



Toward an improved description of the physics of two-phase flow

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The present work incorporates the effects of interface dynamics into the theoretical description of two-phase flow in a porous medium. This advance offers the potential for improved understanding and modeling of multiphase flow processes. To provide background for this work, the traditional approach to describing two-phase flow in porous media is reviewed. The universally employed empirical extension of Darcy's Law for single-phase flow to two-phase flow situations is rejected as arbitrary and subject to severe shortcomings. Burial of dynamic effects into relative permeability and capillary pressure hysteresis is shown to be an unsatisfactory theoretical construct for modeling the actual processes occurring in two-phase flow. Examination of the traditional theory at equilibrium shows that interfacial forces actually present in multiphase systems have been overlooked causing the theory to provide contradictory results. To overcome these problems, a general theory of two-phase flow is proposed that is based on the basic principles of mass, momentum, and energy conservation and the second law of thermodynamics. This theory accounts, in a systematic way, for interfacial forces that are known to have an important effect on the movement of fluid phases in a porous medium. A new equation of momentum balance accounting for the presence of interfaces and their energetics is developed. This equation reduces to Darcy's Law for the special case of single-phase flow. The extended theory has the potential to describe phenomena unaccounted for by the traditional theory and thus provides a basis for scientific understanding of the physics of two-phase flow. Application of the theory requires experimental study to ascertain the values and precise functional dependence of the constitutive coefficients that arise.

Key words: Unsaturated flow, two-phase flow, Darcy's law, interfacial areas, capillary pressure

INTRODUCTION

In 1856, Henry Darcy published the results of his work on flow of water through sand including the empirical result that has come to be known as Darcy's Law. In its simplest form, the Darcy equation states that the flow of water through a porous medium with a unit cross-sectional area is related to the product of the hydraulic gradient and a constant of proportionality termed the hydraulic conductivity.²⁷ This may be expressed as:

$$Q = -AKJ \quad (1)$$

where Q is the volumetric flow rate, A is the cross-sectional area, K is the hydraulic conductivity, and J is the hydraulic gradient. Evidence of the profound impact Darcy's Law has had in the study of groundwater hydrology is the fact that the publication of Darcy's work has been referred to as 'The birth of groundwater hydrology as a quantitative science'.¹² Darcy's original law was found to be valid for slow, steady, one-dimensional flow through a homogeneous and isotropic sand. However, during the subsequent century, interest in groundwater hydraulics, petroleum reservoir exploration, infiltration, transient flow, anisotropic and heterogeneous systems, and multidimensional flow has resulted in extensions of Darcy's Law forms applicable

to multi-fluid phase systems such as:

$$\mathbf{q}^\alpha = -\mathbf{K}^\alpha \cdot \mathbf{J}^\alpha \quad (2)$$

where \mathbf{q}^α is the volumetric flow rate per unit area vector of the α -phase fluid, \mathbf{K}^α is the hydraulic conductivity tensor of the α -phase and is a function of the viscosity and saturation of the α -phase, and \mathbf{J}^α is the hydraulic gradient vector that accounts for pressure, gravitational and interphase effects. Despite occasional criticisms expressed about the validity of this generalization, equation (2) is considered today to be a fundamental principle in analysis of porous media flows.²⁵

Although Darcy's Law retains widespread utility, one cannot help but wonder about the wisdom of relying on 'generalization' of the simple empirical eqn (1) to describe complex phenomena. Equation (2) provides no additional physical insight into phenomena of importance when examining complex systems. Indeed it seems that most of the dynamics of, for example, a multiphase flow system are accounted for by ascribing a complex hysteretic functional form to the permeability tensor. Use of eqn (1) as a basis for obtaining a flow equation for complex multiphase systems having the form of eqn (2) seems unwise. An analogous development might be to begin with the ideal gas law:

$$PV = nRT \quad (3)$$

and base the kinetic theory of gases on finding increasingly complex forms for the ideal gas constant R . In this latter case, it is much more satisfying, and theoretically rewarding, to begin with a general formulation and find that eqn (3) applies as a simplification of that formulation under limiting conditions. Similar conclusions can be reached in considering the wisdom of using Fick's Law of chemical diffusion or Fourier's Law of heat conduction as foundational relations applicable to complex systems simply through generalization of the diffusivity or conductivity parameter.

In many fields of study, insights have been gathered through the centuries. Simple formulas have been reached that correlate various aspects of system behavior. Some have been found useful for a time but then have been debunked. March²³ provides the interesting case of Aristotle's statement that a falling body instantly acquires its speed of fall which was not refuted until the 17th century when Galileo insisted that in the absence of resistance, all bodies will fall and accelerate at the same rate. If nothing else, this example points out the hazards of building a theory on an empirical observation. In groundwater hydrology, this approach has been the norm. Darcy's Law has been considered as an end in itself, and theoretical studies have tended to use the ability to arrive at this relation as an acid test of the merit of the theory.

Although Darcy's Law can be obtained as a special case of the momentum equation for porous media flow,

the need exists to build on basic principles of mass, momentum, and energy conservation to obtain equations that account for and describe the physics of these flows. Confounding this task is the fact that the scale of the equations describing the porous media flow must be the same as the scale of observation. It is fruitless, for example, to appeal to contact angle of a fluid–fluid interface on the walls of a pore to quantitatively describe the effect of those interfaces on a sample of rock with a 5 cm characteristic length. Thus the need exists to build fundamental equations at the macroscopic scale, the scale of observation, which account for the physics of flow and transport in porous media. These equations must account for the effect of quantities such as saturation and interfacial area per unit volume, quantities that do not exist at a smaller scale. The equations should, of course, reduce to Darcy's Law under certain circumstances as this equation is particularly robust for slow flow of a single fluid phase in a homogeneous medium. However, the approach must also provide equations that account for additional phenomena that impact the flow, for example in the multiphase case, and present an experimental and/or computational challenge to determine circumstances when those phenomena might be important. If advances in understanding of subsurface processes are to occur, the governing equations invoked must be based on physical principles, not merely on an extension of a simple correlation.

Similar ideas were expressed almost 40 years ago by Babcock and Overstreet.^{2,3} They succinctly describe two guidelines for a correct application of thermodynamics to a heterogeneous system:

First, the number of properties that must be fixed in order to define the state of a given system must be established experimentally. ... Thus, the number of differential terms required to specify the total differential in some given property can be known only from experimental observation of the system. ... Second, ... it is essential that all thermodynamic formulations be written only in terms of macroscopic properties of the system, that is, in terms of state variables.

For a salt-free soil–water system, they proposed temperature, pressure, and water content as independent state variables. They realized that such microscopic effects as fluid–fluid surface curvature and solid–fluid interaction forces must somehow be accounted for by macroscopic variables. Unfortunately, these ideas have not been widely adopted; and a macroscopic thermodynamic theory of two-phase flow has not developed. Because of this, much confusion, particularly due to mixing of microscale and macroscale concepts, persists in basic thermodynamic concepts for subsurface multiphase flow systems. Recent advances in the development

of macroscopic conservation laws and constitutive equations for two-phase flow in porous media¹³⁻¹⁶ have provided the underpinning needed to formulate a thermodynamic theory of porous media flow and transport systematically.

This paper reviews the traditional theory of two-phase flow in porous media. Some of the inherent inconsistencies in this theory that arise because the flow is required to be governed by the extended Darcy's Law are discussed. Next the results of a systematic transformation from the microscale to the macroscale are presented and the consequences of this theory are examined. This extended theory is shown to require knowledge of additional parameters in comparison to the standard theory, but the potential for this theory to account for phenomena overlooked in the traditional theory is demonstrated.

THE TRADITIONAL THEORY OF TWO-PHASE FLOW IN A POROUS MEDIUM

In this section, the basic equations typically employed to describe two-phase flow in a porous medium are reviewed. To facilitate a focused presentation, only a simplified physical system will be discussed.

Consider a porous medium consisting of a homogeneous solid phase saturated with two immiscible and compressible fluids. Let each fluid be composed of a single non-reacting constituent. Define the solid phase such that it behaves as an elastic material undergoing very small deformations. The solid grains are specified as incompressible such that their mass density remains constant. Deformation of the solid skeleton is still possible because of the movement of grains with respect to each other.

To model the fluid flow in this system, the equations of mass and momentum balance for the solid and fluid phases must be solved simultaneously. If the wetting phase is denoted by w , the non-wetting phase by n , and the solid phase by s , mass balance equations for the three phases take the forms:

$$\frac{\partial(\epsilon s^\alpha \rho^\alpha)}{\partial t} + \nabla \cdot (\epsilon s^\alpha \rho^\alpha \mathbf{v}^\alpha) = 0 \quad \alpha = w, n \quad (4a)$$

$$-\frac{\partial \epsilon}{\partial t} + \nabla \cdot [(1 - \epsilon) \mathbf{v}^s] = 0 \quad (4b)$$

where ϵ is porosity, s^α ($\alpha = w, n$) is saturation, ρ^α ($\alpha = w, n$) is mass density and \mathbf{v}^α ($\alpha = w, n, s$) is the velocity vector. Saturations are subject to the restriction:

$$s^w + s^n = 1 \quad (5)$$

Velocities actually solved for in each of the fluid phases are the relative velocities with respect to the solid phase. If the relative fluid velocity is indicated as

$\mathbf{v}^{\alpha,s} = \mathbf{v}^\alpha - \mathbf{v}^s$, eqn (4a) becomes:

$$\begin{aligned} \frac{D^s(\epsilon s^\alpha \rho^\alpha)}{Dt} + \nabla \cdot (\epsilon s^\alpha \rho^\alpha \mathbf{v}^{\alpha,s}) \\ + \epsilon s^\alpha \rho^\alpha \nabla \cdot \mathbf{v}^s = 0 \quad \alpha = w, n \end{aligned} \quad (6)$$

where D^s/Dt is the material derivative moving with the solid such that $D^s/Dt = \partial/\partial t + \mathbf{v}^s \cdot \nabla$. Equation (4b) may also be written, making use of the material derivative, as :

$$-\frac{D^s \epsilon}{Dt} + (1 - \epsilon) \nabla \cdot \mathbf{v}^s = 0 \quad (7)$$

Elimination of $\nabla \cdot \mathbf{v}^s$ between eqns (6) and (7) leads to the mass balance equation for the fluid phases:

$$\begin{aligned} \frac{\epsilon s^\alpha \rho^\alpha}{(1 - \epsilon)} \frac{D^s \epsilon}{Dt} + \frac{D^s(\epsilon s^\alpha \rho^\alpha)}{Dt} \\ + \nabla \cdot (\epsilon s^\alpha \rho^\alpha \mathbf{v}^{\alpha,s}) = 0 \quad \alpha = w, n \end{aligned} \quad (8)$$

The compressibility of the porous matrix may be of importance in the modeling of aquifers, particularly in studying single-phase flow. However, for the case considered here, consolidation that causes changes in porosity will be considered negligible compared to other processes occurring such that eqn (8) may be simplified to the commonly employed form:^{6,10}

$$\frac{\partial(\epsilon s^\alpha \rho^\alpha)}{\partial t} + \nabla \cdot (\epsilon s^\alpha \rho^\alpha \mathbf{v}^{\alpha,s}) = 0 \quad \alpha = w, n \quad (9)$$

The relative fluid velocity is typically taken to be described by a heuristically extended Darcy's equation which makes use of a relative permeability concept. However, in order to frame the discussion in such a way that comparison of this theory with an extended theory is facilitated, the Darcy equation will be presented as it may be developed from the equation of momentum balance using an averaging approach. The macroscopic, or porous media scale, momentum balance for a fluid phase, neglecting macroscopic inertial and viscous effects is:

$$\hat{\mathbf{T}}^\alpha = \nabla(\epsilon s^\alpha p^\alpha) - \epsilon s^\alpha \rho^\alpha \mathbf{g} \quad \alpha = w, n \quad (10)$$

where $\hat{\mathbf{T}}^\alpha$ is the force exerted by the porous medium on the α -phase fluid. This equation is a balance law and, except for the assumption of negligible inertial and viscous terms, is a general form. The crucial step in relating this balance equation to a system of interest is obtaining the appropriate constitutive relationship for $\hat{\mathbf{T}}^\alpha$. By analogy with single-phase theories, it is typically required that:

$$\hat{\mathbf{T}}^\alpha = \hat{\boldsymbol{\tau}}^\alpha + p^\alpha \nabla(\epsilon s^\alpha) \quad \alpha = w, n \quad (11)$$

where $\hat{\boldsymbol{\tau}}^\alpha$ is the non-equilibrium part of $\hat{\mathbf{T}}^\alpha$ such that at equilibrium $\hat{\boldsymbol{\tau}}^\alpha = \hat{\boldsymbol{\tau}}_{\text{eq}}^\alpha = 0$. Relation (11) is either simply assumed or it may be obtained by applying an averaging procedure to the microscopic Navier-Stokes equations. The conclusion that the equilibrium part of $\hat{\mathbf{T}}^\alpha$ equals

$P^\alpha \nabla(\epsilon s^\alpha)$ is standard but nevertheless seems to be deficient and is most probably the source of shortcomings in the traditional two-phase flow theories. (This point will be expanded upon in the next section.) Substitution of eqn (11) into eqn (10) yields:

$$\hat{\tau}^\alpha = \epsilon s^\alpha (\nabla p^\alpha - \rho^\alpha \mathbf{g}) \quad \alpha = w, n \quad (12)$$

To complete the development of the Darcy equation that governs momentum transport in a fluid phase, a constitutive relation must be specified for $\hat{\tau}^\alpha$. This term accounts for the drag exerted by the adjacent phases on phase α . Typically, an expression is selected such that:

$$\begin{aligned} \hat{\tau}^\alpha &= -\mathbf{R}^{\alpha\alpha} \cdot \mathbf{v}^{\alpha,s} - \mathbf{R}^{\alpha\beta} \cdot \mathbf{v}^{\beta,s} \\ \alpha &= w, n; \quad \beta = w, n; \quad \alpha \neq \beta \end{aligned} \quad (13)$$

wherein a linear dependence of the viscous drag forces on the fluid velocities is assumed. Substitution of eqn (13) into eqn (12) yields:

$$\begin{aligned} \mathbf{R}^{\alpha\alpha} \cdot \mathbf{v}^{\alpha,s} + \mathbf{R}^{\alpha\beta} \cdot \mathbf{v}^{\beta,s} &= -\epsilon s^\alpha (\nabla p^\alpha - \rho^\alpha \mathbf{g}) \\ \alpha &= w, n; \quad \beta = w, n; \quad \alpha \neq \beta \end{aligned} \quad (14)$$

Next, neglect the coupling velocity term in eqn (14) that would account for flow in the w -phase (n -phase) due to pressure and gravitational effects in the n -phase (w -phase), and formulate $\mathbf{R}^{\alpha\alpha}$ such that $\mathbf{R}^{\alpha\alpha} = (\epsilon s^\alpha)^2 (\mu^\alpha / k^\alpha) \mathbf{K}^{-1}$. The equation obtained is of the same form for both the wetting and the non-wetting phases:

$$\epsilon s^\alpha \mathbf{v}^{\alpha,s} = -\frac{k^\alpha}{\mu^\alpha} \mathbf{K} \cdot (\nabla p^\alpha - \rho^\alpha \mathbf{g}) \quad \alpha = w, n \quad (15)$$

where \mathbf{K} is the permeability tensor of the porous medium, k^α is the relative permeability coefficient for phase α considered to be known as a function of

saturation, μ^α is the (microscopic) viscosity coefficient of the α -phase, and p^α is the thermodynamic pressure. The product $\epsilon s^\alpha \mathbf{v}^{\alpha,s}$ that appears in both eqns (9) and (15) is commonly denoted as the Darcy velocity $\mathbf{q}^\alpha = \epsilon s^\alpha \mathbf{v}^{\alpha,s}$ and is a superficial velocity of phase α relative to the solid. Thus, with ϵ taken to be a parameter of the multiphase flow problem, eqns (5), (9) and (15) provide nine equations for the 12 unknowns, $s^w, s^n, \rho^w, \rho^n, p^w, p^n, \mathbf{q}^w$ and \mathbf{q}^n .

For the system to be determinate, three more equations must be provided. Two of these are given by equations of state for the fluid phases which are normally stated in the functional forms:

$$\rho^\alpha = \rho^\alpha(p^\alpha, T) \quad \alpha = w, n \quad (16)$$

where T is the temperature of the medium taken to be the same for all phases at a given point. If temperature varies in space and/or in time, an energy balance equation for the system must also be provided. For simplicity, here the temperature is taken to be constant and therefore dependence of fluid properties on T need not be considered.

The final equation of the quasi-equilibrium approach is a relationship between the saturation and the capillary pressure, p^c , which is defined as the difference in fluid pressures:

$$p^c(s^w, T) = p^n - p^w \quad (17)$$

The form of this relationship is specific to the fluid pairs and the porous medium. Saturation–capillary pressure curves are obtained from equilibrium experiments and are not strictly valid under dynamic conditions. Therefore, the system of equations listed here, and collected in Table 1 constitutes a quasi-equilibrium theory. This set of equations is typically taken to be the set of equations that must be simultaneously satisfied to describe two-

Table 1. System of equations for the quasi-equilibrium theory

Equation	Equation form	Parameters
Mass conservation for wetting phase (eqn (9))	$\frac{\partial(\epsilon s^w \rho^w)}{\partial t} + \nabla \cdot (\epsilon s^w \rho^w \mathbf{v}^{w,s}) = 0$	ϵ
Mass conservation for non-wetting phase (eqn (9))	$\frac{\partial(\epsilon s^n \rho^n)}{\partial t} + \nabla \cdot (\epsilon s^n \rho^n \mathbf{v}^{n,s}) = 0$	ϵ
Saturation constraint (eqn (5))	$s^w + s^n = 1$	
Darcy's Law for wetting phase (eqn (15))	$\epsilon s^w \mathbf{v}^{w,s} = -\frac{k^w}{\mu^w} \mathbf{K} \cdot (\nabla p^w - \rho^w \mathbf{g})$	$k^w, \mu^w, \mathbf{K}, \epsilon, \mathbf{g}$
Darcy's Law for non-wetting phase (eqn (15))	$\epsilon s^n \mathbf{v}^{n,s} = -\frac{k^n}{\mu^n} \mathbf{K} \cdot (\nabla p^n - \rho^n \mathbf{g})$	$k^n, \mu^n, \mathbf{K}, \epsilon, \mathbf{g}$
Equation of state for wetting phase (eqn (16))	$\rho^w = \rho^w(p^w, T)$	T
Equation of state for non-wetting phase (eqn (16))	$\rho^n = \rho^n(p^n, T)$	T
Quasi-equilibrium capillary pressure (eqn (17))	$p^c(s^w, T) = p^n - p^w$	$p^c(s^w, T)$

Note: Total set of 12 equations in the 12 unknowns $s^w, \rho^w, \mathbf{v}^{w,s}, s^n, \rho^n, \mathbf{v}^{n,s}, p^w, p^n$.

phase flow in porous media in the traditional theory.^{5,10,24,30}

DISCUSSION OF EQUILIBRIUM FOR THE TRADITIONAL THEORY OF MULTIPHASE FLOW

Limitations of the quasi-equilibrium theory of multiphase flow have been pointed out by many researchers.^{19,28–30} Usually, the absence of coupling terms in Darcy's equations or the hysteresis in the $p^c(s^w)$ relationship have been the focus of discussion. However, other shortcomings of the traditional theory exist which are often overlooked in the literature. Recently, Gray and Hassanizadeh¹⁵ have discussed unsaturated flow theories and identified a number of paradoxes and inconsistencies. These inconsistencies are actually not limited to unsaturated flow and are also encountered in traditional theories of general two-phase flow. For example, note that inversion of state eqns (16) to the form $p^a = p^a(\rho^a, T)$ predicts a dependence of p^w (or p^n) on ρ^w (or ρ^n) but does not predict a dependence of the fluid phase pressure on saturation. On the other hand, eqn (17) suggests the opposite with fluid pressures depending on saturation but not on density. Furthermore, the contention that capillary pressure can attain values much larger than the pressure of the non-wetting phase, implying large negative pressure in the wetting phase, is not acceptable but is a consequence of measurement artifacts. An extensive discussion of the distinction between microscopic and macroscopic capillary pressure has been provided elsewhere.¹⁷ Here some of the implications of the system of equations as listed in Table 1 are examined when two immiscible fluid phases exist at equilibrium in a porous medium.

Consider eqns (15) for each of the fluid phases. These are actually the single-phase flow Darcy equations with modified permeability tensors. The extension of Darcy's equation to two-phase flow is typically done in a somewhat cavalier fashion forcing the equation to fit some dynamic situation with little attention paid to the underlying physics or the equilibrium state. In fact, the only adjustment from the single-phase Darcy equation is the arbitrary multiplication of the permeability tensor by a scale factor referred to as the relative permeability coefficient. Many researchers have discussed the limitations of this approach.^{19,30} In any event, the relative permeability concept fails to alter the equation of force balance for static conditions in two-phase flow as compared to single-phase flow. In other words, in extending single-phase flow theories to multiphase flow, no attention has been given to the very different nature of forces that act in a multiphase system at equilibrium (as well as in the dynamic state). As a result, despite the actual presence of various interfacial forces in multiphase systems, the equation of static equilibrium for such systems is exactly identical to that for a

saturated porous medium. This oversimplification causes the traditional theory to manifest inadequacies in describing a two-phase system at equilibrium as discussed below.

When both of the fluid phases are at equilibrium such that $\mathbf{v}^{w,s} = \mathbf{v}^{n,s} = 0$ eqns (15), or the more basic eqns (12), are commonly reduced to the static pressure expressions:

$$\nabla p^n = \rho^n \mathbf{g} \quad (18a)$$

$$\nabla p^w = \rho^w \mathbf{g} \quad (18b)$$

such that, by eqn (17):

$$\nabla p^c = (\rho^n - \rho^w) \mathbf{g} \quad (18c)$$

According to these relations, pressure in the fluid phases, and thus also the capillary pressure, varies linearly in the vertical direction and will be uniform horizontally. The equilibrium distribution of capillary pressure is, therefore, expected to be independent of fluid saturation, soil type, chemical properties of the fluid and many other properties which might be expected to affect the state of the fluids. No correlation between capillary pressure and pore size distribution is indicated at equilibrium! These requirements seem to be physically unreasonable. At equilibrium, forces other than gravity exist (for example, preferential wetting) which are capable of impacting the pressure distribution in each of the fluids. These effects must be accounted for in an appropriate constitutive expression for the equilibrium part of $\hat{\mathbf{T}}^\alpha$ that arises in eqn (10). Apparently the approximation provided by eqn (11), wherein the equilibrium part of $\hat{\mathbf{T}}^\alpha$ is equal to $p^\alpha \nabla(\epsilon s^\alpha)$, is deficient in this regard.

Gray and Hassanizadeh¹⁴ indicate that the effects of attractive forces between the fluids and the solid appear to be lumped into the standard capillary pressure concept. As another illustration of this fact and of the deficiency of eqn (11), consider the problem of the equilibrium distribution of water in a vertical soil column that has been drained under gravity with the water table as the lower boundary. If the initial state were such that only drainage occurred throughout the soil (i.e. saturation changes are non-positive), no hysteretic effects would be observed and the relation between capillary pressure and saturation should be unique. Water saturation at the equilibrium state is observed to decrease with height above the water table until it reaches 'field capacity' (or the 'irreducible saturation') after which it remains essentially constant. For constant saturation and constant air pressure, according to eqn (17), the water pressure will also be constant. This contradicts eqns (18a)–(18c) because those equations account for no forces other than pressure and gravity.

This point can be illustrated further by considering

the distribution of $\hat{\tau}^w$ corresponding to the observed pressure distribution. From eqn (12), the equilibrium conditions that must apply are:

$$\hat{\tau}_{eq}^w = 0 \quad 0 \leq z \leq h_0 \quad (19a)$$

$$\hat{\tau}_{eq}^w = -\epsilon s^w \rho^w \mathbf{g} \quad h_0 \leq z \leq \infty \quad (19b)$$

where h_0 is some coordinate in the vertical direction. This is a strange result. It indicates that in some regions, there is no force exerted by the porous medium on water, whereas in some other parts, the porous medium does exert a force equal and opposite to the force of gravity. This must be the force of attraction of water by solid. There is no reason for this force to be absent in lower parts of an unsaturated soil profile or when water movement takes place. Furthermore, eqn (19b) violates the definition of $\hat{\tau}^w$ in eqn (11) as the portion of $\hat{\mathbf{T}}^w$ that is zero at equilibrium.

One may attempt to explain this paradox in two different ways. The first is to say that p^c is infinity at field capacity (or irreducible saturation) so that $\partial p^c / \partial z$ is non-zero and equal to $(\rho^w - \rho^n)g$. However, if this relation holds, the capillary pressure would reach an infinite value only at an infinite distance above the groundwater table. However, since field capacity is reached at a finite distance above the groundwater table, this result is inconsistent. A second explanation might be that at field capacity, hydraulic conductivity is zero so that there is no flow. This explanation would satisfy the equality imposed by eqn (15). By this explanation, $\nabla p^\alpha - \rho^\alpha \mathbf{g}$ would not have to be zero at field capacity. Nevertheless, this argument is flawed because for all cases where hydraulic conductivity is zero such that its inverse does not exist, eqn (15) is not attainable from eqn (14). In any event, at equilibrium or at field capacity, eqns (18a)–(18c) must apply in violation of this second explanation. Thus, because these equations cannot apply, the approximations involved in obtaining eqns (11) and (15) are apparently too simplistic.

To carry the discussion further, consider a porous medium at equilibrium containing one continuous fluid phase and one discontinuous fluid phase. Situations of this type of practical importance are oil ganglia in a reservoir after secondary recovery, brine in oil reservoirs, oil products in groundwater, vapor (and steam) in geothermal reservoirs, and unsaturated soil at a state of either near-saturation or irreducible saturation. According to eqn (18a), the average pressure in a discontinuous, immobile α -phase would increase with depth linearly such that $p^\alpha = p_0 + \rho^\alpha g z$. However such a simple pressure distribution cannot describe the conditions in the discontinuous α -phase. Rather, the pressure of the discontinuous phase is determined by the pressure of the continuous phase surrounding it, as well as the capillary pressure. In other words, one would expect a coupling in the pressure distribution of the two fluids depending on the medium geometry, saturation, and

other fluid properties. Thus the traditional Darcy's equation may seem to be inapplicable to cases where one phase is discontinuous. However, in practice, eqn (15) is applied to the full range of saturations and to the study of problems such as the movement of oil ganglia.

The oversimplified nature of eqns (18a)–(18c) becomes even more evident when one considers the pressure distribution in the horizontal direction. The horizontal components of eqns (18a)–(18c) predict no horizontal gradient in fluid pressures and capillary pressure at equilibrium, regardless of soil condition and medium inhomogeneities. For homogeneous media, the absence of horizontal fluid pressure gradients also implies that no horizontal gradient in saturation will exist at equilibrium except possibly at locations where a change of the dynamic situation from drying to wetting, or vice versa, has occurred.

To investigate whether the latter is true, a series of simple and somewhat primitive experiments were performed. In these experiments, a number glass tubes with constant diameters ranging from 5.6 to 9.2 mm were packed to a length of about 50 cm with a dry, well-sorted sand. Cotton balls were placed at the end of the packed region to keep the sand in place while allowing the free passage of air. The center of mass of each tube along the axial direction was determined by balancing the tube on a knife edge. Subsequently, an initial uniform saturation moisture distribution was developed in each tube. Enough water was injected into one end of the tube so that some predetermined uniform saturation could be obtained. The actual initial saturations chosen varied among the tubes from $s^w = 0.0$ to $s^w = 0.6$. To ensure that the moisture distribution was uniform, the water was sequentially vaporized in a 104°C oven and condensed in the tube until the balance point of the tube prior to water injection was recovered. This result provides some indication that the tubes were packed uniformly as well as evidence supporting the state of uniform initial saturation. A known amount of water was then injected into one end of a tube so that a state of essentially complete saturation ($s^w = 1$) was obtained over a desired length. The lengths selected ranged from 1/4 to 1/2 of the total tube length. The tubes were placed horizontally in a constant humidity chamber for the subsequent duration of the experiment, approximately one year. The movement of moisture in each tube was monitored by balancing the tube on the edge of a knife to determine its center of gravity. The change in position of this point with time is an indication of moisture movement. Note that if the flow were to continue until uniform moisture distribution were achieved, the tubes would balance at their original, pre-injection, balance points. In all cases, the injection caused an initial displacement of the center of gravity that recovered somewhat in the first four days of the experiment. Following this recovery, additional redistribution was very slow with the actual rate outside the

detection limit of the crude experimental set-up. Typical of the results obtained was a tube with an initial uniform moisture content of $s^w = 0.3$ that was injected with enough additional water to saturate 1/4 of the tube length, assuming no redistribution of water. This injection caused the balance point to displace by 2.75 mm. After two days, the offset had reduced to 1.5 mm, and after a month the balance point was still 1.1 mm from the pre-injection balance point. Measurements were made at intervals of approximately one month, but no reliable measure of additional redistribution was obtained. In none of the tubes did the water redistribute to a uniform state after the injection. Furthermore, visual examination of the tubes indicated that the sand was wetter at one end than at the other. The level of detection of the experimental set-up was not sufficient to determine the rate of distribution occurring after 300 days although there is no evidence that a steady state profile was actually achieved.

These experiments indicate that even large gradients in saturation and capillary pressure in the horizontal direction can be sustained for a long time. Although the rough experiments reported are not conclusive, two explanations for the observed large horizontal capillary pressure gradients may apply.

One explanation is that the end of the tube where injection occurred goes into drainage while the other end undergoes imbibition. Therefore, hysteresis would cause different $p^c(s^w)$ curves to be operating simultaneously. Indeed, it is possible to have equal values of p^c for different saturations. However, given the large difference in saturations along the tube, this argument is not completely satisfactory. From the migration of the balance point and visual observation, it could be established that saturation differences along the tube are large (i.e. on the order of 0.7 for the case described above and approaching 1.0 in other cases). No horizontal line exists on a standard $p^c(s^w)$ diagram that has these widely differing values at intercepts with the hysteretic drainage and imbibition curves.

A second possible explanation might be based on eqn (15) with both phases at equilibrium. In this case, $\partial p^\alpha / \partial x$ might be presumed to be large while the relative permeabilities at the region of high saturation gradient are presumed to be close to zero. Thus $\mathbf{v}^{\alpha,s}$ would be very small and no noticeable fluid movement would occur. Although this explanation may have some appeal, ample experimental evidence shows that even at irreducible saturation, fluid movement is possible. In the experiments described above, when a very small amount of water was added to a cotton ball at one end of the tube, a front which was almost stationary for more than 100 days immediately responded and moved forward pulling the added moisture into the tube. This indicates that the relative permeability coefficient at the moisture front is not zero.

In addition to the shortcomings of the traditional

theory of multiphase flow at equilibrium as discussed above, this theory sometimes fails to provide a satisfactory modeling of dynamic situations. Practical difficulties associated with hysteresis in capillary pressure and the relative permeability coefficient further reduce the robustness of present theories. In light of the inconsistencies discussed above (and in Ref. 15) a search for a more complete theory that describes two-phase flow seems worthwhile. Although such a theory will be more complex than the traditional equation set, it provides a foundation from which the importance of a greater number of physical effects can be examined at the macroscale.

FUNDAMENTAL EQUATIONS DESCRIBING TWO-PHASE FLOW IN A POROUS MEDIUM

In an investigation of the fundamentals of present theories of two-phase flow, Hassanizadeh and Gray¹³⁻¹⁶ have re-examined the basic principles describing mass, momentum and energy processes in search of alternative expressions to eqns (11), (12) and (14) that are both consistent and provide a more rigorous theory of two-phase flow in porous media. In this approach, macroscopic equations for balance of mass, momentum, and energy are given for each and every phase and interface. These equations are supplemented by the second law of thermodynamics (the principle of entropy inequality) and constitutive equations relating energy, stress, heat conduction, drag forces, etc., to constitutive variables such as density, saturation, temperature, specific interfacial area, and velocity. In a systematic manner, necessary simplifications are introduced in the balance laws and constitutive relationships in order to obtain field equations for mass, momentum and energy conservation applicable to specific cases of interest.

The equations of mass balance, for compressible fluid phases and an incompressible solid phase, neglecting mass exchange between phases, are identical to eqns (4a), and (4b). Thus the fluid phase continuity equations may be simplified to the same form as eqn (9).

A complete theory for two-phase flow that includes interfaces will also require that the mass and momentum conservation equations for the interfaces be solved. The interface mass equations are of the form:^{13,16}

$$\begin{aligned} \frac{\partial(\Gamma^{\alpha\beta} a^{\alpha\beta})}{\partial t} + \nabla \cdot (\Gamma^{\alpha\beta} a^{\alpha\beta} \mathbf{w}^{\alpha\beta,s}) + \nabla \cdot (\Gamma^{\alpha\beta} a^{\alpha\beta} \mathbf{v}^s) \\ = -\hat{e}_{\alpha\beta}^\alpha - \hat{e}_{\alpha\beta}^\beta + \hat{e}_{wns}^{\alpha\beta} \end{aligned} \quad (20)$$

where $a^{\alpha\beta}$ is the specific area of the $\alpha\beta$ -interface (i.e. the area of $\alpha\beta$ -interface per unit volume of porous medium), $\Gamma^{\alpha\beta}$ is the average mass of the $\alpha\beta$ -interface (i.e. the mass of all $\alpha\beta$ -interfaces in an averaging volume per unit area), $\hat{e}_{\alpha\beta}^\alpha$ is the rate of transfer of mass from the interface to the phase α , $\hat{e}_{wns}^{\alpha\beta}$ is the rate of transfer of

mass from the contact line to the interface, and $\mathbf{w}^{\alpha\beta,s}$ is the average velocity of the $\alpha\beta$ -interface relative to the solid phase. The terms on the right side of this equation account for mass transfer between the interface and the adjacent phases and the interface and the contact line that forms its boundary. Equations of motion for the two fluid phases, neglecting macroscopic inertial and viscous effects, are identical to eqn (10). However, the form of the constitutive relationship for $\hat{\mathbf{T}}^\alpha$, given by eqn (11) for the traditional theory, is dictated by the entropy inequality as:¹⁵

$$\hat{\mathbf{T}}^\alpha = \hat{\tau}^\alpha + p^\alpha \nabla(\epsilon s^\alpha) - \epsilon s^\alpha \rho^\alpha$$

$$\left(\frac{\partial A^\alpha}{\partial \alpha^{wn}} \nabla a^{wn} + \frac{\partial A^\alpha}{\partial \alpha^{as}} \nabla a^{as} + \frac{\partial A^\alpha}{\partial s^w} \nabla s^w + \frac{\partial A^\alpha}{\partial \epsilon} \nabla \epsilon \right)$$

$$\alpha, \beta = w, n \quad (21)$$

where A^α is the macroscopic Helmholtz free energy of the α -phase, assumed to be a function of ρ^α , s^α , a^{wn} , a^{as} , ϵ and T . In this equation, as in eqn (11), $\hat{\tau}^\alpha$ is the non-equilibrium part of $\hat{\mathbf{T}}^\alpha$ and will equal zero at equilibrium. Substitution of eqn (21) into momentum eqn (10) yields:

$$\hat{\tau}^\alpha = \epsilon s^\alpha (\nabla p^\alpha - \rho^\alpha \mathbf{g}) + \epsilon s^\alpha \rho^\alpha$$

$$\left(\frac{\partial A^\alpha}{\partial \alpha^{wn}} \nabla a^{wn} + \frac{\partial A^\alpha}{\partial \alpha^{as}} \nabla a^{as} + \frac{\partial A^\alpha}{\partial s^w} \nabla s^w + \frac{\partial A^\alpha}{\partial \epsilon} \nabla \epsilon \right)$$

$$\alpha, \beta = w, n \quad (22)$$

Note that the terms in parentheses are extra terms in comparison to the traditional theory. These terms do not arise from a linearization procedure but are present because of assumed functional dependence of the macroscopic Helmholtz free energy and account for the effect of interfaces on the state of the system. Under the constitutive assumption of linear dependence of viscous drag forces on velocities, as in eqn (13) but with the coupling term neglected, eqn (22) simplifies to:

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

$$\left(\frac{\partial A^\alpha}{\partial \alpha^{wn}} \nabla a^{wn} + \frac{\partial A^\alpha}{\partial \alpha^{as}} \nabla a^{as} + \frac{\partial A^\alpha}{\partial s^w} \nabla s^w + \frac{\partial A^\alpha}{\partial \epsilon} \nabla \epsilon \right)$$

$$\alpha, \beta = w, n \quad (23)$$

Equations of motion are obtained for interfaces as well. With the macroscopic inertial terms and the coupling terms neglected and the interfacial viscosity considered small, the following equations of motion are obtained:¹⁵

$$\hat{\tau}^{\alpha\beta} = -\mathbf{R}^{\alpha\beta} \cdot \mathbf{w}^{\alpha\beta,s}$$

$$= -\nabla(a^{\alpha\beta} \gamma^{\alpha\beta})$$

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

$$\alpha\beta = wn, ws, ns \quad (24)$$

where $\hat{\tau}^{\alpha\beta}$ accounts for drag on the interface by the surrounding phases and is zero at equilibrium, $\mathbf{R}^{\alpha\beta}$ is a resistance tensor that arises when a linear constitutive form is applied to $\hat{\tau}^{\alpha\beta}$, $\gamma^{\alpha\beta}$ is the macroscopic (or average) interfacial tension, and $A^{\alpha\beta}$ is the macroscopic Helmholtz free energy of the $\alpha\beta$ -interface per unit mass of interface assumed to be a function of $\alpha^{\alpha\beta}$, $\Gamma^{\alpha\beta}$, s^w , ϵ and T .

Quantities appearing in eqns (23) and (24) have been obtained in terms of thermodynamic state variables in Ref.16. The thermodynamic pressure in eqn (23) is related to Helmholtz free energy by:

$$p^\alpha = (\rho^\alpha)^2 \left(\frac{\partial A^\alpha}{\partial \rho^\alpha} \right)_{\epsilon, s^w, a^{\alpha\beta}, T} \quad \alpha = w, n \quad (25a)$$

which implies that:

$$p^\alpha = p^\alpha(\rho^\alpha, T, \epsilon, s^w, a^{\alpha\beta}) \quad \alpha = w, n \quad (25b)$$

The macroscopic interfacial tension is given by:

$$\gamma^{\alpha\beta} = -(\Gamma^{\alpha\beta})^2 \left(\frac{\partial A^{\alpha\beta}}{\partial \Gamma^{\alpha\beta}} \right)_{a^{\alpha\beta}, T, s^w}$$

$$= -a^{\alpha\beta} \Gamma^{\alpha\beta} \left(\frac{\partial A^{\alpha\beta}}{\partial a^{\alpha\beta}} \right)_{\Gamma^{\alpha\beta}, T, s^w}$$

$$\alpha\beta = wn, ws, ns \quad (26)$$

The macroscopic capillary pressure is related to other thermodynamic properties by:

$$p^c = -\rho^w s^w \left(\frac{\partial A^w}{\partial s^w} \right) - \rho^n s^n \left(\frac{\partial A^n}{\partial s^n} \right)$$

$$- \sum_{\alpha\beta} \frac{a^{\alpha\beta} \Gamma^{\alpha\beta}}{\epsilon} \left(\frac{\partial A^{\alpha\beta}}{\partial s^w} \right) \quad (27a)$$

and the difference in the fluid pressures is given by the linearized relation:

$$p^n - p^w = p^c - L \frac{\partial s^w}{\partial t} \quad (27b)$$

where L is a material coefficient. A similar relation to this last one has been given for $\partial a^{\alpha\beta} / \partial t$ for each of the interfaces:¹⁵

$$\frac{\partial a^{wn}}{\partial t} = -\Pi^{wn} \left(s^w \rho^w \frac{\partial A^w}{\partial a^{wn}} + s^n \rho^n \frac{\partial A^n}{\partial a^{wn}} \right) \quad (28a)$$

$$\frac{\partial a^{ws}}{\partial t} = -\Pi^{ws} \left(\epsilon s^w \rho^w \frac{\partial A^w}{\partial a^{ws}} + (1 - \epsilon) \rho^s \frac{\partial A^s}{\partial a^{ws}} \right) \quad (28b)$$

$$\frac{\partial a^{ns}}{\partial t} = -\Pi^{ns} \left(\epsilon s^n \rho^n \frac{\partial A^n}{\partial a^{ns}} + (1 - \epsilon) \rho^s \frac{\partial A^s}{\partial a^{ns}} \right) \quad (28c)$$

In each of these equations, the quantity in parentheses on the right side will be zero at equilibrium. This completes the full set of equations. Note that the tensors $\mathbf{R}^{\alpha\alpha}$ and $\mathbf{R}^{\alpha\beta}$ are both positive semi-definite, scalars p^α ,

$\gamma^{\alpha\beta}$, L and $\Pi^{\alpha\beta}$ are non-negative, and these quantities may depend on density, temperature, porosity, saturation, and specific interfacial area of the corresponding phase or interface.

Equations (5), (9), (20) and (23)–(28c) are the complete set of equations comprising the non-equilibrium theory that may be solved for the variables ρ^α , p^α , s^α , $a^{\alpha\beta}$, $\Gamma^{\alpha\beta}$ and $\gamma^{\alpha\beta}$ for $\alpha = w, n$ and $\alpha\beta = wn, ws, ns$. Although this set of equations is considerably more complex than that listed in Table 1, it offers a much greater potential for modeling the complex processes affecting two-phase fluid flow in a porous medium. In particular, explicit modeling of the full dynamics of the interfaces, an important feature of multiphase systems, is now possible. Fortunately, for many practical cases of interest, the basic equations may be significantly simplified while still accounting for the important influence of the interfaces. One set of assumptions that still results in a fairly general theory of two-phase flow is considered in the next section.

PROPOSED GENERAL THEORY OF TWO-PHASE FLOW IN A POROUS MEDIUM

The balance equations for the interfaces that supplement the equations for the phases provide a formidable set of governing equations. Additionally, the requirement that all the parameters identified for the problem be determined makes simulation of any complete system a daunting, if not overwhelming, task. However, under a set of assumptions that are essentially quasi-equilibrium assumptions for the interfaces, a more tractable set of equations can be obtained that still represents a significant extension of the traditional theory. The limits of applicability of these equations will have to be verified through experimental studies.

The equations of mass balance in the proposed theory are kept in their general form given by eqn (9). For special cases, such as incompressible flow, simplifications are possible. The equations of motion for the fluid phases are obtained from eqn (23). Except for the case of shrinking and swelling media, the effect of porosity changes on the free energy is expected to be negligible. For this situation, or when $\nabla\epsilon = 0$, with $\mathbf{R}^{\alpha\alpha}$ set equal to $\epsilon^2\mu^\alpha\mathbf{K}^{\alpha-1}$, the following equations of motion for two-phase flow are obtained:

$$\epsilon s^w \mathbf{v}^{w,s} = -\frac{s^{w2}\mathbf{K}^w}{\mu^w} \cdot \left[(\nabla p^w - \rho^w \mathbf{g}) + \frac{\lambda^{wn}}{a^{wn}} \nabla a^{wn} - \frac{\lambda^{ws}}{a^{ws}} \nabla a^{ws} + \frac{\Omega^w}{s^w} \nabla s^w \right] \quad (29a)$$

$$\epsilon s^n \mathbf{v}^{n,s} = -\frac{s^{n2}\mathbf{K}^n}{\mu^n} \cdot \left[(\nabla p^n - \rho^n \mathbf{g}) - \frac{\lambda^{nw}}{a^{wn}} \nabla a^{wn} - \frac{\lambda^{ns}}{a^{ns}} \nabla a^{ns} + \frac{\Omega^n}{s^n} \nabla s^n \right] \quad (29b)$$

where \mathbf{K}^α is the permeability tensor for the α -phase and other coefficients are defined and constrained by:

$$\Omega^\alpha = s^\alpha \rho^\alpha \frac{\partial A^\alpha}{\partial s^\alpha} \geq 0 \quad \alpha = w, n \quad (30a)$$

with:

$$\Omega^\alpha = 0 \quad \text{at} \quad s^w = 0, 1 \quad \alpha = w, n \quad (30b)$$

$$\lambda^{\alpha s} = -\rho^\alpha a^{\alpha s} \frac{\partial A^\alpha}{\partial a^{\alpha s}} \geq 0 \quad \alpha = w, n \quad (31a)$$

with:

$$\lambda^{\alpha s} \rightarrow 0 \quad \text{as} \quad a^{\alpha s} \rightarrow a^\alpha \quad \alpha = w, n \quad (31b)$$

$$\lambda^{wn} = \rho^w a^{wn} \frac{\partial A^w}{\partial a^{wn}} \geq 0 \quad (32b)$$

with:

$$\lambda^{wn} \rightarrow 0 \quad \text{as} \quad a^{wn} \rightarrow 0 \quad (32b)$$

$$\lambda^{nw} = -\rho^n a^{wn} \frac{\partial A^n}{\partial a^{wn}} \geq 0 \quad (33a)$$

with:

$$\lambda^{nw} \rightarrow 0 \quad \text{as} \quad a^{wn} \rightarrow 0 \quad (33b)$$

The coefficients in these definitions depend on s^w , a^{ns} , a^{ws} and a^{wn} (as well as density and temperature) and have units of energy per unit volume of the fluid phase. Note that if $\partial a^{wn}/\partial t$ is small, eqn (28a) provides the additional equality:

$$s^w \lambda^{wn} = s^n \lambda^{nw} \quad (34)$$

The sense of the coefficients defined in eqns (30a)–(34) are chosen on intuitive grounds based on qualitative information and general knowledge of system behavior. For example, a wetting phase entering a porous medium is known to release energy in the form of heat of wetting.^{5,8,26,30} During the wetting process, s^w increases, s^n decreases, a^{ws} is non-negative (i.e. positive when wetting fluid displaces non-wetting fluid in contact with the solid but zero at saturations where the wetting fluid already completely coats the solid), and a^{ns} is non-negative. In this process, energy is expended by the wetting phase to drive the non-wetting phase, whose energy increases, out of the porous medium. Energy is released by the destruction of interfaces between the solid and the non-wetting fluid and is expended in forming interfaces between the solid and the wetting fluid. At low saturations of the wetting phase, the magnitude of the heat of wetting is particularly large and the specific

interfacial area between the solid and wetting fluid is small. Conversely, when the saturation of the wetting phase is large, the heat of wetting is small and the interfacial area between the solid and the non-wetting fluid is small. Thus as saturation is increasing, the amount of heat released per unit of invading fluid will decrease. Based on these considerations, one may propose the following with $\alpha = w, n$:

$$\frac{\partial A^\alpha}{\partial s^\alpha} \geq 0 \quad \text{with} \quad \frac{\partial A^\alpha}{\partial s^\alpha} \rightarrow 0 \quad \text{as} \quad s^\alpha \rightarrow 1 \quad (35a)$$

and

$$\frac{\partial A^\alpha}{\partial a^{\alpha s}} \leq 0 \quad \text{with} \quad \frac{\partial A^\alpha}{\partial a^{\alpha s}} \rightarrow 0 \quad \text{as} \quad a^{\alpha s} \rightarrow a^s \quad (35b)$$

Similar indications may be found for the coefficients $\partial A^w/\partial a^{wn}$ and $\partial A^n/\partial a^{wn}$. It is important to bear in mind that the determination of the sense of these coefficients is somewhat speculative. For instance, the quantity $\partial A^\alpha/\partial s^\alpha$ must be evaluated with all other independent variables, such as $a^{\alpha\beta}$, remaining constant. Such thermodynamic changes are very difficult to envisage. Ultimately, the postulated sense of the coefficients in eqns (29a) and (29b) must be verified by experiment. The indications given in eqns (30a)–(33b) are certainly subject to adjustment in the face of evidence provided in future studies. Indeed, it is possible that experimental evidence might indicate that $\partial A^\alpha/\partial s^\alpha$ undergoes a change in sign over the full range of saturations.

Next, consider the equations of motion of the interfaces as given by eqn (24). This equation relates the dynamics of an $\alpha\beta$ -interface to the saturation gradient and the intrinsic properties of the interface. Again, neglect the term accounting for the effects of porosity on the motion. If the interface movement is not of direct interest or of importance to the bulk phase movement, this equation may be simplified by setting the left side, the resistance tensor times the relative interfacial velocity, to zero. Furthermore, consider the effects of gravity on the interface movement to be negligible (i.e. the mass per unit area of interface to be negligible). Then summation of eqn (24) over the wn, ws and ns interfaces yields:

$$\begin{aligned} & -\nabla(a^{wn}\gamma^{wn} + a^{ws}\gamma^{ws} + a^{ns}\gamma^{ns}) + \left(\Gamma^{wn}a^{wn} \frac{\partial A^{wn}}{\partial s^w} \right. \\ & \left. + \Gamma^{ws}a^{ws} \frac{\partial A^{ws}}{\partial s^w} + \Gamma^{ns}a^{ns} \frac{\partial A^{ns}}{\partial s^w} \right) \nabla s^w = 0 \end{aligned} \quad (36)$$

Now, eqn (27a) for the capillary pressure, making use of the definition of Ω^α given in eqn (30a), may be substituted into the group of terms in the second parentheses to obtain:

$$\begin{aligned} & -\nabla(a^{wn}\gamma^{wn} + a^{ws}\gamma^{ws} + a^{ns}\gamma^{ns}) \\ & + \epsilon(\Omega^n - \Omega^w - p^c) \nabla s^w = 0 \end{aligned} \quad (37)$$

Further simplify the system by restricting attention to the case of intermediate saturations such that all $\gamma^{\alpha\beta}$ are constants, $a^{ws} = a^s$, and $a^{ns} = 0$. Then eqn (37) reduces further to:

$$-\gamma^{wn} \nabla a^{wn} + \epsilon(\Omega^n - \Omega^w - p^c) \nabla s^w = 0 \quad (38)$$

Substitution of eqn (38) into eqns (29a) and (29b) for the case where $\nabla a^{ws} = \nabla a^{ns} = 0$ yields:

$$\begin{aligned} \epsilon s^w \mathbf{v}^{w,s} = & -\frac{(s^w)^2 \mathbf{K}^w}{\mu^w} \cdot \left[(\nabla p^w - \rho^w \mathbf{g}) \right. \\ & \left. + \left(\frac{\epsilon(\Omega^n - \Omega^w - p^c) \lambda^{wn}}{\gamma^{wn} a^{wn}} + \frac{\Omega^w}{s^w} \right) \nabla s^w \right] \end{aligned} \quad (39a)$$

$$\begin{aligned} \epsilon s^n \mathbf{v}^{n,s} = & -\frac{(s^n)^2 \mathbf{K}^n}{\mu^n} \cdot \left[(\nabla p^n - \rho^n \mathbf{g}) \right. \\ & \left. - \left(\frac{\epsilon(\Omega^n - \Omega^w - p^c) \lambda^{nw}}{\gamma^{wn} a^{wn}} + \frac{\Omega^n}{s^n} \right) \nabla s^w \right] \end{aligned} \quad (39b)$$

The equations needed to model the intermediate saturation system are summarized in Table 2. Note that in this table, simplified functional dependence is indicated for several unknowns. For example, the capillary pressure depends on densities and interfacial areas between the solid and fluids as well as on the indicated saturation and interfacial areas between the fluids. For convenience, and in recognition of the fact that the equations listed are simplified from the general theory, only functional dependences that are expected to be important to consider are indicated.

Several comments are important concerning the information in Table 2. It must be remembered that the equations listed are obtained as a simplification of the general theory based on some observations of system behavior. Additionally the restrictions have been applied that the porosity, ϵ , is constant, the specific surface of the solid is constant, the wetting phase completely coats the solid (thereby ensuring that $\nabla a^{ws} = \nabla a^{ns} = 0$), and the dynamics of the interfaces (i.e. their velocities) do not impact the overall system behavior. Note that although vector equations are usually counted as three equations, the final equation in the table, eqn (38), is a compatibility condition between a^{wn} and s^w and actually provides only one constraint. In a one-dimensional situation, it provides a one-to-one relationship between a^{wn} and s^w through a constant of integration obtained by solving a particular problem subject to its appropriate boundary and initial conditions. The value of the constant is expected to be different for imbibition and drainage problems such that for the same saturation value, a range of specific interfacial areas would be obtained depending on the initial and boundary conditions. For two- or three-dimensional problems, the additional equations are needed to determine the dependencies of the constant of integration on the

Table 2. A simplified system of equations based on the proposed theory

Equation	Equation form	Parameters
Mass conservation for wetting phase (eqn (9))	$\frac{\partial(\epsilon s^w \rho^w)}{\partial t} + \nabla \cdot (\epsilon s^w \rho^w \mathbf{v}^{w,s}) = 0$	ϵ
Mass conservation for non-wetting phase (eqn (9))	$\frac{\partial(\epsilon s^n \rho^n)}{\partial t} + \nabla \cdot (\epsilon s^n \rho^n \mathbf{v}^{n,s}) = 0$	ϵ
Saturation constraint (eqn (5))	$s^w + s^n = 1$	
Momentum for wetting phase (eqn (29a))	$\epsilon s^w \mathbf{v}^{w,s} = -\frac{(s^w)^2 \mathbf{K}^w}{\mu^w} \cdot \left[(\nabla p^w - \rho^w \mathbf{g}) + \left(\frac{\epsilon(\Omega^n - \Omega^w - p^c) \lambda^{wn}}{\gamma^{wn} a^{wn}} + \frac{\Omega^w}{s^w} \right) \nabla s^w \right]$	$\mu^w, \mathbf{K}^w, \epsilon, \Omega^w, \Omega^n, \gamma^{wn}, \lambda^{wn}, \mathbf{g}$
Momentum for non-wetting phase (eqn (29b))	$\epsilon s^n \mathbf{v}^{n,s} = -\frac{(s^n)^2 \mathbf{K}^n}{\mu^n} \cdot \left[(\nabla p^n - \rho^n \mathbf{g}) - \left(\frac{\epsilon(\Omega^n - \Omega^w - p^c) \lambda^{nw}}{\gamma^{wn} a^{wn}} + \frac{\Omega^n}{s^n} \right) \nabla s^w \right]$	$\mu^n, \mathbf{K}^n, \epsilon, \Omega^w, \Omega^n, \gamma^{wn}, \lambda^{nw}, \mathbf{g}$
Equation of state for wetting phase (eqn (16))	$\rho^w = \rho^w(p^w, T)$	T
Equation of state for non-wetting phase (eqn (16))	$\rho^n = \rho^n(p^n, T)$	T
Capillary pressure equation of state	$p^c = p^c(s^w, a^{wn}, T)$	T
Capillary pressure dynamics (eqn (27b))	$L \frac{\partial s^w}{\partial t} = p^c - (p^n - p^w)$	L
Interfacial area between the fluid phases (eqn (38))	$-\gamma^{wn} \nabla a^{wn} + \epsilon(\Omega^n - \Omega^w - p^c) \nabla s^w = 0$	$\gamma^{wn}, \epsilon, \Omega^w, \Omega^n$

Note: Total set of 14 equations in the 14 unknowns $s^w, \rho^w, \mathbf{v}^{w,s}, s^n, \rho^n, \mathbf{v}^{n,s}, p^w, p^n, p^c, a^{wn}$.

second and third coordinates. Thus Table 2 consists of 14 equations in the 14 unknowns as indicated. All parameters in the equation are expected to be positive.

In the next section, the proposed general two-phase flow theory is discussed further and its potential for resolving the inconsistencies present in the traditional theory is illustrated.

DISCUSSION OF THE PROPOSED SIMPLIFIED THEORY OF TWO-PHASE FLOW

The general set of equations presented here provide a firm foundation for a theoretically sound model of two-phase flow in porous media. The ultimate utility of any proposed theory remains to be determined from physical experiments. The general set of equations provides a significant and long-term experimental challenge. The simplified set appearing in Table 2 is also challenging, but appears to be tractable. Despite the lack of quantitative information on the values of new coefficients appearing in those equations, some insight that will prove valuable as a preliminary to experimental study may be gained by

examining the theory for some particular situations under certain simplifying assumptions.

Single-phase flow with $s^w = 1$

When there is only a single fluid present in the porous medium, in this case taken to be the one designated as the wetting phase w , no equations for the non-wetting fluid, for capillary pressure, or for interfaces between the fluids are necessary. The mass conservation equation is as given by eqn (9) unless compressibility of the solid phase is important, in which case eqn (8) should be used along with some constitutive expression for $D^s \epsilon / Dt$. Note that in single-phase flow, matrix compressibility is of more importance than in multiphase flow. The momentum balance equation is obtained from eqn (29a) simplified by the observation that the coefficient multiplying ∇s^w is zero by constraints (30a)–(33b). Thus the momentum balance for a single phase reduces directly to the classical form of Darcy's Law:

$$\epsilon \mathbf{v}^{w,s} = -\frac{\mathbf{K}^w}{\mu^w} \cdot [(\nabla p^w - \rho^w \mathbf{g})] \quad (40)$$

The coefficient \mathbf{K}^w is thus the saturated permeability tensor when $s^w = 1$. The procedure illustrated here whereby a general theory reduces to the standard single phase theory under the appropriate assumptions is preferable to the usual approach whereby the theory for flow of more than one phase is extrapolated from the equations for single-phase flow. The opportunity to be led astray in following the latter approach should be evident.

Vertical equilibrium distribution of two fluids in a porous medium

As discussed previously, the existing theories of two-phase flow predict that the pressure of each constant density fluid will decrease linearly upward, independently of each other, and regardless of the porous medium properties (cf. eqns (18a) and (18b)). The proposed theory, however, predicts a dependence of fluid pressure, capillary pressure, and saturation on the medium properties. At equilibrium in a homogeneous porous medium, the dynamic equation for capillary pressure, (eqn (27b)), and momentum equations (29a) and (29b), reduce respectively to:

$$p^c(s^w, a^{wn}) = p^n - p^w \quad (41a)$$

$$\nabla p^w - \rho^w \mathbf{g} + \left[\frac{\epsilon(\Omega^n - \Omega^w - p^c)\lambda^{wn}}{\gamma^{wn} a^{wn}} + \frac{\Omega^w}{s^w} \right] \nabla s^w = 0 \quad (41b)$$

and

$$\nabla p^n - \rho^n \mathbf{g} - \left[\frac{\epsilon(\Omega^n - \Omega^w - p^c)\lambda^{nw}}{\gamma^{wn} a^{wn}} + \frac{\Omega^n}{s^w} \right] \nabla s^w = 0 \quad (41c)$$

Subtract eqn (41b) from eqn (41c) and eliminate $p^n - p^w$ using eqn (41a) to obtain:

$$\nabla p^c - (\rho^n - \rho^w) \mathbf{g} - \left[\frac{\epsilon(\Omega^n - \Omega^w - p^c)(\lambda^{nw} + \lambda^{wn})}{\gamma^{wn} a^{wn}} + \frac{\Omega^n}{s^n} + \frac{\Omega^w}{s^w} \right] \nabla s^w = 0 \quad (42)$$

Because of the dependence of p^c on saturation and interfacial area, application of the chain rule and then use of eqn (38) yields:

$$\begin{aligned} \nabla p^c &= \frac{\partial p^c}{\partial s^w} \nabla s^w + \frac{\partial p^c}{\partial a^{wn}} \nabla a^{wn} \\ &= \left[\frac{\partial p^c}{\partial s^w} + \frac{\epsilon(\Omega^n - \Omega^w - p^c)}{\gamma^{wn}} \frac{\partial p^c}{\partial a^{wn}} \right] \nabla s^w \end{aligned} \quad (43)$$

This equation may now be used to eliminate the gradient of capillary pressure from equation (42). If equation (34) is also invoked, the equilibrium relationship for the

vertical saturation profile may be expressed as:

$$\begin{aligned} \left[\frac{\partial p^c}{\partial s^w} - \frac{\Omega^n}{s^n} - \frac{\Omega^w}{s^w} + \frac{\epsilon(\Omega^n - \Omega^w - p^c)}{\gamma^{wn} a^{wn}} \right. \\ \left. \left(a^{wn} \frac{\partial p^c}{\partial a^{wn}} - \frac{\lambda^{nw}}{s^w} \right) \right] \nabla s^w = (\rho^n - \rho^w) \mathbf{g} \end{aligned} \quad (44)$$

Equation (44) may be used in conjunction with eqns (41b) and (41c) to obtain the pressure profiles in each phase as functions of the fluid and solid phase properties.

Incompressible two-phase flow

The mass conservation equation for an incompressible fluid takes on a simplified form since the density may be removed from the equation. For the current case, the momentum equations, (29a) and (29b), will be substituted into the mass conservation equations, eqn (9) for each of the phases, to eliminate the velocity. Additionally when a fluid is incompressible, its equation of state becomes unnecessary as the density is known and the pressure becomes an unknown of the theory to be obtained as a function of space and time. Furthermore, the dependence of equation parameters, including capillary pressure, on fluid densities is not taken into consideration. Under these conditions, the proposed theory of Table 2 reduces to the following set of equations to be solved for s^w , a^{wn} , p^w , p^n :

$$\begin{aligned} \epsilon \frac{\partial s^w}{\partial t} - \nabla \cdot \left\{ \frac{(s^w)^2 \mathbf{K}^w}{\mu^w} \cdot \left[(\nabla p^w - \rho^w \mathbf{g}) \right. \right. \\ \left. \left. + \left(\frac{\epsilon(\Omega^n - \Omega^w - p^c)\lambda^{wn}}{\gamma^{wn} a^{wn}} + \frac{\Omega^w}{s^w} \right) \nabla s^w \right] \right\} = 0 \end{aligned} \quad (45)$$

$$\begin{aligned} \epsilon \frac{\partial s^w}{\partial t} + \nabla \cdot \left\{ \frac{(1-s^w)^2 \mathbf{K}^n}{\mu^n} \cdot \left[(\nabla p^n - \rho^n \mathbf{g}) \right. \right. \\ \left. \left. - \left(\frac{\epsilon(\Omega^n - \Omega^w - p^c)\lambda^{nw}}{\gamma^{wn} a^{wn}} + \frac{\Omega^n}{1-s^w} \right) \nabla s^w \right] \right\} = 0 \end{aligned} \quad (46)$$

$$L \frac{\partial s^w}{\partial t} = p^c(s^w, a^{wn}) - p^n + p^w \quad (47)$$

$$-\gamma^{wn} \nabla a^{wn} + \epsilon(\Omega^n - \Omega^w - p^c) \nabla s^w = 0 \quad (48)$$

where γ^{wn} , Ω^w , Ω^n , λ^{wn} , λ^{nw} , \mathbf{K}^w , \mathbf{K}^n , L and p^c must be provided as functions of a^{wn} and s^w . Although even this simplified set of equations may seem to require a daunting amount of support information, the expectation exists that complex functional dependences found in the traditional theory will be much simplified here because the parameters capture the actual physics of the problem rather than being merely quantities used to correlate some data. For example, in the most favorable case, the permeability tensors, \mathbf{K}^w and \mathbf{K}^n , may be equal to each other and to the saturated permeability

coefficient of the medium. Additionally, the inclusion of the dependence of capillary pressure on interfacial area as well as saturation is expected to eliminate the apparent hysteresis. Equations (45)–(48) are the appropriate equations to employ in simulating the horizontal tube experiments discussed previously.

THE CONCEPT OF TOTAL POTENTIAL FOR TWO-PHASE FLOW

The concept of a total potential for flow and the components of this potential have been topics of much theoretical inquiry in soil physics.^{2–4,9,11,21,22} Bolt and Miller⁷ define the total potential as the minimum energy per unit mass of water that must be expended in order to transport an infinitesimal test body of water from a specified reference state to any point within the liquid phase of a soil–water system which is in a state of rest. This concept has been introduced intuitively and by analogy with the energy potential defined for free bulk water as a single phase. As a result, some disagreement and confusion has persisted in translating the qualitative definition of potential into a mathematical expression. For example, while the non-gravitational part of the total potential of salt-free water is typically postulated to depend on temperature and pressure only, Babcock and Overstreet² propose a dependence on water content (or saturation) as well in the following formula for the change in chemical potential:

$$d\mu^w = \frac{1}{\rho^w} dp - \eta^w dT + \frac{\partial \mu^w}{\partial (\epsilon s^w)} d(\epsilon s^w) \quad (49)$$

where η^w is entropy. In this equation, all effects related to the water–air interfaces and the soil–water interaction are considered to be accounted for by the last term. Also, p refers to the external pressure of the environment on the soil and not to the average pore pressure of the water.

A formula for the change in free energy of water and a definition of the total potential can be obtained from the results of the general theory presented in the previous section. Let the Gibb's free energy function for an α -phase, G^α , and for an $\alpha\beta$ -interface defined as:

$$G^\alpha = A^\alpha + \frac{p^\alpha}{\rho^\alpha} \quad \alpha = w, n \quad (50a)$$

$$G^{\alpha\beta} = A^{\alpha\beta} - \frac{\gamma^{\alpha\beta}}{\Gamma^{\alpha\beta}} \quad \alpha\beta = wn, ws, ns \quad (50b)$$

Based on the functional dependence of the Helmholtz free energies and the thermodynamic relationships (25a) and (26), one can show that:

$$dG^\alpha = \frac{1}{\rho^\alpha} dp^\alpha + \frac{\partial A^\alpha}{\partial a^{wn}} da^{wn} + \frac{\partial A^\alpha}{\partial a^{as}} da^{as} + \frac{\partial A^\alpha}{\partial s^w} ds^w + \frac{\partial A^\alpha}{\partial \epsilon} d\epsilon \quad \alpha = w, n \quad (51a)$$

$$dG^{\alpha\beta} = -\frac{1}{a^{\alpha\beta}\Gamma^{\alpha\beta}} d(a^{\alpha\beta}\gamma^{\alpha\beta}) + \frac{\partial A^{\alpha\beta}}{\partial s^w} ds^w + \frac{\partial A^{\alpha\beta}}{\partial \epsilon} d\epsilon \quad \alpha\beta = wn, ws, ns \quad (51b)$$

Therefore eqns (23) and (24) may be rewritten, respectively, as:

$$\mathbf{R}^{\alpha\alpha} \cdot \mathbf{v}^{\alpha,s} = -\epsilon s^\alpha \rho^\alpha (\nabla G^\alpha - \mathbf{g}) \quad \alpha = w, n \quad (52)$$

$$\mathbf{R}^{\alpha\beta} \cdot \mathbf{w}^{\alpha\beta,s} = -a^{\alpha\beta} \Gamma^{\alpha\beta} (\nabla G^{\alpha\beta} - \mathbf{g}) \quad \alpha\beta = wn, ws, ns \quad (53)$$

Although not considered here, a similar equation that applies to the solid phase may also be obtained. If the gravity is written in terms of a potential ϕ , such that $\mathbf{g} = -\nabla\phi$, eqns (52) and (53) reduce, respectively, to:

$$\mathbf{R}^{\alpha\alpha} \cdot \mathbf{v}^{\alpha,s} = -\epsilon s^\alpha \rho^\alpha \nabla \Phi^\alpha \quad \alpha = w, n \quad (54)$$

$$\mathbf{R}^{\alpha\beta} \cdot \mathbf{w}^{\alpha\beta,s} = -a^{\alpha\beta} \Gamma^{\alpha\beta} \nabla \Phi^{\alpha\beta} \quad \alpha\beta = wn, ws, ns \quad (55)$$

where $\Phi^{w\alpha}$ and $\Phi^{\alpha\beta}$ are the 'total potential' for a phase or interface, respectively, defined by:

$$\Phi^\alpha = G^\alpha + \phi \quad \alpha = w, n \quad (56a)$$

$$\Phi^{\alpha\beta} = G^{\alpha\beta} + \phi \quad \alpha\beta = wn, ws, ns \quad (56b)$$

Equations (54) and (55) imply that at equilibrium, the total potential for a phase will be constant throughout the medium. Furthermore, flow in a porous medium is explicitly related to a gradient of total potential for each phase and interface, the potential being the sum of Gibb's free energy and gravitational energy. This flow would be such that it occurs from regions of high potential to regions of low potential.

For the case of saturated, flow of phase w in a porous medium where the fluid phase density is a function of pressure only, Φ^w/g is simply equal to Hubbert's potential and, from eqn (51a):

$$\nabla G^w = \nabla p^w / \rho^w \quad (57)$$

Then equation (52) reduces directly to the standard form of Darcy's Law. However, for the case of two-phase flow where the free energy depends on saturation and specific interfacial area, such a simplification of eqns (51a) and (52) to the traditional form of Darcy's Law is not possible.

Despite this fact, the simplification to Darcy's Law is commonly applied in the study of unsaturated flow in soils. Although tensiometers and/or pressure plates are often used to measure a quantity referred to as matric potential or soil water potential, this quantity is simply treated as the water pressure or capillary pressure. Capillary pressure versus saturation curves obtained are used to estimate air–water interface curvature.¹⁰ Additionally, matric potential is generally defined to

be equal to $z + p^w/\rho^w g$ where z is an elevation.²⁰ In view of eqns (51a) and (51b), this understanding is overly simplistic. The quantity actually measured by a tensiometer is the free energy of the water phase and not the capillary pressure.^{3,7} Evidence supporting this can be obtained by comparing the implications of eqns (15) and (52) in the context of a column of partially saturated soil in contact with a water table at its lower boundary. For both these equations to apply, the equality given in eqn (57) must be satisfied. However, in light of eqn (51a), either the equality is not satisfied or the quantity actually used in eqn (15) must not really be p^w but some other quantity that is measured. In fact, this quantity is the free energy. The assumption implicit in standard measurements of capillary pressure is that the pressure of water in the measuring instrument is equal to the soil water pressure. This assumption has been shown to be invalid, except possibly for high saturation states, by Babcock and Overstreet.²

CONCLUSION

The extrapolation of Darcy's equation of saturated flow to describe two-phase flow in porous media is considered to be scientifically unacceptable in that it does not necessarily account for the operative physical process. Rather, the fundamental equations describing two-phase flow must be obtained from the basic principles of physics. The traditional relative permeability concept, introduced in the extended Darcy's equation, does not properly account for differences in physical processes that occur in single- and two-phase flow systems. In particular, the use of relative permeability fails to provide any improvement in modeling equilibrium states. Despite the very different nature of the forces acting in a multiphase system in comparison to a single-phase system, the equations of static equilibrium for both systems are exactly identical in the traditional approach.

The two phase flow theory formulated in this work is derived from basic principles of continuum physics and eliminates the specific shortcomings of the traditional theories of two-phase flow described earlier herein. Main features of the proposed theory are:

- Interfaces are explicitly accounted for in the macroscopic equations of motion for phases. Thus, the effect of interfacial forces on the motion of phases is modelled via their corresponding energy effects.
- Specific interfacial area as well as saturation appear as system variables in the governing equations. This feature is expected to eliminate hysteresis in the functional form of capillary pressure.
- The equation of motion for a fluid phase, eqn (23), contains some new terms which will be non-zero

even at equilibrium. These terms are due to the presence of interfaces and they will be identically zero for saturated porous media.

The equations presented do require some experimental and computational work to determine their range of applicability and the forms of the coefficients.

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REFERENCES

1. Aoda, T., Yoshida, S., Nakano, T. & Yamada, A., The fundamental studies of the rain infiltration into the sandy soil considering the hysteresis. *Transactions of the Japanese Society of Irrigation and Drainage Reclamation Engineering*, **157** (1992) 35–44.
2. Babcock, K.L. & Overstreet, R., Thermodynamics of soil moisture: a new application. *Soil Science*, **80**(1955) 257–63.
3. Babcock, K.L. & Overstreet, R., The extra-thermodynamics of soil moisture. *Soil Science*, **83** (1957) 455–64.
4. Babcock, K.L. & Overstreet, R., A note on the 'Buckingham' equation. *Soil Science*, **84** (1957) 341–43.
5. Bear, J., *Dynamics of Fluids in Porous Media*. Elsevier, New York, 1972
6. Bear, J., *Hydraulics of Groundwater Flow*. McGraw-Hill, New York, 1979
7. Bolt, G.H. & Miller R.D., Calculation of total and component potentials of water in soil. *Transactions of American Geophysical Union*, **39** (1958) 917–28.
8. Collins, R.E., *Flow of Fluids Through Porous Materials*. Reinhold, New York, 1961.
9. Day, P.R., The moisture potential in soils. *Soil Science*, **54** (1942) 391–400.
10. De Marsily, G., *Quantitative Hydrogeology, Groundwater Hydrology for Engineers*. Academic, Orlando, 1986.
11. Edlefsen, N.E. & Anderson, A.B.C., Thermodynamics of soil moisture. *Hilgardia*, **15** (1943) 31–298.
12. Freeze, R.A. & Cherry, J.A., *Groundwater*. Prentice-Hall, Englewood Cliffs, 1979.
13. Gray, W.G. & Hassanizadeh, S.M., Averaging theorems and averaged equations for transport of interface properties in multiphase systems. *International Journal of Multiphase Flow*, **15** (1989) 81–95.
14. Gray, W.G. & Hassanizadeh, S.M., Paradoxes and realities in unsaturated flow theory. *Water Resources Research*, **27** (1991) 1847–54.
15. Gray, W.G. & Hassanizadeh, S.M., Unsaturated flow theory including interfacial phenomena. *Water Resources Research* **27** (1991) 1855–63.
16. Hassanizadeh, S.M. & Gray, W.G., Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries. *Advances in Water Resources*, **13** (1990) 169–86.

17. Hassanizadeh, S.M. & Gray, W.G., Thermodynamic basis of capillary pressure in porous media. *Water Resources Research* (submitted, 1993).
18. Hillel, D., *Fundamentals of Soil Physics*. Academic Press, New York, 1980.
19. Kalaydjian, F., A macroscopic description of multiphase flow involving spacetime evolution of fluid/fluid interface. *Transport in Porous Media*, **2** (1987) 537–52.
20. Koorevaar, P., Menelik, G. & Dirksen, C. *Elements of Soil Physics*. Elsevier, Amsterdam, 1983.
21. Low, P.F., Force fields and chemical equilibrium in heterogeneous systems with special reference to soils. *Soil Science*, **71** (1951) 409–18.
22. Low, P.F. & Deming, J.M., Movement and equilibrium of water in heterogeneous systems with special reference to soils. *Soil Science*, **75** (1953) 187–202.
23. March, R.H., *Physics for poets*. McGraw-Hill, New York, 1970.
24. Marle, C.M., From the pore scale to the macroscopic scale: Equations governing multiphase fluid flow through porous media. In *Proceedings of Euromech 143*, ed. A Verruigt & Barends, F.B.J. A.A. Balkema, Rotterdam, 1981, pp. 57–61.
25. McWhorter, D. & Sunada, D.K., *Ground-water Hydrology and Hydraulics*. Water Resources Publications, Fort Collins, 1977.
26. Miller, C.A. & Neogi, P., *Interfacial Phenomena*. Marcel Dekker, New York, 1985.
27. National Research Council, *Ground Water Models, Scientific and Regulatory Applications*. National Academy Press, Washington, DC, 1990.
28. Rose, W., Some problems connected with the use of classical descriptions of fluid/fluid displacement processes. In *Fundamentals of Transport Processes in Porous Media*. Elsevier, Amsterdam, 1972, pp. 229–40.
29. Rose, W., Measuring transport coefficients necessary for the description of coupled two-phase flow of immiscible fluids in porous media. *Transport in Porous Media*, **3** (1988) 163–71.
30. Scheidegger, A.E., *The Physics of Flow through Porous Media*, 3rd edn. University of Toronto Press, Toronto, 1974.
31. Slattery, J.C., Multiphase viscoelastic flow through porous media. *AIChE J.*, **14** (1968) 50–6.