

# Thermodynamics and constitutive theory for multiphase porous-media flow considering internal geometric constraints

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This paper provides the thermodynamic approach and constitutive theory for closure of the conservation equations for multiphase flow in porous media. The starting point for the analysis is the balance equations of mass, momentum, and energy for two fluid phases, a solid phase, the interfaces between the phases and the common lines where interfaces meet. These equations have been derived at the macroscale, a scale on the order of tens of pore diameters. Additionally, the entropy inequality for the multiphase system at this scale is utilized. The internal energy at the macroscale is postulated to depend thermodynamically on the extensive properties of the system. This energy is then decomposed to provide energy forms for each of the system components. To obtain constitutive information from the entropy inequality, information about the mechanical behavior of the internal geometric structure of the phase distributions must be known. This information is obtained from averaging theorems, thermodynamic analysis, and from linearization of the entropy inequality at near equilibrium conditions. The final forms of the equations developed show that capillary pressure is a function of interphase area per unit volume as well as saturation. The standard equations used to model multiphase flow are found to be very restricted forms of the general equations, and the assumptions that are needed for these equations to hold are identified. © 1999 Elsevier Science Ltd. All rights reserved.

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## NOMENCLATURE

$\mathcal{A}^\alpha$	surface area forming the boundary of the $\alpha$ phase	$c_{\alpha}^{\alpha\beta}$	accounts for contribution to the energy of the $\alpha\beta$ interphase of the $\alpha$ phase
$\mathcal{A}^{\alpha\beta}$	surface area of $\alpha\beta$ -interface	$c_{wns}^{\alpha\beta}$	accounts for contributions to the energy of the $\alpha\beta$ interface of the $wns$ common line
$a^\alpha$	specific interfacial area of the boundary of the $\alpha$ phase (area per unit of system volume)	$c_{\alpha\beta}^{wns}$	accounts for contributions to the energy of the $wns$ common line of the $\alpha\beta$ interface
$a^{\alpha\beta}$	specific interfacial area of $\alpha\beta$ -interface (area per unit of system volume)	$\mathbf{d}^\alpha$	deformation rate tensor of an $\alpha$ phase
$b^\alpha$	external supply of entropy to the $\alpha$ phase	$\mathbf{d}^{\alpha\beta}$	deformation rate tensor of an $\alpha\beta$ interface
$b^{\alpha\beta}$	external supply of entropy to the $\alpha\beta$ interface	$\mathbf{d}^{wns}$	deformation rate tensor of a $wns$ common line
$b^{wns}$	external supply of entropy to the $wns$ common line	$\mathbf{d}^m$	deformation rate tensor: phase ( $m = \alpha$ ), interface ( $m = \alpha\beta$ ), or common line ( $m = wns$ )
$\mathbf{b}^m$	tensor used to write the outline form of the entropy inequality in eqn (39)	$E^\alpha$	internal energy of $\alpha$ phase per mass of $\alpha$ phase
$c_{\alpha}^\alpha$	accounts for contribution to the energy of the $\alpha$ phase of the $\alpha\beta$ interface	$E^{\alpha\beta}$	internal energy of $\alpha\beta$ interface per mass of $\alpha\beta$ interface
		$E^{wns}$	internal energy of $wns$ common line per mass of $wns$ common line

$\hat{E}^\alpha$	internal energy of the $\alpha$ phase per unit volume of system	$\hat{\mathbf{T}}_{\alpha\beta}^\alpha$	force exerted on the $\alpha$ -phase by the $\alpha\beta$ -interface
$\hat{E}^{\alpha\beta}$	internal energy of the $\alpha\beta$ interface per unit volume of system	$\hat{\mathbf{T}}_{wns}^{\alpha\beta}$	force exerted on the $\alpha\beta$ -interface by the $wns$ common line
$\hat{E}^{wns}$	internal energy of the $wns$ common line per unit volume of system	$\mathbf{t}^\alpha$	stress tensor for the $\alpha$ phase
$E^\alpha$	extensive internal energy of the $\alpha$ phase	$\mathbf{t}^{\alpha\beta}$	stress tensor for the $\alpha\beta$ interface
$E^{\alpha\beta}$	extensive internal energy of the $\alpha\beta$ interface	$\mathbf{t}^{wns}$	stress tensor for the $wns$ common line
$E^{wns}$	extensive internal energy of the $wns$ common line	$\mathbf{u}$	velocity of a common line
$\mathbf{E}^s$	Lagrangian strain tensor of the solid phase	$\mathcal{V}^\alpha$	volume of $\alpha$ -phase
$\hat{e}_{\alpha\beta}^\alpha$	rate of transfer of mass from $\alpha\beta$ -interface to the $\alpha$ -phase	$\mathcal{V}_0^s$	reference volume of solid phase
$\hat{e}_{wns}^{\alpha\beta}$	rate of transfer of mass from $wns$ common line to the $\alpha\beta$ -interface	$\mathbf{v}^\alpha$	velocity of the $\alpha$ phase
$\mathbf{e}^m$	term accounting for the multipliers of velocity in outline entropy inequality (39)	$\mathbf{v}^{\alpha\beta}$	velocity of the $\alpha\beta$ interface
$\mathbf{F}^s$	displacement vector of the solid phase	$\mathbf{v}^{wns}$	velocity of the $wns$ common line
$\mathbf{g}^\alpha$	external supply of momentum to the $\alpha$ phase	$\mathbf{v}^{\alpha,\alpha\beta}$	velocity of the $\alpha$ phase relative to the velocity of the $\alpha\beta$ interface, $\mathbf{v}^\alpha - \mathbf{v}^{\alpha\beta}$
$\mathbf{g}^{\alpha\beta}$	external supply of momentum to the $\alpha\beta$ interface	$\mathbf{v}^{\alpha\beta,wns}$	velocity of the $\alpha\beta$ interface relative to the velocity of the $wns$ common line, $\mathbf{v}^{\alpha\beta} - \mathbf{v}^{wns}$
$\mathbf{g}^{wns}$	external supply of momentum to the $wns$ common line	$\mathbf{w}$	velocity of an interface
$h^\alpha$	external supply of energy to the $\alpha$ phase	$\mathbf{X}^s$	reference position of a solid phase ‘particle’
$h^{\alpha\beta}$	external supply of energy to the $\alpha\beta$ interface	$\mathbf{x}$	spatial position of a solid phase ‘particle’
$h^{wns}$	external supply of energy to the $wns$ common line	$x_s^{ns}$	fraction of the solid phase surface in contact with the non-wetting phase
$\mathbf{I}$	identity tensor	$x_s^{ws}$	fraction of the solid phase surface in contact with the wetting phase
$J_s^s$	average curvature of the solid surface calculated with $\mathbf{n}^s$ positive	<i>Greek symbols</i>	
$J_{\alpha\beta}^\alpha$	average curvature of the $\alpha\beta$ calculated with $\mathbf{n}^\alpha$ positive	$\gamma^{\alpha\beta}$	surface tension of $\alpha\beta$ -interface
$j$	jacobian of the motion of the solid phase	$\gamma^{wns}$	lineal tension of $wns$ -common line
$L$	material coefficients (with various superscripts and subscripts)	$\epsilon$	porosity of the medium
$\mathcal{L}^{wns}$	common line length	$\epsilon^\alpha$	volume fraction of $\alpha$ -phase
$l^{wns}$	specific length of $wns$ common line (length per unit volume of medium)	$\hat{\eta}^\alpha$	entropy of $\alpha$ phase per unit volume of system
$\mathcal{M}^\alpha$	mass of $\alpha$ phase	$\hat{\eta}^{\alpha\beta}$	entropy of $\alpha\beta$ interface per unit volume of system
$\mathcal{M}^{\alpha\beta}$	mass of $\alpha\beta$ interface	$\hat{\eta}^{wns}$	entropy of $wns$ common line per unit volume of system
$\mathcal{M}^{wns}$	mass of $wns$ common line	$\theta$	temperature
$\mathbf{n}^\alpha$	unit vector normal to and pointing outward from the surface of the $\alpha$ phase	$\theta^\alpha$	temperature of the $\alpha$ phase
$\mathbf{p}$	unit vector in direction of average principal curvature of the $wns$ common line	$\theta^{\alpha\beta}$	temperature of the $\alpha\beta$ interface
$p^\alpha$	pressure of $\alpha$ -phase	$\theta^{wns}$	temperature of the $wns$ common line
$\hat{Q}_{\alpha\beta}^\alpha$	energy transferred to the $\alpha$ -phase from the $\alpha\beta$ -interface	$\theta^{\alpha,\alpha\beta}$	temperature difference, $\theta^\alpha - \theta^{\alpha\beta}$
$\hat{Q}_{wns}^{\alpha\beta}$	energy transferred to the $\alpha\beta$ -interface from the $wns$ common line	$\theta^{\alpha\beta,wns}$	temperature difference, $\theta^{\alpha\beta} - \theta^{wns}$
$\mathbf{q}$	effective total heat conduction vector	$\kappa$	average principal curvature of the common line
$\mathbf{q}^\alpha$	heat conduction vector for the $\alpha$ phase	$\kappa_n$	average normal curvature of the common line with respect to the $s$ surface
$\mathbf{q}^{\alpha\beta}$	heat conduction vector for the $\alpha\beta$ interface	$\kappa_g^{ws}$	average geodesic curvature of the common line with respect to the $ws$ surface
$\mathbf{q}^{wns}$	heat conduction vector for the $wns$ common line	$\lambda$	unit vector tangent to the $wns$ common line
$S^\alpha$	entropy of the $\alpha$ phase	$\mu^\alpha$	chemical potential of the $\alpha$ phase
$S^{\alpha\beta}$	entropy of the $\alpha\beta$ interface	$\mu^{\alpha\beta}$	chemical potential of the $\alpha\beta$ interface
$S^{wns}$	entropy of the $wns$ common line	$\mu^{wns}$	chemical potential of the $wns$ common line
$s^\alpha$	saturation of the $\alpha$ -phase, volume fraction of void space occupied by fluid phase $\alpha$	$\nu^{\alpha\beta}$	unit vector on the common line normal to $\lambda$ and tangent to the $\alpha\beta$ interface
		$\rho^\alpha$	density of $\alpha$ phase, mass of $\alpha$ phase per volume of $\alpha$ phase
		$\rho^{\alpha\beta}$	density of $\alpha\beta$ interface, mass of $\alpha\beta$ interface per area of $\alpha\beta$ interface
		$\rho^{wns}$	density of $wns$ common line, mass of $wns$ common line per length of $wns$ common line

$\sigma^s$	stress in the solid due to deformation
$\sigma^{\alpha s}$	stress in the $\alpha$ -solid interface due to solid deformation
$\tau$	quantities defined in the text (with subscripts and superscripts) that are zero at equilibrium
$\Phi$	average contact angle between the $w$ and $s$ phases
$\phi^\alpha$	entropy conduction vector of the $\alpha$ phase
$\phi^{\alpha\beta}$	entropy conduction vector of the $\alpha\beta$ interface
$\phi^{wns}$	entropy conduction vector of the $wns$ common line
$\hat{\Omega}^\alpha$	grand canonical potential of the $\alpha$ phase per unit volume of system
$\hat{\Omega}^{\alpha\beta}$	grand canonical potential of the $\alpha\beta$ interface per unit volume of system
$\hat{\Omega}^{wns}$	grand canonical potential of the $wns$ common line per unit volume of system

#### Special symbols

$D^\alpha/Dt$	material time derivative following the motion in the $\alpha$ phase, $\partial/\partial t + \mathbf{v}^\alpha \cdot \nabla$
$D^{\alpha\beta}/Dt$	material time derivative following the motion in the $\alpha\beta$ interface, $\partial/\partial t + \mathbf{v}^{\alpha\beta} \cdot \nabla$
$D^{wns}/Dt$	material time derivative following the motion in the $wns$ common line, $\partial/\partial t + \mathbf{v}^{wns} \cdot \nabla$
$\sum_{\beta \neq \alpha}$	summation over all phases except $\alpha$ -phase
$\nabla$	gradient operator with respect to spatial coordinates
$\nabla_{\mathbf{x}}$	gradient operator with respect to reference coordinates

#### Superscripts and subscripts

$n$	non-wetting phase
$s$	solid phase
$w$	wetting phase
$ns$	non-wetting–solid interface
$wn$	wetting–non-wetting interface
$ws$	wetting–solid interface

## 1 INTRODUCTION

Accurate description of multiphase flow in porous media requires that a number of system intricacies be accounted for. These include the presence of juxtaposed phases and their interfaces, the complicated geometry of pores, fluid dynamics giving rise to appearance and disappearance of interfaces, pendular rings of a wetting phase, ganglia of the non-wetting phase, and the behavior of films. A variety of forces, due to viscous effects, gravity, interfacial tension, and pressure are simultaneously present and influencing system behavior. A fundamental question in modeling the flow of fluids in porous media is how much detail should be included in such models. In virtually all laboratory and field scale models, microscale details (i.e., pore geometry and flow variations within those pores) are impossible to include

and are not actually needed. However, manifestation of those details at the macroscale (a scale involving tens to hundreds of pores) must be preserved. Traditionally, porosity and fluid saturations, concepts that do not exist at the microscale, are included in macroscale porous media theories to account for the presence of multiple phases at a point in a macroscale continuum. However, these additional variables have proven insufficient to account for all important microscale processes that influence macroscale behavior. Because of the dynamic motion of the fluids, many configurations and distributions of the fluids are possible for a given saturation. Even at equilibrium, different distributions of fluids could exist at a prescribed saturation such that the balances of forces on the fluid are satisfied.

This matter has received attention in recent years and thermodynamic theories have been developed wherein interfacial effects are explicitly included.<sup>10,18,20,26,27</sup> In these theories, in addition to porosity and saturation, specific interfacial area, the amount of interfacial area between two phases per unit volume of the system, is introduced as a macroscale independent variable. This variable is of importance in studies of mass transfer among phases of a porous medium and thus is of wide interest. A number of procedures involving network models and experimental methods have been developed for measurement of interfacial areas.<sup>13,36,40,43</sup>

Porous media systems that involve flow of two or more fluids may also have common lines, curves formed in those instances when three different interface types come together. The common lines may play an important role in the movement of fluids and interfaces. Indeed, in a capillary tube where a meniscus between fluids is at rest, flow can be initiated only if the balance of forces on the common line, as well as the balance on the phases and the meniscus, is perturbed. Thus, the question arises as to how the presence of common lines and the thermodynamic properties of those lines affect the macroscale flow processes in porous media. This question, and more general questions regarding the degree of detail that must be incorporated into macroscale theories, can be investigated only if appropriate conservation equations for the common lines are available. Subsequent to the development of a general theory, information obtained from experiments and observations may be used to evaluate the relative significance of various phenomena accounted for in the theory. At that point, simplifications can be made that eliminate unimportant terms from the modeling process. It is important to observe that by starting from a general formulation, one is forced to make explicit assumptions to arrive at equations to be used in a modeling exercise. Then, if the exercise proves unsuccessful, the source of the difficulty will lie in the approximations made. If, on the other hand, one begins with simple equations based on empirical or intuitive ideas, the cause of the failure of such equations cannot be inferred.

In this work, the results from a general thermodynamic theory are developed where the effects of both interfaces and common lines have been taken into account. The

procedure for developing usable equations for the simulation of multiphase subsurface flow involves six steps:

- *Derivation of conservation equations for phases, interfaces, and common lines at the porous media scale, the macroscale, and of the entropy inequality for the system.* Work to do this has been ongoing for many years. Initially, the work considered only phases; and balance laws studied were restricted to conservation of mass and momentum, e.g. Ref. <sup>47</sup>. The dissertation of Hassanizadeh<sup>22</sup> and the papers by Hassanizadeh and Gray<sup>23–25</sup> employed an averaging theory that extended this approach to inclusion of the energy equation and entropy inequality. Subsequent to this, Gray and Hassanizadeh<sup>18</sup> developed averaging theorems for interfaces and developed conservation relations for the interface properties as well. Finally, theorems for averaging over common lines were developed by Gray et al.<sup>21</sup> and have been employed in a paper by Gray and Hassanizadeh<sup>20</sup>. This latter reference, in fact, presents the set of averaged equations of mass, momentum, and energy conservation for phases, interfaces, and common lines that form the basis for a general study of multiphase flow.
- *Postulation of thermodynamic dependences of the energy on independent variables for phases, interfaces, and common lines and incorporation of these postulates into the entropy inequality.* This task is one that has not, heretofore, been addressed thoroughly for macroscale system representation. There is a need to ensure that the fundamental ideas of thermodynamics are not neglected when making use of the principles of continuum mechanics. Note that classical thermodynamics deals with equilibrium systems only while continuum mechanics deals with both equilibrium states and the transitions when a system is not at equilibrium. Nevertheless, it is important that the continuum mechanical description reduce to the classical thermodynamic one at steady state. Thermodynamics requires that consistent and systematic postulates be made concerning the dependence of internal energy on independent variables. The presence of interfaces adds the complication of excess surface properties such as mass per unit area and interfacial tension that must be accounted for in a conceptually and quantitatively consistent manner (surface excess properties from a microscale Gibbsian perspective are discussed, for example, in Miller and Neogi<sup>34</sup> and Gaydos *et al.*<sup>17</sup>). Then, from the postulated forms, relations among variables and insights into system behavior can be obtained. One of the most useful approaches for postulating the thermodynamic dependence of internal energy is the approach advocated in Callen<sup>12</sup> and Bailyn<sup>9</sup> and, used to advantage by Gaydos *et al.*<sup>17</sup> in a study of microscopic capillarity, whereby the extensive energy is considered to be a function of the extensive variables of the system. With this approach, confusion about differences among Helmholtz potential, Gibbs potential, grand canonical potential, and enthalpy are diminished as they are simply mathematical rearrangements of the original postulated form for internal energy. Insights gained from applying microscale-based thermodynamic postulates to multiphase systems (e.g. Refs <sup>1–4,15,34,35,37</sup>) are extremely valuable in formulating a macroscale theory, but do not replace the need for formulation of that theory in terms of macroscale variables. To develop the macroscale thermodynamics, the postulative approach of Callen<sup>12</sup> will be employed after extension to the macroscale perspective. The philosophy of Callen<sup>12</sup> is employed herein to obtain thermodynamic relations that are appropriate for a macroscale description of a porous media system. One important point is that from the perspective of the macroscale, the system is composed of coexisting phases at a point and not juxtaposed phases, interfaces, and common lines. Thus, in fact, the energy postulate should be made in terms of all components. The decomposition of the internal energy for the total system to the component parts describing each phase, interface, and common line must be undertaken with caution.
- *Determination of mechanical equilibrium constraints and their incorporation into the entropy inequality.* Although the geometric variables including porosity, saturation, areas per volume, and common line length per volume are independent variables, their deviations around an equilibrium state are not (e.g., a change in saturation of one fluid would be expected to cause a change in the amount of area bounding that fluid). These considerations give rise to employment of the averaging theorems to obtain relations among changes in geometric variables. These relations are useful in deriving both thermodynamic equilibrium conditions and dynamic relations between changes in geometric variables and the thermodynamic state of the system.
- *Exploitation of the entropy inequality to obtain equations that describe equilibrium system behavior.* The entropy inequality provides a condition that requires a system to be at its minimum energy state when at equilibrium. It also provides some guidance on allowable dependences of functions on independent variables. Furthermore, it provides guidance on the positivity or negativity of some coefficients by forbidding, for example, up-gradient flow or transfer of heat from a cold body to a warmer one or flow in a direction opposite to a gradient in potential. A theoretical tool exists for developing

constitutive functions in a systematic manner that is based on the second law of thermodynamics. The procedure of Coleman and Noll<sup>14</sup> was applied to single phase systems to assure that the second law of thermodynamics is not violated by constitutive assumptions. Complementing this work are extensions and variations that consider multiphase mixtures and interfaces (e.g., Refs<sup>19,25,38,45</sup>). Here, the macroscale entropy inequality will be exploited while taking into account constraints obtained from the geometric relations.

- *Linearization of some of the constitutive functions to obtain conservation equations with their coefficients capable of modeling dynamic systems.* Although the localization theory for a three phase system provides 35 balance equations of mass, momentum, and energy for the phases, interfaces, and common lines, it also contains 150 constitutive functions that must be specified. The dependence of these functions on other system parameters are obtained under some assumptions. Also, the functional forms of the dependences of the stress tensors are obtained. However, in general, the actual functional relations between the constitutive functions and their independent variables are not known except at equilibrium. For example, at equilibrium the heat conduction vector is zero; but the general functional representation of this vector in terms of independent variables is not known at an arbitrary state of disequilibrium. Thus a compromise must be employed whereby functional forms are obtained 'near' equilibrium. Experimental and computational studies must subsequently be undertaken to determine the definition of 'nearness'. By this approach, which is similar to taking a Taylor series expansion of a function and ignoring higher order terms, results such as the heat conduction vector being proportional to the temperature gradient and a velocity proportional to a potential gradient are obtained. Because multiphase porous media flows are typically slow, they also satisfy the conditions of being 'near enough' to equilibrium that this linearization procedure provides relations appropriate for many physical situations. It is important to note, however, that although the equations are linearized, the coefficients that arise still may have complex dependence on system parameters (e.g., relative permeability, which is traditionally simplified to be a function of saturation). Identification of those coefficients remains a challenging task.
- *Determination of the physical interpretation of the coefficients, as possible, using geometric approximations that provide insight into required laboratory measurements.* It is important that the theoretical procedure not simply be a propagator of unknown coefficients that have no chance of being measured or even understood. Therefore,

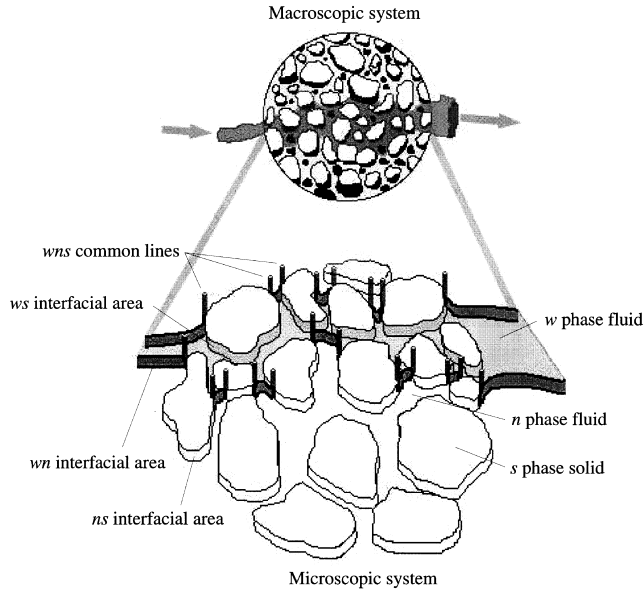
effort must be made to allow insightful study of the new coefficients through laboratory and computer experimentation. Thus, although a general formulation is employed, it is simplified to a manageable, yet still challenging, set of equations that can be effectively studied. As progress is made in parameterizing these systems, the approximations employed can be relaxed so that more complex systems may be studied.

The first of the above steps was carried out by Gray and Hassanizadeh<sup>20</sup> for the general case including an arbitrary number of phases, interfaces, common lines, and common points. Here, the conservation equations developed in that paper will be simplified to the case of three phases (wetting phase  $w$ , non-wetting phase  $n$ , and solid phase  $s$ ) prior to continuing the systematic approach to addressing thermodynamic and geometric issues. The result of this study is a 'workable' set of equations that arises from examination of a three-phase system, composed of a solid and two fluids. Additionally, the assumptions needed to reduce the general set of equations to the set traditionally used to model a three-phase system are made explicit.

## 2 CONSERVATION EQUATIONS

Fig. 1 depicts a three-phase system consisting of a solid and two fluid phases, denoted by  $s$ ,  $w$ , and  $n$ , respectively. The  $w$  phase will be referred to as the wetting phase because it preferentially wets the solid relative to the non-wetting  $n$  phase. The phases are separated by three different interfaces denoted as  $wn$ ,  $ws$ , and  $ns$  where the paired indices refer to the phases on each side of the interface and the order of the indices is inconsequential. Additionally, a  $wns$  common line may exist. The three-phase system is a simplification of a more general case involving more phases in that no common points exist. General macroscale equations describing conservation of mass, momentum, and energy for phases and interfaces have been developed previously.<sup>18,23</sup> These have been collected, and equations for common lines and common points have been derived along with the entropy inequality for the system.<sup>20</sup> Here, these will be simplified to the forms needed to describe a three-phase system. The reduction to the required forms is a straightforward manipulation of the general forms with the main differences being that summations over common lines reduce to terms involving the single common line and terms relating to transfer processes at common points are zero since no common points exist for a three-phase system.

In addition, for convenience rather than necessity, the energy densities will be expressed per unit mass and per unit of system volume. Therefore, with  $E^\alpha$  being the internal energy of the  $\alpha$  phase per unit mass of  $\alpha$  phase,  $\hat{E}^\alpha$  will indicate the  $\alpha$  phase energy per unit volume of porous medium. These two energy densities are related by  $\hat{E}^\alpha = \rho^\alpha \epsilon^\alpha E^\alpha$ . For an interface,  $E^{\alpha\beta}$  is the excess internal



**Fig. 1.** Depiction of a three-phase system at a macroscale point (top) and from the microscale perspective (bottom) with notation employed to identify phases, interfaces, and the common line.

energy of the  $\alpha\beta$  interface per unit mass of interface while  $\hat{E}^{\alpha\beta} = \rho^{\alpha\beta} a^{\alpha\beta} E^{\alpha\beta}$  is the excess energy per unit volume of the system. Finally, the common line energy per unit mass of common line is denoted as  $E^{wns}$  while the common line internal energy per unit volume of the system is  $\hat{E}^{wns} = \rho^{wns} l^{wns} E^{wns}$ . Note that in the case of massless interfaces and common lines, the energies per unit volume are still directly meaningful functions, while the product of mass density times energy per mass must be evaluated in the limit as the density approaches zero.

The objective of this section is to provide the needed balance equations rather than reproduce their derivation from the earlier general work.<sup>20</sup>

### 2.1 Phase conservation equations

The balance equations for the three-phase system are essentially unchanged from the general case with more phases. For the current study, each phase may have two different kinds of interfaces at its boundary. For example, the phase is bounded by some combination of  $wn$  and  $ws$  interfaces. The balance equations for the phases are as follows:

*Macroscale mass conservation for the  $\alpha$ -phase*

$$\frac{D^\alpha(\epsilon^\alpha \rho^\alpha)}{Dt} + \epsilon^\alpha \rho^\alpha \nabla \cdot \mathbf{v}^\alpha = \sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^\alpha \quad \alpha = w, n, s \quad (1)$$

*Macroscale momentum conservation for the  $\alpha$ -phase*

$$\epsilon^\alpha \rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} - \nabla \cdot (\epsilon^\alpha \mathbf{t}^\alpha) - \epsilon^\alpha \rho^\alpha \mathbf{g}^\alpha = \sum_{\beta \neq \alpha} \hat{\mathbf{T}}_{\alpha\beta}^\alpha \quad \alpha = w, n, s \quad (2)$$

*Macroscale energy conservation for the  $\alpha$ -phase*

$$\begin{aligned} \frac{D^\alpha \hat{E}^\alpha}{Dt} - \nabla \cdot (\epsilon^\alpha \mathbf{q}^\alpha) - (\epsilon^\alpha \mathbf{t}^\alpha - \hat{E}^\alpha \mathbf{I}) : \nabla \mathbf{v}^\alpha - \epsilon^\alpha \rho^\alpha h^\alpha \\ = E^\alpha \sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^\alpha + \sum_{\beta \neq \alpha} \hat{Q}_{\alpha\beta}^\alpha \quad \alpha = w, n, s \end{aligned} \quad (3)$$

The terms on the right side of the equations account for exchanges with the bounding interfaces. The complete notation used is provided at the beginning of the text.

### 2.2 Interface conservation equations

These equations express conservation of mass, momentum, and energy of the interface. The interfaces may exchange properties with adjacent phases and with the common line. The balance equations are as follows:

*Macroscale mass conservation for the  $\alpha\beta$ -interface*

$$\begin{aligned} \frac{D^{\alpha\beta}(a^{\alpha\beta} \rho^{\alpha\beta})}{Dt} + a^{\alpha\beta} \rho^{\alpha\beta} \nabla \cdot \mathbf{v}^{\alpha\beta} = -(\hat{e}_{\alpha\beta}^\alpha + \hat{e}_{\alpha\beta}^\beta) + \hat{e}_{wns}^{\alpha\beta} \\ \alpha\beta = wn, ws, ns \end{aligned} \quad (4)$$

*Macroscale momentum conservation for the  $\alpha\beta$ -interface*

$$\begin{aligned} a^{\alpha\beta} \rho^{\alpha\beta} \frac{D^{\alpha\beta} \mathbf{v}^{\alpha\beta}}{Dt} - \nabla \cdot (a^{\alpha\beta} \mathbf{t}^{\alpha\beta}) - a^{\alpha\beta} \rho^{\alpha\beta} \mathbf{g}^{\alpha\beta} \\ = - \sum_{i=\alpha, \beta} (\hat{e}_{\alpha\beta}^i \mathbf{v}^{i, \alpha\beta} + \hat{\mathbf{T}}_{\alpha\beta}^i) + \hat{\mathbf{T}}_{wns}^{\alpha\beta} \quad \alpha\beta = wn, ws, ns \end{aligned} \quad (5)$$

*Macroscale energy conservation for the  $\alpha\beta$ -interface*

$$\begin{aligned} \frac{D^{\alpha\beta} \hat{E}^{\alpha\beta}}{Dt} - \nabla \cdot (a^{\alpha\beta} \mathbf{q}^{\alpha\beta}) - (a^{\alpha\beta} \mathbf{t}^{\alpha\beta} - \hat{E}^{\alpha\beta} \mathbf{I}) : \nabla \mathbf{v}^{\alpha\beta} - a^{\alpha\beta} \rho^{\alpha\beta} h^{\alpha\beta} \\ = - \sum_{i=\alpha, \beta} \{ \hat{e}_{\alpha\beta}^i [E^i + (\mathbf{v}^{i, \alpha\beta})^2/2] + \hat{\mathbf{T}}_{\alpha\beta}^i \cdot \mathbf{v}^{i, \alpha\beta} + \hat{Q}_{\alpha\beta}^i \} \\ + E^{\alpha\beta} \hat{e}_{wns}^{\alpha\beta} + \hat{Q}_{wns}^{\alpha\beta} \end{aligned} \quad (6)$$

### 2.3 Common line conservation equations

The balance equations for the common line account for the properties of the common line and the exchange of those properties with the interfaces that meet to form the common line. The appropriate equations for the case where there are three phases, and thus only one common line and no common points, are as follows.

*Macroscale mass conservation for the wns-common line*

$$\frac{D^{wns}(l^{wns} \rho^{wns})}{Dt} + l^{wns} \rho^{wns} \nabla \cdot \mathbf{v}^{wns} = -(\hat{e}_{wns}^{wn} + \hat{e}_{wns}^{ws} + \hat{e}_{wns}^{ns}) \quad (7)$$

Macroscale momentum balance for the wns-common line

$$l^{wns} \rho^{wns} \frac{D^{wns} \mathbf{v}^{wns}}{Dt} - \nabla \cdot (l^{wns} \mathbf{t}^{wns}) - l^{wns} \rho^{wns} \mathbf{g}^{wns} = - \sum_{ij=wn,ws,ns} (\hat{e}_{wns}^{ij} \mathbf{v}^{ij,wns} + \hat{\mathbf{T}}_{wns}^{ij}) \quad (8)$$

Macroscale energy conservation for the wns-common line

$$\frac{D^{wns} \hat{E}^{wns}}{Dt} - \nabla \cdot (l^{wns} \mathbf{q}^{wns}) - (l^{wns} \mathbf{t}^{wns} - \hat{E}^{wns} \mathbf{I}) : \nabla \mathbf{v}^{wns} - l^{wns} \rho^{wns} h^{wns} = - \sum_{ij=wn,ws,ns} \{ \hat{e}_{wns}^{ij} [E^{ij} + (\mathbf{v}^{ij,wns})^2/2] + \hat{\mathbf{T}}_{wns}^{ij} \cdot \mathbf{v}^{ij,wns} + \hat{Q}_{wns}^{ij} \} \quad (9)$$

## 2.4 Entropy inequality

An entropy inequality has been derived for each phase, interface, and the common line as discussed in Gray and Hassanizadeh.<sup>20</sup> However, the entropy exchange terms between the different components prevent the individual inequalities from being particularly useful. The power of the entropy inequalities comes in calculating their sum such that the exchange terms cancel. The combined entropy inequality for the three phase system takes the form:

$$\begin{aligned} \Lambda = & \sum_{\alpha} \left\{ \frac{D^{\alpha} \hat{\eta}^{\alpha}}{Dt} + \hat{\eta}^{\alpha} \mathbf{I} : \nabla \mathbf{v}^{\alpha} - \nabla \cdot (\epsilon^{\alpha} \phi^{\alpha}) - \epsilon^{\alpha} \rho^{\alpha} b^{\alpha} \right\} \\ & + \sum_{\alpha\beta} \left\{ \frac{D^{\alpha\beta} \hat{\eta}^{\alpha\beta}}{Dt} + \hat{\eta}^{\alpha\beta} \mathbf{I} : \nabla \mathbf{v}^{\alpha\beta} - \nabla \cdot (a^{\alpha\beta} \phi^{\alpha\beta}) \right. \\ & \left. - a^{\alpha\beta} \rho^{\alpha\beta} b^{\alpha\beta} - \eta^{\alpha\beta} \sum_{i=\alpha,\beta} \hat{e}_{\alpha\beta}^i \right\} + \frac{D^{wns} \hat{\eta}^{wns}}{Dt} \\ & + \hat{\eta}^{wns} \mathbf{I} : \nabla \mathbf{v}^{wns} - \nabla \cdot (l^{wns} \phi^{wns}) - l^{wns} \rho^{wns} b^{wns} \\ & - \eta^{wns} \sum_{ij=wn,ws,ns} \hat{e}_{wns}^{ij} \geq 0 \end{aligned} \quad (10)$$

## 3 IDENTIFICATION OF UNKNOWNNS

For the conservation equations to be useful in an application, some determination must be made of the functional forms of the variables that appear in these equations. In fact, for the three phase system, there are a total of 35 conservation equations (for each phase, interface, and common line there is one mass conservation equation, three momentum equations, and one energy equation). For these equations, the following 35 variables will be designated as primary

physical independent variables:

- 15 phase properties:  $\rho^w, \rho^n, \rho^s, \mathbf{v}^w, \mathbf{v}^n, \mathbf{F}^s, \theta^w, \theta^n, \theta^s$
- 15 interface properties:  $\rho^{wn}, \rho^{ws}, \rho^{ns}, \mathbf{v}^{wn}, \mathbf{v}^{ws}, \mathbf{v}^{ns}, \theta^{wn}, \theta^{ws}, \theta^{ns}$
- 5 common line properties:  $\rho^{wns}, \mathbf{v}^{wns}, \theta^{wns}$

In addition to these quantities, six primary geometric independent variables appear in the equations which account for the distributions of phases, interfaces, and common line in the system. These variables are:

- 6 geometric variables:  $\epsilon, s^w, a^{wn}, a^{ws}, a^{ns}, l^{wns}$

It is important to note that the six dynamic geometric variables, not present in a microscale formulation but arising at the macroscale, provide an excess of unknowns over and above the 35 primary variables that are associated with the 35 balance equations. The development of equations that describe the dynamics of the macroscale geometry is a significant challenge.

Finally, there are additional quantities appearing in the equation that must be expressed as constitutive functions of the physical and geometric variables. These quantities are:

- 75 functions from the phase equations:

$$\hat{E}^{\alpha}, \mathbf{t}^{\alpha}, \hat{\mathbf{T}}_{\alpha\beta}^{\alpha}, \mathbf{q}^{\alpha}, \hat{Q}_{\alpha\beta}^{\alpha}, \hat{\eta}^{\alpha}, \hat{e}_{\alpha\beta}^{\alpha}, \phi^{\alpha}, b^{\alpha};$$

$$\alpha = w, n, s; \quad \alpha\beta = wn, ws, ns$$

- 60 functions from the interface equations:

$$\hat{E}^{\alpha\beta}, \mathbf{t}^{\alpha\beta}, \hat{\mathbf{T}}_{wns}^{\alpha\beta}, \mathbf{q}^{\alpha\beta}, \hat{Q}_{wns}^{\alpha\beta}, \hat{\eta}^{\alpha\beta}, \hat{e}_{wns}^{\alpha\beta}, \phi^{\alpha\beta}, b^{\alpha\beta};$$

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

- 15 functions from the common line equation:

$$\hat{E}^{wns}, \mathbf{t}^{wns}, \mathbf{q}^{wns}, \hat{\eta}^{wns}, \phi^{wns}, b^{wns}$$

Thus to close the system and have a set of equations that can be used to model the three phase system, there is a need for 150 constitutive functions of the physical properties and geometric variables, as well as the six additional relations among the geometric and physical parameters. The constitutive functions will be assumed to be expressible as functions of the 35 independent variables, the geometric variables, and gradients of some of these quantities.

**Assumption I** The 150 constitutive functions may be expressed in terms of the following set of independent variables:

$$\begin{aligned} \mathbf{z} = & \{ \rho^w, \rho^n, \rho^s, \mathbf{v}^w, \mathbf{v}^n, \mathbf{F}^s, \theta^w, \theta^n, \theta^s, \epsilon, s^w, \nabla \theta^w, \nabla \theta^n, \nabla \theta^s, \nabla \epsilon, \\ & \nabla s^w, \rho^{wn}, \rho^{ws}, \rho^{ns}, \mathbf{v}^{wn}, \mathbf{v}^{ws}, \mathbf{v}^{ns}, \theta^{wn}, \theta^{ws}, \theta^{ns}, a^{wn}, a^{ws}, a^{ns}, \\ & \nabla \theta^{wn}, \nabla \theta^{ws}, \nabla \theta^{ns}, \nabla a^{wn}, \nabla a^{ws}, \nabla a^{ns}, \rho^{wns}, \mathbf{v}^{wns}, \theta^{wns}, \\ & l^{wns}, \nabla \theta^{wns}, \nabla l^{wns} \} \end{aligned} \quad (11)$$

Inclusion of other variables in this list (e.g.  $\mathbf{d}^w, \nabla^2 \theta^{wn}$ ) is certainly possible, and may even be necessary in order to describe some processes, but the above list is considered to

be adequate for description of the porous media systems under study here. Should the resulting equations prove to be incapable of describing a process of interest, then it may be necessary to propose an expanded list of independent variables.

Determination of the constitutive functions such that the equation system may be closed is certainly a significant task, but one that can be accomplished with a combination of systematic thermodynamic postulates, reasonable geometric conditions, exploitation of the entropy inequality, and laboratory verification. The theoretical steps to be employed will be demonstrated next.

#### 4 THERMODYNAMIC ASSUMPTIONS AND RELATIONS

One of the important challenges to obtaining a complete theory of multi-phase flow is the postulation of the appropriate thermodynamics. Here, an approach is followed that is based on the key assumption:

**Assumption II** The dependence of energy of the phases, interfaces, and common lines on the independent variables is the same function whether or not the full multi-phase system is at equilibrium.

This assumption, which means that energy is a function of a subset of the independent variables in list (11), may limit the theory such that it applies only to slowly changing systems, but this is the case in most porous media flow situations. An advantageous consequence of this assumption is that some mathematically complex relations involving the dependence of energy on quantities such as velocity or temperature gradient which are of little physical consequence do not arise. The postulated dependences will be made with the total energy being dependent on extensive properties of the phases, interfaces, and common line. The postulates of dependence of energy on the physical and geometric variables are made in a manner consistent with the philosophy of Callen<sup>12</sup> for microscopic systems but is more general.

##### 4.1 System thermodynamics

For the system consisting of phases, interfaces, and the common line in which points are viewed from the macroscale perspective, the energy is postulated to be a function of the entropies of the system components, the mass of each component, and the geometric extents such that:

$$E = E(S^w, S^n, S^s, S^{wn}, S^{ws}, S^{ns}, S^{wns}, M^w, M^n, M^s, M^{wn}, M^{ws}, M^{ns}, M^{wns}, V^w, V^n, V^s, V_0 \mathbf{E}^s, \mathcal{A}^{wn}, \mathcal{A}^{ws}, \mathcal{A}^{ns}, \mathcal{L}^{wns}). \quad (12)$$

All variables written in script are extensive variables. Many useful relations describing the equilibrium thermodynamic behavior of the multiphase system as a whole may be

derived based on postulate (12). However, the goal of this work is to obtain a dynamic description of the multi-phase system at the macroscale and the contribution of each component of the system to the dynamic behavior. For example, when not at equilibrium, phases, interfaces, and common lines co-existing at a macroscopic point might not be at the same temperature. Therefore, to describe such a situation, it is necessary to decompose the functional form of the energy given by postulate (12) into its component parts at each macroscale point and treat those separately. The path to such a decomposition is not entirely obvious and certainly is not unique.

One necessary part of the decomposition is to require that the total system energy be equivalent to the sum of its component parts from the phases, interfaces, and common lines such that:

$$E = E^w + E^n + E^s + E^{wn} + E^{ws} + E^{ns} + E^{wns}. \quad (13)$$

The next step is to determine the functional dependence of each of the seven components. The most general proposal for such dependence would be to allow each of the component energies to depend on the full list of extensive variables of the system, as in eqn (12). Although this formulation is attractive because of its generality, it lacks appeal because it fails to dismiss negligible interactions among system components such that the system description obtained is unnecessarily complex from a mathematical perspective. Thus, an alternative more restrictive approach will be followed here for specifying the dependence of the energy on extensive variables that allows for some coupling of the thermodynamic properties of components, but not all possible couplings. It must be emphasized that this restriction may limit the general applicability of the theory, but it is proposed as a reasonable compromise among generality, the need to relate the theory to a real system, and the couplings that are expected to be important. The assumption that will be employed is as follows:

**Assumption III** A multiphase system is composed of phases, interfaces, and common lines which will be referred to as components. The total energy of each component will be assumed to be a function of the entropy of that component, the geometric extensive variable of that component, the mass of that component, and the geometric extensive variables of all microscopically adjacent components.

Inherent in Assumption III is the restriction that components only impact the thermodynamics of other components with which they have physical contact. Additionally, postulation of the functional dependence of the macroscale energy of a component on the geometric properties of an adjacent component, but not on the mass of these components, is analogous to approaches taken by Li and Neumann<sup>32</sup> and Hirasaki<sup>29</sup> in their studies of films at the microscale. The thermodynamic dependence of the internal energy of a component on the geometric properties of the adjacent components is expected to be important only when



the average microscale distance between points in each component is small (e.g., in thin films or for highly dispersed phases, interfaces and common lines). In addition, the functional dependences obtained by Assumption III must still lead to thermodynamic relations involving component properties consistent with the thermodynamic analysis of the system as a whole.

## 4.2 Constitutive postulates for phase energy functions

The dependence of energy of the fluid phases on their properties is postulated as:

$$\mathcal{E}^w = \mathcal{E}^w(S^w, \mathcal{V}^w, \mathcal{M}^w, \mathcal{A}^{wn}, \mathcal{A}^{ws}) \quad (14a)$$

$$\mathcal{E}^n = \mathcal{E}^n(S^n, \mathcal{V}^n, \mathcal{M}^n, \mathcal{A}^{wn}, \mathcal{A}^{ns}) \quad (14b)$$

The solid phase energy depends on the state of strain of the solid<sup>9</sup> such that it is expressed as:

$$\mathcal{E}^s = \mathcal{E}^s(S^s, \mathcal{V}_0^s \mathbf{E}^s, \mathcal{M}^s, \mathcal{A}^{ws}, \mathcal{A}^{ns}) \quad (14c)$$

The inclusion of a dependence on the interfacial areas in these expressions is a departure from the type of postulate made when a system is to be modeled at the microscale. This is to account for changes in energy that may occur when the amount of surface area per volume of phase is large. Additionally, note that the nature of a solid accounts for its energy being postulated as depending on the state of deformation rather than its volume. From these equations, because energy is a homogeneous first order function,<sup>9,12</sup> the Euler forms of the energy are:

$$\mathcal{E}^w = \theta^w S^w - p^w \mathcal{V}^w + \mu^w \mathcal{M}^w + c_{wn}^w \mathcal{A}^{wn} + c_{ws}^w \mathcal{A}^{ws} \quad (15a)$$

$$\mathcal{E}^n = \theta^n S^n - p^n \mathcal{V}^n + \mu^n \mathcal{M}^n + c_{wn}^n \mathcal{A}^{wn} + c_{ns}^n \mathcal{A}^{ns} \quad (15b)$$

and

$$\mathcal{E}^s = \theta^s S^s - \sigma^s : \mathcal{V}_0^s \mathbf{E}^s + \mu^s \mathcal{M}^s + c_{ws}^s \mathcal{A}^{ws} + c_{ns}^s \mathcal{A}^{ns} \quad (15c)$$

As an example, note that the partial derivative of  $\mathcal{E}^w$  with respect to one of its independent variables, as listed in eqn (14a), is simply equal to the coefficient of that variable in eqn (15a). Similar observations apply for all the phase energies as well as the interface and common line energies to be discussed subsequently.

Now convert eqns (15a), (15b) and (15c) such that they are on a per unit system volume basis:

$$\begin{aligned} \hat{\mathcal{E}}^w(\hat{\eta}^w, \epsilon^w, \epsilon^w \rho^w, a^{wn}, a^{ws}) \\ = \theta^w \hat{\eta}^w - p^w \epsilon^w + \mu^w \epsilon^w \rho^w + c_{wn}^w a^{wn} + c_{ws}^w a^{ws} \end{aligned} \quad (16a)$$

$$\begin{aligned} \hat{\mathcal{E}}^n(\hat{\eta}^n, \epsilon^n, \epsilon^n \rho^n, a^{wn}, a^{ns}) \\ = \theta^n \hat{\eta}^n - p^n \epsilon^n + \mu^n \epsilon^n \rho^n + c_{wn}^n a^{wn} + c_{ns}^n a^{ns} \end{aligned} \quad (16b)$$

$$\begin{aligned} \hat{\mathcal{E}}^s\left(\hat{\eta}^s, \frac{\epsilon^s \mathbf{E}^s}{j}, \epsilon^s \rho^s, a^{ws}, a^{ns}\right) \\ = \theta^s \hat{\eta}^s - \sigma^s : \epsilon^s \mathbf{E}^s / j + \mu^s \epsilon^s \rho^s + c_{ws}^s a^{ws} + c_{ns}^s a^{ns} \end{aligned} \quad (16c)$$

Make use of the definition of the grand canonical potential:

$$\hat{\Omega}^\alpha = \hat{\mathcal{E}}^\alpha - \theta^\alpha \hat{\eta}^\alpha - \mu^\alpha \epsilon^\alpha \rho^\alpha. \quad (17)$$

and employ Legendre transformations on  $\hat{\eta}^\alpha$  and  $\epsilon^\alpha \rho^\alpha$  to obtain:

$$\hat{\Omega}^w(\theta^w, \epsilon^w, \mu^w, a^{wn}, a^{ws}) = -p^w \epsilon^w + c_{wn}^w a^{wn} + c_{ws}^w a^{ws} \quad (18a)$$

$$\hat{\Omega}^n(\theta^n, \epsilon^n, \mu^n, a^{wn}, a^{ns}) = -p^n \epsilon^n + c_{wn}^n a^{wn} + c_{ns}^n a^{ns} \quad (18b)$$

$$\hat{\Omega}^s\left(\hat{\theta}^s, \frac{\epsilon^s \mathbf{E}^s}{j}, \mu^s, a^{ws}, a^{ns}\right) = -\sigma^s : \epsilon^s \mathbf{E}^s / j + c_{ws}^s a^{ws} + c_{ns}^s a^{ns} \quad (18c)$$

where

$$\frac{\partial \hat{\Omega}^\alpha}{\partial \theta^\alpha} = -\hat{\eta}^\alpha \quad (18d)$$

$$\frac{\partial \hat{\Omega}^\alpha}{\partial \epsilon^\alpha} = -p^\alpha \quad \alpha = w, n \quad (18e)$$

$$\frac{\partial \hat{\Omega}^s}{\partial (\epsilon^s \mathbf{E}^s / j)} = -\sigma^s \quad (18f)$$

$$\frac{\partial \hat{\Omega}^\alpha}{\partial \mu^\alpha} = -\epsilon^\alpha \rho^\alpha \quad (18g)$$

$$\frac{\partial \hat{\Omega}^\alpha}{\partial a^{\alpha\beta}} = c_{\alpha\beta}^\alpha. \quad (18h)$$

For eqns (16a), (16b) and (16c), it is also worth noting that their respective Gibbs–Duhem equations are:

$$0 = \hat{\eta}^w d\theta^w - \epsilon^w dp^w + \epsilon^w \rho^w d\mu^w + a^{wn} dc_{wn}^w + a^{ws} dc_{ws}^w \quad (19a)$$

$$0 = \hat{\eta}^n d\theta^n - \epsilon^n dp^n + \epsilon^n \rho^n d\mu^n + a^{wn} dc_{wn}^n + a^{ns} dc_{ns}^n \quad (19b)$$

and

$$0 = \hat{\eta}^s d\theta^s - \frac{\epsilon^s \mathbf{E}^s}{j} : d\sigma^s + \epsilon^s \rho^s d\mu^s + a^{ws} dc_{ws}^s + a^{ns} dc_{ns}^s. \quad (19c)$$

## 4.3 Constitutive postulates for interfacial energy functions

The dependence of the internal energy of the interfaces on their properties are postulated as:

$$\mathcal{E}^{wn} = \mathcal{E}^{wn}(S^{wn}, \mathcal{A}^{wn}, \mathcal{M}^{wn}, \mathcal{V}^w, \mathcal{V}^n, \mathcal{L}^{wns}) \quad (20a)$$

$$\mathcal{E}^{ws} = \mathcal{E}^{ws}(S^{ws}, \mathcal{A}^{ws}, \mathcal{M}^{ws}, \mathcal{V}^w, \mathcal{V}_0^s \mathbf{E}^s, \mathcal{L}^{wns}) \quad (20b)$$

$$\mathcal{E}^{ns} = \mathcal{E}^{ns}(S^{ns}, \mathcal{A}^{ns}, \mathcal{M}^{ns}, \mathcal{V}^n, \mathcal{V}_0^s \mathbf{E}^s, \mathcal{L}^{wns}) \quad (20c)$$

Here the common line length is included as an indicator of the length of the boundary of the interface, a measure of whether the microscale areas are small and distributed or large. The inclusion of the volumes of the adjacent fluid phases and the strain tensor of the adjacent solid phase adds generality that may be important when the amount of volume per area is small. The Euler forms of the energy equations are:

$$\begin{aligned} \mathcal{E}^{wn} &= \theta^{wn} \mathcal{S}^{wn} + \gamma^{wn} \mathcal{A}^{wn} + \mu^{wn} \mathcal{M}^{wn} - c_w^{wn} \mathcal{V}^w \\ &\quad - c_n^{wn} \mathcal{V}^n - c_{wns}^{wn} \mathcal{L}^{wns} \end{aligned} \quad (21a)$$

$$\begin{aligned} \mathcal{E}^{ws} &= \theta^{ws} \mathcal{S}^{ws} + \gamma^{ws} \mathcal{A}^{ws} + \mu^{ws} \mathcal{M}^{ws} - c_w^{ws} \mathcal{V}^w \\ &\quad - \sigma^{ws} : \mathcal{V}_0^s \mathbf{E}^s - c_{wns}^{ws} \mathcal{L}^{wns} \end{aligned} \quad (21b)$$

$$\begin{aligned} \mathcal{E}^{ns} &= \theta^{ns} \mathcal{S}^{ns} + \gamma^{ns} \mathcal{A}^{ns} + \mu^{ns} \mathcal{M}^{ns} - c_n^{ns} \mathcal{V}^n \\ &\quad - \sigma^{ns} : \mathcal{V}_0^s \mathbf{E}^s - c_{wns}^{ns} \mathcal{L}^{wns} \end{aligned} \quad (21c)$$

Conversion of these expressions to a per-unit-volume basis where  $\hat{E}^{\alpha\beta}$  is the energy per unit volume of medium gives:

$$\begin{aligned} \hat{E}^{wn} &= \hat{E}^{wn}(\hat{\eta}^{wn}, a^{wn}, a^{wn} \rho^{wn}, \epsilon^w, \epsilon^n, l^{wns}) \\ &= \theta^{wn} \hat{\eta}^{wn} + \gamma^{wn} a^{wn} + \mu^{wn} a^{wn} \rho^{wn} - c_w^{wn} \epsilon^w \\ &\quad - c_n^{wn} \epsilon^n - c_{wns}^{wn} l^{wns} \end{aligned} \quad (22a)$$

$$\begin{aligned} \hat{E}^{ws} &= \hat{E}^{ws}(\hat{\eta}^{ws}, a^{ws}, a^{ws} \rho^{ws}, \epsilon^w, \epsilon^s \mathbf{E}^s / j, l^{wns}) \\ &= \theta^{ws} \hat{\eta}^{ws} + \gamma^{ws} a^{ws} + \mu^{ws} a^{ws} \rho^{ws} - c_w^{ws} \epsilon^w \\ &\quad - \sigma^{ws} : \epsilon^s \mathbf{E}^s / j - c_{wns}^{ws} l^{wns} \end{aligned} \quad (22b)$$

$$\begin{aligned} \hat{E}^{ns} &= \hat{E}^{ns}(\hat{\eta}^{ns}, a^{ns}, a^{ns} \rho^{ns}, \epsilon^n, \epsilon^s \mathbf{E}^s / j, l^{wns}) \\ &= \theta^{ns} \hat{\eta}^{ns} + \gamma^{ns} a^{ns} + \mu^{ns} a^{ns} \rho^{ns} - c_n^{ns} \epsilon^n \\ &\quad - \sigma^{ns} : \epsilon^s \mathbf{E}^s / j - c_{wns}^{ns} l^{wns} \end{aligned} \quad (22c)$$

Make use of the definition of the grand canonical potential of the form:

$$\hat{\Omega}^{\alpha\beta} = \hat{E}^{\alpha\beta} - \theta^{\alpha\beta} \hat{\eta}^{\alpha\beta} - \mu^{\alpha\beta} a^{\alpha\beta} \rho^{\alpha\beta} \quad (23)$$

and Legendre transformation of the independent variables  $\hat{\eta}^{\alpha\beta}$  and  $a^{\alpha\beta} \rho^{\alpha\beta}$  to obtain:

$$\begin{aligned} \hat{\Omega}^{wn} &= \hat{\Omega}^{wn}(\theta^{wn}, a^{wn}, \mu^{wn}, \epsilon^w, \epsilon^n, l^{wns}) \\ &= \gamma^{wn} a^{wn} - c_w^{wn} \epsilon^w - c_n^{wn} \epsilon^n - c_{wns}^{wn} l^{wns} \end{aligned} \quad (24a)$$

$$\begin{aligned} \hat{\Omega}^{ws} &= \hat{\Omega}^{ws}(\theta^{ws}, a^{ws}, \mu^{ws}, \epsilon^w, \epsilon^s \mathbf{E}^s / j, l^{wns}) \\ &= \gamma^{ws} a^{ws} - c_w^{ws} \epsilon^w - \sigma^{ws} : \epsilon^s \mathbf{E}^s / j - c_{wns}^{ws} l^{wns} \end{aligned} \quad (24b)$$

$$\begin{aligned} \hat{\Omega}^{ns} &= \hat{\Omega}^{ns}(\theta^{ns}, a^{ns}, \mu^{ns}, \epsilon^n, \epsilon^s \mathbf{E}^s / j, l^{wns}) \\ &= \gamma^{ns} a^{ns} - c_n^{ns} \epsilon^n - \sigma^{ns} : \epsilon^s \mathbf{E}^s / j - c_{wns}^{ns} l^{wns} \end{aligned} \quad (24c)$$

where

$$\frac{\partial \hat{\Omega}^{\alpha\beta}}{\partial \theta^{\alpha\beta}} = -\hat{\eta}^{\alpha\beta} \quad (24d)$$

$$\frac{\partial \hat{\Omega}^{\alpha\beta}}{\partial a^{\alpha\beta}} = \gamma^{\alpha\beta} \quad (24e)$$

$$\frac{\partial \hat{\Omega}^{\alpha\beta}}{\partial \mu^{\alpha\beta}} = -a^{\alpha\beta} \rho^{\alpha\beta} \quad (24f)$$

$$\frac{\partial \hat{\Omega}^{\alpha\beta}}{\partial \epsilon^\alpha} = -c_\alpha^{\alpha\beta} \quad (24g)$$

$$\frac{\partial \hat{\Omega}^{\alpha\beta}}{\partial (\epsilon^s \mathbf{E}^s / j)} = -\sigma^{\alpha\beta} \quad (24h)$$

$$\frac{\partial \hat{\Omega}^{\alpha\beta}}{\partial l^{wns}} = -c_{wns}^{\alpha\beta} \quad (24i)$$

From eqns (22a), (22b) and (22c), the Gibbs–Duhem equations for the interfacial energies are obtained, respectively, as:

$$\begin{aligned} 0 &= \hat{\eta}^{wn} d\theta^{wn} + a^{wn} d\gamma^{wn} + a^{wn} \rho^{wn} d\mu^{wn} - \epsilon^w dc_w^{wn} \\ &\quad - \epsilon^n dc_n^{wn} - l^{wns} dc_{wns}^{wn} \end{aligned} \quad (25a)$$

$$\begin{aligned} 0 &= \hat{\eta}^{ws} d\theta^{ws} + a^{ws} d\gamma^{ws} + a^{ws} \rho^{ws} d\mu^{ws} - \epsilon^w dc_w^{ws} \\ &\quad - \frac{\epsilon^s \mathbf{E}^s}{j} : d\sigma^{ws} - l^{wns} dc_{wns}^{ws} \end{aligned} \quad (25b)$$

and

$$\begin{aligned} 0 &= \hat{\eta}^{ns} d\theta^{ns} + a^{ns} d\gamma^{ns} + a^{ns} \rho^{ns} d\mu^{ns} - \epsilon^n dc_n^{ns} \\ &\quad - \frac{\epsilon^s \mathbf{E}^s}{j} : d\sigma^{ns} - l^{wns} dc_{wns}^{ns} \end{aligned} \quad (25c)$$

#### 4.4 Constitutive postulate for the common line energy function

The three-phase system under consideration may have a common line, but no common points. The dependence of the internal energy of the common line on its extensive variables is postulated as:

$$\mathcal{E}^{wns} = \mathcal{E}^{wns}(\mathcal{S}^{wns}, \mathcal{L}^{wns}, \mathcal{M}^{wns}, \mathcal{A}^{wn}, \mathcal{A}^{ws}, \mathcal{A}^{ns}) \quad (26)$$

The Euler form of the common line energy equation is:

$$\begin{aligned} \mathcal{E}^{wns} &= \theta^{wns} \mathcal{S}^{wns} - \gamma^{wns} \mathcal{L}^{wns} + \mu^{wns} \mathcal{M}^{wns} + c_{wn}^{wns} \mathcal{A}^{wn} \\ &\quad + c_{ws}^{wns} \mathcal{A}^{ws} + c_{ns}^{wns} \mathcal{A}^{ns} \end{aligned} \quad (27)$$

Conversion of this expression to a per-unit-volume basis where  $\hat{E}^{wns}$  is the energy per unit volume of system gives:

$$\begin{aligned} \hat{E}^{wns} &= \hat{E}^{wns}(\hat{\eta}^{wns}, l^{wns}, l^{wns} \rho^{wns}, a^{wn}, a^{ws}, a^{ns}) \\ &= \theta^{wns} \hat{\eta}^{wns} - \gamma^{wns} l^{wns} + \mu^{wns} l^{wns} \rho^{wns} + c_{wn}^{wns} a^{wn} \\ &\quad + c_{ws}^{wns} a^{ws} + c_{ns}^{wns} a^{ns} \end{aligned} \quad (28)$$

Make use of the definition of the grand canonical potential:

$$\hat{\Omega}^{wns} = \hat{E}^{wns} - \theta^{wns} \hat{\eta}^{wns} - \mu^{wns} l^{wns} \rho^{wns} \quad (29)$$

and apply a Legendre transformation to the variables  $\hat{\eta}^{wns}$

and  $l^{wns} \rho^{wns}$  to obtain:

$$\begin{aligned} \hat{\Omega}^{wns}(\theta^{wns}, l^{wns}, \mu^{wns}, a^{wn}, a^{ws}, a^{ns}) \\ = -\gamma^{wns} l^{wns} + c_{wn}^{wns} a^{wn} + c_{ws}^{wns} a^{ws} + c_{ns}^{wns} a^{ns} \end{aligned} \quad (30a)$$

where

$$\frac{\partial \hat{\Omega}^{wns}}{\partial \theta^{wns}} = -\hat{\eta}^{wns} \quad (30b)$$

$$\frac{\partial \hat{\Omega}^{wns}}{\partial l^{wns}} = -\gamma^{wns} \quad (30c)$$

$$\frac{\partial \hat{\Omega}^{wns}}{\partial \mu^{wns}} = -l^{wns} \rho^{wns} \quad (30d)$$

$$\frac{\partial \hat{\Omega}^{wns}}{\partial a^{\alpha\beta}} = c_{\alpha\beta}^{wns} \quad (30e)$$

The Gibbs–Duhem equation for the common line is obtained from the differential of eqn (28) as:

$$\begin{aligned} 0 = \hat{\eta}^{wns} d\theta^{wns} - l^{wns} d\gamma^{wns} + l^{wns} \rho^{wns} d\mu^{wns} + a^{wn} dc_{wn}^{wns} \\ + a^{ws} dc_{ws}^{wns} + a^{ns} dc_{ns}^{wns} \end{aligned} \quad (31)$$

The grand canonical potentials developed above are useful functions for incorporation into the entropy inequality so that some information concerning constitutive functions may be obtained. They will be expanded in terms of their independent variables in the next section.

## 5 EXPANSION OF ENTROPY INEQUALITY FUNCTIONS IN TERMS OF INDEPENDENT VARIABLES

The grand canonical potentials have been defined in eqns (17), (23) and (29). The material derivatives of these equations are calculated and then used to eliminate the material derivatives of entropy in eqn (10). Then the mass and energy conservation equations are substituted in to eliminate the material derivatives of mass per volume and internal energy per volume and obtain the following form.

*Entropy inequality for three-phase system*

$$\begin{aligned} - \sum_{\alpha} \frac{1}{\theta^{\alpha}} \left[ \frac{D^{\alpha} \hat{\Omega}^{\alpha}}{Dt} + \hat{\eta}^{\alpha} \frac{D^{\alpha} \theta^{\alpha}}{Dt} + \epsilon^{\alpha} \rho^{\alpha} \frac{D^{\alpha} \mu^{\alpha}}{Dt} \right] \\ + \sum_{\alpha} \frac{1}{\theta^{\alpha}} (\epsilon^{\alpha} \mathbf{t}^{\alpha} - \hat{\Omega}^{\alpha} \mathbf{I}) : \mathbf{d}^{\alpha} \\ - \sum_{\alpha\beta} \frac{1}{\theta^{\alpha\beta}} \left[ \frac{D^{\alpha\beta} \hat{\Omega}^{\alpha\beta}}{Dt} + \hat{\eta}^{\alpha\beta} \frac{D^{\alpha\beta} \theta^{\alpha\beta}}{Dt} + a^{\alpha\beta} \rho^{\alpha\beta} \frac{D^{\alpha\beta} \mu^{\alpha\beta}}{Dt} \right] \\ + \sum_{\alpha\beta} \frac{1}{\theta^{\alpha\beta}} (a^{\alpha\beta} \mathbf{t}^{\alpha\beta} - \hat{\Omega}^{\alpha\beta} \mathbf{I}) : \mathbf{d}^{\alpha\beta} \end{aligned}$$

$$\begin{aligned} - \frac{1}{\theta^{wns}} \left[ \frac{D^{wns} \hat{\Omega}^{wns}}{Dt} + \hat{\eta}^{wns} \frac{D^{wns} \theta^{wns}}{Dt} + l^{wns} \rho^{wns} \frac{D^{wns} \mu^{wns}}{Dt} \right] \\ + \frac{1}{\theta^{wns}} (l^{wns} \mathbf{t}^{wns} - \hat{\Omega}^{wns} \mathbf{I}) : \mathbf{d}^{wns} \\ - \sum_{\alpha\beta} \frac{1}{\theta^{wns}} \hat{\mathbf{T}}_{wns}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta, wns} - \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{1}{\theta^{\alpha\beta}} \hat{\mathbf{T}}_{\alpha\beta}^{\alpha} \cdot \mathbf{v}^{\alpha, \alpha\beta} \\ + \sum_{\alpha} \frac{\epsilon^{\alpha}}{(\theta^{\alpha})^2} \mathbf{q}^{\alpha} \cdot \nabla \theta^{\alpha} + \sum_{\alpha\beta} \frac{a^{\alpha\beta}}{(\theta^{\alpha\beta})^2} \mathbf{q}^{\alpha\beta} \cdot \nabla \theta^{\alpha\beta} \\ + \frac{l^{wns}}{(\theta^{wns})^2} \mathbf{q}^{wns} \cdot \nabla \theta^{wns} - \sum_{\alpha} \nabla \cdot \left[ \epsilon^{\alpha} \left( \phi^{\alpha} - \frac{\mathbf{q}^{\alpha}}{\theta^{\alpha}} \right) \right] \\ - \sum_{\alpha\beta} \nabla \cdot \left[ a^{\alpha\beta} \left( \phi^{\alpha\beta} - \frac{\mathbf{q}^{\alpha\beta}}{\theta^{\alpha\beta}} \right) \right] - \nabla \cdot \left[ l^{wns} \left( \phi^{wns} - \frac{\mathbf{q}^{wns}}{\theta^{wns}} \right) \right] \\ - \sum_{\alpha} \left[ \epsilon^{\alpha} \rho^{\alpha} \left( b^{\alpha} - \frac{h^{\alpha}}{\theta^{\alpha}} \right) \right] - \sum_{\alpha\beta} \left[ a^{\alpha\beta} \rho^{\alpha\beta} \left( b^{\alpha\beta} - \frac{h^{\alpha\beta}}{\theta^{\alpha\beta}} \right) \right] \\ - l^{wns} \rho^{wns} \left( b^{wns} - \frac{h^{wns}}{\theta^{wns}} \right) \\ - \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\hat{\epsilon}_{\alpha\beta}^{\alpha}}{\theta^{\alpha\beta}} \left[ \frac{\Omega^{\alpha} \theta^{\alpha, \alpha\beta}}{\theta^{\alpha}} + \eta^{\alpha} \theta^{\alpha, \alpha\beta} + \mu^{\alpha, \alpha\beta} + \frac{1}{2} (v^{\alpha, \alpha\beta})^2 \right] \\ - \sum_{\alpha\beta} \frac{\hat{\epsilon}_{wns}^{\alpha\beta}}{\theta^{wns}} \left[ \frac{\Omega^{\alpha\beta} \theta^{\alpha\beta, wns}}{\theta^{\alpha\beta}} + \eta^{\alpha\beta} \theta^{\alpha\beta, wns} \right. \\ \left. + \mu^{\alpha\beta, wns} + \frac{1}{2} (v^{\alpha\beta, wns})^2 \right] - \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\theta^{\alpha, \alpha\beta}}{\theta^{\alpha} \theta^{\alpha\beta}} \hat{\mathcal{Q}}_{\alpha\beta}^{\alpha} \\ - \sum_{\alpha\beta} \frac{\theta^{\alpha\beta, wns}}{\theta^{\alpha\beta} \theta^{wns}} \hat{\mathcal{Q}}_{wns}^{\alpha\beta} \geq 0 \end{aligned} \quad (32)$$

An alternative to substitution of the conservation equations into the entropy inequality was proposed by Liu<sup>33</sup> whereby the conservation equations are multiplied by a Lagrange multiplier and added to the entropy inequality as constraints. A variation on the Lagrange multiplier approach has also been used by Murad *et al.*<sup>39</sup> with success in the study of swelling clays. However, the eventual results obtained using the Lagrange multiplier approach in the current study would not be different from those obtained using the substitution approach.

To exploit eqn (32), it is necessary to expand the material derivatives of the grand canonical potential in terms of the independent variables. This is done in Appendix A for the phases, interfaces, and the common line taking into account supplemental information provided by the conservation equations. Substitution of the expansions provided by eqns (88), (93), (96), (99) and (102) into entropy inequality (32) provides the form of the entropy inequality consistent with the thermodynamic postulates employed thus far:

Entropy inequality for three-phase system

$$\begin{aligned}
\Lambda = & \left\{ \frac{\epsilon^s}{j} \left[ \frac{\sigma^s}{\theta^s} + \frac{\sigma^{ws}}{\theta^{ws}} + \frac{\sigma^{ns}}{\theta^{ns}} \right] : [(\nabla_{\mathbf{x}} \mathbf{F}^s)(\nabla_{\mathbf{x}} \mathbf{F}^s)^T - \mathbf{E}^s \mathbf{I}] \right. \\
& + \frac{1}{\theta^s} [\epsilon^s \mathbf{t}^s - \hat{\Omega}^s \mathbf{I}] : \mathbf{d}^s + \sum_{\alpha=w,n} \frac{1}{\theta^\alpha} (\epsilon^\alpha \mathbf{t}^\alpha - \hat{\Omega}^\alpha \mathbf{I}) : \mathbf{d}^\alpha \\
& + \sum_{\alpha\beta} \frac{1}{\theta^{\alpha\beta}} (a^{\alpha\beta} \mathbf{t}^{\alpha\beta} - \hat{\Omega}^{\alpha\beta} \mathbf{I}) : \mathbf{d}^{\alpha\beta} \\
& + \frac{1}{\theta^{wns}} (l^{wns} \mathbf{t}^{wns} - \hat{\Omega}^{wns} \mathbf{I}) : \mathbf{d}^{wns} \\
& + \sum_{\alpha=w,n} \left[ \left( \sum_{\beta \neq \alpha} \frac{c_\alpha^{\alpha\beta}}{\theta^{\alpha\beta}} + \frac{p^\alpha}{\theta^\alpha} \right) \frac{D^s \epsilon^\alpha}{Dt} \right] \\
& + \left( \frac{\sigma^{ws}}{\theta^{ws}} + \frac{\sigma^{ns}}{\theta^{ns}} + \frac{\sigma^s}{\theta^s} \right) : \left( \frac{\mathbf{E}^s}{j} \right) \frac{D^s \epsilon^s}{Dt} \\
& - \sum_{\alpha\beta} \left( \frac{c_{\alpha\beta}^\alpha}{\theta^\alpha} + \frac{c_{\alpha\beta}^\beta}{\theta^\beta} + \frac{c_{\alpha\beta}^{wns}}{\theta^{wns}} + \frac{\gamma^{\alpha\beta}}{\theta^{\alpha\beta}} \right) \frac{D^s a^{\alpha\beta}}{Dt} \\
& + \left( \frac{c_{wns}^{wn}}{\theta^{wn}} + \frac{c_{wns}^{ws}}{\theta^{ws}} + \frac{c_{wns}^{ns}}{\theta^{ns}} + \frac{\gamma^{wns}}{\theta^{wns}} \right) \frac{D^s l^{wns}}{Dt} \\
& - \sum_{\alpha=w,n} \frac{1}{\theta^\alpha} \mathbf{v}^{\alpha,s} \cdot [-p^\alpha \nabla \epsilon^\alpha + c_{wn}^\alpha \nabla a^{wn} + c_{\alpha s}^\alpha \nabla a^{\alpha s}] \\
& - \frac{1}{\theta^{wn}} \mathbf{v}^{wn,s} \cdot [\gamma^{wn} \nabla a^{wn} - c_w^{wn} \nabla \epsilon^w - c_n^{wn} \nabla \epsilon^n - c_{wns}^{wn} \nabla l^{wns}] \\
& - \sum_{\alpha=w,n} \frac{1}{\theta^{\alpha s}} \mathbf{v}^{\alpha s,s} \cdot \left[ \gamma^{\alpha s} \nabla a^{\alpha s} - c_\alpha^{\alpha s} \nabla \epsilon^\alpha - \sigma^{\alpha s} : \nabla \left( \frac{\epsilon^s \mathbf{E}^s}{j} \right) \right. \\
& \left. - c_{wns}^{\alpha s} \nabla l^{wns} \right] - \frac{1}{\theta^{wns}} \mathbf{v}^{wns,s} \cdot [-\gamma^{wns} \nabla l^{wns} + c_{wn}^{wns} \nabla a^{wn} \\
& + c_{ws}^{wns} \nabla a^{ws} + c_{ns}^{wns} \nabla a^{ns}] - \sum_{\alpha\beta} \frac{1}{\theta^{wns}} \hat{\mathbf{T}}_{wns}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta,wns} \\
& - \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{1}{\theta^{\alpha\beta}} \hat{\mathbf{T}}_{\alpha\beta}^\alpha \cdot \mathbf{v}^{\alpha,\alpha\beta} + \sum_{\alpha} \frac{\epsilon^\alpha}{(\theta^\alpha)^2} \mathbf{q}^\alpha \cdot \nabla \theta^\alpha \\
& + \sum_{\alpha\beta} \frac{a^{\alpha\beta}}{(\theta^{\alpha\beta})^2} \mathbf{q}^{\alpha\beta} \cdot \nabla \theta^{\alpha\beta} + \frac{l^{wns}}{(\theta^{wns})^2} \mathbf{q}^{wns} \cdot \nabla \theta^{wns} \\
& - \sum_{\alpha} \nabla \cdot \left[ \epsilon^\alpha \left( \phi^\alpha - \frac{\mathbf{q}^\alpha}{\theta^\alpha} \right) \right] \\
& - \sum_{\alpha\beta} \nabla \cdot \left[ a^{\alpha\beta} \left( \phi^{\alpha\beta} - \frac{\mathbf{q}^{\alpha\beta}}{\theta^{\alpha\beta}} \right) \right] \\
& - \nabla \cdot \left[ l^{wns} \left( \phi^{wns} - \frac{\mathbf{q}^{wns}}{\theta^{wns}} \right) \right] - \sum_{\alpha} \left[ \epsilon^\alpha \rho^\alpha \left( b^\alpha - \frac{h^\alpha}{\theta^\alpha} \right) \right] \\
& - \sum_{\alpha\beta} \left[ a^{\alpha\beta} \rho^{\alpha\beta} \left( b^{\alpha\beta} - \frac{h^{\alpha\beta}}{\theta^{\alpha\beta}} \right) \right] \\
& - l^{wns} \rho^{wns} \left( b^{wns} - \frac{h^{wns}}{\theta^{wns}} \right)
\end{aligned}$$

$$\begin{aligned}
& - \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\hat{\epsilon}_{\alpha\beta}^\alpha}{\theta^{\alpha\beta}} \left[ \frac{\Omega^{\alpha} \theta^{\alpha,\alpha\beta}}{\theta^\alpha} + \eta^{\alpha} \theta^{\alpha,\alpha\beta} + \mu^{\alpha,\alpha\beta} + \frac{1}{2} (v^{\alpha,\alpha\beta})^2 \right] \\
& - \sum_{\alpha\beta} \frac{\hat{\epsilon}_{wns}^{\alpha\beta}}{\theta^{wns}} \left[ \frac{\Omega^{\alpha\beta} \theta^{\alpha\beta,wns}}{\theta^{\alpha\beta}} + \eta^{\alpha\beta} \theta^{\alpha\beta,wns} \right. \\
& \left. + \mu^{\alpha\beta,wns} + \frac{1}{2} (v^{\alpha\beta,wns})^2 \right] - \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\theta^{\alpha,\alpha\beta}}{\theta^\alpha \theta^{\alpha\beta}} \hat{\mathcal{Q}}_{\alpha\beta}^\alpha \\
& - \sum_{\alpha\beta} \frac{\theta^{\alpha\beta,wns}}{\theta^{\alpha\beta} \theta^{wns}} \hat{\mathcal{Q}}_{wns}^{\alpha\beta} \geq 0
\end{aligned} \tag{33}$$

At this point, simplifying assumptions will be made that impose some restrictions on the dynamic system behavior, but nevertheless leave the system sufficiently general to describe many physical realizations.

**Assumption IV** The fluids and solid are assumed to form simple thermodynamic systems<sup>16</sup> such that:

$$\phi^\alpha - \frac{\mathbf{q}^\alpha}{\theta^\alpha} = 0; \quad b^\alpha - \frac{h^\alpha}{\theta^\alpha} = 0 \quad \alpha = w, n, s \tag{34a}$$

$$\phi^{\alpha\beta} - \frac{\mathbf{q}^{\alpha\beta}}{\theta^{\alpha\beta}} = 0; \quad b^{\alpha\beta} - \frac{h^{\alpha\beta}}{\theta^{\alpha\beta}} = 0 \quad \alpha\beta = wn, ws, ns \tag{34b}$$

and

$$\phi^{wns} - \frac{\mathbf{q}^{wns}}{\theta^{wns}} = 0; \quad b^{wns} - \frac{h^{wns}}{\theta^{wns}} = 0 \tag{34c}$$

These relations are appropriate for many systems, but will have to be modified in the future when considering multi-constituent phases.

**Assumption V** Any changes in temperature are assumed to occur slowly enough that the temperature at a macroscopic point in the system is unique (i.e., the phase, interface, and common line temperatures at a point are equal).

Note that this restriction does not preclude the existence of temperature gradients in the system or restrict the study to isothermal cases. It is a reasonable assumption for systems in which the dynamic changes are occurring slowly enough for the temperature to locally equilibrate.

In addition to these assumptions, some identities and definitions will be used to reorganize the terms involving material derivatives of void fractions and interfacial areas. First, recall that the void fractions of the phases may be expressed in terms of the porosity,  $\epsilon$ , and the saturations of the fluid phases according to:

$$\epsilon^s = 1 - \epsilon \tag{35a}$$

$$\epsilon^w = s^w \epsilon \tag{35b}$$

$$\epsilon^n = s^n \epsilon = (1 - s^w) \epsilon. \tag{35c}$$

These identities indicate that only two parameters are needed to identify the void fractions of the phases. In

addition because the three phase system consists of a very slightly deformable matrix plus the wetting and non-wetting fluids, it will be convenient to replace the two variables  $a^{ws}$  and  $a^{ns}$  by the variables  $x_s^{ws}$  and  $a^s$  in the material derivative of a fluid solid interfacial area where:

$$a^s = a^{ws} + a^{ns} \quad (36a)$$

and

$$x_s^{ws} = a^{ws}/a^s = 1 - x_s^{ns}. \quad (36b)$$

It must be emphasized that this change in geometric variables in no way diminishes the generality of the formulation but is convenient in considering the internal geometry of the system.

Application of constraints (34a) through (34c) to entropy inequality (33), multiplication by the single temperature, and use of the alternative geometric variables as convenient restates the entropy inequality as follows.

#### Uni-thermal entropy inequality for three-phase system

$$\begin{aligned} \theta \Lambda = & \left\{ \frac{\epsilon^s}{j} [\sigma^s + \sigma^{ws} + \sigma^{ns}] : [(\nabla_{\mathbf{x}} \mathbf{F}^s)(\nabla_{\mathbf{x}} \mathbf{F}^s)^T - \mathbf{E}^s \mathbf{I}] \right. \\ & + \epsilon^s \mathbf{t}^s - \hat{\Omega}^s \mathbf{I} \Big\} : \mathbf{d}^s + \sum_{\alpha=w,n} (\epsilon^\alpha \mathbf{t}^\alpha - \hat{\Omega}^\alpha \mathbf{I}) : \mathbf{d}^\alpha \\ & + \sum_{\alpha\beta} (a^{\alpha\beta} \mathbf{t}^{\alpha\beta} - \hat{\Omega}^{\alpha\beta} \mathbf{I}) : \mathbf{d}^{\alpha\beta} + (l^{wns} \mathbf{t}^{wns} - \hat{\Omega}^{wns} \mathbf{I}) : \mathbf{d}^{wns} \\ & - \left[ (\sigma^s + \sigma^{ws} + \sigma^{ns}) : \frac{\mathbf{E}^s}{j} - s^w (c_w^{ws} + c_w^{wn} + p^w) \right. \\ & - s^n (c_n^{ns} + c_n^{wn} + p^n) \Big] \frac{D^s \epsilon}{Dt} \\ & - \epsilon [(c_n^{ns} + c_n^{wn} + p^n) - (c_w^{ws} + c_w^{wn} + p^w)] \frac{D^s s^w}{Dt} \\ & - [x_s^{ws} (c_{ws}^w + c_{ws}^s + c_{ws}^{wns} + \gamma^{ws}) \\ & + x_s^{ns} (c_{ns}^n + c_{ns}^s + c_{ns}^{wns} + \gamma^{ns})] \frac{D^s a^s}{Dt} \\ & - a^s [(c_{ws}^w + c_{ws}^s + c_{ws}^{wns} + \gamma^{ws}) \\ & - (c_{ns}^n + c_{ns}^s + c_{ns}^{wns} + \gamma^{ns})] \frac{D^s x_s^{ws}}{Dt} \\ & - (c_{wn}^w + c_{wn}^n + c_{wn}^{wns} + \gamma^{wn}) \frac{D^s a^{wn}}{Dt} \\ & + (c_{wns}^{wn} + c_{wns}^{ws} + c_{wns}^{ns} + \gamma^{wns}) \frac{D^s l^{wns}}{Dt} \\ & - \sum_{\alpha=w,n} \mathbf{v}^{\alpha,s} \cdot [\hat{\mathbf{T}}_{wn}^\alpha + \hat{\mathbf{T}}_{cs}^\alpha - p^\alpha \nabla \epsilon^\alpha + c_{wn}^\alpha \nabla a^{wn} \\ & + c_{cs}^\alpha \nabla a^{\alpha s}] - \mathbf{v}^{wn,s} \cdot [\hat{\mathbf{T}}_{wns}^{wn} - \hat{\mathbf{T}}_{wn}^w - \hat{\mathbf{T}}_{wn}^n + \gamma^{wn} \nabla a^{wn} \\ & - c_w^{wn} \nabla \epsilon^w - c_n^{wn} \nabla \epsilon^n - c_{wns}^{wn} \nabla l^{wns}] \end{aligned}$$

$$\begin{aligned} & - \sum_{\alpha=w,n} \mathbf{v}^{\alpha,s} \cdot [\hat{\mathbf{T}}_{wns}^{\alpha s} - \hat{\mathbf{T}}_{cs}^\alpha - \hat{\mathbf{T}}_{cs}^s + \gamma^{\alpha s} \nabla a^{\alpha s} - c_{cs}^{\alpha s} \nabla \epsilon^\alpha \\ & - \sigma^{\alpha s} : \nabla \left( \frac{\epsilon^s \mathbf{E}^s}{j} \right) - c_{wns}^{\alpha s} \nabla l^{wns}] \\ & - \mathbf{v}^{wns,s} \cdot [\hat{\mathbf{T}}_{wns}^{wn} - \hat{\mathbf{T}}_{wns}^{ws} - \hat{\mathbf{T}}_{wns}^{ns} - \gamma^{wns} \nabla l^{wns} \\ & + c_{wn}^{wns} \nabla a^{wn} + c_{ws}^{wns} \nabla a^{ws} + c_{ns}^{wns} \nabla a^{ns}] + \sum_{\alpha} \frac{\epsilon^\alpha}{\theta} \mathbf{q}^\alpha \cdot \nabla \theta \\ & + \sum_{\alpha\beta} \frac{a^{\alpha\beta}}{\theta} \mathbf{q}^{\alpha\beta} \cdot \nabla \theta + \frac{l^{wns}}{\theta} \mathbf{q}^{wns} \cdot \nabla \theta \\ & - \sum_{\alpha} \sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^\alpha \left[ (\mu^\alpha - \mu^{\alpha\beta}) + \frac{1}{2} (v^{\alpha,\alpha\beta})^2 \right] \\ & - \sum_{\alpha\beta} \hat{e}_{wns}^{\alpha\beta} \left[ (\mu^{\alpha\beta} - \mu^{wns}) + \frac{1}{2} (v^{\alpha\beta,wns})^2 \right] \geq 0 \quad (37) \end{aligned}$$

This form of the entropy inequality is still very general, and contains significant challenges for determining the appropriate balance equations, at least in part because of the interactions among the phases, interfaces, and common lines as accounted for in the thermodynamic postulates that lead to the 'c' coefficients. An additional complicating factor lies in the absence of enough equations to completely determine the system. As was mentioned earlier, equations for the geometric parameters are needed but not available. Nevertheless, this inequality does provide a path to appropriate forms of the governing conservation equations for certain conditions that will require experimental support. However, it is useful to consider some of the features of the inequality and discuss how it might be employed most effectively.

## 6 CONSIDERATIONS FOR THE ENTROPY INEQUALITY

To facilitate this general discussion of the entropy inequality, a notationally representative form of eqn (37) will be employed that accounts for all the types of terms encountered, but leaves out the complete superscript notation and assumes summation over repeated indices. First, it can be shown that summation of the component grand canonical potentials gives the system grand canonical potential:

$$\hat{\Omega} = \hat{\Omega}^w + \hat{\Omega}^n + \hat{\Omega}^s + \hat{\Omega}^{wn} + \hat{\Omega}^{ws} + \hat{\Omega}^{ns} + \hat{\Omega}^{wns} \quad (38a)$$

whose functional dependence, for the unithermal case, may be expressed as:

$$\hat{\Omega} = \hat{\Omega}(\theta, \mu^w, \mu^n, \mu^s, \mu^{wn}, \mu^{ws}, \mu^{ns}, \mu^{wns}, \mathbf{E}^s/j, \epsilon, s^w, a^s, x_s^{ws}, a^{wn}, l^{wns}) \quad (38b)$$

The Lagrangian time derivative of  $\hat{\Omega}$  moving at the solid phase velocity taken while holding the first nine variables listed in eqn (38b) constant (i.e., the temperature, chemical

potentials, and solid deformation divided by the jacobian) can be shown to be equal to the sum of the six terms involving material derivatives in eqn (37). Thus the entropy inequality in outline form is:

$$\theta \Lambda = \mathbf{b}^m : \mathbf{d}^m - \mathbf{v}^{m,s} \cdot \mathbf{e}^m + \frac{\mathbf{q}}{\theta} \cdot \nabla \theta - \frac{D^s \hat{\Omega}}{Dt} \Big|_{\theta, \mu^i, \mathbf{E}^s f_j} - f_m^r \hat{e}_m^r \geq 0 \quad (39)$$

where summation over the repeated indices  $m$  and  $r$  is presumed with these indices taking on the values  $w, n, s, wn, ws, ns, wns$ ; the notation  $\mu^i$  indicates that all seven of the chemical potentials are being held constant when evaluating the Lagrangian time derivative; and  $\mathbf{b}^m$ ,  $\mathbf{e}^m$ ,  $\mathbf{q}$ , and  $\hat{e}_m^r$  are functions of the variables,  $\mathbf{z}$ , in list (11). It is useful to note that each of the terms in this equation will be zero at equilibrium. An important obstacle to proper exploitation of the inequality is the equation deficit that has arisen because of the geometric variables. The absence of additional equations in terms of the six geometric variables is the reason the time derivative of the grand canonical potential remains explicitly present in the entropy inequality.

Balance equations in these geometric terms are needed but, at present, are not definitively available. However, some approximations may be made that allow one to proceed forward to obtain reasonable approximations. The derivation of the approximations used here is found in Appendix B. The procedure is based strictly on the application of averaging theorems to the geometric regions with no consideration given to thermodynamic constraints. The following three relations are obtained which can be used to eliminate  $D^s a^s/Dt$ ,  $D^s a^{wn}/Dt$ , and  $D^s l^{wns}/Dt$  from the entropy inequality:

$$\frac{D^s a^s}{Dt} + J_s^s \frac{D^s \epsilon}{Dt} = 0 \quad (40)$$

$$\frac{D^s a^{wn}}{Dt} - J_{wn}^w \epsilon \frac{D^s s^w}{Dt} - a^s \cos \Phi \frac{D^s x_s^{ws}}{Dt} = 0 \quad (41)$$

$$\frac{D^s l^{wns}}{Dt} + \kappa_g^{ws} a^s \frac{D^s x_s^{ws}}{Dt} = 0. \quad (42)$$

A difficulty with these three relations is the fact that four new variables are introduced relating to the macroscale average curvature of the interface ( $J_s^s$  for the solid surface as defined in eqn (108); and  $J_{wn}^w$  for the interface between the fluids as defined in eqn (126)), a macroscale measure of the contact angle  $\Phi$  defined in eqn (137), and a macroscale measure of the geodesic curvature of the common line  $\kappa_g^{ws}$  as provided in eqn (145b). It should not be surprising that such parameters arise as they account for the way that microscale differences in geometric structure evidence themselves at the macroscale. In Appendix C, the relationship of these four variables to thermodynamic quantities are developed based on material to be presented subsequently in the main body of text. Thus, if the equilibrium functional form of the energy is known, these coefficients can be

determined. Typically, such a full representation will not be known, however, and the parameters will be specified based on experimental measurements of specific processes.

Although these three equations can be imposed as additional constraints on the system, a three-equation deficit still remains that must be overcome to deal with the terms  $D^s \epsilon/Dt$ ,  $D^s s^w/Dt$ , and  $D^s x_s^{ws}/Dt$  that survive in the entropy inequality. Note, however, that if more precise balance equations for the material derivatives of the geometric quantities become available, the final system of governing equations for porous media flow can be improved or made more generally applicable.

With the geometric constraints incorporated, exploitation of the entropy inequality will make use of an assumption concerning the remaining three time derivatives of geometric quantities. This may be stated as follows:

**Assumption VI** Three additional balance equations for the geometric quantities involving their material derivatives, although unknown, are such that they do not alter the terms in the entropy inequality of the form  $\mathbf{b}^m : \mathbf{d}^m$ ,  $\mathbf{v}^{m,s} \cdot \mathbf{e}^m$ ,  $\mathbf{q} \cdot \nabla \theta$ , and  $f_m^r \hat{e}_m^r$ .

This assumption may seem rather speculative, but, in fact, it is operationally equivalent to stating that the equation deficit may be overcome by considering ‘near equilibrium’ conditions such that  $D^s \epsilon/Dt$ ,  $D^s s^w/Dt$ , and  $D^s x_s^{ws}/Dt$  may be taken as being proportional to their multipliers in the entropy inequality. The physical basis for making this assumption is the expectation that the changes in the geometry of the phases, interfaces, and common line should not have an impact on the mechanisms of heat transfer, mass exchange, or stress within each of these regions. Certainly, if the results obtained under the limitations of this assumption turn out to be without merit, an alternative strategy will have to be developed for overcoming the lack of governing equations.

The impact of Assumption VI is to allow the exploitation of the entropy inequality to be separated into two primary steps. The first step involves determination of the conservation equations for the system. This step makes use of the following observations and manipulations with respect to eqn (39).

- Because the symmetric rate of strain tensors  $\mathbf{d}^m$ , for all  $m$  are not included in list (11) as independent variables of the system, the entropy production may not depend on these quantities. Therefore each of the quantities in eqn (37) represented by  $\mathbf{b}^m$  in eqn (39) must be zero.
- Each of the quantities in eqn (37) represented as  $\mathbf{e}^m$  (i.e. the quantities that are dotted with velocity vectors) will be zero at equilibrium. A truncated Taylor expansion of these quantities in terms of the independent variables of the problem provides an approximation for  $\mathbf{e}^m$  as being linear proportional to the relative velocities (with respect to the solid

phase) of component  $m$  and of the components of the system that are in contact with  $m$ . Although the quantities  $\mathbf{e}^m$  would also be linearly proportional to  $\nabla\theta$ , this effect is not considered in the present derivation.

- The heat conduction vector,  $\mathbf{q}$ , is zero at equilibrium and is proportional to  $\nabla\theta$  when determined from a truncated Taylor series expansion. Dependence of  $\mathbf{q}$  on the velocities is not considered here.
- The mass exchange terms,  $\hat{e}_m^r$ , are each zero at equilibrium. Under the assumption that each term is dependent only on the state of the  $m$  and  $r$  components, a truncated Taylor series expansion allows each term to be expressed as proportional to  $f_m^r$ .

The completion of this step provides governing conservation equations with constitutive coefficients.

The set of equations, however, still must be closed in a second step that provides three auxiliary conditions for the rates of change of the three geometric properties that remain in the entropy inequality. As mentioned, these terms will be obtained by linearization at 'near equilibrium' conditions in terms of their multipliers in the entropy inequality. Again, it must be emphasized that the relations developed in this second step will be approximate and subject to improvement in the future.

In the next section the first step will be implemented to develop the equations of mass and momentum conservation. For simplicity, the energy equations will not be written explicitly as emphasis will be focused on the flow equations. The energy equations may be obtained directly by substitution of the constitutive forms into the general expressions.

## 7 MASS AND MOMENTUM BALANCES

The development of the conservation equations will proceed according to step one as outlined above. Because none of the constitutive functions are considered to depend on the symmetric strain tensors, the coefficients of  $\mathbf{d}^\alpha$ ,  $\mathbf{d}^{\alpha\beta}$ , and  $\mathbf{d}^{wns}$  must be zero. From inequality (37) and the expression for the grand canonical potential in eqns (18a)–(18c), (24a)–(24c) and (30a), the following forms of the stress tensor are obtained:

$$\epsilon^\alpha \mathbf{t}^\alpha = \hat{\Omega}^\alpha \mathbf{I} = (-p^\alpha \epsilon^\alpha + c_{wn}^\alpha a^{wn} + c_{\alpha s}^\alpha a^{\alpha s}) \mathbf{I} \quad \alpha = w, n \quad (43a)$$

$$\epsilon^s \mathbf{t}^s = \hat{\Omega}^s \mathbf{I} - \frac{\epsilon^s}{j} [\sigma^s + \sigma^{ws} + \sigma^{ns}] : [(\nabla_x \mathbf{F}^s)(\nabla_x \mathbf{F}^s)^T - \mathbf{E}^s \mathbf{I}] \quad (43b)$$

$$a^{wn} \mathbf{t}^{wn} = \hat{\Omega}^{wn} \mathbf{I} = (\gamma^{wn} a^{wn} - c_w^{wn} \epsilon^w - c_n^{wn} \epsilon^n - c_{wns}^{wn} l^{wns}) \mathbf{I} \quad (43c)$$

$$a^{\alpha s} \mathbf{t}^{\alpha s} = \hat{\Omega}^{\alpha s} \mathbf{I} = (\gamma^{\alpha s} a^{\alpha s} - c_\alpha^{\alpha s} \epsilon^\alpha - \epsilon^s \sigma^{\alpha s} : \mathbf{E}^s / j - c_{wns}^{\alpha s} l^{wns}) \mathbf{I} \quad \alpha = w, n \quad ((43d))$$

$$l^{wns} \mathbf{t}^{wns} = \hat{\Omega}^{wns} \mathbf{I} = (-\gamma^{wns} l^{wns} + c_{wn}^{wns} a^{wn} + c_{ws}^{wns} a^{ws} + c_{ns}^{wns} a^{ns}) \mathbf{I} \quad (43e)$$

The terms that multiply the velocities in inequality (37) will be zero at equilibrium. Therefore, the following definitions apply where all the  $\tau_v$  quantities are zero at equilibrium:

$$\tau_v^\alpha = -(\hat{\mathbf{T}}_{\alpha s}^\alpha + \hat{\mathbf{T}}_{wn}^\alpha) + p^\alpha \nabla \epsilon^\alpha - c_{wn}^\alpha \nabla a^{wn} - c_{\alpha s}^\alpha \nabla a^{\alpha s} \quad \alpha = w, n \quad (44a)$$

$$\tau_v^{wn} = \hat{\mathbf{T}}_{wn}^w + \hat{\mathbf{T}}_{wn}^n - \hat{\mathbf{T}}_{wns}^{wn} - \gamma^{wn} \nabla a^{wn} + c_w^{wn} \nabla \epsilon^w + c_n^{wn} \nabla \epsilon^n + c_{wns}^{wn} \nabla l^{wns} \quad (44b)$$

$$\tau_v^{\alpha s} = \hat{\mathbf{T}}_{\alpha s}^\alpha + \hat{\mathbf{T}}_{\alpha s}^s - \hat{\mathbf{T}}_{wns}^{\alpha s} - \gamma^{\alpha s} \nabla a^{\alpha s} + c_\alpha^{\alpha s} \nabla \epsilon^\alpha + \sigma^{\alpha s} : \nabla \left( \frac{\epsilon^s \mathbf{E}^s}{j} \right) + c_{wns}^{\alpha s} \nabla l^{wns} \quad \alpha = w, n \quad (44c)$$

$$\tau_v^{wns} = \hat{\mathbf{T}}_{wns}^{wn} + \hat{\mathbf{T}}_{wns}^{ws} + \hat{\mathbf{T}}_{wns}^{ns} + \gamma^{wns} \nabla l^{wns} - c_{wn}^{wns} \nabla a^{wn} - c_{ws}^{wns} \nabla a^{ws} - c_{ns}^{wns} \nabla a^{ns} \quad (44d)$$

The summation of terms that multiply the temperature gradient in the entropy inequality will also be zero at equilibrium. This sum is denoted as  $\mathbf{q}$  such that:

$$\mathbf{q} = \epsilon^w \mathbf{q}^w + \epsilon^n \mathbf{q}^n + \epsilon^s \mathbf{q}^s + a^{wn} \mathbf{q}^{wn} + a^{ws} \mathbf{q}^{ws} + a^{ns} \mathbf{q}^{ns} + l^{wns} \mathbf{q}^{wns} \quad (45)$$

Finally, the quantities that multiply the phase exchange terms must also be zero at equilibrium such that the following quantities may be defined, which are zero at equilibrium:

$$\tau_{\alpha\beta}^\alpha = \mu^{\alpha\beta} - \mu^\alpha - \frac{1}{2}(v^{\alpha, \alpha\beta})^2 \quad (46a)$$

$$\tau_{wns}^{\alpha\beta} = \mu^{wns} - \mu^{\alpha\beta} - \frac{1}{2}(v^{\alpha\beta, wns})^2 \quad (46b)$$

Substitution of eqns (43a), (43b), (43c), (43d), (43e), (44a), (44b), (44c), (45), (46a) and (46b) into inequality (37), with the terms relating to the material derivatives of the geometric properties expressed in terms of the material derivative of the grand canonical potential yields the following.

*The residual entropy inequality*

$$\begin{aligned} \theta \Lambda = & \sum_{\alpha=w, n} \mathbf{v}^{\alpha, s} \cdot \tau_v^\alpha + \sum_{\alpha\beta} \mathbf{v}^{\alpha\beta, s} \cdot \tau_v^{\alpha\beta} + \mathbf{v}^{wns, s} \cdot \tau_v^{wns} \\ & + \frac{\mathbf{q}}{\theta} \cdot \nabla \theta - \frac{D^s \hat{\Omega}}{Dt} \Big|_{\theta, \mu^m, \mathbf{E}^s / j} + \sum_{\alpha} \sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^\alpha \tau_{\alpha\beta}^\alpha \\ & + \sum_{\alpha\beta} \hat{e}_{wns}^{\alpha\beta} \tau_{wns}^{\alpha\beta} \geq 0 \end{aligned} \quad (47)$$

As a consequence of these relations, some of the constitutive forms required in the conservation equations may be

deduced. Here attention is focused on the mass and momentum equations for the fluids and the interfaces. Substitution of the definitions in eqns (43a) and (44a) into the phase mass and momentum conservation equations yields the following.

*Macroscale mass conservation for the  $\alpha$ -phase*

$$\frac{D^\alpha(\epsilon^\alpha \rho^\alpha)}{Dt} + \epsilon^\alpha \rho^\alpha \nabla \cdot \mathbf{v}^\alpha = \sum_{\beta \neq \alpha} \hat{e}_{\alpha\beta}^\alpha \quad \alpha = w, n \quad (48)$$

*Macroscale momentum conservation for the  $\alpha$ -phase*

$$\begin{aligned} \epsilon^\alpha \rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} + \epsilon^\alpha \nabla p^\alpha - a^{wn} \nabla c_{wn}^\alpha - a^{\alpha s} \nabla c_{\alpha s}^\alpha \\ - \epsilon^\alpha \rho^\alpha \mathbf{g}^\alpha = -\boldsymbol{\tau}_v^\alpha \quad \alpha = w, n \end{aligned} \quad (49)$$

For an interface between phases, the form of the mass conservation equation is the same regardless of the type of interface. Thus, the mass balance equation is as in eqn (4).

*Macroscale mass conservation for the  $\alpha\beta$ -interface*

$$\begin{aligned} \frac{D^{\alpha\beta}(a^{\alpha\beta} \rho^{\alpha\beta})}{Dt} + a^{\alpha\beta} \rho^{\alpha\beta} \nabla \cdot \mathbf{v}^{\alpha\beta} \\ = -(\hat{e}_{\alpha\beta}^\alpha + \hat{e}_{\alpha\beta}^\beta) + \hat{e}_{wns}^{\alpha\beta} \quad \alpha\beta = wn, ws, ns \end{aligned} \quad (50)$$

For the fluid–fluid interface, the constitutive relations of importance are given in eqns (43c) and (44b) while the constitutive forms for the fluid–solid interfaces are given in eqns (43d) and (44c). After application of these expressions to eqn (5), the momentum balances are of the following form.

*Macroscale momentum conservation for the  $\alpha\beta$ -interface*

$$\begin{aligned} a^{wn} \rho^{wn} \frac{D^{wn} \mathbf{v}^{wn}}{Dt} - a^{wn} \nabla \gamma^{wn} + \epsilon^w \nabla c_w^{wn} + \epsilon^n \nabla c_n^{wn} \\ + l^{wns} \nabla c_{wns}^{wn} - a^{wn} \rho^{wn} \mathbf{g}^{wn} = - \sum_{i=w,n} \hat{e}_{wn}^i \mathbf{v}^{i,wn} - \boldsymbol{\tau}_v^{wn} \end{aligned} \quad (51a)$$

and

$$\begin{aligned} a^{\alpha s} \rho^{\alpha s} \frac{D^{\alpha s} \mathbf{v}^{\alpha s}}{Dt} - a^{\alpha s} \nabla \gamma^{\alpha s} + \epsilon^\alpha \nabla c_\alpha^{\alpha s} + \frac{\epsilon^s \mathbf{E}^s}{j} : \nabla \boldsymbol{\sigma}^{\alpha s} \\ + l^{wns} \nabla c_{wns}^{\alpha s} - a^{\alpha s} \rho^{\alpha s} \mathbf{g}^{\alpha s} = - \sum_{i=\alpha,s} \hat{e}_{wn}^i \mathbf{v}^{i,\alpha s} - \boldsymbol{\tau}_v^{\alpha s} \end{aligned} \quad (51b)$$

For the common line, the constitutive relations of importance are given in eqns (43e) and (44d). These do not alter the mass conservation equation for the common line so that the flow equations are as follows.

*Macroscale mass conservation for the wns-common line*

$$\frac{D^{wns}(l^{wns} \rho^{wns})}{Dt} + l^{wns} \rho^{wns} \nabla \cdot \mathbf{v}^{wns} = -(\hat{e}_{wns}^{wn} + \hat{e}_{wns}^{ws} + \hat{e}_{wns}^{ns}) \quad (52)$$

*Macroscale momentum balance for the wns-common line*

$$\begin{aligned} l^{wns} \rho^{wns} \frac{D^{wns} \mathbf{v}^{wns}}{Dt} + l^{wns} \nabla \gamma^{wns} - a^{wn} \nabla c_{wn}^{wns} - a^{ws} \nabla c_{ws}^{wns} \\ - a^{ns} \nabla c_{ns}^{wns} - l^{wns} \rho^{wns} \mathbf{g}^{wns} \\ = - \sum_{ij=wn,ws,ns} \hat{e}_{wns}^{ij} \mathbf{v}^{ij,wns} - \boldsymbol{\tau}_v^{wns} \end{aligned} \quad (53)$$

Consider a linearization of residual entropy inequality (47) whereby each of the quantities  $\boldsymbol{\tau}_v^m$  is obtained from a Taylor series expansion around the velocity terms for phases, interfaces, and common lines with which the  $m$ th part of the system is in contact. Movement of a phase with respect to the solid will be resisted due to viscous effects. However, movement of any of the interfaces adjacent to that phase will tend to encourage movement of the phase; this phenomenon has been called a viscous coupling effect by Rose.<sup>41</sup> Therefore, the linearizations are expressed as follows where it might be expected that all the coefficients are positive semi-definite tensors and the impact of the  $\mathbf{r}$  coefficients will be less than that of the  $\mathbf{R}$  terms:

$$\boldsymbol{\tau}_v^\alpha = \mathbf{R}^\alpha \cdot \mathbf{v}^{\alpha,s} - \mathbf{r}_{\alpha s}^\alpha \cdot \mathbf{v}^{\alpha s,s} - \mathbf{r}_{wn}^\alpha \cdot \mathbf{v}^{wn,s} \quad \alpha = w, n \quad (54a)$$

$$\boldsymbol{\tau}_v^{wn} = \mathbf{R}^{wn} \cdot \mathbf{v}^{wn,s} - \mathbf{r}_w^{wn} \cdot \mathbf{v}^{w,s} - \mathbf{r}_n^{wn} \cdot \mathbf{v}^{n,s} - \mathbf{r}_{wns}^{wn} \cdot \mathbf{v}^{wns,s} \quad (54b)$$

$$\boldsymbol{\tau}_v^{\alpha s} = \mathbf{R}^{\alpha s} \cdot \mathbf{v}^{\alpha s,s} - \mathbf{r}_\alpha^{\alpha s} \cdot \mathbf{v}^{\alpha,s} - \mathbf{r}_{wns}^{\alpha s} \cdot \mathbf{v}^{wns,s} \quad \alpha = w, n \quad (54c)$$

$$\boldsymbol{\tau}_v^{wns} = \mathbf{R}^{wns} \cdot \mathbf{v}^{wns,s} - \mathbf{r}_{wn}^{wns} \cdot \mathbf{v}^{wn,s} - \mathbf{r}_{ws}^{wns} \cdot \mathbf{v}^{ws,s} - \mathbf{r}_{ns}^{wns} \cdot \mathbf{v}^{ns,s} \quad (54d)$$

Note that in obtaining this expression, the possible expression of  $\boldsymbol{\tau}_v^m$  as a linear function of  $\nabla \theta$  has not been included. If the temperature gradient is high, an additional term expressing proportionality to the temperature gradient may be a needed addition to eqns (54a), (54b), (54c) and (54d). Similarly to the neglect of dependence of velocity deviation terms on  $\nabla \theta$ , the dependence of the heat conduction on velocity will also be considered unimportant. Thus the linearized version of the heat conduction vector will be:

$$\mathbf{q} = \mathbf{K} \cdot \nabla \theta. \quad (55)$$

For use in the energy equations for the phases, interfaces and common lines, the linearized heat conduction vectors of each component may be taken to be similar in form to eqn (55), each with its own conductivity tensor.

The terms  $\hat{e}_{\alpha\beta}^\alpha$  and  $\hat{e}_{wns}^{\alpha\beta}$  associated with phase change will also be linearized as functions of their coefficients in the



entropy inequality. Interactions between competing mass exchange processes will be assumed to be negligible such that cross terms may be neglected to obtain:

$$\hat{e}_{\alpha\beta}^{\alpha} = L_{\alpha\beta}^{\alpha} \tau_{\alpha\beta}^{\alpha} \quad (56a)$$

and

$$\hat{e}_{wns}^{\alpha\beta} = L_{wns}^{\alpha\beta} \tau_{wns}^{\alpha\beta} \quad (56b)$$

Note that if the  $\alpha\beta$  interface is massless:

$$\hat{e}_{\alpha\beta}^{\alpha} + \hat{e}_{\alpha\beta}^{\beta} = 0 \quad (57a)$$

and the linearized expression for mass exchange becomes:

$$\hat{e}_{\alpha\beta}^{\alpha} = L_{\alpha\beta}^{\alpha} (\tau_{\alpha\beta}^{\alpha} - \tau_{\alpha\beta}^{\beta}). \quad (57b)$$

If the  $wns$  common line is massless:

$$\hat{e}_{wns}^{wn} + \hat{e}_{wns}^{ws} + \hat{e}_{wns}^{ns} = 0 \quad (58a)$$

such that only two of the expressions for mass exchange between the interfaces and the common line are independent. Thus, the linearized exchange terms may be expressed as:

$$\hat{e}_{wns}^{\alpha\beta} = L_{wns}^{\alpha\beta} (\tau_{wns}^{\alpha\beta} - \tau_{wns}^{ns}) \quad \alpha\beta = wn, ws \quad (58b)$$

If both an  $\alpha\beta$  interface and the common line are massless, then:

$$\hat{e}_{wns}^{\alpha\beta} = 0. \quad (59)$$

Substitution of the linearizations provided by eqns (54a), (54b), (54c), (54d)–(56a) and (56b) into the mass and momentum conservation equations of the last section and into the residual entropy inequality, as appropriate, and neglecting advective terms, terms involving velocity squared, and the impact of phase change on the momentum equations yields the following.

*Macroscale mass conservation for the  $\alpha$ -phase*

$$\frac{D^{\alpha}(\epsilon^{\alpha} \rho^{\alpha})}{Dt} + \epsilon^{\alpha} \rho^{\alpha} \nabla \cdot \mathbf{v}^{\alpha} = \sum_{\beta \neq \alpha} L_{\alpha\beta}^{\alpha} (\mu^{\alpha\beta} - \mu^{\alpha}) \quad \alpha = w, n \quad (60)$$

*Macroscale momentum conservation for the  $\alpha$ -phase*

$$\begin{aligned} & -\epsilon^{\alpha} (\nabla p^{\alpha} - \rho^{\alpha} \mathbf{g}^{\alpha}) + a^{wn} \nabla c_{wn}^{\alpha} + a^{\alpha s} \nabla c_{\alpha s}^{\alpha} \\ & = \mathbf{R}^{\alpha} \cdot \mathbf{v}^{\alpha, s} - \mathbf{r}_{\alpha s}^{\alpha} \cdot \mathbf{v}^{\alpha s, s} - \mathbf{r}_{wn}^{\alpha} \cdot \mathbf{v}^{wn, s} \end{aligned} \quad (61)$$

*Macroscale mass conservation for the  $\alpha\beta$ -interface*

$$\begin{aligned} & \frac{D^{\alpha\beta}(a^{\alpha\beta} \rho^{\alpha\beta})}{Dt} + a^{\alpha\beta} \rho^{\alpha\beta} \nabla \cdot \mathbf{v}^{\alpha\beta} \\ & = -[L_{\alpha\beta}^{\alpha} (\mu^{\alpha\beta} - \mu^{\alpha}) + L_{\alpha\beta}^{\beta} (\mu^{\alpha\beta} - \mu^{\beta})] \\ & \quad + L_{wns}^{\alpha\beta} (\mu^{wns} - \mu^{\alpha\beta}) \quad \alpha\beta = wn, ws, ns \end{aligned} \quad (62)$$

*Macroscale momentum conservation for the  $\alpha\beta$ -interfaces*

$$\begin{aligned} & a^{wn} (\nabla \gamma^{wn} + \rho^{wn} \mathbf{g}^{wn}) - \epsilon^w \nabla c_w^{wn} - \epsilon^n \nabla c_n^{wn} - l^{wns} \nabla c_{wns}^{wn} \\ & = \mathbf{R}^{wn} \cdot \mathbf{v}^{wn, s} - \mathbf{r}_w^{wn} \cdot \mathbf{v}^{w, s} - \mathbf{r}_n^{wn} \cdot \mathbf{v}^{n, s} - \mathbf{r}_{wns}^{wn} \cdot \mathbf{v}^{wns, s} \end{aligned} \quad (63a)$$

$$\begin{aligned} & a^{\alpha s} (\nabla \gamma^{\alpha s} + \rho^{\alpha s} \mathbf{g}^{\alpha s}) - \epsilon^{\alpha} \nabla c_{\alpha}^{\alpha s} - \frac{\epsilon^s \mathbf{E}^s}{j} : \nabla \boldsymbol{\sigma}^{\alpha s} - l^{wns} \nabla c_{wns}^{\alpha s} \\ & = \mathbf{R}^{\alpha s} \cdot \mathbf{v}^{\alpha s, s} - \mathbf{r}_{\alpha}^{\alpha s} \cdot \mathbf{v}^{\alpha, s} - \mathbf{r}_{wns}^{\alpha s} \cdot \mathbf{v}^{wns, s} \quad \alpha = w, n \end{aligned} \quad (63b)$$

*Macroscale mass conservation for the  $wns$ -common line*

$$\begin{aligned} & \frac{D^{wns}(l^{wns} \rho^{wns})}{Dt} + l^{wns} \rho^{wns} \nabla \cdot \mathbf{v}^{wns} \\ & = - \sum_{\alpha\beta} L_{wns}^{\alpha\beta} (\mu^{wns} - \mu^{\alpha\beta}) \end{aligned} \quad (64)$$

*Macroscale momentum balance for the  $wns$ -common line*

$$\begin{aligned} & -l^{wns} (\nabla \gamma^{wns} - \rho^{wns} \mathbf{g}^{wns}) + a^{wn} \nabla c_{wn}^{wns} \\ & \quad + a^{ws} \nabla c_{ws}^{wns} + a^{ns} \nabla c_{ns}^{wns} \\ & = \mathbf{R}^{wns} \cdot \mathbf{v}^{wns, s} - \mathbf{r}_{wn}^{wns} \cdot \mathbf{v}^{wn, s} - \mathbf{r}_{ws}^{wns} \cdot \mathbf{v}^{ws, s} - \mathbf{r}_{ns}^{wns} \cdot \mathbf{v}^{ns, s} \end{aligned} \quad (65)$$

*The residual entropy inequality*

$$\begin{aligned} \theta \Lambda = & \sum_{\alpha = w, n} \mathbf{v}^{\alpha, s} \cdot \mathbf{R}^{\alpha} \cdot \mathbf{v}^{\alpha, s} + \sum_{\alpha\beta} \mathbf{v}^{\alpha\beta, s} \cdot \mathbf{R}^{\alpha\beta} \cdot \mathbf{v}^{\alpha\beta, s} \\ & + \mathbf{v}^{wns, s} \cdot \mathbf{R}^{wns} \cdot \mathbf{v}^{wns, s} \\ & - \sum_{\alpha = w, n} \sum_{\beta \neq \alpha} \mathbf{v}^{\alpha, s} \cdot [\mathbf{r}_{\alpha\beta}^{\alpha} + (\mathbf{r}_{\alpha}^{\alpha\beta})^T] \cdot \mathbf{v}^{\alpha\beta, s} \\ & - \sum_{\alpha\beta} \mathbf{v}^{\alpha\beta, s} \cdot [\mathbf{r}_{wns}^{\alpha\beta} + (\mathbf{r}_{\alpha\beta}^{wns})^T] \cdot \mathbf{v}^{wns, s} + \frac{1}{\theta} (\nabla \theta) \cdot \mathbf{K} \cdot \nabla \theta \\ & + \sum_{\alpha} \sum_{\beta \neq \alpha} L_{\alpha\beta}^{\alpha} [\mu^{\alpha\beta} - \mu^{\alpha}]^2 + \sum_{\alpha\beta} L_{wns}^{\alpha\beta} [\mu^{wns} - \mu^{\alpha\beta}]^2 \\ & - \left. \frac{D^s \hat{\Omega}}{Dt} \right|_{\theta, \mu^m, \mathbf{E}^s / j} \geq 0 \end{aligned} \quad (66)$$

If desired, Gibbs–Duhem eqn (19a) or eqn (19b) may be substituted into the phase momentum eqn (61) to obtain the alternative form:

$$\begin{aligned} & -\epsilon^{\alpha} (\rho^{\alpha} \nabla \mu^{\alpha} + \hat{\eta}^{\alpha} \nabla \theta^{\alpha} - \rho^{\alpha} \mathbf{g}^{\alpha}) \\ & = \mathbf{R}^{\alpha} \cdot \mathbf{v}^{\alpha, s} - \mathbf{r}_{\alpha s}^{\alpha} \cdot \mathbf{v}^{\alpha s, s} - \mathbf{r}_{wn}^{\alpha} \cdot \mathbf{v}^{wn, s} \quad \alpha = w, n \end{aligned} \quad (67)$$

Similar substitutions of Gibbs–Duhem eqns (25a), (25b) and (25c) may be made into the corresponding interface momentum eqns (63a) and (63b). For the case of a massless interface, only the term involving the temperature gradient

will survive on the left side of the interface momentum equation after this substitution has been made. For the common line, Gibbs–Duhem eqn (31) may be used to express the driving force for the flow as found on the left side of eqn (65) in terms of the chemical potential, gravity, and the temperature gradient. If the common line is massless, this chemical potential and gravitational terms will drop out. In the remainder of this text, the momentum equations in terms of the chemical potential will not be examined.

In eqns (60)–(66), the scalar coefficients  $L$  that appear are non-negative. When the solid material is isotropic, the flow resistance tensors are diagonal such that  $\mathbf{R} = R\mathbf{I}$  and  $\mathbf{r} = r\mathbf{I}$ . Eqns (60)–(65) are a set of 24 equations. If the thermodynamic constitutive forms for the energy of the phases, interfaces, and common lines are available such that the chemical potentials ( $\mu$ ), interfacial tensions ( $\gamma$ ), pressures ( $p$ ), and component interaction terms ( $c$ ) are known as functions of the primary variables, these 24 equations contain 30 unknowns (6 densities, 18 velocity components, and the 6 geometric parameters). Thus solution of these equations requires that information about the geometric parameters be available in the form of six equations or constitutive forms. Three of these six restrictions have been approximated as eqns (40)–(42). The remaining set of three equations will be developed based on the entropy inequality (66) and the thermodynamic postulates.

## 8 SUPPLEMENTARY GEOMETRIC CONDITIONS

The material derivative of the grand canonical potential that appears in eqn (66), which is equal to the sum of all the terms in eqn (37) involving time derivatives of geometric properties, can now be employed to obtain the required three additional conditions to close the system. Expansion of this term and insertion of the constraints provided in eqns (40)–(42) provides the following identity which can be substituted into residual entropy inequality (66):

$$\begin{aligned} -\frac{D^s \hat{\Omega}}{Dt} \Big|_{\theta, \mu^m, \mathbf{E}^s/j} &= -[(\sigma^{ws} + \sigma^{ns} + \sigma^s) : \mathbf{E}^s/j] \\ &- s^w(c_w^{ws} + c_w^{wn} + p^w) - s^n(c_n^{ns} + c_n^{wn} + p^n) \\ &- J_s^s x_s^{ws}(c_{ws}^w + c_{ws}^s + c_{ws}^{wns} + \gamma^{ws}) \\ &- J_s^s x_s^{ns}(c_{ns}^n + c_{ns}^s + c_{ns}^{wns} + \gamma^{ns}) \Big] \frac{D^s \epsilon}{Dt} \\ &- \epsilon[(c_n^{ns} + c_n^{wn} + p^n) - (c_w^{ws} + c_w^{wn} + p^w) \\ &+ J_{wn}^w(c_{wn}^w + c_{wn}^n + c_{wn}^{wns} + \gamma^{wn})] \frac{D^s s^w}{Dt} \\ &- a^s[(c_{ws}^w + c_{ws}^s + c_{ws}^{wns} + \gamma^{ws}) - (c_{ns}^n + c_{ns}^s + c_{ns}^{wns} + \gamma^{ns}) \\ &+ (c_{wn}^w + c_{wn}^n + c_{wn}^{wns} + \gamma^{wn}) \cos \Phi \\ &+ (c_{wns}^w + c_{wns}^s + c_{wns}^{ns} + \gamma^{wns}) \kappa_g^s] \frac{D^s x_s^{ws}}{Dt} \end{aligned} \quad (68)$$

Each of the time derivatives in this equation will be zero at equilibrium. If they are linearized in terms of the velocities and the temperature gradient using Taylor series expansions, the coefficients that appear in the expansion will be vectors. Because such coefficients must be isotropic, and the only isotropic vector is the null vector, the time derivatives  $D^s \epsilon/Dt$ ,  $D^s s^w/Dt$ , and  $D^s x_s^{ws}/Dt$  cannot be linearized as expansions in terms of vector quantities. The simplest linearization approach is to require that the coefficients of each of the three derivatives as given in eqn (68) be zero at equilibrium and assume that each derivative is linearly proportional to that coefficient. A more general approach would involve each derivative being linearly proportional to all three of the coefficients, but this will not be employed here. Therefore, the following linearized relations are assumed to apply:

$$\begin{aligned} L_\epsilon \frac{D^s \epsilon}{Dt} &= -[(\sigma^{ws} + \sigma^{ns} + \sigma^s) : \mathbf{E}^s/j - s^w(c_w^{ws} + c_w^{wn} + p^w) \\ &- s^n(c_n^{ns} + c_n^{wn} + p^n) - J_s^s x_s^{ws}(c_{ws}^w + c_{ws}^s + c_{ws}^{wns} + \gamma^{ws}) \\ &- J_s^s x_s^{ns}(c_{ns}^n + c_{ns}^s + c_{ns}^{wns} + \gamma^{ns})] \end{aligned} \quad (69)$$

$$\begin{aligned} L_s^w \frac{D^s s^w}{Dt} &= -\epsilon[(c_n^{ns} + c_n^{wn} + p^n) - (c_w^{ws} + c_w^{wn} + p^w) \\ &+ J_{wn}^w(c_{wn}^w + c_{wn}^n + c_{wn}^{wns} + \gamma^{wn})] \end{aligned} \quad (70)$$

$$\begin{aligned} L_x^{ws} \frac{D^s x_s^{ws}}{Dt} &= -a^s[(c_{ws}^w + c_{ws}^s + c_{ws}^{wns} + \gamma^{ws}) \\ &- (c_{ns}^n + c_{ns}^s + c_{ns}^{wns} + \gamma^{ns}) \\ &+ (c_{wn}^w + c_{wn}^n + c_{wn}^{wns} + \gamma^{wn}) \cos \Phi \\ &+ (c_{wns}^w + c_{wns}^s + c_{wns}^{ns} + \gamma^{wns}) \kappa_g^s] \end{aligned} \quad (71)$$

In these three equations, the multipliers of the time derivatives must be non-negative to assure that the entropy inequality is not violated. At equilibrium, the right side of each of these equations is zero. The derivation in Appendix C relates the geometric quantities in the right side of these equations to thermodynamic definitions such that:

$$J_s^s(a^s, \epsilon) = -\left(\frac{\partial a^s}{\partial \epsilon}\right)_{\theta, \mu^m, \mathbf{E}^s/j, a^{wn}, l^{wns}, s^w, x_s^{ws}, \hat{\Omega}} \quad (72)$$

$$J_{wn}^w(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon) = \frac{1}{\epsilon} \left(\frac{\partial a^{wn}}{\partial s^w}\right)_{\theta, \mu^m, \mathbf{E}^s/j, \epsilon, a^s, x_s^{ws}, l^{wns}, \hat{\Omega}} \quad (73)$$

$$\cos[\Phi(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon)] = \frac{1}{a^s} \left(\frac{\partial a^{wn}}{\partial x_s^{ws}}\right)_{\theta, \mu^m, \mathbf{E}^s/j, s^w, \epsilon, a^s, \hat{\Omega}} \quad (74)$$

$$\kappa_g^s(x_s^{ws}, l^{wns}, a^s) = -\frac{1}{a^s} \left(\frac{\partial l^{wns}}{\partial x_s^{ws}}\right)_{\theta, \mu^m, \mathbf{E}^s/j, s^w, \epsilon, a^s, \hat{\Omega}} \quad (75)$$

Thus eqns (40)–(42), (60)–(65) and (69)–(71) constitute a closed set of equations that can be used to model two-phase

flow in porous media. To demonstrate the utility of the equations, an example of a simple system that they describe will be presented.

## 9 EXAMPLE: SLOWLY-DEFORMING SOLID; NO PHASE CHANGE; NEGLIGIBLE INTERACTIONS

This example is presented so that the assumptions needed to simplify the general equations to those commonly used in multiphase porous media models will be explicitly identified. Heretofore, the assumptions have been intrinsic to the model and thus paths to improved models based on relaxed assumptions have not been apparent. The first set of assumptions to be applied are the following.

- The system is isothermal such that the dependence of equations and coefficients on temperature need not be considered.
- Transfer of material between phases is negligible. This is enforced mathematically in the general equation set either by setting the phase change terms ( $\hat{e}_{\alpha\beta}^{\alpha}$  and  $\hat{e}_{wns}^{\alpha\beta}$ ) to zero or by requiring the chemical potentials of the mass in each of the phases, interfaces, and the common line to be equal.
- The interfaces and common lines are taken to be massless ( $\rho^{\alpha\beta}$  and  $\rho^{wns}$  are zero). This assumption eliminates the need to consider the interface and common line mass balance equations in the formulation.
- The surface tensions of the interfaces and the lineal tension of the common line may all be treated as constants. This assumption eliminates the need to consider the momentum balance equations for the interfaces and common lines in the formulation.
- The velocities of the interfaces and common lines do not impact the phase velocities such that they can be neglected in the flow equations for the phases. This assumption allows the terms on the right side of flow eqn (61) with resistance coefficients of the form  $\mathbf{r}_{\alpha\beta}^{\alpha}$  to be neglected.
- The decomposition of the energy function into its component parts may be accomplished without considering the interactive effects of a phase with its boundaries, of an interface with the adjacent phases and its common line boundary, and of a common line with its adjacent interfaces. This assumption allows all the coefficients 'c' in the governing equations to be set to zero.
- The deformation of the solid matrix is such that the porosity and area of the solid phase may be considered to be time invariant. Thus eqns (40) and (69) are not needed as  $\epsilon$  and  $a^s$  are spatially dependent specified parameters of the problem.

These assumptions reduce the system of equations to the following set of 12 equations in the 14 variables  $\rho^w, \rho^n, s^w, \mathbf{v}^w, \mathbf{v}^n, p^w, p^n, a^{wn}, x_s^{ws},$  and  $l^{wns}$ .

*Macroscale mass conservation for the  $\alpha$ -phase*

$$\frac{D^\alpha(\epsilon^\alpha \rho^\alpha)}{Dt} + \epsilon^\alpha \rho^\alpha \nabla \cdot \mathbf{v}^\alpha = 0 \quad \alpha = w, n \quad (76)$$

*Macroscale momentum conservation for the  $\alpha$ -phase*

$$-\epsilon^\alpha (\nabla p^\alpha - \rho^\alpha \mathbf{g}^\alpha) = \mathbf{R}^\alpha \cdot \mathbf{v}^{\alpha,s} \quad \alpha = w, n \quad (77)$$

*Constitutive equation for the fluid–fluid interface*

$$\frac{D^s a^{wn}}{Dt} - J_{wn}^w \epsilon \frac{D^s s^w}{Dt} - a^s \cos \Phi \frac{D^s x_s^{ws}}{Dt} = 0 \quad (78)$$

*Constitutive equation for the common line*

$$\frac{D^s l^{wns}}{Dt} + \kappa_g^{ws} a^s \frac{D^s x_s^{ws}}{Dt} = 0 \quad (79)$$

*Constitutive equation for saturation*

$$L_s^w \frac{D^s s^w}{Dt} = -\epsilon [p^n - p^w + J_{wn}^w \gamma^{wn}] \quad (80)$$

*Constitutive equation for wetted fraction of solid surface*

$$L_x^{ws} \frac{D^s x_s^{ws}}{Dt} = -a^s [\gamma^{ws} - \gamma^{ns} + \gamma^{wn} \cos \Phi + \kappa_g^{ws} \gamma^{wns}] \quad (81)$$

Two equations of state for the density in terms of pressure (for the isothermal system), as alternatives to the functional form of the energy functions of the phases, must be specified to obtain an equal number of equations and primary unknowns.

*Equation of state*

$$\rho^\alpha = \rho^\alpha(p^\alpha) \quad \alpha = w, n \quad (82)$$

Functional forms must be available for the following quantities:

$$J_{wn}^w = J_{wn}^w(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon) \quad (83a)$$

$$\cos \Phi = \cos \Phi(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon) \quad (83b)$$

$$\kappa_g^{ws} = \kappa_g^{ws}(x_s^{ws}, l^{wns}, a^s) \quad (83c)$$

These quantities are, respectively, the average fluid–fluid interfacial curvature, the cosine of the average contact angle of the wetting phase with the solid, and the average geodesic curvature, with respect to the interface between the wetting and solid phases, of the common line. The influence of dynamic conditions on these quantities must also be accounted for. Note also that eqn (80) provides the equilibrium condition on the pressure difference between the two fluid phases. This capillary pressure,  $p^c$ , is defined

such that:

$$p^c(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon) = -\gamma^{wn} J_{wn}^w \\ = -\frac{\gamma^{wn}}{\epsilon} \left( \frac{\partial a^{wn}}{\partial s^w} \right)_{\theta, \mu^m, E^s/j, \epsilon, \alpha^s, x_s^{ws}, l^{wns}, \hat{\Omega}} \quad (84)$$

Therefore, the equilibrium condition resulting from eqn (80) is:

$$p^n - p^w - p^c = 0 \quad (85)$$

Capillary pressure is usually obtained experimentally as a function of saturation only. However, the derivation here indicates that it actually has a broader functional dependence. The parameters  $\mathbf{R}^w$ ,  $\mathbf{R}^n$ ,  $L_s^w$ , and  $L_x^{ws}$  that appear in the equations must be specified in order to mathematically complete the system.

Although the set of eqns (76)–(84) employs a large number of simplifications, they must be simplified further to obtain the most widely used set of equations by making the additional assumptions.

- There is no explicit dependence of the system behavior on the interfacial area between the fluid phases  $a^{wn}$ , the fraction of the solid phase surface in contact with the wetting fluid  $x_s^{ws}$ , or the common line length  $l^{wns}$ . As a consequence, these variables may be eliminated from the problem along with eqns (78), (79) and (81); and the functions in eqns (83b) and (83c) are not required. The capillary pressure in eqn (84) and, de facto, the fluid–fluid interfacial curvature  $J_{wn}^w$ , are assigned reduced functional forms such that they depend only on saturation, the specified solid surface area, and the specified system porosity.
- The disequilibrium between the capillary pressure and the pressures in the phases may be neglected so that eqn (80) may be replaced by its equilibrium form as given in eqn (85) with  $p^c = p^c(s^w)$ .

The equations obtained with these additional assumptions are those commonly employed in modeling multiphase systems. Through the years, a large amount of effort has been put into obtaining the functional form of the dependence of the coefficients  $\mathbf{R}^w$  and  $\mathbf{R}^n$  (or their inverses which are related to relative permeability) on  $s^w$  and of the equilibrium  $p^c(s^w)$  relation such that dynamic systems can be studied (e.g., Refs 6,7,11,28,30,31,42,44,46). However, much less effort has been expended in determining which of the simplifying assumptions made in developing the governing equations and restricting the functional dependences of these quantities to saturation only are violated in the systems under study (e.g., Ref 8). These violations carry much of the responsibility for difficulties in obtaining robust and accurate models.

## 10 CONCLUSION

The derivation of equations of flow of two immiscible fluids in a porous media system has been achieved. The derivation

requires that the entropy inequality, subjected to internal geometric constraints, be applied to gain constitutive forms that close the system. Even in a simplified system, knowledge of the evolution of the interfacial area between phases and of the functional form of the capillary pressure is essential to a model that is based on the system physics. Here, assumptions were identified that the flow system must satisfy if the standard multiphase equations are to be used. Thus, consideration of a problem of interest in light of these assumptions may lead one to conclude that a model more complex than the simplified form is required. These more complex models carry with them the burden of requiring more complete thermodynamic relations for the phases, interfaces, and common lines and more parameters that must be measured. However, the physical processes that each of these parameters account for are known; and this should give rise to innovative experimental and simulation programs that allow for their quantification. Thus a route to more complete models has been developed which is followed by eliminating assumptions made to the general model. This is a more satisfying route than one that is based on heuristic addition of terms to simple equations that seem to be helpful in allowing the model to match data.

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## APPENDIX A. EXPANSIONS OF GRAND CANONICAL POTENTIALS

Incorporation of the Lagrangian time derivative of the grand canonical potential into the entropy inequality requires that the derivative be expanded in terms of the independent variables. These expansions are obtained in this appendix.

### Fluid phases

For a fluid phase, from eqns (18a) and (18b), the derivative of the grand canonical potential is:

$$\begin{aligned} \frac{D^\alpha \hat{\Omega}^\alpha}{Dt} = & \frac{\partial \hat{\Omega}^\alpha}{\partial \theta^\alpha} \frac{D^\alpha \theta^\alpha}{Dt} + \frac{\partial \hat{\Omega}^\alpha}{\partial \epsilon^\alpha} \frac{D^\alpha \epsilon^\alpha}{Dt} + \frac{\partial \hat{\Omega}^\alpha}{\partial \mu^\alpha} \frac{D^\alpha \mu^\alpha}{Dt} \\ & + \frac{\partial \hat{\Omega}^\alpha}{\partial a^{wn}} \frac{D^\alpha a^{wn}}{Dt} + \frac{\partial \hat{\Omega}^\alpha}{\partial a^{\alpha s}} \frac{D^\alpha a^{\alpha s}}{Dt} \end{aligned} \quad (A1)$$

It will be convenient to have the material derivatives of the geometric properties written with respect to the solid phase velocity. Thus eqn (A1) becomes:

$$\begin{aligned} -\frac{1}{\theta^\alpha} \frac{D^\alpha \hat{\Omega}^\alpha}{Dt} = & -\frac{1}{\theta^\alpha} \frac{\partial \hat{\Omega}^\alpha}{\partial \theta^\alpha} \frac{D^\alpha \theta^\alpha}{Dt} - \frac{1}{\theta^\alpha} \frac{\partial \hat{\Omega}^\alpha}{\partial \epsilon^\alpha} \frac{D^\alpha \epsilon^\alpha}{Dt} \\ & - \frac{1}{\theta^\alpha} \frac{\partial \hat{\Omega}^\alpha}{\partial \mu^\alpha} \frac{D^\alpha \mu^\alpha}{Dt} - \frac{1}{\theta^\alpha} \frac{\partial \hat{\Omega}^\alpha}{\partial a^{wn}} \frac{D^\alpha a^{wn}}{Dt} - \frac{1}{\theta^\alpha} \frac{\partial \hat{\Omega}^\alpha}{\partial a^{\alpha s}} \frac{D^\alpha a^{\alpha s}}{Dt} \\ & - \frac{1}{\theta^\alpha} \mathbf{v}^{\alpha, s} \cdot \left[ \frac{\partial \hat{\Omega}^\alpha}{\partial \epsilon^\alpha} \nabla \epsilon^\alpha + \frac{\partial \hat{\Omega}^\alpha}{\partial a^{wn}} \nabla a^{wn} + \frac{\partial \hat{\Omega}^\alpha}{\partial a^{\alpha s}} \nabla a^{\alpha s} \right] \end{aligned} \quad (A2)$$

Now use of definitions (18d) through (18h) allows rewriting of this equation as:

$$\begin{aligned} -\frac{1}{\theta^\alpha} \frac{D^\alpha \hat{\Omega}^\alpha}{Dt} = & \frac{\hat{\eta}^\alpha}{\theta^\alpha} \frac{D^\alpha \theta^\alpha}{Dt} + \frac{p^\alpha}{\theta^\alpha} \frac{D^\alpha \epsilon^\alpha}{Dt} + \frac{\epsilon^\alpha \rho^\alpha}{\theta^\alpha} \frac{D^\alpha \mu^\alpha}{Dt} \\ & - \frac{c_{wn}^\alpha}{\theta^\alpha} \frac{D^\alpha a^{wn}}{Dt} - \frac{c_{\alpha s}^\alpha}{\theta^\alpha} \frac{D^\alpha a^{\alpha s}}{Dt} \\ & - \frac{1}{\theta^\alpha} \mathbf{v}^{\alpha, s} \cdot [-p^\alpha \nabla \epsilon^\alpha + c_{wn}^\alpha \nabla a^{wn} + c_{\alpha s}^\alpha \nabla a^{\alpha s}] \end{aligned} \quad (A3)$$

### Solid phase

For the solid, eqn (18c) indicates that the grand canonical potential depends on the Lagrangian strain tensor,  $\mathbf{E}^s$ , and the macroscale jacobian,  $j$ . Note that the symmetric Lagrangian strain tensor, with components  $\mathbf{E}_{KL}^s$ , behaves according

to Eringen:<sup>16</sup>

$$\frac{D^s \mathbf{E}^s}{Dt} = \mathbf{d}^s : (\nabla_{\mathbf{x}} \mathbf{F}^s)(\nabla_{\mathbf{x}} \mathbf{F}^s)^T \quad (A4)$$

where

$$x = \mathbf{F}^s(\mathbf{X}^s, t) \quad (A5)$$

and  $\nabla_{\mathbf{x}} \mathbf{F}^s$  is the deformation gradient. The macroscale jacobian of the solid phase deformation,  $j$ , accounts for a change in volume and is governed by the equation:

$$\frac{D^s j}{Dt} = j \mathbf{d}^s : \mathbf{I} \quad (A6)$$

Application of the chain rule to expand eqn (18c) gives:

$$\begin{aligned} \frac{D^s \hat{\Omega}^s}{Dt} = & \frac{\partial \hat{\Omega}^s}{\partial \theta^s} \frac{D^s \theta^s}{Dt} + \frac{\partial \hat{\Omega}^s}{\partial (\epsilon^s \mathbf{E}^s / j)} : \left[ \frac{\mathbf{E}^s D^s \epsilon^s}{j} + \frac{\epsilon^s D^s \mathbf{E}^s}{j} - \frac{\epsilon^s \mathbf{E}^s D^s j}{j^2} \right] \\ & + \frac{\partial \hat{\Omega}^s}{\partial \mu^s} \frac{D^s \mu^s}{Dt} + \frac{\partial \hat{\Omega}^s}{\partial a^{ws}} \frac{D^s a^{ws}}{Dt} + \frac{\partial \hat{\Omega}^s}{\partial a^{ns}} \frac{D^s a^{ns}}{Dt} \end{aligned} \quad (A7)$$

Substitution of eqns (A4) and (A6) into this expression yields:

$$\begin{aligned} -\frac{1}{\theta^s} \frac{D^s \hat{\Omega}^s}{Dt} = & -\frac{1}{\theta^s} \frac{\partial \hat{\Omega}^s}{\partial \theta^s} \frac{D^s \theta^s}{Dt} - \frac{1}{\theta^s} \frac{\partial \hat{\Omega}^s}{\partial (\epsilon^s \mathbf{E}^s / j)} : \frac{\mathbf{E}^s D^s \epsilon^s}{j} \\ & - \frac{1}{\theta^s} \left\{ \frac{\partial \hat{\Omega}^s}{\partial (\epsilon^s \mathbf{E}^s / j)} \frac{\epsilon^s}{j} : [(\nabla_{\mathbf{x}} \mathbf{F}^s)(\nabla_{\mathbf{x}} \mathbf{F}^s)^T - \mathbf{E}^s \mathbf{I}] \right\} : \mathbf{d}^s \\ & - \frac{1}{\theta^s} \frac{\partial \hat{\Omega}^s}{\partial \mu^s} \frac{D^s \mu^s}{Dt} - \frac{1}{\theta^s} \frac{\partial \hat{\Omega}^s}{\partial a^{ws}} \frac{D^s a^{ws}}{Dt} - \frac{1}{\theta^s} \frac{\partial \hat{\Omega}^s}{\partial a^{ns}} \frac{D^s a^{ns}}{Dt} \end{aligned} \quad (A8)$$

Use of definitions (18d) through (18h) allows simplification of the notation in this expression to the form:

$$\begin{aligned} -\frac{1}{\theta^s} \frac{D^s \hat{\Omega}^s}{Dt} = & \frac{\hat{\eta}^s}{\theta^s} \frac{D^s \theta^s}{Dt} + \frac{\sigma^s : \mathbf{E}^s / j}{\theta^s} \frac{D^s \epsilon^s}{Dt} \\ & - \frac{1}{\theta^s} \left\{ -\frac{\epsilon^s}{j} \sigma^s : [(\nabla_{\mathbf{x}} \mathbf{F}^s)(\nabla_{\mathbf{x}} \mathbf{F}^s)^T - \mathbf{E}^s \mathbf{I}] \right\} : \mathbf{d}^s \\ & + \frac{\epsilon^s \rho^s}{\theta^s} \frac{D^s \mu^s}{Dt} - \frac{c_{ws}^s}{\theta^s} \frac{D^s a^{ws}}{Dt} - \frac{c_{ns}^s}{\theta^s} \frac{D^s a^{ns}}{Dt} \end{aligned} \quad (A9)$$

### Fluid–fluid interface

The functional form of the grand canonical potential of the interface between the wetting and non-wetting phases, as given in eqn (24a), can be expanded such that:

$$\begin{aligned} \frac{D^{wn} \hat{\Omega}^{wn}}{Dt} = & \frac{\partial \hat{\Omega}^{wn}}{\partial \theta^{wn}} \frac{D^{wn} \theta^{wn}}{Dt} + \frac{\partial \hat{\Omega}^{wn}}{\partial a^{wn}} \frac{D^{wn} a^{wn}}{Dt} + \frac{\partial \hat{\Omega}^{wn}}{\partial \mu^{wn}} \frac{D^{wn} \mu^{wn}}{Dt} \\ & + \frac{\partial \hat{\Omega}^{wn}}{\partial \epsilon^{ws}} \frac{D^{wn} \epsilon^{ws}}{Dt} + \frac{\partial \hat{\Omega}^{wn}}{\partial \epsilon^{ns}} \frac{D^{wn} \epsilon^{ns}}{Dt} + \frac{\partial \hat{\Omega}^{wn}}{\partial l^{wns}} \frac{D^{wn} l^{wns}}{Dt} \end{aligned} \quad (A10)$$

Expression of all the material derivatives of the geometric

properties in terms of the solid phase velocity yields:

$$\begin{aligned}
 -\frac{1}{\theta^{wn}} \frac{D^{wn} \hat{\Omega}^{wn}}{Dt} &= -\frac{1}{\theta^{wn}} \frac{\partial \hat{\Omega}^{wn}}{\partial \theta^{wn}} \frac{D^{wn} \theta^{wn}}{Dt} - \frac{1}{\theta^{wn}} \frac{\partial \hat{\Omega}^{wn}}{\partial a^{wn}} \frac{D^s a^{wn}}{Dt} \\
 &- \frac{1}{\theta^{wn}} \frac{\partial \hat{\Omega}^{wn}}{\partial \mu^{wn}} \frac{D^{wn} \mu^{wn}}{Dt} - \frac{1}{\theta^{wn}} \frac{\partial \hat{\Omega}^{wn}}{\partial \epsilon^w} \frac{D^s \epsilon^w}{Dt} \\
 &- \frac{1}{\theta^{wn}} \frac{\partial \hat{\Omega}^{wn}}{\partial \epsilon^n} \frac{D^s \epsilon^n}{Dt} - \frac{1}{\theta^{wn}} \frac{\partial \hat{\Omega}^{wn}}{\partial l^{wns}} \frac{D^s l^{wns}}{Dt} \\
 &- \frac{1}{\theta^{wn}} \mathbf{v}^{wn,s} \cdot \left[ \frac{\partial \hat{\Omega}^{wn}}{\partial a^{wn}} \nabla a^{wn} + \sum_{i=w,n} \frac{\partial \hat{\Omega}^{wn}}{\partial \epsilon^i} \nabla \epsilon^i + \frac{\partial \hat{\Omega}^{wn}}{\partial l^{wns}} \nabla l^{wns} \right]
 \end{aligned} \quad (A11)$$

Use of definitions (24d) through (24i) simplifies this expression to:

$$\begin{aligned}
 -\frac{1}{\theta^{wn}} \frac{D^{wn} \hat{\Omega}^{wn}}{Dt} &= \frac{\hat{\eta}^{wn}}{\theta^{wn}} \frac{D^{wn} \theta^{wn}}{Dt} - \frac{\gamma^{wn}}{\theta^{wn}} \frac{D^s a^{wn}}{Dt} \\
 &+ \frac{a^{wn} \rho^{wn}}{\theta^{wn}} \frac{D^{wn} \mu^{wn}}{Dt} + \frac{c_w^{wn}}{\theta^{wn}} \frac{D^s \epsilon^w}{Dt} + \frac{c_n^{wn}}{\theta^{wn}} \frac{D^s \epsilon^n}{Dt} \\
 &+ \frac{c_{wns}^{wn}}{\theta^{wn}} \frac{D^s l^{wns}}{Dt} - \frac{1}{\theta^{wn}} \mathbf{v}^{wn,s} \cdot [\gamma^{wn} \nabla a^{wn} - c_w^{wn} \nabla \epsilon^w \\
 &- c_n^{wn} \nabla \epsilon^n - c_{wns}^{wn} \nabla l^{wns}].
 \end{aligned} \quad (A12)$$

### Fluid–solid interface

Similarly, based on eqns (24b) and (24c), the functional form of the grand canonical potential of a fluid–solid interface can be expanded such that:

$$\begin{aligned}
 \frac{D^{\alpha s} \hat{\Omega}^{\alpha s}}{Dt} &= \frac{\partial \hat{\Omega}^{\alpha s}}{\partial \theta^{\alpha s}} \frac{D^{\alpha s} \theta^{\alpha s}}{Dt} + \frac{\partial \hat{\Omega}^{\alpha s}}{\partial a^{\alpha s}} \frac{D^{\alpha s} a^{\alpha s}}{Dt} + \frac{\partial \hat{\Omega}^{\alpha s}}{\partial \mu^{\alpha s}} \frac{D^{\alpha s} \mu^{\alpha s}}{Dt} \\
 &+ \frac{\partial \hat{\Omega}^{\alpha s}}{\partial \epsilon^\alpha} \frac{D^{\alpha s} \epsilon^\alpha}{Dt} + \frac{\partial \hat{\Omega}^{\alpha s}}{\partial (\epsilon^s \mathbf{E}^s / j)} : \frac{D^{\alpha s} (\epsilon^s \mathbf{E}^s / j)}{Dt} \\
 &+ \frac{\partial \hat{\Omega}^{\alpha s}}{\partial l^{wns}} \frac{D^{\alpha s} l^{wns}}{Dt}.
 \end{aligned} \quad (A13)$$

Substitution of kinematic eqns (A4) and (A6) into this expression along with expression of all the material derivatives of the geometric properties in terms of the solid phase velocity yields:

$$\begin{aligned}
 -\frac{1}{\theta^{\alpha s}} \frac{D^{\alpha s} \hat{\Omega}^{\alpha s}}{Dt} &= -\frac{1}{\theta^{\alpha s}} \frac{\partial \hat{\Omega}^{\alpha s}}{\partial \theta^{\alpha s}} \frac{D^{\alpha s} \theta^{\alpha s}}{Dt} - \frac{1}{\theta^{\alpha s}} \frac{\partial \hat{\Omega}^{\alpha s}}{\partial a^{\alpha s}} \frac{D^s a^{\alpha s}}{Dt} \\
 &- \frac{1}{\theta^{\alpha s}} \frac{\partial \hat{\Omega}^{\alpha s}}{\partial \mu^{\alpha s}} \frac{D^{\alpha s} \mu^{\alpha s}}{Dt} - \frac{1}{\theta^{\alpha s}} \frac{\partial \hat{\Omega}^{\alpha s}}{\partial \epsilon^\alpha} \frac{D^s \epsilon^\alpha}{Dt} \\
 &- \frac{1}{\theta^{\alpha s}} \frac{\partial \hat{\Omega}^{\alpha s}}{\partial (\epsilon^s \mathbf{E}^s / j)} : \frac{\mathbf{E}^s D^s \epsilon^s}{j Dt} - \frac{1}{\theta^{\alpha s}} \frac{\partial \hat{\Omega}^{\alpha s}}{\partial l^{wns}} \frac{D^s l^{wns}}{Dt} \\
 &- \frac{1}{\theta^{\alpha s}} \frac{\partial \hat{\Omega}^{\alpha s}}{\partial (\epsilon^s \mathbf{E}^s / j)} : \left[ \frac{\epsilon^s}{j} (\nabla_{\mathbf{x}} \mathbf{F}^s) (\nabla_{\mathbf{x}} \mathbf{F}^s)^T - \frac{\epsilon^s \mathbf{E}^s}{j} \mathbf{I} \right] : \mathbf{d}^s
 \end{aligned}$$

$$\begin{aligned}
 &- \frac{1}{\theta^{\alpha s}} \mathbf{v}^{\alpha s,s} \cdot \left[ \frac{\partial \hat{\Omega}^{\alpha s}}{\partial a^{\alpha s}} \nabla a^{\alpha s} + \frac{\partial \hat{\Omega}^{\alpha s}}{\partial \epsilon^\alpha} \nabla \epsilon^\alpha + \frac{\partial \hat{\Omega}^{\alpha s}}{\partial (\epsilon^s \mathbf{E}^s / j)} : \nabla \left( \frac{\epsilon^s \mathbf{E}^s}{j} \right) \right. \\
 &\left. + \frac{\partial \hat{\Omega}^{\alpha s}}{\partial l^{wns}} \nabla l^{wns} \right]
 \end{aligned} \quad (A14)$$

Substitution of definitions (24d) through (24i) into this equation results in the form:

$$\begin{aligned}
 -\frac{1}{\theta^{\alpha s}} \frac{D^{\alpha s} \hat{\Omega}^{\alpha s}}{Dt} &= \frac{\hat{\eta}^{\alpha s}}{\theta^{\alpha s}} \frac{D^{\alpha s} \theta^{\alpha s}}{Dt} - \frac{\gamma^{\alpha s}}{\theta^{\alpha s}} \frac{D^s a^{\alpha s}}{Dt} + \frac{a^{\alpha s} \rho^{\alpha s}}{\theta^{\alpha s}} \frac{D^{\alpha s} \mu^{\alpha s}}{Dt} \\
 &+ \frac{c_\alpha^{\alpha s}}{\theta^{\alpha s}} \frac{D^s \epsilon^\alpha}{Dt} + \frac{\sigma^{\alpha s} : \mathbf{E}^s D^s \epsilon^s}{\theta^{\alpha s} j Dt} + \frac{c_{wns}^{\alpha s}}{\theta^{\alpha s}} \frac{D^s l^{wns}}{Dt} \\
 &+ \frac{1}{\theta^{\alpha s}} \left\{ \frac{\epsilon^s}{j} \sigma^{\alpha s} : [(\nabla_{\mathbf{x}} \mathbf{F}^s) (\nabla_{\mathbf{x}} \mathbf{F}^s)^T - \mathbf{E}^s \mathbf{I}] \right\} : \mathbf{d}^s \\
 &- \frac{1}{\theta^{\alpha s}} \mathbf{v}^{\alpha s,s} \cdot \left[ \gamma^{\alpha s} \nabla a^{\alpha s} - c_\alpha^{\alpha s} \nabla \epsilon^\alpha - \sigma^{\alpha s} : \nabla \left( \frac{\epsilon^s \mathbf{E}^s}{j} \right) \right. \\
 &\left. - c_{wns}^{\alpha s} \nabla l^{wns} \right].
 \end{aligned} \quad (A15)$$

### Common line

Finally, from eqn (30a) for the common line, expansion of the grand canonical potential yields:

$$\begin{aligned}
 \frac{D^{wns} \hat{\Omega}^{wns}}{Dt} &= \frac{\partial \hat{\Omega}^{wns}}{\partial \theta^{wns}} \frac{D^{wns} \theta^{wns}}{Dt} + \frac{\partial \hat{\Omega}^{wns}}{\partial l^{wns}} \frac{D^{wns} l^{wns}}{Dt} \\
 &+ \frac{\partial \hat{\Omega}^{wns}}{\partial \mu^{wns}} \frac{D^{wns} \mu^{wns}}{Dt} + \sum_{ij=wn,ws,ns} \frac{\partial \hat{\Omega}^{wns}}{\partial a^{ij}} \frac{D^{wns} a^{ij}}{Dt}
 \end{aligned} \quad (A16)$$

With the material derivatives of geometric properties taken with respect to the solid phase, eqn (A16) becomes:

$$\begin{aligned}
 -\frac{1}{\theta^{wns}} \frac{D^{wns} \hat{\Omega}^{wns}}{Dt} &= -\frac{1}{\theta^{wns}} \frac{\partial \hat{\Omega}^{wns}}{\partial \theta^{wns}} \frac{D^{wns} \theta^{wns}}{Dt} \\
 &- \frac{1}{\theta^{wns}} \frac{\partial \hat{\Omega}^{wns}}{\partial l^{wns}} \frac{D^s l^{wns}}{Dt} - \frac{1}{\theta^{wns}} \frac{\partial \hat{\Omega}^{wns}}{\partial \mu^{wns}} \frac{D^s \mu^{wns}}{Dt} \\
 &- \frac{1}{\theta^{wns}} \sum_{ij=wn,ws,ns} \frac{\partial \hat{\Omega}^{wns}}{\partial a^{ij}} \frac{D^s a^{ij}}{Dt} \\
 &- \frac{1}{\theta^{wns}} \mathbf{v}^{wns,s} \cdot \left[ \frac{\partial \hat{\Omega}^{wns}}{\partial l^{wns}} \nabla l^{wns} + \sum_{ij=wn,ws,ns} \frac{\partial \hat{\Omega}^{wns}}{\partial a^{ij}} \nabla a^{ij} \right]
 \end{aligned} \quad (A17)$$

Then from the definitions in eqns (30b), (30c), (30d) and (30e), this equation reduces to:

$$\begin{aligned}
 -\frac{1}{\theta^{wns}} \frac{D^{wns} \hat{\Omega}^{wns}}{Dt} &= \frac{\hat{\eta}^{wns}}{\theta^{wns}} \frac{D^{wns} \theta^{wns}}{Dt} + \frac{\gamma^{wns}}{\theta^{wns}} \frac{D^s l^{wns}}{Dt} \\
 &+ \frac{l^{wns} \rho^{wns}}{\theta^{wns}} \frac{D^s \mu^{wns}}{Dt} - \frac{1}{\theta^{wns}} \sum_{ij=wn,ws,ns} c_{ij}^{wns} \frac{D^s a^{ij}}{Dt}
 \end{aligned}$$

$$-\frac{1}{\theta^{wns}} \mathbf{v}^{wns, s} \cdot \left[ -\gamma^{wns} \nabla l^{wns} + \sum_{ij=wn, ws, ns} c_{ij}^{wns} \nabla a^{ij} \right] \quad (\text{A18})$$

## APPENDIX B. GEOMETRIC CONSTRAINTS

For proper exploitation of the entropy inequality, information is needed concerning the relations among changes in the geometric variables. As a first step toward obtaining geometric relations, consider the solid phase. The following relations for the void fraction follow directly and exactly from the averaging theorems<sup>21</sup> and for systems with one solid phase and two fluid phases. Integration is performed over the surface area of the solid,  $\mathcal{A}^s$ , that is contained in an averaging volume. The following equations result, respectively, from the averaging theorems for a time derivative and for the gradient of a constant:

$$\frac{\partial \epsilon^s}{\partial t} = \frac{1}{\delta V} \int_{\mathcal{A}^s} \mathbf{n}^s \cdot \mathbf{w} \, d\mathcal{A} \quad (\text{B1})$$

$$\nabla \epsilon^s = -\frac{1}{\delta V} \int_{\mathcal{A}^s} \mathbf{n}^s \, d\mathcal{A}. \quad (\text{B2})$$

The material derivative obtained using the macroscale solid phase velocity is obtained as the sum of eqn (B1) and the macroscale velocity dotted with eqn (B2):

$$\frac{D^s \epsilon}{Dt} = -\frac{1}{\delta V} \int_{\mathcal{A}^s} \mathbf{n}^s \cdot (\mathbf{w} - \mathbf{v}^s) \, d\mathcal{A} \quad (\text{B3})$$

where the fact that  $\epsilon^s = 1 - \epsilon$  has been employed.

To obtain an equation for the time derivative of the solid phase surface area contained within an averaging volume, the surficial averaging theorem may be applied to a constant surface property to obtain:

$$\frac{\partial a^s}{\partial t} = -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^s} (\mathbf{w} \cdot \mathbf{n}^s) \mathbf{n}^s \, d\mathcal{A} + \frac{1}{\delta V} \int_{\mathcal{A}^s} (\nabla \cdot \mathbf{n}^s) (\mathbf{n}^s \cdot \mathbf{w}) \, d\mathcal{A} \quad (\text{B4})$$

This equation may be approximated by estimating the average of the products appearing in these integrals as the product of the average of each of the quantities. Then an order of magnitude estimate of the relative importance of the three terms is obtained as:

$$\begin{aligned} \frac{\partial a^s}{\partial t} = & -\frac{1}{\delta V} \nabla \cdot \left[ \frac{1}{\mathcal{A}^s} \left( \int_{\mathcal{A}^s} \mathbf{w} \cdot \mathbf{n}^s \, d\mathcal{A} \right) \left( \int_{\mathcal{A}^s} \mathbf{n}^s \, d\mathcal{A} \right) \right] \\ & + \frac{J_s^s}{\delta V} \int_{\mathcal{A}^s} \mathbf{n}^s \cdot \mathbf{w} \, d\mathcal{A} \end{aligned} \quad (\text{B5})$$

where the average curvature of the solid surface calculated on the basis of the unit normal in the direction pointing outward from the solid,  $J_s^s$  is defined as:

$$J_s^s = \frac{1}{\mathcal{A}^s} \int_{\mathcal{A}^s} \nabla \cdot \mathbf{n}^s \, d\mathcal{A} \quad (\text{B6})$$

and is of the order of magnitude  $a^s/\epsilon^s$ . Now substitute into eqn (B5) to eliminate each of the integral terms using eqns

(B1) and (B2) and obtain:

$$\frac{\partial a^s}{\partial t} = \nabla \cdot \left[ \frac{1}{a^s} \left( \frac{\partial \epsilon^s}{\partial t} \right) (\nabla \epsilon^s) \right] + J_s^s \frac{\partial \epsilon^s}{\partial t} \quad (\text{B7})$$

Expansion of the second term in eqn (B7) yields:

$$\begin{aligned} \frac{\partial a^s}{\partial t} = & -\frac{1}{(a^s)^2} \left( \frac{\partial \epsilon^s}{\partial t} \right) (\nabla \epsilon^s \cdot \nabla a^s) + \frac{1}{2a^s} \frac{\partial}{\partial t} (\nabla \epsilon^s \cdot \nabla \epsilon^s) \\ & + \frac{1}{a^s} \left( \frac{\partial \epsilon^s}{\partial t} \right) \nabla^2 \epsilon^s + J_s^s \frac{\partial \epsilon^s}{\partial t} \end{aligned} \quad (\text{B8})$$

or, after rearrangement:

$$\begin{aligned} \frac{\partial a^s}{\partial t} = & \left[ J_s^s + \frac{1}{a^s} \nabla^2 \epsilon^s - \frac{1}{(a^s)^2} (\nabla \epsilon^s \cdot \nabla a^s) \right] \frac{\partial \epsilon^s}{\partial t} \\ & + \frac{1}{2a^s} \frac{\partial}{\partial t} (\nabla \epsilon^s \cdot \nabla \epsilon^s) \end{aligned} \quad (\text{B9})$$

For a porous medium, the radius of a grain is much smaller than the average volume characteristic dimension so that:

$$|J_s^s| \gg \frac{1}{a^s} |\nabla^2 \epsilon^s| \quad (\text{B10})$$

$$|J_s^s| \gg \frac{1}{(a^s)^2} |\nabla \epsilon^s \cdot \nabla a^s| \quad (\text{B11})$$

and

$$|J_s^s \frac{\partial \epsilon^s}{\partial t}| \gg \frac{1}{2a^s} \left| \frac{\partial}{\partial t} (\nabla \epsilon^s \cdot \nabla \epsilon^s) \right| \quad (\text{B12})$$

Therefore, eqn (B9) simplifies to:

$$\frac{\partial a^s}{\partial t} = J_s^s \frac{\partial \epsilon^s}{\partial t} \quad (\text{B13})$$

Then, if the velocity of the solid is small, as it is for most porous media situations, the Lagrangian time derivative moving with the solid is a reasonable approximation to the partial time derivative such that eqn (B13) may be approximated as:

$$\frac{D^s a^s}{Dt} = J_s^s \frac{D^s \epsilon^s}{Dt} \quad (\text{B14})$$

or, since  $\epsilon^s = 1 - \epsilon$ :

*Constitutive equation for solid phase surface*

$$\frac{D^s a^s}{Dt} + J_s^s \frac{D^s \epsilon}{Dt} = 0 \quad (\text{B15})$$

such that

$$J_s^s = J_s^s(a^s, \epsilon) \quad (\text{B16})$$

Now, as a prelude to the development of other constitutive forms, the time averaging theorems (as found in Ref.<sup>5</sup> or Ref.<sup>47</sup> for a volume; Ref.<sup>18</sup> for a surface; and Ref.<sup>21</sup> for a common line) applied to a constant yield the following relations for a volume fraction, area per volume, and common line length per volume are stated as follows



where the integrations are over the appropriate region within an averaging volume:

$$\frac{\partial \epsilon^\alpha}{\partial t} = \frac{1}{\delta V} \int_{\mathcal{A}^{\alpha\beta}} \mathbf{n}^\alpha \cdot \mathbf{w} \, d\mathcal{A} + \frac{1}{\delta V} \int_{\mathcal{A}^{\alpha\gamma}} \mathbf{n}^\alpha \cdot \mathbf{w} \, d\mathcal{A} \quad (\text{B17})$$

$$\begin{aligned} \frac{\partial a^{\alpha\beta}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^{\alpha\beta}} \mathbf{w} \cdot \mathbf{n}^\alpha \mathbf{n}^\alpha \, d\mathcal{A} \\ &= \frac{1}{\delta V} \int_{\mathcal{A}^{\alpha\beta}} (\nabla \cdot \mathbf{n}^\alpha) \mathbf{n}^\alpha \cdot \mathbf{w} \, d\mathcal{A} + \frac{1}{\delta V} \int_{\mathcal{L}^{\alpha\beta}} \mathbf{v}^{\alpha\beta} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B18})$$

$$\frac{\partial l^{\alpha\beta}}{\partial t} = -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{L}^{\alpha\beta}} \mathbf{u} \cdot (\mathbf{I} - \lambda\lambda) \, d\mathcal{L} - \frac{1}{\delta V} \int_{\mathcal{L}^{\alpha\beta}} \lambda \cdot \nabla \lambda \cdot \mathbf{u} \, d\mathcal{L} \quad (\text{B19})$$

The objective in manipulating these equations, which are obtained directly from the averaging theorems, will be to eliminate the integrals that appear and replace them with derivatives of the geometric properties of the system.

For the wetting phase, the following may be obtained from eqn (B17) since  $\epsilon^w = \epsilon s^w$ :

$$s^w \frac{\partial \epsilon}{\partial t} + \epsilon \frac{\partial s^w}{\partial t} = \frac{1}{\delta V} \int_{\mathcal{A}^{wn}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} + \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \quad (\text{B20})$$

For the interfaces between the wetting and non-wetting phases, eqn (B18) becomes:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^{wn}} \mathbf{w} \cdot \mathbf{n}^w \mathbf{n}^w \, d\mathcal{A} \\ &+ \frac{1}{\delta V} \int_{\mathcal{A}^{wn}} (\nabla \cdot \mathbf{n}^w) \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \\ &+ \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{v}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B21})$$

while for the interface between the wetting and solid phases, it takes the following form:

$$\begin{aligned} x_s^{ws} \frac{\partial a^s}{\partial t} + a^s \frac{\partial x_s^{ws}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^{ws}} \mathbf{w} \cdot \mathbf{n}^s \mathbf{n}^s \, d\mathcal{A} \\ &+ \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} (\nabla \cdot \mathbf{n}^s) \mathbf{n}^s \cdot \mathbf{w} \, d\mathcal{A} + \frac{1}{\delta V} \int_{\mathcal{L}^{ws}} \mathbf{v}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B22})$$

Now rearrange eqn (B22) such that the terms on the right are all on the order of the rate of change of  $a^s$  or less and thus are smaller than the terms on the left:

$$\begin{aligned} a^s \frac{\partial x_s^{ws}}{\partial t} - \frac{1}{\delta V} \int_{\mathcal{L}^{ws}} \mathbf{v}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \\ = -x_s^{ws} \frac{\partial a^s}{\partial t} - \frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^{ws}} \mathbf{w} \cdot \mathbf{n}^s \mathbf{n}^s \, d\mathcal{A} \\ + \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} (\nabla \cdot \mathbf{n}^s) \mathbf{n}^s \cdot \mathbf{w} \, d\mathcal{A} \end{aligned} \quad (\text{B23})$$

Therefore, a reasonable approximation is to retain only the terms on the left such that:

$$a^s \frac{\partial x_s^{ws}}{\partial t} - \frac{1}{\delta V} \int_{\mathcal{L}^{ws}} \mathbf{v}^{ws} \cdot \mathbf{u} \, d\mathcal{L} = 0 \quad (\text{B24})$$

For the interface between the fluids, eqn (B21) may be written:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^{wn}} \mathbf{w} \cdot \mathbf{n}^w \mathbf{n}^w \, d\mathcal{A} \\ &+ \frac{J_{wn}^w}{\delta V} \int_{\mathcal{A}^{wn}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} + \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{v}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B25})$$

where the macroscale measure of the interfacial curvature,  $J_{wn}^w$ , is defined as:

$$J_{wn}^w = \frac{1}{\mathcal{A}^{wn}} \int_{\mathcal{A}^{wn}} (\nabla \cdot \mathbf{n}^w) \, d\mathcal{A} \quad (\text{B26})$$

Now add and subtract a term to this equation so that the second integral is over the entire  $\omega$  surface:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^{wn}} \mathbf{w} \cdot \mathbf{n}^w \mathbf{n}^w \, d\mathcal{A} \\ &+ J_{wn}^w \left[ \frac{1}{\delta V} \int_{\mathcal{A}^w} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} - \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \right] \\ &+ \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{v}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B27})$$

Substitution of eqn (B20) for the first term in the brackets yields:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^{wn}} \mathbf{w} \cdot \mathbf{n}^w \mathbf{n}^w \, d\mathcal{A} \\ &+ J_{wn}^w \left[ \frac{\partial \epsilon^w}{\partial t} - \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \right] \\ &+ \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{v}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B28})$$

Since the normal velocity of the solid surface is of a smaller order of magnitude than the velocity of the fluid–fluid interface, eqn (B28) may be approximated by writing the first integral as being over the entire wetting phase surface such that:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \int_{\mathcal{A}^w} (\mathbf{w} \cdot \mathbf{n}^w) \mathbf{n}^w \, d\mathcal{A} \\ &+ J_{wn}^w \left[ \frac{\partial \epsilon^w}{\partial t} - \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \right] \\ &+ \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{v}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B29})$$

Now if the correlation between  $\mathbf{w} \cdot \mathbf{n}^w$  and  $\mathbf{n}^w$  is neglected in the first term on the right such that the average of the integral of their product is approximated as the product of their averages, this equation becomes:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} &= -\frac{1}{\delta V} \nabla \cdot \left[ \frac{1}{\mathcal{A}^w} \left( \int_{\mathcal{A}^w} \mathbf{w} \cdot \mathbf{n}^w \, d\mathcal{S} \right) \left( \int_{\mathcal{A}^w} \mathbf{n}^w \, d\mathcal{S} \right) \right] \\ &+ J_{wn}^w \left[ \frac{\partial \epsilon^w}{\partial t} - \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \right] \\ &+ \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{v}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B30})$$

or

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} = & \nabla \cdot \left[ \frac{1}{a^w} \left( \frac{\partial \epsilon^w}{\partial t} \right) (\nabla \epsilon^w) \right] \\ & + J_{wn}^w \left[ \frac{\partial \epsilon^w}{\partial t} - \frac{1}{\delta V} \int_{\mathcal{A}^{ws}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \right] \\ & + \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{p}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B31})$$

Expansion of the derivatives on the right side and collection of terms yields:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} = & \left[ J_{wn}^w + \frac{1}{a^w} \nabla^2 \epsilon^w - \frac{1}{(a^w)^2} (\nabla a^w \cdot \nabla \epsilon^w) \right] \frac{\partial \epsilon^w}{\partial t} \\ & + \frac{1}{2a^w} \frac{\partial}{\partial t} (\nabla \epsilon^w \cdot \nabla \epsilon^w) - \frac{J_{wn}^w}{\delta V} \int_{\mathcal{A}^{ws}} \mathbf{n}^w \cdot \mathbf{w} \, d\mathcal{A} \\ & + \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{p}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B32})$$

Now if the terms of lower order of magnitude (i.e., those relating to changes due to solid movement as opposed to fluid movement) are neglected, this equation simplifies to:

$$\frac{\partial a^{wn}}{\partial t} - J_{wn}^w \epsilon \frac{\partial s^w}{\partial t} = \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{p}^{wn} \cdot \mathbf{u} \, d\mathcal{L} \quad (\text{B33})$$

Next, note that the normal to the edge of the interface at the common line is also normal to the common line such that:

$$\mathbf{p}^{wn} = (\mathbf{n}^s \cdot \mathbf{p}^{wn}) \mathbf{n}^s + (\mathbf{p}^{ws} \cdot \mathbf{p}^{wn}) \mathbf{p}^{ws} \quad (\text{B34})$$

Therefore, eqn (B33) becomes:

$$\begin{aligned} \frac{\partial a^{wn}}{\partial t} - J_{wn}^w \epsilon \frac{\partial s^w}{\partial t} = & \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} (\mathbf{n}^s \cdot \mathbf{p}^{wn}) \mathbf{n}^s \cdot \mathbf{u} \, d\mathcal{L} \\ & + \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} (\mathbf{p}^{ws} \cdot \mathbf{p}^{wn}) \mathbf{p}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B35})$$

The first integral involves the velocity of the common line normal to the solid grain, which is small in comparison to the velocity tangential to the grain. Thus the first integral may be neglected in comparison to the second to obtain:

$$\frac{\partial a^{wn}}{\partial t} - J_{wn}^w \epsilon \frac{\partial s^w}{\partial t} = \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} (\mathbf{p}^{ws} \cdot \mathbf{p}^{wn}) \mathbf{p}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \quad (\text{B36})$$

Now define a dynamic macroscale contact angle,  $\Phi$ , according to:

$$\cos \Phi = \frac{1}{l^{wns} \delta V} \int_{\mathcal{L}^{wns}} (\mathbf{p}^{ws} \cdot \mathbf{p}^{wn}) \, d\mathcal{L} \quad (\text{B37})$$

so that eqn (B36) becomes:

$$\frac{\partial a^{wn}}{\partial t} - J_{wn}^w \epsilon \frac{\partial s^w}{\partial t} = \frac{\cos \Phi}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{p}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \quad (\text{B38})$$

Substitution of eqn (B24) into this expression yields:

$$\frac{\partial a^{wn}}{\partial t} - J_{wn}^w \epsilon \frac{\partial s^w}{\partial t} - a^s \cos \Phi \frac{\partial x_s^{ws}}{\partial t} = 0 \quad (\text{B39})$$

Since the solid velocity is assumed small, the partial derivative may be replaced by the total derivative moving with the solid phase to obtain:

*Constitutive equation for the interface*

$$\frac{D^s a^{wn}}{Dt} - J_{wn}^w \epsilon \frac{D^s s^w}{Dt} - a^s \cos \Phi \frac{D^s x_s^{ws}}{Dt} = 0 \quad (\text{B40})$$

where

$$J_{wn}^w = J_{wn}^w(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon) \quad (\text{B41})$$

and

$$\cos \Phi = \cos \Phi(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon) \quad (\text{B42})$$

Next consider the equation for the common line given by eqn (B19). For this equation, the divergence term is also small in relation to the remaining terms so that:

$$\frac{\partial l^{wns}}{\partial t} = - \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \mathbf{u} \, d\mathcal{L} \quad (\text{B43})$$

The principal curvature of the common line is defined as:

$$\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} = \kappa \mathbf{p} = \kappa (\mathbf{p} \cdot \mathbf{n}^s) \mathbf{n}^s + \kappa (\mathbf{p} \cdot \mathbf{p}^{ws}) \mathbf{p}^{ws} \quad (\text{B44})$$

where  $\kappa$  is the magnitude of the principal curvature and  $\mathbf{p}$  is the principal unit normal to the line. Therefore, eqn (B43) becomes:

$$\begin{aligned} \frac{\partial l^{wns}}{\partial t} = & - \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \kappa (\mathbf{p} \cdot \mathbf{n}^s) \mathbf{n}^s \cdot \mathbf{u} \, d\mathcal{L} \\ & - \frac{1}{\delta V} \int_{\mathcal{L}^{wns}} \kappa (\mathbf{p} \cdot \mathbf{p}^{ws}) \mathbf{p}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \end{aligned} \quad (\text{B45})$$

The quantity  $\kappa (\mathbf{p} \cdot \mathbf{n}^s)$  is the normal curvature and  $\kappa (\mathbf{p} \cdot \mathbf{p}^{ws})$  is the geodesic curvature. If the average of these over the common line are indicated as  $\kappa_n$  and  $\kappa_g^{ws}$ , respectively, then eqn (B45) may be approximated as:

$$\frac{\partial l^{wns}}{\partial t} = - \frac{\kappa_n}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{n}^s \cdot \mathbf{u} \, d\mathcal{L} - \frac{\kappa_g^{ws}}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{p}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \quad (\text{B46})$$

where

$$\kappa_n = \frac{1}{\mathcal{L}^{wns}} \int_{\mathcal{L}^{wns}} \kappa (\mathbf{p} \cdot \mathbf{n}^s) \, d\mathcal{L} \quad (\text{B47})$$

and

$$\kappa_g^{ws} = \frac{1}{\mathcal{L}^{wns}} \int_{\mathcal{L}^{wns}} \kappa (\mathbf{p} \cdot \mathbf{p}^{ws}) \, d\mathcal{L} \quad (\text{B48})$$

The first integral is small in comparison with the second since it involves movement normal to the solid grain, so that this equation approximates further to:

$$\frac{\partial l^{wns}}{\partial t} = \frac{\kappa_g^{ws}}{\delta V} \int_{\mathcal{L}^{wns}} \mathbf{p}^{ws} \cdot \mathbf{u} \, d\mathcal{L} \quad (\text{B49})$$

Substitution of eqn (B24) into this expression yields:

$$\frac{\partial l^{wns}}{\partial t} + \kappa_g^{ws} a^s \frac{\partial x_s^{ws}}{\partial t} = 0 \quad (\text{B50})$$

Once again, because the velocity of the solid phase is small, the partial derivatives may be replaced by total derivatives moving with respect to the solid phase to obtain the following.

Constitutive equation for the common line

$$\frac{D^s l^{wns}}{Dt} + \kappa_g^s a^s \frac{D^s x_s^{ws}}{Dt} = 0 \quad (B51)$$

where

$$\kappa_g = \kappa_g(x_s^{ws}, l^{wns}, a^s) \quad (B52)$$

## APPENDIX C. THERMODYNAMIC EQUILIBRIUM INFORMATION

A state of stable thermodynamic equilibrium of the total system is one for which the grand canonical potential of the system is less than it is for any other thermodynamic state having the same temperature, chemical potential, and geometric parameters.<sup>17</sup> Thus the equilibrium state is a state of minimum energy. Therefore, deviations in the independent variables around this equilibrium state will cause no change in the energy. In the entropy inequality, the energy form that is minimized at equilibrium is the grand canonical potential. The expression for a deviation in this quantity is:

$$\begin{aligned} d\hat{\Omega}|_{\theta, \mu^m, \mathbf{E}^s/j} = & \epsilon [(c_n^{ns} + c_n^{wn} + p^n) - (c_w^{ws} + c_w^{wn} + p^w)] ds^w \\ & + [(\sigma^{ws} + \sigma^{ns} + \sigma^s) : \mathbf{E}^s/j - s^w(c_w^{ws} + c_w^{wn} + p^w) \\ & - s^n(c_n^{ns} + c_n^{wn} + p^n)] d\epsilon + [x_s^{ws}(c_w^{ws} + c_w^{wn} + c_w^{wns} + \gamma^{ws}) \\ & + x_s^{ns}(c_n^{ns} + c_n^{wn} + c_n^{wns} + \gamma^{ns})] da^s \\ & + a^s [(c_w^{ws} + c_w^{wn} + c_w^{wns} + \gamma^{ws}) \\ & - (c_n^{ns} + c_n^{wn} + c_n^{wns} + \gamma^{ns})] dx_s^{ws} \\ & + (c_w^{wn} + c_w^{wn} + c_w^{wns} + \gamma^{wn}) da^{wn} \\ & - (c_w^{wn} + c_w^{wns} + c_w^{wns} + \gamma^{wns}) dl^{wns} \end{aligned} \quad (C1)$$

where  $\theta$ ,  $\mu^m$ , and  $\mathbf{E}^s/j$  are held constant to coincide with the conditions of entropy inequality (37) as indicated in the compressed representation (39). The goal of this analysis is to examine this equation in light of eqn (69) through (71). Since the right sides of these equations are zero at equilibrium, an examination of the conditions giving rise to that equilibrium state will provide information about the relation of the coefficients that appear to the thermodynamic state.

The first study involves examination of eqn (151) to obtain conditions where its right side is of similar form to the right side of eqn (69). This is obtained by holding some of the independent variables constant while evaluating the change in  $\hat{\Omega}$  with respect to the void fraction such that:

$$\begin{aligned} \frac{\partial \hat{\Omega}}{\partial \epsilon} \Big|_{\theta, \mu^m, \mathbf{E}^s/j, a^{wn}, l^{wns}, s^w, x_s^{ws}} \\ = \left[ \frac{(\sigma^{ws} + \sigma^{ns} + \sigma^s) : \mathbf{E}^s}{j} - s^w(c_w^{ws} + c_w^{wn} + p^w) \right] \end{aligned}$$

$$\begin{aligned} - s^n(c_n^{ns} + c_n^{wn} + p^n) \Big] + [x_s^{ws}(c_w^{ws} + c_w^{wn} + c_w^{wns} + \gamma^{ws}) \\ + x_s^{ns}(c_n^{ns} + c_n^{wn} + c_n^{wns} + \gamma^{ns})] \frac{\partial a^s}{\partial \epsilon} \end{aligned} \quad (C2)$$

At equilibrium, the left side of this equation will be zero since  $\hat{\Omega}$  will be at a minimum. A comparison of the right side of this equation with eqns (69) and (B16) yields:

$$J_s^s(a^s, \epsilon) = - \left( \frac{\partial a^s}{\partial \epsilon} \right)_{\theta, \mu^m, \mathbf{E}^s/j, a^{wn}, l^{wns}, s^w, x_s^{ws}, \hat{\Omega}} \quad (C3)$$

Next, eqn (C1) will be examined for equilibrium conditions such that its right side is of similar form to the right side of eqn (70). Evaluation of the partial derivative of  $\hat{\Omega}$  with respect to saturation  $s^w$  while holding other independent variables constant yields:

$$\begin{aligned} \frac{\partial \hat{\Omega}}{\partial s^w} \Big|_{\theta, \mu^m, \mathbf{E}^s/j, \epsilon, a^s, x_s^{ws}, l^{wns}} \\ = \epsilon [(c_n^{ns} + c_n^{wn} + p^n) - (c_w^{ws} + c_w^{wn} + p^w)] \\ + (c_w^{wn} + c_w^{wn} + c_w^{wns} + \gamma^{wn}) \frac{\partial a^{wn}}{\partial s^w} \end{aligned} \quad (C4)$$

Comparison of this equation with eqns (70) and (B42) yields:

$$J_{wn}^w(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon) = \frac{1}{\epsilon} \left( \frac{\partial a^{wn}}{\partial s^w} \right)_{\theta, \mu^m, \mathbf{E}^s/j, \epsilon, a^s, x_s^{ws}, l^{wns}, \hat{\Omega}} \quad (C5)$$

Finally, the differential of the grand canonical potential near equilibrium conditions will be examined to determine if the coefficients that appear in eqn (71) can be related to thermodynamic variables. The differential of  $\hat{\Omega}$  while holding  $s^w$ ,  $\epsilon$ , and  $a^s$  constant may be obtained directly from eqn (C1). Then, if  $\hat{\Omega}$  is also held constant, since its variation will be zero at an equilibrium state, the following equation results:

$$\begin{aligned} d\hat{\Omega}|_{\theta, \mu^m, \mathbf{E}^s/j, \epsilon, a^s, \hat{\Omega}} = 0 \\ = a^s [(c_w^{ws} + c_w^{wn} + c_w^{wns} + \gamma^{ws}) \\ - (c_n^{ns} + c_n^{wn} + c_n^{wns} + \gamma^{ns})] dx_s^{ws} \\ + (c_w^{wn} + c_w^{wn} + c_w^{wns} + \gamma^{wn}) da^{wn} \\ - (c_w^{wn} + c_w^{wns} + c_w^{wns} + \gamma^{wns}) dl^{wns} \end{aligned} \quad (C6)$$

Comparison of this equation with the right side of eqn (71) at equilibrium and invoking the functional dependence indicated in eqns (B42) and (B52) yields:

$$\cos[\Phi(s^w, a^{wn}, x_s^{ws}, a^s, \epsilon)] = \frac{1}{a^s} \left( \frac{\partial a^{wn}}{\partial x_s^{ws}} \right)_{\theta, \mu^m, \mathbf{E}^s/j, s^w, \epsilon, a^s, \hat{\Omega}} \quad (C7)$$

$$\kappa_g(x_s^{ws}, l^{wns}, a^s) = - \frac{1}{a^s} \left( \frac{\partial l^{wns}}{\partial x_s^{ws}} \right)_{\theta, \mu^m, \mathbf{E}^s/j, s^w, \epsilon, a^s, \hat{\Omega}} \quad (C8)$$