

Continuum Percolation Theory for Water Retention and Hydraulic Conductivity of Fractal Soils: Estimation of the Critical Volume Fraction for Percolation and Extension to Non-Equilibrium

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Abstract

Systematic experimental deviations from theoretical predictions derived for water retention characteristics of fractal porous media have previously been interpreted in terms of continuum percolation theory (at low moisture contents, below the critical volume fraction of water, α_c , capillary flow ceases). In other work, continuum percolation theory was applied to find the hydraulic conductivity as a function of saturation for saturations high enough to guarantee percolation of capillary flow. Now these two problems are further linked, using percolation theory to estimate non-equilibrium water contents at matric potential values such that the equilibrium water content is too low for percolation of capillary flow paths. Also an analytical scheme is developed to allow an estimation of the value of α_c from physical parameters.

1. Introduction

Recently I applied percolation theory, Hunt, 2001, to derive an expression for the unsaturated hydraulic conductivity, K , of “random fractal” porous media (such as described by Tyler and Wheatcraft, 1990, or Rieu and Sposito, 1991) in terms of the saturated hydraulic conductivity, K_s , and the relative saturation, S , $K=f(K_s,S)$. Unambiguous comparison with experiment required the fractal dimensionality for the pore space, D , (obtainable from the particle-size distribution, PSD) and the critical volume fraction for percolation, α_c . The relationship between K and K_s was shown, Hunt, 2001, in accord with numerical simulations of Perrier et al., 1995, although there were complications at lower saturations due to hysteretic effects of drainage and imbibition. The relationship between K and K_s was also found to agree with experimental results for the McGee Ranch soil at the US Department of Energy Hanford site over 4 orders of magnitude, Hunt, 2001; Hunt and Gee, 2002a. Although no adjustable parameters were used in this comparison, some uncertainty existed in the choice of a value for α_c . When tested on the more complex North Caisson (NC) soil, an appropriate generalization of the simple model led to agreement within approximately 20% over the full saturation range and 6 orders of magnitude of the hydraulic conductivity, Hunt and Gee, 2002a. Thus, to the extent that a given soil can be represented with (generalized) fractal models, and that hysteresis can be neglected (or averaged over), percolation theory appears to be a very promising technique for finding $K(K_s,S)$.

In Hunt and Gee, 2002b, water retention curves appropriate for fractal media were compared with experimental water retention data, Freeman, 1995; Khaleel and Freeman, 1995. In nearly all of 43 cases from the US Department of Energy Hanford site the predicted water retention curve was in excellent agreement with experiment. In this case D was again obtained from the PSD, while the air entry head was needed as a fit parameter. Below some fairly well-defined value of the water content, θ_d , experimental results deviated from the fractal prediction. This deviation was interpreted in the context of continuum percolation theory; thus it was suggested that in most cases the deviation was due to a break-up of the network of pore space connected by continuous capillary

flow and that $\theta_d = \alpha_c$ (although in some cases, for which $K(\theta_d) \leq 5 \times 10^{-8}$ cm/s, $\theta_d > \alpha_c$ was the result). As a test of the suggestion, θ_d was compared with a phenomenological relationship for the threshold moisture content, (called θ_t , by Moldrup et al., 2001) at which solute diffusion vanishes. In Moldrup et al., 2001, $\theta_t = 0.039[SA_{vol}]^{0.52}$ where SA_{vol} is the surface area to volume ratio of the soil. Using a calculation of SA_{vol} from the random fractal model, the measured θ_d was compared with the Moldrup et al., 2001 relation for θ_t . R^2 for this correlation was about 0.85. In view of the interpretation $\theta_d = \alpha_c$ we concluded that we had shown it possible to find at least a good approximation to α_c from SA_{vol} . The ability to find α_c from SA_{vol} made it possible, in principle, to predict the functional dependence of $K(S)/K_S$ on S from physical measurements only and bypass the necessity for complex and expensive hydraulic measurements of partially saturated soils. Here I estimate α_c from the PSD and the porosity.

This identification $\theta_t = \alpha_c$ also implied the relevance of percolation theory to solute transport. The fact that the vanishing of the diffusion constant for solute transport is a linear function of $\theta - \alpha_c$ implicates percolation theory here as well, since this difference is just the inverse of the characteristic distance, Λ , between nodes, Stauffer, 1979, in a continuous flow network at moisture content θ if percolation requires a minimum θ of α_c . In other words, Λ diverges as $(\theta - \alpha_c)^{-1}$.

The following research questions now become of interest. 1) Is it possible rigorously to derive the result for the diffusion constant proportional to Λ^{-1} ? Possibly, but this task is deferred to a later date. 2) Is it possible to predict the form of the water retention curve at moisture contents below the percolation threshold? The basis for such a relationship is laid here using percolation theory. Since most phenomenological expressions for the water retention characteristics of a porous medium are designed to cover all ranges of moisture content, it is clear that the water retention characteristics above and below the threshold are rather generally related. In this context, the fact that certain aspects of percolation theory are universal, Stauffer, 1979, suggests its suitability for connecting these two regimes, and I do derive here a time-dependent result for the water retention

characteristics in this low moisture regime. This relationship, however, is not tested by comparison with experimental results, as such results with precise time measurements are not readily available. On the other hand, unless specific assumptions are made regarding the time allowed for equilibration for given changes in matric potential, it is difficult to make concrete predictions for comparison with experiment.

As a final note, values obtained for α_c from both calculations as well as the regression against the Moldrup et al., 2001, relationship for θ_t are inserted into the relationship for K/K_S in the cases previously discussed, the McGee Ranch and North Caisson soils from the Hanford site. The previous close correspondence with experiment is improved.

In section 2 the material necessary to introduce the soil structure is reviewed. In section 3, a short review of the previous calculations for the hydraulic conductivity under both saturated and unsaturated conditions is given, as well as expressions for the water retention curve. An important point of section 3 is to introduce the percolation probability, which ultimately allows description of clusters of pores with particular characteristics in terms of the cluster statistics of percolation as well as the fraction of pores connected to the infinite cluster. In section 4, a brief estimate of α_c is given, and its predictive capability is compared with the Moldrup et al., 2001, empirical relationship. In section 5, two descriptions of non-equilibrium calculations of water retention characteristics are given for the particular case of a thin sample. (For thicker samples, the non-uniform vertical distribution of moisture will ultimately require solution of Richard's equation, but using the non-equilibrium constitutive relations derived here). Then a general condition defining equilibrium response is given. Necessary scaling relations associated with the percolation probability are discussed in the appendix.

2. Soil structure background

The reader is referred to the work of Rieu and Sposito, 1991, denoted subsequently by RS, for detailed discussion of the appropriate structure for discrete, deterministic fractals. I use a power law probability distribution function, pdf, of pore sizes over a finite range

of size, from a minimum of r_0 to a maximum of r_m . This is supposed compatible with a random fractal structure, in which, in the mean, the geometrical relationships between successive pore classes are satisfied, allowing identical representation of the *statistics* of pore classes to that satisfied by a deterministic fractal. The power law pore size distribution is given in terms of the fractal dimensionality, D , and the porosity, ϕ , is found from D and the ratio of r_0 to r_m

$$1 - \left(\frac{r_0}{r_m} \right)^{3-D} = \phi \quad (1)$$

This relationship was derived initially by RS for a discrete random fractal, and was used as a guideline for results from the continuous random fractal approach, Hunt, 2001; Hunt and Gee, 2002a. The probability, $P(r_i)$, that a given pore had radius r_i was then,

$$P(r_i) \propto r_i^{-D} \quad (2)$$

where r_i takes on discrete values with successive ratios, q_r . For a continuous range of pore sizes, the appropriate modification to yield the probability $W(r)dr$ of measuring a pore radius between r and $r+dr$ is as follows, Hunt and Gee, 2002a,

$$W(r)dr = \frac{3-D}{r_m^{3-D}} r^{-1-D} dr \quad (3)$$

The reduction in the power by 1 is necessary to allow an integral over a finite range of r (e.g., one size class, from r_i to $q_r r_i = r_{i+1}$) to yield r^{-D} , corresponding to the discrete case. The normalization constant, $(3-D)/r_m^{(3-D)}$ has been chosen consistent with a pore volume r^3 , so that the porosity associated with pores of radius between r and $r+dr$ is,

$$d\phi = r^3 \frac{3-D}{r_m^{3-D}} r^{-1-D} \quad (4)$$

If a specific pore geometry is considered (so that a pore volume is written as the product of r^3 and a numerical factor) then the normalization constant must be adapted accordingly, so that the total porosity, ϕ , defined next, still agrees with (1). The total porosity is the integral of $d\phi$ over all pore sizes from the smallest at r_0 to the largest at r_m ,

$$\frac{(3-D_r)}{r_m^{3-D_r}} \int_{r_0}^{r_m} \left(\frac{dr}{r} \right) r^3 r^{-D_r} = 1 - \left(\frac{r_0}{r_m} \right)^{3-D} = \phi \quad (5)$$

in agreement with RS.

It is also possible to find an expression for the surface area to volume ratio of a given soil in a random fractal model. This has been done in Hunt and Gee, 2002b, but does not require much discussion in this context. The important points are, that no particular pore or particle geometry was assumed, with a surface area of a given particle taken as the radius squared, its volume the radius cubed, whereas volume was taken as a proxy for mass. Thus the calculation does not actually give the measured SA_{vol} , (in m^2/g) but a quantity proportional to SA_{vol} with an unknown proportionality constant. The calculation is supposed to give, however, the correct dependence of SA_{vol} on maximum particle size, as well as fractal dimensionality. First it was assumed that both pore volume and solid volume are “fractal,” and that the solid fractal dimensionality, D_s , is related to the pore volume in the same way that the pore space fractal dimensionality is related to the solid volume,

$$D_s = 3 - \frac{\log(\phi)}{\log\left(\frac{r_0}{r_m}\right)} \quad (6)$$

Eqn(1), if solved for D , using the substitution $\phi \rightarrow 1-\phi$ yields eqn(6). Using (6) it is possible to calculate the ratio of the total solid surface area to the total solid volume as follows (such a calculation allows double-counting of surfaces shared by neighboring particles),

$$SA_{vol} \propto \frac{\int_{r_0}^{r_m} r^2 r^{-1-D_s} dr}{\int_{r_0}^{r_m} r^3 r^{-1-D_s} dr} = \left(\frac{3-D_s}{2-D_s}\right) \frac{1}{r_m} \left[\frac{\left(\frac{r_m}{r_0}\right)^{D_s-2} - 1}{1-\phi} \right] \quad (7)$$

Eqn(7) will be used in the expression for α_c .

3. Hydraulic conductivity for capillary flow

The system is envisioned to consist of a network of connections between pores. The connections between pores are denoted as hydraulic conductances, with values of the conductance consistent with a generalized Poiseuille's Law for flow. These conductances can, in principle be determined from numerical solution of the Navier-Stokes equation at the pore scale, allowing values of a pore radius, r , and length, l , to be obtained as appropriate substitutes for r and l of a right cylindrical tube, but which have a specific interpretation in terms of the geometry of a pore throat. For a self-similar network the important point is that whatever these geometrical factors are, they remain the same at all length scales, allowing scaling analysis to find the ratio of hydraulic conductances at different length scales. As a consequence it proves possible to find expressions for the

hydraulic conductivity at arbitrary saturation, $K(S)$, in terms of the saturated value of the hydraulic conductivity, K_S .

The saturated hydraulic conductivity for a regular network was best obtained, Bernabe and Bruderer, 1998, through application of critical path analysis, Katz and Thompson, 1986. While this result does not, by itself, guarantee a similar result for unsaturated media, the same conclusion has also been reached regarding the electrical conductivities of disordered solids, [see, for example, Hunt, 2002, the articles therein, and the articles referred to], and is independent of the particular model of conduction. Critical path analysis, developed originally in solid state physics, Ambegaokar et al.; 1971; Pollak, 1972, yields directly the smallest value of the conductance on the most highly conducting path of infinite extent by equating the critical quantile of the conductance distribution (measured from the largest conductance in the system) with the bond percolation probability, p_c . Such an operation is most clearly appropriate when the local conductances connect sites on a regular lattice. When pore lengths can vary over orders of magnitude, the random network becomes more difficult to envision and construct, and the choice of a critical bond percolation probability is made difficult. In this case, critical path analysis may be applied in the form of continuum percolation, Hunt, 2001.

When a well-defined fraction, α_c , of a large volume is occupied by small volumes, or particles, of a given type A, (under certain clearly defined conditions, such as the shapes of the individual “particles” A, and any correlations between shape and orientation, or in the placements of the individual particles) the particles A must form a continuous connected network, Stauffer and Aharony, 1994. It is, in general, a difficult problem to find the particular value of α_c for an arbitrary choice of individual volume shapes and correlations, but a scheme for estimating α_c is given in section 4. Given a value of α_c , however, the method of finding the saturated hydraulic conductivity is simply to find the largest value of the smallest pore that water must traverse in order to build an infinite, interconnected path of capillary flow “tubes.” An integral over the differential porosity from the minimum necessary pore size for continuous flow to the largest pore size in the system must therefore yield the critical volume fraction for percolation as follows,

$$\left[\frac{3 - D_r}{r_m^{3-D_r}} \right] \int_{r_c}^{r_m} r^{2-D_r} dr = \alpha_c \quad (8)$$

which yields,

$$r_c = r_m [1 - \alpha_c]^{1/(3-D_r)} \quad (9)$$

Using eqn(9) for r_c it is possible to write for the limiting hydraulic conductance at full saturation,

$$g_c^h = \left[\frac{\pi}{8C\mu} \right] r_c^3 = \left[\frac{\pi}{8C\mu} \right] r_m^3 [1 - \alpha_c]^{3/(3-D_r)} \quad (10)$$

if, as consistent with fractal geometry, the pore aspect ratio is taken to be a constant, C , independent of size, i.e. $l=Cr$. Then the pore volume becomes Cr^3 , but the normalization constant is reduced by C and all present results are unaffected. As discussed, Hunt, 2001; Hunt and Gee, 2002a, the hydraulic conductivity involves other length scales as well, and need not conform to Miller-Miller similitude, Miller and Miller, 1956, but for representing the ratio of $K(S)$ to K_S , the limiting hydraulic conductance is likely sufficient. Assuming that the critical volume fraction, α_c , must remain the same for all saturations allows the controlling radius, r_c , at arbitrary saturation ultimately to be written in terms of its value at complete saturation, making possible the discovery of the relationship between $K(S)$ and K_S as a function of S . To do this it is necessary first to find a result for the *equilibrium* saturation of the porous medium. I assume that, in

equilibrium, all pores larger than a given size $r_>$ are empty, and all smaller pores are full. This is justifiable in terms of the assumed self-similarity, i.e. that there is a one-to-one correspondence between pore radius (that appears above in, e.g., Poiseuille's Law) and pore curvature, and that all pores larger than $r_>$ will have characteristic curvatures less than that accommodated at the particular value of the matric potential. The problem can thus be formulated either of two ways, to find $r_>$ as a function of S , or to find the matric potential, h , as a function of S . For the former we write (as in Hunt and Gee, 2002a),

$$S = \left(\frac{1}{\phi} \right) \left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_0}^{r_>} dr r^{2-D} = \frac{1}{\phi} \frac{[r_>^{3-D} - r_0^{3-D}]}{r_m^{3-D}} \quad (11)$$

which yields,

$$r_> = \left[S r_m^{3-D} + (1-S) r_0^{3-D} \right]^{1/(3-D)} \quad (12)$$

Repeating the procedure used to generate eqn(8) leads to the following expression for arbitrary saturation, S ,

$$\alpha_c = \left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_c}^{r_>} dr r^{2-D} = \left(\frac{r_>}{r_m} \right)^{3-D} - \left(\frac{r_c}{r_m} \right)^{3-D} \quad (13)$$

The result of eqn(13) using eqn(12) for $r_>$ as a function of saturation yields

$$r_c(S) = r_c(S=1) \left[1 - \phi \frac{1-S}{1-\alpha_c} \right]^{1/(3-D)} \quad (14)$$

which allows the controlling hydraulic conductance at arbitrary saturation to be written in terms of its value at full saturation thus,

$$g = g_s \left[1 - \phi \frac{1-S}{1-\alpha_c} \right]^{3/(3-D_r)} \quad (15)$$

This result has been tested and found to yield the hydraulic conductivity in agreement with experiment without use of adjustable parameters, although there was initially some uncertainty in the choice of the critical volume fraction for percolation, α_c .

For later use it is necessary also to give the dependence of the saturation on the matric potential, h . This was done as follows. Eqn(11) can be rewritten in terms of a suction pressure, such that $r > -A/h$, with A a constant, which depends on pore geometry, but whose value is not required if one is prepared to use its value at “air-entry,” h_A , as a parameter. In other words, for a matric potential h , all pores with $r > -A/h$ are empty of water, while if $h \geq h_A$, the medium is saturated. Thus,

$$S = \left(\frac{1}{\phi} \right) \left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_0}^{-A/h} dr r^{2-D} \quad (16)$$

$$1 = \left(\frac{1}{\phi} \right) \left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_0}^{-A/h_A} dr r^{2-D} \quad (17)$$

Combining these two expressions gives,

$$S = 1 - \left(\frac{1}{\phi} \right) \left[1 - \left(\frac{h}{h_A} \right)^{D-3} \right] \quad (18)$$

4. Estimation of the critical volume fraction for percolation

Clearly water flows through most saturated soils reasonably quickly, and typically by means of “capillary flow.” This is evidenced by the fact that it is difficult to keep soil saturated under the influence of gravity. Thus at full saturation, there is usually no question that the volume fraction associated with capillary flow percolates. But it is also clear that only a certain fraction of that water can be removed before the capillary flow paths break up into isolated regions. This concept can be easily introduced for the following network of tubes, which can serve as a model for either a bond or a continuum percolation problem. The advantage to such a network is that it allows the identification of an unknown quantity (α_c) in terms of a known quantity (p_c).

Consider a simple cubic lattice, in which right circular cylindrical tubes of equal radius and length connect all lattice sites. The tubes occupy a fraction of the total volume of space equal to the porosity of the system, ϕ . The bond percolation probability, p_c , for a three-dimensional simple cubic lattice is $\frac{1}{4}$. Thus, when $\frac{1}{4}$ of the tubes are full of water, it will be possible for water to flow from one side of the lattice to the other by capillary flow without any interruptions, or breaks in flow. If $\frac{1}{4}$ of the tubes are full of water, then by definition the saturation at the critical volume fraction for percolation is $\frac{1}{4}$, whatever the value of ϕ is (i.e., whatever the dimensions of the tubes) and α_c is in this case $\frac{1}{4}\phi$. But in the general case of continuum percolation, the critical volume fraction for percolation is typically around 15-16%, Stauffer and Aharony, 1994. Thus, if it is guaranteed that the pore space in a porous medium percolates, it should be reasonable to choose a critical volume fraction in the range $\frac{1}{4}\phi$ to $\frac{1}{6}\phi$. According to the result of Vyssotsky et al., 1961, the critical bond percolation probability, p_c , satisfies the approximate equality,

$Zp_c=d/(d-1)$, where Z is the number of nearest neighbors, and d is the dimensionality of the system (3, in our case). The value $1/4$ is obtained for p_c on the simple cubic lattice because $Z=6$ [$6(1/4)=3/2$]; a value of $1/6$ would require $Z=9$ (which is not possible for any regular lattice, but is not an unreasonable mean value for a random system). So as a first approximation for α_c one could write,

$$\alpha_c = \frac{1}{6}\phi \quad (19)$$

(one could take the proportionality to be $1/4$, but $1/6$ seems to work better).

As a higher order approximation, however, one can propose the following. For fine soils with a high clay fraction, neighboring clay grains may be close enough together so that capillary flow as such between the individual clay grains does not occur. This suggestion is motivated partly by experimental results, which clearly show that α_c can be as large as 0.2, even when porosity is only ca. 0.5. In this case, flow through the narrowest spaces in the system may be similar in character to film flow along the faces of particles at very low moisture contents, Blunt and Scher, 1995; Tokunaga and Wan; 1997, Toledo et al., 1995. If this suggestion is valid, then those “bonds,” or connections between pores, which happen to have radii less than some size proportional to the clay grains (with $r < 2\mu\text{m}$), may not support capillary flow. A very simple such concept allows the possibility of a surface layer, Δ in thickness, with $\Delta \approx 0.5\mu\text{m}$, along each grain, which does not support capillary flow. Choosing a layer twice the thickness, or $1/2$ the thickness, does not change the results much. Such layers comprise a certain fraction of the pore space, which is then supposed not to contribute to capillary flow. Thus the minimum water content for a continuous network of capillary flow must occupy the volume, $1/6\phi$, plus the surface layers, (even though the latter do not contribute to capillary flow, they contribute to the water content). Such a volume is easily representable in terms of the contribution to SA_{vol} from the smallest particles (less than $\Delta=0.5\mu\text{m}$ in radius).

$$\alpha_c \approx \left(\frac{1}{6}\phi\right) + \frac{3-D_s}{r_m^{2-D_s}} \int_{r_0}^{2\Delta} r^{2-D} dr \quad (20)$$

Use of 2Δ as the upper limit is a result of integrating over pore space rather than over particle sizes; if a pore is not twice the width of the surface zone, the surface zones will adjoin. The result of the integration can be expressed (using $\Delta = \delta + r_0/2$)

$$\alpha_c = \left(\frac{7}{6}\phi\right) - 1 + \left(\frac{r_0 + 2\delta}{r_m}\right)^{3-D} \quad (21)$$

or cast in the following way by using the approximation $(1+x)^{3-D} = 1 + (3-D)x$, and substituting eqn(7) for SA_{vol} ,

$$\alpha_c = \left(\frac{1}{6}\phi\right) + (3-D) \left[\frac{2r_m(D_s - 2)SA_{vol}}{(3-D_s)r_0 \left\{ \left[\frac{r_m}{r_0}\right]^{D_s-2} - 1 \right\}} - 1 \right] \left(\frac{r_0}{r_m}\right)^{3-D} \quad (22)$$

Eqn(21) and eqn(22) have somewhat similar general forms to the Moldrup et al., 2001, relationship for $\theta_d(SA_{vol})$. To use eqn(21) or eqn(22), I tried $r_0 < 1\mu\text{m}$ so that $\delta = 0.5\mu\text{m} - r_0/2 > 0$. In either form, it is possible to compare the result with experimental observations for θ_d , and these results are given in Fig. 1 and Fig. 2. Eqn(21) (eqn(22)) has R^2 of about 0.83 (0.79), similar to the result, 0.85, for predicting θ_d from the Moldrup et al., 2001, relationship, Fig. 3. Thus from a practical view of how best to find α_c , it would seem that all three calculations are roughly equally useful, but the approximate equality of the R^2 values for all three methods is probably more a result of the experimental uncertainty in

its determination (the original value of R^2 reported by Moldrup et al., 2001, 0.99, is clearly superior to anything discussed here), so that use of the Moldrup relation might be more accurate here as well, if experimental results for θ_d had had less scatter. Eqn(21) has proved more valuable than eqn(22) in finding α_c because the slope of the correlation is more nearly 1.

Using eqn(21) for α_c , or simply the regression determined for the Moldrup et al., 2001, empirical relationship, gives a critical volume fraction of 0.10 for the McGee Ranch soil, and a critical volume fraction of 0.08 for the North Caisson soil, instead of the estimated values, 0.15 and 0.095, respectively from Hunt and Gee, 2002a. Comparisons with experiment, Rockhold et al., 1988, of the results for the hydraulic conductivity of these soils as a function of moisture content (or saturation) using the estimated, Hunt and Gee, 2002a, vs. the calculated values of α_c are plotted in Fig. (4ab) and in Fig. (5ab). Although the hydraulic conductivity is not a particularly sensitive function of α_c , improvements in the scheme for finding α_c appear to result in improvements in estimating $K(S)$.

5. Non-equilibrium calculations

Non-equilibrium properties depend on the entire history of the system since it was last in equilibrium. Many different factors can affect non-equilibrium properties, but I will only be concerned with those, which can be related to percolation theory. Reasons for this restriction range from the practical to the theoretical and include: 1) Such complications have never before been considered quantitatively, 2) Neglect of percolation theory has led to inconsistencies of interpretation in the past (for example, tortuosity has been used as an ad hoc adjustable parameter, rather than as a well-defined consequence of the importance of percolation theory to flow), 3) Percolation theory concerns effects which are due to incomplete connectivity, rather than those, e.g., of local geometry. The latter should probably tend to cancel as a function of S in a self-similar medium, whereas the effects of incomplete connectivity should be large, 4) percolation theory offers a degree of universality to interpretation, particularly when the important behavior can be

interpreted as being expressible in terms of a “nearness” to percolation, or in terms of a function of the difference of some probability, p , and its critical value for percolation, p_c .

Edge effects, while potentially important, and also treatable in percolation theory, Hunt, 1998, will not be considered here. In analogy with calculations of finite size effects on the hydraulic conductivity, clusters of larger pores in direct contact with an edge, but not with the infinite cluster (which can therefore rapidly empty on reduction of h below h_A) are assumed important only in systems of linear dimension several hundred pore separations or less, perhaps relevant in decimeter sized samples of coarse sands. However, such edge effects are emphasized when soil columns are very short compared to their width. This is because equilibration is less dependent on flow within the medium, and associated connectivity questions (percolation) when a larger fraction of the medium is in direct contact with the external forcing.

Two general approaches to the non-equilibrium problem are given. The first assumes that no other mechanism for flow exists other than capillary flow, and the method is developed so as to omit any time dependence. While this approach is simpler, it is thus also less general, i.e. it could only apply for cases where $K(S=\alpha_c/\phi) \gg K_{ff}$ (K_{ff} =effective conductivity due to film flow), and when the time for adjustment to a new matric potential is too small for low conductive pathways through film flow to make a significant effect. Thus it is intended to be applicable to experiments with rapid reduction in matric potential, but with relatively high values of the hydraulic conductivity due to capillary flow, e.g., in coarse sands at higher saturations. But if experimenters followed this approach closely, water contents less than α_c would never be reached on experimental time scales.

It is argued in the appendix that a reasonable estimate, for all $\theta > \alpha_c$, for the probability, P , that a given water-filled pore is attached to the infinite cluster of water-filled pores is (eqn(A.3)),

$$P = \frac{(\theta - \alpha_c)^\beta}{(\phi - \alpha_c)^\beta} \quad (23)$$

Note that $P(\theta=\phi)=1$, when all pores are filled with water. In fact, eqn(23) probably overestimates the fraction of sites cut off from capillary flow, but other choices of θ for normalizing P to 1 appear arbitrary. The following results are written for a process where the matric head is lowered from h_A , the air entry head, by discrete steps with h_i the i^{th} value of the matric potential, h_{i-1} the previous value, and so on. The expression for the moisture content is now modified as follows,

$$\theta_i = \left\{ \left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_0}^{-A/h_i} r^{2-D} dr + \left(\frac{3-D}{r_m^{3-D}} \right) \int_{-A/h_i}^{-A/h_{i-1}} r^{2-D} dr \left[1 - \left(\frac{\theta_{i-1}^{eq} - \alpha_c}{\phi - \delta_i - \alpha_c} \right)^\beta \right] + \dots \right. \\ \left. \left(\frac{3-D}{r_m^{3-D}} \right) \int_{-A/h_{i-1}}^{-A/h_{i-2}} r^{2-D} dr \left[1 - \left(\frac{\theta_{i-2}^{eq} - \alpha_c}{\phi - \delta_{i-1} - \alpha_c} \right)^\beta \right] + \dots \right\}. \quad (24)$$

where $\delta_i(\theta) = \theta_{i-1} - \theta_{i-1}^{eq}$. The numerator refers to the equilibrium value of the previous moisture content, θ_i , and $\delta_i(\theta)$ is introduced into the denominator because the water content remaining in the medium (after the i^{th} operation) in pores larger than those, which in equilibrium should be empty of water, does not contribute to either the volume of water on the percolation cluster, nor to the volume of water, which should be required (say through reimbibition) to guarantee that all pores are connected to the infinite cluster. Thus this modification involves a renormalization, which is accomplished with the mathematical operation of subtracting $\delta_i(\theta)$ from both the numerator and the denominator of the actual value of $(\theta - \alpha_c)/(\phi - \alpha_c)$. The non-equilibrium nature of the problem is explicit in eqn(24); the recursive nature of this equation implies that the water content at any value of θ , for which the factor in $\theta - \alpha_c$ is appreciably less than 1, is dependent on previous values of θ .

The imbibition problem considered is somewhat different, in that I start with a system, which is assumed to have a lower moisture content than required for percolation of water-filled pores. Thus this condition cannot have been reached exclusively by the procedure above. Until an infinite pathway can be connected, there is no way to get moisture into the majority of the smallest pores (the fraction of pores connected to the largest clusters is negligible except in systems small enough for edge effects to be important). Once the infinite pathway is connected, moisture can start in. When the matric potential is increased to $-A/r_c$, ($r_c = -A/h_c$) defined as follows, it will be possible for water to enter into more than just the few pores along the edge.

$$\alpha_c = \left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_0}^{-A/h_c} r^{2-D} dr \quad (25)$$

Then, upon subsequent increase of the head to the value h , the moisture content will be given by (provided again that insufficient time for equilibration by the effects of film flow is allowed),

$$\theta = \left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_0}^{-A/h} r^{2-D} dr \left[\frac{(A/h)^{3-D} - (A/h_c)^{3-D}}{(A/h_A)^{3-D} - (A/h_c)^{3-D}} \right]^\beta \quad (26)$$

In order to obtain eqn(26), the factor with $(\theta - \alpha_c)^\beta$ was expressed in terms of the hydraulic head along the lines of eqn(25), which implies that the fraction of accessible pores is essentially set by a water entry matric potential, and is not dependent on the history of the sample. Thus, to the extent that eqn(26) is accurate, the implication is that the process of imbibition is less strongly hysteretic than that of drainage, but this is partly because no

residual water content was considered in the development. If there was some small water content, θ_r , remaining in the soil from a previous drainage experiment (thus present in larger pores than would be the case in equilibrium), then the value of h_c should be altered as follows,

$$\alpha_c = \frac{3-D}{r_m^{3-D}} \int_{r_0}^{-A/h_c} r^{2-D} dr + \theta_r \quad (27)$$

Experiments leaving a significant amount of moisture, such as accounted for in eqn(27) would tend to reduce hysteretic effects by making it easier for a rapidly dried sample to reimbibe. However, the obvious aspect, which has been neglected, is that during the process where the head is increased again, the water content is still higher than the equilibrium value for a given h , and the tendency will be for continued drainage. The next treatment is more likely to capture typical hysteretic effects, if extended to imbibition.

A Non-equilibrium Experiment

The pressure plate experiment, developed by Richards, Richards and Fireman 1943; Richards 1948, has become the standard method for measuring water retention characteristics of soils, Clapp and Hornberger 1978; Rawls et al. 1982. But there may be significant problems with equilibration in many cases, Gee et al., 2002.

A typical experimental arrangement consists of a soil column of cross-sectional area w^2 and height d sitting on a pressure plate of area w^2 and thickness of d_0 within a chamber full of air at an initial pressure, $-h_i$, which may be different from atmospheric pressure. The air in the chamber is then pressurized, pushing water out through the plate at the bottom. Different plates are used for different pressure ranges, because it is important that the plate conductivity on the one hand not be too low relative to that of the soil or equilibration is hindered, but on the other hand, not too high, else the plate saturation may also change during the course of an experiment. In any case experimental estimates of

moisture contents in equilibrium with a particular pressure, θ^{eq} , are not necessarily trivial, and a typical method to estimate them is to wait until outflow has materially decreased or stopped (i.e., too low to measure in reasonable time), assuming that equilibrium has then occurred. The cessation of drainage, however, often takes longer than several weeks, particularly for finer-textured soils. In order to avoid long and uncertain waiting times, Stol (1965) suggested a means to estimate equilibrium water contents by using an analytical (nomograph) method that requires estimating both soil and plate conductances to predict the final drainage curve. Topp et al. (1993) suggested fitting the time dependent weight loss or changes in volume outflow (after 48 hours) to an exponential function. An exponential function is consistent with treating the change in the water content of the soil with changes in h in terms of an h -dependent capacitance, i.e., with assuming that the pressure gradient in the soil diminishes as it equilibrates, in analogy to the charge on a capacitor after a change in voltage. Here, we treat a linearized version of the problem, but anticipate that our calculated time and the relaxation time of Topp et al., 1993, should be related. In any case, using this method, Topp et al. (1993) estimated equilibration times of up to 25 days for 76-mm-high cores. The question is what fraction of water remains in the soil a time t after the application of pressure $-h_f > -h_i$, presuming that equilibration at $-h_i$ was possible?

This problem really has two parts, as the approximation applied below is not correct, that the hydraulic head everywhere in the soil column is h_f , immediately after application of the pressure. In fact, the soil column develops a pressure gradient in excess of that induced by gravity. Nevertheless, we propose to use this approximation in order to find the basis of dividing up the water content to be evacuated as coming from two sources: one from the pores connected with the percolation “path,” and one from pores which must be evacuated through film flow because of the lack of a connection with a path. This type of partition could then be used in a simulation of Richard’s equation to develop the flow and matric potential as a function of time and height. Lacking such a numerical approximation, the expressions developed here are probably directly applicable only when $d/w \ll 1$, i.e. in the case where height of the soil column is small compared with its width.

First it is necessary to define the following hydraulic conductivity symbols: K_0 is the plate hydraulic conductivity, K_{pm} is the capillary flow hydraulic conductivity, and K_{ff} is the film flow hydraulic conductivity. K_{ff} is not calculated in the present work, but for reference to K_{ff} in fractal media, see Toledo et al., 1995. In experiments at PNNL, (Gee, 2001, personal communication) K_0 can be as small as 10^{-9} cm/s.

If equilibrium is reached, the volume of water lost from the soil will be, V_w

$$V_w = \phi dw^2 \left\{ \left[1 - \frac{1}{\phi} \left(\left[\frac{h_A}{h_f} \right]^{3-D} - 1 + \phi \right) \right] - \left[1 - \frac{1}{\phi} \left(\left[\frac{h_A}{h_i} \right]^{3-D} - 1 + \phi \right) \right] \right\} \quad (28)$$

Eqn(28) for V_w is just a fancier version of,

$$V_w = dw^2 \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] = \phi dw^2 (S_i - S_f) \quad (29)$$

It is assumed to begin with that all this water can exit the porous medium by capillary conduction. If this is not the case, then there are additional complications to be dealt with later. V_w will be lost through the resistance of the plate, which is

$$R_h = \frac{d_0}{w^2 K_o} \quad (30)$$

where d_0 is the thickness of the plate, and K_0 is its hydraulic conductivity. But the water cannot be removed from the soil more slowly than it would be through the pressure gradient induced by gravity, so that a minimum $\Delta P=d$ for the soil, while $\Delta P=h$ for the plate. As long as the resistance of the plate is much larger than that of the soil,

$$t = \frac{V_w}{dV_w/dt} = \frac{\left(dw^2 \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] \right)}{w^2 \left(\frac{h}{d_0} \right) K_0} = \left(\frac{dd_0}{hK_0} \right) \phi(S_i - S_f) \quad (31)$$

If the resistance of the “porous medium” is larger, then,

$$t = \frac{V_w}{dV_w/dt} = \frac{\left(dw^2 \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] \right)}{w^2 \left(\frac{h}{h} \right) K_{pm}} = \frac{d\phi(S_i - S_f)}{K_{pm}} \quad (32)$$

Actually it is not precisely the resistance ratio, which is relevant. In fact, it is the ratio $(h/d_0)K_0/K_{pm}$. When this ratio is 1, eqn(31) and eqn(32) are equivalent. For the McGee Ranch soil, $\phi=0.445$, at the lowest water content, $S\phi=0.15$, the matric potential was $h=-300\text{cm}$, and the factor proportional to the water lost is very nearly 0.3. It is possible then to generate a rough estimate of the time for drying of the soil to a moisture content of 0.15, if this process takes place in a single step. If $K_0=10^{-9}\text{cm/s}$, and the ratio $d/d_0=10$ (5cm/5mm), then $t=28\text{days}$. If K_0 is enough larger so that the limiting conductance is the McGee Ranch soil, itself, then t can be 17 days (to reach a head of -300cm). In this calculation, however, I have used the K from this lowest water content, on the order of

10^{-6} cm/s (with $d_0/h=0.5/300$), although obviously a continuously changing K should be used, with the assumption that the system is equilibrating. No hysteresis effects have been incorporated into this expression.

There are several possible hysteresis effects to consider. One is that as the water content is reduced, and the conductivity of the medium approaches that of the ceramic plate, some pores with water will be cut off from the path of drainage, and will not be able to drain within the time set by the hydraulic conductivity of the medium. This is ultimately a result of pore-scale heterogeneity, in which the conductivity of the medium is determined by the optimal path (with larger K) of flow, and not by the average path of flow. As long as, e.g., a mean hydraulic conductivity of the medium is larger than the hydraulic conductivity of the plate, this is not a significant problem.

Some other complications develop already for $\theta > \alpha_c$. As in the previous non-equilibrium calculations, some of the “pores” which would admit capillary flow because they are still “full” are cut off from the conducting path, while others are connected. Since the fraction of water-filled pores connected to the infinite cluster is called P , the fraction not connected to the infinite path, is,

$$1 - P = 1 - \frac{(\theta - \alpha_c)^\beta}{(\phi - \alpha_c)^\beta} \quad (33)$$

Suppose that the water content of the medium is to be lowered from θ_i to θ_f by staying in equilibrium. Then we can break up the process as follows: the water to be removed that is directly connected to the network with K_{pm} is,

$$(\theta_i - \theta_f) \frac{(\theta_i - \alpha_c)^\beta}{(\phi - \alpha_c)^\beta} \quad (34)$$

The remaining fraction is,

$$(\theta_i - \theta_f) \left[1 - \frac{(\theta_i - \alpha_c)^\beta}{(\phi - \alpha_c)^\beta} \right] \quad (35)$$

If sufficient time is allowed, both of these fractions can be removed, and the total water lost is still the value given in eqn(28), or

$$V_w = dw^2 \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] \frac{(\theta_i - \alpha_c)^\beta}{(\phi - \alpha_c)^\beta} + dw^2 \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] \left[1 - \frac{(\theta_i - \alpha_c)^\beta}{(\phi - \alpha_c)^\beta} \right] \quad (36)$$

But with different time scales (of the different physical processes) associated with these two terms, the water lost may be something different from eqn(36) (consistent with eqn(29)) in an experiment of finite duration. This is a relatively simple partition with complications coming only in the time scales for flow on and off the infinite cluster.

The time dependence is controlled by flow path lengths. The water directly connected to the infinite cluster must flow a distance on the order of d , but at the relatively high rate given by the critical conductance for capillary flow. The remaining water must first reach the infinite cluster by the much slower means of film flow. Even though the latter distance is much less, the conducting mechanism may be so much slower that there can be a significant time lag. The distance, L_a , this water must travel before it reaches the infinite cluster is on the order of a typical separation of flow paths. The typical separation of flow paths is given by the same general result, eqn(A.6), that defines the correlation length, or largest cluster of water-filled pores at water contents less than critical percolation. But much of this distance is composed of transit through finite clusters,

which admit capillary flow. If constrained to flow through the finite clusters, the composite water path will have the tortuosity associated with flow along the infinite cluster right at percolation. This path length is longer than the correlation length, and is given by, $L \propto (p-p_c)^{-1}$. On the other hand, the large clusters right near percolation are identically tortuous, so the sum of the lengths of the paths inside the clusters is also proportional to L . Since the path length is the difference between these two lengths, it is likely not to be a critical (scaling) function of the variables $p-p_c$ at all. As a consequence, the path length through the air filled pores should be expressible in terms of the fraction of pore space which is air filled. Assuming that L_a normalizes to a quantity closely related to the minimum air-filled pore size at the critical volume fraction of air for percolation ($r_m(1-\alpha_c)^{1/(3-D)}$), I find the length in air to be,

$$L_a \approx r_m (1 - \alpha_c)^{\frac{1}{3-D}} \left(\frac{\phi - \theta}{\alpha_c} \right) \quad (37)$$

where the subscript a stands for air. In eqn(37) use was made of the fact that if the largest water-filled (thus smallest air filled pore) pore has $r=r_m[1-\alpha_c]^{1/(3-D)}$, the air-filled pores just percolate, in analogy with the corresponding derivation in the appendix of χ for the water-filled pores. Also, when $\theta=\phi-\alpha_c$, the numerator and denominator are equal, and the distance is roughly the size of the smallest air-filled pore. L_a does not change rapidly at any volumetric water content larger than α_c , so that the time required for water to reach the infinite water cluster does not change rapidly in the vicinity of $\theta=\alpha_c$.

Then it is possible to modify eqn(36) by including factors linear in time, t , such that the product of t and the relevant hydraulic conductivity is equal to the distance of flow (this assumption ignores the geometrical factors associated with the film flow towards the quasi one-dimensional elements of the infinite cluster as well as changes in the pressure gradient due to the flow itself). The result is eqn(38),

$$\begin{aligned}
 \theta_f = \theta_i - & \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] \left[\frac{\left(\frac{h_A}{h_{i1}} \right)^{3-D} - \alpha_c + (\phi - 1)}{\phi - \alpha_c} \right]^\beta \times \\
 & \left[\frac{t}{d} K_{pm} H \left(1 - \frac{tK_{pm}}{d} \right) + H \left(\frac{tK_{pm}}{d} - 1 \right) \right] \\
 - & \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] \left\{ 1 - \left[\frac{\left(\frac{h_A}{h_i} \right)^{3-D} - \alpha_c + (\phi - 1)}{\phi - \alpha_c} \right]^\beta \right\} \times \\
 & \left[[t - t_0] \frac{K_{pm}}{d} H \left(1 - \frac{tK_{pm}}{d} + \frac{t_0 K_{pm}}{d} \right) + H \left(\frac{tK_{pm}}{d} - \frac{t_0 K_{pm}}{d} - 1 \right) \right]
 \end{aligned} \tag{38}$$

with

$$t_0 \approx \left[\frac{\phi - \theta}{\alpha_c} \right] \frac{r_m}{K_{ff}} [1 - \alpha_c]^{1/(3-D)} \tag{39}$$

In these expressions, $H(x)$ is the Heaviside step function of argument x , which essentially changes the functional form from linear in the time to constant, after the equilibrium change in water content has occurred. Such an abrupt change is clearly an oversimplification, in line with similar approximations that, e.g., were associated with ignoring the dependence of water content and matric potential on column height. The first term accounts, as above, for the amount of water, which is removed directly from the medium by the conducting paths, and the time involved for this volume transfer is taken process, the approximation has been made that water migrating to the infinite cluster does not arrive until a ‘delay time,’ t_0 , which represents the typical time water flows to the

infinite cluster by film flow. Of course, this is also an oversimplification, and, in reality, this travel time is distributed about t_0 .

Next it is necessary to consider the drainage of water at very low water contents, so that percolation of capillary flow no longer exists. Although up to now, I have considered that the critical volume fraction for percolation defines the point at which the continuous path for capillary flow breaks up into isolated clusters, the largest finite cluster may still be as long as the height of the system for water contents very slightly below α_c . Thus, if the distance water must travel by film flow is equal to the height of the soil column less the correlation length for water filled pores, it is not until that correlation length is actually smaller than the system dimension, that it is certain that (nearly) all water will have to be transported by film flow. At water contents below

$$\theta = \alpha_c - \frac{r_m}{d}(\phi - \alpha_c)^{1/\nu} \quad (40)$$

the correlation length for water-filled pores is shorter than the system height. At, and below, this water content, film flow is required for any further removal of water from the system. Clearly, if $d \gg r_m$, this water content is scarcely different from the critical volume fraction. For this considered range of water contents, it is possible to write, in analogy with eqn(37),

$$\theta_f = \theta_i - \left[\left(\frac{h_A}{h_i} \right)^{3-D} - \left(\frac{h_A}{h_f} \right)^{3-D} \right] \left[\frac{\left(\frac{h_A}{h_{i1}} \right)^{3-D} - \alpha_c + (\phi - 1)}{\phi - \alpha_c} \right]^\beta \times \left[\frac{t}{d - r_m \left(\frac{\phi - \alpha_c}{\alpha_c - \theta} \right)} K_{ff} H \left(1 - \frac{tK_{ff}}{d - r_m \left(\frac{\phi - \alpha_c}{\alpha_c - \theta} \right)} \right) + H \left(\frac{tK_{ff}}{d - r_m \left(\frac{\phi - \alpha_c}{\alpha_c - \theta} \right)} - 1 \right) \right] \quad (41)$$

and for moisture contents much below the critical volume fraction, the time involved for equilibration rapidly approaches d/K_{ff} , which can be very large indeed, if film flow is orders of magnitude smaller than capillary flow (if the latter can result in drainage time of 2 weeks, 3 orders of magnitude longer is already 40 years. At some point vapor phase transport takes over, and the film-flow mechanism becomes less important, but this is a topic beyond the scope of the present paper.

The reason why deviations of $\theta(h)$ from the equilibrium prediction tend to be small for $\theta > \alpha_c$, is that the time required for the transport by film flow is given by the ratio of a microscopic length (i.e., pore size) to K_{ff} . However, for $\theta < \alpha_c$, all water removed must be transported by film flow, so there is a rapid cross-over in the equilibration time to a value given by the ratio of the sample size to K_{ff} , which can be very large.

Implications for purely kinetic problems with equilibration

The previous treatment of non-equilibration for the two separate cases of $\theta > \alpha_c$ and $\theta < \alpha_c$ is illuminating. First, note that for a given value of $h > h_c$, (at which percolation of capillary flow ceases), the results here imply potential variability in S , but without corresponding variability in K , because by definition the water, which may be stranded in the sample, does not connect to the percolation path. Thus, these results imply that $K(S)$

should show more effects of hysteresis than $K(h)$. In particular, $K(S)$ would often be measured as too low, since for a given K , S would be too large. In fact, however, the experimental problem in this range is generally opposite; $K(h)$ shows more effects of hysteresis than does $K(S)$, and the measured value of $K(h)$ is likely to be too high, Hunt and Gee, 2002b. As a consequence I conclude that the major cause of hysteresis for $\theta < \alpha_c$ is not a result of uncertain connectivity, even though questions of connectivity clearly dominate the situation for $\theta < \alpha_c$. For $\theta > \alpha_c$ it appears as though the major cause of hysteresis must be related to the occurrence of very small values of K arising from capillary flow, in accord with Hunt and Gee, 2002b. Since then equilibration occurs by capillary transport of water, but the transport process is simply too slow on typical experimental time scales, the system falls out of equilibrium due to kinetic effects. Such a result is familiar from the “kinetic” glass transition in viscous liquids (where as heat is removed, the rate at which heat can be removed diminishes rapidly). The glass transition temperature can be predicted by equating experimental and relaxational time scales. Can the same be done here?

In analogy with the results of the glass transition, Hunt, 1991, I write,

$$\frac{\Delta h / \Delta t}{dh / d\theta} \equiv \frac{dh / dt}{dh / d\theta} = \frac{K(h)}{d} \quad (42)$$

where the left-hand side of the equation is essentially a desired rate of change of moisture content with time in terms of steps of Δh and allowed equilibration times Δt , and the right-hand side is the limiting rate of change of moisture content with time. When $K(h)$ has diminished to the point that these two quantities are equal, the system will fall out of equilibrium unless Δt is increased. Using the fractal descriptions in the text eqn(42) can be rewritten,

$$\frac{\Delta h}{\Delta t} = \left(\frac{1}{3-D} \right) \left(\frac{h_A K_S}{d} \right) [1 + \theta - \phi]^{1/(3-D)} \left[1 - \frac{1 - \left(\frac{h_A}{h} \right)^{3-D}}{1 - \alpha_c} \right]^{\frac{3}{3-D}} \quad (43)$$

where the final factor is just $K(h)/K_S$, obtained from substituting eqn(18) for $S(h)$ into eqn(15) for $K(S)$. Using Δh as, say, 10cm, $d=5$ cm, and $D=2.83$, eqn(42) implies a value for Δt of about 12 days if K is 10^{-6} cm/s (at $\theta \approx 0.15$), and about 4 minutes, at $K=10^{-3}$ cm/s (at full saturation). These results are in rough agreement with the prediction of eqn(32) for the McGee Ranch soil. The analogous procedure in viscous liquids leads to a transcendental equation in the temperature, and greater conceptual difficulties.

The reason, why small values of K tend to lead to overpredictions of $K(h)$ for low h , is that in that case the excess water content is not a result of a drop in connectivity, but simply of the slower rate, at which the water is removed, and as a consequence, K is overestimated as well as S , so that the dependence of $K(S)$ is less affected. But $K(h)$ is noticeably overestimated. In other words, $h(S)$ tends to curve upward ($-h$ increases more rapidly than it should), but the upward curvature of $\log[K(h)]$ vs. h is accentuated as well (K diminishes less rapidly than it should) and the two effects tend to cancel in $K(S)$. Precisely this tendency was shown to exist, Hunt and Gee, 2002b, in experiments, Khaleel and Relyea, 2001, from the Hanford site in coarse sands at low values of θ , but with $\theta > \alpha_c$.

Conclusions

Further investigations into the role of continuum percolation in wetting and drying of porous media have been carried out. The chief new work has involved: 1) an analytical approximation for the critical volume fraction for percolation (and use of two values thereof in existing formulas for previously described soils) and 2) derivation of non-equilibrium moisture retention characteristics. Derivations of non-equilibrium moisture retention characteristics were accomplished using percolation theory, under the assumption that the dominant reason for lack of equilibration was due to problems with

connectivity. Two different approaches were taken; one was the development of a recursive relationship for the water content in terms of a series of rapid, discrete reductions in the matric potential (excluding any time dependence), while the second approach generated explicit time dependences. The latter should prove useful for estimating water contents in the low saturation regime, where equilibration is difficult because of the necessity of invoking film-flow (when capillary flow paths do not connect). The former may be of some use in experiments at higher moisture contents, but it is likely that effects of reduced connectivity in this regime are of secondary importance to problems in equilibration arising from very low values of the hydraulic conductivity due to capillary flow, and a general relationship for estimating the equilibration time for this case is given. It is hoped that most experimental procedures can be described using some combination of these means, or at least straightforward generalizations thereof.

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Appendix

Here I give arguments for the specific choices of the scaling relationships for the fraction of "sites" (water-filled pores) connected to the infinite cluster for $\theta > \alpha_c$, and for the correlation length, or linear dimension of the largest cluster of connected water-filled pores for $\theta < \alpha_c$.

At saturation $S < 1$, in equilibrium, not all water-filled pores are connected to the infinitely large, interconnected cluster of water-filled pores. A general relationship from percolation theory, Stauffer, 1979, is that the fraction of sites, P , connected to the infinite cluster is,

$$P \propto (p - p_c)^\beta \quad (\text{A.1})$$

where the critical exponent, $\beta \approx 0.4$ in three dimensional systems, and where p is the fraction of occupied sites in site percolation, the fraction of connected bonds in bond percolation, or the volume fraction in continuum percolation. The value of p , for which percolation occurs, is called p_c . In the present case of continuum percolation, the moisture content is the variable analogous to p , and its critical value for percolation has been called α_c . Thus,

$$P \propto (\theta - \alpha_c)^\beta \quad (\text{A.2})$$

(A.2) is more helpful as an equality, but there are no general guidelines for choosing the constant of proportionality. I wish to use proportionality (A.2) for the entire range of relevant values of θ , but strictly speaking proportionality (A.2) is only valid in the vicinity of α_c . Nevertheless, an approximate equality can be obtained by constraining the value of P in the limit of $\theta \rightarrow \phi$ to be 1. Since, in actuality, P is probably very nearly 1 at considerably smaller values of θ , this approximation should tend to underestimate P throughout the range of $\theta > \alpha_c$, but any other choice, in the absence of direct simulations, would be arbitrary. The result of applying this constraint is that,

$$P = \frac{(\theta - \alpha_c)^\beta}{(\phi - \alpha_c)^\beta} \quad (\text{A.3})$$

Another required quantity is the linear dimension, χ , of the largest cluster of interconnected sites when $p < p_c$. It is known that, Stauffer, 1979,

$$\chi = \chi_0 (p_c - p)^{-\nu} \quad (\text{A.4})$$

where χ_0 is a fundamental length scale appropriate to the particular problem, and $\nu=0.88$ is a critical exponent. Then, with the same identifications as above,

$$\chi = \chi_0 (\alpha_c - \theta)^{-\nu} \quad (\text{A.5})$$

Clearly, in the limit $\theta \rightarrow 0$, χ must be r_0 , so that one could make the approximation

$$\chi = r_0 \left(\frac{\alpha_c}{\alpha_c - \theta} \right)^\nu \quad (\text{A.6})$$

But since the percolation expression for χ is valid only for θ 'near' α_c , it is probably better to use a fundamental pore length scale for χ , which is accurate in the vicinity of α_c , rather than to use r_0 . Such a length is given by r^* , defined through,

$$\left(\frac{3-D}{r_m^{3-D}} \right) \int_{r_0}^{r^*} r^{2-D} dr = \alpha_c \quad (\text{A.7})$$

because (A.7) defines the largest water-filled pore right at the critical volume fraction of water. Solution of (A.7) yields,

$$r^* = r_m [1 + \alpha_c - \phi]^{1/(3-D)} \quad (\text{A.8})$$

Now it is possible to write,

$$\chi = r_m [1 + \alpha_c - \phi]^{1/(3-D)} \left[\frac{\alpha_c}{\alpha_c - \theta} \right]^v \quad (\text{A.9})$$

This form is somewhat of a hybrid, with the fundamental length scale defined right at percolation. Consequently the scaling of the power through the condition at zero moisture is no longer quite correct; to modify this it would be necessary to put an explicit moisture content dependence into the length scale (prefactor), and eqn(A.9) tends to overestimate the value of the correlation length at low moisture contents. But to make further modifications would imply an accuracy, which does not exist anyway; any result in the form of eqn(A.9) can not be relied on to give an accurate result in the limit of zero moisture content, and this will be regarded as the best estimate. Furthermore, at moisture contents substantially above zero, vapor phase transport will dominate, and all formulations of the hydraulic conductivity based either on film flow or capillary flow cease to be valid.

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Figure Captions

Figure 1. Correlation of predictions of eqn(21) for the critical volume fraction for percolation, α_c , with results for the moisture content, θ_d , at which experiment and the predictions of fractal theory deviate. Note that not only is $R^2=0.83$, the proportionality is also nearly an equality, with the slope, 0.83, only slightly less than 1. This deviation of the slope is probably due mainly to the lack of kinetic equilibration in many of the coarser soils at low moisture contents (but still above α_c), which prevents the regression line from intersecting the x -axis at the origin. This can be roughly checked; pick $x=0.2$, for which $y=0.2$ would produce a unit slope, if $(x,y)=(0,0)$ were also on the curve. Using the regression formula, $y=0.831x+0.0375$ leads to $y=0.204$.

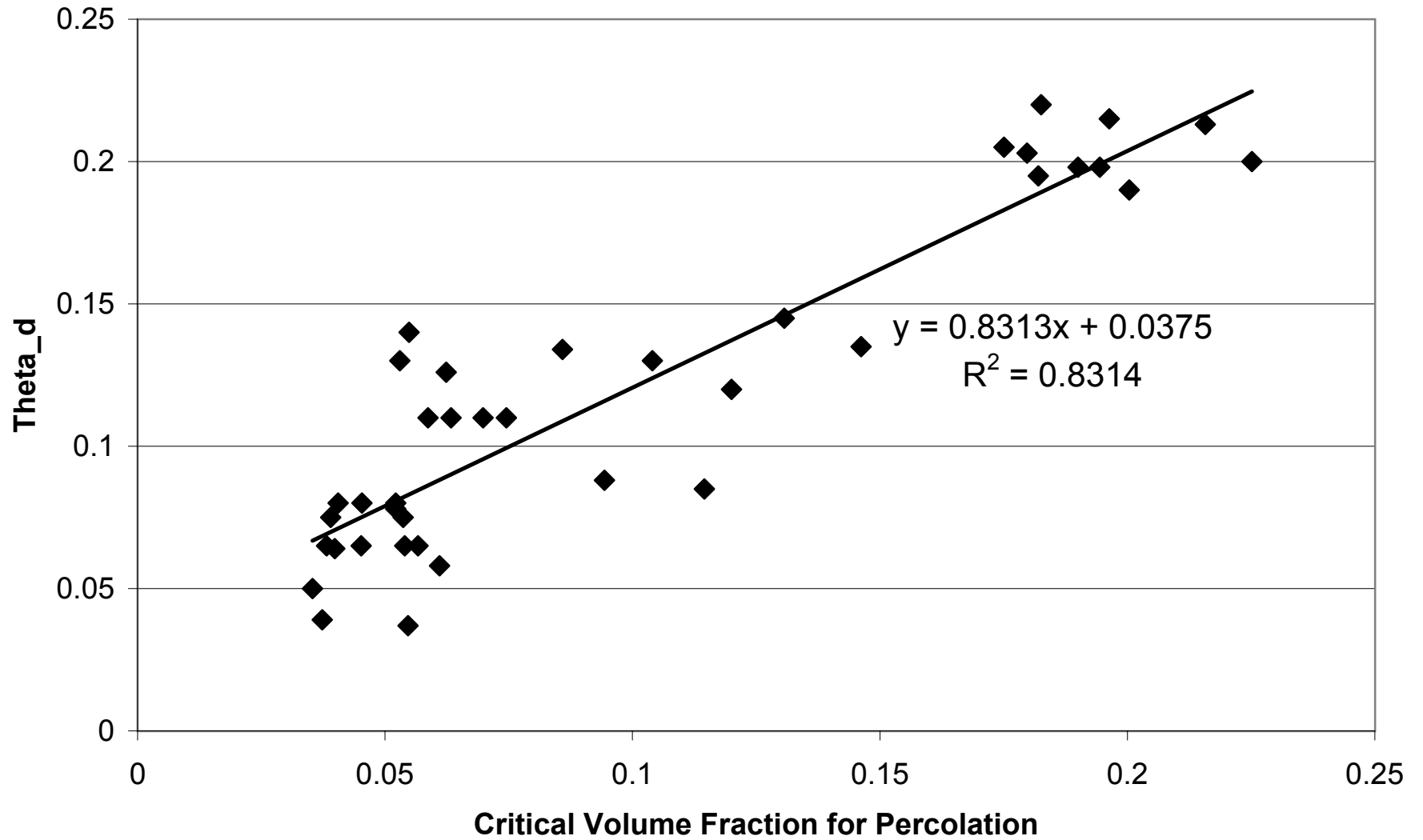
Figure 2. Correlation of prediction of eqn(22) for α_c with results for θ_d . The poorer fit (as well as the smaller value of R^2) suggests that the linear approximation is not as accurate.

Figure 3. Correlation of the Moldrup et al., 2001, relationship for θ_t with the observed θ_d .

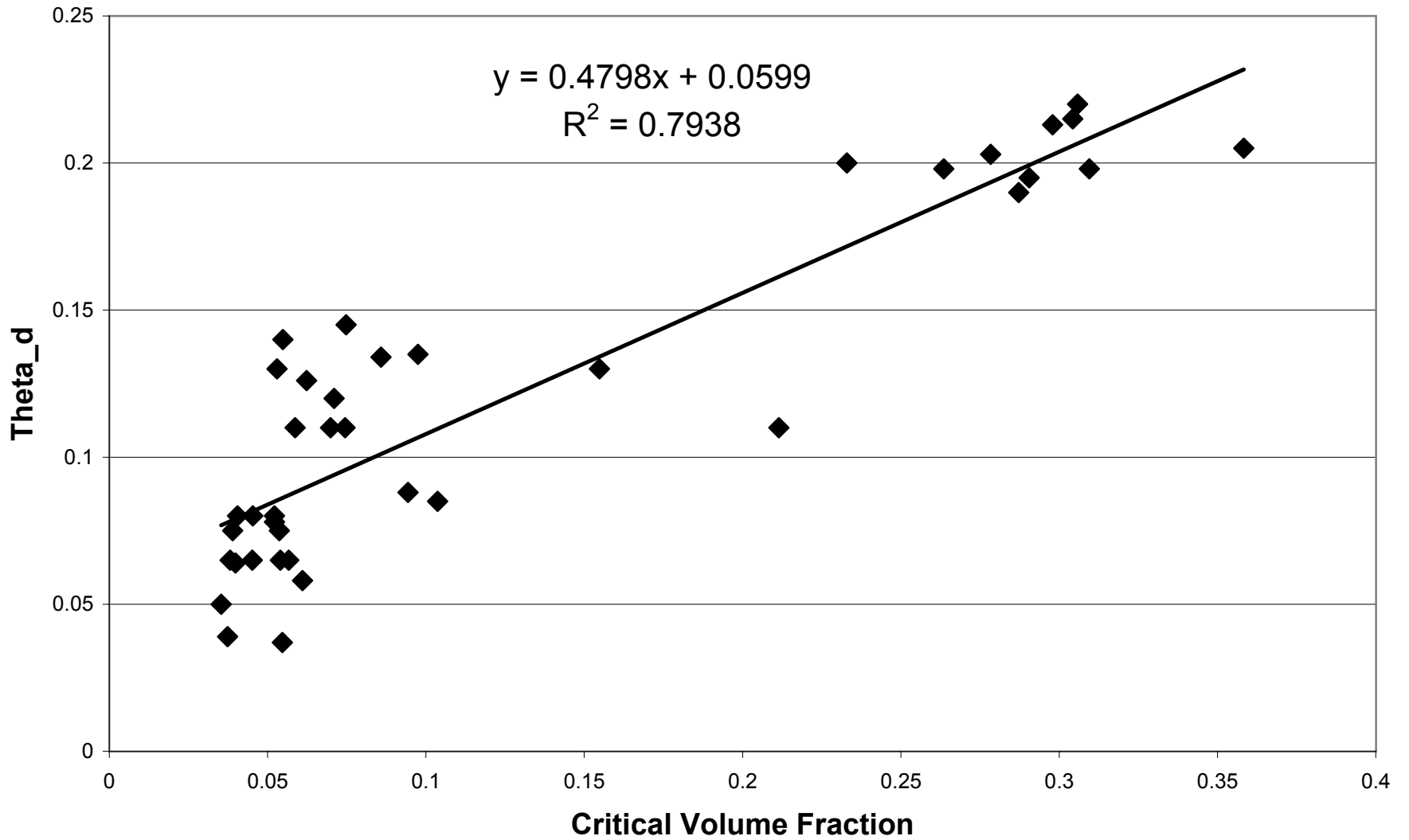
Figure 4. Comparisons of predictions and experiment for $K(S)$ in the McGee Ranch soil. Panel a gives the comparison using an estimation of $\alpha_c = 0.15$, while panel b gives the comparison using the calculated (or regressed) value of $\alpha_c = 0.10$.

Figure 5. The analogous figure for $K(S)$ in the North Caisson soil with $\alpha_c = 0.095$ in panel a, and the regressed value of $\alpha_c = 0.08$ in panel b.

Theta_d vs Percolation Threshold eqn(21)



Theta_d vs. Percolation Threshold eqn(22)



Correlation of Threshold Moisture and Surface Area

