

Published in final edited form as:

*Adv Water Resour.* 2011 June ; 34(6): 770–778. doi:10.1016/j.advwatres.2011.04.001.

## TCAT Analysis of Capillary Pressure in Non-equilibrium, Two-fluid-phase, Porous Medium Systems

William G. Gray\* and Cass T. Miller

Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, North Carolina 27599-7431, USA

Cass T. Miller: casey\_miller@unc.edu

### Abstract

Standard models of flow of two immiscible fluids in a porous medium make use of an expression for the dependence of capillary pressure on the saturation of a fluid phase. Data to support the mathematical expression is most often obtained through a sequence of equilibrium experiments. In addition to such expressions being hysteretic, recent experimental and theoretical studies have suggested that the equilibrium functional forms obtained may be inadequate for modeling dynamic systems. This situation has led to efforts to express relaxation of a system to an equilibrium capillary pressure in relation to the rate of change of saturation. Here, based on insights gained from the thermodynamically constrained averaging theory (TCAT) we propose that dynamic processes are related to changes in interfacial area between phases as well as saturation. A more complete formulation of capillary pressure dynamics is presented leading to an equation that is suitable for experimental study.

### Keywords

thermodynamically constrained averaging theory; dynamics; thermodynamics; interfacial areas

## 1 Introduction

When modeling flow of two immiscible fluids in porous media, the capillary pressure between the fluids is typically modeled as a function of the saturation of one of the fluids according to  $p^c = f(s^w)$ . This capillary pressure function is also set equal to the pressure in the non-wetting phase minus the pressure in the wetting phase. This approach suffers from two major shortcomings.

First, the capillary pressure, although measured at equilibrium, is not a unique function of saturation. At the same saturation, capillary pressure is found to be higher following a drainage event than following an imbibition event. All values between the high and low equilibrium capillary pressure at a particular saturation can be reached as equilibrium values by creatively using sequences of wetting and drying steps. This situation suggests that capillary pressure may be a function of other variables in addition to saturation [7, 16]. In

---

© 2011 Elsevier Ltd. All rights reserved.

\*Corresponding author: GrayWG@unc.edu (William G. Gray.).

**Publisher's Disclaimer:** This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

fact, this should not be surprising. At the microscale, the capillary pressure is dependent upon the properties of an interface and is equal to the interfacial tension multiplied by the interfacial curvature. This functional dependence is unique. Thus, suggesting that the averaged capillary pressure is a function only of saturation implies that saturation is a surrogate for curvature. Depending on how a fluid is distributed in the pore space, its surface area may take on different forms and curvatures. Thus rather than concluding that the macroscale capillary function is intrinsically hysteretic, it is reasonable to consider that the functional dependence is incomplete when cast in terms of fluid saturations alone. As a first step toward reducing hysteresis, one can obtain expressions for capillary pressure as a function of interfacial area between fluids as well as saturation [4, 18, 19].

The second shortcoming relates not to the functional form of the equilibrium capillary pressure relationship but to setting it equal to the pressure difference between phases. Because the capillary pressure is a property of an interface, it relates to the difference in pressure at the interfaces at equilibrium. Although the error is likely small in most cases, the distinction between a pressure averaged over a phase and averaged over a fluid-fluid interface is typically ignored. Furthermore, for a dynamic system, capillary pressure is not equal to a difference in fluid-phase pressures. During a redistribution of phases in a region, saturation, interfacial curvature, interfacial tension, and pressures will all be changing. The requirement that an interface thermodynamic property be equal to a difference in properties of adjacent phases seems unreasonable. The difference in phase pressures is sometimes referred to as a “dynamic capillary pressure” [3, 6, 17]. However, this is a misnomer as a dynamic capillary pressure should refer to a transient value of an interface property, such as capillary pressure and/or curvature. For example, the expression “dynamic capillary pressure” has been employed more appropriately to describe relations that are proportional to the interfacial tension [5, 23].

Because capillary pressure is equal to the pressure difference between phases only at equilibrium, efforts have been made to develop equations that account for system dynamics. The first attempts to account for this disequilibrium seem to have been in the 1970's [1, 21]. As described in Barenblatt et al. [2], one approach to accounting for the disequilibrium is to make use of a transient effective saturation. Stauffer [21] postulated that the disequilibrium is proportional to the rate of change of saturation. The difference between an observed  $p^c$  and an equilibrium thermodynamic form of this function has also been hypothesized to be proportional to the rate of change of saturation [13]. A more complex analysis based on rational thermodynamics postulated to hold at the macroscale has also led to a similar relation [10].

Despite these advances in modeling the dynamics of capillarity, the models are still lacking. Efforts to obtain values for the coefficient that appears in dynamic models have shown a wide range of variability [11, 15, 20, 22]. One reason for variability in coefficients is that they are being used to account for some physics that are otherwise overlooked in the problem formulation. In the present instance, it seems likely that relaxation to an equilibrium capillary pressure expression would involve both saturation adjustments and redistribution of fluid within the medium. This redistribution could involve reshaping of interfaces (and thus alteration of the capillary pressure of the interface) as well as formation and destruction of interfaces. These processes can occur at constant pressure, but the current formulations would only allow for disequilibrium due to changing saturation.

This unsatisfactory situation is due, at least in part, to the use of a postulated rational thermodynamic formulation at the macroscale. Such a formulation is useful in allowing for dependence on an expanded set of variables to be employed. However, this approach overlooks subscale variations in thermodynamic variables such as interfacial area density.

However, the thermodynamically constrained averaging theory (TCAT) offers a means to develop an improved dynamic expression. TCAT involves averaging established microscale thermodynamic principles to the macroscale. In doing so, it inherently assures consistency between microscale and macroscale forms. Additionally, terms arise naturally that account for microscale variations in macroscale quantities.

Here, we will review the expression that arises in the full TCAT formulation of two-fluid-phase flow. We will then work with this expression to develop expressions for dynamics in the capillary pressure equation. We note that this formulation allows for relaxation to equilibrium based on both saturation changes and changes in interfacial area density. The functional forms generated can be studied experimentally or through highly resolved microscale simulations to obtain values or functional forms for the coefficients that appear in the closure relations that are derived.

## 2 Entropy Inequality Force-Flux Pair

A full TCAT analysis has been performed for two-fluid-phase flow in porous media [12]. As part of this analysis a term arises in the entropy inequality that hints at a useful and desired force-flux form. This expression is denoted here as  $\theta^{\overline{wn}} T_\eta$  with

$$\theta^{\overline{wn}} T_\eta = \langle \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^s) [p_w - p_n - (\nabla' \cdot \mathbf{n}_w) \gamma_{wn} + \rho_{wn} \mathbf{n}_w \cdot \mathbf{g}] \rangle_{\Omega_{wn}, \Omega} \geq 0 \quad (1)$$

where  $T_\eta$  is the actual term that appears in the entropy inequality and  $\theta^{\overline{wn}}$  is the macroscale temperature of the  $wn$  interface obtained using microscale entropy per area of the interface used as a weighting function in averaging it from the microscale. The microscale terms inside the averaging operator are beautifully arranged into a force-flux form. This is the term that gives rise to dynamic aspects of capillary pressure. However, converting the microscale form to a macroscale force-flux pair is not straightforward. Here, we will examine this term in detail with the objective of analyzing existing formulations for capillary pressure, and we will also provide an improved formulation.

We note that a full formulation would require consideration of other force-flux types of expressions to account for cross-coupling of phenomena. Here we will not make use of these couplings as they are thought to be of lesser importance than the terms that appear in Eqn (1). As insights grow, it may be deemed appropriate to make use of these other forces that impact relaxation of capillary pressure toward equilibrium.

## 3 Definitions

For convenience, let us first define some of the macroscale quantities that will appear in the subsequent discussions. First denote as  $A_{wn}$  one of the microscale quantities that appears in Eqn (1) according to

$$A_{wn} = \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^s). \quad (2)$$

This quantity is averaged over the  $wn$  interface so that we obtain the macroscale quantity:

$$\overline{A}^{\overline{wn}} = \mathcal{E}^{wn} A^{wn} = \langle \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^s) \rangle_{\Omega_{wn}, \Omega}. \quad (3)$$

Similarly, we can define the macroscale quantity  $B_{wn}$  as:

$$B_{wn} = \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^s) \nabla' \cdot \mathbf{n}_w. \quad (4)$$

The microscale curvature of the interface is denoted as  $J_w$  where:

$$J_w = \nabla' \cdot \mathbf{n}_w. \quad (5)$$

so that:

$$B_{wn} = J_w A_{wn}. \quad (6)$$

Then the macroscale average of  $B_{wn}$  is

$$\overline{B^{wn}} = \varepsilon^{wn} B^{wn} = \langle \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^s) \nabla' \cdot \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega}. \quad (7)$$

The macroscale average of the curvature is defined as:

$$J_w^{wn} = \langle \nabla' \cdot \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega_{wn}}. \quad (8)$$

Although microscale quantities  $A_{wn}$  and  $B_{wn}$  are directly related as in Eqn (6), a corresponding macroscale relation between  $\overline{A^{wn}}$  and  $\overline{B^{wn}}$  will only exist necessarily when  $J_w$  is constant within the averaging volume. We use  $J_{wc}$  to denote the constant value of microscale curvature in this situation where

$$J_{wc} = J_w = J_w^{wn}, \quad (9)$$

when  $J_w$  is a constant. Thus, when the microscale curvature is constant:

$$\overline{B^{wn}} = J_{wc} \overline{A^{wn}}. \quad (10)$$

At equilibrium, Eqn (9) will apply. This relation may also apply in other situations, for example in the case of spherical gas bubbles expanding in a liquid phase.

For shorthand convenience, we will use the designation

$$P_{wn} = p_w - p_n + \rho_{wn} \mathbf{n}_w \cdot \mathbf{g} \quad (11)$$

to indicate the microscale pressure difference between the wetting and non-wetting phases as modified due to the mass contained in the interface between the phases. The macroscale counterpart of this quantity is:

$$P^{wn} = \langle P_{wn} \rangle_{\Omega_{wn}, \Omega_{wn}} = P_w^{wn} - P_n^{wn} + \rho^{wn} \mathbf{n}_w^{\overline{wn}} \cdot \mathbf{g}, \quad (12)$$

where  $P_w^{wn}$  ( $P_n^{wn}$ ) is the microscale pressure of the  $w(n)$  phase averaged over the  $wn$  interface and  $\mathbf{n}_w^{\overline{wn}}$  is the  $wn$  interfacial density weighted average of the normal to the  $wn$  interface oriented to be positive outward from the  $w$  phase. Making use of the notational conveniences, we may rewrite Eqn (1) in three equivalent alternative forms:

$$\theta^{\overline{wn}} T_\eta = \langle A_{wn} (P_{wn} - J_w \gamma_{wn}) \rangle_{\Omega_{wn}, \Omega} \geq 0 \quad (13)$$

or

$$\theta^{\overline{wn}} T_\eta = \left\langle B_{wn} \left( \frac{P_{wn}}{J_w} - \gamma_{wn} \right) \right\rangle_{\Omega_{wn}, \Omega} \geq 0 \quad (14)$$

or

$$\theta^{\overline{wn}} T_\eta = \langle A_{wn} P_{wn} - B_{wn} \gamma_{wn} \rangle_{\Omega_{wn}, \Omega} \geq 0. \quad (15)$$

Note that the first two forms involve products of factors that all go to zero at equilibrium. Thus, these are in force-flux forms at the microscale. However, Eqn (15) is not in this form. Thus, it is more difficult to see how to make use of Eqn (15) in determining macroscale closure relations for the dynamic evolution of pressure.

One additional term that arises involves the average of the difference between the microscale and macroscale curvature multiplied by  $A_{wn}$ , which is denoted as  $e^{\overline{wn}}$  according to:

$$e^{\overline{wn}} = \langle (J_w - J_w^{wn}) \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^s) \rangle_{\Omega_{wn}, \Omega}, \quad (16)$$

which may be integrated to:

$$e^{\overline{wn}} = B^{\overline{wn}} - J_w^{wn} A^{\overline{wn}}. \quad (17)$$

The quantity  $e^{\overline{wn}}$  equals zero at equilibrium and also under dynamic conditions when  $J_w^{wn} = J_w^c$ .

With various macroscale quantities defined, we now perform some manipulations aimed at examining the possibility of rearranging Eqn (1), or its equivalent forms of Eqns (13)–(15) to obtain macroscale force-flux pairs. As will be seen, this task cannot be accomplished solely in terms of the macroscale variables thus far defined.

#### 4 Analysis Based on $A_{wn}$

For this analysis, we start with Eqn (13). We add and subtract macroscale terms to obtain:

$$\overline{\theta}^{\overline{wn}} T_\eta = \langle A_{wn}(P^{wn} - J_w^{wn} \gamma^{wn}) \rangle_{\Omega_{wn}, \Omega} + \langle A_{wn}(P_{wn} - P^{wn} - J_w \gamma_{wn} + J_w^{wn} \gamma^{wn}) \rangle_{\Omega_{wn}, \Omega} \geq 0. \quad (18)$$

The first term may be integrated directly since the macroscale quantity may be removed from the averaging operator. This calculation gives:

$$\overline{\theta}^{\overline{wn}} T_\eta = A^{\overline{wn}} (P^{wn} - J_w^{wn} \gamma^{wn}) + \langle A_{wn}(P_{wn} - P^{wn} - J_w \gamma_{wn} + J_w^{wn} \gamma^{wn}) \rangle_{\Omega_{wn}, \Omega} \geq 0. \quad (19)$$

For convenience, we will write this as the leading term plus an error term,  $e_A^{\overline{wn}}$ , such that:

$$\overline{\theta}^{\overline{wn}} T_\eta = A^{\overline{wn}} (P^{wn} - J_w^{wn} \gamma^{wn}) + e_A^{\overline{wn}} \geq 0, \quad (20)$$

where:

$$e_A^{\overline{wn}} = \langle A_{wn}(P_{wn} - P^{wn} - J_w \gamma_{wn} + J_w^{wn} \gamma^{wn}) \rangle_{\Omega_{wn}, \Omega}. \quad (21)$$

Alternatively, we can rearrange this error expression to:

$$e_A^{\overline{wn}} = \left\langle A_{wn} \left[ (P_{wn} - \gamma_{wn} J_w) - J_w^{wn} \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) \right] \right\rangle_{\Omega_{wn}, \Omega}. \quad (22)$$

In both of these forms of the error term, quantities that go to zero at equilibrium are contained in parentheses and multiply  $A_{wn}$ . As demonstrated by Eqn (20), the force-flux form in terms of macroscale quantities cannot be achieved unless the term  $e_A^{\overline{wn}}$  is properly accounted for.

#### 5 Analysis Based on $B_{wn}$

For this assessment, we also start with Eqn (13) for convenience. Multiply the factors together to obtain the expanded expression:

$$\overline{\theta}^{\overline{wn}} T_\eta = \langle A_{wn} P_{wn} - A_{wn} J_w \gamma_{wn} \rangle_{\Omega_{wn}, \Omega} \geq 0. \quad (23)$$

Then addition and subtraction of the term  $A_{wn} P_{wn} J_w / J_w^{wn}$  yields:

$$\overline{\theta}^{\overline{wn}} T_\eta = \left\langle A_{wn} \frac{P_{wn}}{J_w^{wn}} J_w + A_{wn} P_{wn} - A_{wn} \frac{P_{wn}}{J_w^{wn}} J_w - A_{wn} J_w \gamma_{wn} \right\rangle_{\Omega_{wn}, \Omega} \geq 0. \quad (24)$$

Eqn (24) may be factored to:

$$\theta^{\overline{\overline{wn}}} T_\eta = \left\langle A_{wn} J_w \left( \frac{P_{wn}}{J_w^{wn}} - \gamma_{wn} \right) + A_{wn} P_{wn} \left( 1 - \frac{J_w}{J_w^{wn}} \right) \right\rangle_{\Omega_{wn}, \Omega} \geq 0 \quad (25)$$

or:

$$\theta^{\overline{\overline{wn}}} T_\eta = \left\langle B_{wn} \left( \frac{P_{wn}}{J_w^{wn}} - \gamma_{wn} \right) + A_{wn} P_{wn} \left( 1 - \frac{J_w}{J_w^{wn}} \right) \right\rangle_{\Omega_{wn}, \Omega} \geq 0. \quad (26)$$

Now addition and subtraction of the quantity  $B_{wn}(P^{wn} - \gamma^{wn} J_w^{wn})/J_w^{wn}$  yields:

$$\theta^{\overline{\overline{wn}}} T_\eta = \left\langle B_{wn} \left( \frac{P_{wn}}{J_w^{wn}} - \gamma^{wn} \right) \right\rangle_{\Omega_{wn}, \Omega} + \left\langle B_{wn} \left( \frac{P_{wn} - P^{wn}}{J_w^{wn}} - \gamma_{wn} + \gamma^{wn} \right) \right\rangle_{\Omega_{wn}, \Omega} + \left\langle A_{wn} P_{wn} \left( 1 - \frac{J_w}{J_w^{wn}} \right) \right\rangle_{\Omega_{wn}, \Omega} \geq 0. \quad (27)$$

The first term may be integrated to provide:

$$\theta^{\overline{\overline{wn}}} T_\eta = B^{\overline{\overline{wn}}} \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) + e_B^{\overline{\overline{wn}}} \geq 0. \quad (28)$$

where:

$$e_B^{\overline{\overline{wn}}} = \left\langle B_{wn} \left( \frac{P_{wn} - P^{wn}}{J_w^{wn}} - \gamma_{wn} + \gamma^{wn} \right) \right\rangle_{\Omega_{wn}, \Omega} + \left\langle A_{wn} P_{wn} \left( 1 - \frac{J_w}{J_w^{wn}} \right) \right\rangle_{\Omega_{wn}, \Omega}. \quad (29)$$

To prepare this error to be compared with  $e_A^{\overline{\overline{wn}}}$ , we first rearrange this expression to:

$$e_B^{\overline{\overline{wn}}} = \left\langle A_{wn} \left( \frac{P_{wn} J_w^{wn} - P^{wn} J_w}{J_w^{wn}} - \gamma_{wn} J_w + \gamma^{wn} J_w \right) \right\rangle_{\Omega_{wn}, \Omega} \quad (30)$$

and then to:

$$e_B^{\overline{\overline{wn}}} = \left\langle A_{wn} \left[ (P_{wn} - \gamma_{wn} J_w) - J_w \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) \right] \right\rangle_{\Omega_{wn}, \Omega}. \quad (31)$$

We note that  $e_B^{\overline{\overline{wn}}}$  will be equal to zero at equilibrium since both  $A_{wn}$  and the factors in parentheses in this equation will be zero at equilibrium. Furthermore, Eqn (28) indicates that  $e_B^{\overline{\overline{wn}}}$  must be properly accounted for to obtain a macroscale force-flux form.

## 6 Comparison of the Error Terms

Eqns (20) and (28) would be macroscale force-flux pairs if  $e_A^{\overline{\overline{wn}}}$  and  $e_B^{\overline{\overline{wn}}}$ , respectively, were zero or were themselves macroscale force flux pairs. However, neither of these circumstances will necessarily be the case. Comparison of Eqns (22) and (31) reveals that

$e_A^{\overline{wn}}$  and  $e_B^{\overline{wn}}$  differ only by the scale of the curvature that multiplies the second term in parentheses. Therefore, we can subtract these two error terms to obtain:

$$e_B^{\overline{wn}} = e_A^{\overline{wn}} - \left\langle A_{wn}(J_w - J_w^{wn}) \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) \right\rangle_{\Omega_{wn}, \Omega}. \quad (32)$$

The integral expression can be evaluated exactly making use of definition Eqn (16) to obtain:

$$e_B^{\overline{wn}} = e_A^{\overline{wn}} - \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) e^{\overline{wn}}. \quad (33)$$

## 7 Approximations

To this point, none of the equations and identities developed involve any approximations.

However, the five variables  $A^{\overline{wn}}$ ,  $B^{\overline{wn}}$ ,  $e_A^{\overline{wn}}$ ,  $e_B^{\overline{wn}}$ , and  $e^{\overline{wn}}$  have not been specified in terms of physical macroscale quantities. To be able to proceed toward useful expressions for the system dynamics involving capillary pressure, we need to evaluate these terms. Exact expressions are not attainable in general. However, under conditions that are commonly encountered in porous medium flows, approximations with minimal error are achievable. We will now develop some approximations that will prove to be helpful. To be clear, in contrast to the derivation that has preceded, these approximations may be subjected to improvement based on new insights or information. We believe, however, that the forms to be proposed are quite workable and useful, and are certainly improvements compared to currently used formulas for the analysis of the dynamics of capillary pressure evolution.

The need to obtain expressions for  $A^{\overline{wn}}$  and  $B^{\overline{wn}}$  in the study of the evolution of interfacial areas has led to some work to obtain these in [8]. Neither quantity can be evaluated exactly, but some reasonable approximations have been obtained. These expressions are based on the exploitation of the averaging theorems as applied to volumes, surfaces, and curves.

It has been shown [8] that if one considers any motion of the solid-phase surface to be independent of the fluid phase it contacts, the expression for  $A^{\overline{wn}}$  is:

$$A^{\overline{wn}} = \varepsilon \frac{D^{\overline{s}} s^w}{Dt} + (s^w - \chi_{ws}^{ss}) \frac{D^{\overline{s}} \varepsilon}{Dt}, \quad (34)$$

where  $\varepsilon$  is the porosity,  $s^w$  is the saturation of the  $w$  phase,  $\chi_{ws}^{ss}$  is the fraction of solid surface in contact with the  $w$  phase, and the material derivative moving with the average velocity of the solid phase is given by:

$$\frac{D^{\overline{s}}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^{\overline{s}} \cdot \nabla. \quad (35)$$

When the solid-phase dynamics are very slow in comparison to the redistribution of the fluids in the pores, as is usually the case, Eqn (34) may be simplified to:



$$A^{\overline{\overline{wn}}} = \varepsilon \frac{\partial s^{wn}}{\partial t}. \quad (36)$$

Eqn (36) is exact for the case of a non-deforming solid with time independent porosity.

The evaluation of  $B^{\overline{\overline{wn}}}$  is more difficult. For this term, we will make use of the [2, (3, 0), 0] averaging theorems [9]. When applied to averaging of a constant, the time averaging theorem T[2, (3, 0), 0] provides:

$$\langle (\nabla' \cdot \mathbf{n}_w) \mathbf{n}_w \cdot \mathbf{v}_{wn} \rangle_{\Omega_{wn}, \Omega} = \frac{\partial \varepsilon^{wn}}{\partial t} + \nabla \cdot \langle \mathbf{n}_w \mathbf{n}_w \cdot \mathbf{v}_{wn} \rangle_{\Omega_{wn}, \Omega} - \langle \mathbf{n}_{wn} \cdot \mathbf{v}_{wns} \rangle_{\Omega_{wns}, \Omega}. \quad (37)$$

The averaging theorem for the gradient of a function, G[2, (3, 0), 0], provides the following identity when the function is a constant:

$$-\langle (\nabla' \cdot \mathbf{n}_w) \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega} = \nabla \varepsilon^{wn} - \nabla \cdot \langle \mathbf{n}_w \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega} + \langle \mathbf{n}_{wn} \rangle_{\Omega_{wns}, \Omega}. \quad (38)$$

The dot product of Eqn (38) with the macroscale solid-phase velocity gives:

$$-\langle (\nabla' \cdot \mathbf{n}_w) \mathbf{n}_w \cdot \mathbf{v}^{\overline{s}} \rangle_{\Omega_{wn}, \Omega} = \mathbf{v}^{\overline{s}} \cdot \nabla \varepsilon^{wn} - \nabla \cdot \langle \mathbf{n}_w \mathbf{n}_w \cdot \mathbf{v}^{\overline{s}} \rangle_{\Omega_{wn}, \Omega} + \langle \mathbf{n}_w \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega} : \mathbf{d}^{\overline{s}} + \langle \mathbf{n}_{wn} \cdot \mathbf{v}^{\overline{s}} \rangle_{\Omega_{wns}, \Omega}. \quad (39)$$

Addition of Eqns (37) and (39) provides:

$$\langle (\nabla' \cdot \mathbf{n}_w) \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}) \rangle_{\Omega_{wn}, \Omega} = \frac{D^{\overline{s}} \varepsilon^{wn}}{Dt} + \nabla \cdot \langle \mathbf{n}_w \mathbf{n}_w \cdot (\mathbf{v}_{wn} - \mathbf{v}^{\overline{s}}) \rangle_{\Omega_{wn}, \Omega} - \langle \mathbf{n}_{wn} \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}) \rangle_{\Omega_{wns}, \Omega} + \langle \mathbf{n}_w \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega} : \mathbf{d}^{\overline{s}}, \quad (40)$$

where the quantity on the left is  $B^{\overline{\overline{wn}}}$ . A useful rearrangement can be obtained by adding and subtracting  $\mathbf{v}^{\overline{wn}}$  to the second term on the right. With this step, and evaluating other integrals as possible, we obtain:

$$B^{\overline{\overline{wn}}} = \frac{D^{\overline{s}} \varepsilon^{wn}}{Dt} + \nabla \cdot [\varepsilon^{wn} \mathbf{G}^{wn} \cdot (\mathbf{v}^{\overline{wn}} - \mathbf{v}^{\overline{s}})] + \nabla \cdot [\varepsilon^{wn} (\mathbf{w}^{\overline{\overline{wn}}} - \mathbf{G}^{wn} \cdot \mathbf{v}^{\overline{wn}})] + \varepsilon^{wn} \mathbf{G}^{wn} : \mathbf{d}^{\overline{s}} - \langle \mathbf{n}_{wn} \cdot (\mathbf{v}_{wns} - \mathbf{v}^{\overline{s}}) \rangle_{\Omega_{wns}, \Omega}, \quad (41)$$

where the rate of strain tensor for the solid is defined as:

$$\mathbf{d}^{\overline{s}} = \frac{1}{2} \left[ \nabla \mathbf{v}^{\overline{s}} + (\nabla \mathbf{v}^{\overline{s}})^T \right], \quad (42)$$

$\mathbf{w}^{\overline{\overline{wn}}}$  is the average of the normal velocity of the  $wn$  interface defined as:

$$\mathbf{w}^{\overline{\overline{wn}}} = \langle \mathbf{n}_w \mathbf{n}_w \cdot \mathbf{v}_{wn} \rangle_{\Omega_{wn}, \Omega}, \quad (43)$$

and  $\mathbf{G}^{wn}$  is the macroscale orientation tensor for the interface defined as:

$$\mathbf{G}^{wn} = \langle \mathbf{n}_w \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega_{wn}}. \quad (44)$$

No approximations have been used in developing Eqn (41), but the last term is an integral term that cannot be evaluated exactly. This integral accounts for the movement of the common curve relative to the average solid-phase velocity.

The integral in Eqn (41) may be approximated following [8] as:

$$\langle \mathbf{n}_{wn} \cdot (\mathbf{v}_{wns} - \mathbf{v}^s) \rangle_{\Omega_{wns}, \Omega} = \varepsilon^{ss} \frac{D^s \chi_{ws}^{ss}}{Dt} \overline{\cos \varphi^{ws, wn}} - \frac{\varepsilon^{wns}}{\varepsilon^{ss}} \frac{D^s \varepsilon^s}{Dt} \overline{\sin \varphi^{ws, wn}}, \quad (45)$$

where  $\varepsilon^{ss}$  is the solid-phase surface per unit volume,  $\chi_{ws}^{ss}$  is the fraction of the solid-phase surface in contact with the  $w$  phase,  $\overline{\varphi^{ws, wn}}$  is the average contact angle at the solid surface between the  $ws$  and  $wn$  interfaces, and  $\varepsilon^{wns}$  is the common curve length per unit volume. This approximate relation assumes that the contact angle average is decoupled from the velocity of the common curve. This approximation inherently neglects the contributions of the dynamic nature of the contact angle to the changes in  $\varepsilon^{wn}$ . For the case where the contact angle within an averaging volume is approximately constant, the approximation is exact. Substitution of Eqn (45) into Eqn (41) and cancellation of terms involving  $\mathbf{G}^{wn} \cdot \mathbf{v}^{wn}$  yields an approximate expression for  $B^{\overline{wn}}$  in the form:

$$B^{\overline{wn}} = \frac{D^s \varepsilon^{wn}}{Dt} + \nabla \cdot [\varepsilon^{sn} (\mathbf{w}^{\overline{wn}} - \mathbf{G}^{wn} \cdot \mathbf{v}^s)] + \varepsilon^{wn} \mathbf{G}^{wn} : \mathbf{d}^s - \varepsilon^{ss} \frac{D^s \chi_{ws}^{ss}}{Dt} \overline{\cos \varphi^{ws, wn}} + \frac{\varepsilon^{wns}}{\varepsilon^{ss}} \frac{D^s \varepsilon^s}{Dt} \overline{\sin \varphi^{ws, wn}}. \quad (46)$$

When the solid-phase movement is insignificant, this expression reduces further to:

$$B^{\overline{wn}} = \frac{\partial \varepsilon^{wn}}{\partial t} + \nabla \cdot (\varepsilon^{wn} \mathbf{w}^{\overline{wn}}) - \frac{\partial \varepsilon^{ws}}{\partial t} \overline{\cos \varphi^{ws, wn}}. \quad (47)$$

We can obtain an alternative approximation for  $B^{\overline{wn}}$  based on the identity of Eqn (17). Arrangement of this equation yields:

$$B^{\overline{wn}} = J_w^{wn} A^{\overline{wn}} + e^{\overline{wn}}. \quad (48)$$

Approximation of this expression proceeds first by substituting Eqn (34) to eliminate  $A^{\overline{wn}}$  so that we have:

$$B^{\overline{wn}} = J_w^{wn} \left( \frac{D^s \varepsilon^w}{Dt} + \chi_{ws}^{ss} \frac{D^s \varepsilon^s}{Dt} \right) + e^{\overline{wn}}. \quad (49)$$

In [8], arguments were made that because  $e^{\overline{wn}}$  accounts for movement of the  $wn$  interfaces when the microscale interfacial curvature within the averaging volume is not constant, it may be approximated using a linear representation as:

$$e^{\overline{\overline{wn}}} = -\widehat{k}^{wn}(\varepsilon^{wn} - \varepsilon_{eq}^{wn}), \quad (50)$$

where  $\widehat{k}^{wn}$  is a parameter that may depend on system variables, and  $\varepsilon_{eq}^{wn}$  is the equilibrium value of  $\varepsilon^{wn}$ . With this expression, Eqn (49) provides an alternative approximation to  $B^{\overline{\overline{wn}}}$ :

$$B^{\overline{\overline{wn}}} = J_w^{wn} \left( \frac{D^s \varepsilon^w}{Dt} + \chi_{ws}^{ss} \frac{D^s \varepsilon^s}{Dt} \right) - \widehat{k}^{wn}(\varepsilon^{wn} - \varepsilon_{eq}^{wn}). \quad (51)$$

This form also may be simplified for the case where the solid is relatively immobile to the expression:

$$B^{\overline{\overline{wn}}} = J_w^{wn} \frac{\partial \varepsilon^w}{\partial t} - \widehat{k}^{wn}(\varepsilon^{wn} - \varepsilon_{eq}^{wn}). \quad (52)$$

Eqns (46) and (51) are alternative forms. Additionally, their simplified versions based on relatively slow solid dynamics given in Eqns (47) and (52) may be used interchangeably.

Although we have expressions for averages of  $A_{wn}$  and  $B_{wn}$ , we cannot make use of these directly in Eqn (20) or Eqn (28) to obtain a force-flux pair in terms of macroscale physical variables because of the presence of the residual terms  $e_A^{\overline{\overline{wn}}}$  and  $e_B^{\overline{\overline{wn}}}$ . Thus to proceed with this analysis, we must make suitable approximations for these residual terms under various conditions. One way to do this is to consider the way in which experimental studies are performed to determine capillary pressure-saturation relations [14].

## 8 Estimates of Residual Terms

The relationship between capillary pressure and fluid saturation is typically investigated experimentally by making stepwise changes in the difference between the pressure of the two fluids and allowing the system to equilibrate before quantifying the resultant fluid saturations. The equilibration process involves rearrangement and reshaping of the interface surfaces as well as flow of the phases into or out of the study cell. It is reasonable to consider that the pressures of the phases and the interfacial tension are constant during the equilibration process. Thus we will consider the case where:

$$P_{wn} = P^{wn} \quad (53)$$

and:

$$\gamma_{wn} = \gamma^{wn}. \quad (54)$$

With these stipulations, Eqn (22) for  $e_A^{\overline{\overline{wn}}}$  simplifies to:

$$e_A^{\overline{\overline{wn}}} = -\gamma^{wn} \langle A_{wn} (J_w - J_w^{wn}) \rangle_{\Omega_{wn}, \Omega} = -\gamma^{wn} e^{\overline{\overline{wn}}}. \quad (55)$$

This suggests further that the more general Eqn (22) be arranged to the following form:

$$e_A^{\overline{\overline{wn}}} = -\gamma^{wn} e^{\overline{\overline{wn}}} + \langle A_{wn}(P_{wn} - P^{wn}) - B_{wn}(\gamma_{wn} - \gamma^{wn}) \rangle_{\Omega_{wn}, \Omega}. \quad (56)$$

For purposes of subsequent discussion, we denote the error due to the difference in pressure differences and surface tension differences between the microscale and macroscale, respectively, as:

$$e_p^{\overline{\overline{wn}}} = \langle A_{wn}(P_{wn} - P^{wn}) \rangle_{\Omega_{wn}, \Omega} \quad (57)$$

and:

$$e_\gamma^{\overline{\overline{wn}}} = \langle B_{wn}(\gamma_{wn} - \gamma^{wn}) \rangle_{\Omega_{wn}, \Omega}. \quad (58)$$

Therefore Eqn (56) may be written as:

$$e_A^{wn} = -\gamma^{wn} e^{\overline{\overline{wn}}} + e_p^{\overline{\overline{wn}}} - e_\gamma^{\overline{\overline{wn}}}. \quad (59)$$

In this expression,  $e^{\overline{\overline{wn}}}$  accounts for disequilibrium due to the distribution of the microscale interfacial curvature within the REV,  $e_p^{\overline{\overline{wn}}}$  accounts for the distribution of pressure differences across an interface, and  $e_\gamma^{\overline{\overline{wn}}}$  accounts for the distribution of interfacial tension. Thus whenever variability of either curvature, pressure difference, or interfacial tension within the REV may be considered negligible, its corresponding residual term may be neglected in the formulation.

For the special case under consideration here with the pressure difference and interfacial tension distributions neglected, Eqn (31) for  $e_B^{\overline{\overline{wn}}}$  reduces to:

$$e_B^{\overline{\overline{wn}}} = -\frac{P^{wn}}{J_w^{wn}} \langle A_{wn}(J_w - J_w^{wn}) \rangle_{\Omega_{wn}, \Omega} = -\frac{P^{wn}}{J_w^{wn}} e^{\overline{\overline{wn}}}. \quad (60)$$

Therefore rearrangement of Eqn (31) such that this portion of the error is the leading term gives:

$$e_B^{\overline{\overline{wn}}} = -\frac{P^{wn}}{J_w^{wn}} e^{\overline{\overline{wn}}} + \langle A_{wn}(P_{wn} - P^{wn}) - B_{wn}(\gamma_{wn} - \gamma^{wn}) \rangle_{\Omega_{wn}, \Omega} \quad (61)$$

or, making use of definitions given in Eqns (57) and (58):

$$e_B^{\overline{\overline{wn}}} = -\frac{P^{wn}}{J_w^{wn}} e^{\overline{\overline{wn}}} + e_p^{\overline{\overline{wn}}} - e_\gamma^{\overline{\overline{wn}}}. \quad (62)$$

Based on these expressions, we will be neglecting  $e_p^{\overline{\overline{wn}}}$  and  $e_\gamma^{\overline{\overline{wn}}}$ . Typically studies of capillary pressure relations are performed under conditions where the interfacial tension is a constant.

This, of course, precludes the study of cases where the interfacial tension is evolving due to coincident heat transfer or compositional changes of the phases. The neglect of  $e_p^{\overline{wn}}$  is employed in consideration of the fact that pressure equilibration occurs at a faster rate than the shape of the interface, which will reshape in response to the pressure in the phases.

Finally, in cases where  $J_w = J_{wc}$ , we obtain  $e_A^{\overline{wn}} = e_B^{\overline{wn}} = 0$ . This corresponds to a case where the microscale interfacial curvature within the averaging region is a function of time, but has the same value at any point on any interface segment as the system approaches equilibrium.

## 9 Expressions for Capillary Pressure Evolution

Eqn (59) is the general expression for  $e_A^{\overline{wn}}$ . When disequilibrium due to a non-uniform pressure difference profile and non-uniformity in surface tension are ignored, substitution back into Eqn (20) provides the relation:

$$\theta^{\overline{wn}} T_\eta = A^{\overline{wn}} (P^{wn} - J_w^{wn} \gamma^{wn}) - \gamma^{wn} e^{\overline{wn}} \geq 0, \quad (63)$$

or after substitution of the approximation given by Eqn (50):

$$\theta^{\overline{wn}} T_\eta = A^{\overline{wn}} (P^{wn} - J_w^{wn} \gamma^{wn}) + \gamma^{wn} \widehat{k}^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \geq 0. \quad (64)$$

The coefficient  $\widehat{k}^{wn}$  is a function of system variables. In an effort to obtain a force-flux form, let us write this coefficient in terms of another variable  $\widehat{k}_1^{wn}$  where:

$$\widehat{k}^{wn} = \left( \frac{J_w^{wn} \gamma^{wn}}{P^{wn}} - 1 \right) \widehat{k}_1^{wn}. \quad (65)$$

Substitution of Eqn (65) into Eqn (64) and rearrangement gives:

$$\theta^{\overline{wn}} T_\eta = \left[ A^{\overline{wn}} - \frac{\gamma^{wn}}{P^{wn}} \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] (P^{wn} - J_w^{wn} \gamma^{wn}) \geq 0. \quad (66)$$

This is a force-flux form that suggests the linear relation:

$$\widehat{\tau}_A \left[ A^{\overline{wn}} - \frac{\gamma^{wn}}{P^{wn}} \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] = P^{wn} - J_w^{wn} \gamma^{wn}. \quad (67)$$

Then substitution of the approximation for  $A^{\overline{wn}}$  as given by Eqn (34) and for  $P^{wn}$  as given by Eqn (12) yields:

$$\widehat{\tau}_A \left[ \varepsilon \frac{D^s s^w}{Dt} + (s^w - \chi_{ws}^{ss}) \frac{D^s \varepsilon}{Dt} - \frac{\gamma^{wn}}{p_w^{wn} - p_n^{wn} + \rho^{wn} \mathbf{n}_w^{\overline{wn}} \cdot \mathbf{g}} \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] = p_w^{wn} - p_n^{wn} + \rho^{wn} \mathbf{n}_w^{\overline{wn}} \cdot \mathbf{g} - J_w^{wn} \gamma^{wn}. \quad (68)$$

For purposes of examining the most important processes, we can consider the solid-phase motion to occur at a much longer time scale than the time scale over which fluid-fluid

interface dynamics are operative. Also, consider the mass per area of the interface to be negligible and denote the capillary pressure as:

$$p^c = -\gamma^{wn} J_w^{wn}. \quad (69)$$

Thus Eqn (68) becomes:

$$\widehat{\tau}_A \left[ \varepsilon \frac{\partial s^w}{\partial t} + \frac{\gamma^{wn}}{p_n^{wn} - p_w^{wn}} \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] = p_w^{wn} - p_n^{wn} + p^c. \quad (70)$$

This is an extended form of the usual equation for relaxation of the capillary pressure to equilibrium. Before discussing this relation further and considering special cases, we will develop an alternative form based on Eqn (28).

Substitution of the expression in Eqn (62) into Eqn (28) retaining only the term accounting for disequilibrium in curvature gives:

$$\theta^{\overline{wn}} T_\eta = B^{\overline{wn}} \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) - \frac{P^{wn}}{J_w^{wn}} e^{\overline{wn}} \geq 0. \quad (71)$$

Substitution of Eqns (50) and (65) into Eqn (71) yields:

$$\theta^{\overline{wn}} T_\eta = B^{\overline{wn}} \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) + \frac{P^{wn}}{J_w^{wn}} \widehat{k}_1^{wn} \left( \frac{J_w^{wn} \gamma^{wn}}{P^{wn}} - 1 \right) (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \geq 0. \quad (72)$$

This relation can be rearranged into the force-flux form:

$$\theta^{\overline{wn}} T_\eta = \left[ B^{\overline{wn}} - \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] \left( \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn} \right) \geq 0. \quad (73)$$

This suggests the linear relation:

$$\widehat{\tau}_B \left[ B^{\overline{wn}} - \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] = \frac{P^{wn}}{J_w^{wn}} - \gamma^{wn}. \quad (74)$$

Then substitution of Eqn (46) and introduction of the expression for pressure from Eqn (12) into Eqn (74) gives:

$$\begin{aligned} \widehat{\tau}_B \left\{ \frac{D^{\overline{s}} \varepsilon^{wn}}{Dt} + \nabla \cdot \left[ \varepsilon^{wn} (\mathbf{w}^{\overline{wn}} - \mathbf{G}^{wn} \cdot \mathbf{v}^{\overline{s}}) \right] + \varepsilon^{wn} \mathbf{G}^{wn} : \mathbf{d}^{\overline{s}} - \varepsilon^{ss} \frac{D^{\overline{s}} \chi_{ws}^{ss}}{Dt} \cos \varphi^{\overline{ws,wn}} + \frac{\varepsilon^{wns}}{\varepsilon^{ss}} \frac{D^{\overline{s}} \varepsilon^s}{Dt} \sin \varphi^{\overline{ws,wn}} - \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right\} \\ = \frac{p_w^{wn} - p_n^{wn} + \rho^{wn} \mathbf{n}_w^{\overline{wn}} \cdot \mathbf{g}}{J_w^{wn}} - \gamma^{wn}. \end{aligned} \quad (75)$$

This general form is simplified when the interfacial density per area is negligible and the solid-phase dynamics can be ignored to obtain:

$$\widehat{\tau}_B \left[ \frac{\partial \varepsilon^{wn}}{\partial t} + \nabla \cdot (\varepsilon^{wn} \mathbf{w}^{wn}) - \frac{\partial \varepsilon^{ws}}{\partial t} \cos \varphi^{ws,wn} - \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] = \frac{P_w^{wn} - P_n^{wn} + P^c}{J_w^{wn}}. \quad (76)$$

Despite their different appearance, Eqns (70) and (76) must be equivalent forms since they were developed under the same set of assumptions. Because of the equivalent definitions of  $B^{wn}$  given by Eqns (47) and (52), it is straightforward to rearrange Eqn (76) to show that:

$$\widehat{\tau}_A = (J_w^{wn})^2 \widehat{\tau}_B. \quad (77)$$

Eqn (76) indicates that the relaxation to equilibrium can be monitored in terms of the interfacial area density changes without inclusion of the rate of change of saturation. However, this approach does require knowledge of the average of the normal component of the microscale  $wn$  interface velocity, the rate of change of the  $ws$  interfacial area density, and the contact angle. Eqn (70), though no more valid than Eqn (76), seems easier to work with.

## 10 Discussion

The combination of terms that has resulted from the TCAT analysis, including averaging of thermodynamic relations, has given rise to Eqn (20), which can be rewritten making use of Eqns (12), (36), (59), and (69) as:

$$\overline{\theta^{wn}} T_\eta = \varepsilon \frac{\partial s^w}{\partial t} (P_w^{wn} - P_n^{wn} + \rho^{wn} \mathbf{n}_w^{wn} \cdot \mathbf{g} + P^c) - \gamma^{wn} e^{wn} + e_p^{wn} - e_\gamma^{wn} \geq 0. \quad (78)$$

This equation is obtained with the following considerations:

- solid-phase dynamics are considered to be negligible in comparison to fluid-phase dynamics related to capillary pressure transients;
- the phase pressures that impact capillary pressure dynamics are the averages of the fluid-phase pressures over the fluid-fluid interfaces;
- capillary pressure at the macroscale is the average interfacial tension multiplied by the average interfacial curvature;
- $e^{wn}$  relates to the dynamics of interface reconfiguration during dynamic changes of capillary pressure and is zero when the microscale interfacial curvature is constant and at equilibrium;
- $e_p^{wn}$  relates to the dynamics of pressure equilibration within an averaging volume and is zero when the difference between microscale fluid-phase pressures is constant and at equilibrium; and
- $e_\gamma^{wn}$  relates to the dynamics of interfacial tension and is zero when the microscale interfacial tension is constant and at equilibrium.

We can now examine some special cases, proceeding from the simplest to the more complex.

## 10.1 Equilibrium

The equilibrium statement of a capillary pressure relation arises directly from the microscale rather than as a special case of Eqn (78). At any point on the interface, the microscale capillary pressure,  $p_c$  is defined as:

$$p_c = -\gamma_{wn} \mathbf{J}_w. \quad (79)$$

This definition is independent of the pressures in the fluids on each side of the interface. At equilibrium, the statement of a balance of forces at a microscale point on the interface is:

$$p_w - p_n + \rho_{wn} \mathbf{n}_w \cdot \mathbf{g} + p_c = 0. \quad (80)$$

Averaging of this expression over the interface then yields:

$$p_w^{wn} - p_n^{wn} + \rho^{wn} \mathbf{n}_w^{\overline{wn}} \cdot \mathbf{g} + p^c = 0. \quad (81)$$

When the product of the density of the interface with the average vertical component of the unit normal outward from the phase on the interface is negligible, the term accounting for a pressure jump across the interface due to gravity can be neglected. Additionally, the distinction between the fluid-phase pressure averaged over that phase or averaged over the fluid-fluid interface is typically implicitly considered to be unimportant so that the equilibrium capillary pressure is given as:

$$p^w - p^n + p^c = 0. \quad (82)$$

## 10.2 Simple Dynamic Model

The simple dynamic model is one that has appeared as the model for inclusion of capillary dynamics. In fact, it is a simplified model of these dynamics. To obtain this model

proceeding from Eqn (78), one assumes that the pressure difference deviation term,  $e_p^{\overline{wn}}$ , and the interfacial tension deviation term,  $e_\gamma^{\overline{wn}}$ , are both negligible. Of particular note is the fact that the term,  $e^{\overline{wn}}$ , involving rearrangement of the interfacial curvature distribution is also neglected. Additionally, the interfacial mass density term is considered small, and the surface average pressures are replaced by the volume averaged pressures so that Eqn (78) is reduced to:

$$\theta^{\overline{wn}} T_\eta = \varepsilon \frac{\partial s^w}{\partial t} (p^w - p^n + p^c) \geq 0. \quad (83)$$

Then, based on the idea that this is a force-flux form, the linearized expression is given as:

$$\widehat{\tau}_A \varepsilon \frac{\partial s^w}{\partial t} = p^w - p^n + p^c, \quad (84)$$

which may alternatively be obtained directly by manipulating Eqn (70).



This equation indicates that the only dynamic process that gives rise to disequilibrium between capillary pressure and the phase pressures is the rate of change of saturation. This is an important observation on a number of scores. First, the formulation of Eqn (84) is obtained directly when using a rational thermodynamics approach at the macroscale. Such an approach inherently applies the concept of local equilibrium to an averaging volume such that thermodynamic variables are ascribed at that scale. Thus, specification of capillary pressure as a single variable at that scale overlooks the possibility of subscale variation of this thermodynamic property. On the other hand, if one makes use of the TCAT approach and averages microscale thermodynamics to the macroscale, the impact of subscale variations is retained in the formulation. It can be eliminated through assumptions, but one is forced to identify explicitly any assumptions and therefore consider them as sources of error in matching data to theory.

Second, Eqn (84) does not account properly for disequilibrium due to the dynamics of interfacial rearrangement at constant saturation. This process would seem to be important. In fact, when running an experiment to measure the capillary pressure-saturation relation, some relaxation of the system will occur even after the flow into the test cell has ceased. The rearrangement of interfaces is an important process that is not accounted for in the expression on the left side of Eqn (84). This means that experimental observations employed to obtain the parameter,  $\hat{\tau}_A$ , by measuring pressures and saturation as a function of time will not provide particularly useful information if interface non-uniformities are important. The problem is that based on Eqn (84),  $\hat{\tau}_A$  will have to serve as the parameter that relates to the influence of saturation changes on capillary dynamics and also will have to account for the physical dynamics of interface reshaping as embodied in the term  $e^{\overline{wn}}$ . Not surprisingly, experimental studies have demonstrated great variability in  $\hat{\tau}_A$ , which has not been explained. Based on the present analysis, at least one component of this variability seems to lie in the neglect of some of the system dynamics in formulating the equation for capillary pressure evolution. When the curvature is uniform within the averaging volume, Eqn (84) might seem to have greater utility in modeling the system. However, the presence of a solid phase with its distribution of pore sizes and corners would seem to preclude the case of uniform curvature in most instances.

### 10.3 More Complete Dynamic Model

With reference to Eqn (78), a complete model of capillary dynamics will result if all of the terms are accounted for in the formulation. However, in most studies, the interfacial tension is considered constant so that  $e^{\overline{wn}}$  as defined in Eqn (58) will be zero. Additionally, the difference in pressure difference is expected to become uniform much more quickly than the interfaces will reach a uniform profile. Therefore,  $e_p^{\overline{wn}}$  can be neglected relative to  $\gamma^{wn} e^{\overline{wn}}$ , except, perhaps, at very small times after a change in pressure. The challenge then becomes to develop a form for  $e^{\overline{wn}}$  that both properly accounts for the physics and is useful in obtaining a linearized force-flux form. In [8], the assumption was made that  $e^{\overline{wn}}$  is linearly proportional to  $\varepsilon^{wn} - \varepsilon_{eq}^{wn}$  where  $\varepsilon_{eq}^{wn} = \varepsilon_{eq}^{wn}(s^w, J_w^{wn})$  and the coefficient of proportionality is denoted as  $\hat{k}^{wn}$ . Whether, indeed, this relation is linear should be studied experimentally. The state function  $\varepsilon_{eq}^{wn}(s^w, J_w^{wn})$  is an inversion of the function  $p^c(s^w, e^{wn})/\gamma^{wn}$  obtained under equilibrium conditions. This observation carries the implication that if  $p^c$  is not a function of  $e^{wn}$ , then the importance of  $e^{\overline{wn}}$  in describing capillary dynamics is negligible. The parameter  $\hat{k}^{wn}$  must be a function of system properties, and the considerations for obtaining the force-flux form have resulted in the form given by Eqn (65), indicate it can be expressed in terms of the macroscale variables when contributions due to interface density are negligible as:

$$\widehat{k}^{wn} = \left( \frac{p^c}{p^n - p^w} - 1 \right) \widehat{k}_1^{wn}. \quad (85)$$

For the case where the macroscale fluid pressure obtained as an average over the  $wn$  interface is approximately equal to the average of the pressure over its phase, Eqn (70) becomes:

$$\widehat{\tau}_A \left[ \varepsilon \frac{\partial s^w}{\partial t} + \frac{\gamma^{wn}}{p^n - p^w} \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] = p^w - p^n + p^c. \quad (86)$$

This equation contains two parameters that must be obtained to model capillary dynamics. Experimental studies may indicate an appropriate functional form for  $\widehat{\tau}_A$  and for  $\widehat{k}_1^{wn}$ . For the expressions here, if they are treated as constants, we see that the approach of the interfacial area densities to equilibrium will be slower at small saturations where  $p^n - p^w$  becomes large. This seems reasonable from physical considerations of the reduced mobility of the wetting phase at low saturations and also has implications for the measurements of the equilibrium capillary pressure as a function of saturation and interfacial area. Measurements made at low saturations will require a longer equilibration time than those made at larger saturations.

Finally, based on Eqns (76) and (77) as well as the considerations in this section, the alternative to Eqn (86) that can be used to model capillary dynamics is:

$$\widehat{\tau}_A \frac{\gamma^{wn}}{p^c} \left[ \frac{\partial \varepsilon^{wn}}{\partial t} + \nabla \cdot (\varepsilon^{wn} \mathbf{w}^{wn}) - \frac{\partial \varepsilon^{ws}}{\partial t} \cos \varphi^{ws,wn} - \widehat{k}_1^{wn} (\varepsilon^{wn} - \varepsilon_{eq}^{wn}) \right] = -(p^w - p^n + p^c). \quad (87)$$

This equation can be compared to Eqn (86). Note that the right sides differ only by a minus sign. Therefore, the expression in brackets in Eqn (87) scaled by  $-\gamma^{wn}/p^c$  will equal the expression in brackets in Eqn (86). This equality is consistent with the evolution equation for  $\varepsilon^{wn}$  derived in [8].

## 11 Conclusion

The issue of capillary dynamics is one that has received increasing interest in modeling multiphase fluid flow in porous media. Here, we have shown that based on thermodynamic expressions averaged from the microscale to the macroscale, the relaxation of a system toward the equilibrium equality between fluid pressure differences and capillary pressure is dependent on both the rate of change of saturation and the rate of adjustment of the interfacial area density to an equilibrium configuration. This latter feature does not emerge in methods that propose system thermodynamics at the macroscale. Based on the TCAT approach to thermodynamics, the elements and assumptions that are incorporated in a dynamic expression for capillary pressure dynamics become explicit. The expectation that interface rearrangement as well as saturation changes are important to the dynamics suggests that efforts to parameterize an equation that does not account for this process neglects important system physics.

## Acknowledgments

This work was supported by National Science Foundation grant ATM-0941235, Department of Energy grant DE-SC0002163, and National Institute of Environmental Health Sciences grant P42 ES05948.

## Abbreviations

### Roman letters

$A$	velocity of the normal fluid-fluid interface velocity relative to the macroscale solid-phase velocity
$B$	velocity of the normal fluid-fluid interface velocity relative to the macroscale solid-phase velocity multiplied by the interfacial curvature
$\mathbf{d}$	rate of strain tensor
$\overline{e}^{wn}$	error or deviation terms relating to interface curvature dynamics
$\overline{e}_p^{wn}$	error or deviation terms relating to pressure dynamics
$\overline{e}_\gamma^{wn}$	error or deviation terms relating to interfacial tension dynamics
$\mathbf{G}$	geometric orientation tensor
$\mathbf{g}$	gravity vector
$J_w$	microscale surface curvature defined as the surface divergence of the outward normal from phase $w$
$J_{wc}$	denotes case when $J_w$ is constant within an REV
$J_w^{wn}$	macroscale surface curvature defined as the average over the $wn$ interface of the surface divergence of the outward normal from phase $w$
$\hat{k}^{wn}$	generation rate coefficient for interfacial area
$\widehat{k}_1^{wn}$	modified generation rate coefficient for interfacial area
$\mathbf{n}_w$	outward normal vector from $w$ phase on its boundary
$\overline{\mathbf{n}}_w^{wn}$	$= \langle \mathbf{n}_w \rangle_{\Omega_{wn}, \Omega_{wn}, \rho_{wn}}$ , density weighted average of $\mathbf{n}_w$ over the $wn$ interface
$\mathbf{n}_{wn}$	tangent vector to the $wn$ surface and outward normal from the bounding common curve $wns$
$P_{wn}$	microscale function at the fluid-fluid interface equal to the pressure in the wetting phase minus the pressure in the non-wetting phase plus the jump in pressure due to the density of the material in the interface and gravity
$\overline{P}^{wn}$	average of $P_{wn}$ over the $wn$ interface
$p$	fluid pressure
$s$	saturation
$T_\eta$	term appearing in the full entropy inequality
$t$	time
$\mathbf{v}$	velocity
$\overline{\mathbf{w}}^{wn}$	average of the normal component of the velocity of the $wn$ interface over the $wn$ interface

**Greek letters**

$\gamma$	interfacial tension
$\varepsilon$	porosity
$\varepsilon^s$	volume fraction of the $s$ phase
$\varepsilon^{ss}$	specific surface area of the $s$ phase
$\varepsilon^w$	volume fraction of the $w$ phase
$\varepsilon^{wn}$	area of the $wn$ interface per averaging volume
$\varepsilon^{wns}$	length of the $wns$ common curve per averaging volume
$\theta$	temperature
$\rho$	mass density
$\hat{\tau}$	coefficient in linearized force-flux relation for capillary pressure dynamics
$\overline{\varphi}_{ws,wn}$	average contact angle between the $ws$ and $wn$ interfaces
$\chi_{ws}^{ss}$	fraction of the solid surface in contact with the $w$ phase
$\Omega$	spatial domain of the averaging volume
$\Omega_{wn}$	domain of the $wn$ interface within the averaging volume

**Subscripts (for microscale) and superscripts (for macroscale)**

$A$	subscript associated with average of $A$
$B$	subscript associated with average of $B$
$c$	constant value
$c$	used with $p$ to indicate capillary pressure
<b>eq</b>	equilibrium value
$n$	non-wetting-phase qualifier
$ns$	qualifier for interface formed by the intersection of the non-wetting and solid phases
$s$	solid-phase qualifier
$ss$	solid surface qualifier
$w$	wetting-phase qualifier
$wn$	qualifier for interface formed by the intersection of wetting and non-wetting phases
$wns$	qualifier for common curve formed by the intersection of the wetting, non-wetting, and solid phases
$ws$	qualifier for interface formed by the intersection of wetting and solid phases

**Symbols**

$\nabla'$	surface divergence vector
–	above a superscript refers to a density weighted macroscale average
=	above a superscript refers to a uniquely defined macroscale average with the definition provided in the text

$\mathbf{t}$	vector tangent to a surface
$\wedge$	a parameter defined at the scale indicated by the subscript or superscript on the parameter
$\langle F_\alpha \rangle_{\Omega_b, \Omega_c, f}$	$= \left( \int_{\Omega_b} f F_\alpha \, d\mathbf{r} \right) / \left( \int_{\Omega_c} f \, d\mathbf{r} \right)$ , general average of a property associated with entity $\alpha$
$\langle F_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha}$	$= F^\alpha = \left( \int_{\Omega_\alpha} F_\alpha \, d\mathbf{r} \right) / \left( \int_{\Omega_\alpha} d\mathbf{r} \right)$ , macroscale volume average of a phase (interface) property over the phase (interface)
$\langle F_\alpha \rangle_{\Omega_\alpha, \Omega_\alpha, \rho_\alpha}$	$= F^{\bar{\alpha}} = \left( \int_{\Omega_\alpha} \rho_\alpha F_\alpha \, d\mathbf{r} \right) / \left( \int_{\Omega_\alpha} \rho_\alpha \, d\mathbf{r} \right)$ , density weighted macroscale average of a property of an entity over that entity
$F_\alpha^{\alpha\beta}$	$= \langle F_\alpha \rangle_{\Omega_{\alpha\beta}, \Omega_{\alpha\beta}}$ , average of a property of phase $\alpha$ over the $\alpha\beta$ interface
$\mathbf{D}^{\bar{\alpha}}/\mathbf{D}t$	material derivative, $\partial/\partial t + \mathbf{v}^{\bar{\alpha}} \cdot \nabla$

### Abbreviations

<b>REV</b>	representative elementary volume for averaging from the microscale to the macroscale
<b>TCAT</b>	thermodynamically constrained averaging theory

### References

1. Barenblatt GI. Flow of two immiscible fluids in homogeneous porous medium (in Russian). *Izv AN SSSR, Mekh Zhidk i Gaza*. 1971; 5:144–151.
2. Barenblatt, GI.; Patzek, TW.; Silin, DB. The mathematical model of non-equilibrium effects in water-oil displacement. *Proceedings of the SPE/DOE 13th Symposium on Improved Oil Recovery*, number SPE75169; Tulsa, OK. 13–17 April 2002;
3. Beliaev AY, Hassanizadeh SM. A theoretical model of hysteresis and dynamic effects in the capillary relation for two-phase flow in porous media. *Transport in Porous Media*. 2001; 43:487–510.
4. Chen D, Pyrak-Nolte LJ, Griffin J, Giordano NN. Measurement of interfacial area per volume for drainage and imbibition. *Water Resources Research*. 2007; 43:10.1029/2007WR006021
5. de Gennes PG. Dynamic capillary pressure in porous media. *Europhysics Letters*. 1988; 5:689–691.
6. Gamps-Roach G, O’Carroll DM, Newson TA, Sakaki T, Illangasekare TH. Experimental investigation of dynamic effects in capillary pressure: Grain size dependency and upscaling. *Water Resources Research*. 2010; 46(W08544)10.1029/2009WR008881
7. Gray WG, Hassanizadeh SM. Paradoxes and realities in unsaturated flow theory. *Water Resources Research*. 1991; 27(8):1847–1854.
8. Gray WG, Miller CT. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 8. Interface and common curve dynamics. *Advances in Water Resources*. 2010; 10.1016/j.advwatres.2010.01.010
9. Gray, WG.; Leijnse, A.; Kolar, RL.; Blain, CA. *Mathematical Tools for Changing Spatial Scales in the Analysis of Physical Systems*. CRC Press; Boca Raton: 1993.
10. Hassanizadeh SM, Gray WG. Mechanics and thermodynamics of multiphase flow in porous media including interphase boundaries. *Advances in Water Resources*. 1990; 13(4):169–186.

11. Hassanizadeh SM, Celia MA, Dahle HK. Dynamic effect in the capillary pressure-saturation relationship and its impact on unsaturated flow. *Vadose Zone Journal*. 2002; 1:38–57.
12. Jackson ABS, Miller CT, Gray WG. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 6. Two-fluid-phase flow. *Advances in Water Resources*. 2009; 32(6):779–795.
13. Kalaydjian F. A macroscopic description of multiphase flow in porous media involving spacetime evolution of fluid/fluid interface. *Transport in Porous Media*. 1987; 2:537–552.
14. Miller CT, Christakos G, Imhoff PT, McBride JF, Pedit JA, Trangenstein JA. Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches. *Advances in Water Resources*. 1998; 21(2):77–120.
15. Mirzaei M, Das DB. Dynamic effects in capillary pressure-saturations relationships for two-phase flow in 3D porous media: Implications of micro-heterogeneities. *Chemical Engineering Science*. 2007; 62(7):1927–1947.
16. Morrow NR. Irreducible wetting-phase saturations in porous media. *Chemical Engineering Science*. 1970; 25:1799–1815.
17. Papafotiou, A. Master's thesis. Universität Stuttgart; 2004. Interpretation of simulation results including a dynamic capillary pressure relationship.
18. Porter ML, Schaap MG, Wildenschild D. Lattice-Boltzmann simulations of the capillary pressure-saturation-interfacial area relationship for porous media. *Advances in Water Resources*. 2009; 32(11):1632–1640.
19. Reeves PC, Celia MA. A functional relationship between capillary pressure, saturation, and interfacial area as revealed by a pore-scale network model. *Water Resources Research*. 1996; 32(8):2345–2358.
20. Sakaki T, O'Carroll DM, Illangasekare TH. Direct quantification of dynamic effects in capillary pressure for drainage-wetting cycles. *Vadose Zone Journal*. 2010; 9:424–437.
21. Stauffer, F. Time dependence of the relations between capillary pressure, water content and conductivity during drainage of porous media. *International IAHR Symposium on Scale Effects in Porous Media*; Thessaloniki, Greece. 1978.
22. Tsakiroglou CD, Theodoropoulou MA, Karoutsos V. Nonequilibrium capillary pressure and relative permeability curves of porous media. *AIChE Journal*. October; 2003 49(10):2472–2486.
23. Weitz DA, Stokes JP, Ball RC, Kushnick AP. Dynamic capillary pressure in porous media: Origin of the viscous-fingering length scale. *Physical Review Letters*. 1987; 59(26):2967–2969. [PubMed: 10035699]