Modeling and simulation of macrocapillarity

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Abstract. Macroscopic capillarity. or macrocapillarity for short, refers to capillary phenomena occurring during twophase and multiphase flow in porous media. Wetting phenomena and hysteresis in porous media are at present poorly understood in the sense that neither in physics nor in engineering a fully predictive theory seems to exist, that can describe or predict all observations. This paper extends the constitutive assumptions of a recent approach based on the concept of hydraulic percolation of fluid phases. The theory proposed here allows prediction of residual saturations. It can describe displacement processes in which imbibition and drainage occur simultaneously. This contrasts with the established traditional theory where capillary forces are lumped into capillary pressure function and relative permeabilities, and these functions need to be specified for each displacement process as input. Contrary to the traditional theory the approach advanced here allows to predict capillary pressure saturation relations as output.

Keywords: capillarity, hysteresis, residual saturation, multiphase flow, porous media, immiscible displacement

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INTRODUCTION

A predictive macroscopic theory of two phase fluid flow inside a rigid porous medium is a longstanding and unsolved problem in statistical and computational physics of fluids, soft matter, and disordered systems [1, 2, 3, 4, 5, 6]. Describing and predicting the flow of two immiscible and incompressible fluids through a complex disordered geometry is not only of interest for statistical physics, but also of significant practical importance for many applied sciences such as hydrology, petroleum engineering and other applied fields [7, 8, 9, 10].

Many authors have proposed microscopic models (e.g. network models) to predict macroscopic immiscible displacement in porous media. An important motivation for these investigations are the longstanding unsolved problems with the traditional macroscopic equations that are based on the concepts of capillary pressure and relative permeabilities (see e.g. [7, 9]). In particular, one fundamental problem is the nonuniqueness of the capillary pressure as function of saturation. Other problems with the capillary pressure are its hysteresis, process dependence and dynamic effects such as dependence on velocities or rates of saturation change. Residual saturations are not constant parameters as it is assumed in the traditional macroscopic theory. Experimental observations show instead that residual saturations vary as functions of position and time. Most practitioners ignore these problems and continue to use the traditional set of equations, and many physicists are following their lead by calculating effective relative permeabilities pertaining to the traditional theory.

Droplets or ganglia of one fluid phase hinder the flow of the other fluid phase.

Experimental observations of this basic phenomenon abound [11, 12, 13, 14, 15, 16, 17, 18]. It is therefore surprising that the importance of hydraulic percolation for theoretical modeling of two phase flow seems to have remained unnoticed until recently [19, 20, 21, 22, 23, 24, 25].

Given that a basic constitutive approach to hydraulic percolation for macroscopic capillarity has been presented in [22, 23, 24] my objective in this paper is to extend that basic approach towards a more realistic description. Let me begin the discussion with the mathematical ingredients of the hydraulic percolation approach. One ingredient is the introduction of four phases instead of two, a second are balance laws for volume mass and momentum, and the third are the constitutive assumptions. It is the third ingredient where extensions and modifications of the assumptions in [22, 23, 24] will be made. An extensive discussion of the modified constitutive assumptions as well as their consequences and comparison to previous theories cannot be presented due to the page limit. More details will be given elsewhere.

DEFINITION OF PHASES

A porous sample $\mathbb{S}=(\mathbb{P}\cup\mathbb{M})\subset\mathbb{R}^3$ consists of a subset \mathbb{P} (called pore space) and a subset M (called matrix). The pore space P contains two immiscible fluids, namely a wetting fluid, called water and denoted as W, plus a nonwetting fluid, called oil and denoted as O.

Each of the two fluids W, O consists of disjoint and pathconnected subsets (regions) $\mathbb{W}_i, \mathbb{O}_i$. More precisely one has

$$\mathbb{W} = \bigcup_{i=1}^{N_{\mathbb{W}}} \mathbb{W}_{i}$$

$$\mathbb{O} = \bigcup_{i=1}^{N_{\mathbb{O}}} \mathbb{O}_{i}$$
(1a)

$$\mathbb{O} = \bigcup_{i=1}^{N_{\mathbb{O}}} \mathbb{O}_i \tag{1b}$$

where the subsets $\mathbb{W}_i, \mathbb{O}_i$ are mutually disjoint, and each of them is pathconnected. A set is called pathconnected if any two of its points can be connected by a path contained inside the set. The sets are called mutually disjoint if $\mathbb{O}_i \cap \mathbb{O}_j = \emptyset$ and $\mathbb{W}_i \cap \mathbb{W}_j = \emptyset$ holds for all $i \neq j$. The integers $N_{\mathbb{W}}, N_{\mathbb{O}}$ give the total number of pathconnected subsets for water resp. oil. These numbers vary with time, as do the regions $\mathbb{W}_i, \mathbb{O}_i$.

Now define percolating $(\mathbb{F}_1, \mathbb{F}_3)$ and nonpercolating $(\mathbb{F}_2, \mathbb{F}_4)$ fluid regions by classifying the subsets $\mathbb{W}_i, \mathbb{O}_i$ as to whether they have empty or nonempty intersection with the sample boundary ∂S . More formally, define

$$\mathbb{F}_1 = \bigcup_{\substack{i=1\\ \partial \mathbb{W}_i \cap \partial \mathbb{S} \neq \emptyset}}^{N_{\mathbb{W}}} \mathbb{W}_i \tag{2a}$$

$$\mathbb{F}_{2} = \bigcup_{\substack{i=1\\ \partial \mathbb{W}_{i} \cap \partial \mathbb{S} = \emptyset}}^{N_{\mathbb{W}}} \mathbb{W}_{i} \tag{2b}$$

$$\mathbb{F}_{3} = \bigcup_{\substack{i=1\\\partial \mathbb{O}_{i} \cap \partial \mathbb{S} \neq \emptyset}}^{N_{\mathbb{O}}} \mathbb{O}_{i} \tag{2c}$$

$$\mathbb{F}_{1} = \bigcup_{\substack{i=1\\ \partial \mathbb{W}_{i} \cap \partial \mathbb{S} \neq \emptyset}}^{N_{\mathbb{W}}} \mathbb{W}_{i} \qquad (2a)$$

$$\mathbb{F}_{2} = \bigcup_{\substack{i=1\\ \partial \mathbb{W}_{i} \cap \partial \mathbb{S} = \emptyset}}^{N_{\mathbb{W}}} \mathbb{W}_{i} \qquad (2b)$$

$$\mathbb{F}_{3} = \bigcup_{\substack{i=1\\ \partial \mathbb{Q}_{i} \cap \partial \mathbb{S} \neq \emptyset}}^{N_{\mathbb{Q}}} \mathbb{Q}_{i} \qquad (2c)$$

$$\mathbb{F}_{4} = \bigcup_{\substack{i=1\\ \partial \mathbb{Q}_{i} \cap \partial \mathbb{S} = \emptyset}}^{N_{\mathbb{Q}}} \mathbb{Q}_{i} \qquad (2d)$$

so that \mathbb{F}_1 is the union of all regions \mathbb{W}_i , and \mathbb{F}_3 is the union of all regions \mathbb{O}_i , that have nonempty intersection with the sample boundary ∂S . Similarly \mathbb{F}_2 is the union of all regions \mathbb{W}_i that have empty intersection with $\partial \mathbb{S}$, and similarly for \mathbb{F}_4 . In this way each point in \mathbb{P} belongs to one of four regions \mathbb{F}_i , i = 1, 2, 3, 4. This results in a total of four fluid phases called percolating resp. nonpercolating water, and percolating resp. nonpercolating oil. The index i = 5 will be used for the rigid matrix M.

BALANCE LAWS

Let $V=V_{\mathbb{S}}$ denote the sample volume, $V_{\mathbb{P}}$ denote the volume of pore space, $V_{\mathbb{W}}$ the volume filled with water, $V_{\mathbb{Q}}$ the volume filled with oil, $V_{\mathbb{M}} = V_{5}$ the volume occupied by matrix, and $V_i = V_{\mathbb{F}_i}$ the volumes of the subsets $\mathbb{F}_i \subset \mathbb{S}, i = 1, 2, 3, 4$. The volumes are defined as

$$V_{\mathbb{G}} = \int_{\mathbb{R}^3} \chi_{\mathbb{G}}(\mathbf{y}) d^3 \mathbf{y}$$
 (3)

where $i = \mathbb{F}_1, \mathbb{F}_2, \mathbb{F}_3, \mathbb{F}_4, \mathbb{S}, \mathbb{P}, \mathbb{M}, \mathbb{W}, \mathbb{O}$, and

$$\chi_{\mathbb{G}}(\mathbf{y}) = \begin{cases} 1 & , \mathbf{y} \in \mathbb{G} \\ 0 & , \mathbf{y} \notin \mathbb{G} \end{cases} \tag{4}$$

is the characteristic function of a set G. Then volume conservation implies

$$V_{\mathbb{S}} = V = V_{\mathbb{P}} + V_{\mathbb{M}} = V_{\mathbb{W}} + V_{\mathbb{O}} + V_{\mathbb{M}} = \sum_{i=1}^{5} V_{i}$$
 (5a)

$$V_{\mathbb{W}} = V_1 + V_2 \tag{5b}$$

$$V_{\mathbb{O}} = V_3 + V_4 \tag{5c}$$

where $V_5 = V_{\mathbb{M}}$. The volume fraction $\phi = V_{\mathbb{P}}/V$ is called total or global porosity. The volume fraction $V_{\mathbb{W}}/V_{\mathbb{P}} = (V_{\mathbb{W}}/V)/\phi$ is the total or global water saturation, and analogous intensive quantities can be defined for the other phases.

Often the saturations are not constant but vary on macroscopic scales. Local volume fractions are defined by introducing a one parameter family of functions $X^{\varepsilon}_{\mathbb{G}}: \mathbb{R}^3 \times \mathbb{R}^3 \to \mathbb{R}$ by defining $X^1(\mathbf{x},\mathbf{x}) = \chi_{\mathbb{G}}(\mathbf{x})$ on the diagonal and then extending it as

$$X_{\mathbb{C}_{\tau}}^{\varepsilon}(\mathbf{x},\mathbf{y}) = X_{\mathbb{C}_{\tau}}^{1}(\mathbf{x},\mathbf{x}/\varepsilon) \tag{6}$$

to the full space. Here $\varepsilon > 0$ is the scale separation parameter, and $y = x/\varepsilon$ is the fast variable. For an infinite sample $\mathbb{S} = \mathbb{R}^3$ the local volume fractions may be defined as

$$\phi_{\mathbb{G}}(\mathbf{x}) = \lim_{\varepsilon \to 0} \frac{3\varepsilon^3}{4\pi} \int_{\mathbb{B}(\mathbf{x}, 1/\varepsilon)} X_{\mathbb{G}}^{\varepsilon}(\mathbf{x}, \mathbf{y}) d^3 \mathbf{y}$$
 (7)

where $\mathbb{G} = \mathbb{F}_1, \mathbb{F}_2, \mathbb{F}_3, \mathbb{F}_4, \mathbb{S}, \mathbb{P}, \mathbb{M}, \mathbb{W}, \mathbb{O}$, and $\mathbb{B}(\mathbf{x}, 1/\varepsilon)$ is a sphere of radius $1/\varepsilon$ centered at \mathbf{x} with volume $4\pi/(3\varepsilon^3)$. In the following it is assumed that the limit exists, but may in general depend also on time so that the local volume fractions $\phi_i(\mathbf{x}, t)$ become position and time dependent. Local volume conservation implies the relations

$$\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 = 1 \tag{8a}$$

$$S_1 + S_2 + S_3 + S_4 = 1$$
 (8b)

$$1 - \phi = \phi_5 \tag{8c}$$

where $\phi_i = \phi S_i$ (i = 1, 2, 3, 4) are volume fractions, and S_i are saturations. The water saturation is defined as $S_{\mathbb{W}} = S_1 + S_2$, and the oil saturation as $S_{\mathbb{Q}} = 1 - S_{\mathbb{W}} = S_3 + S_4$. The general law of mass balance in differential form reads (i = 1, 2, 3, 4)

$$\frac{\partial (\phi_i \rho_i)}{\partial t} + \nabla \cdot (\phi_i \rho_i \mathbf{v}_i) = M_i = \sum_{i=1}^5 M_{ij}$$
(9)

where $\rho_i(\mathbf{x},t)$, $\phi_i(\mathbf{x},t)$, $\mathbf{v}_i(\mathbf{x},t)$ denote mass density, volume fraction and velocity of phase $i = \mathbb{W}$, \mathbb{O} as functions of position $\mathbf{x} \in \mathbb{S} \subset \mathbb{R}^3$ and time $t \in \mathbb{R}_+$. Exchange of mass between the two phases is described by mass transfer rates M_i giving the amount of mass by which phase i changes per unit time and volume. The rate M_{ij} is the rate of mass transfer from phase j into phase i.

The law of momentum balance is formulated as (i = 1, 2, 3, 4)

$$\phi_i \rho_i \frac{D^i}{D^i} \mathbf{v}_i - \phi_i \nabla \cdot \Sigma_i - \phi_i \mathbf{F}_i = \mathbf{m}_i - \mathbf{v}_i M_i$$
(10)

where Σ_i is the stress tensor in the *i*th phase, \mathbf{F}_i is the body force per unit volume acting on the *i*th phase, \mathbf{m}_i is the momentum transfer into phase *i* from all the other phases, and

$$\frac{\mathbf{D}^{i}}{\mathbf{D}t} = \frac{\partial}{\partial t} + \mathbf{v}_{i} \cdot \nabla \tag{11}$$

denotes the material derivative for phase $i = \mathbb{W}, \mathbb{O}$.

CONSTITUTIVE ASSUMPTIONS

The porous medium is assumed to be macroscopically homogeneous

$$\phi(\mathbf{x}) = \phi = \text{const} \tag{12}$$

although this assumption rarely holds in practice [26]. Let us further assume that the fluids are incompressible so that

$$\rho_1(\mathbf{x},t) = \rho_{\mathbb{W}} \tag{13a}$$

$$\rho_2(\mathbf{x},t) = \rho_{\mathbb{W}} \tag{13b}$$

$$\rho_3(\mathbf{x},t) = \rho_{\mathbb{O}} \tag{13c}$$

$$\rho_4(\mathbf{x},t) = \rho_{\mathbb{O}} \tag{13d}$$

where the constants $\rho_{\mathbb{W}}$, $\rho_{\mathbb{Q}}$ are independent of **x** and *t*.

Flows through porous media often have low Reynolds numbers. Thus accelerations and the inertial term

$$\frac{\mathbf{D}^i}{\mathbf{D}t}\mathbf{v}_i = 0 \tag{14}$$

can be neglected in the momentum balance equation (10).

The momentum transfer into phase i from all the other phases is assumed to arise from viscous drag,

$$\mathbf{m}_i = \sum_{j=1}^5 R_{ij}(\mathbf{v}_j - \mathbf{v}_i) \tag{15}$$

with resistance coefficients R_{ij} quantifying the loss due to viscous friction between phase i and j. The matrix is assumed to be rigid so that $\mathbf{v}_5 = 0$. Hence $-R_{i5}\mathbf{v}_i$ is the momentum transfer from the wall into phase i. Then

$$\mathbf{m}_1 = R_{13}(\mathbf{v}_3 - \mathbf{v}_1) + R_{14}(\mathbf{v}_4 - \mathbf{v}_1) - R_{15}\mathbf{v}_1$$
 (16a)

$$\mathbf{m}_2 = R_{23}(\mathbf{v}_3 - \mathbf{v}_2) + R_{24}(\mathbf{v}_4 - \mathbf{v}_2) - R_{25}\mathbf{v}_2$$
 (16b)

$$\mathbf{m}_3 = R_{31}(\mathbf{v}_1 - \mathbf{v}_3) + R_{32}(\mathbf{v}_2 - \mathbf{v}_3) - R_{35}\mathbf{v}_3$$
 (16c)

$$\mathbf{m}_4 = R_{41}(\mathbf{v}_1 - \mathbf{v}_4) + R_{42}(\mathbf{v}_2 - \mathbf{v}_4) - R_{45}\mathbf{v}_4$$
 (16d)

where $R_{12} = 0$ and $R_{34} = 0$ was used because there is no common interface and hence no direct viscous interaction between these phase pairs. The viscous resistance coefficients R_{ij} may be rewritten in term of dimensionless coefficients r_{ij} as

$$R_{ij} = \mu_{\mathbb{W}} k^{-1} r_{ij}, \qquad i = 1, 2$$
 (17a)
 $R_{ij} = \mu_{\mathbb{Q}} k^{-1} r_{ij}, \qquad i = 3, 4$ (17b)

$$R_{ij} = \mu_{\mathbb{O}} k^{-1} r_{ij}, \qquad i = 3,4$$
 (17b)

where $\mu_{\mathbb{W}}, \mu_{\mathbb{O}}$ are the viscosities of water and oil, k is the absolute permeability tensor of the medium, and r_{ij} are dimensionless viscous drag coefficients. Each R_{ij} is a 3 × 3matrix. In practice viscous coupling terms between the two fluid phases are often neglected.

The stress tensor is written as a pressure term plus a capillary correction term. The reference pressure for the nonpercolating phases is the pressure of the surrounding percolating phase [24]. Thus

$$\Sigma_1 = -P_{\mathbb{W}} \mathbf{1} + \Sigma_{c1} \tag{18a}$$

$$\Sigma_2 = -P_{\mathbb{O}} \mathbf{1} + \Sigma_{C2} \tag{18b}$$

$$\Sigma_3 = -P_{\mathbb{O}} \mathbf{1} + \Sigma_{c3} \tag{18c}$$

$$\Sigma_4 = -P_{\mathbb{W}} \mathbf{1} + \Sigma_{c4}, \tag{18d}$$

where Σ_{ci} are capillary stresses resulting from the presence of fluid-fluid and fluid-matrix interfaces.

Similarly, the body forces are augmented with capillary body forces as

$$\mathbf{F}_i = \rho_i \mathbf{g} + \mathbf{F}_{ci} \tag{19}$$

with i = 1, 2, 3, 4. The capillary body forces \mathbf{F}_{ci} are responsible for keeping the trapped fluids inside the medium. They are assumed to be potential forces

$$\mathbf{F}_{ci} = -\nabla \Pi_{ci} \tag{20}$$

where Π_{ci} are the capillary potentials.

One has considerable freedom to specify the capillary stresses Σ_{ci} and potentials Π_{ci} . General thermodynamic considerations suggest ideas to restrict this freedom. Let F denote the total Helmholtz free energy of the system with and oil-water interface, and let $F_{\mathbb{W}}$ and $F_{\mathbb{O}}$ denote the individual Helmholtz free energies of bulk water and bulk oil. Then [27, 28]

$$dF = -P_{\mathbb{W}} dV_{\mathbb{W}} - P_{\mathbb{O}} dV_{\mathbb{O}} + \sigma_{\mathbb{W}\mathbb{O}} d\widetilde{A}_{\mathbb{W}\mathbb{O}} + \sigma_{\mathbb{W}\mathbb{M}} d\widetilde{A}_{\mathbb{W}\mathbb{M}} + \sigma_{\mathbb{O}\mathbb{M}} d\widetilde{A}_{\mathbb{O}\mathbb{M}}$$
(21)

where $P_{\mathbb{W}}, P_{\mathbb{O}}$ are the oil and water pressure, $V_{\mathbb{W}}, V_{\mathbb{O}}$ are the volumes of oil and water, and $\widetilde{A}_{\mathbb{WO}}, \widetilde{A}_{\mathbb{WM}}, \widetilde{A}_{\mathbb{OM}}$ are the total interfacial areas between oil and water, water and matrix, resp. oil and matrix. The oil-water surface tension $\sigma_{\mathbb{WO}}$ and the fluid-matrix interfacial tensions $\sigma_{\mathbb{WM}}, \sigma_{\mathbb{OM}}$ are related by Youngs equation

$$\sigma_{\text{OM}} = \sigma_{\text{WM}} + \sigma_{\text{WO}} \cos(\vartheta) \tag{22}$$

where ϑ is the contact angle of water. The interfacial areas obey

$$\widetilde{A}_{\mathbb{W}\mathbb{O}} = \widetilde{A}_{31} + \widetilde{A}_{32} + \widetilde{A}_{41} + \widetilde{A}_{42} \tag{23}$$

$$\widetilde{A}_{\mathbb{PM}} = \widetilde{A}_{\mathbb{WM}} + \widetilde{A}_{\mathbb{OM}}$$
 (24)

$$\widetilde{A}_{\mathbb{WM}} = \widetilde{A}_{15} + \widetilde{A}_{25} \tag{25}$$

$$\widetilde{A}_{\mathbb{OM}} = \widetilde{A}_{35} + \widetilde{A}_{45} \tag{26}$$

where \widetilde{A}_{ij} is the total interfacial area between phase i and j, and the volumes are related by eqs. (5b) and (5c).

In equilibrium dF = 0 holds. Also, sample volume and internal surface are constant because the porous medium is rigid. This implies dV = 0 and $d\widetilde{A}_{\mathbb{PM}} = 0$. Using eq. (5c) one arrives at

$$0 = P_{\mathbb{O}} - P_{\mathbb{W}} + \sigma_{\mathbb{WO}} \left(\frac{\partial \widetilde{A}_{\mathbb{WO}}}{\partial V_{\mathbb{W}}} - \cos \vartheta \frac{\partial \widetilde{A}_{\mathbb{WM}}}{\partial V_{\mathbb{W}}} \right)$$
(27)

where Youngs equation (22) was also used.

These considerations suggest one particular way to specify the capillary stresses and potentials. Following earlier ideas [24] the capillary stresses are specified as

$$\Sigma_{c1} = 0 \tag{28a}$$

$$\Sigma_{c2} = -\frac{\sigma_{\mathbb{W}\mathbb{O}}}{\phi} \frac{\partial A_{\mathbb{W}\mathbb{O}}}{\partial S_{\mathbb{W}}} \tag{28b}$$

$$\Sigma_{c3} = 0 \tag{28c}$$

$$\Sigma_{c4} = -\Sigma_{c2} \tag{28d}$$

where local equilibrium was assumed and intensive quantities (per unit volume of porous medium) were introduced. The capillary potentials may be associated with the last term in eq. (27). They are specified as

$$\Pi_{c1} = 0 \tag{29a}$$

$$\Pi_{c2} = \frac{\sigma_{\mathbb{WO}}}{\phi} \cos \vartheta \frac{\partial A_{\mathbb{WM}}}{\partial S_{\mathbb{W}}}$$
 (29b)

$$\Pi_{c3} = 0 \tag{29c}$$

$$\Pi_{c4} = -\Pi_{c2} \tag{29d}$$

in analogy with [23, 24].

The mass transfer rates are $M_i = \sum_{j=1}^5 M_{ij}$ where M_{ij} is the mass transfer rate from phase j into phase i. Neglecting chemical reactions one assumes $M_{ij} = 0$ for all pairs (i,j) except the pairs (1,2),(2,1),(3,4),(4,3). These remaining transfer rates are assumed to be given as

$$M_{12} = -M_{21} = \phi \rho_{\mathbb{W}} \left\{ [b_1(1 - S_2) - b_2 S_2] \Theta_{\mathbb{W}}^* + \eta_2 \left(\frac{S_2 - S_2^*}{S_{\mathbb{W}}^* - S_{\mathbb{W}}} \right) \frac{\partial S_{\mathbb{W}}}{\partial t} \right\} (30a)$$

$$M_{34} = -M_{43} = \phi \rho_{\mathbb{O}} \left\{ [b_3(1 - S_4) - b_4 S_4] \Theta_{\mathbb{O}}^* + \eta_4 \left(\frac{S_4 - S_4^*}{S_{\mathbb{O}}^* - S_{\mathbb{O}}} \right) \frac{\partial S_{\mathbb{O}}}{\partial t} \right\}$$
(30b)

with

$$S_{\mathbb{W}}^* = \Theta\left(\frac{\tau_{\mathbb{W}}\partial S_{\mathbb{W}}}{\partial t}\right) + S_2^* - S_4^*$$
 (31a)

$$S_{\mathbb{O}}^* = 1 - S_{\mathbb{W}}^* \tag{31b}$$

$$S_2^* = \min(S_{\mathbb{W}}, S_{\mathbb{W}i}) \left[1 - \Theta\left(\frac{\tau_{\mathbb{W}} \partial S_{\mathbb{W}}}{\partial t}\right) \right]$$
 (31c)

$$S_4^* = \min(S_{\mathbb{O}}, S_{\mathbb{O}\mathbf{r}})\Theta\left(\frac{\tau_{\mathbb{W}}\partial S_{\mathbb{W}}}{\partial t}\right)$$
 (31d)

as in [22, 23, 24]. The limiting saturations for S_2 , S_4 , called irreducible water resp. residual oil saturation,

$$S_{Wi} = S_{Wi}(\mathbf{v}_1, \mathbf{v}_3) = \frac{b_1(\mathbf{v}_1, \mathbf{v}_3)}{b_1(\mathbf{v}_1, \mathbf{v}_3) + b_2(\mathbf{v}_1, \mathbf{v}_3)}$$
 (32a)

$$S_{\mathbb{O}_{\mathbf{r}}} = S_{\mathbb{O}_{\mathbf{r}}}(\mathbf{v}_1, \mathbf{v}_3) = \frac{b_3(\mathbf{v}_1, \mathbf{v}_3)}{b_3(\mathbf{v}_1, \mathbf{v}_3) + b_4(\mathbf{v}_1, \mathbf{v}_3)}$$
 (32b)

are velocity dependent, because they depend on the velocity dependent "reaction rates" $b_i(\mathbf{v}_1,\mathbf{v}_3), i=1,2,3,4$. The relation between residual oil saturation $S_{\mathbb{O}_{\Gamma}}$ and flow velocity is also known as capillary correlation or capillary desaturation curve [29, 30, 31]. The factors $\Theta_{\mathbb{W}}^*$, $\Theta_{\mathbb{O}}^*$ are defined as

$$\Theta_{\mathbb{W}}^{*} = \left\{ \Theta(\cos \vartheta) + [1 - \Theta(\cos \vartheta)] \Theta(S_2 - S_{\mathbb{W}i}^{0}) \right\}$$
 (33a)

$$\Theta_{\mathbb{O}}^{*} = \left\{ \Theta(\cos\vartheta)\Theta(S_4 - S_{\mathbb{O}r}^0) + [1 - \Theta(\cos\vartheta)] \right\}$$
 (33b)

where ϑ denotes the contact angle of water,

$$S_{\mathbb{W}i}^{0} = \lim_{\mathbf{v} \to 0} S_{\mathbb{W}i}(\mathbf{v}, \mathbf{v}) \tag{34a}$$

$$S^0_{\mathbb{O}\mathbf{r}} = \lim_{\mathbf{v} \to 0} S_{\mathbb{O}\mathbf{r}}(\mathbf{v}, \mathbf{v}).$$
 (34b)

are the low velocity limits of $S_{\mathbb{W}_i}, S_{\mathbb{O}_r}$, and

$$\Theta(x) = \begin{cases} 1 & , x > 0 \\ 0 & , x \le 0 \end{cases} \tag{35}$$

denotes the Heaviside unit step function. The velocity dependent "reaction rates" b_i are chosen such that they vanish for vanishing velocities. In this paper it will be assumed

that

$$b_1 = b_1(\mathbf{v}_1, \mathbf{v}_3) = \tau_{\mathbb{W}}^3 A^4 \mathbf{v}_1^2 \mathbf{v}_3^2$$
 (36a)

$$b_2 = b_2(\mathbf{v}_1, \mathbf{v}_3) = \tau_{\mathbb{W}}^3 A^4 \mathbf{v}_3^4 \left(\frac{1 - S_{\mathbb{W}_i}^0}{S_{\mathbb{W}_i}^0} \right)$$
 (36b)

$$b_3 = b_3(\mathbf{v}_1, \mathbf{v}_3) = \tau_0^3 A^4 \mathbf{v}_1^2 \mathbf{v}_3^2$$
 (36c)

$$b_4 = b_4(\mathbf{v}_1, \mathbf{v}_3) = \tau_{\mathbb{O}}^3 A^4 \mathbf{v}_1^4 \left(\frac{1 - S_{\mathbb{O}r}^0}{S_{\mathbb{O}r}^0} \right)$$
 (36d)

consistent with eq. (34). The parameters $\tau_{\mathbb{W}}$, $\tau_{\mathbb{O}}$ are time scales, and η_2 , η_4 , b_{ij} are dimensionless constants.

The first terms in the curly brackets of (30) model an equilibrium reaction between nonpercolating and percolating fluids. The reaction, i.e. breakup and coalescence, takes only place when both percolating phases move, i.e. have nonvanishing velocity. The prefactors $\Theta_{\mathbb{W}}^*$, $\Theta_{\mathbb{O}}^*$ reproduce the experimental observation that nonpercolating nonwetting fluid phases show little breakup or coalescence below the low velocity limit of the residual nonwetting saturation. The prefactors also ensure that sign and dimensions are correct.

The specific internal surfaces $A_{\mathbb{WO}}, A_{\mathbb{WM}}$ depend on saturation. Here it is assumed that

$$A_{\mathbb{WM}} = A_{\mathbb{PM}} S_{\mathbb{W}}. \tag{37}$$

The dependence of $A_{\mathbb{WO}}(S_1, S_2, S_3, S_4)$ is suggested by inverting the classic hydraulic radius theory

$$k = C_1 \frac{S_1^3}{A_1^2} = C_3 \frac{S_3^3}{A_3^2} \tag{38}$$

where $A_1 = A_{31} + A_{41} + A_{51}$ and $A_3 = A_{31} + A_{32} + A_{35}$.

Finally, the system is closed selfconsistently using the condition

$$0 = \left(\frac{R_{13}}{\phi_{1}} + \frac{R_{14}}{\phi_{1}} + \frac{R_{15}}{\phi_{1}} + \frac{R_{31}}{\phi_{3}} - \frac{R_{41}}{\phi_{4}} + \frac{M_{1}}{\phi_{1}}\right) \mathbf{v}_{1} + \rho_{1} \frac{D^{1}}{Dt} \mathbf{v}_{1}$$

$$+ \left(-\frac{R_{23}}{\phi_{2}} - \frac{R_{24}}{\phi_{2}} - \frac{R_{25}}{\phi_{2}} + \frac{R_{32}}{\phi_{3}} - \frac{R_{42}}{\phi_{4}} + \frac{M_{1}}{\phi_{2}}\right) \mathbf{v}_{2} - \rho_{2} \frac{D^{2}}{Dt} \mathbf{v}_{2}$$

$$+ \left(-\frac{R_{13}}{\phi_{1}} + \frac{R_{23}}{\phi_{2}} - \frac{R_{31}}{\phi_{3}} - \frac{R_{32}}{\phi_{3}} - \frac{R_{35}}{\phi_{3}} - \frac{M_{3}}{\phi_{3}}\right) \mathbf{v}_{3} - \rho_{3} \frac{D^{3}}{Dt} \mathbf{v}_{3}$$

$$+ \left(-\frac{R_{14}}{\phi_{1}} + \frac{R_{24}}{\phi_{2}} + \frac{R_{41}}{\phi_{4}} + \frac{R_{42}}{\phi_{4}} + \frac{R_{45}}{\phi_{4}} - \frac{M_{3}}{\phi_{4}}\right) \mathbf{v}_{4} + \rho_{4} \frac{D^{4}}{Dt} \mathbf{v}_{4}$$

$$(39)$$

written here in its most general form. It is obtained by demanding that the closure condition should be consistent with the capillary pressure saturation relation obtained in the residual decoupling limit (see [22, 23, 24]).

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