



PERGAMON

International Journal of Multiphase Flow 26 (2000) 467–501

International Journal of
**Multiphase
Flow**

www.elsevier.com/locate/ijmulflow

Macroscale equilibrium conditions for two-phase flow in porous media

William G. Gray*,¹

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA

Received 20 April 1998; received in revised form 16 March 1999

Abstract

Flow in porous media is typically modeled at a length scale, referred to as the macroscale, such that a point of the system encompasses tens to hundreds of pore diameters. For such a system description, thermodynamic equilibrium conditions involve equality of the temperatures and chemical potentials of the system components at a point as well as mechanical conditions expressing an equilibration of forces at interfaces between phases and at common lines where interfaces come together. These force balances must be expressed in terms of macroscale thermodynamic variables and are obtained here. In addition, perturbations from the equilibrium state involve changes in the macroscale variables describing the amount of volume of a phase, area of an interface, or length of common line per volume of the system. A variational analysis provides the expressions for independent variations of these quantities, important information for completion of a continuum mechanical description of the system physics involving exploitation of the entropy inequality. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Porous media; Multiphase; Thermodynamics; Averaging theory; Continuum mechanics; Interfacial area; Unsaturated flow

1. Introduction

The primary problem to be considered here relates to the determination of the conditions of

* Corresponding author. Tel.: +1-219-631-5380; fax: +1-219-631-9236.

E-mail address: william.g.gray.3@nd.edu (W.G. Gray).

¹ Work completed while on leave at: Centre for Water Research; University of Western Australia, Nedlands, Western Australia 6907.

equilibrium for flow of two immiscible fluids in a porous medium. This situation will be referred to as two-phase flow because the solid phase, although it may deform slightly, does not flow in the same sense that the fluids do. Such flow systems may be studied at different scales. The microscale is a continuum length scale that is much smaller than the diameter of a pore. Studies at the microscale would consider flow profiles within the pores of the juxtaposed phases that are separated by interfaces. These interfaces could meet at common lines (if there are at least three phases present), and the common lines could meet at common points (when there are four or more phases present). Boruvka and Neumann (1977) have studied general multiphase systems at the microscale and determined conditions of thermodynamic and mechanical equilibrium.

On the other hand, the study of two-phase flow in naturally occurring media and in the laboratory is typically carried out at a macroscale, a length scale on the order of tens to hundreds of pore diameters. To obtain conservation equations at this scale, averaging theorems for the phases (Whitaker, 1967; Anderson and Jackson, 1967; Gray and Lee, 1977) have been employed such that quantities appearing in the equations (i.e., density, velocity, etc.) are in fact average values from a region surrounding a point of interest. This approach has been extended by Gray and Hassanizadeh (1989) and Gray et al. (1993) to include averaging theorems for interfacial properties and common lines. Gray and Hassanizadeh (1998) have used a localization approach to develop conservation equations for phases, interfaces, common lines, and common points (which will be referred to collectively as components) at the macroscale. Any macroscale point in the system will have values of velocity, and other properties, for each component. Note that this is conceptually different from the continuum microscale wherein, for example, only one phase will be present at a point and thus only one velocity. At this scale, phases are juxtaposed. In contrast, at a macroscale point, values of a property corresponding

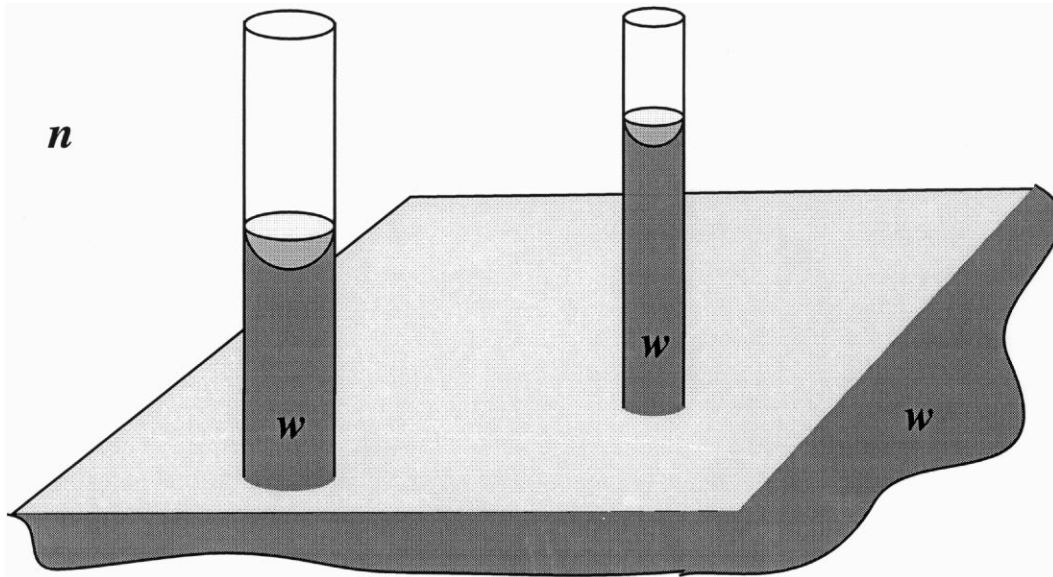


Fig. 1. Fluid reservoir with two capillary tubes of different diameters.

to each system component exist and a geometric density is assigned to each component (volume per volume for a phase, area per volume for an interface, line length per volume for a common line, or number of points per volume for common points) to complete the characterization of the system. At any macroscale point the geometric densities are important parameters, and their presence in the conservation equations for macroscale systems is one of the chief features that distinguishes macroscale analysis from microscale analysis.

Important issues involve determination of equilibrium conditions for a macroscale thermodynamic system and relations among changes in the geometric densities near equilibrium. In this study, the macroscale thermodynamic equations will be investigated to obtain conditions of mechanical equilibrium. The approach to be followed is based on that employed by Boruvka and Neumann (1977) and Gaydos et al. (1996) for microscale systems and follows from the macroscale entropy inequality for two-phase flow derived by Gray (1999).

2. Motivation and need

The need for thermodynamic equilibrium relations at the macroscale can be seen by considering the simple system depicted in Fig. 1. The figure depicts two glass capillary tubes of different diameters that are inserted into a reservoir of fluid (designated as the w phase) that preferentially wets the tubes compared to air (denoted as n , or non-wetting, phase). For convenience, let the contact angle between the fluid and the glass be zero. Thus the interfaces between the two fluids within the capillary tubes are essentially hemispherical. At the interface between the fluids in each tube, the capillary pressure is given by:

$$p_c = -\sigma_{wn}j_{wn}^w \quad (1)$$

where σ_{wn} is the microscale interfacial tension, $j_{wn}^w = \nabla^s \cdot \mathbf{n}^w$ is the interfacial curvature with \mathbf{n}^w being the unit normal on the interface positive outward from the w phase, and ∇^s is the surficial operator used to take the surficial divergence. For the present case where the interface is a hemisphere, $j_{wn}^w = -2/R$ at each point on the interface when R is the radius of the tube. In the smaller tube, the capillary rise is higher, the curvature of the interface is greater, and the capillary pressure is greater. Indeed, when looking at the interface in each of the tubes, determination of the interfacial curvature, and thus the capillary pressure, is straightforward. On the other hand, if one has to consider the capillary tubes as part of a system, it is not at all clear what should be identified as the ‘capillary pressure’ of that system. Certainly the interfaces within the tubes would contribute to such a determination as might the curvature of the interface between the fluids exterior to the capillary tubes. In any event, a definition of the ‘capillary pressure’ would be subject to interpretation, even for the simple system in the figure.

The concept of capillary pressure in a porous medium is far more complex than that for a simple system composed of several capillary tubes. Hassanizadeh and Gray (1993) have considered some of the similarities and differences between capillary pressure as viewed from the micro- and macroscales. Despite that effort, and those of other researchers (e.g., Kalaydjian, 1987; Pavone, 1989) the comment of Scheidegger (1974) still holds true: “A consistent theory of capillary pressure in porous solids should provide an explanation of the fundamental relationship between saturation and capillary pressure (or interfacial curvature).

To date, this does not seem to have been obtained.” One of the aspects of porous media fluids that precludes the simple definition of capillary pressure is the fact that, in contrast to the capillary tube where the interface adopts its shape without influence of the solid, the shape of the fluid–fluid interface in a porous system is impacted by the solid. For example, when a thin film coats a solid, the curvature of the interface between the two fluids will be a function of the shape of the solid as well as of the interaction of the adjacent fluids. Thus, although one can examine the curvature at every point on the fluid–fluid interface from the microscale perspective and obtain values of the capillary pressure, a macroscale description of the capillary pressure, including tens of pores, requires that these point effects be somehow integrated.

At the microscale, thermodynamic equilibrium conditions may be obtained. For example, the pressure difference between two fluids at a point on an interface between the fluids is equal to the capillary pressure. If one is to successfully apply macroscale theories to the description of multiphase flows in porous media, it is necessary to derive analogous mechanical conditions for equilibrium. These conditions must apply at the macroscale, and there seems to be no obvious way to infer these conditions as an integrated effect of the microscale conditions. Thus, the purpose of the present manuscript is to obtain porous media scale conditions of macroscale thermodynamic equilibrium. The variational procedure followed makes use of the quantities related to the geometry of the distribution of phases in a porous medium. These quantities, referred to as geometric densities since they involve amounts of phase volume, interfacial area, and common line length per system volume, do not exist at the microscale; and thus the equilibrium conditions must be derived from the thermodynamics postulated at the macroscale.

3. Microscale energy equations for a three-phase system

Consideration of the energy state of a system composed of two fluids (the w and n phases) and a solid (the s phase) requires that the energy associated with the phases, interfaces, and common lines be accounted for. For an α -phase, where $\alpha = w, n, \text{ or } s$, the microscale internal energy per volume is expressed according to the standard thermodynamic relation (Callen, 1985; Bailyn, 1994):

$$e_\alpha(\eta_\alpha, \rho_{\alpha i}) = \theta_\alpha \eta_\alpha - p_\alpha + \sum_i \mu_{\alpha i} \rho_{\alpha i} \quad (2)$$

where e_α is the microscale internal energy per volume, θ_α is the microscale temperature, η_α is the microscale entropy per volume, p_α is the microscale pressure in the α -phase, $\rho_{\alpha i}$ is the microscale mass of species i per unit volume of phase α , and $\mu_{\alpha i}$ is the microscale chemical potential of species i in the α -phase. For this relation, the temperature and chemical potential are defined, respectively, as:

$$\theta_\alpha = \frac{\partial e_\alpha}{\partial \eta_\alpha} \quad (3a)$$

and:

$$\mu_{xi} = \frac{\partial e_\alpha}{\partial \rho_{xi}} \quad (3b)$$

The density of the phase is related to the species densities by:

$$\rho_\alpha = \sum_i \rho_{xi} \quad (4)$$

Although it is possible to derive the solid phase pressure using the Lagrangian strain tensor (Bailyn, 1994), this extension will not significantly alter the derivation of the equilibrium conditions that follows.

The total energy of the phase per volume at equilibrium includes the gravitational potential energy φ_α which is related to the gravitational acceleration according to $\mathbf{g} = -\nabla\varphi_\alpha$. Therefore, total microscale energy per volume for the α -phase is:

$$e_{\alpha T} = e_\alpha + \sum_i \rho_{xi} \varphi_\alpha = e_\alpha + \rho_\alpha \varphi_\alpha \quad (5)$$

For an $\alpha\beta$ interface separating the α - and β -phases, where $\alpha\beta = wn, ws,$ or ns , the microscale internal energy per area, $e_{\alpha\beta}$, is expressed according to the classical relation:

$$e_{\alpha\beta}(\eta_{\alpha\beta}, \rho_{\alpha\beta i}) = \theta_{\alpha\beta} \eta_{\alpha\beta} + \sigma_{\alpha\beta} + \sum_i \mu_{\alpha\beta i} \rho_{\alpha\beta i} \quad (6)$$

where $\theta_{\alpha\beta}$ is the microscale temperature, $\eta_{\alpha\beta}$ is the microscale entropy per area, $\sigma_{\alpha\beta}$ is the interfacial tension of the $\alpha\beta$ interface, $\rho_{\alpha\beta i}$ is the microscale mass of species i per unit area of interface $\alpha\beta$, and $\mu_{\alpha\beta i}$ is the microscale chemical potential of species i in the $\alpha\beta$ interface. For this relation, the temperature and chemical potential are defined by:

$$\theta_{\alpha\beta} = \frac{\partial e_{\alpha\beta}}{\partial \eta_{\alpha\beta}} \quad (7a)$$

and:

$$\mu_{\alpha\beta i} = \frac{\partial e_{\alpha\beta}}{\partial \rho_{\alpha\beta i}} \quad (7b)$$

The mass density of the interface is obtained from the species densities as:

$$\rho_{\alpha\beta} = \sum_i \rho_{\alpha\beta i} \quad (8)$$

Here, following Gibbs (1948), the microscale interfacial energy is considered to be independent of the curvature of the interface. Boruvka and Neumann (1977) and Boruvka et al. (1985) have provided an extension to this expression that includes the dependence of interfacial energy on the first and second curvatures as microscale independent variables. They have shown that this is necessary for interfaces with very high curvature, a situation that will be neglected here. The total energy density of the interface at equilibrium includes the gravitational potential energy

$\varphi_{\alpha\beta}$ which is related to the gravitational acceleration according to $\mathbf{g} = -\nabla\varphi_{\alpha\beta}$. Therefore, total microscale energy per area for the $\alpha\beta$ interface is:

$$e_{\alpha\beta T} = e_{\alpha\beta} + \sum_i \rho_{\alpha\beta i} \varphi_{\alpha\beta} = e_{\alpha\beta} + \rho_{\alpha\beta} \varphi_{\alpha\beta} \quad (9)$$

For a wns common line, the microscale internal energy per common line length is:

$$e_{wns}(\eta_{wns}, \rho_{wnsi}) = \theta_{wns} \eta_{wns} - \sigma_{wns} + \sum_i \mu_{wnsi} \rho_{wnsi} \quad (10)$$

where θ_{wns} is the microscale temperature, η_{wns} is the microscale entropy per unit length, σ_{wns} is the lineal tension, ρ_{wnsi} is the microscale mass of species i per unit length of common line, and μ_{wnsi} is the microscale chemical potential of species i in the line. Boruvka and Neumann (1977) have included some of the microscale geometric properties of the common line as independent variables, but these effects will be considered small. For this equation, the temperature and chemical potential are defined by:

$$\theta_{wns} = \frac{\partial e_{wns}}{\partial \eta_{wns}} \quad (11a)$$

and:

$$\mu_{wnsi} = \frac{\partial e_{wns}}{\partial \rho_{wnsi}} \quad (11b)$$

The mass density of the phase is described by:

$$\rho_{wns} = \sum_i \rho_{wnsi} \quad (12)$$

The total energy per unit length of a point on the common line at equilibrium includes the gravitational potential energy φ_{wns} , which is related to the gravitational acceleration according to $\mathbf{g} = -\nabla\varphi_{wns}$. Therefore, total microscale energy per length for the wns common line is:

$$e_{wnsT} = e_{wns} + \sum_i \rho_{wnsi} \varphi_{wns} = e_{wns} + \rho_{wns} \varphi_{wns} \quad (13)$$

The relations for the energy in this section will be used in conjunction with a variational analysis to determine the necessary conditions for microscale thermodynamic equilibrium. This will be done after considering the counterparts to these energy equations obtained from a macroscale perspective.

4. Macroscale energy equations for a three-phase system

At the macroscale, energies for the phases, interfaces and common line will all be expressed on a per unit averaging volume basis. Since each component occupies only a portion of that

volume, this must be accounted for in the list of independent variables. Additionally, because the integration to the macroscale involves a loss of information concerning the actual geometric configuration that is observable at the microscale, the possibility exists that one or more additional independent variables will be required to describe the internal energy dependence. These variables will be included in the list of variables along with appropriate potentials. Additionally, the notational convention will be adopted such that superscripts will be used with macroscale variables where subscripts were used with their microscale counterparts. A microscale idealization of a three-phase system is provided in Fig. 2. Note that in actuality the notation $a^{\alpha\beta}$ will be used to indicate the amount of interfacial area between the α - and β - phases per averaging volume and l^{wns} will denote the common line length per volume.

For the α -phase, the macroscale internal energy per volume is expressed according to the relation:

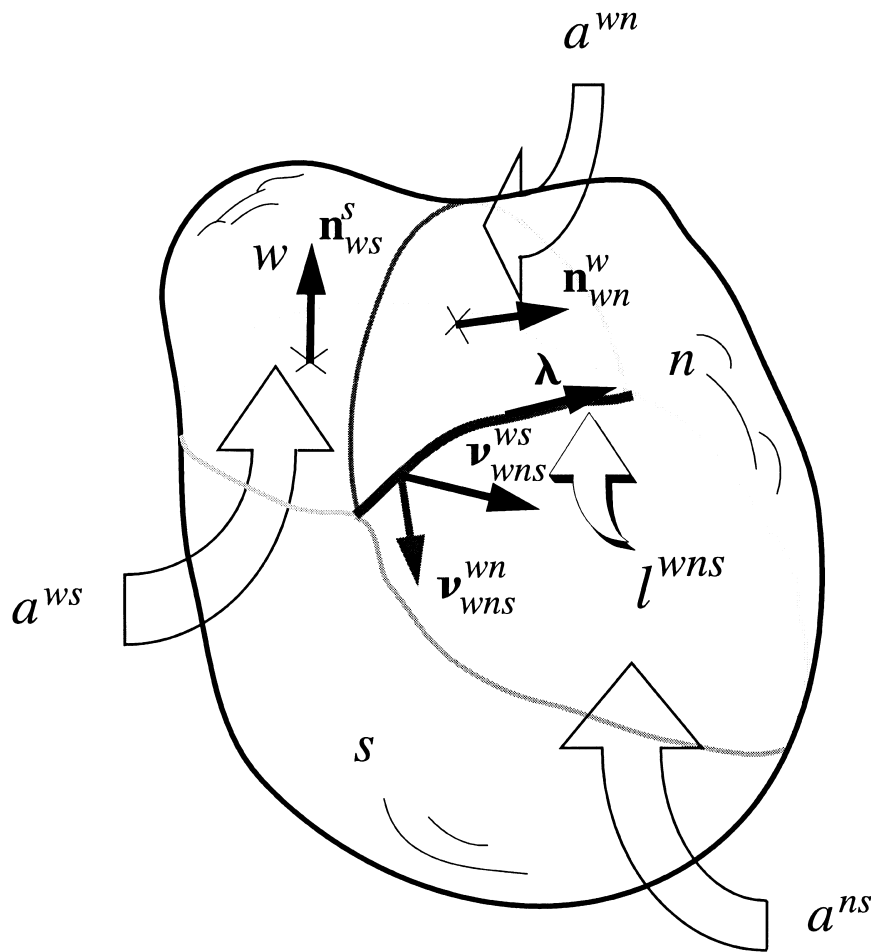


Fig. 2. Schematic diagram of a three-phase wns system as viewed from the microscale perspective. Phases, interfaces, and common line are indicated as are some of the unit vectors of importance in the analysis.

$$\hat{E}^\alpha(\hat{\eta}^\alpha, \varepsilon^\alpha, \rho^{\alpha i}) = \theta^\alpha \hat{\eta}^\alpha - p^\alpha \varepsilon^\alpha + \sum_i \mu^{\alpha i} \rho^{\alpha i} \varepsilon^\alpha \quad (14)$$

where θ^α is the macroscale temperature, $\hat{\eta}^\alpha$ is the macroscale entropy of the α -phase per averaging volume, p^α is the macroscale pressure in the α -phase, ε^α is the volume fraction of α -phase (i.e., the volume of α -phase per averaging volume), $\rho^{\alpha i}$ is the macroscale mass of species i per volume of phase α within an averaging volume, and $\mu^{\alpha i}$ is the macroscale chemical potential of species i in the α -phase. Based on Eq. (14), the temperature, pressure, chemical potential, and additional potentials are obtained as:

$$\theta^\alpha = \frac{\partial \hat{E}^\alpha}{\partial \hat{\eta}^\alpha} \quad (15a)$$

$$p^\alpha = -\frac{\partial \hat{E}^\alpha}{\partial \varepsilon^\alpha} \quad (15b)$$

and

$$\mu^{\alpha i} = \frac{\partial \hat{E}^\alpha}{\partial (\varepsilon^\alpha \rho^{\alpha i})} \quad (15c)$$

The macroscale mass density of the phase is obtained from the species densities as:

$$\rho^\alpha = \sum_i \rho^{\alpha i} \quad (16)$$

The total energy of the phase at equilibrium includes the gravitational potential energy φ^α which is related to the gravitational acceleration according to $\mathbf{g} = -\nabla\varphi^\alpha$. Therefore, the total macroscale α -phase energy per macroscale volume is:

$$\hat{E}_T^\alpha = \hat{E}^\alpha + \sum_i \varepsilon^\alpha \rho^{\alpha i} \varphi^\alpha = \hat{E}^\alpha + \varepsilon^\alpha \rho^\alpha \varphi^\alpha \quad (17)$$

For an $\alpha\beta$ interface, the macroscale internal energy per unit system volume is:

$$\hat{E}^{\alpha\beta}(\hat{\eta}^{\alpha\beta}, a^{\alpha\beta}, \rho^{\alpha\beta i}) = \theta^{\alpha\beta} \hat{\eta}^{\alpha\beta} + \sigma^{\alpha\beta} a^{\alpha\beta} + \sum_i \mu^{\alpha\beta i} \rho^{\alpha\beta i} a^{\alpha\beta} \quad (18)$$

where $\theta^{\alpha\beta}$ is the macroscale temperature, $\hat{\eta}^{\alpha\beta}$ is the macroscale entropy of the $\alpha\beta$ interface per macroscale volume, $\sigma^{\alpha\beta}$ is the macroscale surface tension of the $\alpha\beta$ interface, $a^{\alpha\beta}$ is the area of the $\alpha\beta$ interface per averaging volume, $\rho^{\alpha\beta i}$ is the macroscale mass of species i per unit area of $\alpha\beta$ interface, and $\mu^{\alpha\beta i}$ is the macroscale chemical potential of species i in the $\alpha\beta$ interface. Based on Eq. (18), the temperature, interfacial tension, and chemical potentials are obtained as:

$$\theta^{\alpha\beta} = \frac{\partial \hat{E}^{\alpha\beta}}{\partial \hat{\eta}^{\alpha\beta}} \quad (19a)$$

$$\sigma^{\alpha\beta} = \frac{\partial \hat{E}^{\alpha\beta}}{\partial a^{\alpha\beta}} \tag{19b}$$

and:

$$\mu^{\alpha\beta i} = \frac{\partial \hat{E}^{\alpha\beta}}{\partial (a^{\alpha\beta} \rho^{\alpha\beta i})} \tag{19c}$$

The macroscale mass density of the interface is the mass per unit area and is given by:

$$\rho^{\alpha\beta} = \sum_i \rho^{\alpha\beta i} \tag{20}$$

The total energy of the interface at equilibrium includes the gravitational potential energy $\varphi^{\alpha\beta}$ where $\mathbf{g} = -\nabla\varphi^{\alpha\beta}$. Therefore, the total macroscale energy of the $\alpha\beta$ interface per macroscale volume is:

$$\hat{E}_T^{\alpha\beta} = \hat{E}^{\alpha\beta} + \sum_i a^{\alpha\beta} \rho^{\alpha\beta i} \varphi^{\alpha\beta} = \hat{E}^{\alpha\beta} + a^{\alpha\beta} \rho^{\alpha\beta} \varphi^{\alpha\beta} \tag{21}$$

For a wns common line, the macroscale internal energy per macroscale volume of the mixture is expressed according to the relation:

$$\hat{E}^{wns}(\hat{\eta}^{wns}, l^{wns}, \rho^{wnsi}) = \theta^{wns} \hat{\eta}^{wns} - \sigma^{wns} l^{wns} + \sum_i \mu^{wnsi} \rho^{wnsi} l^{wns} \tag{22}$$

where θ^{wns} is the macroscale temperature, $\hat{\eta}^{wns}$ is the macroscale entropy of the wns common line per volume, σ^{wns} is the macroscale lineal tension of the wns common line, l^{wns} is the length of the wns common line per macroscale volume, ρ^{wnsi} is the macroscale mass of species i per unit length of wns common line, and μ^{wnsi} is the macroscale chemical potential of species i on the wns common line. Based on Eq. (22), the temperature, lineal tension, chemical potential, and additional potentials are defined, respectively, as:

$$\theta^{wns} = \frac{\partial \hat{E}^{wns}}{\partial \hat{\eta}^{wns}} \tag{23a}$$

$$\sigma^{wns} = -\frac{\partial \hat{E}^{wns}}{\partial l^{wns}} \tag{23b}$$

and:

$$\mu^{wnsi} = \frac{\partial \hat{E}^{wns}}{\partial (l^{wns} \rho^{wnsi})} \tag{23c}$$

The macroscale mass density of the common line is the mass per unit length and is given by:

$$\rho^{wns} = \sum_i \rho^{wnsi} \quad (24)$$

The total energy of the common line at equilibrium includes the gravitational potential energy φ^{wns} , where $\mathbf{g} = -\nabla\varphi^{wns}$. Therefore, the total macroscale energy of the wns common line per volume:

$$\hat{E}_T^{wns} = \hat{E}^{wns} + \sum_i l^{wns} \rho^{wnsi} \varphi^{wns} = \hat{E}^{wns} + l^{wns} \rho^{wns} \varphi^{wns} \quad (25)$$

The total energy per unit volume at a macroscale point is obtained as the sum of the energies of the phases, interfaces, and common line at that point:

$$E_T = \hat{E}_T^w + \hat{E}_T^n + \hat{E}_T^s + \hat{E}_T^{wn} + \hat{E}_T^{ws} + \hat{E}_T^{ns} + \hat{E}_T^{wns} \quad (26)$$

This is different from the microscale perspective where the energy at a point is described by a single phase, interface, or common line present at that point.

5. The variational expressions

The variational problem to be considered is designed to determine the thermodynamic and mechanical constraints such that the system will be at a state of minimum energy at equilibrium. This problem is attacked by considering portions of the domain isolated from other portions. Since the derivations of variational equations for phase, interface, and common line properties distract from the central theme of this paper, they are provided in Appendix A. The results are indicated here for continuity of the text.

The variation of the total amount of a property of the α -phase within a system of interest is obtained in Eq. (A14) as:

$$\delta\mathcal{B}^\alpha = \int_{\mathcal{V}} \bar{\delta}\hat{B}^\alpha d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V} \int_{V^\alpha} \bar{\delta}b_\alpha dV \right] d\mathcal{V} + \int_{\mathcal{V}} \left[\sum_{\beta \neq \alpha} \frac{1}{V} \int_{A^{\alpha\beta}} b_\alpha \delta\xi \cdot \mathbf{n}_{\alpha\beta}^\alpha dA \right] d\mathcal{V} \quad (27)$$

In this expression, \mathcal{V} is the total volume of the system, V is the averaging volume whose size, shape, and orientation is independent of position in the system, V^α is the volume of α -phase within the averaging volume, and $A^{\alpha\beta}$ is the boundary between the α - and β -phases within the averaging volume. The unit vector $\mathbf{n}_{\alpha\beta}^\alpha$ is normal to the $\alpha\beta$ interface and oriented positive outward from the α -phase (e.g. see \mathbf{n}_{ws}^s in Fig. 2). The microscale quantity of interest, b_α is a function of position as well as of other quantities. A location in space \mathbf{r} is written in terms of the location of the centroid of the averaging volume, \mathbf{x} , and the location relative to that centroid, ξ , as $\mathbf{r} = \mathbf{x} + \xi$. The microscale density of the quantity of interest, b_α , is thus a function of $\mathbf{x} + \xi$, the macroscale quantity, \hat{B}^α is a function of \mathbf{x} , and the total of the property for the entire system, \mathcal{B}^α , is independent of space. In the equation, the variation $\bar{\delta}$ is a variation holding the \mathbf{x} coordinates constant and δ is a variation taken holding both \mathbf{x} and ξ constant. Thus both variations are fixed point in that the variations are taken holding the spatial coordinates constant. In Eq. (27), the quantity after the first equal sign is of importance

in obtaining the macroscale conditions of equilibrium while the quantity after the second equal sign is important for obtaining equilibrium conditions at the microscale.

The variation of the total amount of a property of an $\alpha\beta$ interface within a system of interest is obtained in Eq. (A29) as:

$$\begin{aligned} \delta\mathcal{B}^{\alpha\beta} &= \int_{\mathcal{V}} \bar{\delta}\hat{\mathcal{B}}^{\alpha\beta} d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V} \int_{A^{\alpha\beta}} \bar{\delta}_s b_{\alpha\beta} dA \right] d\mathcal{V} \\ &+ \int_{\mathcal{V}} \left[\frac{1}{V} \int_{A^{\alpha\beta}} b_{\alpha\beta} \nabla_{\xi} \cdot \mathbf{n}_{\alpha\beta}^{\alpha} \delta\xi \cdot \mathbf{n}_{\alpha\beta}^{\alpha} dA \right] d\mathcal{V} + \int_{\mathcal{V}} \left[\frac{1}{V} \int_{C^{wns}} b_{\alpha\beta} \delta\xi \cdot \mathbf{v}_{wns}^{\alpha\beta} dC \right] d\mathcal{V} \end{aligned} \tag{28}$$

In this equation, C^{wns} is the total length of the common line within an averaging volume. The unit vector $\mathbf{v}_{wns}^{\alpha\beta}$ is normal to the common line, oriented tangent to and pointing outward from the $\alpha\beta$ interface (For example, see \mathbf{v}_{wns}^{wn} in Fig. 2). The new variation in this equation is $\bar{\delta}_s$ which is a fixed point variation holding the \mathbf{x} coordinates and the microscale surficial coordinates constant. The variation of the total amount of an interface property near equilibrium is expressed in terms of the macroscale situation using the first equal sign and in terms of the microscale variation using the second equal sign in Eq. (28).

For the common line, the variational equation is derived as Eq. (A38):

$$\begin{aligned} \delta\mathcal{B}^{wns} &= \int_{\mathcal{V}} \bar{\delta}\hat{\mathcal{B}}^{wns} d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V} \int_{C^{wns}} \bar{\delta}_c b_{wns} dC \right] d\mathcal{V} \\ &- \int_{\mathcal{V}} \left[\frac{1}{V} \int_{C^{wns}} b_{wns} \boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \delta\xi dC \right] d\mathcal{V} \end{aligned} \tag{29}$$

The variation in this equation, $\bar{\delta}_c$ is fixed point holding the macroscale coordinates constant and the coordinate along the curve constant. In addition, the microscale unit vector $\boldsymbol{\lambda}$ which is tangent to the common line appears in this equation. Note that $\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda}$ is the microscale curvature of the common line.

6. Equilibrium conditions for a two-phase system

For purposes of illustration, a two-phase system will be analyzed to obtain both the microscopic and macroscopic equilibrium constraints. The development will be patterned after that of Boruvka and Neumann (1977) who have obtained microscale constraints for multiphase systems. The unconstrained problem that must be solved is the minimization of the functional:

$$\mathcal{F} = \mathcal{E}_T - T\mathcal{S} - \sum_i M_i \mathcal{M}^i \tag{30}$$

where T and M_i are Lagrange multipliers, \mathcal{E}_T is the total energy of the system, \mathcal{S} is the total entropy, and \mathcal{M}_i is the total mass of species i in the system. The minimization problem may be expressed as:

$$\delta \mathcal{F} = \delta \mathcal{E}_T - T \delta \mathcal{S} - \sum_i M_i \delta \mathcal{M}^i = 0 \quad (31)$$

If a system is composed of two-phases designated as the w and n phases, there will be no common lines and Eq. (31) may be stated as:

$$\delta \mathcal{F}^w + \delta \mathcal{F}^n + \delta \mathcal{F}^{wn} = 0 \quad (32)$$

Thus, variational equilibrium considerations will involve only Eqs. (27) and (28) without integration over a common line. The microscale variational problem involves the integrals of the microscale quantities as derived in the second equalities of Eqs. (27) and (28) such that use of the microscale counterparts to \mathcal{F}^w , \mathcal{F}^n , and \mathcal{F}^{wn} in Eq. (32) provides the minimization problem in the form:

$$\begin{aligned} & \sum_{\alpha=w,n} \int_{\mathcal{V}^\alpha} \left[\frac{1}{V} \int_{V^\alpha} \bar{\delta} f_\alpha \, dV \right] d\mathcal{V} + \sum_{\alpha=w,n} \int_{\mathcal{V}^\alpha} \left[\frac{1}{V} \int_{A^{wn}} f_\alpha \delta \boldsymbol{\xi} \cdot \mathbf{n}_{wn}^\alpha \, dA \right] d\mathcal{V} \\ & + \int_{\mathcal{V}^\alpha} \left[\frac{1}{V} \int_{A^{wn}} \bar{\delta}_s f_{wn} \, dA \right] d\mathcal{V} + \int_{\mathcal{V}^\alpha} \left[\frac{1}{V} \int_{A^{wn}} f_{wn} \nabla_\xi \cdot \mathbf{n}_{wn}^w \delta \boldsymbol{\xi} \cdot \mathbf{n}_{wn}^w \, dA \right] d\mathcal{V} = 0 \end{aligned} \quad (33)$$

Substitution of the elements that comprise the microscale functionals f_w , f_n , and f_{wn} and considering only the integrand of the global integral gives:

$$\begin{aligned} & \sum_{\alpha=w,n} \int_{V^\alpha} \bar{\delta} \left[e_\alpha + \rho_\alpha \varphi_\alpha - T \eta_\alpha - \sum_i M_i \rho_{\alpha i} \right] dV \\ & + \sum_{\alpha=w,n} \int_{A^{wn}} \left[e_\alpha + \rho_\alpha \varphi_\alpha - T \eta_\alpha - \sum_i M_i \rho_{\alpha i} \right] \delta \boldsymbol{\xi} \cdot \mathbf{n}_{wn}^\alpha \, dA \\ & + \int_{A^{wn}} \bar{\delta}_s \left[e_{wn} + \rho_{wn} \varphi_{wn} - T \eta_{wn} - \sum_i M_i \rho_{wni} \right] dA \\ & + \int_{A^{wn}} \left[e_{wn} + \rho_{wn} \varphi_{wn} - T \eta_{wn} - \sum_i M_i \rho_{wni} \right] \nabla_\xi \cdot \mathbf{n}_{wn}^w \delta \boldsymbol{\xi} \cdot \mathbf{n}_{wn}^w \, dA = 0 \end{aligned} \quad (34)$$

Application of the fixed point variations and substitution of the expressions for the microscale energy as given in Eqs. (2) and (6) yields:

$$\begin{aligned}
 & \sum_{\alpha=w,n} \int_{V^\alpha} \left[(\theta_\alpha - T) \bar{\delta} \eta_\alpha + \sum_i (\varphi_\alpha + \mu_{\alpha i} - M_i) \bar{\delta} \rho_\alpha^i \right] dV \\
 & + \sum_{\alpha=w,n} \int_{A^{wn}} \left[(\theta_\alpha - T) \eta_\alpha + \sum_i (\varphi_\alpha + \mu_{\alpha i} - M_i) \rho_{\alpha i} - p_\alpha \right] \delta \xi \cdot \mathbf{n}_{wn}^\alpha dA \\
 & + \int_{A^{wn}} \left[(\theta_{wn} - T) \bar{\delta}_s \eta_{wn} + \sum_i (\varphi_{wn} + \mu_{wni} - M_i) \bar{\delta}_s \rho_{wni} \right] dA \\
 & + \int_{A^{wn}} \left[(\theta_{wn} - T) \eta_{wn} + \sum_i (\varphi_{wn} + \mu_{wni} - M_i) \rho_{wni} + \sigma_{wn} \right] \nabla_\xi \cdot \mathbf{n}_{wn}^w \delta \xi \cdot \mathbf{n}_{wn}^w dA = 0
 \end{aligned} \tag{35}$$

In this equation, the multipliers of the variations of entropy and the mass densities must be zero if the equation is to apply for arbitrary variations such that two condition of equilibrium are:

$$T = \theta_w = \theta_n = \theta_{wn} \tag{36}$$

and:

$$M_i = \varphi_w + \mu_{wi} = \varphi_n + \mu_{ni} = \varphi_{wn} + \mu_{wni} \tag{37}$$

The first equation is the condition for thermal equilibrium and the second is the condition for chemical equilibrium. With these conditions employed, Eq. (35) simplifies to:

$$\int_{A^{wn}} [p_n - p_w + \sigma_{wn} \nabla_\xi \cdot \mathbf{n}_{wn}^w] \delta \xi \cdot \mathbf{n}_{wn}^w dA = 0 \tag{38}$$

where use has been made of the fact that $\mathbf{n}_{wn}^w = -\mathbf{n}_{wn}^n$. The quantity $\nabla_\xi \cdot \mathbf{n}_{wn}^w$ is the curvature of the interface based on a normal pointing out from the *w* phase such that the final equilibrium constraint is:

$$p_n - p_w + j_{wn}^w \sigma_{wn} = 0 \tag{39a}$$

where:

$$j_{wn}^w = \nabla_\xi \cdot \mathbf{n}_{wn}^w \tag{39b}$$

and $j_{wn}^w \sigma_{wn}$ is the capillary pressure. Condition (39a) is a classical result known as the Young–Laplace equation. This is the condition for mechanical equilibrium that supplements the thermal and chemical equilibrium constraints.

Next the macroscale equilibrium conditions will be examined with respect to Eqs. (27) and (28). Application of the first equality in these equations transforms Eq. (32) into a variational problem in terms of macroscale quantities:

$$\int_{\mathcal{V}} \bar{\delta} \hat{F}^w d\mathcal{V} + \int_{\mathcal{V}} \bar{\delta} \hat{F}^n d\mathcal{V} + \int_{\mathcal{V}} \bar{\delta} \hat{F}^{wn} d\mathcal{V} = 0 \tag{40}$$

Substitution of the elements that comprise the macroscale functional expands this equation to:

$$\begin{aligned} & \int_{\mathcal{V}^c} \bar{\delta} \left(\hat{E}^w + \varepsilon^w \rho^w \varphi^w - T \hat{\eta}^w - \sum_i M_i \varepsilon^w \rho^{wi} \right) d\mathcal{V}^c \\ & + \int_{\mathcal{V}^c} \bar{\delta} \left(\hat{E}^n + \varepsilon^n \rho^n \varphi^n - T \hat{\eta}^n - \sum_i M_i \varepsilon^n \rho^{ni} \right) d\mathcal{V}^c \\ & + \int_{\mathcal{V}^c} \bar{\delta} \left(\hat{E}^{wn} + a^{wn} \rho^{wn} \varphi^{wn} - T \hat{\eta}^{wn} - \sum_i M_i \varepsilon^{wn} \rho^{wni} \right) d\mathcal{V}^c = 0 \end{aligned} \quad (41)$$

Now apply the fixed point variations to expand these expressions using the functional dependence of energy on independent variables indicated in Eqs. (14) and (18) to obtain:

$$\begin{aligned} & \int_{\mathcal{V}^c} \left[(\theta^w - T) \bar{\delta} \hat{\eta}^w + \sum_i (\varphi^w + \mu^w - M_i) \bar{\delta} (\varepsilon^w \rho^{wi}) - p^w \bar{\delta} \varepsilon^w \right] d\mathcal{V}^c \\ & + \int_{\mathcal{V}^c} \left[(\theta^n - T) \bar{\delta} \hat{\eta}^n + \sum_i (\varphi^n + \mu^n - M_i) \bar{\delta} (\varepsilon^n \rho^{ni}) - p^n \bar{\delta} \varepsilon^n \right] d\mathcal{V}^c \\ & + \int_{\mathcal{V}^c} \left[(\theta^{wn} - T) \bar{\delta} \hat{\eta}^{wn} + \sum_i (\varphi^{wn} + \mu^{wn} - M_i) \bar{\delta} (a^{wn} \rho^{wni}) + \sigma^{wn} \bar{\delta} a^{wn} \right] d\mathcal{V}^c = 0 \end{aligned} \quad (42)$$

The thermal and chemical equilibrium conditions are obtained by setting the coefficients of the entropy and density variations to zero and are analogous to those at the microscale:

$$T = \theta^w = \theta^n = \theta^{wn} \quad (43)$$

and:

$$M_i = \varphi^w + \mu^{wi} = \varphi^n + \mu^{ni} = \varphi^{wn} + \mu^{wni} \quad (44)$$

In fact, these relations indicate that microscopic and macroscopic equilibrium temperatures and chemical potentials are equal. With these conditions imposed, the residual of the variational equation is:

$$\int_{\mathcal{V}^c} \left[-p^w \bar{\delta} \varepsilon^w - p^n \bar{\delta} \varepsilon^n + \sigma^{wn} \bar{\delta} a^{wn} \right] d\mathcal{V}^c = 0 \quad (45)$$

From this equation, it is clear that if the variations in volume fractions and area density are independent, the equilibrium condition is that each of the macroscale pressures and the interfacial tension must be zero. Since experimental observations indicate that this is not the case, the variations of the various geometric quantities must be somehow related. These relations are determined by examining the variations in terms of their microscale precursors.

First of all, based on Eq. (27), with $b_w = b_n = 1$, the variations of each of the volume

fractions may be expressed, respectively, as:

$$\bar{\delta}\varepsilon^w = \frac{1}{V} \int_{A^{wn}} \delta\xi \cdot \mathbf{n}_{wn}^w \, dA \tag{46a}$$

and:

$$\bar{\delta}\varepsilon^n = \frac{1}{V} \int_{A^{wn}} \delta\xi \cdot \mathbf{n}_{wn}^n \, dA \tag{46b}$$

Since $\mathbf{n}_{wn}^w = -\mathbf{n}_{wn}^n$ it must be true that:

$$\bar{\delta}\varepsilon^n + \bar{\delta}\varepsilon^w = 0 \tag{47}$$

This expression may be considered obvious in that the definition of the volume fraction dictates that the sum of the two void fractions must equal 1 at all times. However, it is worth noting that relation (47) has been developed here using much different reasoning based on the variational analysis and is applied only at near equilibrium conditions.

Based on Eq. (28) with $b_{wn} = 1$, the relation for the variation of the areal density may be obtained. For the two-phase case, there is no common line so the expression for $\bar{\delta}a^{wn}$ is:

$$\bar{\delta}a^{wn} = \frac{1}{V} \int_{A^{wn}} \nabla_\xi \cdot \mathbf{n}_{wn}^w \delta\xi \cdot \mathbf{n}_{wn}^w \, dA \tag{48}$$

Inspection of this equation reveals that for the case of spherical interfaces of uniform curvature, the quantity $\nabla_\xi \cdot \mathbf{n}_{wn}^w$ will not depend on ξ and could be removed from the integrand. This would provide an immediate relation between $\bar{\delta}a^{wn}$ and $\bar{\delta}\varepsilon^w$. In the more general case where the interface is not necessarily spherical, a macroscale variable J_{wn}^w may be introduced such that it can be moved inside of the integral over the microscale areal coordinates. Thus Eq. (46a) may be written:

$$J_{wn}^w \bar{\delta}\varepsilon^w = \frac{1}{V} \int_{A^{wn}} J_{wn}^w \delta\xi \cdot \mathbf{n}_{wn}^w \, dA \tag{49}$$

Subtraction of Eq. (49) from Eq. (48) yields:

$$\bar{\delta}a^{wn} - J_{wn}^w \bar{\delta}\varepsilon^w = \frac{1}{V} \int_{A^{wn}} (\nabla_\xi \cdot \mathbf{n}_{wn}^w - J_{wn}^w) \delta\xi \cdot \mathbf{n}_{wn}^w \, dA \tag{50}$$

Thus J_{wn}^w is a measure of the macroscale curvature and can be selected such that the right side of Eq. (50) is zero and:

$$\bar{\delta}a^{wn} - J_{wn}^w \bar{\delta}\varepsilon^w = 0 \tag{51}$$

Based on insights from Eqs. (47) and (51) such that $\bar{\delta}\varepsilon^n$ and $\bar{\delta}a^{wn}$ may each be expressed in terms of $\bar{\delta}\varepsilon^w$, Eq. (45) is rearranged to the near-equilibrium form:

$$\int_{\mathcal{V}^c} [(p^n - p^w + \sigma^{wn} J_{wn}^w) \bar{\delta}\varepsilon^w] \, d\mathcal{V}^c = 0 \tag{52}$$

For the integral to be zero for any variation of ε^w and also independent of the size of the system considered, the macroscale equilibrium condition is:

$$p^n - p^w + \sigma^{wn} J_{wn}^w = 0 \quad (53)$$

where $\sigma^{wn} J_{wn}^w$ is the macroscale capillary pressure. Although this equation is clearly similar in form to the microscale equilibrium condition derived previously as Eq. (39a), in fact it is quite different in interpretation. First, although this equation looks like its microscopic counterpart, the quantities are macroscopic values characteristic of an averaging volume. Thus equilibrium relation (53) is not merely a direct average of its microscale counterpart as has been asserted, for example, in Nitao and Bear (1996). In fact, no averaging of pressure or interfacial tension was performed to obtain Eq. (53) as these quantities are defined directly at the macroscale.

Second, whereas the microscopic capillary pressure is defined as the product of the microscale interfacial tension and the microscale curvature (which is a function of the actual geometry of the interface) the macroscopic capillary pressure is seen to be defined uniquely as the product of the macroscale interfacial tension and a measure of the macroscale curvature of the interfaces within the averaging volume. Thus, macroscale curvature cannot be expressed in terms of microscale variables but is actually a function of the volume fraction and the area density. This assertion may be seen quantitatively by working with the total grand canonical potential of the system, $\hat{\Omega}_T$, defined using Legendre transformations on the total internal energy (Callen, 1985; Gray, 1999) such that:

$$\hat{\Omega}_T = \hat{\Omega}_T^w + \hat{\Omega}_T^n + \hat{\Omega}_T^{wn} \quad (54a)$$

where:

$$\hat{\Omega}_T^\alpha(\theta^\alpha, \mu^\alpha + \varphi^\alpha, \varepsilon^\alpha) = \hat{E}^\alpha - \theta^\alpha \hat{\eta}^\alpha - (\mu^\alpha + \varphi^\alpha) \varepsilon^\alpha \rho^\alpha = -p^\alpha \varepsilon^\alpha \quad \alpha = w, n \quad (54b)$$

$$\hat{\Omega}_T^{wn}(\theta^{wn}, \mu^{wn} + \varphi^{wn}, a^{wn}) = \hat{E}^{wn} - \theta^{wn} \hat{\eta}^{wn} - (\mu^{wn} + \varphi^{wn}) a^{wn} \rho^{wn} = \sigma^{wn} a^{wn} \quad (54c)$$

When equilibrium conditions (43) and (44) are enforced, the differential change in the total grand canonical potential is:

$$d\hat{\Omega}_T|_{\theta, \mu + \varphi} = (p^n - p^w) d\varepsilon^w + \sigma^{wn} da^{wn} \quad (55)$$

Comparison of Eqs. (55) and (53) provides the relation for the macroscale effective curvature in terms of macroscale variables as:

$$J_{wn}^w = \left(\frac{\partial a^{wn}}{\partial \varepsilon^w} \right)_{\theta, \mu + \varphi, \hat{\Omega}_T} \quad (56)$$

This is quite different in substance from its microscale counterpart, Eq. (39b). Finally, the near equilibrium relation (51) between changes in macroscale volume fractions and interfacial areal densities can be used to gain additional insight into transient processes and constitutive relations needed for the study of dynamic systems at the macroscale.

7. Equilibrium conditions for a general three-phase system

In the analysis of two-phase systems, the microscale situation was examined primarily to demonstrate the contrast with the macroscale case. For the three-phase system, the analysis presented here will be restricted to the macroscale case. The study will nevertheless require that the microscale geometry of the system be transformed so that it can be accounted for from the macroscale perspective. In particular it is important to consider the microscale angles at which the interfaces meet at a common line, as depicted in Fig. 3.

For a multiphase system, the constraints that result for thermal and chemical potential equilibrium are direct extensions of those for the two-phase case found in Eqs. (43) and (44). These conditions state that at all macroscale points of the system in all phases, interfaces, common lines, and common points, the temperatures must be equal; and the chemical plus gravitational potentials must be equal. The part of the equation that remains to be examined for mechanical equilibrium for a three-phase system is:

$$\int_{\mathcal{V}^c} \bar{\delta} \hat{\Omega}_T |_{\theta, \mu + \varphi} d\mathcal{V}^c = \int_{\mathcal{V}^c} [-p^w \bar{\delta} \varepsilon^w - p^n \bar{\delta} \varepsilon^n - p^s \bar{\delta} \varepsilon^s + \sigma^{wn} \bar{\delta} a^{wn} + \sigma^{ws} \bar{\delta} a^{ws} + \sigma^{ns} \bar{\delta} a^{ns} - \sigma^{wns} \bar{\delta} l^{wns}] d\mathcal{V}^c = 0 \tag{57}$$

To obtain the conditions of equilibrium, the dependence of the variations that appear in this equation on each other must be ascertained such that the integrand on the right side is zero.

For the volume fractions, the three equations that express their variations are obtained based on Eq. (27) with $b_\alpha = 1$ for each α -phase as:

$$\bar{\delta} \varepsilon^w = \frac{1}{V} \int_{A^{wn}} \delta \xi \cdot \mathbf{n}_{wn}^w dA + \frac{1}{V} \int_{A^{ws}} \delta \xi \cdot \mathbf{n}_{ws}^w dA \tag{58a}$$

$$\bar{\delta} \varepsilon^n = \frac{1}{V} \int_{A^{wn}} \delta \xi \cdot \mathbf{n}_{wn}^n dA + \frac{1}{V} \int_{A^{ns}} \delta \xi \cdot \mathbf{n}_{ns}^n dA \tag{58b}$$

and:

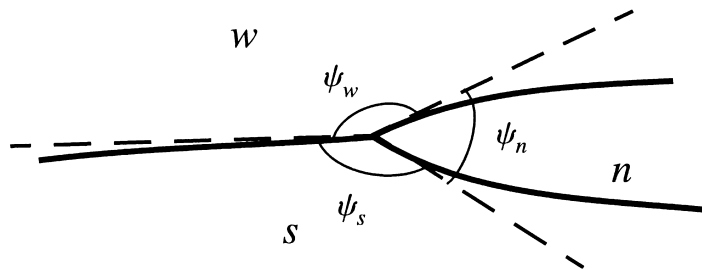


Fig. 3. Three phase w, n, s system with interfaces between phases (dark curves) and angles of intersection, ψ_α , at the common line indicated.

$$\bar{\delta}\varepsilon^s = \frac{1}{V} \int_{A^{ws}} \delta\xi \cdot \mathbf{n}_{ws}^s \, dA + \frac{1}{V} \int_{A^{ns}} \delta\xi \cdot \mathbf{n}_{ns}^s \, dA \quad (58c)$$

Because $\mathbf{n}_{\alpha\beta}^\alpha = -\mathbf{n}_{\alpha\beta}^\beta$ these three variational expressions for the volume fractions are actually written in terms of three independent integrals involving the variation $\delta\xi$.

For the interfaces, the equations for the macroscale area densities are based on Eq. (28) with $b_{\alpha\beta} = 1$ and have the forms:

$$\bar{\delta}a^{wn} = \frac{1}{V} \int_{A^{wn}} \nabla_\xi \cdot \mathbf{n}_{wn}^w \delta\xi \cdot \mathbf{n}_{wn}^w \, dA + \frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{v}_{wns}^{wn} \, dC \quad (59a)$$

$$\bar{\delta}a^{ws} = \frac{1}{V} \int_{A^{ws}} \nabla_\xi \cdot \mathbf{n}_{ws}^s \delta\xi \cdot \mathbf{n}_{ws}^s \, dA + \frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{v}_{wns}^{ws} \, dC \quad (59b)$$

and:

$$\bar{\delta}a^{ns} = \frac{1}{V} \int_{A^{ns}} \nabla_\xi \cdot \mathbf{n}_{ns}^s \delta\xi \cdot \mathbf{n}_{ns}^s \, dA + \frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{v}_{wns}^{ns} \, dC \quad (59c)$$

To make use of these relations, it is useful to define macroscale curvatures, $J_{\alpha\beta}^\alpha(\mathbf{x})$ which are thus functions of the macroscale coordinates but are constants with respect to the integrations over ξ coordinates such that:

$$\frac{1}{V} \int_{A^{\alpha\beta}} (\nabla_\xi \cdot \mathbf{n}_{\alpha\beta}^\alpha - J_{\alpha\beta}^\alpha) \delta\xi \cdot \mathbf{n}_{\alpha\beta}^\alpha \, dA = 0 \quad (60)$$

Additionally, it is useful to express the three different unit vectors that appear in the integrals over the common line in terms of an orthonormal pair of unit vectors according to:

$$\mathbf{v}_{wns}^{wn} = \cos \psi_w \mathbf{v}_{wns}^{ws} - \sin \psi_w \mathbf{n}_{wns}^s \quad (61a)$$

and:

$$\mathbf{v}_{wns}^{ns} = \cos \psi_s \mathbf{v}_{wns}^{ws} + \sin \psi_s \mathbf{n}_{wns}^s \quad (61b)$$

Now introduce a pair of macroscale function types that will be defined by:

$$\frac{1}{V} \int_{C^{wns}} (\cos \psi_\alpha - \cos \Psi^\alpha) \delta\xi \cdot \mathbf{v}_{wns}^{ws} \, dC = 0 \quad (62a)$$

and:

$$\frac{1}{V} \int_{C^{wns}} (\sin \psi_\alpha - \sin \Psi^\alpha) \delta\xi \cdot \mathbf{n}_{wns}^s \, dC = 0 \quad (62b)$$

The macroscale functions of \mathbf{x} designated as $\cos \Psi^\alpha$ and $\sin \Psi^\alpha$ are conceptually some average cosine and sine functions of the microscale angle ψ_α along the common line within an averaging volume. However, these are not true sine and cosine functions because their sum squared is not necessarily equal to 1 for all distributions of angles that could exist within an

averaging volume. The notation adopted is used to indicate the interpretation of the functions that appear. Use of Eqs. (60)–(62b) in Eqs. (59a)–(59c) provides:

$$\begin{aligned} \bar{\delta}a^{wn} = & J_{wn}^w \left[\frac{1}{V} \int_{A^{wn}} \delta\xi \cdot \mathbf{n}_{wn}^w \, dA \right] + \cos \Psi^w \left[\frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{v}_{wns}^{ws} \, dC \right] \\ & - \sin \Psi^w \left[\frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{n}_{ws}^s \, dC \right] \end{aligned} \tag{63a}$$

$$\bar{\delta}a^{ws} = J_{ws}^s \left[\frac{1}{V} \int_{A^{ws}} \delta\xi \cdot \mathbf{n}_{ws}^s \, dA \right] + \left[\frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{v}_{wns}^{ws} \, dC \right] \tag{63b}$$

$$\begin{aligned} \bar{\delta}a^{ns} = & J_{ns}^s \left[\frac{1}{V} \int_{A^{ns}} \delta\xi \cdot \mathbf{n}_{ns}^s \, dA \right] + \cos \Psi^s \left[\frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{v}_{wns}^{ws} \, dC \right] \\ & + \sin \Psi^s \left[\frac{1}{V} \int_{C^{wns}} \delta\xi \cdot \mathbf{n}_{ws}^s \, dC \right] \end{aligned} \tag{63c}$$

The integrals over the areas that appear in these expressions have already appeared in Eqs. (58a)–(58c) for the variations of the void fractions. Two different additional integrals appear over the common line. Thus the variations of the six volume and areal geometric densities are expressible in terms of five independent variations.

The variational expression for the common line length per volume is obtained from Eq. (28) for the case where $b_{wns} = 1$ such that:

$$\bar{\delta}l^{wns} = -\frac{1}{V} \int_{C^{wns}} \boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \delta\xi \, dC \tag{64}$$

where $\boldsymbol{\lambda}$ is the tangent to the common line and $\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda}$ is the curvature of the line. This vector is orthogonal to $\boldsymbol{\lambda}$ such that it can be expressed in terms of any pair of orthonormal vectors that are normal to the common line. For instance, in terms of the pair of vectors \mathbf{v}_{wns}^{ws} and \mathbf{n}_{ws}^s :

$$\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} = (\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \mathbf{v}_{wns}^{ws}) \mathbf{v}_{wns}^{ws} + (\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \mathbf{n}_{ws}^s) \mathbf{n}_{ws}^s \tag{65}$$

Substitution of this equation into Eq. (64) gives the form of the variational expression:

$$\bar{\delta}l^{wns} = -\frac{1}{V} \int_{C^{wns}} (\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \mathbf{v}_{wns}^{ws}) \mathbf{v}_{wns}^{ws} \cdot \delta\xi \, dC - \frac{1}{V} \int_{C^{wns}} (\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \mathbf{n}_{ws}^s) \mathbf{n}_{ws}^s \cdot \delta\xi \, dC \tag{66}$$

In these two integrals, the first quantity in parentheses is the microscale geodesic curvature, $\kappa_g(\mathbf{x} + \boldsymbol{\xi})$ while the second quantity in parentheses is the microscale normal curvature, $\kappa_n(\mathbf{x} + \boldsymbol{\xi})$, with respect to the ws interfacial surface. Effective macroscale geodesic and normal curvatures, indicated as $\kappa^G(\mathbf{x})$ and $\kappa^N(\mathbf{x})$ respectively can be defined such that:

$$\frac{1}{V} \int_{C^{wns}} \left[(\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \mathbf{v}_{wns}^{ws}) - \kappa^G \right] \mathbf{v}_{wns}^{ws} \cdot \delta\xi \, dC = 0 \tag{67a}$$

and:

$$\frac{1}{V} \int_{C^{wns}} \left[(\boldsymbol{\lambda} \cdot \nabla \boldsymbol{\lambda} \cdot \mathbf{n}_{ws}^s) - \kappa^N \right] \mathbf{n}_{ws}^s \cdot \delta \boldsymbol{\xi} \, dC = 0 \quad (67b)$$

Making use of these relations in Eq. (66), one obtains:

$$\bar{\delta} l^{wns} = -\kappa^G \left[\frac{1}{V} \int_{C^{wns}} \mathbf{v}_{wns}^{ws} \cdot \delta \boldsymbol{\xi} \, dC \right] - \kappa^N \left[\frac{1}{V} \int_{C^{wns}} \mathbf{n}_{ws}^s \cdot \delta \boldsymbol{\xi} \, dC \right] \quad (68)$$

This expression does not contain any integrals that have not already appeared in the expressions (63a) through (63c) for the interfacial areas. Thus the variations in the seven geometric densities at equilibrium conditions may be expressed in terms of five independent variations. Therefore, there will be five equilibrium conditions and two relations among the variations in the geometric densities.

Substitution of Eqs. (58a)–(58c), (63a)–(63c), and (68) into the integrand of Eq. (57) yields:

$$\begin{aligned} \delta \hat{\Omega}_T |_{\theta, \mu + \varphi} = & \left[-p^w + p^n + \sigma^{wn} J_{wn}^w \right] \left[\frac{1}{V} \int_{A^{wn}} \delta \boldsymbol{\xi} \cdot \mathbf{n}_{wn}^w \, dA \right] + \left[p^w - p^s + \sigma^{ws} J_{ws}^s \right] \\ & \times \left[\frac{1}{V} \int_{A^{ws}} \delta \boldsymbol{\xi} \cdot \mathbf{n}_{ws}^s \, dA \right] + \left[p^n - p^s + \sigma^{ns} J_{ns}^s \right] \left[\frac{1}{V} \int_{A^{ns}} \delta \boldsymbol{\xi} \cdot \mathbf{n}_{ns}^s \, dA \right] \\ & + \left[\sigma^{wn} \cos \Psi^w + \sigma^{ws} + \sigma^{ns} \cos \Psi^s + \sigma^{wns} \kappa^G \right] \left[\frac{1}{V} \int_{C^{wns}} \mathbf{v}_{wns}^{ws} \cdot \delta \boldsymbol{\xi} \, dC \right] \\ & + \left[-\sigma^{wn} \sin \Psi^w + \sigma^{ns} \sin \Psi^s + \sigma^{wns} \kappa^N \right] \left[\frac{1}{V} \int_{C^{wns}} \mathbf{n}_{ws}^s \cdot \delta \boldsymbol{\xi} \, dC \right] = 0 \end{aligned} \quad (69)$$

For the equality to be satisfied, each of the coefficients of the integral variations must be zero. Thus the equilibrium conditions for a general three-phase system are:

$$-p^w + p^n + \sigma^{wn} J_{wn}^w = 0 \quad (70a)$$

$$p^w - p^s + \sigma^{ws} J_{ws}^s = 0 \quad (70b)$$

$$p^n - p^s + \sigma^{ns} J_{ns}^s = 0 \quad (70c)$$

$$\sigma^{wn} \cos \Psi^w + \sigma^{ws} + \sigma^{ns} \cos \Psi^s + \sigma^{wns} \kappa^G = 0 \quad (70d)$$

$$-\sigma^{wn} \sin \Psi^w + \sigma^{ns} \sin \Psi^s + \sigma^{wns} \kappa^N = 0 \quad (70e)$$

The two equilibrium relations among variations in the geometric properties may be obtained from manipulation of Eqs. (58a)–(58c), (63a)–(63c) and (68) as:

$$\bar{\delta} \varepsilon^w + \bar{\delta} \varepsilon^n + \bar{\delta} \varepsilon^s = 0 \quad (71a)$$

and:

$$\begin{aligned}
 & [\kappa^N J_{ns}^s + J_{ws}^s (\kappa^N \cos \Psi^s - \kappa^G \sin \Psi^s)] \{ \bar{\delta} a^{wn} - J_{wn}^w \bar{\delta} \varepsilon^w \} \\
 & + [\kappa^N J_{wn}^w - J_{ws}^s (\kappa^N \cos \Psi^w + \kappa^G \sin \Psi^w)] \{ \bar{\delta} a^{ns} - J_{ns}^s \bar{\delta} \varepsilon^s \} \\
 & - [J_{wn}^w (\kappa^N \cos \Psi^s - \kappa^G \sin \Psi^s) + J_{ns}^s (\kappa^N \cos \Psi^w + \kappa^G \sin \Psi^w)] \bar{\delta} a^{ws} \\
 & + [J_{wn}^w \sin \Psi^s - J_{ns}^s \sin \Psi^w - J_{ws}^s \sin(\Psi^s + \Psi^w)] \bar{\delta} l^{wns} = 0
 \end{aligned} \tag{71b}$$

With these relations employed, the integrand in Eq. (57) may be rearranged to obtain the equilibrium expression:

$$\begin{aligned}
 & [J_{ws}^s (\kappa^N \cos \Psi^w + \kappa^G \sin \Psi^w) - \kappa^N J_{wn}^w] \bar{\delta} \hat{\Omega}_T |_{\theta, \mu + \varphi} = [-p^w + p^n + \sigma^{wn} J_{wn}^w] \\
 & \times [(\kappa^N \cos \Psi^w + \kappa^G \sin \Psi^w) (J_{ws}^s \bar{\delta} \varepsilon^w + \bar{\delta} a^{ws}) - \kappa^N \bar{\delta} a^{wn} + \sin \Psi^w \bar{\delta} l^{wns}] \\
 & + [p^w - p^s + \sigma^{ws} J_{ws}^s] [(\kappa^N \cos \Psi^w + \kappa^G \sin \Psi^w) \bar{\delta} a^{ws} + \kappa^N (J_{wn}^w \bar{\delta} \varepsilon^w - \bar{\delta} a^{wn}) + \sin \Psi^w \bar{\delta} l^{wns}] \\
 & + [p^n - p^s + \sigma^{ns} J_{ns}^s] [(\kappa^N \cos \Psi^w + \kappa^G \sin \Psi^w) (-J_{ws}^s \bar{\delta} \varepsilon^w - J_{ws}^s \bar{\delta} a^{ws}) \\
 & + \kappa^N (J_{wn}^w \bar{\delta} \varepsilon^n + \bar{\delta} a^{wn}) - \sin \Psi^w \bar{\delta} l^{wns}] + [\sigma^{wn} \cos \Psi^w + \sigma^{ws} + \sigma^{ns} \cos \Psi^s + \sigma^{wns} \kappa^G] \\
 & \times [\kappa^N (J_{ws}^s \bar{\delta} a^{wn} - J_{wn}^w \bar{\delta} a^{ws} - J_{ws}^s J_{ws}^w \bar{\delta} \varepsilon^w) - J_{ws}^s \sin \Psi^w \bar{\delta} l^{wns}] \\
 & + [-\sigma^{wn} \sin \Psi^w + \sigma^{ns} \sin \Psi^s + \sigma^{wns} \kappa^N] \\
 & \times [(J_{wn}^w - J_{ws}^s \cos \Psi^w) \bar{\delta} l^{wns} - \kappa^G (J_{wn}^w \bar{\delta} a^{ws} + J_{ws}^s \bar{\delta} a^{wn} - J_{wn}^w J_{ws}^s \bar{\delta} \varepsilon^w)] = 0
 \end{aligned} \tag{72}$$

The utility of this equation is that it provides the equilibrium thermodynamic situation as being composed of a sum of five products of terms, for which each factor is zero at equilibrium. This quality can be useful in studying dynamic systems.

It may seem reasonable that the above relations can be considered to hold for the case where one of the phases is a solid. However, this is not so. In fact, the above manipulations were performed where the degenerate cases, such as when any of the angles is an integer multiple of $\pi/2$, have been ignored. Since the case of a solid phase and two immiscible fluids is an important one, and is also a degenerate case of the above analysis, it will be treated explicitly in the next section.

8. Mechanical equilibrium for two fluids and one solid phase

Consideration of this system follows along the lines of the previous analysis, but some of the unique characteristics of a solid are incorporated. (58a)–(58c), (63a)–(63c), and (68) provide the initial forms for the variations of the geometric quantities. The solid phase is considered to be smooth such that $\Psi^s = \pi$. Then, a variational expression may be written for the total solid phase as a sum of Eqs. (63b) and (63c):

$$\bar{\delta}a^s = \bar{\delta}a^{ws} + \bar{\delta}a^{ns} = J_{ws}^s \left[\frac{1}{V} \int_{A^{ws}} \delta\xi \cdot \mathbf{n}_{ws}^s \, dA \right] + J_{ns}^s \left[\frac{1}{V} \int_{A^{ns}} \delta\xi \cdot \mathbf{n}_{ns}^s \, dA \right] \quad (73)$$

Alternatively, a variational expression may be obtained for a^s directly using Eq. (27) as:

$$\bar{\delta}a^s = J^s \left[\frac{1}{V} \int_{A^s} \delta\xi \cdot \mathbf{n}^s \, dA \right] \quad (74)$$

where J^s is the effective curvature of the solid phase surface, \mathbf{n}^s is the unit normal on the solid surface, and $A^s = A^{ws} + A^{ns}$ is the total solid phase surface. The effective curvature is reasonably considered to be a weighted average of J_{ws}^s and J_{ns}^s according to the expression:

$$J^s = x_s^{ws} J_{ws}^s + x_s^{ns} J_{ns}^s \quad (75)$$

where x_s^{ws} is the fraction of the solid phase surface in contact with the w phase and x_s^{ns} is the fraction of the solid phase surface in contact with the n phase such that $x_s^{ws} + x_s^{ns} = 1$. Substitution of Eq. (75) into Eq. (74) and subtraction of the result from Eq. (73) yields:

$$\begin{aligned} 0 = & J_{ws}^s \left[\frac{1}{V} \int_{A^{ws}} \delta\xi \cdot \mathbf{n}_{ws}^s \, dA - x_s^{ws} \frac{1}{V} \int_{A^s} \delta\xi \cdot \mathbf{n}^s \, dA \right] \\ & + J_{ns}^s \left[\frac{1}{V} \int_{A^{ns}} \delta\xi \cdot \mathbf{n}_{ns}^s \, dA - x_s^{ns} \frac{1}{V} \int_{A^s} \delta\xi \cdot \mathbf{n}^s \, dA \right] \end{aligned} \quad (76)$$

For this equation to hold for all cases, the variations must be related according to:

$$x_s^{ns} \frac{1}{V} \int_{A^{ws}} \delta\xi \cdot \mathbf{n}_{ws}^s \, dA = x_s^{ws} \frac{1}{V} \int_{A^{ns}} \delta\xi \cdot \mathbf{n}_{ns}^s \, dA \quad (77)$$

With these conditions imposed, Eq. (69), for a solid being one of the three phases, is:

$$\begin{aligned}
 \delta \hat{Q}_T|_{\theta, \mu + \varphi} = & \left[p^n - p^w + \sigma^{wn} J_{wn}^w \right] \left[\frac{1}{V} \int_{A^{wn}} \delta \xi \cdot \mathbf{n}_{wn}^w \, dA \right] \\
 & + \left[x_s^{ws} p^w + x_s^{ns} p^n - p^s + x_s^{ws} \sigma^{ws} J_{ws}^s + x_s^{ns} \sigma^{ns} J_{ns}^s \right] \left[\frac{1}{x_s^{ws} V} \int_{A^{ws}} \delta \xi \cdot \mathbf{n}_{ws}^s \, dA \right] \\
 & + \left[\sigma^{wn} \cos \Psi^s + \sigma^{ws} - \sigma^{ns} + \sigma^{wns} \kappa^G \right] \left[\frac{1}{V} \int_{C^{wns}} v_{wns}^{ws} \cdot \delta \xi \, dC \right] \\
 & + \left[\sigma^{wns} \kappa^N - \sigma^{wn} \sin \Psi^w \right] \left[\frac{1}{V} \int_{C^{wns}} \mathbf{n}_{ws}^s \cdot \delta \xi \, dC \right] = 0
 \end{aligned} \tag{78}$$

For the equality to be satisfied for the variation around equilibrium, the coefficients of the integrals must each be zero so that when one phase of a three-phase system is a solid, four mechanical equilibrium conditions result (rather than the five conditions for the more general case):

$$p^n - p^w + \sigma^{wn} J_{wn}^w = 0 \tag{79a}$$

$$x_s^{ws} p^w + x_s^{ns} p^n - p^s + x_s^{ws} \sigma^{ws} J_{ws}^s + x_s^{ns} \sigma^{ns} J_{ns}^s = 0 \tag{79b}$$

$$\sigma^{wn} \cos \Psi^w + \sigma^{ws} - \sigma^{ns} + \sigma^{wns} \kappa^G = 0 \tag{79c}$$

$$\sigma^{wns} \kappa^N - \sigma^{wn} \sin \Psi^w = 0 \tag{79d}$$

Since there are seven geometric parameters and only four independent variations, there must be three variational relations involving only the geometric parameters. Although these relations may be derived directly, it is more convenient to work with parameters that are commonly employed in porous media studies. The three volume density parameters, $\varepsilon^w, \varepsilon^n$, and ε^s , are related to the porosity, ε , and the saturations of each of the fluids, s^w and s^n , respectively by:

$$\varepsilon^s = 1 - \varepsilon \tag{80a}$$

$$\varepsilon^w = \varepsilon s^w \tag{80b}$$

$$\varepsilon^n = \varepsilon s^n \tag{80c}$$

where $s^w + s^n = 1$. Also the area densities of the solid phases are related to the total solid surface area and the fraction of the area in contact with each phase according to:

$$a^{ws} = x_s^{ws} a^s \tag{81a}$$

$$a^{ns} = (1 - x_s^{ws}) a^s \tag{81b}$$

Thus with the seven geometric parameters transformed to $\varepsilon, s^w, s^n, a^s, x_s^{ws}, a^{wn}$, and l^{wns} , the three

relations among the parameters are derived as:

$$\bar{\delta}s^w + \bar{\delta}s^n = 0 \quad (82a)$$

$$\bar{\delta}a^s + J^s \bar{\delta}\varepsilon = 0 \quad (82b)$$

and:

$$\begin{aligned} \bar{\delta}a^{wn} - \varepsilon J_{wn}^w \bar{\delta}s^w - a^s \left[\cos \Psi^w + \frac{\kappa^G \sin \Psi^w}{\kappa^N} \right] \bar{\delta}x_s^{ws} - \frac{\sin \Psi^w}{\kappa^N} \bar{\delta}l^{wns} \\ + \left[J_{wn}^w (x_s^{ws} - s^w) - x_s^{ws} x_s^{ns} (J_{ws}^s - J_{ns}^s) \left(\cos \Psi^w + \frac{\kappa^G \sin \Psi^w}{\kappa^N} \right) \right] \bar{\delta}\varepsilon = 0 \end{aligned} \quad (82c)$$

With these relations, the integrand in Eq. (57) may be rearranged to the form:

$$\begin{aligned} \bar{\delta}\hat{\Omega}_T|_{\theta, \mu+\varphi} = & -[x_s^{ws} p^w + x_s^{ns} p^n - p^s + x_s^{ws} \sigma^{ws} J_{ws}^s + x_s^{ns} \sigma^{ns} J_{ns}^s] [\bar{\delta}\varepsilon] \\ & + [p^n - p^w + \sigma^{wn} J_{wn}^w] [\varepsilon \bar{\delta}s^w + (s^w - x_s^{ws}) \bar{\delta}\varepsilon] \\ & + [\sigma^{wn} \cos \Psi^w + \sigma^{ws} - \sigma^{ns} + \sigma^{wns} \kappa^G] [a^s \bar{\delta}x_s^{ws} + x_s^{ns} x_s^{ws} (J_{ws}^s - J_{ns}^s) \bar{\delta}\varepsilon] \\ & - \frac{1}{\kappa^N} [\sigma^{wns} \kappa^N - \sigma^{wn} \sin \Psi^w] [\bar{\delta}l^{wns} + \kappa^G a^s \bar{\delta}x_s^{ws} + \kappa^G x_s^{ns} x_s^{ws} (J_{ws}^s - J_{ns}^s) \bar{\delta}\varepsilon] \end{aligned} \quad (83)$$

This arrangement provides the set of four products of pairs of terms in square brackets. For these products, the first of each pair is zero at equilibrium by Eqs. (79a)–(79d) and the second in each product is an independent variation.

All terms in these equilibrium constraints are thermodynamic variables. The definitions of the macroscale curvatures and angles may be obtained from the functional dependence of the grand canonical potential on the geometric densities by taking derivatives while holding some parameters constant so that an equilibrium condition is recovered. Then a term by term comparison of the equilibrium condition with the result obtained from the differentiation processes leads to the following definitions:

$$J_{ws}^s = - \left(\frac{\partial a^s}{\partial \varepsilon} \right)_{\varepsilon^n, a^{wn}, a^{ns}, l^{wns}, \hat{\Omega}, \theta, \mu+\varphi} \quad (84a)$$

$$J_{ns}^s = - \left(\frac{\partial a^s}{\partial \varepsilon} \right)_{\varepsilon^w, a^{wn}, a^{ws}, l^{wns}, \hat{\Omega}, \theta, \mu+\varphi} \quad (84b)$$

$$J_{wn}^w = \frac{1}{\varepsilon} \left(\frac{\partial a^{wn}}{\partial s^w} \right)_{\varepsilon, a^s, x_s^{ws}, l^{wns}, \hat{\Omega}, \theta, \mu+\varphi} \quad (84c)$$

$$\cos \Psi^w = \frac{1}{a^s} \left(\frac{\partial a^{wn}}{\partial x_s^{ws}} \right)_{\varepsilon, s^w, a^s, \hat{\Omega}, \theta, \mu + \varphi} \tag{84d}$$

$$\kappa^G = -\frac{1}{a^s} \left(\frac{\partial l^{wns}}{\partial x_s^{ws}} \right)_{\varepsilon, s^w, a^s, \hat{\Omega}, \theta, \mu + \varphi} \tag{84e}$$

$$\frac{\sin \Psi^w}{\kappa^N} = -\left(\frac{\partial a^{wn}}{\partial l^{wns}} \right)_{\varepsilon, s^w, a^s, x_s^{ws}, \hat{\Omega}, \theta, \mu + \varphi} \tag{84f}$$

9. Discussion of results

The preceding analysis has provided a basis for the study of the thermodynamic behavior of multiphase systems at the macroscale by deriving the conditions for mechanical equilibrium in such systems. In particular, since porous media flow is typically studied at a scale encompassing tens to hundreds of pore diameters, it is important to have conditions for equilibrium at that scale as well as some information concerning which variations in the position of the interface between phases and of the location of the common line are independent. It is worthwhile to examine each of the four conditions of equilibrium obtained for a system composed of a solid and two fluids, as listed in Eqs. (79a)–(79d), and indicate some of the insights into physical processes that they provide.

Eq. (79a) is an important macroscale relation that leads to the definition of the capillary pressure at the macroscale. Since capillary pressure is the difference between the nonwetting and wetting phase pressures, the definition of macroscale capillary pressure is:

$$P^c = -\sigma^{wn} J_{wn}^w \tag{85}$$

This equation is the macroscale analogue of Eq. (1). However, at the macroscale the expression for J_{wn}^w is not obtained directly from the curvature at points on the interface but from Eq. (84c) as the change of interfacial area between fluid phases with respect to the change in volume of the wetting phase. It is important to note that although P^c is traditionally tabulated as a non-unique function of saturation, in fact it seems to depend on the interfacial area and common line densities as well. Failure to include these dependences may account for the non-uniqueness of the plots of capillary pressure vs. saturation.

Eq. (79b) indicates that the macroscale equilibrium solid phase pressure is equal to a sum of the effects of wetting and non-wetting phase pressures and the fluid solid interfacial tension effects weighted by the fraction of the solid phase surface in contact with each fluid. This is a physically reasonable result and represents an extension to the form of the equilibrium relation typically employed for effective stress in a solid (Bishop, 1959; Fredlund and Rahardjo, 1993; Lewis and Schrefler, 1998; Hassanizadeh and Gray, 1990; Gray, 1999) in which the equilibrium pressure of the solid phase is a weighted sum of the fluid phase pressures with a typical weighting being the saturation. This older approximate formulation is likely reasonable in many cases and is simpler to work with because of its use of saturations rather than aerial

fractions (i.e., it does not require that one solve for surface aerial fractions). Indeed, when the solid phase deformation is of negligible importance, the weighting coefficients for the fluid pressures are not significant to the description of the fluid flow. However, if the deformation of the solid is of primary interest, the extended expression for the solid pressure in terms of the adjacent fluid and interface properties may be important.

The microscale analogue to Eq. (79c) may be obtained as a balance of forces tangent to the surface on a common line but is usually given for porous media without accounting for the line tension (e.g. Schiegg, 1986). When the balance is made in a vertical capillary tube, the geodesic curvature is zero and thus the usual equation is complete without line tension effects. The macroscale parameter $\cos \Psi^s$ accounts for the effective contact angle between the wetting phase and the solid in the porous medium. It is related to the macroscale aerial densities of the wn interface and the ws interface through Eq. (84d). Note that variable contact angles may be accounted for as the macroscale term listed as a ‘cos’ function is actually a measure of relative changes in surface area.

Eq. (79d) is actually a macroscale force balance on a contact line in the direction normal to the surface. To understand its physical meaning, it is useful to consider its microscale counterpart. This balance is typically ignored in considering common line dynamics. Note that although it is common to consider systems for which the water solid contact angle is taken to be zero degrees, such a system would require that there be no common line tension. For example, for a single vertical capillary tube, the normal curvature of the common line is $1/R$ so that the microscale equation for the contact angle would be:

$$\sin \psi_w = \frac{\sigma_{wns}}{R\sigma_{wn}} \quad (86)$$

Thus if $\psi_w = 0$, the lineal tension, σ_{wns} must be zero. The macroscale equation derived here indicates how the macroscale effective normal curvature of the common line and the effective contact angle are related to the fluid–fluid interfacial tension and the common line tension. The effective quantity is obtained through Eq. (84f) as a change in the wn interfacial area density with respect to the wns common line length density.

In addition to the equilibrium conditions obtained, this analysis provides information concerning the number of independent variations of geometric densities that can be accommodated at the macroscale. In fact, the form provided by Eq. (83) will prove to be of great utility in supporting the analysis of the fully dynamic system. Gray (1999) has previously obtained an approximation to Eq. (83), but the more complete form here also offers the possibility of obtaining improved closure equations for the full description of multiphase flow in porous media.

10. Conclusion

Macroscale thermodynamic representation of two-phase flow in porous media differs from the representation at the microscale because geometric densities must be included in the formulation as independent variables. The volume fractions of the system components, the amounts of the various interfacial areas per unit volume, and the common line length per

volume at a point contribute to the definition of the thermodynamic state at that point. A variational analysis of the system thermodynamics has provided macroscale relations among the pressures, surface tensions, lineal tension, effective contact angle, effective interfacial curvatures, and effective common line curvature that must be satisfied at the equilibrium state. Additionally, information about the required relations among variations of the geometric densities motivates the appropriate rearrangement of the dynamic entropy inequality such that near-equilibrium, linearized equations for the geometric quantities may be obtained to close the problem formulation. By basing the analysis of the changes of geometric parameters on a variational approach rather than on investigation of the averaging theorems as in Gray (1999), it is possible to reduce the number of approximations that must be made and therefore obtain more complete dynamic equations for the geometric variables.

Acknowledgements

This work was supported, in part, by the U.S. Department of Energy under grant DE-FG07-96ER14701 and by a subgrant from Cornell University of U.S. Department of Energy grant DE-FG07-96ER14703. The author was a Gladden Visiting Fellow at the Centre for Water Research at the University of Western Australia during the latter stages of this work.

Appendix. Derivation of variational relations

A.1. Derivation of variations for phase properties

Here the property of a phase will be considered. At the microscale, the amount of the property per unit volume (i.e. the density of the property) will be denoted as b_α . Since averaging will be done to the macroscale, b_α may be a function of the microscale thermodynamic parameters of the system and of $\mathbf{x} + \boldsymbol{\xi}$, where \mathbf{x} is the location of the centroid of the averaging volume and $\boldsymbol{\xi}$ is the distance from this centroid to a microscale point of interest. The macroscale density of the quantity for the α -phase will be denoted as \hat{B}^α . Note that for convenience this quantity is defined per unit volume of the averaging volume, not just per volume of α phase. The macroscale property \hat{B}^α is a function of the macroscale thermodynamic parameters of the system and of the location of the averaging volume, \mathbf{x} . The total amount of the property of interest in volume \mathcal{V} is denoted as \mathcal{B}^α and is related to its macroscale and microscale counterparts by:

$$\mathcal{B}^\alpha = \int_{\mathcal{V}} \hat{B}^\alpha d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V} \int_{V^\alpha} b_\alpha dV \right] d\mathcal{V} \quad (\text{A1})$$

where V is the averaging volume and V^α is the volume occupied by the α -phase within the averaging volume.

Now consider the variation of the first equality in Eq. (A1). This may be expressed as:

$$\delta \mathcal{B}^\alpha = \delta \int_{\mathcal{V}} \hat{B}^\alpha d\mathcal{V} \quad (\text{A2})$$

The generalized function as employed in Gray et al. (1993) will be used here also to convert the variation of the integral to the integral of a variation. For convenience, the generalized function $\gamma(\mathbf{x})$ that has a value of 1 within the volume and zero elsewhere will be introduced to convert the integral over the system volume to an integral over all space:

$$\delta \mathcal{B}^\alpha = \delta \int_{\mathcal{V}_\infty} \hat{B}^\alpha(\mathbf{x})\gamma(\mathbf{x}) d\mathcal{V} \quad (\text{A3})$$

The dependence on spatial coordinates of quantities in the integrand is listed here just for emphasis, but will not be included in subsequent forms. Because the integration volume is now fixed in size and not subject to variations, the variation may be moved inside the integral to obtain:

$$\delta \mathcal{B}^\alpha = \int_{\mathcal{V}_\infty} \delta \hat{B}^\alpha \gamma d\mathcal{V} + \int_{\mathcal{V}_\infty} \hat{B}^\alpha \delta \gamma d\mathcal{V} \quad (\text{A4})$$

The variation $\delta \hat{B}^\alpha$ is in an integral whose integration region is unchanging. This is equivalent to a fixed point variation in the original volume of integration. Note that the location is fixed with respect to the \mathbf{x} coordinate, and this fixed point variation will be denoted as $\bar{\delta}$. In the second integral on the right side, make use of the fact that:

$$\delta \gamma = -\delta \mathbf{x} \cdot \nabla_{\mathbf{x}} \gamma \quad (\text{A5})$$

where $\nabla_{\mathbf{x}}$ is the nabla operator in terms of \mathbf{x} coordinates so that Eq. (A4) now becomes:

$$\delta \mathcal{B}^\alpha = \int_{\mathcal{V}} \bar{\delta} \hat{B}^\alpha d\mathcal{V} - \int_{\mathcal{V}_\infty} \hat{B}^\alpha \delta \mathbf{x} \cdot \nabla_{\mathbf{x}} \gamma d\mathcal{V} \quad (\text{A6})$$

The quantity $\nabla_{\mathbf{x}} \gamma$ in an integrand of a volume integral converts the integral to a boundary integral such that:

$$\delta \mathcal{B}^\alpha = \int_{\mathcal{V}} \bar{\delta} \hat{B}^\alpha d\mathcal{V} + \int_{\mathcal{A}} \hat{B}^\alpha \delta \mathbf{x} \cdot \mathbf{n} d\mathcal{A} \quad (\text{A7})$$

where \mathbf{n} is the unit normal pointing outward from the region of interest and \mathcal{A} is the surface bounding \mathcal{V} .

Next it will be useful to obtain an expression for $\bar{\delta} \hat{B}^\alpha$, the fixed point macroscale variation that appears in Eq. (A7) in terms of the variation at the microscale. From the equality in Eq. (A1):

$$\bar{\delta} \hat{B}^\alpha = \bar{\delta} \left[\frac{1}{V} \int_{V^\alpha} b_\alpha dV \right] \quad (\text{A8})$$

It is useful to emphasize that the variational operator $\bar{\delta}$ is fixed point with respect to the \mathbf{x} coordinate system but not with respect to the ξ coordinates. Introduce the distribution

function $\gamma^\alpha(\mathbf{x} + \boldsymbol{\xi})$ which is 1 in the α -phase and zero elsewhere and the distribution function $\gamma(\boldsymbol{\xi})$ which is 1 within the averaging volume of interest and zero elsewhere. Because the averaging volume shape, size, and orientation is independent of its location in space, γ does not depend on \mathbf{x} . Thus the integral in Eq. (A8) can be written as being over all space according to:

$$\bar{\delta}\hat{B}^\alpha = \bar{\delta}\left[\frac{1}{V}\int_{V_\infty} b_\alpha(\mathbf{x} + \boldsymbol{\xi})\gamma^\alpha(\mathbf{x} + \boldsymbol{\xi})\gamma(\boldsymbol{\xi}) dV\right] \tag{A9}$$

where the coordinate dependences have been explicitly indicated and the integration is over the $\boldsymbol{\xi}$ coordinates. Since both V and the volume of integration are constant, the fixed point variational operator may be moved inside the integral to obtain:

$$\bar{\delta}\hat{B}^\alpha = \frac{1}{V}\int_{V_\infty} \bar{\delta}b_\alpha\gamma^\alpha\gamma dV + \frac{1}{V_\infty}\int_{V_\infty} b_\alpha\bar{\delta}\gamma^\alpha\gamma dV \tag{A10}$$

where use has been made of the fact that a fixed point variation of $\gamma(\boldsymbol{\xi})$ will be zero, which physically corresponds to the condition of a non-varying averaging volume. The variation in the first integral converts to a fixed point variation with respect to both \mathbf{x} and $\boldsymbol{\xi}$ coordinates when the integration region reverts back to the averaging volume, and the fixed point variation of γ^α is defined by:

$$\bar{\delta}\gamma^\alpha = -\delta\boldsymbol{\xi} \cdot \nabla_{\boldsymbol{\xi}}\gamma^\alpha \tag{A11}$$

Thus, Eq. (A10) becomes:

$$\bar{\delta}\hat{B}^\alpha = \frac{1}{V}\int_{V^\alpha} \bar{\bar{\delta}}b_\alpha dV - \frac{1}{V}\int_{V_\infty} b_\alpha\delta\boldsymbol{\xi} \cdot \nabla_{\boldsymbol{\xi}}\gamma^\alpha\gamma dV \tag{A12}$$

In the second integral, the quantity $\nabla_{\boldsymbol{\xi}}\gamma^\alpha$ converts integration over the volume to integration over the interface between the α -phase and all other phases and γ restricts the integral to the interfaces within the averaging volume so that the expression for the variation is:

$$\bar{\delta}\hat{B}^\alpha = \frac{1}{V}\int_{V^\alpha} \bar{\bar{\delta}}b_\alpha dV + \sum_{\beta \neq \alpha} \frac{1}{V}\int_{A^{\alpha\beta}} b_\alpha\delta\boldsymbol{\xi} \cdot \mathbf{n}_{\alpha\beta}^\alpha dA \tag{A13}$$

where $\bar{\bar{\delta}}$ is a variation with both spatial coordinates fixed, $A^{\alpha\beta}$ is the interface between the α - and β -phases, and $\mathbf{n}_{\alpha\beta}^\alpha$ is the unit normal to the $\alpha\beta$ interface positive outward from the α -phase.

Combination of Eq. (A13) with Eq. (A7) for the case where the global volume does not interact with its surroundings such that $\delta\mathbf{x} \cdot \mathbf{n} = 0$ on \mathcal{A} provides the variational equalities essential to the study of mechanical equilibrium of phases:

$$\delta\mathcal{B}^\alpha = \int_{\mathcal{V}} \bar{\delta}\hat{B}^\alpha d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V}\int_{V^\alpha} \bar{\bar{\delta}}b_\alpha dV\right] d\mathcal{V} + \int_{\mathcal{V}} \left[\sum_{\beta \neq \alpha} \frac{1}{V}\int_{A^{\alpha\beta}} b_\alpha\delta\boldsymbol{\xi} \cdot \mathbf{n}_{\alpha\beta}^\alpha dA\right] d\mathcal{V} \tag{A14}$$

A2. Derivation of variations for interface properties

Here the property of an interface will be considered. At the microscale, the amount of the property per unit area (i.e. the density of the property) will be denoted as $b_{\alpha\beta}$. Since averaging will be done to the macroscale, $b_{\alpha\beta}$ will be a function of the thermodynamic parameters of the interface and of the spatial position $\mathbf{x} + \boldsymbol{\xi}$, where \mathbf{x} is the centroid of the averaging volume and $\boldsymbol{\xi}$ is the distance from this centroid to the point on the surface. Of course, the dependence on all three of the microscale coordinates of a surface property may be transformed to a dependence on the two surficial coordinates. The macroscale density of the property for the $\alpha\beta$ interface will be denoted as $\hat{B}^{\alpha\beta}$. As for the phase, this quantity is defined per unit of averaging volume. Thus $\hat{B}^{\alpha\beta}$ is the amount of interface property per averaging volume. The macroscale property $\hat{B}^{\alpha\beta}$ may be a function of macroscale thermodynamic parameters of the averaging volume and of \mathbf{x} . Then the total amount of the property of interest is denoted as $\mathcal{B}^{\alpha\beta}$ and is related to its microscale and macroscale counterparts by:

$$\mathcal{B}^{\alpha\beta} = \int_{\mathcal{V}} \hat{B}^{\alpha\beta} d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V} \int_{A^{\alpha\beta}} b_{\alpha\beta} dA \right] d\mathcal{V} \quad (\text{A15})$$

Now consider the variation of the first equality in Eq. (A15). This may be expressed as:

$$\delta \mathcal{B}^{\alpha\beta} = \delta \int_{\mathcal{V}} \hat{B}^{\alpha\beta} d\mathcal{V} \quad (\text{A16})$$

The generalized function may be employed as previously in Eqs. (A3) through Eq. (A7) to obtain:

$$\delta \mathcal{B}^{\alpha\beta} = \int_{\mathcal{V}} \bar{\delta} \hat{B}^{\alpha\beta} d\mathcal{V} + \int_{\mathcal{A}} \hat{B}^{\alpha\beta} \delta \mathbf{x} \cdot \mathbf{n} d\mathcal{A} \quad (\text{A17})$$

where \mathbf{n} is the unit normal positive outward on the surface of the region of interest.

Next it will be useful to obtain an expression for $\bar{\delta} \hat{B}^{\alpha\beta}$, the fixed point macroscale variation that appears in Eq. (A17), in terms of the variation at the microscale. The derivation is different from that for a phase. From the equality in Eq. (A15):

$$\bar{\delta} \hat{B}^{\alpha\beta} = \bar{\delta} \left[\frac{1}{V} \int_{A^{\alpha\beta}} b_{\alpha} dA \right] \quad (\text{A18})$$

Introduce the surface distribution function $\gamma^{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi})$ which is 1 on the $\alpha\beta$ interface and zero elsewhere on a closed surface enclosing the α phase. Also employ $\gamma(\boldsymbol{\xi})$ which is 1 within the averaging volume of interest and zero elsewhere. Thus, Eq. (A18) becomes:

$$\bar{\delta} \hat{B}^{\alpha\beta} = \bar{\delta} \left[\frac{1}{V} \int_{A_{\infty}} b_{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}) \gamma^{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}) \gamma(\boldsymbol{\xi}) dA \right] \quad (\text{A19})$$

where A_{∞} is the boundary of the constructed closed volume. This surface integral may be converted to a volume integral over all space using the distribution function $\gamma^{\alpha}(\mathbf{x} + \boldsymbol{\xi})$ as in Gray et al. (1993) to obtain:

$$\bar{\delta} \hat{B}^{\alpha\beta} = -\bar{\delta} \left[\frac{1}{V} \int_{V_\infty} b_{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}) \gamma^{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}) \gamma(\boldsymbol{\xi}) \mathbf{n}_{\alpha\beta}^\alpha(\mathbf{x} + \boldsymbol{\xi}) \cdot \nabla_\xi \gamma^\alpha(\mathbf{x} + \boldsymbol{\xi}) dV \right] \quad (\text{A20})$$

where the coordinate dependences have been explicitly indicated and integration is over the $\boldsymbol{\xi}$ coordinates. The fixed point variational operator may be moved inside the integral since the volume is constant to obtain:

$$\begin{aligned} \bar{\delta} \hat{B}^{\alpha\beta} &= -\frac{1}{V} \int_{V_\infty} \bar{\delta} b_{\alpha\beta} \gamma^{\alpha\beta} \gamma \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi \gamma^\alpha dV - \frac{1}{V} \int_{V_\infty} b_{\alpha\beta} \bar{\delta} \gamma^{\alpha\beta} \gamma \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi \gamma^\alpha dV \\ &\quad - \frac{1}{V} \int_{V_\infty} b_{\alpha\beta} \gamma^{\alpha\beta} \gamma \mathbf{n}_{\alpha\beta}^\alpha \cdot \bar{\delta} (\nabla_\xi \gamma^\alpha) dV \end{aligned} \quad (\text{A21})$$

where use has been made of the facts that $\bar{\delta} \gamma(\boldsymbol{\xi}) = 0$ because the averaging volume is constrained to be fixed and that $\bar{\delta} \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi \gamma^\alpha = 0$ because $\mathbf{n}_{\alpha\beta}^\alpha$ and $\nabla_\xi \gamma^\alpha$ are co-linear. The variation in the first integral converts to a fixed point variation with respect to the \mathbf{x} and $\boldsymbol{\xi}$ coordinates when the integration region reverts back to the integration area. The fixed point variation of $\gamma^{\alpha\beta}$ is defined analogously to the fixed point variation of γ^α in Eq. (A11):

$$\bar{\delta} \gamma^{\alpha\beta} = -\delta \boldsymbol{\xi} \cdot \nabla_\xi \gamma^{\alpha\beta} \quad (\text{A22})$$

where ∇_ξ^s is the surface gradient operator. Thus, Eq. (A21) becomes:

$$\begin{aligned} \bar{\delta} \hat{B}^{\alpha\beta} &= \frac{1}{V} \int_{A^{\alpha\beta}} \bar{\delta} b_{\alpha\beta} dA + \frac{1}{V} \int_{V_\infty} b_{\alpha\beta} \delta \boldsymbol{\xi} \cdot \nabla_\xi^s \gamma^{\alpha\beta} \gamma \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi \gamma^\alpha dV \\ &\quad + \frac{1}{V} \int_{V_\infty} b_{\alpha\beta} \gamma^{\alpha\beta} \gamma \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi (\delta \boldsymbol{\xi} \cdot \nabla_\xi \gamma^\alpha) dV \end{aligned} \quad (\text{A23})$$

In the second integral, the quantity $\nabla_\xi \gamma^\alpha$ converts the domain of integration from the volume to the $\alpha\beta$ interface, and the quantity $\nabla_\xi^s \gamma^{\alpha\beta}$ converts the domain of integration to the common line. Thus the equation simplifies to:

$$\begin{aligned} \bar{\delta} \hat{B}^{\alpha\beta} &= \frac{1}{V} \int_{A^{\alpha\beta}} \bar{\delta} b_{\alpha\beta} dA + \frac{1}{V} \int_{C^{wns}} b_{\alpha\beta} \delta \boldsymbol{\xi} \cdot \mathbf{v}_{wns}^{\alpha\beta} dC \\ &\quad + \frac{1}{V} \int_{V_\infty} b_{\alpha\beta} \gamma^{\alpha\beta} \gamma \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi (\delta \boldsymbol{\xi} \cdot \nabla_\xi \gamma^\alpha) dV \end{aligned} \quad (\text{A24})$$

where C^{wns} is the common line within the averaging volume and $\mathbf{v}_{wns}^{\alpha\beta}$ is a unit vector normal to the common line and tangent to the $\alpha\beta$ interface positive outward from the interface. The last integral in this equation requires some particular attention. Apply the divergence theorem to this term and note that the integral over the surface at infinity will be zero so that:

$$\frac{1}{V} \int_{V_\infty} b_{\alpha\beta} \gamma^{\alpha\beta} \gamma \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi (\delta \boldsymbol{\xi} \cdot \nabla_\xi \gamma^\alpha) dV = -\frac{1}{V} \int_{V_\infty} \delta \boldsymbol{\xi} \cdot \nabla_\xi \gamma^\alpha \nabla_\xi \cdot (\mathbf{n}_{\alpha\beta}^\alpha b_{\alpha\beta} \gamma^{\alpha\beta} \gamma) dV \quad (\text{A25})$$

Then expand the divergence operator and return the integral over the infinite volume to

integrals over the appropriate surfaces and common line yielding:

$$\begin{aligned} \frac{1}{V} \int_{V_\infty} b_{\alpha\beta} \gamma^{\alpha\beta} \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi (\delta \xi \cdot \nabla_\xi \gamma^\alpha) dV &= \frac{1}{V} \int_{A^{\alpha\beta}} b_{\alpha\beta} \nabla_\xi \cdot \mathbf{n}_{\alpha\beta}^\alpha \delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha dA \\ &+ \frac{1}{V} \int_{A^{\alpha\beta}} \delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi b_{\alpha\beta} dA - \frac{1}{V} \int_{C_{\text{ext}}} \delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha (\mathbf{n}_{\alpha\beta}^\alpha \cdot \mathbf{n}^\alpha) b_{\alpha\beta} dC \end{aligned} \quad (\text{A26})$$

where C_{ext} is the common line on the boundary of the averaging volume formed by the intersection of the $\alpha\beta$ interface with this surface. Use has been made of the fact that $\mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla \gamma^{\alpha\beta} = 0$. The last integral in this equation will be set to zero by requiring that the variational analysis be performed with no exchange of work with regions outside the averaging volume such that $\delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha = 0$ on C_{ext} . Substitution of Eq. (A26) into Eq. (A24) provides the equation for the fixed point variation:

$$\begin{aligned} \bar{\delta} \hat{B}^{\alpha\beta} &= \frac{1}{V} \int_{A^{\alpha\beta}} \left(\bar{\delta} b_{\alpha\beta} + \delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi b_{\alpha\beta} \right) dA + \frac{1}{V} \int_{A^{\alpha\beta}} b_{\alpha\beta} \nabla_\xi \cdot \mathbf{n}_{\alpha\beta}^\alpha \delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha dA \\ &+ \frac{1}{V} \int_{C_{\text{wns}}} b_{\alpha\beta} \delta \xi \cdot \mathbf{v}_{\text{wns}}^{\alpha\beta} dC \end{aligned} \quad (\text{A27})$$

The second term in the first integral in this equation accounts for variation due to movement normal to the surface. Since the fixed point variation is with all coordinates held constant, this integrand suggests the definition:

$$\bar{\delta}_s b_{\alpha\beta} = \bar{\delta} b_{\alpha\beta} + \delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha \mathbf{n}_{\alpha\beta}^\alpha \cdot \nabla_\xi b_{\alpha\beta} \quad (\text{A28})$$

where $\bar{\delta}_s$ is a fixed point variation with all the macroscale coordinates and the two surface coordinates fixed.

Combination of Eq. (A27) with Eq. (A17) for the case where the global volume does not interact with its surroundings such that $\delta \mathbf{x} \cdot \mathbf{n} = 0$ on \mathcal{A} provides the variational equality essential to the study of an interface in the three-phase system

$$\begin{aligned} \delta \mathcal{B}^{\alpha\beta} &= \int_{\mathcal{V}'} \bar{\delta} \hat{B}^{\alpha\beta} d\mathcal{V}' = \int_{\mathcal{V}'} \left[\frac{1}{V} \int_{A^{\alpha\beta}} \bar{\delta}_s b_{\alpha\beta} dA \right] d\mathcal{V}' \\ &+ \int_{\mathcal{V}'} \left[\frac{1}{V} \int_{A^{\alpha\beta}} b_{\alpha\beta} \nabla_\xi \cdot \mathbf{n}_{\alpha\beta}^\alpha \delta \xi \cdot \mathbf{n}_{\alpha\beta}^\alpha dA \right] d\mathcal{V}' + \int_{\mathcal{V}'} \left[\frac{1}{V} \int_{C_{\text{wns}}} b_{\alpha\beta} \delta \xi \cdot \mathbf{v}_{\text{wns}}^{\alpha\beta} dC \right] d\mathcal{V}' \end{aligned} \quad (\text{A29})$$

A3. Derivation of variations for common line properties

Here the property of a common line in a three-phase system will be considered. At the microscale, the amount of the property per unit length (i.e. the density of the property) will be denoted as b_{wns} . The microscale unit vector tangent to the common line is designated as λ . Since averaging is to be done to the macroscale, b_{wns} will be a function of $\mathbf{x} + \xi$, where \mathbf{x} is the centroid of the averaging volume and ξ is the distance from this centroid to the point on the

common line, as well as of the thermodynamic parameters of the interface. The macroscale density of the quantity for the *wns* common line will be denoted as \hat{B}^{wns} . As for the phase and interface, this quantity is defined per unit of averaging volume. Thus \hat{B}^{wns} is the amount of common line property per volume under study. The macroscale property \hat{B}^{wns} is a function of \mathbf{x} as well as the macroscale thermodynamic parameters of the system. Then the total amount of the property of interest is denoted as \mathcal{B}^{wns} and is related to its microscale and macroscale counterparts by:

$$\mathcal{B}^{wns} = \int_{\mathcal{V}} \hat{B}^{wns} d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V} \int_{C^{wns}} b_{wns} dC \right] d\mathcal{V} \tag{A30}$$

Now consider the variation of the first equality in Eq. (A30). This may be expressed as:

$$\delta \mathcal{B}^{wns} = \delta \int_{\mathcal{V}} \hat{B}^{wns} d\mathcal{V} \tag{A31}$$

The generalized function may be employed as previously in Eqs. (A3)–(A7) to obtain:

$$\delta \mathcal{B}^{wns} = \int_{\mathcal{V}} \bar{\delta} \hat{B}^{wns} d\mathcal{V} + \int_{\mathcal{A}} \hat{B}^{wns} \delta \mathbf{x} \cdot \mathbf{n} d\mathcal{A} \tag{A32}$$

where \mathbf{n} is the unit normal pointing outward from the region of interest.

Next it will be useful to obtain an expression for $\bar{\delta} \hat{B}^{wns}$, the fixed point macroscale variation that appears in Eq. (A32), in terms of the variation at the microscale. The derivation is different from that for phases and interfaces. From the equality in Eq. (A30):

$$\bar{\delta} \hat{B}^{wns} = \bar{\delta} \left[\frac{1}{V} \int_{C^{wns}} b_{wns} dC \right] \tag{A33}$$

Introduce the lineal distribution function $\gamma^{wns}(\mathbf{x} + \boldsymbol{\xi})$ which is 1 on the *wns* line and zero elsewhere on a closed curve enclosing the boundary of the α phase. Also employ $\gamma(\boldsymbol{\xi})$ which is 1 within the averaging volume of interest and zero elsewhere. Thus Eq. (A33) becomes:

$$\bar{\delta} \hat{B}^{wns} = \bar{\delta} \left[\frac{1}{V} \int_{C_{\infty}} b_{wns}(\mathbf{x} + \boldsymbol{\xi}) \gamma^{wns}(\mathbf{x} + \boldsymbol{\xi}) \gamma(\boldsymbol{\xi}) dC \right] \tag{A34}$$

This curve integral may be converted to a volume integral over all space using the distribution functions $\gamma^{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi})$ and $\gamma^{\alpha}(\mathbf{x} + \boldsymbol{\xi})$ as in Gray et al. (1993) for arbitrary selection of the phase α and the interface $\alpha\beta$ to obtain:

$$\bar{\delta} \hat{B}^{wns} = \bar{\delta} \left[\frac{1}{V} \int_{V_{\infty}} b_{wns}(\mathbf{x} + \boldsymbol{\xi}) \gamma^{wns}(\mathbf{x} + \boldsymbol{\xi}) \gamma(\boldsymbol{\xi}) \mathbf{v}^{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}) \cdot \nabla_{\boldsymbol{\xi}} \gamma^{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}) \mathbf{n}_{\alpha\beta}^{\alpha}(\mathbf{x} + \boldsymbol{\xi}) \cdot \nabla_{\boldsymbol{\xi}} \gamma^{\alpha}(\mathbf{x} + \boldsymbol{\xi}) dV \right] \tag{A35}$$

where the coordinate dependences have been explicitly indicated. Manipulations of this equation are completely analogous to but lengthier than those performed previously. In the

derivation, the condition is applied to ensure no exchange of mechanical work with the surroundings that $\delta\xi \cdot \lambda = 0$ at the locations where the common line pierces the surface of the averaging volume. The equation obtained for the fixed point variation is:

$$\bar{\delta}\hat{B}^{wns} = \frac{1}{V} \int_{C^{wns}} \bar{\delta}_c b_{wns} dC - \frac{1}{V} \int_{C^{wns}} b_{wns} \lambda \cdot \nabla_\xi \lambda \cdot \delta\xi dC \quad (A36)$$

where the fixed point variation indicated is one with the macroscale \mathbf{x} and microscale λ coordinates fixed such that:

$$\bar{\delta}_c b_{wns} = \bar{\delta} b_{wns} + \delta\xi \cdot \nabla_\xi b_{wns} - \delta\xi \cdot \lambda \lambda \cdot \nabla b_{wns} \quad (A37)$$

Combination of Eq. (A36) with Eq. (A32) for the case where the global volume does not interact with its surroundings such that $\delta\mathbf{x} \cdot \mathbf{n} = 0$ on \mathcal{A} provides the variational equalities essential to the study of common lines for the three-phase system:

$$\begin{aligned} \delta\mathcal{B}^{wns} &= \int_{\mathcal{V}} \bar{\delta}\hat{B}^{wns} d\mathcal{V} = \int_{\mathcal{V}} \left[\frac{1}{V} \int_{C^{wns}} \bar{\delta}_c b_{wns} dC \right] d\mathcal{V} \\ &\quad - \int_{\mathcal{V}} \left[\frac{1}{V} \int_{C^{wns}} b_{wns} \lambda \cdot \nabla_\xi \lambda \cdot \delta\xi dC \right] d\mathcal{V} \end{aligned} \quad (A38)$$

References

- Anderson, T.B., Jackson, R., 1967. A fluid mechanical description of fluidized beds. *Industrial and Engineering Chemistry Fundamentals* 6, 527–539.
- Bailyn, M., 1994. *A Survey of Thermodynamics*. American Institute of Physics Press, New York.
- Bishop, A.W., 1959. The principle of effective stress. *Teknisk Ukeblad* 39, 859–863.
- Boruvka, L., Neumann, A.W., 1977. Generalization of the classical theory of capillarity. *Journal of Chemical Physics* 66 (12), 5464–5476.
- Boruvka, L., Rotenberg, Y., Neumann, A.W., 1985. Free energy formulation of the theory of capillarity. *Langmuir* 1 (1), 40–44.
- Callen, H.B., 1985. *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed. Wiley, New York.
- Fredlund, D.G., Rahardjo, H., 1993. *Soil Mechanics for Unsaturated Soils*. Wiley, New York.
- Gaydos, J., Rotenberg, Y., Boruvka, L., Chen, P., Neumann, A.W., 1996. The generalized theory of capillarity. In: Neumann, A.W., Spelt, J.K. (Eds.), *Applied Surface Thermodynamics Surfactant Science Series*, 63. Marcel Dekker, New York, pp. 1–51.
- Gibbs, J.W., 1948. *Collected Works, Volume I*. Yale University Press, New Haven.
- Gray, W.G., 1999. Thermodynamics and constitutive theory for multiphase porous-media flow considering internal geometric constraints. *Advances in Water Resources* 22 (5), 521–547.
- Gray, W.G., Hassanizadeh, S.M., 1989. Averaging theorems and averaged equations for transport of interface properties in multiphase systems. *International Journal of Multiphase Flow* 15 (1), 81–95.
- Gray, W.G., Hassanizadeh, S.M., 1998. Macroscale continuum mechanics for multiphase porousmedia flow including phases, interfaces, common lines, and common points. *Advances in Water Resources* 21, 261–281.
- Gray, W.G., Lee, P.C.Y., 1977. On the theorems for local volume averaging of multi-phase systems. *International Journal Multiphase Flow* 3, 333–340.

- Gray, W.G., Leijnse, A., Kolar, R.L., Blain, C.A., 1993. *Mathematical Tools for Changing Spatial Scales in the Analysis of Physical Systems*. CRC Press, Boca Raton.
- Hassanizadeh, S.M., Gray, W.G., 1990. Mechanics and thermodynamics of multiphase flow in porous media including interface boundaries. *Advances in Water Resources* 13 (4), 169–186.
- Hassanizadeh, S.M., Gray, W.G., 1993. Thermodynamic basis of capillary pressure in porous media. *Water Resources Research* 29 (10), 3389–3405.
- Kalaydjian, F., 1987. A macroscopic description of multiphase flow involving spacetime evolution of fluid/fluid interface. *Transport in Porous Media* 2, 537–552.
- Lewis, R.W., Schrefler, B.A., 1998. *The Finite Element Method in the Static and Dynamic Deformation and Consolidation of Porous Media*, 2nd ed. Wiley, New York.
- Nitao, J.J., Bear, J., 1996. Potential and their role in transport in porous media. *Water Resources Research* 32 (2), 225–250.
- Pavone, D., 1989. Macroscopic equations derived from space averaging for immiscible two-phase flow in porous media. *Revue de l'Institut Francais du Pétrole* 44 (1), 29–41.
- Scheidegger, A.E., 1974. *The Physics of Flow through Porous Media*, 3rd ed. University of Toronto Press, Toronto.
- Schiegg, H.O. Evaluation and Treatment of Cases of Oil Damage with Regard to Groundwater Protection, In: Albertson, M. et al. Swiss Federal Office of the Environment, LTWS #20, 1986.
- Whitaker, S., 1967. Diffusion and dispersion in porous media. *American Institute of Chemical Engineers Journal* 13, 420–427.