

Paradoxes and Realities in Unsaturated Flow Theory

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In currently applied theory of unsaturated flow, paradoxes exist concerning the equation of state for the water phase, the idea of a water phase at negative absolute pressure, the applicability of the hydrostatic pressure gradient at equilibrium, and the lack of explicit inclusion of interface effects in the problem formulation. The theory of unsaturated flow presented here eliminates those paradoxes and indicates that the hysteresis in capillary pressure and relative permeability may be accounted for by allowing these quantities to depend on interfacial area as well as saturation. The wettability potential is shown to be a thermodynamic function which is important in describing unsaturated flow processes. The momentum balance equation for the interface between the air and water phases also contributes to a systematic and tractable set of equations which describe unsaturated flow.

INTRODUCTION

The study of movement and distribution of water in unsaturated porous media is important as a naturally occurring process and in engineering design of soil barriers to the spreading of buried hazardous waste. *Hillel* [1971] states that physical and mathematical description of water movement in unsaturated porous media dates back to the turn of the present century. Early theories were obtained by simply extending concepts and ideas from less complicated systems and situations. Predictably, some of those theories were unable to account for complexities of a dynamic soil-water-air system. Despite many advancements achieved in the science of soil physics in the last forty years, certain shortcomings of the basic equations persist. *Hillel* [1971, p. 3] warns against overlooking the limitations of present theories of soil physics in stating,

In applying to the soil oversimplified concepts and theories borrowed from simpler or "purer" systems, we must be careful not to take our models too seriously or literally. Present-day theories of soil physics should therefore be taken with a grain or two of salt, as they were developed by entirely fallible (though courageous) soil physicists desperately attempting to make their system manageable by simplifying it. As the science develops, however, its tools are becoming more sophisticated and capable of handling some of the complexities which previous soil physicists therefore disregarded.

In developing more general and elaborate theories of unsaturated flow, one can no more rely on borrowing and extending ideas and equations from simpler systems such as saturated porous media. Instead, the reverse procedure must be followed. That is, one must start with a general description of an unsaturated system which includes all basic features and phenomena of interest and then proceed to simpler models by making appropriate assumptions; the saturated flow equations should be the end product or most simplified form obtained. Important features of an unsaturated medium that must be explicitly incorporated in a

mathematical model are a description of the mass, momentum, and energy exchanges within and between the solid phase, two-fluid phases, and three interfaces. These processes are only implicit in the celebrated Darcy-Buckingham equation. This equation is, in form, identical to Darcy's saturated flow equation, but the permeability coefficient and water pressure are interpreted differently to account for the presence of the air phase. Despite the warnings of *Hillel* [1971], this interpretation has been carried too far in implying that water phase bulk "pressure" may be less than absolute zero. Although water, under certain conditions, exhibits appreciable tensile strength, it does not do so in contact with air. When the (absolute) water pressure approaches the vapor pressure, the water will begin to evaporate.

Another difficulty in the present theories of unsaturated flow is providing an acceptable explanation for the hysteresis effects in the capillary pressure-saturation relation. The literature on unsaturated flow commonly adds disclaimers that the equations for unsaturated flow are limited in applicability by hysteresis effects [*Scheidegger*, 1974; *Hillel*, 1980; *de Marsily*, 1986]. Although the problem is well recognized, little evidence exists that it is being addressed effectively. Indeed, simulation models of unsaturated flow for today's high speed computers (e.g., discussed by *Huyakorn and Pinder* [1983] and *Bear and Verruijt* [1987]) are still based on the Darcy-Buckingham formulation of the momentum equation [*Darcy*, 1856; *Buckingham*, 1907] in conjunction with *Richards'* [1931] form of the mass balance equation. The last half century has mainly seen basic advances occurring in the measurement of the coefficients which appear in the governing equation, such as relative permeability and capillary pressure, and in improving computational algorithms for simulation of the nonlinear problem. *Schiegg* [1986] has provided a very detailed experimental and theoretical study of multiphase flow phenomena, including microscopic interfacial phenomena, which provides good insight into the many aspects of unsaturated flow which must be accounted for in a complete mathematical description.

The authors of the current paper have undertaken a series of articles [*Hassanizadeh and Gray*, 1990; *Gray and Has-*

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sanizadeh, 1989, this issue] which have had as their goal the incorporation of the interface thermodynamics into the equations describing multiphase flow. On the basis of the strategy of proceeding from the general to the specific, an unsaturated medium is modeled at the microscale as a union of three phases and three interfaces each with its own thermodynamic behavior. Standard balance laws of mass, momentum, energy, and entropy are given for each and every phase and interface. Certain restrictive relations ensure the compatibility of the thermodynamics of the phases and interfaces. The microscopic balance laws and restrictions are then averaged on the basis of a systematic averaging procedure [Gray and Hassanizadeh, 1989]. The macroscopic balance laws are supplemented with constitutive relationships which are proposed on the basis of physical understanding of the behavior of the phases and interfaces. The second law of thermodynamics and certain other physical and mathematical principles are exploited to ensure the physical and mathematical admissibility of the constitutive model [Hassanizadeh and Gray, 1990]. Afterward, a series of practical assumptions about the unsaturated flow system are employed to arrive at successively simpler models [Gray and Hassanizadeh, this issue]. In all of these models the basic features of the system are preserved, and many of the shortcomings of present theories are avoided. In the present work some shortcomings of the currently used equations are first examined. Then the simplest set of new equations is presented, and improvement offered by these equations is noted.

STANDARD UNSATURATED FLOW EQUATIONS

The modeling of unsaturated water flow in a partially saturated medium usually involves solution of the mass and momentum conservation equations for the water phase while the air phase is assumed to be at constant atmospheric pressure. Here, as a point of departure for the ensuing discussion, these equations will be presented. The equations are written at a scale assumed to be representative of the porous medium.

The mass balance equation for the water is [e.g., Bear, 1979]

$$\frac{\partial \varepsilon s^w \rho^w}{\partial t} + \nabla \cdot (\varepsilon s^w \rho^w \mathbf{v}^{w,s}) + \nabla \cdot (\varepsilon s^w \rho^w \mathbf{v}^s) = 0 \quad (1)$$

where ε is the porosity, ρ^w is the mass of water per unit volume of water, s^w is the water saturation, $\mathbf{v}^{w,s}$ is the velocity of the water phase with respect to the solid phase, and \mathbf{v}^s is the velocity of the solid phase. The velocity of the solid is usually expressed in terms of the deformation of the medium. Here, where the discussion is intended to focus on the water phase, the last term in (1) will be simply left as is with the understanding that it must be accounted for using a constitutive theory or the solid phase conservation equations.

The momentum equation for the water phase is given by Darcy's law generalized to allow for relative permeability:

$$\varepsilon s^w \mathbf{v}^{w,s} = -\frac{k^w K}{\mu} \cdot (\nabla p^w - \rho^w \mathbf{g}) \quad (2)$$

where p^w is the pressure in the water phase, K is the permeability of the medium, μ is the specified microscopic

viscosity of water, and k^w is the relative permeability taken to be a function of saturation and varying from zero to one. In (1) and (2), ε and K are considered to be parameters of the medium which must be prescribed. Thus the four equations above (the scalar continuity equation and the three components of the momentum equation) must be solved for the seven unknowns s^w , p^w , ρ^w , k^w , and $\mathbf{v}^{w,s}$. Three additional conditions are then required for the system to be determinate.

Typically, the water density may be assumed constant in a soil-water system. However, in a more general development and especially when the pressure is considered to vary by tens of bars, an equation of state is needed and written in the form

$$\rho^w = \rho^w(p^w, T) \quad (3)$$

where T is the temperature which will be considered to be a constant in this discussion. The remaining two conditions come from laboratory determination of relative permeability and capillary pressure as functions of saturation (and T) such that

$$k^w = k^w(s^w, T) \quad (4)$$

$$P_{st}^c = P_{st}^c(s^w, T) \quad (5)$$

where P_{st}^c is used to denote the standard definition of capillary pressure. Relations (4) and (5) are hysteretic functions of s^w in that they may take on more than one value for a prescribed saturation. The use of P_{st}^c adds an additional variable to the system, but capillary pressure is taken to be the difference between the constant atmospheric air pressure p^a and the water phase pressure p^w , or

$$P_{st}^c(s^w, T) = p^a - p^w \quad (6)$$

This set of eight equations (note that vector equation (2) is actually three equations) and constitutive relations comprises a set of conditions which, when supplemented by initial and boundary conditions, can be used to determine the water distribution and velocity field during the unsaturated flow process.

Although the preceding equations admit a solution and represent the state of the art in modeling unsaturated flow, some significant difficulties and paradoxes arise in considering the implications of these equations. These will be discussed in the next section, prior to proposing an alternative set of equations obtained by averaging and then application of a constitutive theory which both reveals macroscopic thermodynamics and assures that the second law of thermodynamics is not violated.

DISCUSSION OF PARADOXES

In considering the above system of equations and trying to relate them to the physical system under consideration, a variety of inconsistencies arise. Some are qualitative in nature while others give quantitative cause to reconsider various aspects of (1) through (6). Some of these difficulties, by themselves, recommend rejection of the preceding equations while others are best viewed in light of the package of arguments. Indeed, the reasons we present for rejecting the current formulation of unsaturated flow equations are most

likely not exhaustive. They nevertheless, we believe, constitute a compelling case.

Paradox 1: Equations of State

The form of equation of state (3) for the macroscopic density of the water phase is proposed by analogy with the equation of state used to describe single-phase fluids at the microscale. However, when used in describing water at the macroscale as a constituent in a multiphase system, this relation is inconsistent. To confirm this, invert (3) to obtain p^w in terms of ρ^w as

$$p^w = p^w(\rho^w, T) \tag{7}$$

This inversion is admissible because $\partial p^w / \partial \rho^w$ is positive for water. Equation (7) indicates that the pressure in the water phase is completely determined if the density and temperature of that phase are known. On the other hand, (6) may be rearranged to obtain

$$p^w = p^a - P_{st}^c(s^w) \tag{8}$$

For unsaturated flow, where the air pressure is considered constant at a particular temperature, this equation indicates that the pressure in the water phase is completely determined if the saturation of the water phase is known. Thus a paradox arises in that (7) indicates that p^w depends on ρ^w but not s^w , while (8) indicates just the opposite.

The contradictory functional dependence of p^w on independent variables suggests that neither (7) nor (8) adequately serves as an equation of state for the water. Indeed, a more general form intuitively seems appropriate such as

$$p^w = p^w(\rho^w, T, s^w) \tag{9}$$

An equation of state of this form or with dependence on even more independent variables would have to be formulated at the macroscale and could not be obtained as a simple extension of a single phase microscopic equation of state. This is, perhaps, most easily seen to be the case by noting that the concept of saturation does not even exist at the microscale where a point is either in the water, air, or soil phase.

Although (9) eliminates the contradiction of (7) and (8), it raises significant questions about the thermodynamics of multiphase systems in general when considered at the macroscale. If pressure of a phase is a function of saturation, this will impact the overall thermodynamic description of the system. For example, for a single phase homogeneous fluid at the microscale, the Helmholtz free energy per unit mass, A , is of the form

$$A = A(\rho, T) \tag{10a}$$

From thermodynamic considerations it is also known that the pressure in the fluid is related to the Helmholtz free energy by

$$p(\rho, T) = \rho^2 \left(\frac{\partial A}{\partial \rho} \right)_T \tag{10b}$$

However, in the macroscale situation where p^w depends on saturation as well as density and temperature, the existence of a macroscopic analogue to (10a) and (10b) is not obvious. One could postulate a Helmholtz free energy such that

$$A^w = A^w(\rho^w, T, s^w) \tag{11a}$$

but this would not necessarily imply that

$$p^w(\rho^w, T, s^w) = \rho^{w2} \left(\frac{\partial A^w}{\partial \rho^w} \right)_{T, s^w} \tag{11b}$$

where p^w in this equation is the equilibrium value of stress in the water. A relation such as (11b) would need to be proven before it could be applied to a multiphase flow or unsaturated flow problem.

The paradox involving the equation of state of the water phase for an unsaturated flow problem suggests the need for such equations to be formulated at the macroscale. This requirement carries with it the burden of deriving macroscale thermodynamic relations among macroscopic variables.

Paradox 2: The Range of Values for P_{st}^c

As noted in (6), for unsaturated flow problems, capillary pressure is taken to be the air phase pressure minus the water phase pressure. The minimum pressure that can be achieved in a bulk fluid phase is absolute zero. For virtually all natural soils the equilibrium pressure in the water phase is less than that in the air phase such that capillary pressure is positive. Thus if air is at 1 atm. pressure, one would expect (for natural soils) that P_{st}^c would be bounded by

$$0 \leq P_{st}^c \leq 1 \text{ atm} \tag{12}$$

Indeed, a water pressure approaching absolute zero would seem to imply that a condition of no water phase molecules present is approached. A bulk water phase pressure less than absolute zero seems physically unrealistic. *Koorevaar et al.* [1983] flatly state that negative absolute pressures do not exist. Nevertheless, unsaturated flow literature consistently and almost casually refers to capillary pressures more than 1 order of magnitude greater than 1 atm. even when the air phase pressure is atmospheric. For example, *de Marsily* [1986] indicates that the wilting point of certain plants is reached when the capillary pressure is of the order of 15 atm. He then uses this information to calculate a mean curvature radius of the water menisci in an unsaturated medium. Also, according to *Hillel* [1980], negative pressure potential of soil water up to 100 bars is conceivable. The concept of a bulk water phase under such large negative pressures is, at best, difficult to conceptualize.

De Marsily [1986] provides an informative description of the measurement of capillary pressure in a porous medium using a porous cup tensiometer. Water inside the cup achieves pressure equilibrium with the water in the soil, and the pressure in the cup is measured using a manometer. *De Marsily* indicates that this device can be used to measure the capillary pressure up to about 0.9 atm. At that point the water in the cup begins to boil. This observation is not surprising in view of the expected upper limit on P_{st}^c of 1 atm. when the air is at ambient pressure. *Kirkham* [1964], however, says that tensiometers operate only up to about 0.85 atm. of tension and attributes their subsequent failure to dissolved air and the impurities in the soil water which reduce the water's tensile strength. *De Marsily* [1986] and also *Hillel* [1980] note that in making laboratory measurements of P_{st}^c as a function of saturation, the air pressure may

be raised artificially in a pressurized closed circuit to allow values of P_{st}^c greater than 1 atm. to be achieved. This also seems reasonable and in accord with the reasoning which led up to (12). However, in regard to a further discussion by de Marsily of an indirect method for measuring $P_{st}^c > 1$ atm. under field conditions, questions remain as to whether the quantity being measured is actually related solely to the difference in pressures of the water and air phase (e.g., the attraction of the solid phase for the fluid phase could influence the measurements). Indeed, numerous indications exist in the literature that externally measured capillary pressure near residual saturation loses significance with respect to conditions within the porous medium [Harris and Morrow, 1964; Morrow and Harris, 1965; Morrow, 1970].

A statement that pressure in the bulk water phase may take on values less than absolute zero seems to be a conceptualization of or accounting for other processes which are occurring. De Marsily [1986, p. 33] confirms this idea quite succinctly when he states "These high negative pressures (less than absolute zero) to which the water in an unsaturated medium may be subjected should not surprise us; they measure, in reality, a state of energy of the water in the soil, i.e., the quantity of energy needed to extract a molecule that is bound to the solid by electrostatic forces." Indeed, energy may be required to extract water from a porous medium when that water is bound to the solid matrix. However, to quantify this energy in terms of a physically unrealistic negative pressure in the water phase and to use this pressure to calculate a radius of curvature for the menisci cannot be justified. Hillel [1980] discusses the total soil-water potential composed of gravitational potential, pressure (or matric) potential, osmotic potential, and other forces as the driving force for unsaturated flow. He emphasizes that the matric potential includes the effect of attraction of the solid matrix for water as well as the soil water pressure potential. This is a standard statement in the soil physics literature, and it is an acceptable definition. However, to equate this potential with $p^w/\rho^w g$ and identify the measured forces at all saturation values with the soil water pressure is unacceptable and goes against the very definition of matric potential just cited.

Bolt and Miller [1958] provide an informative and comprehensive discussion of various forces active in a soil water system at the microscopic level. They employ the electric double layer theory to compute various components of the total potential at different points within the soil water. They conclude that pressure in soil water under most conditions will remain greater than zero, and the apparently large values of soil moisture tension are artifacts accounted for by adsorption potential (attraction of water by soil grains). The question that remains is how to resolve pressure and adsorption effects at the macroscale. Furthermore, the need to accommodate these effects properly in a momentum balance equation, such as a generalization of Darcy's law, remains.

On the other hand, Bear [1979] defines the capillary head as the driving force for unsaturated flow as being composed of potential energy (i.e., elevation) and water pressure components. At the very least, some thermodynamic clarification of the mechanisms which contribute to unsaturated flow seems warranted.

Paradox 3: Equilibrium Pressure

From (2), provided $k^w K/\mu$ is not zero, when the velocity of the water phase with respect to the solid phase is zero, the pressure distribution in the water phase will be hydrostatic, or

$$\nabla p^w = \rho^w g \quad (13)$$

Common practice [e.g., Bear, 1972; de Marsily, 1986] is to integrate this in the vertical, or z direction with z positive downward, assuming ρ^w is constant to obtain:

$$p^w - p^a = \rho^w g z \quad (14)$$

where $z = 0$ is the location of $p^w = p^a$. Then invoking (6), one obtains

$$\frac{P_{st}^c(s^w)}{\rho^w g} = -z \quad (15)$$

which indicates that at equilibrium, P_{st}^c is a linear function of elevation in the unsaturated zone and, in fact, depends only upon z , increasing with distance above the water table. However, one would expect the capillary pressure to depend on soil parameters and soil type.

Equation (15) is troublesome for at least two reasons. First of all, this equation is obtained under the assumption of constant ρ^w . For a pressure change in the water phase of the order of tens of atmospheres (as the standard theory predicts when pressure crosses absolute zero into the questionable negative pressure range), one might expect the variation in ρ^w to be important. In fact, in view of the previously mentioned interpretation of high negative pressure as being related to electrostatic binding of water molecules to solid surfaces, one might further expect this binding to cause a significant change in the density of the water phase. This comment questions the validity of integrating (13) to obtain relation (15), but it does not address the validity of (13) itself. However, (13) does not seem to be a universally reasonable condition for equilibrium.

Equation (13) is a macroscopic statement of hydrostatic equilibrium. The anticipation that this will apply at equilibrium stems from the generally invoked microscopic observation that as long as the water phase is continuous, two points at hydrostatic equilibrium separated by a vertical distance Δr from each other will have a pressure difference of $\rho^w g \Delta z$ [de Marsily, 1986]. However, in the case of unsaturated flow it is likely that hydrostatic equilibrium as given by (13) does not apply at the macroscale. The observation that water is attracted to the solid grains implies that, although the water may be continuous, the pressure at a point is not necessarily equal to the weight per unit area of the column of water above that point. The pressure gradient will be less than hydrostatic because of the attraction of the solid grains.

The common practice of determining the vertical saturation profile in a soil by use of (15) is therefore called into question here because (1) constraint (12) which requires nonnegative absolute pressure is violated, (2) equation (15) ignores variation of density with pressure over allegedly large pressure ranges, and (3) the vertical pressure gradient is less than hydrostatic because the attraction of the solid phase for the wetting phase effectively exerts an upward force on the water.

Paradox 4: Interface Effects

Multiphase flow in porous media, including unsaturated flow, differs from single-phase flow in large part because of the dynamics of the interfaces. The relative amounts of interface between the solid and each of the fluid phases may change as the fluids move through the system, but the total amount and position of the solid-fluid interface is usually slower varying or constant. On the other hand, the interfaces between the two fluids, air and water, will be strongly dependent on the amounts of each fluid present as well as the direction of flow. For example, when the saturation of water, s^w , is 1 or 0, the amount of air-water interface per unit volume, a^{wa} , will be zero. At an intermediate saturation, a^{wa} would be expected to change with saturation and to also depend on whether imbibition or drainage is taking place or has just occurred. The presence of the air-water interfaces and the pressure difference across them are extremely important, as they affect the response of the system to imposed pressure gradients.

Because of the importance of a^{wa} and its effect on the dynamics of water movement, one might expect appropriate balance laws governing the change of properties of interfaces to be used along with bulk phase equations in developing a basic theory of unsaturated flow. Instead, equations of unsaturated flow have been empirically obtained by modifying the equations of single-phase flow and introducing the relative permeability. Taking equations appropriate for single-phase flow which have been simplified from general forms by certain assumptions and then making these simple forms more complex by introducing new parameters is not systematic. A more rigorous approach, one offering the possibility of capturing the true physics of multiphase flow, starts from fundamental general balance equations, including equations for the interfaces, and arrives at suitable multiphase equations by making consistent and identifiable assumptions. In the absence of interfaces or under certain simplifying assumptions, the relatively complex multiphase equations should simplify to single-phase equations as a special case (and not the other way around!).

PROPOSED THEORY AND EQUATIONS

Because of the questions raised by the preceding four paradoxes, a systematic theoretical approach is warranted for examining the equations describing unsaturated flow. Such an approach is available based on averaging theory for microscopic phase and interface equations in conjunction with constitutive theory of continuum mechanics. By this approach, macroscale (i.e., porous medium scale) equations are obtained by integrating the equations of mass, momentum, and energy conservation for each phase and interface over a representative elementary volume of porous medium. This gives rise to a set of $5N(N+1)/2$ equations where N is the number of phases (i.e., $N=3$ for the unsaturated flow problem). However, this set of equations contains many more unknowns than equations and cannot be solved without developing constitutive relations for the excess variables. For example, the average macroscopic stress tensor of each phase must be postulated to be a function of certain independent variables. General functional dependences must also be postulated for other phase and interface properties without knowing the actual form of these dependences at the outset. Restrictions on these general constitutive

functions are obtained by applying the second law of thermodynamics and some other physical and mathematical principles using the Coleman and Noll method [Hassanizadeh and Gray, 1990]. This procedure provides two very important sets of information concerning the multiphase flow systems. First, thermodynamic relationships involving macroscopic energies, temperature, density, etc., are obtained. These relations, sometimes similar to but not directly inferable from microscopic thermodynamic relations, are important for a complete mathematical description of the changes which occur in the system due to adjustment of the temperature, the pressure of the water phase, surface tension, etc. Second, the entropy inequality excludes some functional dependences as being incompatible with the requirements of the second law of thermodynamics. It should be noted that this procedure examines thermodynamically allowable functional dependences but does not necessarily determine actual dependencies or the explicit functional form.

Examination of the entropy inequality and the balance equations at equilibrium provides further information concerning the multiphase system. For example, at equilibrium the net heat conduction in all phases and interfaces will be zero, and at a given point, the Gibbs free energy per unit mass will be equal in all phases and interfaces. Further development of the equations then requires laboratory determination of certain quantities. To both simplify the laboratory work and also obtain a reasonable first theoretical cut at what the laboratory will hopefully confirm, dependent variables may be linearized in terms of some of the independent variables. This step in the development is approximate and may prove fruitless when subjected to laboratory verification. However, this linearization is effectively a Taylor series expansion around the equilibrium state with higher order terms neglected. Laboratory studies would then be aimed at determining the range of validity of this approximation, that is, how far from equilibrium the linear representation is suitable.

The full details of the procedure for a general multiphase flow are quite lengthy and encumbered with notational complexities. They have been presented in detail by Hassanizadeh and Gray [1990] and in an abbreviated exposition tailored to unsaturated flow by Gray and Hassanizadeh [this issue]. The equations to be discussed now are proposed, based on Gray and Hassanizadeh [this issue], as an alternative to equations (1) through (6).

The mass balance equation, with the assumption that the rate of exchange of water mass with the wa or ws interface is negligible is identical to (1):

$$\frac{\partial \epsilon s^w \rho^w}{\partial t} + \nabla \cdot (\epsilon s^w \rho^w \mathbf{v}^{w,s}) + \nabla \cdot (\epsilon s^w \rho^w \mathbf{v}^s) = 0 \quad (16)$$

The momentum balance equation for the case where the advective terms are small, the porosity is constant, the solid matric surface is totally wetted by the water (thus $a^{as} = 0$ and a^{ws} is constant), and the drag between the water phase and the interfaces is linear takes the form [Gray and Hassanizadeh, this issue]

$$\epsilon s^w \mathbf{v}^{w,s} = -\frac{k^w K}{\mu} \cdot \left[\nabla p^w - \rho^w \mathbf{g} + (\Omega^w - \Omega^a) \frac{\nabla s^w}{s^w} \right] \quad (17)$$

where the pressure gradient in the air phase is considered negligible.

The water phase pressure depends on saturation and the area of air-water interface per unit volume as well as density and temperature such that $p^w = p^w(\rho^w, T, s^w, a^{wa})$, or inversely,

$$\rho^w = \rho^w(p^w, T, s^w, a^{wa}) \quad (18)$$

The quantity Ω^α is called the wettability potential of each phase (α being w or a) and is obtained from the thermodynamic development as

$$\Omega^\alpha(\rho^\alpha, T, s^w, a^{wa}) = \frac{1}{\rho^\alpha s^\alpha} \left(\frac{\partial A^\alpha}{\partial s^\alpha} \right)_{\rho^\alpha, T, a^{wa}} \quad (19)$$

where $A^\alpha(\rho^\alpha, T, s^w, a^{wa})$ is the macroscopic Helmholtz free energy per unit mass of phase α . Note that because of the presence of an extra term in (17) as compared to (2) the relative permeability k^w is not necessarily the same function in the two equations. However, for the case of saturated flow when $s^w = 1$, (17) and (2) reduce to the same form. In the absence of experimental work which likely indicate that k^w depends primarily on s^w and a^{wa} , the theory here allows a general dependence of k^w on independent variables. For the current exposition where a^{as} , a^{ws} , and ε are constant the functional dependence of k^w will be indicated as

$$k^w = k^w(s^w, a^{wa}, \rho^w, T) \quad (20)$$

Use of the general theoretical framework results in a most interesting expansion on the concept of capillary pressure. Capillary pressure is determined to be a thermodynamic property which is defined independently from the pressures in the bulk phases as [Gray and Hassanizadeh, this issue]

$$p^c = -\Omega^w + \Omega^a - \sum_{\alpha\beta} \frac{\gamma^{\alpha\beta}}{\varepsilon} \left(\frac{\partial a^{\alpha\beta}}{\partial s^w} \right)_{A^{\alpha\beta}, \Gamma^{\alpha\beta}, T} \quad (21)$$

where $\gamma^{\alpha\beta}$ is the macroscale interfacial tension given by

$$\gamma^{\alpha\beta}(\Gamma^{\alpha\beta}, T, s^w, a^{\alpha\beta}) = \left[\frac{\partial A^{\alpha\beta}}{\partial \left(\frac{1}{\Gamma^{\alpha\beta}} \right)} \right]_{a^{\alpha\beta}, T, s^w} \quad (22)$$

with $\Gamma^{\alpha\beta}$ the mass per unit area of $\alpha\beta$ interface and $A^{\alpha\beta}$ the Helmholtz free energy per unit mass of $\alpha\beta$ interface. This capillary pressure, defined in (21), is dependent on s^w and a^{wa} as well as densities, temperature, and the other interface areas. Additionally, when the system is at equilibrium such that \dot{s}^w is zero, the entropy inequality indicates that p^c is equal to the difference between p^a and p^w , or

$$p^c = (p^a - p^w)_e \quad (23)$$

Note that this expression is not a definition but a derived relationship between two independent quantities, p^c and $p^a - p^w$, at equilibrium. A linearized approximation arising from the entropy inequality which relates p^c to $p^a - p^w$ when the system is not at equilibrium takes the form

$$\dot{s}^w \cong \frac{\partial s^w}{\partial t} = -\Pi^w(p^a - p^w - p^c) \quad (24)$$

where Π^w is a material coefficient which must be determined experimentally and, in general, may depend on ρ^α , ε , s^w ,

$\Gamma^{\alpha\beta}$, $a^{\alpha\beta}$, and T . If Π^w is very large, (23) is approached as a quasi-equilibrium approximation. This approximation is commonly invoked and is advocated by Marle [1981] based on experimental findings of Brown [1951] and Jeanson and Dufort [1965].

A final equation which has been obtained as the momentum balance for the a^{wa} interface when the water completely coats the solid is [Gray and Hassanizadeh, this issue]

$$\varepsilon(p^c + \Omega^w - \Omega^a)\nabla s^w + \gamma^{wa}\nabla a^{wa} = -a^{wa}(\nabla\gamma^{wa} + \Gamma^{wa}g) \quad (25)$$

When the influence of gravity on the interfaces is negligible and the gradient of interfacial tension is also neglected, (25) simplifies to

$$\varepsilon(p^c + \Omega^w - \Omega^a)\nabla s^w + \gamma^{wa}\nabla a^{wa} = 0 \quad (26)$$

This equation, although a vector equation, provides one constraint which insures compatibility between a^{wa} and s^w .

On the basis of the equations presented here, a theory of unsaturated flow may be applied which, with limitations clearly identified, avoids the paradoxes of current unsaturated flow theory. The system posed is one where the saturation is above the irreducible saturation and the porosity is constant such that a^{ws} is constant and a^{as} is zero. The dynamics are also considered slow enough that capillary pressure may be considered to be equal to the air phase pressure minus the water phase pressure. The theory proposed here indicates that capillary pressure is a function of s^w and a^{wa} and also requires that the relative wettability potential, $\Omega^w - \Omega^a$, be available as a function of s^w and a^{wa} at a fixed temperature. The proposed theory is compared to the standard theory in Table 1.

DISCUSSION OF THE PROPOSED THEORY AND EQUATIONS

The first paradox raised concerning the standard formulation involved the question of the inclusion of s^w among the variables in an equation of state. In the proposed formulation the result that p^w depends on s^w is a direct consequence of the expectation that the free energy will depend on saturation. This is known to be the case at the macroscale in that introduction of water into a partially saturated medium results in the production of heat due to wetting. Note that the equation of state for the water and the air are of the forms $p^w = p^w(\rho^w, T, s^w, a^{wa})$ and $p^a = p^a(\rho^a, T, s^a, a^{wa})$. Thus $p^a - p^w$ is not a function only of saturation but depends on the interfacial area as well as densities and temperature.

The capillary pressure as provided by (21) is the net energy per unit volume of pore space that would be released per unit change in saturation. When the air and water phases are at equilibrium within this pore, $p^c = (p^a - p^w)_e$. Therefore at equilibrium, p^c is a unique function of ρ^w , ρ^a , T , s^w , and a^{wa} . However, inclusion of a^{wa} in the measurement of capillary pressure is generally ignored. Instead, p^c is typically measured only as a function of s^w (at a particular T), with the result that p^c is not a unique function of s^w (i.e., hysteresis occurs).

The general thermodynamic expression for capillary pressure given by (21) allows for dependence of capillary pressure on s^w , $a^{\alpha\beta}$, ρ^α , $\Gamma^{\alpha\beta}$, and T . Of this group, the

TABLE 1. Comparison of Standard and Proposed Theories

	Standard Theory	Proposed Theory
Dynamic equations		
Water phase continuity	$\frac{\partial \varepsilon s^w \rho^w}{\partial t} + \nabla \cdot (\varepsilon s^w \rho^w \mathbf{v}^{w,s}) + \nabla \cdot (\varepsilon s^w \rho^w \mathbf{v}^s) = 0$	$\frac{\partial \varepsilon s^w \rho^w}{\partial t} + \nabla \cdot (\varepsilon s^w \rho^w \mathbf{v}^{w,s}) + \nabla \cdot (\varepsilon s^w \rho^w \mathbf{v}^s) = 0$
Water phase momentum (three equations)	$\varepsilon s^w \mathbf{v}^{w,s} = -\frac{k^w K}{\mu} \cdot (\nabla p^w - \rho^w \mathbf{g})$	$\varepsilon s^w \mathbf{v}^{w,s} = -\frac{k^w K}{\mu} \cdot \left[\nabla p^w - \rho^w \mathbf{g} + \left(\frac{\Omega^w - \Omega^a}{s^w} \right) \nabla s^w \right]$
Equilibrium capillary pressure Water-air interface momentum	$P_{st}^c = p^a - p^w$...	$p^c = (p^a - p^w)_e$ $\varepsilon(p^c + \Omega^w - \Omega^a) \nabla s^w + \gamma^{wa} \nabla a^{wa} = 0$
Auxiliary conditions		
Equation of state	$\rho^w = \rho^w(p^w, T)$	$\rho^w = \rho^w(p^w, T, s^w, a^{wa})$
Capillary pressure	$P_{st}^c = P_{st}^c(s^w, T)$	$p^c = p^c(s^w, a^{wa}, T)$
Relative permeability	$k^w = k^w(s^w, T)$	$k^w = k^w(s^w, a^{wa}, T)$
Relative wettability	...	$\Omega^w - \Omega^a = F(s^w, a^{wa}, T)$
Parameters plus permeability	$\rho^a, p^a, \varepsilon, T, K$	$\rho^a, p^a, \varepsilon, T, K, a^{ws}, a^{as}, \gamma^{wa}$
Unknowns	$\rho^w, s^w, \mathbf{v}^{w,s}, P_{st}^c, p^w, k^w$	$\rho^w, s^w, \mathbf{v}^{w,s}, p^c, p^w, k^w, a^{wa}, (\Omega^w - \Omega^a)$

variables s^w and a^{wa} (at fixed T) seem to offer the greatest insight into hysteresis. From microscale considerations, hysteresis is considered to be due to the range of values the contact angle of the wa interface with solid may take on, depending whether imbibition or drainage is taking place. Depending on the contact angle, the shape and size of the interface will change. At the macroscale this microscopic behavior is reflected in a^{wa} , the area of water-air interface per unit volume. Therefore equilibrium plots of p^c versus s^w and a^{wa} will likely capture most of the functional dependence and be free of the hysteresis loop which appears when dependence on a^{wa} is not considered. (One can think of the p^c versus s^w plot exhibiting hysteresis as a projection or collapse of the $p^c(s^w, a^{wa})$ surface onto the a^{wa} plane.)

The second paradox concerns the idea that the water phase can be at negative absolute pressure. This concept is used, in fact, to account for the bonds between the water and the soil. However, allowing energy effects to be accounted for by a physically unreasonable pressure in the water phase is, at best, confusing.

Some insight into this may be obtained by comparing the respective flow equations (2) and (17). Designate the water pressure that appears in (2) as $p_{(2)}^w$. If the coefficients in (2) and (17) are taken to be equal, then the equations will be identical if

$$-\nabla p_{(2)}^w = -\nabla p^w - \frac{(\Omega^w - \Omega^a)}{s^w} \nabla s^w \quad (27)$$

Addition of ∇p^a to both sides of this equation and noting that $p^a - p_{(2)}^w = P_{st}^c$ gives

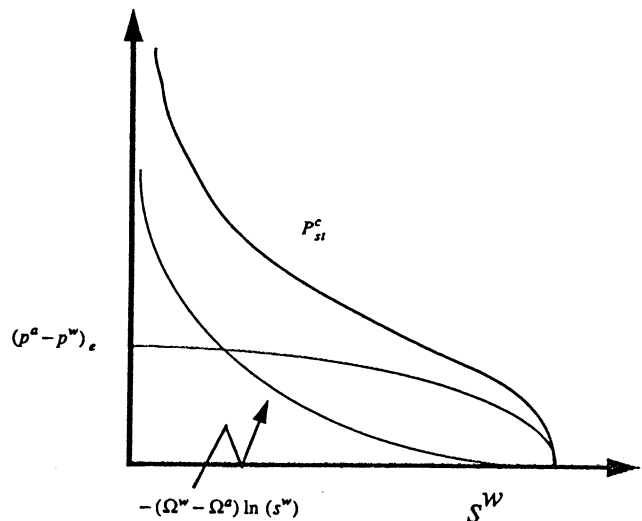
$$\nabla P_{st}^c = \nabla(p^a - p^w) - \frac{(\Omega^w - \Omega^a)}{s^w} \nabla s^w \quad (28)$$

As a crude idealization (which neglects hysteresis) made solely to gain insight, consider Ω^w and Ω^a to be constants. Although probably not strictly correct, this approximation is at least consistent with the expectation that $\partial A^a / \partial s^a$ is greatest when s^a is small (i.e., at a low saturation, the interaction of a phase with other phases will be greater than at high saturation). With this approximation, integration of (28) yields

$$P_{st}^c \equiv (p^a - p^w) - (\Omega^w - \Omega^a) \ln(s^w) \quad (29)$$

When the system is at equilibrium, $(p^a - p^w)_e = p^c$, where p^c is the capillary pressure as obtained in this work. When $s^w = 1$, $p^a - p^w$ will be zero but will asymptotically approach its maximum of 1 atm. as saturation becomes very small. An idealization of this curve is sketched in Figure 1. A curve representing the shape of the function $-(\Omega^w - \Omega^a) \ln(s^w)$ also appears in Figure 1. Addition of the two curves gives the heavier curve in the figure, which indeed is similar in character to plots of P_{st}^c versus s^w which appear in the literature. The term $(\Omega^w - \Omega^a) \ln(s^w)$, or more generally $\int_1^{s^w} [(\Omega^w - \Omega^a)/s^w] ds^w$ should be understood to account macroscopically for the attraction forces between the solid and fluid phases which become especially important at lower saturations. Furthermore, the fact that $\Omega^w - \Omega^a$ likely increases with decreasing s^w and is also dependent on a^{wa} makes the actual identification of P_{st}^c as a single curve plotted versus s^w , as in Figure 1, only a schematization.

This exercise is not proposed as a theoretically justifiable simplification but is only intended to provide qualitative


 Fig. 1. Schematic plot of constituents of P_{st}^c versus saturation.

evidence that the actual theory presented here properly identifies p^c as the difference between the air and water phase pressures at equilibrium. On the other hand, P_{st}^c , by accounting for pressure differences as well as energy effects, leads to the physically unreasonable concept of negative absolute pressure in the water phase. Furthermore, if dependence of p^a , p^w , Ω^a , and Ω^w on a^{wa} is included in (28), integration is not possible such that identification of P_{st}^c as matric potential is not possible.

The form of the flow equation obtained here also eliminates the questions raised concerning the hydrostatic pressure. Under the approximation that ρ^w and $\Omega^w - \Omega^a$ are constant and with z positive downward such that $p^w = p^a$ at $z = 0$, (17) indicates

$$p^w - p^a \approx \rho^w g z - (\Omega^w - \Omega^a) \ln(s^w) \quad (30)$$

Thus the vertical pressure gradient is less than hydrostatic, as would be expected when the water is attracted to the solid. (It must be emphasized that approximation of $\Omega^w - \Omega^a$ as a constant is not a part of the theory but is only employed for illustrative purposes to obtain (29) and (30) which give an indication of the effect of the additional terms obtained in the general theory.)

Finally, the theory presented here takes explicit account of the interfaces. The inclusion of the equations of movement of these interfaces leads to a thermodynamic definition of surface tension at the macroscale and provides an expanded definition of capillary pressure, equation (21), with the ability to account for hysteresis. The set of governing equations actually considered, as in Table 1, is a simplified set appropriate for unsaturated flow when the air phase movement and its property variations are negligible and the dynamics of the solid phase and the interfaces can be accounted for. The formal framework outlined by Gray and Hassanizadeh [this issue] provides governing equations for the air, water, and solid phases as well as for the interfaces which can be applied as needed when experimental support to identify the coefficients is available. In short, the theory presented here eliminates paradoxes in the currently applied theory by making use of the thermodynamic functions Ω^w and Ω^a and accounting for hysteresis as being due to the range of values that a^{wa} may take on at a particular saturation.

CONCLUSION

This paper has compared the equations traditionally used to describe unsaturated flow problems with those obtained from averaging theory coupled with a thermodynamic analysis. The former are obtained as an intuitive extension of Darcy's law, while the latter are simplified forms of a general set of equations obtained from basic principles of continuum mechanics. In light of the results discussed here, a better understanding of the physical processes involved is possible, including proper interpretation of capillary pressure in relation to energy changes within the system and its equality to $p^a - p^w$ at equilibrium, the elimination of the unsatisfying and unrealistic concept of negative absolute pressure of the water phase, and the introduction of the wettability potential as an important thermodynamic property in multiphase flow. This results in a new term in the Darcy equation which must be properly accounted for in modeling unsaturated flow. The extra term accounts for changes in the energy of the water

phase due to changes in saturation and is expected to be of particular importance at lower saturations. The equations developed here reduce to the normal equations for single-phase water flow in a porous medium when the saturation of water is 1.

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REFERENCES

- Bear, J., *Hydraulics of Groundwater*, McGraw-Hill, New York, 1979.
- Bear, J., and A. Verruijt, *Modeling Groundwater Flow and Pollution*, D. Reidel, Hingham, Mass., 1987.
- Bolt, G. H., and R. D. Miller, Calculation of total and component potentials of water in soil, *Eos Trans AGU*, 39, 917-928, 1958.
- Brown, H. H., Capillary pressure investigations, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, 192, 67, 1951.
- Buckingham, E., Studies on the movement of soil moisture, *Bull. 38*, Bureau of Soils U.S. Dep. of Agric., Washington, D. C., 1907.
- Darcy, H., *Les Fontaines Publiques de la Ville de Dijon*, Dalmont, Paris, 1856.
- de Marsily, G., *Quantitative Hydrogeology, Groundwater Hydrology for Engineers*, Academic, San Diego, Calif., 1986.
- 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, Unsaturated flow theory including interfacial phenomena, *Water Resour. Res.*, this issue.
- Harris, C. C., and N. R. Morrow, Pendular moisture in packings of equal spheres, *Nature*, 203, 706-708, 1964.
- 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., *Soil and Water; Physical Principles and Processes*, Academic, San Diego, Calif., 1971.
- Hillel, D., *Fundamentals of Soil Physics*, Academic, San Diego, Calif., 1980.
- Huyakorn, P. S., and G. F. Pinder, *Computational Methods in Subsurface Flow*, Academic, San Diego, Calif., 1983.
- Jeanson, B., and J. Dufort, Mesure de la pression capillaire en écoulement diphasique, *Intern. Rep. 1227*, Institut Francais du Pétrole, Lyon, 1965.
- Kirkham, D., Soil physics, in *Handbook of Applied Hydrology*, sect. 5, edited by V. T. Chow, McGraw-Hill, New York, 1964.
- Koorevaar, P., G. Menelik, and C. Dirksen, *Elements of Soil Physics*, Elsevier, New York, 1983.
- Marle, C. M., *Multiphase Flow in Porous Media*, Gulf Publishing, Houston, Tex., 1981.
- Morrow, N. R., Physics and thermodynamics of capillary action in porous media, in *Flow Through Porous Media*, pp. 104-128, American Chemical Society, Washington, D. C., 1970.
- Morrow, N. R., and C. C. Harris, Capillary equilibrium in porous materials, *Soc. Pet. Eng. J.*, 5, 15-24, 1965.
- Richards, L. A., Capillary conduction of liquids through porous mediums, *Physics*, 1, 318-333, 1931.
- Scheidegger, A. E., *The Physics of Flow through Porous Media*, 3rd ed., University of Toronto Press, Toronto, Ont., 1974.
- Schiegg, H. O., Physical and mathematical fundamental principles, in *Evaluation and Treatment of Cases of Oil Damage With Regard to Groundwater Protection* (in German), edited by M. Albertson et al., section 1.4, Swiss Federal Office of the Environment, Zurich, 1986.

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