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# 2 Advanced Theories of Two-Phase Flow in Porous Media

*S. Majid Hassanizadeh*

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## 2.1 INTRODUCTION

Fluid-filled porous media are ubiquitous in many natural and industrial systems. The working of these systems is controlled and/or affected by the movement of fluids, solutes, particles, and heat through them. Examples of natural porous media and corresponding processes are the flow of oil, gas, and water in oil reservoirs; the potential mobilization of methane in gas hydrates; the flow of nonaqueous phase liquids (NAPLs) in contaminated aquifers; the storage of CO<sub>2</sub>, nuclear waste, other hazardous wastes, and heat in the subsurface; the flow of fluids in biological tissues; and melting and metamorphism of snow. Examples of industrial porous media and corresponding processes are the drying of paper pulp, the adsorption of liquids in diapers and similar absorbing products, gas and water management in fuel cells, and the drying of foods, building materials, detergent tablets, and filters.

Many physical, chemical, and thermal processes (such as fluid flow, diffusion, capillarity, dissolution, adsorption, clogging, degradation, and swelling) occur in these materials. For the design, operation, and maintenance of porous media systems, it is extremely important to understand these processes, describe them quantitatively (by mathematical models), and compute solutions to the governing equations. One would expect that for such a vast range of highly important systems and for complex processes occurring therein, a well-founded science with deep roots in fundamental principles of physics and mechanics should have been developed. Indeed, governing equations embedded in mathematical models of complex porous media systems should originate from rigorous derivations following a systematic approach. But the main equations used in porous media models are relatively simple equations, often borrowed from other disciplines: Darcy's law for flow, Fick's law for solute transport, Fourier's law for heat transfer, and Hooke's law of elasticity

for deformation. These equations, which form cornerstones of conceptual and computational models of flow and transport in deformable porous media at all scales, were originally presented for simple systems. During the last century, these equations have been adopted in an ad hoc fashion in order to be applicable to complex porous media processes, but with superficial modifications only. The complexities of coupled multiphase flow and reactive transport in deformable porous media were not taken into account. It is thus no surprise that, in almost all cases, our models have failed to provide acceptable descriptions of complex porous media. There are many examples. Hereunder, I give a few examples from the energy sector.

In petroleum engineering, predictions of oil or gas production from a well are almost always significantly different from observed production. So, after some time, the model input parameters are changed to match historical production data (this is called “history matching”). Then, new predictions are made, which are usually in error again. So, the cycle is repeated. The subsurface sequestration of  $\text{CO}_2$  involves complex processes too. In the case of injection of  $\text{CO}_2$  into brine reservoirs, one has to deal with three-phase flow (brine, gaseous  $\text{CO}_2$ , and supercritical  $\text{CO}_2$ ), dissolution of  $\text{CO}_2$  into brine, reactions with the solid phases, and deformation of the porous medium. The design of such operations, the prediction of their performance, and safety of  $\text{CO}_2$  sequestration are dependent on our models. Currently, there are major concerns about multiphase flow models being able to provide adequate certainty in this regard. Among other factors, this has hampered the decision-making process, while urgent measures are needed.

Another area where reliable multiphase flow models are urgently needed relates to the fate of huge reservoirs of gas hydrates. At numerous locations around the world, large quantities of methane gas are trapped inside “cages” of water ice molecules in sediments beneath the oceans and in the permafrost regions. This compound is referred to as gas hydrates and has the potential of not only being a blessing but also a curse. On the one hand, these are vast sources of energy if harvested. On the other hand, they could be destabilized as a result of the varying pressure–temperature conditions due to climate change, potentially leading to a catastrophic release of methane and causing an abrupt global warming much worse than what we are experiencing today. Various processes that need to be modeled include heat diffusion, hydration and dissociation, osmosis, sediment matrix deformation, methane oxidation, and movement of gas bubbles and water (two-phase flow). Gas bubbles will exist mainly as a discontinuous phase. But current models of two-phase flow are only valid for continuous phases. So any modeling study of the potentials for the exploitation of these resources or the threat posed by them will be done with a defective model.

The final example relates to what is considered to be the ultimate source of clean energy, namely, a “hydrogen fuel cell.” In a hydrogen fuel cell, energy from oxidation of hydrogen is harnessed, producing water as the only waste. Here again, the central process is the simultaneous movement of water and gasses in layers of porous media. As some layers are hydrophobic, water is formed and moves as droplets, that is, as a discontinuous phase. So current theories of two-phase flow are inappropriate for modeling fuel cells. Many more examples from other sectors can be given.

Obviously, much is needed for improving the quality of our model predictions, including methods for characterization of the media and more robust numerical methods. But a central element, which is at the heart of any model, is the set of equations used for describing the main processes. Our current theories of multiphase flow and transport in porous media are simply outdated and insufficient for modeling systems described earlier. A central issue in formulating theories of multiphase flow is the proper choice of state variables and developing appropriate governing equations for describing the system under consideration. In current theories of two-phase flow, the state variables are considered to be two fluid pressures and the saturation of one of the phases. In this chapter, we show that these three variables are not sufficient to fully characterize the state of two-phase flow in a porous medium. One needs to add another macroscale state variable that contains information about the subscale distribution of the phases.

First, we discuss the shortcomings of current theories of two-phase flow. Then, we provide an alternative and improved theory with roots in rational thermodynamics. We introduce specific

interfacial area (area of fluid–fluid interfaces per unit volume of porous medium) as a new state variable. We present theoretical, experimental, and computational evidences to support new concepts and equations presented here.

## 2.2 CRITICAL EVALUATION OF CURRENT TWO-PHASE FLOW THEORY

### 2.2.1 BRIEF DESCRIPTION OF CURRENT THEORY

Consider the flow of two or more immiscible incompressible fluids in a porous medium. The central equation in current models of multiphase flow is Darcy’s law. This is an empirical equation that was originally proposed by Henry Darcy in 1856 for describing *1D steady-state flow of incompressible water in saturated homogeneous isotropic rigid sandy soil under constant temperature* in a form equivalent to the following:

$$\mathbf{q} = -\frac{\mathbf{k}}{\mu} \cdot (\nabla P - \rho \mathbf{g}) \quad (2.1)$$

where

- $\mathbf{q}$  [ $\text{LT}^{-1}$ ] is the fluid phase apparent velocity vector
- $\mathbf{k}$  [ $\text{L}^2$ ] is the intrinsic permeability tensor
- $\mu$  [ $\text{ML}^{-1}\text{T}^{-1}$ ] is the dynamic viscosity
- $P$  [ $\text{ML}^{-1}\text{T}^{-2}$ ] is the fluid phase pressure
- $\rho$  [ $\text{ML}^{-3}$ ] is the fluid mass density
- $\mathbf{g}$  [ $\text{LT}^{-2}$ ] is the gravity vector

In the course of the last century, this equation has been used, almost without any alteration, to describe much more complex systems, namely, *3D unsteady flow of two or more compressible fluids, with any amount of dissolved matter, in heterogeneous anisotropic deformable porous media under nonisothermal conditions*. One would expect a much more complex equation, which would account for many additional physical phenomena in such complex systems. But the so-called “generalized” Darcy’s law has the same form as Equation 2.1 (Helmig, 1997):

$$\mathbf{q}^\alpha = -\frac{k_{r\alpha} \mathbf{k}}{\mu^\alpha} \cdot (\nabla P_\alpha - \rho^\alpha \mathbf{g}) \quad \alpha = w, n \quad (2.2)$$

where

- subscript  $\alpha (= w, n)$  refers to the fluid phase under consideration
- $w$  denotes the wetting phase, which preferably wets the porous solid
- $n$  denotes the nonwetting phase for which the solid has less affinity

The only new element in Equation 2.2 is the relative permeability  $k_{r\alpha}$  [–], which scales the saturated intrinsic permeability such that the influence on the flow of one phase due to the presence of other phases is taken into account. The relative permeability is assumed to be an algebraic function of saturation only.

The governing equation for saturation is based on the principle of conservation of mass, which for incompressible fluids reduces to the conservation of volume:

$$\phi \frac{\partial S^\alpha}{\partial t} + \nabla \cdot \mathbf{q}^\alpha = 0 \quad \alpha = w, n \quad (2.3)$$

where

- $\phi$  [–] is the porosity
- $S^\alpha$  [–] is the fluid phase saturation

Equations 2.2 and 2.3 are supplemented by the so-called capillary pressure equation

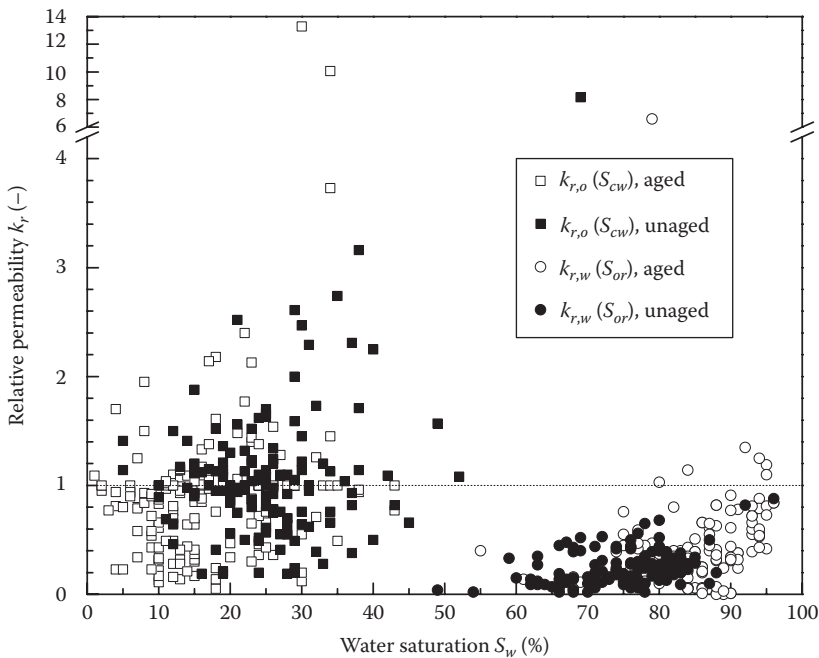
$$P_n - P_w = P_c(S^w) \quad (2.4)$$

where  $P_c$  [ $\text{ML}^{-1}\text{T}^{-2}$ ] is capillary pressure. When more fluid phases are present, Equations 2.2 through 2.4 are simply repeated for each additional phase, as if there are no other forces active, regardless of how many phases fill out the pore space.

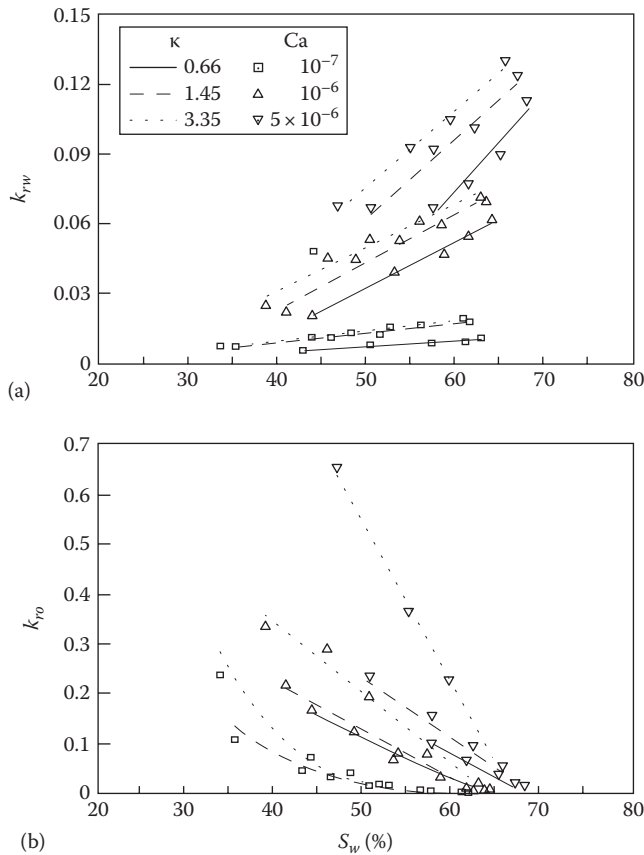
### 2.2.2 CRITICISMS OF DARCY'S LAW

Let us compare Equations 2.1 and 2.2. It is evident that, despite the much more complex nature of multiphase systems compared to the flow of water in saturated sand, the driving force in all cases is assumed to be  $\nabla P - \rho\mathbf{g}$  for each phase. The relative permeability coefficient is given the task of accounting for the complexities of multiphase flow dynamics. Theoretically, this is the coefficient of proportionality in the linear relationship between flow velocity,  $\mathbf{q}^\alpha$ , and the driving force,  $\nabla P_\alpha - \rho^\alpha\mathbf{g}$ . It is supposed to be a known function of saturation, and its value must vary between zero and unity. Yet values of relative permeability as large as 14 have been reported in the literature; see Figure 2.1.

Furthermore, there is ample evidence that the relative permeability depends not only on saturation but also on many other variables. In particular, its dependence on capillary number ( $N_c = \mu v/\sigma$ , where  $v$  is the average flow velocity and  $\sigma$  is the fluid–fluid interfacial tension) and therefore indirectly on pressure gradient or flow velocity has been established through both computational and experimental studies. For example, Figure 2.2 from Constantinides and Payatakes (1996) shows very significant changes in the relative permeability of both phases due to changes in average capillary number. Similar results were obtained in numerical studies of Avraam and Payatakes (1995),



**FIGURE 2.1** Relative permeability values much larger than unity are reported. (From Berg, S. et al., *Trans. Porous Media*, 74, 275–292, 2008.)

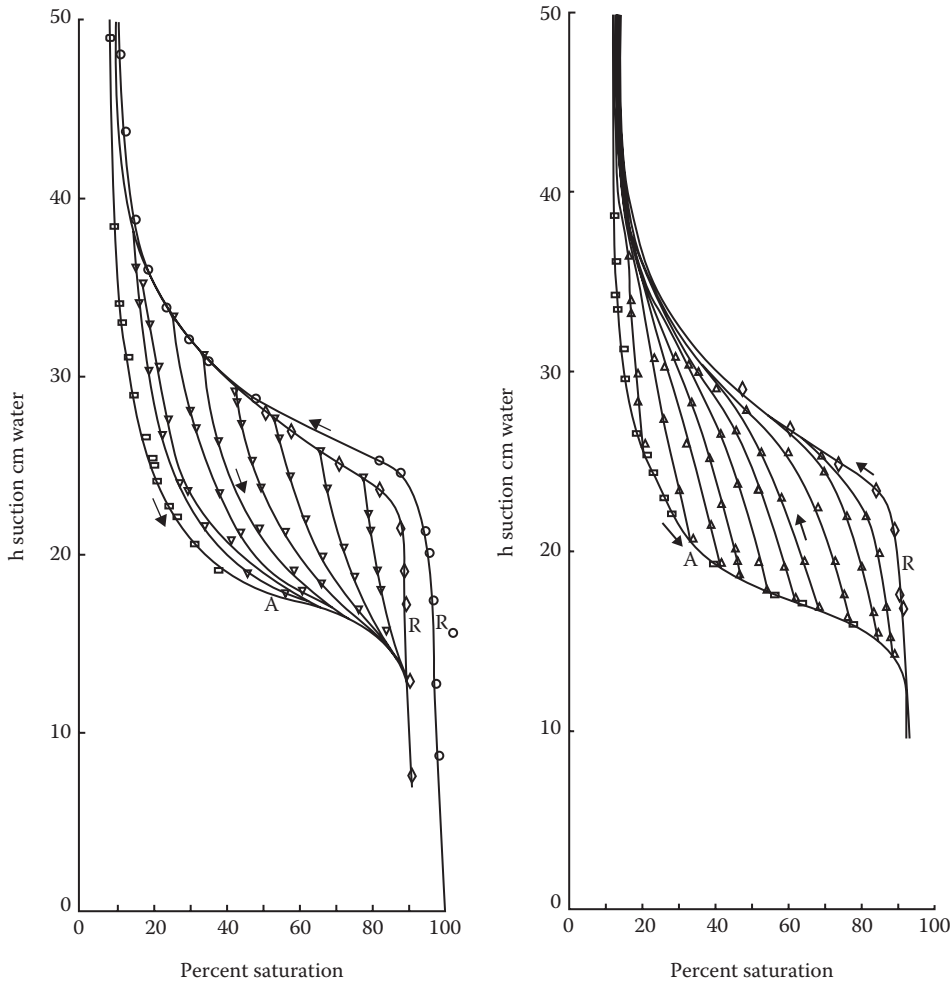


**FIGURE 2.2** Relative permeability for (a) wetting phase and (b) nonwetting phase. They are not just a function of saturation but depend on capillary number, that is, indirectly on the pressure gradient or flow velocity. (From Constantinides, G.N. and Payatakes, A.C., *AIChE J.*, 42, 369, 1996.)

Ataie-Ashtiani et al. (2002), and Li et al. (2005) and in experimental works of Boom et al. (1995, 1996), Henderson et al. (1996, 2000), Skauge et al. (2001), and Bartley and Ruth (2001). Dependence of relative permeability on flow velocity or pressure gradient obviously violates the underlying assumption of linear dependence between  $q^\alpha$  and  $\nabla P_\alpha - \rho^\alpha \mathbf{g}$ . So either the relationship is not linear or other forces need to be included. We know of course that other forces, such as interfacial forces, are present. In fact, the pore space is simultaneously occupied by two or more phases, which are separated by fluid–fluid interfaces. The interaction between the phases takes place through these interfaces. These interfaces play a central role in many processes and effects, such as capillarity, dissolution, adsorption of surfactants, transport of colloids and microorganisms in the unsaturated zone, evaporation, drying processes, and deformation of unsaturated soil. But, in current theories of multiphase flow, interfaces and their characteristics are completely absent! One would expect forces that control the movement of interfaces to be also present in the governing equations of multiphase flow. Also, mass and heat transfer coefficients should depend on the amount of fluid–fluid interfaces.

### 2.2.3 CRITICISMS OF CAPILLARITY THEORY

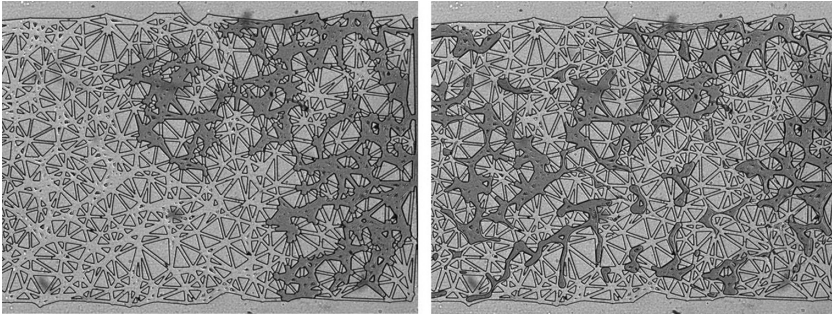
Major shortcomings and inconsistencies are also found in the macroscale capillary Equation 2.4. This equation was proposed empirically too; it is an ad hoc extension of the pore-scale Young–Laplace equation that is valid under equilibrium conditions. While Equation 2.4 prescribes a one-to-one



**FIGURE 2.3** Equilibrium capillary pressure–saturation curves. (Adapted from Morrow, N.R. and Harris, C.C., *Soc. Petrol. Eng. J.*, 5, 15, 1965.)

relationship between fluid pressure difference and saturation, in practice, we have a strongly hysteretic and time-dependent function. In the literature, one commonly speaks of a capillary pressure–saturation curve. But, in practice, there exist many curves for the same porous medium. Typically measured capillary pressure curves are shown in Figure 2.3. It is evident that one has a primary drainage curve (i.e., reducing the wetting phase saturation from unity to some irreducible value); there is a main hysteresis loop (consisting of main drainage and imbibition curves), a large number of primary scanning loops, and a myriad of scanning loops of secondary, tertiary, and higher degrees. In fact, any point within the main hysteresis loop could be a potential equilibrium state of the porous medium.

Typical capillary pressure–saturation graphs (e.g., Figure 2.3) show that for any given saturation, the porous medium may attain a wide range of capillary pressure values. This is because a given volume of the fluid may be distributed within the pores in many different ways. Each distribution will have its own capillary pressure. This is very well evident in the images taken from quasistatic drainage and imbibition experiments in our micromodel, shown in Figure 2.4. The two images are from the same porous medium. White triangles are the solid phase. Darker areas show the nonwetting phase, whereas the wetting phase has a light color. The left image shows a stage



**FIGURE 2.4** Images taken from quasistatic experiments in a micromodel. They are from primary drainage and main imbibition stages. (From Karadimitriou, N.K., Two-phase flow experimental studies in micro-models, PhD thesis, Utrecht University, Department of Earth Sciences, Utrecht, the Netherlands, 2013.)

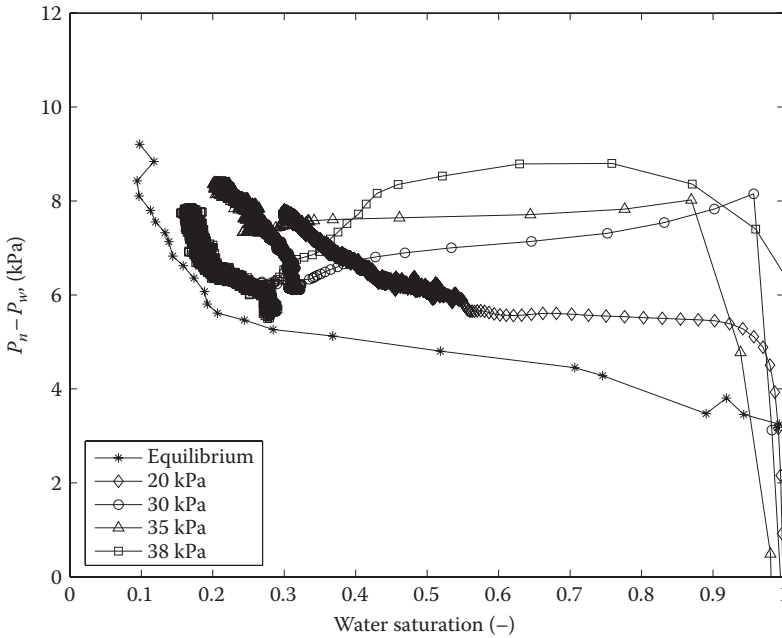
during primary drainage. The right image was obtained during imbibition after main drainage had occurred. The overall wetting phase saturation in both images is 76%, but the average capillary pressure values in the left and right images are 4340 and 2200 Pa, respectively. *This makes it evident that in addition to saturation, another state variable is needed to specify the equilibrium state of the system.* In fact, we need a macroscale variable to account for the difference in fluid distributions in these two stages. We believe this variable can be linked to the area of interfaces separating the two fluids. Indeed, the total interfacial areas in the left and right images are significantly different; they are 18.32 and 30.56 mm<sup>2</sup>, respectively.

There is another major issue with Equation 2.4. As mentioned earlier, capillary pressure–saturation curves are measured under equilibrium (no flow) conditions. They are subsequently used to simulate (very) dynamic processes! There are many situations where the timescale of the processes is much smaller than the timescale of  $P_c$ - $S^w$  measurements. For example, in the modeling of paper pulp drying process, the capillary pressure curve for the water-adsorbing felt (which is used to absorb water out of the pulp) is measured under quasistatic conditions. It takes around 24 h to obtain it, and then it is used to model a process that takes only a fraction of a second (Iliev et al., 2012)! Another example is when there is a rainfall-induced landslide, where there are fast changes in saturation and pore pressure. Under those conditions, equilibrium  $P_c$ - $S^w$  curve cannot be really used (see Nikoee et al., 2013 for a discussion). There are many other examples from natural and industrial porous media where equilibrium capillary pressure and relative permeability curves are used to model very fast processes. Numerous studies have shown that under flow conditions,  $P_n - P_w$  is not equal to  $P_c$ . A detailed review of the literature is found in Hassanizadeh et al. (2002) and Diamantopoulos and Durner (2012). Results of our measurements of  $P_n - P_w$  at a point in a column during a primary drainage process (Bottero et al., 2011) are shown in Figure 2.5. The lowest curve is the equilibrium  $P_c$ - $S^w$  curve. The other curves are plots of  $P_n - P_w$  as a function of  $S^w$  under flow conditions at various injection pressures of 20, 30, 35, and 38 kPa. Clearly, there is a huge difference between dynamic  $P_n - P_w$  and the capillary pressure curve. The higher the injection pressure (and thus the saturation change with time), the larger the difference is. So the underlying premise of Equation 2.4 is simply not valid.

## 2.3 THERMODYNAMICALLY BASED EQUATIONS OF TWO-PHASE FLOW

### 2.3.1 AVERAGING–THERMODYNAMIC APPROACH

This is a systematic framework for the derivation of physically based governing equations of flow and transport in porous media, which has its roots in the principles of rational thermodynamics. Governing equations at a given scale are composed of two ingredients: conservation laws and constitutive equations. In this approach, we use the volume averaging method to derive conservation



**FIGURE 2.5** Curves of pressure difference  $P_n - P_w$  versus saturation under dynamic conditions at various injection pressures of 20, 30, 35, and 38 kPa. The lowest curve is the equilibrium  $P_c$ - $S^w$  curve. (From Bottero, S., *Advances in theories of capillarity in porous media*, PhD thesis, Utrecht University, Department of Earth Sciences, Utrecht, the Netherlands, November 2009.)

laws at the scale of interest, based on the description at a lower scale (see, e.g., Hassanizadeh and Gray, 1979a,b). Then, we employ the principle of rational thermodynamics to derive constitutive laws at the scale of interest (see, e.g., Hassanizadeh and Gray, 1980). This is based on the application of the second law of thermodynamics, which is also called the entropy inequality. The approach allows us to develop general equations for complex systems and then systematically simplify them to obtain equations for simpler systems.

### 2.3.2 NEW TWO-PHASE FLOW THEORY

Hassanizadeh and Gray (1990) have employed the averaging–thermodynamic approach to derive a new theory of two-phase flow in porous media. The new theory has four major new features, compared to the traditional approach, as explained shortly. These equations are devoid of the shortcomings of the traditional two-phase flow theory discussed earlier. First, mass balance laws are presented and then simplified equations of momentum balance.

As explained in the previous section, one would expect fluid–fluid interfaces and solid–fluid interfaces to play an important role in macroscale description of two-phase flow. Indeed, the application of volume averaging technique results in the definition of macroscale quantities not only for fluids and solid phases but also for phase interfaces. Macroscale quantities for phases are the same as the traditional ones: average mass density  $\rho^\alpha$  and velocity vector  $\mathbf{v}^\alpha$  [ $\text{LT}^{-1}$ ], fluid phase saturations  $S^\alpha$ , and pressures  $P^\alpha$ . Similar macroscale quantities were found for interfaces: the average interfacial mass density  $\Gamma^{\alpha\beta}$  ( $\alpha\beta = wn, ns, ws$ ) [ $\text{ML}^{-2}$ ], defined as the total mass of  $\alpha\beta$  interfaces per area of those interfaces within a given volume; interfacial velocity vector  $\mathbf{w}^{\alpha\beta}$  [ $\text{LT}^{-1}$ ], average interfacial tension  $\sigma^{\alpha\beta}$  [ $\text{MT}^{-2}$ ]; and specific interfacial area  $a^{\alpha\beta}$  [ $\text{L}^{-1}$ ]. The latter is defined as the area of  $\alpha\beta$  interfaces per unit volume of the porous medium.

The macroscale mass balance equations for fluid phases and interfaces are found, respectively, to be (Gray and Hassanizadeh, 1989)

$$\frac{\partial \phi S^\alpha \rho^\alpha}{\partial t} + \nabla \cdot (\phi S^\alpha \rho^\alpha \mathbf{v}^\alpha) = \sum_{\beta \neq \alpha} E_{\alpha\beta}^{\alpha\beta}; \quad \alpha = w, n \tag{2.5}$$

$$\frac{\partial a^{\alpha\beta} \Gamma^{\alpha\beta}}{\partial t} + \nabla \cdot (a^{\alpha\beta} \Gamma^{\alpha\beta} \mathbf{w}^{\alpha\beta}) = E_\alpha^{\alpha\beta} + E_\beta^{\alpha\beta} + E^{\alpha\beta\gamma} \tag{2.6}$$

where

$E_\alpha^{\alpha\beta}$  [ML<sup>-3</sup>T<sup>-1</sup>] is the rate of exchange of mass between  $\alpha$ -phase and  $\alpha\beta$ -interface

$E^{\alpha\beta\gamma}$  [ML<sup>-3</sup>T<sup>-1</sup>] is the rate of exchange of mass between  $\alpha\beta$  interface and  $\alpha\beta\gamma$  common line (where the three interfaces come together)

Similar balance equations were derived by Marle (1982) and were used by Cushman and coworkers (see, e.g., Achanta et al., 1994; Bennethum and Cushman, 1996; Murad and Cushman, 1996).

Balance laws were also derived for momentum, energy, and entropy of phases and interfaces (Gray and Hassanizadeh, 1989). They were complemented by constitutive equations, and by employing the rational thermodynamics approach, Hassanizadeh and Gray (1990) derived the following simplified and linearized momentum balance equations for fluid phases and fluid–fluid interfaces, respectively:

$$\nabla P_\alpha - \rho_\alpha \mathbf{g} - \lambda_s^\alpha \nabla S^\alpha - \lambda_a^\alpha \nabla a^{wn} + R^\alpha \mathbf{v}^\alpha = 0; \quad \alpha = w, n \tag{2.7}$$

$$\nabla (a^{wn} \mathbf{o}^{wn}) + \Psi^{wn} \nabla S^w + R^{wn} \mathbf{w}^{wn} = 0 \tag{2.8}$$

↑  
interfacial tension

where

$R^\alpha$  [ML<sup>-3</sup>T<sup>-1</sup>] and  $R^{wn}$  [ML<sup>-3</sup>T<sup>-1</sup>] are resistance coefficients

$\lambda_s^\alpha$  [ML<sup>-1</sup>T<sup>-2</sup>],  $\lambda_a^\alpha$  [MT<sup>-2</sup>], and  $\Psi^{wn}$  [ML<sup>-1</sup>T<sup>-2</sup>] are material coefficients (all of them may be functions of  $S^w$  and  $a^{\alpha\beta}$ )

The gravity term has been neglected in Equation 2.8.

Equations 2.5 and 2.6 can be further simplified if we assume that phase mass densities and the interfacial mass density are constant. These are reasonable assumptions for isothermal situations and in the absence of surfactants. Thus, those equations can be divided by  $\rho^\alpha$  and  $\Gamma^{\alpha\beta}$ , respectively, to obtain the following volume balance and area balance equations:

$$\frac{\partial \phi S^\alpha}{\partial t} + \nabla \cdot (\phi S^\alpha \mathbf{v}^\alpha) = 0; \quad \alpha = w, n \tag{2.9}$$

$$\frac{\partial a^{wn}}{\partial t} + \nabla \cdot (a^{wn} \mathbf{w}^{wn}) = E^{wn} \tag{2.10}$$

where we limit our attention to the fluid–fluid (i.e.,  $wn$ ) interface. The term on the right-hand side of fluid phase mass balance has been neglected as we expect the rate of mass exchange between phases and interfaces to be much smaller than the advective flux of phases. The term on the right-hand side of (2.10),  $E^{wn}$  [L<sup>-1</sup>T<sup>-1</sup>], accounts for the rate of production of fluid–fluid interfaces.

This term is itself a function of saturation and specific interfacial area and their time rate of change. Expressions for such a dependency have been found through pore-network modeling by Joekar-Niasar and Hassanizadeh (2011) and by analyzing results of micromodel experiments by Karadimitriou et al. (2014a).

Next, simplified momentum balance Equations 2.7 and 2.8 are rearranged in order to obtain equations for macroscopic velocities. In the case of Equation 2.8, we assume the interfacial tension  $\sigma^{\alpha\beta}$  to be constant, so that it can be absorbed into other material coefficients. Thus, we obtain the following Darcy-type equations for the movement of fluid phases and fluid–fluid interfaces:

$$\mathbf{q}^\alpha = -\frac{k_{ra}k}{\mu^\alpha}(\nabla P_\alpha - \rho_\alpha \mathbf{g} - \lambda_s^\alpha \nabla S^\alpha - \lambda_a^\alpha \nabla a^{wn}); \quad \alpha = w, n \quad (2.11)$$

$$\mathbf{w}^{wn} = -K^{wn}(\nabla a^{wn} + \psi^{wn} \nabla S^w) \quad (2.12)$$

New variables in these equations are as follows:  $K^{wn}$  [ $L^3T^{-1}$ ] is interfacial conductivity, and  $\psi^{wn}$  [ $L^{-1}$ ] is a material coefficient, which may still depend on  $S^w$  and  $a^{\alpha\beta}$ .

In addition to an extended Darcy's law for the flow of fluids and the governing equations for specific interfacial area, the rational thermodynamics approach also led to a new hypothesis for the capillary pressure. Based on results of the constitutive theory, Hassanizadeh and Gray (1993a) suggested that the capillary pressure is not only a function of saturation but will also depend on specific interfacial area. They postulated that the hysteretic behavior of  $P_c$ - $S^w$  relationship can be modeled by introducing fluid–fluid specific interfacial area  $a^{\alpha\beta}$  into the  $P_c$ - $S^w$  relationship. Based on this hypothesis, capillary pressure–saturation–specific interfacial area data points from drainage and imbibition processes under equilibrium or/and nonequilibrium conditions would fall on a unique surface. Such a surface can be described by the following formula:

$$f(P_c, S^w, a^{wn}) = 0 \quad (2.13)$$

Henceforth, we refer to this surface as the *interfacial area surface*. Also, unless otherwise stated, with the term “saturation,” we refer to the wetting phase saturation.

One final result of the rational thermodynamics approach was that capillary pressure is not necessarily equal to the difference in fluid pressures. It was shown that Equation 2.4 holds under static conditions only. Under dynamic (flow) conditions, the difference in fluid pressure is not just equal to capillary pressure but includes a nonequilibrium term, given by the following equation (which is a linear approximation):

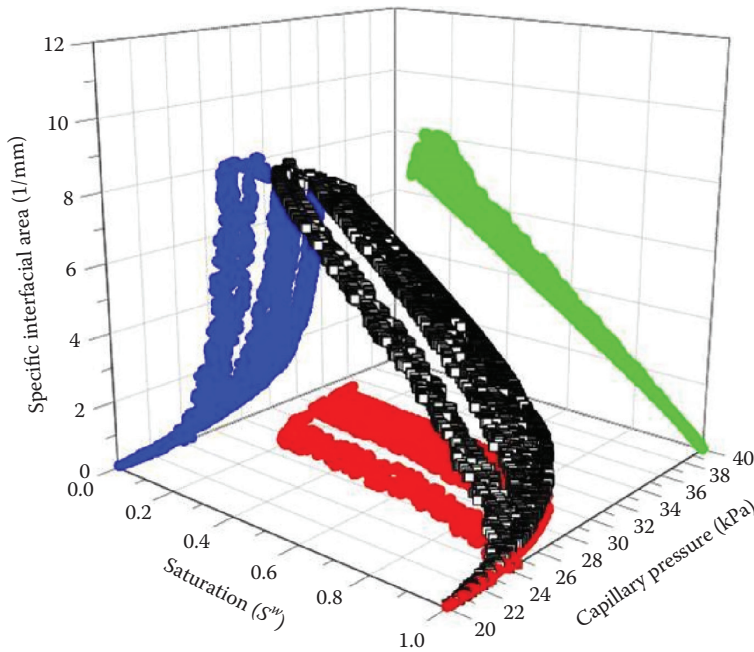
$$P_n - P_w = P_c(S^w, a^{wn}) - \tau \frac{\partial S^w}{\partial t} \quad (2.14)$$

where  $\tau$  [ $ML^{-1}T^{-1}$ ] is a material property, which may still be a function of  $S^w$  and  $a^{wn}$ . This equation is known as the dynamic capillarity formula. The second term on the right-hand side of (2.14) will vanish under equilibrium conditions, but it may be very significant under nonequilibrium conditions.

In the following sections, we discuss the significance of the set of equations developed earlier. In particular, we discuss the role of specific interfacial area and the nonequilibrium capillarity term.

### 2.3.3 EVALUATION OF ROLE OF SPECIFIC INTERFACIAL AREA

A major feature of the new theory is the introduction of specific interfacial area,  $a^{wn}$ , as a new state variable. This is a major departure from the traditional approach where phase saturation and pressures are the only state variables. Given the fact that phenomena such as capillarity and kinetic



**FIGURE 2.6** Schematic representation of  $P_c$ - $S^w$ - $a^{wn}$  surface (shown in black). Its projection onto the  $P_c$ - $S^w$  plane creates the hysteresis domain formed by capillary pressure–saturation curves (shown in red).

mass and heat transfer occur across interfaces, we need a variable that quantifies interfacial configurations. Specific interfacial area is exactly such a variable. As evident from Equation 2.13, the capillary pressure not only is a function of saturation but also depends on the specific interfacial area,  $a^{wn}$ . This means that we do not have capillary pressure–saturation curves, but a capillary pressure–saturation–interfacial area surface, as shown in Figure 2.6. This description of capillarity suggests that the main and scanning hysteresis loops, which we see in Figure 2.3, actually represent a projection of the  $P_c$ - $S^w$ - $a^{wn}$  surface onto the  $P_c$ - $S^w$  plane. This concept is illustrated in Figure 2.6.

Indeed, a growing number of numerical and experimental works show that under quasistatic conditions, drainage and imbibition  $P_c$ - $S^w$ - $a^{wn}$  surfaces (formed by data points from drainage and imbibition experiments, respectively) coincide with each other, within the margin of experimental error. The earliest studies were done by Reeves and Celia (1996), and Held and Celia (2001), who performed quasistatic pore-network modeling. More recent examples of computational studies that prove the existence of interfacial area surface (i.e.,  $P_c$ - $S^w$ - $a^{wn}$  surface) are found in Joekar-Niasar et al. (2008), who also used pore-network modeling, and Porter et al. (2009), who performed lattice Boltzmann simulations. The first experimental evidence for the uniqueness of  $P_c$ - $S^w$ - $a^{wn}$  surface was provided by Cheng et al. (2004) and later by Chen et al. (2007) and Pyrak-Nolte et al. (2008). They performed two-phase flow experiments in a micromodel. A combination of pore-network modeling and micromodel experimental studies was performed by Joekar-Niasar et al. (2009) and Karadimitriou et al. (2013), again showing the existence of the interfacial area surface.

There are many reasons given in the literature for the occurrence of hysteresis in capillary pressure–saturation relationships (see, e.g., Bear, 1972; Morrow, 1970; Morrow and Harris, 1965). But, almost all those reasons tell us that, at the same saturation, fluid distributions are different during drainage and imbibition and interfaces have different curvatures under different conditions. Specific interfacial area is the macroscale variable that quantifies the differences in phase distributions and curvature of interfaces under various conditions. So, in Figure 2.4, the two different states (which are at the same saturation but at two different capillary pressures) are distinguished

by virtue of the differences in specific interfacial area, which are 18.32 and 30.56 mm<sup>2</sup> in the left and right images, respectively. In order to investigate that the inclusion of specific interfacial area will indeed model the capillary hysteretic effect, Niessner and Hassanizadeh (2008) combined the standard volume balance equation and standard Darcy's law (Equation 2.2) with new Equations 2.10 and 2.12 for specific interfacial area and a single interfacial area surface (Equation 2.13) and solved it to model drainage and imbibition processes occurring in the same domain. They compared the results with a standard model, using different capillary pressure curves for drainage and imbibition. They showed that drainage and imbibition processes can be modeled with a single interfacial area surface. In a similar work, Pop et al. (2009) showed that the horizontal redistribution of fluids in a porous medium can be properly modeled with the new theory.

The specific interfacial area is also of great significance on the modeling of kinetic heat and mass transfer processes among phases. Currently, the rate of mass transfer among two immiscible fluids is related to the fluid saturation. But, in fact, as the mass or heat transfer among two phases occurs at their interfaces, the rate of transfer must be related to the amount of interfacial area. The significance of including specific interfacial area in models of heat and mass transfer in two-phase flow has been illustrated numerically by Niessner and Hassanizadeh (2009a,b) and very recently through experiments in micromodels by Karadimitriou et al. (2014b) and Nuske et al. (2014). Recently, Nikoosaei et al. (2012, 2013) have shown that specific interfacial area has to be included in the description of deformation of unsaturated porous media in order to be able to model the observed hysteresis in the effective stress parameter.

### 2.3.4 EVALUATION OF NONEQUILIBRIUM CAPILLARITY EFFECT

The nonequilibrium capillarity Equation 2.14 has been shown to be fully in line with experimental observations. The equation prescribes that under nonequilibrium drainage, where  $-\tau \partial S^w / \partial t$  is positive,  $P_n - P_w$  will be larger than  $P_c$ . This is exactly what we see in Figure 2.5, where curves of nonequilibrium  $P_n - P_w$  lie higher than the drainage capillary pressure curve. Similarly, experimental studies of Oung et al. (2005) showed that under nonequilibrium imbibition, where  $-\tau \partial S^w / \partial t$  is negative,  $P_n - P_w$  will be smaller than  $P_c$ . Data similar to those shown in Figure 2.5 can be used to compute the value of the material coefficient  $\tau$  (see Bottero et al., 2011; Oung et al., 2005). Values of  $\tau$  are found to be in the order of 10<sup>5</sup> kg/m/s. There is a large body of experimental work on determining the validity of the nonequilibrium capillarity Equation 2.14. Examples are the works of O'Carroll et al. (2005), Camps-Roach et al. (2010), and Sakaki et al. (2010).

Some researchers, mainly mathematicians, have shown that the combination of the dynamic capillarity theory and the standard Darcy's law will make it possible to model phenomena that cannot be explained by standard capillarity theory. In particular, they have shown that it can model unstable capillary fingering and nonmonotonic saturation distributions during water infiltration into dry soil (Cuesta et al., 2000; Egorov et al., 2003; Nieber et al., 2005; van Duijn et al., 2007). Dynamic capillary effects have been also studied by means of pore-scale models (Dahle et al., 2005; Joekar-Niasar et al., 2010, 2012). Finally, a number of numerical modelers have incorporated the new capillarity Equation 2.6 in their codes (Manthey, 2006; Manthey et al., 2005).

### 2.3.5 COMMENTS ON THE EXTENDED DARCY'S LAW

As explained in the introduction, computational and experimental works have shown that the linear relationship between flow velocity,  $\mathbf{q}^\alpha$ , and the driving force,  $\nabla P_\alpha - \rho^\alpha \mathbf{g}$ , does not always hold for two-phase flow. This has been evidenced in the fact that the relative permeability could be a function of the flow velocity, among other terms. Now, Equation 2.11 suggests that other forces may play a role in the relationship between  $\mathbf{q}^\alpha$  and  $\nabla P_\alpha - \rho^\alpha \mathbf{g}$ . Let's assume there are flow situations where the last two terms in Equation 2.11 are important. Then, if we leave them out of the equation, their

role has to be taken up by the relative permeability. This may explain why relative permeability is a function of many variables including the capillary number. Tsakiroglou et al. (2004) have shown that the relative permeability curves determined from transient and steady-state experiments are significantly different. This was also found by Joekar-Niasar et al. (2011), who showed that when all terms in Equation 2.11 are included, then the difference between transient and steady-state relative permeability curves disappear. Similar results were found in a study by Niessner et al. (2011). One final comment about Equation 2.11 needs to be made. Hassanizadeh and Gray (1993b) have shown this equation can be recast in the following forms:

$$\mathbf{q}^\alpha = -\rho^\alpha \frac{k_{r\alpha} \mathbf{k}}{\mu^\alpha} \cdot (\nabla G_\alpha - \mathbf{g}) \quad \alpha = w, n \quad (2.15)$$

where  $G_\alpha$  denotes the Gibbs free energy of the fluid phase. This equation suggests that the true driving force for flow of a fluid is the gradient in Gibbs free energy (as well as gravity). In the case of single-phase flow of a fluid, and under isothermal conditions, its Gibbs free energy depends on its mass density only. Then, one can show that (2.15) reduces to the standard Darcy's law for saturated flow. But, in the case of two-phase flow, the Gibbs free energy may depend on saturation and specific interfacial area, in which case an equation similar to (2.11) has to follow.

## 2.4 CONCLUSIONS

For the description of two-phase flow processes, we must introduce a new state variable that accounts for the presence of fluid–fluid interfaces. We define this to be the *specific interfacial area*: the area of fluid–fluid interfaces per unit volume of the medium. The introduction of specific interfacial area allows the modeling of capillary hysteresis. It also allows for the modeling kinetic mass transfer among phases.

The driving forces in Darcy's law should be not only the pressure gradient and gravity but also gradients of saturation and specific interfacial area. The difference in fluid pressures is equal to capillary pressure but only under equilibrium conditions. Under nonequilibrium conditions, the difference in fluid pressures is a function of time rate of change of saturation, as well as saturation. This equation allows for modeling nonmonotonic saturation distributions.

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