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Unsaturated Flow Theory Including Interfacial Phenomena

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The macroscopic porous medium equations for mass, momentum, and energy transport for air, water, and solid phases and the interfaces between these phases are examined in light of the second law of thermodynamics. Attention is focused on the momentum balance for the water phase. Appropriate forms of the momentum balance are obtained, in general, for the slow flow situation and for the case when the water phase completely wets the solid. This last case suggests that the relative wettability of the water and air phases is an important dependent thermodynamic variable which contributes to the hysteretic nature of the capillary pressure versus saturation curve.

INTRODUCTION

One problem of enduring interest in water resources is the unsaturated flow of water in dry or partially saturated soil. This phenomenon has been attacked from experimental and theoretical perspectives since at least the beginning of this century. *Sposito* [1986] attributes the beginnings of the study of soil water flow as a subdiscipline of physics to the fundamental work of *Buckingham* [1907]. The equation still employed today in modeling unsaturated flow is the Darcy-Buckingham equation, an extended version of Darcy's law which allows for a saturation dependent permeability and a capillary potential in place of pressure. *Marino and Luthin* [1982] state that water flow through porous media follows Darcy's law and concur with *Hillel*'s [1980] statement that perhaps the most important difference between unsaturated and saturated flow is in the hydraulic conductivity. *Scheidegger* [1974] notes that extensions of Darcy's law to multiple phase flow is only theoretical speculation. He points to the phenomenon of hysteresis in wettability as indicative of some of the limitations of the approach.

As a logical progression, one should first obtain unsaturated flow equations from basic principles of physics and then infer the saturated flow equations as a special case. The reverse has been the general practice so far. Thus the application of Darcy's law to treat multiphase flow, and in particular unsaturated flow, should be expected to have shortcomings. From a practical point of view the interface between the air and water, a physical boundary which does not exist in single-phase flow, is an important attribute of unsaturated flow. Darcy's law, and its extensions based on redefining single-phase flow parameters, does not account explicitly for such interfaces or for the preferential attraction of one fluid to the solid in comparison to another. This problem has been widely recognized, and as a result, studies of interfacial phenomena have been performed. The work of *Miller and Noegi* [1985] provides extensive information concerning interfacial thermodynamics and that of *Morrow* [1970] provides a succinct discussion of surface energetics and how they are reflected in capillary phenomena. Standard topics for inclusion in books treating multiphase or unsaturated flow are the Young-Laplace equation relating capillary pressure to surface curvature and the attribution of hysteretic effects to contact angle changes between imbibition and drainage, the "ink bottle" effect, and Haines jumps [e.g., *Corey*, 1977; *Hillel*, 1980; *Greenkorn*, 1983; *Bear and Verruijt*, 1987]. All these topics deal with phenomena occurring at the microscale. Nevertheless, the transfer of understanding of microscale occurrences to the porous medium scale has been difficult.

As an indication of the confusion that exists concerning the scale at which equations are formulated, one might consider the Young-Laplace equation. This equation which relates capillary pressure to radius of curvature of an interface between phases is, in fact, merely the equilibrium form of the surface momentum equation at the microscale. The current development is not explicitly concerned with this scale but considers a larger scale, the macroscale. The macroscale is usually not defined precisely but is a length scale small enough to be considered infinitesimal with respect to the length scale of the system under consideration and large enough to provide a function field which does not fluctuate with small changes in the length scale. At the macroscale one does not observe "contact angles" or "curvature of interfaces" but only the impact of these subscale phenomena on the system behavior. This study deals with fully dynamic equations at the macroscale and leads to a definition of capillary pressure which depends on independent variables observed on that scale. The literature sometimes tends to mix scales in that hysteresis in the capillary pressure as a function of saturation is discussed in terms of contact angles. A more systematic approach would provide an explanation for microscopic behavior in terms of microscopic properties and an explanation of macroscopic behavior in terms of macroscopic properties. Thus hysteresis in capillary pressure should be studied in terms of interfacial area per unit volume of medium rather than in terms of the radius of curvature of an interface.

A concurrent line of research is aimed at obtaining theoretically sound understanding of porous media phenomena at the scale consistent with Darcy's law, that is, much greater

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than the scale of a single pore. The technique of averaging equations to affect a change in scale has increased in popularity. The fundamental tools of this approach are averaging theorems which relate the average of a derivative to the derivative of the average, thus allowing a rigorous change in scale [*Anderson and Jackson*, 1967; *Whitaker*, 1967; *Gray and Lee*, 1977]. This technique does indeed produce equations for the water, soil, and air phases, but it also leads to complications in that constitutive relations are needed for the variables that arise because of averaging. Recently, *Gray and Hassanizadeh* [1989] have also provided theorems which allow a change of scale to be accomplished for the interface equations. Although these equations describe interfacial behavior at the macroscale, they compound the overall problem by introducing even more unknowns and functions requiring constitutive approximation.

Fortunately, a tool exists for developing constitutive functions in a systematic manner. This procedure has the attractive feature that it also leads to a consistent thermodynamic description at the macroscale and assures that the second law of thermodynamics is not violated. This method is based on the procedure of *Coleman and Noll* [1963] for exploitation of the entropy inequality. This procedure provides a framework in which assumptions can be consistently employed to simplify the problem description and which helps identify areas of experimental need.

The main purpose of the work here is to provide a fundamental basis on which to advance theories of multiphase flow in general, and unsaturated flow in particular, without appealing to concepts developed for single-phase, saturated flow. Attention is directed primarily at examination of the momentum balance equation for the water phase during unsaturated flow. However, the Coleman and Noll method requires that all balance equations for phases and interfaces be examined simultaneously. Since here the focus will be on momentum transfer, the discussion of constitutive results obtained for the energy equations will be minimized. Furthermore, it must be pointed out that the inclusion of interface balance equations in the overall problem formulation is an important feature in that it allows the dependence of phase properties on interface properties to be consistently treated. Thus although the goal here is to provide insight on the momentum equation for the water phase, the inclusion of phenomena of secondary interest, such as interface momentum, is essential.

BALANCE EQUATIONS

The balance equations on which this theory for unsaturated flow is to be based are obtained by averaging of microscopic equations for each of the phases as well as for the interfaces between phases. In this section an abbreviated description of the procedure employed is presented with more extensive details available in papers by *Gray and Hassanizadeh* [1989] and *Hassanizadeh and Gray* [1990] for a general three-phase system.

Consider a porous media system composed of air, water, and solid phases separated at the microscale by interfaces which possess thermodynamic properties. Microscale balance equations for mass, momentum, energy, and entropy for each bulk phase α are averaged over that phase within a representative elementary volume to obtain macroscale equations of the form

TABLE 1. Symbols Used in (1*b*) to Obtain Specific Balance Formulas for Phase α

Equation	ψ^α	$\mathbf{i}^\alpha$	f^α	$\hat{I}^\alpha_{\alpha\beta}$	Ψ^α
Momentum	$\mathbf{v}^\alpha$	$\mathbf{t}^\alpha$	$\mathbf{g}$	$\hat{\mathbf{T}}^\alpha_{\alpha\beta}$	0
Internal energy	E^α	$\mathbf{q}^\alpha$	h^α	$\hat{Q}^\alpha_{\alpha\beta}$	0
Entropy	η^α	φ^α	b^α	$\hat{\Phi}^\alpha_{\alpha\beta}$	Λ^α

Mass

$$\varepsilon^\alpha \frac{D^\alpha \rho^\alpha}{Dt} + \rho^\alpha \frac{D^\alpha \varepsilon^\alpha}{Dt} + \rho^\alpha \varepsilon^\alpha \nabla \cdot \mathbf{v}^\alpha = \sum_{\beta \neq \alpha} \hat{e}^\alpha_{\alpha\beta} \tag{1a}$$

Momentum, energy, and entropy

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha \psi^\alpha}{Dt} - \nabla \cdot (\varepsilon^\alpha \mathbf{i}^\alpha) - \varepsilon^\alpha \rho^\alpha f^\alpha = \sum_{\beta \neq \alpha} \hat{I}^\alpha_{\alpha\beta} + \Psi^\alpha \tag{1b}$$

where $D^\alpha/Dt = \partial/\partial t + \mathbf{v}^\alpha \cdot \nabla$, $\mathbf{v}^\alpha$ is the velocity of the α phase, ε^α is the volume fraction of phase α, ρ^α is the mass of α per unit volume of α phase, ψ^α is the phase property of interest, $\mathbf{i}^\alpha$ accounts for the dispersive transport of ψ^α, f^α is the external supply of ψ^α, $\hat{e}^\alpha_{\alpha\beta}$ is the rate of transport of mass from the $\alpha\beta$ interface to phase α, $\hat{I}^\alpha_{\alpha\beta}$ is the rate of transport of ψ^α from all $\alpha\beta$ interfaces ($\beta \neq \alpha$) to phase α, and ψ^α is the net rate of production of ψ^α per unit volume of porous medium. Equations (1*a*) and (1*b*) may be written for the air, water, and solid phases by letting α (and β) take on the values a, w, and s, respectively, and letting the $\alpha\beta$ interface be denoted as wa, ws, and as, respectively (note that an $\alpha\beta$ interface is equivalent to a $\beta\alpha$ interface). Symbols for balances of particular properties for (1*b*) are given in Table 1.

In addition, the microscale balance equations for an interface $\alpha\beta$ separating the α and β phases are averaged over the interface within an averaging volume to obtain macroscale equations:

Mass

$$\Gamma^{\alpha\beta} \frac{D^{\alpha\beta} a^{\alpha\beta}}{Dt} + a^{\alpha\beta} \frac{D^{\alpha\beta} \Gamma^{\alpha\beta}}{Dt} + a^{\alpha\beta} \Gamma^{\alpha\beta} \nabla \cdot \mathbf{w}^{\alpha\beta} = -\hat{e}^\alpha_{\alpha\beta} - \hat{e}^\beta_{\alpha\beta} + \hat{e}^{\alpha\beta}_{aws} \tag{2a}$$

Momentum, energy, and entropy

$$a^{\alpha\beta}\Gamma^{\alpha\beta} \frac{D^{\alpha\beta} \psi^{\alpha\beta}}{Dt} - \nabla \cdot (a^{\alpha\beta} \mathbf{i}^{\alpha\beta}) - a^{\alpha\beta}\Gamma^{\alpha\beta} f^{\alpha\beta} = -[\hat{I}^\alpha_{\alpha\beta} + \hat{e}^\alpha_{\alpha\beta}(\psi^\alpha - \psi^{\alpha\beta})] - [\hat{I}^\beta_{\alpha\beta} + \hat{e}^\beta_{\alpha\beta}(\psi^\beta - \psi^{\alpha\beta})] + \hat{I}^{\alpha\beta}_{aws} + \Psi^{\alpha\beta} \tag{2b}$$

where $D^{\alpha\beta}/Dt = \partial/\partial t + \mathbf{w}^{\alpha\beta} \cdot \nabla$, $\mathbf{w}^{\alpha\beta}$ is the velocity of the $\alpha\beta$ interface, $a^{\alpha\beta}$ is the area of the $\alpha\beta$ interface per unit volume of porous medium, $\Gamma^{\alpha\beta}$ is the mass of $\alpha\beta$ per unit area of $\alpha\beta$ interface, $\psi^{\alpha\beta}$ is the interface property of interest, $\mathbf{i}^{\alpha\beta}$ accounts for the rate of transport of $\psi^{\alpha\beta}$ in the interface,

TABLE 2. Symbols Used in (2*b*) to Obtain Specific Balance Formulas for Interface $\alpha\beta$

Equation	$\psi^{\alpha\beta}$	$\mathbf{i}^{\alpha\beta}$	$f^{\alpha\beta}$	$\hat{\imath}_{aws}^{\alpha\beta}$	$\Psi^{\alpha\beta}$
Momentum	$\mathbf{w}^{\alpha\beta}$	$\mathsf{S}^{\alpha\beta}$	$\mathbf{g}$	$\hat{\mathbf{S}}_{aws}^{\alpha\beta}$	0
Internal energy	$E^{\alpha\beta}$	$\mathbf{q}^{\alpha\beta}$	$h^{\alpha\beta}$	$\hat{Q}_{aws}^{\alpha\beta}$	0
Entropy	$\eta^{\alpha\beta}$	$\varphi^{\alpha\beta}$	$b^{\alpha\beta}$	$\hat{\Phi}_{aws}^{\alpha\beta}$	$\Lambda^{\alpha\beta}$

The quantities $\hat{\imath}_{\alpha\beta}^{\alpha}$ and ψ^{α} (2*b*) are the same as for the corresponding phase equation (1*b*).

$f^{\alpha\beta}$ is the external supply of $\psi^{\alpha\beta}$, the terms in brackets on the right side account for transfer of $\psi^{\alpha\beta}$ from the $\alpha\beta$ interface to the α and β phases, $\hat{e}_{aws}^{\alpha\beta}$ accounts for the transport of mass from a contact curve aws (where the three phase interfaces intersect) to the $\alpha\beta$ interface, $\hat{\imath}_{aws}^{\alpha\beta}$ accounts for the transport of $\psi^{\alpha\beta}$ from a contact curve aws to the $\alpha\beta$ interface, and $\Psi^{\alpha\beta}$ is the net rate of production of $\psi^{\alpha\beta}$ per unit volume of porous medium. Equations (2*a*) and (2*b*) are written for each of the three $\alpha\beta$ interfaces, wa, ws, and as. The symbols for balance of particular properties for use in (2*b*) are given in Table 2.

The contact line is considered to possess no properties itself, and therefore the transfer of mass to a contact line is restricted by

$$\sum_{\alpha\beta} \hat{e}_{aws}^{\alpha\beta} = 0 \tag{3a}$$

and the transfer of $\psi^{\alpha\beta}$ to a contact line is restricted by

$$\sum_{\alpha\beta} (\hat{\imath}_{aws}^{\alpha\beta} + \hat{e}_{aws}^{\alpha\beta}\psi^{\alpha\beta}) = 0 \tag{3b}$$

where $\hat{e}_{aws}^{\alpha\beta}$ is the mass transfer to the $\alpha\beta$ interface from other interfaces via the contact line. The stress tensors t^{α} and $\mathsf{S}^{\alpha\beta}$ can be proven to be symmetric. Macroscopic temperature is defined by considering entropy fluxes to be solely due to heat input and considering entropy external source terms to be due only to external energy sources such that $\varphi^{\alpha} = \mathbf{q}^{\alpha}/T^{\alpha}$, $b^{\alpha} = h^{\alpha}/T^{\alpha}$, $\varphi^{\alpha\beta} = \mathbf{q}^{\alpha\beta}/T^{\alpha\beta}$, and $b^{\alpha\beta} = h^{\alpha\beta}/T^{\alpha\beta}$, where T^{α} is the temperature of the α phase, $T^{\alpha\beta}$ is the temperature of the $\alpha\beta$ interface, and the other symbols are given in Tables 1 and 2.

The requirement that the total entropy change for the system must be positive is equivalent to requiring the sum of the entropy production terms in the six entropy equations to be positive. This statement is the second law of thermodynamics and can be mathematically expressed by

$$\Lambda = \sum_{\alpha} \Lambda^{\alpha} + \sum_{\alpha\beta} \Lambda^{\alpha\beta} \geq 0 \tag{4}$$

Because (1) and (2) contain more unknowns than equations, constitutive representations will be needed for some of the variables. Equations (3) and (4) will be used subsequently to restrict the forms of these constitutive relationships as well as to obtain relationships among macroscopic thermodynamic variables.

CONSTITUTIVE THEORY

Equations (1) and (2) comprise 30 equations for 35 primary unknowns:

$$\varepsilon,\ s^{w},\ \rho^{\alpha},\ \mathbf{v}^{w},\ \mathbf{v}^{a},\ \mathbf{F}^{s},\ T^{\alpha},\ a^{\alpha\beta},\ \Gamma^{\alpha\beta},\ \mathbf{w}^{\alpha\beta},\ T^{\alpha\beta} \tag{5}$$

$$\alpha = w, a, s \qquad \alpha\beta = wa, ws, as$$

where $\mathbf{F}^{s}$ is the displacement vector of the solid phase, ε is the void fraction (i.e., $\varepsilon^{s} = 1 - \varepsilon$), and s^{w} is the water phase saturation ($\varepsilon^{w} = s^{w}\varepsilon$ and $\varepsilon^{a} = s^{a}\varepsilon$, where $s^{a} = 1 - s^{w}$). The balance laws obtained from (1) and (2) are supplemented by constitutive relationships for the following unknowns:

$$A^{\alpha},\ A^{\alpha\beta},\ \mathsf{t}^{\alpha},\ \mathsf{S}^{\alpha\beta},\ \hat{\mathbf{T}}_{\alpha\beta}^{\alpha},\ \hat{\mathbf{S}}_{aws}^{\alpha\beta},\ \mathbf{q}^{\alpha},\ \mathbf{q}^{\alpha\beta},$$

$$\hat{Q}_{\alpha\beta}^{\alpha},\ \hat{Q}_{aws}^{\alpha\beta},\ \eta^{\alpha},\ \eta^{\alpha\beta},\ \hat{e}_{\alpha\beta}^{\alpha},\ \hat{e}_{aws}^{\alpha\beta} \tag{6}$$

$$\alpha = w, a, s \qquad \alpha\beta = wa, ws, as$$

where $A^{\alpha}(= E^{\alpha} - T^{\alpha}\eta^{\alpha})$ and $A^{\alpha\beta}(= E^{\alpha\beta} - T^{\alpha\beta}\eta^{\alpha\beta})$ are the Helmholtz free energies per unit mass of the α phase and $\alpha\beta$ interface, respectively. The five-equation deficit for the primary variables in list (5) is eliminated by also requiring constitutive forms for

$$\dot{\varepsilon},\ \dot{s}^{w},\ \dot{a}^{wa},\ \dot{a}^{ws},\ \dot{a}^{as} \tag{7}$$

where the overdot indicates a time derivative taken moving with the solid phase (i.e., $\dot{\varepsilon} = D^{s}\varepsilon/Dt$, etc.). In providing constitutive forms for $\hat{e}_{aws}^{\alpha\beta}$, $\hat{\mathbf{S}}_{aws}^{\alpha\beta}$, and $\hat{Q}_{aws}^{\alpha\beta}$, the constraint equations (3*a*) and (3*b*) must be satisfied.

At this point, to complete the constitutive formulation, the variables listed in (6) and (7) must be allowed to depend on some set of independent variables drawn from the primary variables listed in (5) as well as some time and space derivatives of these variables. This selection of independent variables is crucial to the success of the theory. Not including some independent variables can cause the scope of problems described to be very limited. Allowance for dependence on too many independent variables can lead to equations which are far more general than required. Although such a description is acceptable from the point of view of a theoretical description, on a practical level it makes the manipulations to ensure satisfaction of the entropy inequality excessively complex, and it greatly complicates the laboratory experimental effort which must be undertaken to determine the specific forms of the general constitutive functions and coefficients in the final equations.

The independent variables selected here, which also satisfy the principle of material frame indifference, are

$$\rho^{\alpha},\ \Gamma^{\alpha\beta},\ \mathbf{v}^{\alpha,s},\ \mathbf{w}^{\alpha\beta,s},\ \mathsf{E}^{s},\ T^{\alpha},\ \nabla T^{\alpha},$$

$$\varepsilon,\ \nabla\varepsilon,\ s^{w},\ \nabla s^{w},\ a^{\alpha\beta},\ \nabla a^{\alpha\beta} \tag{8}$$

$$\alpha = w, a, s \qquad \alpha\beta = wa, ws, as$$

where E^{s} is the solid phase stress tensor, and the comma in the superscripts is used to indicate a relative value of velocity (e.g., $\mathbf{v}^{\alpha,s} \equiv \mathbf{v}^{\alpha} - \mathbf{v}^{s}$ and $\mathbf{w}^{\alpha\beta,s} \equiv \mathbf{w}^{\alpha\beta} - \mathbf{v}^{s}$). As a general approach, each variable listed in (6) and (7) would be allowed to depend on all of the variables in list (8). Then application of the entropy inequality serves, with great effort, to eliminate some of the dependences as infeasible. This approach is particularly cumbersome if the Helmholtz free energy is allowed this general dependence because the chain rule for differentiation with respect to time must be applied to each A^α and $A^{\alpha\beta}$ in applying the entropy inequality. Thus a judicious choice of dependence for the free energy can be a great boon in simplifying the subsequent calculations as well as providing a coherent and tractable description of a reasonably general system.

The Helmholtz free energy must describe the thermodynamic state of each phase and interface. For the case of a porous medium, where the free energy is a macroscopic property, the changes in free energy of a phase should be reflective of changes within that phase as well as of interaction between a phase and its surroundings. Here, the dependence will be assumed to be captured adequately for the water phase by allowing its free energy per unit mass, A^w, to depend on the density of the water phase, ρ^w, the temperature of the water phase, T^w, and the amount of bounding area of the water phase within the volume as measured by the area of *wa* interface per unit volume of water, $a^{wa}/(s^w\varepsilon)$, and the area of *ws* interface per unit volume of water, $a^{ws}/(s^w\varepsilon)$. Note that the inclusion of the bounding areas per unit volume of water is a macroscopic measure of the microscopic curvature of the interface between the water phase and the air and solid phases. Inclusion of a^{wa} and a^{ws} among the independent variables is only possible in a context which includes balance equations for the interfaces such that these variables appear in the theory. Of course, the free energy of the water phase might, in reality, also depend on other quantities, such as Γ^{wa} and Γ^{ws}, but these dependencies are assumed to be small. The two area per unit volume variables selected are taken to provide a reasonable indication of the way the water phase is distributed within the porous medium and thus its energy state.

Similar dependences are allowed for the air and solid phases on their bounding areas (i.e., the air phase surface areas per air phase volume are $a^{as}/(s^a\varepsilon)$ and $a^{wa}/(s^a\varepsilon)$, and the solid phase surface areas per unit volume of solid are $a^{as}/(1-\varepsilon)$ and $a^{ws}/(1-\varepsilon)$). The solid is also taken to depend on its strain tensor E^s. Thus for each of the phases the free energy is assumed constitutive dependence on independent variables in list (8) as follows:

$$A^w = A^w(\rho^w, T^w, a^{wa}, a^{ws}, s^w, \varepsilon) \tag{9a}$$

$$A^a = A^a(\rho^a, T^a, a^{wa}, a^{as}, s^w, \varepsilon) \tag{9b}$$

$$A^s = A^s(\rho^s, T^s, \mathsf{E}^s, a^{ws}, a^{as}) \tag{9c}$$

(Note that explicit dependence of A^s on ε is not listed because with $\hat{e}^s_{s\beta}$, ρ^s, and E^s specified, ε is determined.)

By analogous reasoning, the Helmholtz free energy per unit mass of an interface is allowed to depend on its density and temperature as well as its area per unit volume of adjacent phases. Again, the inclusion of independent variables describing area per unit volume provides a measure of the curvature of the interface. There the interfacial free energies are assigned the constitutive dependences

$$A^{wa} = A^{wa}(\Gamma^{wa}, T^{wa}, a^{wa}, s^w, \varepsilon) \tag{10a}$$

$$A^{ws} = A^{ws}(\Gamma^{ws}, T^{ws}, a^{ws}, s^w, \varepsilon) \tag{10b}$$

$$A^{as} = A^{as}(\Gamma^{as}, T^{as}, a^{as}, s^w, \varepsilon) \tag{10c}$$

Although the free energies are restricted to the above dependences, the other constitutive functions are allowed full dependence on all the independent variables. This allowance does not complicate the application of the entropy inequality, but in experimental verification of the theory a reduced dependence is likely to be sought.

ENTROPY INEQUALITY RESULTS

The procedure for application of the entropy inequality has been presented in detail by *Hassanizadeh and Gray* [1990] for the simplified case where the dependence of phase free energy on interfacial area and porosity is not included. Because the manipulations needed here are similar in content through somewhat more complex, they will not be presented in detail. However, the full entropy inequality obtained is presented in the appendix as the precursor of the results to be indicated here.

Because quantities in braces in (A1) are multiplied by $D^\alpha T^\alpha/Dt$, $D^{\alpha\beta}T^{\alpha\beta}/Dt$, d^α, or $\mathsf{d}^{\alpha\beta}$, which are not independent variables, these quantities must be zero. Therefore with introduction of the symbols p^α and $\gamma^{\alpha\beta}$ where

$$p^\alpha = (\rho^\alpha)^2 \frac{\partial A^\alpha}{\partial \rho^\alpha} \qquad \alpha = w, a, s \tag{11a}$$

$$\gamma^{\alpha\beta} = -(\Gamma^{\alpha\beta})^2 \frac{\partial A^{\alpha\beta}}{\partial \Gamma^{\alpha\beta}} = -a^{\alpha\beta}\Gamma^{\alpha\beta} \frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}} \tag{11b}$$

$$\alpha\beta = wa, ws, as$$

the following equations must hold:

$$\mathsf{t}^\alpha = -p^\alpha \mathsf{I} \qquad \alpha = w, a, \tag{12a}$$

$$\mathsf{t}^s = -p^s\mathsf{I} + \mathsf{t}^s_e \tag{12b}$$

$$\mathsf{t}^s_e = \rho^s(GRAD\mathbf{F}^s)^T \cdot \frac{\partial A^s}{\partial \mathsf{E}^s} \cdot (GRAD\mathbf{F}^s) \tag{12c}$$

$$\eta^\alpha = -\frac{\partial A^\alpha}{\partial T^\alpha} \qquad \alpha = w, a, s \tag{13a}$$

$$\eta^{\alpha\beta} = -\frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}} \qquad \alpha\beta = wa, ws, as \tag{13b}$$

$$\mathsf{S}^{\alpha\beta} = \gamma^{\alpha\beta}\mathsf{I} \qquad \alpha\beta = wa, ws, as \tag{14}$$

In these relations, p^α is thus the macroscopic pressure of the α phase, $\gamma^{\alpha\beta}$ is the macroscopic interfacial tension of the $\alpha\beta$ interface, and t^s_e is the effective stress tensor of the solid phase at the macroscale. The second equality in (11*b*) is not readily apparent from (A1) but may be deduced from a similar equation obtained using $\dot{\Gamma}^{\alpha\beta}$ instead of $\dot{a}^{\alpha\beta}$ as dependent variables.

For the remaining discussion a quasi-equilibrium approximation will be used such that the temperatures of each phase and interface at a point in the system are taken to be equal. The condition is not imposed that the temperature is uniform throughout the system but only that at each point one temperature is sufficient to characterize the state. This approximation is not made of necessity but only to simplify the subsequent discussion in which mass and momentum transfer are given primary attention and energy transport is only of secondary interest.

At equilibrium, (i.e., when $\mathbf{v}^{\alpha,s}$, $\mathbf{w}^{\alpha\beta,s}$, ∇T, $\dot{\varepsilon}$, $\dot{s}^w$, $\dot{a}^{\alpha\beta}$, $\hat{e}^\alpha_{\alpha\beta}$, and $\hat{e}^{\alpha\beta}_{aws}$ are zero), the bracketed quantities in (A1) will each be zero. These quantities can thus be expressed as the sum of an equilibrium part and a nonequilibrium part which is zero at equilibrium. Therefore the terms multiplied by $\mathbf{v}^{\alpha,s}$ and $\mathbf{w}^{\alpha\beta,s}$ may be written

$$\sum_{\beta\neq a} \hat{\mathbf{T}}^{\alpha}_{\alpha\beta} = p^{\alpha}\nabla(\varepsilon s^{\alpha}) - \rho^{\alpha}\varepsilon s^{\alpha}\left[\frac{\partial A^{\alpha}}{\partial a^{wa}}\nabla a^{wa} + \frac{\partial A^{\alpha}}{\partial a^{\alpha s}}\nabla a^{\alpha s}\right.$$

$$\left. + \frac{\partial A^{\alpha}}{\partial s^{w}}\nabla s^{w} + \frac{\partial A^{\alpha}}{\partial \varepsilon}\nabla \varepsilon\right] + \hat{\tau}^{\alpha} \qquad \alpha = w,\ a \qquad (15)$$

$$\hat{\mathbf{S}}^{\alpha\beta}_{aws} - \hat{\mathbf{T}}^{\alpha}_{\alpha\beta} - \hat{\mathbf{T}}^{\beta}_{\alpha\beta} = -\Gamma^{\alpha\beta}a^{\alpha\beta}\left[\frac{\partial A^{\alpha\beta}}{\partial s^{w}}\nabla s^{w} + \frac{\partial A^{\alpha\beta}}{\partial \varepsilon}\nabla\varepsilon\right]$$

$$+ \hat{\tau}^{\alpha\beta} \qquad \alpha\beta = wa,\ ws,\ as \qquad (16)$$

where $\hat{\tau}^{\alpha}$ and $\hat{\tau}^{\alpha\beta}$ are zero at equilibrium.

Equations (15) and (16) are conveniently substituted into the momentum balances for the fluid phases and the interfaces, respectively, to yield

$$\rho^{\alpha}\frac{D^{\alpha}\mathbf{v}^{\alpha}}{Dt} + \nabla p^{\alpha} - \rho^{\alpha}\mathbf{g} + \rho^{\alpha}\left[\frac{\partial A^{\alpha}}{\partial a^{wa}}\nabla a^{wa} + \frac{\partial A^{\alpha}}{\partial a^{\alpha s}}\nabla a^{\alpha s}\right.$$

$$\left. + \frac{\partial A^{\alpha}}{\partial s^{w}}\nabla s^{w} + \frac{\partial A^{\alpha}}{\partial \varepsilon}\nabla\varepsilon\right] = \frac{\hat{\tau}^{\alpha}}{\varepsilon s^{\alpha}} \qquad \alpha = w,\ a \qquad (17)$$

$$\Gamma^{\alpha\beta}a^{\alpha\beta}\frac{D^{\alpha\beta}\mathbf{w}^{\alpha\beta}}{Dt} - \nabla(a^{\alpha\beta}\gamma^{\alpha\beta}) - \Gamma^{\alpha\beta}a^{\alpha\beta}\mathbf{g}$$

$$+ \Gamma^{\alpha\beta}a^{\alpha\beta}\left[\frac{\partial A^{\alpha\beta}}{\partial s^{w}}\nabla s^{w} + \frac{\partial A^{\alpha\beta}}{\partial \varepsilon}\nabla\varepsilon\right]$$

$$= \hat{e}^{\alpha}_{\alpha\beta}\mathbf{w}^{\alpha\beta,\alpha} + \hat{e}^{\beta}_{\alpha\beta}\mathbf{w}^{\alpha\beta,\beta} + \hat{\tau}^{\alpha\beta} \qquad (18)$$

$$\alpha\beta = wa,\ ws,\ as$$

These equations will be examined in more detail when linearized constitutive relations for $\hat{\tau}^{\alpha}$ and $\hat{\tau}^{\alpha\beta}$ are employed. However, first some remarks are appropriate concerning other terms in entropy equation (A1) which are zero at equilibrium.

The quantity in brackets multiplying $\dot{\varepsilon}$ must be zero at equilibrium and expresses a relationship among the pressures of the three phases. If the void fraction potential is designated Z, where

$$Z = s^{w}\rho^{w}\varepsilon\frac{\partial A^{w}}{\partial\varepsilon} + s^{a}\rho^{a}\varepsilon\frac{\partial A^{a}}{\partial\varepsilon} + \sum_{\alpha\beta}\Gamma^{\alpha\beta}a^{\alpha\beta}\frac{\partial A^{\alpha\beta}}{\partial\varepsilon} \qquad (19)$$

then the value of this function when the phases and interfaces are at equilibrium is given by

$$Z = (p^{w}s^{w} + p^{a}s^{a} - p^{s})_{e} \qquad (20)$$

Note that when the dependence of the free energies on void fraction is small such that Z is zero, (20) reduces to the commonly employed relation that the pressure in the solid phase is equal to the saturation-weighted sum of pressures in the fluid phases [e.g., *Schrefler et al.*, 1990].

The bracketed quantities which multiply $\dot{a}^{\alpha\beta}$ are also zero at equilibrium and express a relation between the change in free energy of the phases, with the area separating them. The equilibrium relations are

$$\rho^{w}\varepsilon s^{w}\frac{\partial A^{w}}{\partial a^{wa}} + \rho^{a}\varepsilon s^{a}\frac{\partial A^{a}}{\partial a^{wa}} = 0 \qquad (21a)$$

$$\rho^{w}\varepsilon s^{w}\frac{\partial A^{w}}{\partial a^{ws}} + \rho^{s}(1-\varepsilon)\frac{\partial A^{s}}{\partial a^{ws}} = 0 \qquad (21b)$$

$$\rho^{a}\varepsilon s^{a}\frac{\partial A^{a}}{\partial a^{as}} + \rho^{s}(1-\varepsilon)\frac{\partial A^{s}}{\partial a^{as}} = 0 \qquad (21c)$$

The grouping in brackets which multiplies $\dot{s}^{w}$ in (A1) is also zero at equilibrium. Let the capillary pressure p^{c} be defined by

$$\varepsilon p^{c} = -\rho^{w}\varepsilon s^{w}\frac{\partial A^{w}}{\partial s^{w}} - \rho^{a}\varepsilon s^{a}\frac{\partial A^{a}}{\partial s^{w}} - \sum_{\alpha\beta}\Gamma^{\alpha\beta}a^{\alpha\beta}\frac{\partial A^{\alpha\beta}}{\partial s^{w}} \qquad (22)$$

Then at equilibrium the multiplier of $\dot{s}^{w}$ indicates

$$\varepsilon p^{c} = \varepsilon(p^{a} - p^{w})_{e} \qquad (23)$$

The definition of capillary pressure given in (22) provides this function directly and independently of p^{a} and p^{w} and shows that p^{c}, in general, depends on independent variables as follows:

$$p^{c} = p^{c}(s^{w},\ \varepsilon,\ a^{wa},\ a^{ws},\ a^{as},\ \rho^{w},\ \rho^{a},\ T,\ \Gamma^{wa},\ \Gamma^{ws},\ \Gamma^{as}) \qquad (24)$$

At equilibrium the capillary pressure given in (22), with functional dependence as indicated in (24), will be equal to the difference in pressure between the air and water phases. Typically, p^{c} is assumed to be a function of s^{w}, the fluid pairs through ρ^{w} and ρ^{a}, the solid configuration as evidenced in ε, and temperature T. Therefore the principal difference between (24) and the common $p^{c} - s^{w}$ relation lies in the inclusion of interfacial areas and surface densities.

It should be noted that the entropy inequality also provides information regarding the heat flux terms. In particular, at equilibrium, $\mathbf{q}^{\alpha}$, $\mathbf{q}^{\alpha\beta}$, and $\hat{Q}^{\alpha\beta}_{aws}$ are all zero. Furthermore, at equilibrium the Gibbs free energy per unit mass for each phase and interface will be equal. This last result is satisfying in that it is consistent with the microscopic condition of equilibrium.

The equations developed in this section are very rich, general balance relationships. Although the functional dependence of constitutive forms is provided, the specific form is not obtained. Thus the equations are both valuable and difficult to work with because of their generality. In subsequent sections some simplifying assumptions will be made which sequentially will restrict the applicability of the equations to smaller sets of problems. The restrictions which will be applied here are utilized with the intention of obtaining a relatively simple description of unsaturated flow problems. If one is interested in a different flow situation, alternative appropriate restrictions may be applied, or one of the more general cases can be used. The important feature to notice is that the relatively simple equations for unsaturated flow are obtained as a special case of a general theory rooted in conservation principles and not as a generalized case of a simple theory such as Darcy's equation for saturated single-phase flow.

LINEARIZED EQUATIONS OF MOTION

The key postulates to this point regard the functional dependence of the free energy as stated in (9) and (10). These postulates led to the momentum equations (17) and (18) for the fluid phases and the interfaces, respectively, as well as several useful equilibrium relationships given as (20), (21), and (23). The constitutive functions which are zero at equilibrium ($\hat{\tau}^\alpha$, $\hat{\tau}^{\alpha\beta}$, $\dot{s}^w$, $\dot{a}^{\alpha\beta}$, $\dot{\varepsilon}$) will now be linearized in light of the entropy inequality. This is tantamount to making a Taylor series expansion around the equilibrium state and neglecting higher-order terms. The fact that the constitutive assumptions are to be linearized does not influence any conclusions that will be drawn concerning the equilibrium state of the system (i.e., only the dynamic state will be influenced). Attention will be restricted to the constitutive functions important for the momentum equation in that linearizations of constitutive variables in the energy equation will not be considered. A general momentum equation making use of linearized constitutive function will be presented with attention then successively shifted to more specialized cases.

Case 1: Linearized Constitutive Equation With Negligible Mass Transfer Terms

For this case the transfer of mass from the phases to the interfaces will be considered negligible in contributing to momentum transfer. Also, the temperature gradient will not be considered a driving force for the flow. The nonequilibrium term $\hat{\tau}^\alpha$ for phase α which arises from an integration over the interface of the α phase with other phases is assumed to depend on the velocity of that phase and of the bounding interfaces but not on other phase or interface velocities. Thus equation (17) becomes

$$\rho^\alpha \frac{D^\alpha \mathbf{v}^\alpha}{Dt} + \nabla p^\alpha - \rho^\alpha \mathbf{g} + \rho^\alpha$$

$$\cdot \left[\frac{\partial A^\alpha}{\partial a^{wa}} \nabla a^{wa} + \frac{\partial A^\alpha}{\partial a^{\alpha s}} \nabla a^{\alpha s} + \frac{\partial A^\alpha}{\partial s^w} \nabla s^w + \frac{\partial A^\alpha}{\partial \varepsilon} \nabla \varepsilon \right]$$

$$= -\mathsf{R}^\alpha_\alpha \cdot \mathbf{v}^{\alpha,s} - \sum_{\beta \neq \alpha} \mathsf{R}^\alpha_{\alpha\beta} \cdot \mathbf{w}^{\alpha\beta,s} \qquad \alpha = w, a \qquad (25)$$

The variable $\hat{\tau}^{\alpha\beta}$ depends on the interaction of the $\alpha\beta$ interface with the contact curve as well as on the interaction with the two adjacent phases and thus depends on the velocity of the interfaces and of the α and β phases (note that if the phases are present such that no contact curve exists, $\hat{\tau}^{\alpha\beta}$ will not depend on interface velocities other than that of the $\alpha\beta$ interface). The momentum balance equation (18) for the interface is then

$$\Gamma^{\alpha\beta} a^{\alpha\beta} \frac{D^{\alpha\beta} \mathbf{w}^{\alpha\beta}}{Dt} - \nabla(a^{\alpha\beta} \gamma^{\alpha\beta}) - \Gamma^{\alpha\beta} a^{\alpha\beta} \mathbf{g}$$

$$+ \Gamma^{\alpha\beta} a^{\alpha\beta} \left[\frac{\partial A^{\alpha\beta}}{\partial s^w} \nabla s^w + \frac{\partial A^{\alpha\beta}}{\partial \varepsilon} \nabla \varepsilon \right]$$

$$= -\sum_{\gamma\delta} \mathsf{R}^{\alpha\beta}_{\gamma\delta} \cdot \mathbf{w}^{\gamma\delta,s} - \mathsf{R}^{\alpha\beta}_\alpha \cdot \mathbf{v}^{\alpha,s}$$

$$- \mathsf{R}^{\alpha\beta}_\beta \cdot \mathbf{v}^{\beta,s} \qquad \alpha\beta = wa, ws, as \qquad (26)$$

In (25) and (26) the R tensors are functions of the independent variables. Additionally, entropy inequality (A1) restricts these tensors such that R^α_α, $\mathsf{R}^\alpha_{\alpha\beta} + (\mathsf{R}^{\alpha\beta}_\alpha)^T$, and $\mathsf{R}^{\alpha\beta}_{\gamma\delta} + (\mathsf{R}^{\alpha\beta}_{\gamma\delta})^T$ must be positive semidefinite.

The five constitutive functions $\dot{s}^w$, $\dot{\varepsilon}$, and $\dot{a}^{\alpha\beta}$ may be linearized by requiring that each of them be proportional to the term in brackets in the entropy inequality that it multiplies. The expressions obtained are

$$\dot{s}^w = \Pi^w [p^w - p^a + p^c] \qquad (27)$$

$$\dot{\varepsilon}\varepsilon = \Pi^\varepsilon [s^w p^w + s^a p^a - p^s - Z] \qquad (28)$$

$$\dot{a}^{\alpha\beta} = -\Pi^{\alpha\beta} \left[\rho^\alpha \varepsilon^\alpha \frac{\partial A^\alpha}{\partial a^{\alpha\beta}} + \rho^\beta \varepsilon^\beta \frac{\partial A^\beta}{\partial a^{\alpha\beta}} \right] \qquad (29)$$

$$\alpha\beta = wa, ws, as$$

The coefficients of proportionality, Π^w, Π^ε, and $\Pi^{\alpha\beta}$ are dependent upon the independent variables and constrained to be greater than or equal to zero by the entropy inequality.

Case 2: Constant Porosity, Slow Flow, Negligible Cross Terms

When the flow in the porous medium is slow, the advective terms in (25) and (26) are negligible. The cross flow terms in the right side of (25) and (26) which would account for the influence of movement of one phase or interface on the adjacent interfaces will also be neglected. A final stipulation for this case is that the porosity is constant or, more precisely, that the influence of terms involving the porosity gradient on momentum transport is negligible such that the bracketed term on the right side of (28) may be considered to be zero. This is a quasi-equilibrium assumption. Under these conditions the momentum equations (25) and (26) become, respectively,

$$\nabla p^\alpha - \rho^\alpha \mathbf{g} + \rho^\alpha \left[\frac{\partial A^\alpha}{\partial a^{wa}} \nabla a^{wa} + \frac{\partial A^\alpha}{\partial a^{\alpha s}} \nabla a^{\alpha s} + \frac{\partial A^\alpha}{\partial s^w} \nabla s^w \right]$$

$$= -\mathsf{R}^\alpha_\alpha \cdot \mathbf{v}^{\alpha,s} \qquad \alpha = w, a \qquad (30)$$

$$-\nabla(a^{\alpha\beta} \gamma^{\alpha\beta}) - \Gamma^{\alpha\beta} a^{\alpha\beta} \mathbf{g} + \Gamma^{\alpha\beta} a^{\alpha\beta} \left[\frac{\partial A^{\alpha\beta}}{\partial s^w} \nabla s^w \right]$$

$$= -\mathsf{R}^{\alpha\beta}_{\alpha\beta} \cdot \mathbf{w}^{\alpha\beta,s} \qquad \alpha\beta = wa, ws, as \qquad (31)$$

Case 3: Constant a^{ws} and a^{as}

This additional simplification, though perhaps a peculiar one at first thought, is appropriate for many unsaturated flow problems. When the wetting phase saturation is above the irreducible saturation, the water is considered to coat the solid grains. Thus the a^{ws} interface would include all the solid surface area, and a^{as} would be zero. If, as is the case under consideration here, a uniform soil with constant porosity is considered, then a^{ws} will be constant. Indeed, the terms in (30) and (31) involving ∇a^{as} and ∇a^{ws} would seen to be important primarily at very low saturation when part of the solid phase will be in contact with air. Thus the operative momentum equations are obtained from (30) for the air and water phases and from (31) for the *wa* interface as

$$\nabla p^a - \rho^a \mathbf{g} + \rho^a \frac{\partial A^a}{\partial a^{wa}} \nabla a^{wa} + \rho^a \frac{\partial A^a}{\partial s^w} \nabla s^w = -\mathsf{R}^a_a \cdot \mathbf{v}^{a,s} \tag{32a}$$

$$\nabla p^w - \rho^w \mathbf{g} + \rho^w \frac{\partial A^w}{\partial a^{wa}} \nabla a^{wa} + \rho^w \frac{\partial A^w}{\partial s^w} \nabla s^w = -\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} \tag{32b}$$

$$-\nabla(a^{wa}\gamma^{wa}) - \Gamma^{wa}a^{wa}\mathbf{g} + \Gamma^{wa}a^{wa} \frac{\partial A^{wa}}{\partial s^w} \nabla s^w = -\mathsf{R}^{wa}_{wa} \cdot \mathbf{w}^{wa,s} \tag{33}$$

With the thermodynamic coefficients evaluated, these equations may be used to simulate the movement of both the air and water phases during the unsaturated flow process.

Case 4: Air Phase at Constant Pressure and With Negligible Momentum

This case is the simplest one to be considered here and corresponds physically to the case most commonly considered in simulating unsaturated flow. Quasi-equilibrium assumptions are applied so that the bracketed terms on the right side of (27) through (29) are all zero. This assumption implies that the system dynamics do not cause significant deviation from the equilibrium state for these terms. Now multiplication of (32*a*) by s^a and of (32*b*) by s^w and addition of the resulting equations yields

$$\begin{aligned} & s^w\nabla p^w + s^a\nabla p^a - (s^w\rho^w + s^a\rho^a)\mathbf{g} \\ & \quad + \left(\rho^w s^w \frac{\partial A^w}{\partial a^{wa}} + \rho^a s^a \frac{\partial A^a}{\partial a^{wa}}\right)\nabla a^{wa} \\ & \quad + \left(\rho^w s^w \frac{\partial A^w}{\partial s^w} - \rho^a s^a \frac{\partial A^a}{\partial s^a}\right)\nabla s^w \\ & \quad = -s^w\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} - s^a\mathsf{R}^a_a \cdot \mathbf{v}^{a,s} \end{aligned} \tag{34}$$

For the quasi-equilibrium assumption applied to (29) with $\alpha\beta = wa$ (i.e., equilibrium condition (21*a*)) and with (23) for p^c applicable under the quasi-equilibrium approximation applied to (27), equation (34) becomes

$$\begin{aligned} & -s^w\nabla p^c + \nabla p^a - (s^w\rho^w + s^a\rho^a)\mathbf{g} \\ & \quad + \left(\rho^w s^w \frac{\partial A^w}{\partial s^w} - \rho^a s^a \frac{\partial A^a}{\partial s^a}\right)\nabla s^w \\ & \quad = -s^w\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} - s^a\mathsf{R}^a_a \cdot \mathbf{v}^{a,s} \end{aligned} \tag{35}$$

Finally, with p^a assumed constant and atmospheric, with $\mathbf{v}^{a,s}$ small, and because the density of air is much less than that of water, (35) becomes

$$-\nabla p^c - \rho^w\mathbf{g} + (\Omega^w - \Omega^a)\frac{\nabla s^w}{s^w} = -\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} \tag{36}$$

where Ω^α has been called the wettability potential by *Hassanizadeh and Gray* [1990] and is given by

$$\Omega^\alpha = \rho^\alpha s^\alpha \frac{\partial A^\alpha}{\partial s^\alpha} \qquad \alpha = w, a \tag{37}$$

Equation (36) differs from the standard form used to model unsaturated flow in that an extra term is present involving the gradient of saturation. The appearance of the difference is wettability potential in (36) is particularly intriguing in light of *Scheidegger*'s [1974] mention of the need to quantitatively characterize relative wettability. The actual magnitude of this extra term requires experimental study, although its significance seems to be substantial. A fuller discussion of this term appears in the companion paper [*Gray and Hassanizadeh*, this issue].

As an additional note on the coalescence of results in this case, consider (33), the momentum balance for the a^{wa} interface. This equation can be rearranged to the form

$$-\gamma^{wa}\nabla a^{wa} + \Gamma^{wa}a^{wa}\frac{\partial A^w}{\partial s^w}\nabla s^w = a^{wa}(\nabla\gamma^{wa} + \Gamma^{wa}\mathbf{g}) - \mathsf{R}^{wa}_{wa} \cdot \mathbf{w}^{wa,s} \tag{38}$$

Now a quasi-equilibrium assumption is invoked such that the velocity of the *wa* interface is considered to be due primarily to the gravitational force and to gradients in γ^{wa} which arise due to the movement of the adjacent phases. Under this assumption the right side of (38) is zero and the equation reduces to

$$-\gamma^{wa}\nabla a^{wa} + \Gamma^{wa}a^{wa}\frac{\partial A^{wa}}{\partial s^w}\nabla s^w = 0 \tag{39}$$

With a similar quasi-equilibrium assumption applied to (31) for the *ws* interface with a^{ws} also constant, $\partial A^{ws}/\partial s^w$ is seen to be zero. Multiplication of (22) by ∇s^w and application of condition (38) along with $a^{as} = 0$ yields

$$-\gamma^{wa}\nabla a^{wa} - \varepsilon(p^c + \Omega^w - \Omega^a)\nabla s^w = 0 \tag{40}$$

This equation indicates that when a gradient in a^{wa} exists, a gradient in saturation must also exist. However when a gradient in saturation exists, a gradient in the interfacial area need not exist if $p^c = \Omega^a - \Omega^w$. Substitution of (39) into (36) yields

$$-\varepsilon\nabla(p^c s^w) - \rho^w\varepsilon s^w\mathbf{g} - \gamma^{wa}\nabla a^{wa} = -\varepsilon s^w\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} \tag{41}$$

This form of the momentum balance indicates that at equilibrium p^c is not necessarily hydrostatic. The gradient in saturation does not give rise to a unique gradient in a^{wa}. This observation may help explain the presence of hysteresis in unsaturated flow due to the strong dependence of p^c on a^{wa} as well as on s^w.

Another interesting form of the flow equation may be obtained from (34) noting that gradients in temperature, density, porosity, a^{ws}, and a^{as} are zero. On the basis of the functional dependence of Helmholtz free energy given as (9*a*) and (9*b*), (34) becomes

$$\rho^w s^w\left(\frac{1}{\rho^w}\nabla p^w + \nabla A^w - \mathbf{g}\right) + \rho^a s^a\left(\frac{1}{\rho^a}\nabla p^a + \nabla A^a - \mathbf{g}\right) = -s^w\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} - s^a\mathsf{R}^a_a \cdot \mathbf{v}^{a,s} \tag{42}$$

If the saturation conditions are such that the low-density air phase is essentially at equilibrium and gradients in its properties do not affect the momentum transport in the system, then the terms relating to the air phase may be considered negligible in (42). Furthermore, since the Gibbs free energy is related to Helmholtz free energy by $G^w = A^w + p^w/\rho^w$, the last equation becomes

$$\rho^w(\nabla G^w - \mathbf{g}) = -\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} \tag{43}$$

This form of the balance law indicates that the gradient in Gibb's free energy not balanced by gravitational forces is the driving force for the water phase movement.

Finally, it is somewhat satisfying to note that for the special case of fully saturated flow when ∇a^{wa}, ∇s^w, and s^a are zero and s^w is one, (34) simplifies to

$$\nabla p^w - \rho^w \mathbf{g} = -\mathsf{R}^w_w \cdot \mathbf{v}^{w,s} \tag{44}$$

This equation is Darcy's law for saturated flow and is thus seen to be a highly restricted form of the general momentum equation, derived as (17), subjected to the successive application of the conditions of the four cases considered. Although derivation of Darcy's law for saturated flow by the methods presented here may be viewed as mathematical overkill, the fact that this equation can be obtained by simplification of more general forms provides a point of contact of the theory proposed here with the traditional approach.

CONCLUSION

The results in this paper provide a theoretically sound basis on which to pursue modeling of the unsaturated flow process. The inclusion of the balance equations for the interfaces between phases allows explicit dependence of unsaturated flow on the interface dynamics to be included. The momentum equation developed was presented at four different levels of complexity. The simplest form, slow flow in a homogeneous medium of constant porosity with saturation above the irreducible saturation, corresponds to the unsaturated flow problems typically studied. The more complex cases presented here provide equations for multiphase flow when the movement of both fluids is important and when a wetting fluid invades a medium initially saturated with a nonwetting fluid.

Conceptually, the results provided here are consistent. However, to implement these equations, experimental work is required to measure thermodynamic and material coefficients.

APPENDIX: THE ENTROPY INEQUALITY

$$\Lambda = -\sum_{\alpha} \frac{\varepsilon^\alpha \rho^\alpha}{T^\alpha} \frac{D^\alpha T^\alpha}{Dt} \left\{ \frac{\partial A^\alpha}{\partial T^\alpha} + \eta^\alpha \right\}$$

$$-\sum_{\alpha\beta} \frac{a^{\alpha\beta}\Gamma^{\alpha\beta}}{T^{\alpha\beta}} \frac{D^{\alpha\beta}T^{\alpha\beta}}{Dt} \left\{ \frac{\partial A^{\alpha\beta}}{\partial T^{\alpha\beta}} + \eta^{\alpha\beta} \right\}$$

$$+\sum_{\alpha\neq s} \frac{\mathsf{d}^\alpha}{T^\alpha} : \left\{ \varepsilon s^\alpha \left[\mathsf{t}^\alpha + (\rho^\alpha)^2 \frac{\partial A^\alpha}{\partial \rho^\alpha} \mathsf{I} \right] \right\}$$

$$+\frac{(1-\varepsilon)}{T^s} \mathsf{d}^s : \left\{ \mathsf{t}^s + (\rho^s)^2 \frac{\partial A^s}{\partial \rho^s} \mathsf{I} \right.$$

$$\left. - (GRAD\mathbf{F}^s)^T \cdot \frac{\partial A^s}{\partial \mathsf{E}^s} \cdot (GRAD\mathbf{F}^s) \right\}$$

$$+\sum_{\alpha\beta} \frac{\mathsf{d}^{\alpha\beta}}{T^{\alpha\beta}} : \left\{ a^{\alpha\beta} \left(\mathsf{S}^{\alpha\beta} + \Gamma^{\alpha\beta^2} \frac{\partial A^{\alpha\beta}}{\partial \Gamma^{\alpha\beta}} \mathsf{I} \right) \right\}$$

$$+\dot{\varepsilon} \left[\frac{s^w \rho^{w^2}}{T^w} \frac{\partial A^w}{\partial \rho^w} + \frac{s^a \rho^{a^2}}{T^a} \frac{\partial A^a}{\partial \rho^a} - \frac{\rho^{s^2}}{T^s} \frac{\partial A^s}{\partial \rho^s} \right.$$

$$\left. -\sum_{\alpha\neq s} \frac{\rho^\alpha \varepsilon^\alpha}{T^\alpha} \frac{\partial A^\alpha}{\partial \varepsilon} - \sum_{\alpha\beta} \frac{\Gamma^{\alpha\beta} a^{\alpha\beta}}{T^{\alpha\beta}} \frac{\partial A^{\alpha\beta}}{\partial \varepsilon} \right]$$

$$+\sum_{\alpha\neq s} \frac{\mathbf{v}^{\alpha,s}}{T^\alpha} \cdot \left[\rho^{a^2} \frac{\partial A^\alpha}{\partial \rho^\alpha} \nabla(\varepsilon s^\alpha) \right.$$

$$-\rho^\alpha \varepsilon s^\alpha \left(\frac{\partial A^\alpha}{\partial a^{wa}} \nabla a^{wa} + \frac{\partial A^\alpha}{\partial a^{\alpha s}} \nabla a^{\alpha s} + \frac{\partial A^\alpha}{\partial s^w} \nabla s^w \right.$$

$$\left. \left. + \frac{\partial A^\alpha}{\partial \varepsilon} \nabla \varepsilon \right) - \sum_{\beta\neq\alpha} \hat{\mathbf{T}}^\alpha_{\alpha\beta} + \sum_{\beta\neq\alpha} \hat{\mathbf{T}}^\alpha_{\alpha\beta} \frac{T^{\alpha\beta,\alpha}}{T^{\alpha\beta}} \right]$$

$$+\sum_{\alpha\beta} \frac{\mathbf{w}^{\alpha\beta,s}}{T^{\alpha\beta}} \cdot \left[\Gamma^{\alpha\beta^2} \frac{\partial A^{\alpha\beta}}{\partial \Gamma^{\alpha\beta}} \nabla a^{\alpha\beta} \right.$$

$$-\Gamma^{\alpha\beta} a^{\alpha\beta} \left(\frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}} \nabla a^{\alpha\beta} + \frac{\partial A^{\alpha\beta}}{\partial s^w} \nabla s^w + \frac{\partial A^{\alpha\beta}}{\partial \varepsilon} \nabla \varepsilon \right)$$

$$\left. + \hat{\mathbf{T}}^\alpha_{\alpha\beta} + \hat{\mathbf{T}}^\beta_{\alpha\beta} - \hat{\mathbf{S}}^{\alpha\beta}_{aws} - \frac{\hat{\mathbf{S}}^{\alpha\beta}_{aws} T^{\alpha\beta,s}}{T^s} \right]$$

$$+\dot{s}^w \left[\frac{\rho^w \varepsilon}{T^w} \left(\rho^w \frac{\partial A^w}{\partial \rho^w} - s^w \frac{\partial A^w}{\partial s^w} \right) - \frac{\rho^a \varepsilon}{T^a} \left(\rho^a \frac{\partial A^a}{\partial \rho^a} \right. \right.$$

$$\left. \left. + s^a \frac{\partial A^a}{\partial s^w} \right) - \sum_{\alpha\beta} \frac{\Gamma^{\alpha\beta} a^{\alpha\beta}}{T^{\alpha\beta}} \frac{\partial A^{\alpha\beta}}{\partial s^w} \right]$$

$$+\dot{a}^{wa} \left[-\frac{\rho^w \varepsilon s^w}{T^w} \frac{\partial A^w}{\partial a^{wa}} - \frac{\rho^a \varepsilon s^a}{T^a} \frac{\partial A^a}{\partial a^{wa}} \right.$$

$$\left. -\frac{\Gamma^{wa} a^{wa}}{T^{wa}} \frac{\partial A^{\dot{w}a}}{\partial a^{wa}} + \frac{\Gamma^{wa^2}}{T^{wa}} \frac{\partial A^{wa}}{\partial \Gamma^{wa}} \right]$$

$$+\dot{a}^{ws} \left[-\frac{\rho^w \varepsilon s^w}{T^w} \frac{\partial A^w}{\partial a^{ws}} - \frac{\rho^s (1-\varepsilon)}{T^s} \frac{\partial A^s}{\partial a^{ws}} \right.$$

$$
\begin{aligned}
&- \frac{\Gamma^{ws} a^{ws}}{T^{ws}} \frac{\partial A^{ws}}{\partial a^{ws}} + \frac{\Gamma^{ws^2}}{T^{ws}} \frac{\partial A^{ws}}{\partial \Gamma^{ws}} \Bigg] \\
&+ \dot{a}^{as} \Bigg[-\frac{\rho^{a} \varepsilon s^{a}}{T^{a}} \frac{\partial A^{a}}{\partial a^{as}} - \frac{\rho^{s}(1-\varepsilon)}{T^{s}} \frac{\partial A^{s}}{\partial a^{as}} \\
&- \frac{\Gamma^{as} a^{as}}{T^{as}} \frac{\partial A^{as}}{\partial a^{as}} + \frac{\Gamma^{as^2}}{T^{as}} \frac{\partial A^{as}}{\partial \Gamma^{as}} \Bigg] + \sum_{\alpha} \frac{\varepsilon^{\alpha}}{T^{\alpha^2}} \nabla T^{\alpha} \cdot [\mathbf{q}^{\alpha}] \\
&+ \sum_{\alpha} \frac{a^{\alpha\beta}}{T^{\alpha\beta^2}} \nabla T^{\alpha\beta} \cdot [\mathbf{q}^{\alpha\beta}] - \frac{1}{T^{s}} \sum_{\alpha\beta} \frac{T^{\alpha\beta,s}}{T^{\alpha\beta}} [\hat{Q}^{\alpha\beta}_{aws}] \\
&+ \sum_{\alpha} \sum_{\beta\neq\alpha} \frac{T^{\alpha\beta,\alpha}}{T^{\alpha\beta} T^{\alpha}} [\hat{Q}^{\alpha}_{\alpha\beta}] + \sum_{\alpha} \sum_{\beta\neq\alpha} \frac{\hat{e}^{\alpha}_{\alpha\beta}}{T^{\alpha\beta}} \Bigg[G^{\alpha\beta,\alpha} \\
&+ \tfrac{1}{2} (w^{\alpha\beta,s})^2 + \frac{T^{\alpha\beta,\alpha}}{T^{\alpha}} \left(\eta^{\alpha} T^{\alpha} - \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial \rho^{\alpha}} \right) \Bigg] \\
&- \frac{1}{T^{s}} \sum_{\alpha\beta} \hat{e}^{\alpha\beta}_{aws} \Bigg[G^{\alpha\beta,s} + \tfrac{1}{2} (w^{\alpha\beta,s})^2 \\
&+ \frac{T^{\alpha\beta,s}}{T^{\alpha\beta}} \left(\eta^{\alpha\beta} T^{\alpha\beta} + \Gamma^{\alpha\beta} \frac{\partial A^{\alpha\beta}}{\partial \Gamma^{\alpha\beta}} \right) \Bigg] \geq 0 \qquad \text{(A1)}
\end{aligned}
$$

where G^{α} and $G^{\alpha\beta}$ are the Gibbs free energy per unit mass of α phase and $\alpha\beta$ interface, respectively, with $G^{\alpha} = A^{\alpha} + \rho^{\alpha} \partial A^{\alpha} / \partial \rho^{\alpha}$, $G^{\alpha\beta} = A^{\alpha\beta} + \Gamma^{\alpha\beta} \partial A^{\alpha\beta} / \partial \Gamma^{\alpha\beta}$, and $G^{\alpha\beta,\alpha} = G^{\alpha\beta} - G^{\alpha}$.

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REFERENCES

Anderson, T. B., and R. Jackson, A fluid mechanical description of fluidized beds, *Ind. Eng. Chem. Fundam.*, *6*, 527–539, 1967.

Bear, J., and A. Verruijt, *Modeling Groundwater Flow and Pollution*, D. Reidel, Hingham, Mass., 1987.

Buckingham, E., Studies on the movement of soil moisture, *Bull. 38*, Bureau of Soils, U.S. Dep. of Agric., Washington, D. C., 1907.

Coleman, B. D., and W. Noll, The thermodynamics of elastic materials with heat conduction and viscosity, *Arch. Ration. Mech. Anal.*, *13*, 168–178, 1963.

Corey, A. T., *Mechanics of Heterogeneous Fluids in Porous Media*, Water Resources Publications, Fort Collins, Colo., 1977.

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

Gray, W. G., and S. M. Hassanizadeh, Paradoxes and realities in unsaturated flow theory, *Water Resour. Res.*, this issue.

Gray, W. G., and P. C. Y. Lee, On the theorems for local volume averaging of multiphase systems, *Int. J. Multiphase Flow*, *3*, 333–340, 1977.

Greenkorn, R. A., *Flow Phenomena in Porous Media*, Marcel Dekker, New York, 1983.

Hassanizadeh, S. M., and W. G. Gray, Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries, *Adv. Water Resour.*, *13*, 169–186, 1990.

Hillel, D., *Fundamentals of Soil Physics*, Academic, San Diego, Calif., 1980.

Marino, M. A., and J. N. Luthin, *Seepage and Groundwater*, Elsevier, New York, 1982.

Miller, C. A., and P. Noegi, *Interfacial Phenomena*, Marcel Dekker, New York, 1985.

Morrow, N. R., Physics and thermodynamics of capillary action in porous media, in *Flow Through Porous Media*, p. 103, American Chemical Society, Washington, D. C., 1970.

Scheidegger, A. E., *The Physics of Flow through Porous Media*, 3rd ed., University of Toronto Press, Toronto, Ont., 1974.

Schrefler, B. A., L. Simoni, L. Xikui, and O. C. Zienkiewicz, Mechanics of partially saturated porous media, in *Numerical Methods and Constitutive Modelling in Geomechanics*, edited by C. S. Desai and G. Gioda, Springer Verlag, New York, 1990.

Sposito, G., The "physics" of soil water physics, *Water Resour. Res.*, *22*(9), 83S–88S, 1986.

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

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