Simplified thermodynamic model for equilibrium capillary pressure in a fractal porous medium

M. R. Deinert
Theoretical and Applied Mechanics, Cornell University, Ithaca, New York 14850, USA

J.-Y. Parlange
Biological and Environmental Engineering, Cornell University, Ithaca, New York 14850, USA

K. B. Cady
Theoretical and Applied Mechanics, Cornell University, Ithaca, New York 14850, USA

Defining a relation for equilibrium pressure in a porous medium has been difficult to do in terms of readily measurable parameters. We present a simplified analysis of this problem using the first law of thermodynamics combined with a fractal description of a porous system. The results show that the variation in fluid interfacial area with fluid volume, and the respective interfacial surface tensions, are dominant factors determining equilibrium capillary pressure. Departures from equilibrium are seen to occur when fluid-solid contact lines are in movement. By describing the pore space as fractal we are able to obtain an expression for the change in fluid interfacial area with respect to its volume, and the resulting model shows a strong fit to pressure data obtained from a capillary rise experiment conducted in a coarse-grained SiO_2 sand.

INTRODUCTION

Accurately predicting the movement and distribution of fluids in a porous medium is a problem relevant to many disciplines and requires knowledge of the pressure distribution of a fluid within the porous system. Considerable attention has been focused over the years on understanding such pressures and, most recently, on how nonequilibrium capillary pressures in porous media develop. Analyses by some authors indicate a dependence of the capillary pressure on the time rate change of moisture content within the system, suggesting that departures from equilibrium are dependent on the movement of fluid interfaces (e.g., [1–9]). However, the resulting models are often difficult to apply to real systems without considerable simplification, and there is, as yet, a need for more experimental data to fully establish the conditions under which such pressures develop [10].

Even the problem of defining an equilibrium pressure relation for a fluid in a porous medium (such as would be found in a capillary rise experiment) is difficult to do in terms of readily measurable parameters. Work along these lines has been based largely on analyses that define pressure via changes in the free energy of the fluid/media system with respect to its volume. Interfacial area has been shown to be particularly relevant (e.g., [11–13]), and a recent paper by Cheng *et al.* [14] has demonstrated the connection between fluid interfacial area in a porous system and capillary pressure by measuring both directly.

In the present work, we extend the thermodynamic discussion of equilibrium capillary pressure to a fractal medium and consider the conditions under which interfacial area will be the dominant determining factor. We derive such a relation using the first law of thermodynamics applied to a fluid element that distributes itself within a region of a porous medium through a quasistatic process. By describing the pore space as a fractal, we are able to express the change in

fluid interfacial area with respect to volume and achieve a closed-form result for capillary pressure that can be fit to data obtained from a capillary rise experiment conducted in a coarse-grained SiO_2 sand. The pore space of such media is known to exhibit fractal properties (e.g., [15]). The analysis also shows that nonequilibrium capillary pressures will occur when fluid-solid contact lines move within the region of interest and indicates a dependence on the velocity of movement as well as the degree of media saturation.

EQUILIBRIUM FLUID PRESSURE IN A POROUS MEDIUM

Consider an element of wetting fluid that enters a region of porous media under pressure p_w and distributes itself by displacing a nonwetting fluid that is at pressure p_n. Let A be the interfacial area of the fluid (m^2), A_p be the projected interfacial area of the fluid within a representative elementary volume (m^2), $\mathbf{F}$ be the force on the fluid-solid contact line per unit of its length per unit of its velocity (kg/m s), F be the magnitude of the force on the fluid-solid contact line per unit of its length per unit of its velocity (kg/m s), g be the gravitational constant (m/s^2), L be the primary fractal length scale {m}, P_c be the capillary pressure (kg/m s^2), p_n be the pressure in the nonwetting fluid (kg/m s^2), p_w be the pressure in the wetting fluid (kg/m s^2), r be the pore radius (m), S be the entropy of fluid (J/K), s_v be the volume shape factor for wetting fluid in contact with the respective nonwetting phase, s_v be the volume shape factor for wetting fluid in contact with the respective nonwetting phase, T be the fluid temperature (K), U be the internal energy of the fluid (J), REV be the representative elementary volume over which pressure is defined, V_w be the volume of the wetting fluid (m^3), V_n be the volume of the nonwetting fluid (m^3), V_p be the pore volume within a REV (m^3), V_{REV} be the volume of
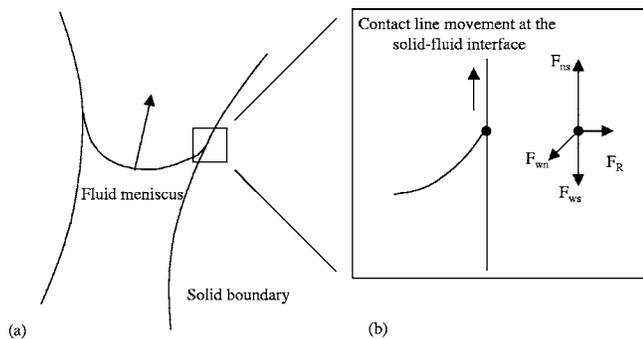
FIG. 1. Schematic of fluid-solid contact line, velocity, and resultant force. (a) Schematic of the fluid-solid contact line for a wetting fluid. (b) Schematic of the contact line and resultant surface force acting on the solid. For equilibrium situations, $F_{(ns,wn,ws)}$ are given by Young's equation [17] and F_R is the resultant force exerted by the solid matrix (e.g., [18]). When the fluid-solid contact line is in motion, viscous drag on the fluid-solid contact line will also be present (e.g., [8]).

a representative elementary volume (REV) (m^3), $\boldsymbol{\nu}$ be the velocity of the fluid-solid contact line in a REV (m/s), ν be the magnitude of the contact line velocity within a REV (m/s), α be the total contact line length per unit of projected area (A_p) in a REV (1/m), β be the fractal scaling factor, $\sigma_{\text{water,air}}$ be the interfacial energy of the water/air boundary (J/m^2), $\sigma_{\text{water,solid}}$ be the interfacial energy of the water/solid boundary (J/m^2), $\sigma_{w,i}$ be the interfacial energy of the wetting fluid in contact with the ith nonwetting phase (J/m^2), ρ_{water} be the density of water (kg/m^3), and θ be the wetting fluid content of the media ($m^3_{\text{fluid}}/m^3_{\text{media}}$).

We adopt the convention that fluid pressure is defined as a quantity averaged over a representative elementary volume (REV) within the soil matrix [16]. Assuming that the surface tensions of the fluid interfaces are functions of temperature only and that the system is taken to be the region occupied by the wetting fluid, then for a constant porosity medium the first law can be written using a control mass formulation,

$$U' = TS' - p_w V'_w - p_n V'_n + \sum \sigma_{w,i} A'_{w,i} + \langle \alpha \mathbf{F} \cdot \boldsymbol{\nu} A_p \nu \rangle. \quad (1)$$

Here work done by the system is taken to be positive and the primes indicate the derivative with respect to time. The last term on the right considers the work done per unit time to move the fluid-solid contact line. (Fig. 1.) Here $\mathbf{F}$ is the force exerted by/on the contact line per unit of its length per unit of its velocity, α is the contact line length per unit of fluid projected area, A_p, $\boldsymbol{\nu}$ is the velocity of the fluid-solid contact line with ν its magnitude, and the average is performed over the REV; see the Appendix. The summed terms account for work corresponding to changes in the interfacial area of the fluid (e.g., [19]), with "w" indicating the wetting phase and "i" the nonwetting phases (i.e., solid matrix or nonwetting phase being displaced). We consider an isothermal, quasistatic process where fluid entropy and internal energy can be considered to be constant. Such a process would approximate a slow capillary rise experiment conducted at constant temperature. Then, Eq. (1) can be reduced to

$$(p_n - p_w)V'_w = -\sum \sigma_{w,i} A'_{w,i} - \langle \alpha \mathbf{F} \cdot \boldsymbol{\nu} A_p \nu \rangle, \quad (2)$$

where we have made use of the fact that $V'_w = -V'_n$. At the end of that process (when $\boldsymbol{\nu}=0$), this can be rearranged to give

$$P_c = -\sum \sigma_{w,i} (\partial A_{w,i}/\partial V)_{U,S,T}. \quad (3)$$

Equation (3) shows that under this idealized model, the equilibrium pressure within the fluid matrix is determined by the change in interfacial areas with respect to fluid volume and can be shown to be a function of the media's saturation. Note that the last term in Eq. (1) only plays a role when the fluid-solid contact lines are in motion, a situation of obvious nonequilibrium.

The result in Eq. (3) differs from that derived by Morrow [12] in that no term for the interfacial energy of the nonwetting fluid-solid interface is included. However, since we define the system as the region occupied by the wetting fluid only, this term is rightly omitted. Equation (3) can also be derived as a subset of the more general analysis of Hassanizadeh and Gray [8]. Note that the restriction of Eq. (3) to a constant entropy process does not violate the condition that spontaneous processes (of which soil wetting is one) proceed toward higher entropy as this requirement pertains to system *and* surroundings. Entropy within the system can be written as

$$S' = S'_{\text{trans}} + S'_{\text{prod}}, \quad (4)$$

where S'_{trans} results from heat and mass transfer into and out of the system and S'_{prod} represents entropy production within the system. The requirement that $S'=0$ stipulates a balance between these terms, which then requires that the entropy of the surroundings increase even if that of the system is constant. Such a situation could well exist for isothermal, quasistatic processes such as those found in a slow capillary rise experiment.

In order to apply Eq. (3), a relation is needed for determining the change in interfacial area with respect to fluid volume, and this can be obtained for a medium whose pore space exhibits fractal properties. A recent study by Bird and Perrier [20] suggests a relation for the pore size in a fractal system after T iterations,

$$r = \beta^T L, \quad (5)$$

where r is the characteristic size, L is the original length scale, and β is a scaling factor. Correspondingly, the number of such pores within a given set is

$$n = (L/r)^D \quad (6)$$

with D the soil fractal dimension [20].

If we assume that "r" represents pore radius, then we can take the interfacial area at a given scale to be $\sim s_a n r^2$ with the corresponding pore volume $\sim s_v n r^3$, where s_a and s_v are shape factors (e.g., 4π and $4/3\pi$, respectively, for a spherical geometry). If we assume that the interfacial areas $A_{w,i}$ are directly proportional to $s_a n r^2$, then the derivatives in Eq. (3) are easily obtained,

$$(\partial A/\partial V) = (\partial A/\partial r)(\partial r/\partial V)$$

$$= (\partial A/\partial r)(\partial V/\partial r)^{-1} = (s_a/s_v)(2 - D)/(3 - D) \ (1/r)$$

$$= f_{w,i}(2 - D)/(3 - D) \ (1/\beta^T L), \tag{7}$$

where $f_{w,i} = s_a/s_v$ for the respective phase. For a situation where water displaces air in a porous medium, Eqs. (3) and (7) can be combined to give

$$P_c = -(f_{\text{water,air}}\sigma_{\text{water,air}} + f_{\text{water,solid}}\sigma_{\text{water,solid}})(2 - D)/(3 - D)$$
$$\times(1/\beta^T L), \tag{8}$$

which, like Eq. (3), is a function of media saturation.

EXPERIMENTAL RESULTS

A capillary rise experiment provides an ideal mechanism for testing Eq. (8). Here fluid is drawn upwards from a saturated region by the network of pores above it with the capillary pressure increasing linearly with height above the saturated level. At any given elevation, small pores fill first with larger ones doing so if their capillarity can overcome the tension in the fluid surrounding them. The size of the largest pores filled therefore decreases with elevation above the saturated region, which leaves an increasing fraction of the pore space empty and results in a decrease in moisture content. For a fractal system, all the pores in a given set are then either filled or empty at a specific capillary pressure. Correspondingly, the value of P_c given by Eq. (8) increases as the size of the largest pores filled, given by $\beta^T L$, decreases. The saturation of the media is defined as $V/V_p = \Sigma s_v n r^3/V_p$. Here V_p is the total pore volume within a REV, V is the volume of water within that pore space, and the sum runs from the largest pore filled (defined by $\beta^T L$) to the smallest, with "T" therefore being directly related to saturation.

An eight-day capillary rise experiment was performed using a 20–30 sieve SiO_2 sand to obtain data on capillary pressure-versus-media saturation. The sand was held in an aluminum chamber with interior dimensions of 1.27 cm/20.3 cm/25.4 cm and the interior faces were treated with a DowCorning silicon release compound in order to render them hydrophobic. The only preparation of the media was a thorough rinse with distilled water. Degassed, distilled water was introduced from the bottom of the chamber until a saturated region 5 cm deep was formed. The chamber was sealed and allowed to equilibrate for 8 days at a constant temperature of 25 °C. The fluid content within the porous medium was measured, at 0.045 cm increments above the saturated region, using neutron radiography as described in Deinert *et al.* [21].

Because the coefficients $f_{w,i}$ are difficult to determine for nonidealized media, the factor $(f_{\text{water,air}}\sigma_{\text{water,air}} + f_{\text{water,solid}}\sigma_{\text{water,solid}})(2-D)/L \ (3-D)$, as well as β were determined by fitting Eq. (8) to data from the capillary rise experiment. Taking the natural log of both sides of Eq. (8), we get

$$\ln(P_c) = \ln[(f_{\text{water,air}}\sigma_{\text{water,air}} + f_{\text{water,solid}}\sigma_{\text{water,solid}})(D$$
$$- 2)/L \ (3 - D)] - T \ln(\beta). \tag{9}$$

Here P_c is the data vector of capillary pressures obtained
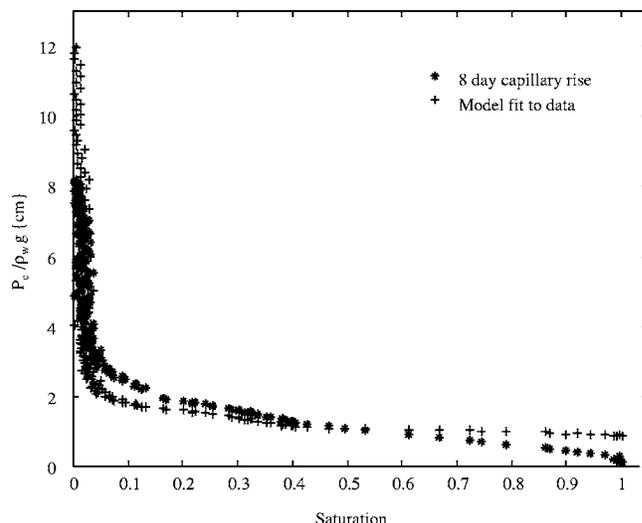

FIG. 2. Eight day capillary rise data and model fit. Data from an 8-day capillary rise experiment are shown along with the best fit of Eq. (8) to those data. The model predicts a higher pressure at low saturation then is shown by the data, however the 8-day capillary rise may not have provided sufficient time for the system to come to a true equilibrium.

experimentally, with T the corresponding fractal iteration vector whose integer components range from 0 to the number of data points. A least-squares method was used in conjunction with Eq. (9) to determine both $(f_{\text{water,air}}\sigma_{\text{water,air}} + f_{\text{water,solid}}\sigma_{\text{water,solid}})(D-2)/L \ (3-D)$ and β.

DISCUSSION

Figure 2 shows a comparison of the data from the capillary rise experiment along with the fit of Eq. (8), which reproduces the shape of the data curve with good fidelity. The model predicts a higher capillary pressure at low saturation then is shown by the data, however the 8-day capillary rise may not have provided sufficient time for the system to come to a true equilibrium. While the total interfacial area in the fractal model goes to zero as V goes to zero, the derivative $\partial A/\partial V$ increases monotonically, which is consistent with the experimental results obtained by Cheng *et al.* [14]. The specific entropy and internal energy of water change by $<0.1\%$ between 0.1 and 1 MPa at 25 °C (e.g., [25]). The capillary rise experiment was conducted at this temperature, and for the pressure ranges shown in Fig. 2 there would have been virtually no change in these quantities, which is consistent with the assumptions under which Eq. (8) was derived. The strong fit of Eq. (8) to data also suggests that the pore space of the media indeed exhibits fractal properties.

For steady moisture content, Eq. (1) indicates that fluid pressure within a porous medium will be a function $P_c(U,S,T,A,V)$. However, as with previous studies (e.g., [2–4,7,8]), Eq. (1) also suggests that movement of the fluid-solid contact lines within a REV will effect the pressure relationship. Indeed, if $P_c(U,S,T,A,V)$ is taken to be the equilibrium pressure function, then, under appropriate conditions, Eq. (1) can be rewritten as

$$P_c = P_c(U,S,T,A,V) - \mu \partial \theta / \partial t, \qquad (10)$$

where the second term on the right considers nonequilibrium effects arising from forces acting on the fluid-solid contact line during its movement (see the Appendix), with θ being the moisture content of the media. As with Eq. (2), the second term on the right side of Eq. (10) represents the work done in moving the total length of the contact line within a REV, but it is now written in a form similar to those found by previous authors (e.g., [9]). While departures from equilibrium pressure are commonly attributed to this term, they would also be expected to occur if temperature gradients were to exist within the system, or if fluid interfacial area varied in time even while moisture content remained fixed.

APPENDIX

Forces that act on the fluid-solid contact line during its movement will cause nonequilibrium effects. Since pressure is defined as a quantity averaged over a REV [16], it is appropriate in Eq. (1) to also consider the average of the energy required per unit time to move the contact line contained within such a region. This quantity is equal to the force exerted by/on the contact line times the velocity at which it moves, averaged over the REV, and can be written as $\langle \alpha \mathbf{F} \cdot \boldsymbol{\nu} \, A_p \nu \rangle$. Here α is the contact line length per unit of projected fluid interfacial area within the REV, A_p, $\boldsymbol{\nu}$ is the velocity of the fluid-solid contact line, ν is the magnitude of that velocity, and $\mathbf{F}$ is the force exerted by/on the contact line per unit of its length per unit of its velocity (see Fig. 3).

When ν does not vary with position over the volume of the integral, the work done per unit time in moving the fluid-solid contact line may be written as $\alpha \langle \mathbf{F} \cdot \boldsymbol{\nu} \rangle A_p \nu$. If the curvature of the menisci with the REV are constant, then by conservation of mass $V'_w = A_p \nu$ and Eq. (2) can be rewritten as

$$P_c V'_w = - \sum \sigma_{w,i} A'_{w,i} - \alpha \langle \mathbf{F} \cdot \boldsymbol{\nu} \rangle V'_w. \qquad (A1)$$

If the magnitude of the interfacial velocity does not vary within the REV, then Eq. (A1) can also be rearranged to give

$$P_c = - \sum \sigma_{w,i} (\partial A_{w,i} / \partial V)_{u,s,T} - \alpha \langle \mathbf{i} \cdot \mathbf{k} / \| \mathbf{i} \cdot \mathbf{k} \| \rangle F V'_w / A_p. \qquad (A2)$$

Here $\mathbf{i}$ and $\mathbf{k}$ are the directions of the force exerted by/on the fluid-solid contact line and the projected area vectors, respectively (see Fig. 3) and where we have again made use of the fact that $V'_w = A_p \nu$. Noting that the moisture content $\theta = V_w / V_{REV}$, V'_w can be written as $V_{REV} |\partial \theta / \partial t|$. The second term on the right-hand side in Eq. (A2) can then be written as $V_{REV} |\partial \theta / \partial t| \alpha \langle \mathbf{i} \cdot \mathbf{k} / \| \mathbf{i} \cdot \mathbf{k} \| \rangle F / A_p$, which is positive when $\langle \mathbf{i} \cdot \mathbf{k} / \| \mathbf{i} \cdot \mathbf{k} \| \rangle$ is positive and negative when it is negative (see Fig. 3). Hence, Eq. (A2) can be written
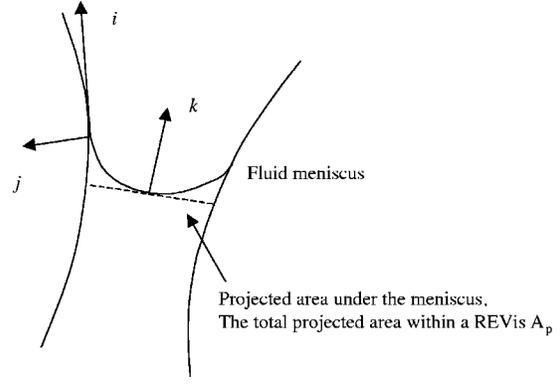

FIG. 3. Projected flow area. When the curvature of the menisci within a REV is constant, the volume flow rate into or out of the REV is given by νA_p, where the magnitude of the contact line and interfacial velocities is assumed to be the same. The unit vectors i,j,k denote the directions of the force on the fluid-solid contact line, the resultant force on the solid matrix, F_R, and the direction in which the projected area moves, respectively. For a wetting fluid, the force on the fluid-solid contact line is in the direction of movement for $\partial \theta / \partial t > 0$ and resists the movement of the fluid-solid contact line when $\partial \theta / \partial t < 0$.

$$P_c = - \sum \sigma_{w,i} (\partial A_{w,i} / \partial V)_{U,S,T} - \mu \partial \theta / \partial t, \qquad (A3)$$

where $\mu = |\alpha F / A_p \int_{REV} \mathbf{i} \cdot \mathbf{k} / \| \mathbf{i} \cdot \mathbf{k} \| dV|$. More generally, if terms for U' and TS' are not dropped from Eq. (1), then

$$P_c = P_c(U,S,T,A,V) - \mu \partial \theta / \partial t, \qquad (A4)$$

where $P_c(U,S,T,A,V)$ is understood to be the equilibrium capillary pressure. Equation (A4) is also obtained by Hassanizadeh and Beliaev [9] through a more general analysis. The coefficient μ takes into consideration the movement of the fluid-solid contact line within a REV and would need to be determined experimentally in all but the simplest of geometries.

Importantly, the parameter α indicates that μ will have some dependence on both media structure and moisture content. While the dependence of $\mathbf{F}$ on contact line velocity was not specified in the above derivation, simulations have shown that the force required to move a contact line through a smooth capillary tube is $\sim \nu$ [1,22] and other studies have obtained predictions of $\sim \nu^x$, with x ranging from 0.4 to 9/7 [23,24]. Experiments done to measure the change in force required to move a capillary interface through glass beads contained in a thin tube have shown a dependence $\sim \nu^{1/2}$ [2]. As a result, it is likely that the second term on the right-hand side of Eq. (2) will increase in magnitude for higher velocities, indicating that μ will be correlated to $\partial \theta / \partial t$.

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