \cos\Phi + \right. \\
&\left. + \gamma^{wns} \kappa^{wns}_G] \int_{C_{wns}} \delta\xi \bullet \boldsymbol{\nu}^{ws}_{wns} \mathrm{d}C \right\} \mathrm{d}\mathcal{V} = 0,
\end{aligned} \tag{33}$$

where the assumption has been employed that on the solid surface the variations are related according to

$$\begin{aligned}
\frac{1}{x^{ws}_s} \int_{S_{ws}} \delta\xi \bullet \mathbf{n}^s_{ws} \mathrm{d}S &= \frac{1}{x^{ns}_s} \int_{S_{ns}} \delta\xi \bullet \mathbf{n}^s_{ns} \mathrm{d}S \\
&= \frac{a^s}{l^{wns}} \int_{C_{wns}} \delta\xi \bullet \mathbf{n}^s_{wns} \mathrm{d}C = \int_{S_s} \delta\xi \bullet \mathbf{n}^s \mathrm{d}S.
\end{aligned} \tag{34}$$

This is a key assumption that essentially states that the variation on the surface is independent of whether the point of interest is on the ws-interface, the ns-interface, or on the common line. This assumption incorporates the difference between the behavior of an interface involving a solid and one involving a fluid into the analysis and considers a solid surface to have a well-defined normal at every microscopic point. With the variations in the three integrals in Equation (33) being independent, the mechanical equilibrium conditions are:

$$p^w - p^n - J^w_{wn} \gamma^{wn} = 0, \tag{35a}$$

$$\begin{aligned}
p^w x^{ws}_s \;+\; p^n x^{ns}_s + \frac{\hat{\Omega}^s}{\epsilon^s} + \gamma^{ws} J^s_{ws} x^{ws}_s + \gamma^{ns} J^s_{ns} x^{ns}_s + \\
+ \;\; \frac{l^{wns}}{a^s} (\gamma^{wns} \kappa^{wns}_N - \gamma^{wn} \sin\Phi) = 0,
\end{aligned} \tag{35b}$$

and

$$\gamma^{ws} - \gamma^{ns} + \gamma^{wn}\cos\Phi + \gamma^{wns}\kappa_G^{wns} = 0, \tag{35c}$$

where the porosity, ϵ, is given by

$$\epsilon = 1 - \epsilon^s = \epsilon^w + \epsilon^n \tag{36a}$$

the fractional solid phase area is

$$x_s^{\alpha s} = a^{\alpha s}/a^s \tag{36b}$$

and the averaged first curvatures of the interfaces have been introduced with

$$J_{\alpha\beta}^{\alpha} = \frac{1}{S_{\alpha\beta}}\int_{S_{\alpha\beta}} \nabla \bullet \mathbf{n}_{\alpha\beta}^{\alpha}\,\mathrm{d}S \tag{36c}$$

and

$$J^s = x_s^{ws}J_{ws}^s + x_s^{ns}J_{ns}^s. \tag{36d}$$

Also, κ_G^{wns} and κ_N^{wns} are the macroscale geodesic and normal curvatures, respectively, obtained as averages of their microscale counterparts over the common line. Similarly, $\cos\Phi$ and $\sin\Phi$ are actually average values of the cosine and sine of the microscale contact angle, respectively, over the common line.

To proceed with the derivation of the dynamic equations, it is necessary to have more information than the equilibrium conditions. In particular, expressions for the three independent variations, the integrals in Equation (33), must be obtained in terms of the variations of the geometric properties. Algebraic manipulations of the expressions for the variations of the geometric densities leads to the expressions for the integrals. Incorporation of the expressions for independent variations into Equation (33) yields

$$\begin{aligned}
&\int_{\mathcal{V}} \{(p^w - p^n - J_{wn}^w\gamma^{wn})[\overline{\delta}\epsilon^w - x_s^{ws}\overline{\delta}\epsilon]\}\,\mathrm{d}\mathcal{V} + \\
&\quad + \int_{\mathcal{V}} \left\{\left[p^w x_s^{ws} + p^n x_s^{ns} + \frac{\hat{\Omega}^s}{\epsilon^s} + \gamma^{ws}J_{ws}^s x_s^{ws} + \gamma^{ns}J_{ns}^s x_s^{ns} + \right.\right. \\
&\quad \left.\left. + \frac{l^{wns}}{a^s}(\gamma^{wns}\kappa_N^{wns} - \gamma^{wn}\sin\Phi)\right][\overline{\delta}\epsilon]\right\}\mathrm{d}\mathcal{V} - \\
&\quad - \int_{\mathcal{V}} \{[\gamma^{ws} - \gamma^{ns} + \gamma^{wn}\cos\Phi + \gamma^{wns}\kappa_G^{wns}] \times \\
&\quad \times [a^s\overline{\delta}x_s^{ws} + x_s^{ws}(J_{ws}^s - J^s)\overline{\delta}\epsilon]\}\,\mathrm{d}\mathcal{V} = 0.
\end{aligned} \tag{37}$$

It is important to note that this relation holds at equilibrium and that each integrand is composed of three pairs of products whose factors are each zero at equilibrium.

This form suggests a rearrangement that will be used in Equation (15) after expansion of the material derivatives of the GCPs in terms of their respective independent variables.

Appendix B: Derivation of Important Geometrical Constraints

From the variational analysis of the macroscale equilibrium conditions, the equilibrium constraint conditions (35a) through (35c) are developed. When the entropy inequality is then arranged such that these groups of terms appear as coefficients of collections of time derivatives, three additional groups remain as contained in the first three terms on the right side of Equation (17) as follows:

$$\begin{aligned}\theta\Lambda \;=\; & -\gamma^{wn}\left\{\frac{D^s a^{wn}}{Dt} - J^w_{wn}\frac{D^s\epsilon^w}{Dt} - (\cos\Phi)a^s\frac{D^s x^{ws}_s}{Dt} + \right.\\ & \left. + \left[x^{ws}_s J^w_{wn} - (\sin\Phi)\frac{l^{wns}}{a^s} - x^{ws}_s(J^s_{ws} - J^s)(\cos\Phi)\right]\frac{D^s\epsilon}{Dt}\right\} - \\ & - (\gamma^{ws}x^{ws}_s + \gamma^{ns}x^{ns}_s)\left[\frac{D^s a^s}{Dt} + J^s\frac{D^s\epsilon}{Dt}\right] + \\ & + \gamma^{wns}\left\{\frac{D^s l^{wns}}{Dt} + \kappa^{wns}_G a^s\frac{D^s x^{ws}_s}{Dt} + \right.\\ & \left. + \left[\kappa^{wns}_G x^{ws}_s(J^s_{ws} - J^s) - \kappa^{wns}_N\frac{l^{wns}}{a^s}\right]\frac{D^s\epsilon}{Dt}\right\} + \ldots . \end{aligned} \tag{38}$$

The problem with these terms stems from the fact that the entropy inequality needs to be arranged such that it consists of a sum of products in which each factor is zero at equilibrium. However, the first factor in each of these terms is a tension term that is not zero. Therefore some manipulations must be performed that will lead to these terms being combined into the entropy equality. This is done by developing relations for each of the second factors in these products in terms of other variables appearing in the entropy inequality. In other words, expressions for A, B, and C in the following expressions are sought:

$$\frac{D^s a^s}{Dt} + (x^{ws}_s J^s_{ws} + x^{ns}_s J^s_{ns})\frac{D^s\epsilon}{Dt} = A, \tag{39}$$

$$\begin{aligned}\frac{D^s a^{wn}}{Dt} \;-\; & J^w_{wn}\frac{D^s\epsilon^w}{Dt} - (\cos\Phi)a^s\frac{D^s x^{ws}_s}{Dt} + \\ & + \left\{x^{ws}_s J^w_{wn} - (\sin\Phi)\frac{l^{wns}}{a^s} - \right.\\ & \left. - \; x^{ws}_s(J^s_{ws} - J^s)(\cos\Phi)\right\}\frac{D^s\epsilon}{Dt} = B, \end{aligned} \tag{40}$$

and

$$\frac{D^s l^{wns}}{Dt} + \kappa_G^{wns} a^s \frac{D^s x_s^{ws}}{Dt} + \left[\kappa_G^{wns} x_s^{ws} (J_{ws}^s - J^s) - \kappa_N^{wns} \frac{l^{wns}}{a^s} \right] \frac{D^s \epsilon}{Dt} = C, \tag{41}$$

where factors A, B, and C are zero at equilibrium conditions. Definitive determination of these factors away from equilibrium would require the existence of universally applicable evolution equations for the geometric properties. In the absence of these equations, reasonable approximations must be developed. The purpose of this appendix is to outline the path to suitable approximations.

First, an approximation for A in Equation (39) will be developed by obtaining expressions for the two material derivatives that appear in the equation. From Gray *et al.* (1993), the following conditions apply for the porosity:

$$\nabla \epsilon = \frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \mathrm{d}S, \tag{42a}$$

$$\frac{\partial \epsilon}{\partial t} = -\frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \bullet \mathbf{w} \mathrm{d}S. \tag{42b}$$

Take the vector product of Equation (42a) with the macroscale velocity of the solid phase, $\mathbf{v}^s$, and add this to Equation (42b) to obtain

$$\frac{D^s \epsilon}{Dt} = \frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \bullet (\mathbf{v}^s - \mathbf{w}) \, \mathrm{d}S \tag{43}$$

It is important to note that the macroscale velocity, $\mathbf{v}^s$ may be moved inside the integral without error.

The material derivative of the surface area of the solid phase may be obtained based on equations from Gray *et al.* (1993) for the gradient and the time derivative. The forms of these equations for the complete solid surface within the averaging volume, δV, are

$$0 = \nabla a^s - \nabla \bullet \left[\frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \mathbf{n}^s \, \mathrm{d}S \right] + \frac{1}{\delta V} \int_{S_s} (\nabla \bullet \mathbf{n}^s) \mathbf{n}^s \mathrm{d}S \tag{44}$$

and

$$0 = \frac{\partial a^s}{\partial t} + \nabla \bullet \left[\frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \mathbf{n}^s \bullet \mathbf{w} \mathrm{d}S \right] - \frac{1}{\delta V} \int_{S_s} (\nabla \bullet \mathbf{n}^s) \mathbf{n}^s \bullet \mathbf{w} \mathrm{d}S. \tag{45}$$

Now take the vector product of Equation (44) with the solid phase macroscale velocity and add the result to Equation (45) to obtain

$$0 = \frac{D^s a^s}{Dt} - \nabla \bullet \left[\frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \mathbf{n}^s \mathrm{d}S \right] \bullet \mathbf{v}^s + \nabla \bullet \left[\frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \mathbf{n}^s \bullet \mathbf{w} \mathrm{d}S \right] + \frac{1}{\delta V} \int_{S_s} (\nabla \bullet \mathbf{n}^s) \mathbf{n}^s \bullet (\mathbf{v}^s - \mathbf{w}) \, \mathrm{d}S. \tag{46}$$

This equation contains no approximations. However the presence of the normal vectors in the integrals makes these difficult to evaluate exactly. Some approximations will be applied. First, define the geometric orientation tensors

$$\mathbf{G}^{\alpha\beta} = \frac{1}{S_{\alpha\beta}} \int_{S_{\alpha\beta}} \mathbf{n}^{\alpha}_{\alpha\beta} \mathbf{n}^{\alpha}_{\alpha\beta} \mathrm{d}S, \qquad \alpha\beta = wn, ws, ns. \tag{47}$$

These tensors account for the directional dependence of the microscopic interfaces as evidenced at the macroscale. Because they are related to the geometric configuration of phases and interfaces, $\mathbf{G}^{\alpha\beta}$ will be functions of some or all of the primary geometric variables, as appropriate, and must be specified or parameterized as secondary geometric variables in the same way as the curvature variables. Note that for equisized spherical particles uniformly packed, the geometric tensors have the property

$$x_s^{ws}\mathbf{G}^{ws} + x_s^{ns}\mathbf{G}^{ns} = \tfrac{1}{3}\mathbf{I}. \tag{48}$$

For a situation where the solid grains are non-spherical but randomly oriented and the fraction of the surface in contact with each of the fluid phases is also randomly oriented, the geometric factors take the form

$$\mathbf{G}^{ws} = \mathbf{G}^{ns} = \tfrac{1}{3}\mathbf{I}. \tag{49}$$

Next, make the approximation that

$$\frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \mathbf{n}^s \bullet \mathbf{w} \mathrm{d}S = a^{ws}\mathbf{G}^{ws} \bullet \mathbf{v}^{ws} + a^{ns}\mathbf{G}^{ns} \bullet \mathbf{v}^{ns}. \tag{50}$$

Behind this approximation are the assumption that variations in the interfacial density are negligible as are the correlations between the geometric factors and the velocity of the interface. Additionally, assume that the correlation between the interfacial curvature and the velocity of the interface is negligible such that

$$\begin{aligned} &\frac{1}{\delta V} \int_{S_s} (\nabla \bullet \mathbf{n}^s)\mathbf{n}^s \bullet (\mathbf{v}^s - \mathbf{w}) \, \mathrm{d}S \\ &\quad = (x_s^{ws} J_{ws}^s + x_s^{ns} J_{ns}^s) \frac{1}{\delta V} \int_{S_s} \mathbf{n}^s \bullet (\mathbf{v} - \mathbf{w}) \, \mathrm{d}S. \end{aligned} \tag{51}$$

Substitution of Equations (43), (47), (50), and (51) into Equation (46) yields

$$\begin{aligned} \frac{D^s a^s}{Dt} \; + \; (x_s^{ws} J_{ws}^s + x_s^{ns} J_{ns}^s) \frac{D^s \epsilon}{Dt} &= -a^{ws}\mathbf{G}^{ws} \colon \mathbf{d}^{ws} - a^{ns}\mathbf{G}^{ns} \colon \mathbf{d}^{ns} - \\ - \; \nabla \bullet (a^{ws}\mathbf{G}^{ws}) \bullet \mathbf{v}^{ws,s} - \nabla \bullet (a^{ns}\mathbf{G}^{ns}) \bullet \mathbf{v}^{ns,s}. & \end{aligned} \tag{52}$$

Therefore the approximation for A in Equation (39) is.

$$\begin{aligned} A = \; - \; a^{ws}\mathbf{G}^{ws} \colon \mathbf{d}^{ws} - a^{ns}\mathbf{G}^{ns} \colon \mathbf{d}^{ns} - \\ - \; \nabla \bullet (a^{ws}\mathbf{G}^{ws}) \bullet \mathbf{v}^{ws,s} - \nabla \bullet (a^{ns}\mathbf{G}^{ns}) \bullet \mathbf{v}^{ns,s}. \end{aligned} \tag{53}$$

The derivation of B in Equation (40) follows along similar lines. It is a lengthier derivation in that four different material derivatives must be examined. The equations involving partial time derivatives and gradients of the geometric densities in terms of integrals may be found in Gray *et al*. (1993). In addition, the macroscale measures of the sine and cosine of the microscale contact angle are defined according to

$$\cos \Phi = \frac{1}{C_{wns}} \int_{C_{wns}} \cos \varphi \, \mathrm{d}C \tag{54a}$$

and

$$\sin \Phi = \frac{1}{C_{wns}} \int_{C_{wns}} \sin \varphi \, \mathrm{d}C. \tag{54b}$$

Also, a geometric factor for a common line with unit tangent vector $\boldsymbol{\lambda}^{wns}$ is given by

$$\mathbf{G}^{wns} = \frac{1}{C_{wns}} \int_{C_{wns}} (\mathbf{I} - \boldsymbol{\lambda}^{wns} \boldsymbol{\lambda}^{wns}) \, \mathrm{d}C. \tag{55}$$

If the common lines are equisized circles with random orientation within the averaging volume, the common line geometric factor has the value

$$\mathbf{G}^{wns} = \frac{2}{3}\mathbf{I}. \tag{56}$$

The curvature of the common line, κ^{wns} is expressed as

$$\boldsymbol{\lambda}^{wns} \bullet \nabla \boldsymbol{\lambda}^{wns} = \boldsymbol{\kappa}^{wns} = \kappa_n^{wns} \mathbf{n}^s + \kappa_g^{wns} \boldsymbol{\nu}_{wns}^{ws}, \tag{57}$$

where κ_n^{wns} is the normal curvature and κ_g^{wns} is the geodesic curvature. The averaged macroscale curvature components are then defined as

$$\kappa_N^{wns} = \frac{1}{C_{wns}} \int_{C_{wns}} \boldsymbol{\lambda}^{wns} \bullet \nabla \boldsymbol{\lambda}^{wns} \bullet \mathbf{n}^s \, \mathrm{d}C = \frac{1}{C_{wns}} \int_{C_{wns}} \kappa_n^{wns} \mathrm{d}C \tag{58a}$$

and

$$\kappa_G^{wns} = \frac{1}{C_{wns}} \int_{C_{wns}} \boldsymbol{\lambda}^{wns} \bullet \nabla \boldsymbol{\lambda}^{wns} \bullet \boldsymbol{\nu}_{wns}^{ws} \mathrm{d}C = \frac{1}{C_{wns}} \int_{C_{wns}} \kappa_g^{wns} \mathrm{d}C. \tag{58b}$$

An important remaining issue is to determine how to treat the integrals over the fluid-solid interfaces. If any grain expansion within an averaging volume is considered to occur uniformly, then two of the surface and common line integrals that arise may be approximated as

$$\frac{1}{\delta V} \int_{S_{ws}} \mathbf{n}_{ws}^s \bullet (\mathbf{w} - \mathbf{v}^s) \mathrm{d}S = -x_s^{ws} \frac{D^s \epsilon}{Dt} \tag{59a}$$

and

$$\frac{1}{\delta V}\int_{C_{wns}} \mathbf{n}^s \bullet (\mathbf{w}-\mathbf{v}^s)\mathrm{d}C = -\frac{l^{wns}}{a^s}\frac{D^s\epsilon}{Dt}. \tag{59b}$$

The preceding approximations may be used along with the expressions for the material derivatives in Equation (40) to obtain the approximate evolutionary equation

$$\begin{aligned}
&\frac{D^s a^{wn}}{Dt} - J^w_{wn}\frac{D^s\epsilon^w}{Dt} - (\cos\Phi)a^s\frac{D^s x^{ws}_s}{Dt} + \\
&\quad + \left\{x^{ws}_s J^w_{wn} - (\sin\Phi)\frac{l^{wns}}{a^s} - x^{ws}_s(J^s_{ws}-J^s)(\cos\Phi)\right\}\frac{D^s\epsilon}{Dt} \\
&= \cos\Phi[\nabla\bullet(x^{ns}_s a^{ws}\mathbf{G}^{ws})\bullet\mathbf{v}^{ws,s} + x^{ns}_s a^{ws}\mathbf{G}^{ws}:\ \mathbf{d}^{ws} - \\
&\quad - \nabla\bullet(x^{ws}_s a^{ns}\mathbf{G}^{ns})\bullet\mathbf{v}^{ns,s} - x^{ws}_s a^{ns}\mathbf{G}^{ns}:\ \mathbf{d}^{ns}] + \\
&\quad + \cos\Phi[a^{ws}\mathbf{G}^{ws}\bullet\mathbf{v}^{ws,s} + a^{ns}\mathbf{G}^{ns}\bullet\mathbf{v}^{ns,s}]\bullet\nabla x^{ws}_s - \\
&\quad - \nabla\bullet[\mathbf{G}^{wn}a^{wn}]\bullet\mathbf{v}^{wn,s} - a^{wn}\mathbf{G}^{wn}:\ \mathbf{d}^{wn}.
\end{aligned} \tag{60}$$

Comparison of this equation with Equation (40) indicates that

$$\begin{aligned}
B\ =\ &\cos\Phi[\nabla\bullet(x^{ns}_s a^{ws}\mathbf{G}^{ws})\bullet\mathbf{v}^{ws,s} + x^{ns}_s a^{ws}\mathbf{G}^{ws}:\ \mathbf{d}^{ws} - \\
&-\nabla\bullet(x^{ws}_s a^{ns}\mathbf{G}^{ns})\bullet\mathbf{v}^{ns,s} - x^{ws}_s a^{ns}\mathbf{G}^{ns}:\mathbf{d}^{ns}] + \\
&+\cos\Phi[a^{ws}\mathbf{G}^{ws}\bullet\mathbf{v}^{ws,s} + a^{ns}\mathbf{G}^{ns}\bullet\mathbf{v}^{ns,s}]\bullet\nabla x^{ws}_s - \\
&-\nabla\bullet[\mathbf{G}^{wn}a^{wn}]\bullet\mathbf{v}^{wn,s} - a^{wn}\mathbf{G}^{wn}:\mathbf{d}^{wn}.
\end{aligned} \tag{61}$$

Finally, an expression for C in Equation (41) is obtained in a straightforward manner. All the preliminary work needed involving relations for the material derivatives is encountered in the derivation of Equation (61). The result obtained after minimal algebra is

$$\begin{aligned}
&\frac{D^s l^{wns}}{Dt} + \kappa^{wns}_G a^s\frac{D^s x^{ws}_s}{Dt} + \left[\kappa^{wns}_G x^{ws}_s(J^s_{ws}-J^s) - \kappa^{wns}_N\frac{l^{wns}}{a^s}\right]\frac{D^s\epsilon}{Dt} \\
&\quad = -\kappa^{wns}_G\nabla\bullet[x^{ns}_s\mathbf{G}^{ws}a^{ws}]\bullet\mathbf{v}^{ws,s} + \kappa^{wns}_G\nabla\bullet[x^{ws}_s\mathbf{G}^{ns}a^{ns}]\bullet\mathbf{v}^{ns,s} - \\
&\qquad - \nabla\bullet[\mathbf{G}^{wns}l^{wns}]\bullet\mathbf{v}^{wns,s} - \\
&\qquad - \kappa^{wns}_G[a^{ws}\mathbf{G}^{ws}\bullet\mathbf{v}^{ws,s} + a^{ns}\mathbf{G}^{ns}\bullet\mathbf{v}^{ns,s}]\bullet\nabla x^{ws}_s - \\
&\qquad - \kappa^{wns}_G x^{ns}_s a^{ws}\mathbf{G}^{ws}:\ \mathbf{d}^{ws} + \kappa^{wns}_G x^{ws}_s a^{ns}\mathbf{G}^{ns}:\ \mathbf{d}^{ns} - \\
&\qquad - l^{wns}\mathbf{G}^{wns}:\ \mathbf{d}^{wns}.
\end{aligned} \tag{62}$$

Comparison of this equation with Equation (41) shows that the right side of Equation (62) is equal to C.

Acknowledgements

This work has been supported, in part, by the Los Alamos National Laboratory which is operated by the University of California for the U.S. Department of Energy. This work was performed at the Lawrence Livermore and Los Alamos National Laboratories under contracts W-7405-ENG-48 and W-7405-ENG-36, respectively, for the U.S. Department of Energy (DOE), as well as at the University of Notre Dame under DOE grant DO-FG07-96ER14701 and NSF grant EAR-9901432.

References

Allen, M. B.: 1984, In: M. B. Allen, G. A. Behie and J. A. Trangenstein (eds), *Multiphase Flow in Porous Media: Mechanics, Mathematics, and Numerics*, Lecture Notes in Engineering, Vol. 34, Springer-Verlag, Berlin.

Bachmat, Y.: 1972, Spatial macroscopization of processes in heterogeneous systems, *Israel J. Technol.* **10**, 391–403.

Bailyn, M.: 1994, *A Survey of Thermodynamics*, American Institute of Physics Press, New York.

Bennethum, L. S.: 1994, Multiscale, hybrid mixture theory for swelling systems with interfaces, Center for Applied Mathematics Technical Report #259, Purdue University.

Bennethum, L. S. and Giorgi, T.: 1997, Generalized Forchheimer equation for two-phase flow based on hybrid mixture theory, *Transport in Porous Media* **26**, 261–275.

Boruvka, L. and Neumann, A. W.: June 1977, Generalization of the classical theory of capillarity, *J. Chem. Phy.* **66**(12), 5464–5476.

Callen, H. B.: 1985, *Thermodynamics and an Introduction to Thermostatistics*, 2nd edn. Wiley, New York.

Eringen, A. C.: 1980, *Mechanics of Continua*, 2nd edn., Krieger, Huntington, New York.

Gray, W. G.: 1999, Thermodynamics and constitutive theory for multiphase porous-media flow considering internal geometric constraints, *Adv. Water Resour.* **22**, 521–547.

Gray, W. G.: 2000, Macroscale equilibrium conditions for two-phase flow in porous media, *Int. J. Multiphase Flow* **26**(3), 467–501.

Gray, W. G. and Hassanizadeh, S. M.: 1989, Averaging theorems and averaged equations for transport of interface properties in multiphase systems, *Int. J. Multiphase Flow* **15**(1), 81–95.

Gray, W. G. and Hassanizadeh, S. M.: 1998, Macroscale continuum mechanics for multiphase porous-media flow including phases, interfaces, common lines, and common points, *Adv. Water Resour.* **21**(4), 261–281.

Gray, W. G., Leijnse, A., Kolar, R. L. and Blain, C. A.: 1993, *Mathematical Tools for Changing Spatial Scales in the Analysis of Physical Systems*, CRC Press, Boca Raton, FL, 240 pp.

Hassanizadeh, M. and Gray, W. G.: 1979, General conservation equations for multi-phase systems, ii. mass, momenta, energy, and entropy equations, *Adv. Water Resour.* **2**(4), 191–203.

Hazlett, R. D., Chen, S. Y. and Soll, W. E.: 1998, Wettability and rate effects on immiscible displacement: lattice Boltzmann simulation in microtomographic images of reservoir rocks, *J. Petrol. Sci. Engng* **20**(3–4), 167–175.

Hilfer, R.: 1998, Macroscopic equations of motion for two-phase flow in porous media, *Phys. Rev. E* **58**(2), 2090–2095.

Hou, S. L., Shan, X. W., Zou, Q. S., Doolen, G. D. and Soll, W. E.: 1997, Evaluation of two lattice Boltzmann models for multiphase flows, *J. Comput. Phys.* **138**(2), 695–713.

Kalaydjian, F.: 1987, A macroscopic description of multiphase flow in porous media involving spacetime evolution of fluid/fluid interface, *Transport in Porous Media* **2**, 537–552.

Kalaydjian, F. J.-M.: 1992, Dynamic capillary pressure curve for water/oil displacement in porous media: theory versus. experiment, SPE Paper 24813, 491–506.

Liu, I.-S.: 1972, Method of Lagrange multipliers for exploitation of the energy principle, *Arch. Ration. Mech. Anal.* **46**, 131–148.

Lowry, M. I. and Miller, C. T.: 1995, Modeling of nonwetting-phase residual in porous-media, *Water Resour. Res.* **31**(3), 455–473.

Montemagno, C. D. and Gray, W. G.: 1995, Photoluminescent volumetric imaging: a technique for the exploration of multiphase flow and transport in porous media, *Geophys. Res. Lett.* **22**(4), 425–428.

Reeves, P. C. and Celia, M. A.: 1996, A functional relationship between capillary pressure, saturation, and interfacial area as revealed by a pore-scale network model, *Water Resour. Res.* **32**(8), 2345–2358.

Schaefer, C. E., DiCarlo, D. A. and Blunt, M. J.: 2000, Experimental measurement of air-water interfacial area during gravity drainage and secondary imbibition in porous media, *Water Resour. Res.* **36**(4), 885–890.

Slattery, J. C.: 1972, *Momentum, Energy, and Mass Transfer in Continua,* McGraw-Hill, New York.

Whitaker, S.: 1967, Diffusion and dispersion in porous media, *AIChE J.* **13**, 420–427.

Whitaker, S.: 1969, Advances in theory of fluid motion in porous media, *Indust. Engng Chem.* **61**, 14–28.

Whitaker, S.: 1998, *The Method of Volume Averaging; Theory and Application of Triansport in Porous Media*, Vol. 13 of Theories and Applications of Transport in Porous Media, Kluwer, Dordrecht.