PERCOLATION THEORY AND NETWORK MODELING APPLICATIONS IN SOIL PHYSICS

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Abstract. The application of percolation theory to porous media is closely tied to network models. A network model is a detailed model of a porous medium, generally incorporating pore-scale descriptions of the medium and the physics of pore-scale events. Network models and percolation theory are complementary: while network models have yielded insight into behavior at the pore scale, percolation theory has shed light, at the larger scale, on the nature and effects of randomness in porous media. This review discusses some basic aspects of percolation theory and its applications, and explores work that explicitly links percolation theory to porous media using network models. We then examine assumptions behind percolation theory and discuss how network models can be adapted to capture the physics of water, air and solute movement in soils. Finally, we look at some current work relating percolation theory and network models to soils.

Key words: Percolation theory, invasion percolation, network models, porous media, soil physics

1. Introduction

Percolation theory is a branch of probability theory dealing with properties of random media. Originally conceived as dealing with crystals, mazes and random media in general (Broadbent and Hammersley, 1957), it now appears in such fields as petroleum engineering, hydrology, fractal mathematics, and the physics of magnetic induction and phase transitions. As explained by the originators of percolation theory (Broadbent and Hammersley, 1957), percolation and diffusion, for example, can both be seen as dealing with fluids in a medium (in a very general sense), but they differ in their emphasis: in diffusion, the randomness "belongs to" the fluid, while in percolation theory, the emphasis is on the randomness of the medium. Several reviews of percolation theory in general (e.g., Shante and Kirkpatrick, 1971; Bunde and Havlin, 1991; Havlin and Bunde, 1991; Stauffer and Aharony, 1992) and in relation to porous media in particular (e.g., Berkowitz and Balberg, 1993) have been published recently. Percolation theory also figures prominently in books on porous media by Dullien (1992), Adler (1992) and Sahimi (1995).

The history of percolation theory as applied to porous media is closely tied to network models. A network model is a detailed model of a porous medium, generally incorporating pore-scale descriptions of the medium and the physics of

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pore-scale events. Network models and percolation theory are complementary: while network models have yielded insight into behavior at the pore scale, percolation theory has shed light on the larger scale behavior, accounting for randomness in porous medium geometry, fluid properties, and their interplay. In each case, behaviors are seen at the large scale (e.g., an assemblage of pores) that are not necessarily predictable at the scale of the individual pore. Network models and their application to porous media were recently reviewed by Ferrand et al. (1990) and Ferrand and Celia (1992). However, the emphasis of their reviews is on network models rather than percolation theory, and it is important to differentiate between the use of pore-scale network models alone, and their use in conjunction with percolation theory.

The objectives of this review are, first, to provide a useful summary and reference work for soil scientists wanting to learn more about percolation theory and network models and their application to soils, and second, to expose some of the many remaining issues and challenges in this field. This review will first briefly sketch some basics of percolation theory, and then explore some mathematical aspects. We then discuss work that explicitly links percolation theory to porous media, often using network models, and consider some applications in more depth. We examine the assumptions behind percolation theory and discuss how network models can be adapted to capture the physics of water, air, and solute movement in soils. Finally, we look at some current work relating percolation theory and network models to soils.

Many basic ideas in percolation can be illustrated quite easily. Suppose we have a large array of squares (Figure 1a). Let us call the line intersections "sites", and the segments connecting them "bonds". In a square lattice one bond is connected to six nearest neighbor bonds, while a site has only four nearest neighbor sites. Suppose that each site exists in only two possible states, 'empty' or 'open' (or 'allowed'; there is no universal terminology to describe these states, and one could just as easily say 'on' or 'off'), with open sites being denoted by the presence of a large dot on the intersection, and suppose further that whether a site is open or empty is random and independent of its neighbors. A bond is assumed to exist between each pair of nearest neighbor sites on the lattice. If half the sites are open (Figure 1b), we see that open sites tend to group into clusters of many shapes and sizes. We can refer to these clusters by their size, i.e., a single open site with no immediate open neighbors is a 1-cluster; two adjacent open sites with no open neighbors form a 2-cluster, and so on.

If the probability p of a site being open increases to 2/3 (Figure 1c), several things happen. Most important, at some probability between 1/2 and 2/3, many of the sites become joined into one giant cluster that spans the entire array both vertically and horizontally. The probability at which this happens (approximately 0.593 for the square lattice sites) is called the critical probability p_c, also known as the percolation threshold. If we imagine that fluid can flow only through bonds that connect open sites (drawn more thickly in Figure 1b,c), then below the threshold the

lattice will have zero conductivity, while above the threshold conductivity will rise as the probability increases. Hence, there is a strong relation between connectivity of the (so-called microscopic) elements of the system and the physical properties of the entire (or so-called macroscopic) system. Second, as the proportion of open sites increases, the proportion of empty sites that have open neighbors also increases. Third, once $p > p_c$, if we run fluid across the lattice through bonds connecting open sites, we will find that some of the bonds (the backbone) have fluid flowing through them, while others are simply isolated dead-ends or dangling branches; the proportion of these branches varies as a function of p. The proportion of open sites belonging to the infinite cluster - in other words, the proportion of open sites that would be penetrated by a fluid at the lattice boundaries – is called the accessibility function. Fourth, the clusters grow larger (and merge) with an increase in p. And finally, the reverse is happening to the empty sites: they are being divided and squeezed into smaller clusters as the probability of open sites increases.

The above example varies only the proportion of open sites, so it is called site percolation. An analogous procedure, called bond percolation, varies the proportion of open bonds. The two are not interchangeable: there is no simple formula that will predict bond percolation from site percolation (although bond problems can be "mapped onto" site problems), and, in fact, p_c for site percolation is always greater than p_c for bond percolation (Fisher, 1961). We will encounter a physical significance to the distinction between bond and site percolation in Section 3 of this review.

The ragged ("ramified") edge of a cluster is reminiscent of fractals, and indeed, clusters near the percolation threshold are known to be fractal (Stauffer and Aharony, 1992). In fact, the fractal dimension of a percolating cluster is the same ($D \approx 1.896$) whether the percolation takes place on square, triangular, honeycomb, Voronoi, or some other kinds of 2D lattices (Figures 2a–d) which differ widely in their connectivity (which can be quantified by the coordination number z, defined as the mean number of bonds per site). The fractal dimension does, however, change with the dimensionality or embedding dimension d of the lattice: percolating clusters on 2D lattices have different fractal dimensions than those on 3D lattices (such as cubic lattices, Figure 2e). We will find other connections between percolation theory and fractals in Sections 2 and 3.

The mathematics of percolation theory can be traced back to Flory (1941) and Stockmayer (1943), who were trying to explain the process of gelation, in which small molecules adhere to larger and larger ones to eventually form a gel. Because these molecules do not loop back on themselves, but rather branch indefinitely, they form a special family of lattices known as Cayley trees (Figure 2f), also called Bethe lattices. These trees have only one possible path connecting any two sites, making them much more amenable to mathematical treatment. As a consequence, much of the mathematics of percolation theory was originally developed on Cayley trees. However, these trees differ topologically from lattices which are multiply connected

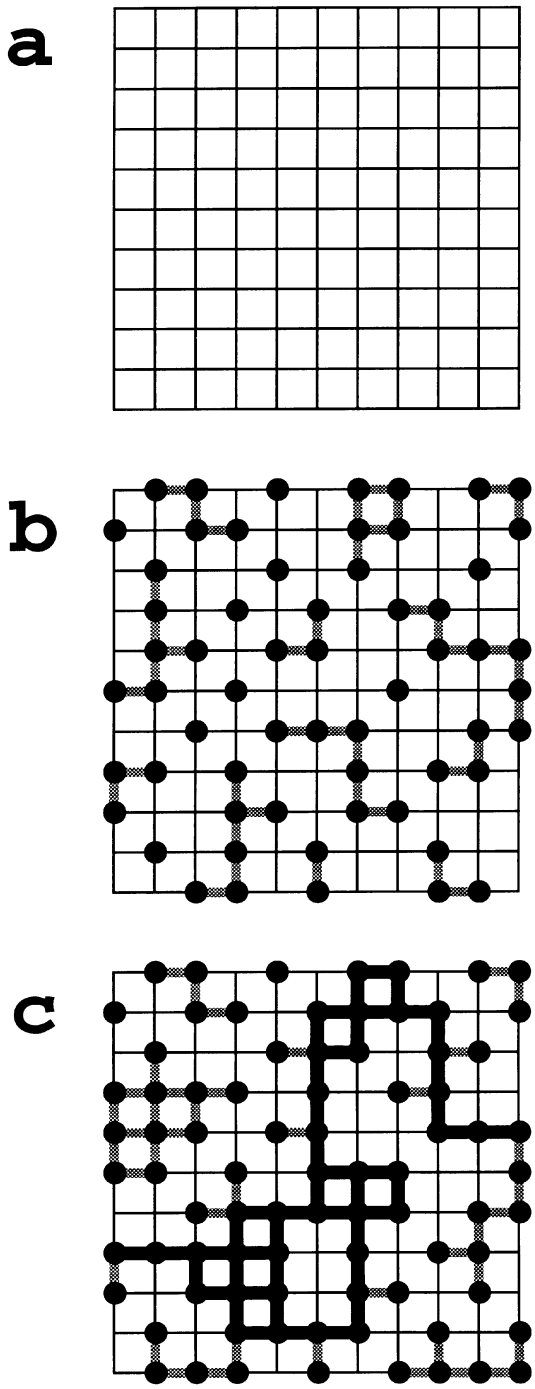

Figure 1. (a): square lattice, (b): square lattice with 50% open sites, (c): square lattice with 67% open sites. In (c), the backbone for flow from left to right is shown with dark bonds, while isolated clusters and dangling branches are shown with light bonds.

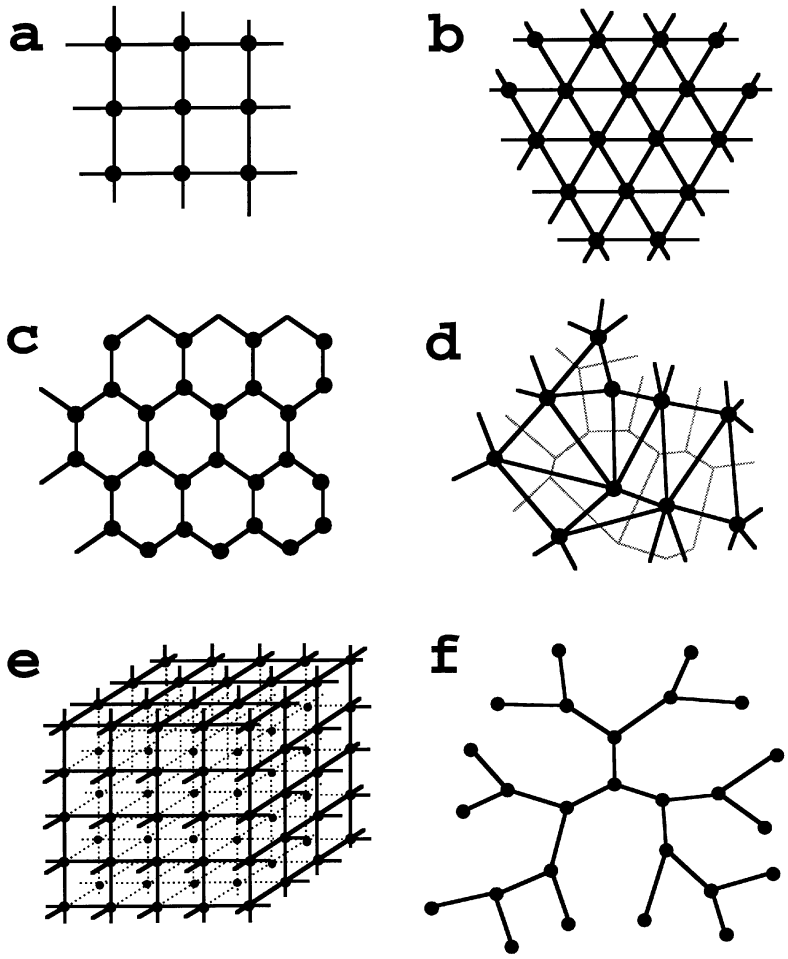

Figure 2. Examples of 2D lattices, with circles representing sites, and dark lines denoting bonds. (a): square ($z = 4$), (b): triangular ($z = 6$), (c): honeycomb ($z = 3$), (d): Voronoi ($\langle z \rangle = 6$), (e): cubic ($z = 6$), and (f): Cayley tree with $z = 3$.

(having loops), like the pore space in a soil, so our discussion will focus on the multiply connected lattices.

The form of percolation of interest to us was developed by Broadbent and Hammersley (1957), who thought of it as a fluid (saturating what we called, above, open sites or bonds) flowing into a maze (the medium). At the time, Broadbent was involved in designing gas masks for use in coal mines (Hammersley and Welsh, 1980). These masks were to use porous carbon granules which would filter the air, with cleaning occurring via surface adsorption. If the pore space within the granules were sufficiently interconnected, gas could penetrate through them and have access to the entire surface area; if not, the granules would not be sufficiently

permeable and so the mask would not work. Hammersley was meanwhile trying to improve Monte Carlo methods for nuclear reactor design, and had organized a symposium (Royal Statistical Society, 1954) to discuss this topic. He became interested in Broadbent's problem, and, according to Sahimi (1984), named it percolation because he thought the fluid flowing into the maze resembled coffee flowing through the grounds in a percolator.

2. The Mathematics of Percolation

Percolation theory and its many variants can be considered as part of a general framework of statistical theories that deal with structural and transport properties in porous media. The literature devoted to percolation theory is enormous, and spans the fields of mathematics and statistical physics, as well as a variety of engineering and other applied disciplines. As such, we shall introduce below only some of the basic features of percolation theory; many other aspects of percolation will be introduced in subsequent sections in the course of discussing its application.

2.1. BASICS AND DEFINITIONS

Many properties of a macroscopic system are essentially determined by the connectivity of the system elements. The properties of a system which emerge at the onset of macroscopic connectivity within it are known as percolation properties. To illustrate the concept of connectivity, consider the square lattice of Figure 1c, in terms of bond percolation. If, for example, the (connected) network of bonds is fully saturated and conducts a fluid, and bonds are randomly removed from the network, the intensity of flow between opposing sides of the network decreases. The question then arises as to the possibility of determining, at one side of the domain, the number of removed bonds by monitoring the fluid flow. In particular, it is of interest to know the number of bonds that must be removed (randomly) in order for no fluid to arrive at the side of the domain. The answer to the second question is given by what is known as the percolation threshold. If the number of bonds is denoted by N, and their number at the threshold is N_c (the "critical" number), one can show (Balberg, 1987; Wong, 1984) that the volumetric fluid flow, Q, will be determined by a power law of the form

$$Q \propto (N - N_c)^{\kappa} \tag{1}$$

where κ is some ("critical") exponent which can be found from theory and/or computer simulation and/or experiment. Such a simple law holds for N relatively close to N_c (typically, for $N/N_c \leq 2$). For much larger N, other considerations can be applied which in many cases lead to other power laws.

The problem described above, and the simple law given by Equation (1) that governs its solution, apply to many kinds of systems, and as such, are much

more general than one might realize at first glance. The above formulation can be used, for example, to describe flow of water in porous rocks, flow of electricity in electrical networks and composite materials, penetration of termites in wood and the spread of fire or epidemics. In a percolation problem, one asks three basic questions: (a) What is the geometrical or physical property (e.g., Q) that is relevant to the connectivity of the system under investigation?, (b) What is the threshold for percolation (i.e., N_c or an equivalent quantity)?, and (c) What is the exponent that describes the behavior of Q near N_c (i.e., κ)? One of the most interesting and useful aspects of percolation theory is that many systems have the same κ. This means that by finding κ for a simple and solvable model, one can predict the value of κ for very complicated systems. This central property of percolation theory is known as "universality". On the other hand, the percolation threshold must be determined separately for each system, although some general guidelines for its determination are available.

Several simple geometrical and statistical concepts are used to quantitatively describe percolation-type systems. To present these concepts, consider the so-called square lattice shown in Figure 1b,c. Each point on the lattice represents a site that is empty or open. A basic assumption of percolation theory is that the process of assigning open sites is random, so that the probability of a site being open is independent of the open/empty assignment of its neighbors or of any other site. Of primary interest is characterization of the system under a given fraction of open sites. For example, assume that there are N_0 sites in the two-dimensional square lattice, with N of them open, as shown in Figure 1b,c. Since the assignment process is random, the probability p of each site being open is simply $p = N/N_0$; this probability is well defined in the $N_0 \to \infty$ limit.

2.2. CLUSTER PROPERTIES

Another concept to be introduced is that of the "cluster", which is simply a group of connected sites. An important question that arises relates to the size distribution of clusters that can be found when the lattice occupation probability is p; cluster size distributions are important in the characterization of interconnected (conducting) groupings of pores or fractures. Cluster sizes may vary, for example, as pores or fractures become disconnected through mechanical or geochemical processes. On a square lattice, to have a 1-cluster, there must be an open site (probability p) surrounded by four empty sites (probability $(1-p)^4$). Hence, the number of 1-clusters will be $N_0 p(1-p)^4$. Similarly, for 2-clusters, the number of such "left-right" clusters is $N_0 p^2(1-p)^6$, and there is the same number of "up-down" clusters. For the limit $N_0 \to \infty$, one may define the number of s-clusters per site, n_s, where s is the number of sites in the cluster (the "size" of the cluster). Thus, it follows that $n_1 = p(1-p)^4$, $n_2 = 2p^2(1-p)^6$, and $n_3 = 2p^3(1-p)^8 + 4p^2(1-p)^7$. The calculation of n_s for larger values of s, for other lattices, and for higher

dimensions, becomes increasingly complicated, but the basic "recipe" is apparent from the above examples.

Following these examples, it is also clear that with increasing p, the probability of finding larger clusters increases. In a finite lattice such as the one shown in Figure 1c, there will be a p value that is sufficiently large to ensure that at least one cluster connects the "bottom" and "top" (or the "left" and "right") ends of the lattice. This value of p, which is well-defined (say, in a computer experiment) when $N_0 \to \infty$, is called the critical probability, and is denoted p_c. The corresponding largest cluster is called the percolation cluster, and the value of p_c is known as the lattice site percolation threshold. The regimes $0 \leq p < p_c$ and $p_c < p \leq 1$ are called the regimes below and above the percolation threshold, respectively. One can generally argue that there is at most one percolation cluster (e.g., Stauffer and Aharony, 1992); this is obvious for the particular two-dimensional case illustrated in Figure 1c. Above the percolation threshold (i.e., for $p > p_c$), one can also determine the probability per site, P, that an open site belongs to the percolation cluster. Since $\Sigma' n_s s$ (where Σ' is the sum over all finite values of s) is the probability per site that the site is open and belongs to a finite cluster, it follows that

$$P = p - \Sigma' n_s s. \tag{2}$$

Furthermore, it can be shown (Stauffer and Aharony, 1992) that the average size of a finite cluster per site (above or below p_c) is $\Sigma' n_s s^2$, which is the weighted average of cluster sizes. Since one is interested in the connectivity between open sites, the common definition of the average finite cluster size, S, is the average cluster size per open site,

$$S = \Sigma' n_s s^2 / p. \tag{3}$$

Since (as shown above) n_s is a polynomial function of p, S can be expressed as a power series of p. For example, in the square lattice with the expressions given above for n_s ($s = 1, 2, 3$), one can readily (although with lengthy calculation) find that $S = 1 + 4p + 12p^2 + 24p^3 + 52p^4 + 108p^5 + 224p^6 + 412p^7 + 844p^8 + 1528p^9 + \cdots$. Following the general expectation (see Equation 1) of a power law behavior, and the particular findings in simple cases (e.g., the one-dimensional lattice where $n_s = p^s(1-p)^2$), one expects that, near p_c, it is possible to approximate a power series such as the one shown above for S by a power law of the form

$$S \propto (p_c - p)^{-\gamma} \tag{4}$$

where γ is an exponent. Indeed, an approximation such as Equation (4) (e.g., Alon et al., 1990) yields for γ the same value as that obtained by computer simulation techniques.

It is found that γ is independent of the particular lattice under consideration, and depends only on the dimensionality of the system. In particular, one finds

that γ = 43/18 for two-dimensional systems, and $\gamma \approx 1.80$ for three-dimensional systems. (A convention in the percolation theory literature is that exact, theoretically derived values are reported as fractions, while approximate values from computer simulations are reported in decimal form). In contrast, the value of p_c depends on the particular lattice, but again the p_c value determined by expressing the series (e.g., Equation 3) with an asymptotic form for S (e.g., Equation 4) is the same as that found by computer simulations for the same lattice (e.g., for the square lattice, $p_c \approx 0.593$). Tables of values of p_c and critical exponents for common two- and three-dimensional lattices can be found, for example, in Stauffer and Aharony (1992). Note that for $p > p_c$, the average cluster size is infinite, but the definitions given here are concerned with finite clusters, and Equation (4) describes their divergence (i.e., approaching infinity) as $p \to p_c$. It has been found, however, that the same γ value describes S for $p > p_c$, and thus Equation (4) holds in this regime, except that one has to replace $(p_c - p)$ by $(p - p_c)$.

So far, we have considered the statistical properties of the clusters. The next property we discuss is the geometrical extent of the cluster. Suppose that the sites of a cluster of size s are located at $\mathbf{r}_i$, where $i = 1, 2, \ldots, s$. The center of mass of the cluster can be defined by $\mathbf{r}_0 = \Sigma \mathbf{r}_i / s$, and thus the so-called radius of gyration of the cluster, R_s, is defined by

$$R_s^2 = \Sigma(|\mathbf{r}_i - \mathbf{r}_0|^2)/s. \tag{5}$$

In other words, R_s can be related to the average distance between any two sites within the same cluster. The average radius of gyration (over all finite clusters) per open site, ξ, can then be defined by

$$\xi^2 = 2\Sigma' R_s^2 n_s s^2 / \Sigma' n_s s^2. \tag{6}$$

Thus, ξ represents the average distance between any two cluster sites, averaged over all finite clusters. The parameter ξ is thus also called the correlation, or connectivity, length. Similar to S, the extent of the average cluster diverges as $p \to p_c$, so that a behavior of the form

$$\xi \propto |p - p_c|^{-\nu} \tag{7}$$

can be expected. It has been shown by various approaches that ν = 4/3 for two-dimensional systems, while $\nu \approx 0.875$ for three-dimensional systems. Two sites are considered correlated if they are connected (i.e., if they belong to the same cluster), and thus ξ, which characterizes the average distance over which two sites are connected, is called the "correlation length" of the system.

To characterize the rather ramified or ragged structure of these clusters, the concepts of self-similarity, fractals and fractal dimension can be used. Objects such as the Koch star and the Sierpinski gasket, which are defined by repetition of simple construction rules, and are exactly self-similar over successive magnifications of

portions of the objects, can be called "exact fractals". Non-exact fractals such as percolation clusters are of course not expected to yield exactly the same picture under successive magnifications. And yet, for any given picture, it is not possible to tell at what magnification (i.e., scale) it was taken. However, as with the Koch curve, there is a well-defined relation between cluster size s and the corresponding cluster radius R_s, such that on average (over clusters of size s), one obtains

$$s \propto R_s^D \tag{8}$$

for all (large enough) s. In particular, any large but finite portion of the percolation cluster can be characterized by this D. Hence the percolation cluster is a "statistical fractal", to be distinguished from the "exact fractal" described above. The approach is similar in 3D: the dimensionality of the Euclidean space is d = 3, while for the percolation cluster, it is $D < 3$ when $p \to p_c$. In fact, noting that $P \propto (p - p_c)^\beta$, it has been shown from purely theoretical arguments using power laws, and confirmed experimentally by computer simulations, that $D = d - \beta/\nu$. In the case of clusters in two-dimensional space, D = 91/48 and β = 5/36, while in three-dimensional space, $D \approx 2.52$ and $\beta \approx 0.41$. Note again that since β and ν are universal, D is universal, and as such is unique for every d (e.g., Stauffer and Aharony, 1992).

Thus, the use of percolation theory allows the quantitative introduction of scaling approaches into the analysis of properties of heterogeneous porous and fractured media. Due to the statistically self-similar (fractal) nature of percolation clusters, which can be used to approximate heterogeneous media, properties arise that are independent of scale, and can in principle be applied equally at the pore, laboratory and field levels.

2.3. FLOW THROUGH PERCOLATION NETWORKS

We now proceed to the issue of conduction through the bonds. Obviously, flow problems are of interest only for $p > p_c$. Note that even in this regime, many of the connected bonds will not have fluid flowing in them, since either they do not belong to the percolating cluster, or they form "dangling branches" (analogous to dead-end pores) which, although filled, do not conduct fluid. The ensemble of bonds through which the fluid can flow is called the "backbone" of the system; when examining single-phase flow problems, it is sufficient to consider only the backbone.

What is the structure of the backbone? Recall that the average diameter of the finite clusters is ξ. Since the backbone is a network that connects the ends of the entire system, the average diameter of the "holes" (i.e., the finite clusters) in the network must be of order ξ. The network then consists of "nodes" (or junctions) and "links" connecting the nodes (e.g., Stanley, 1977). As explained above, the distance from one end of the "link" to the other is of the order of ξ (i.e., the average radius of possible embedded finite clusters), but its actual detailed (tortuous) length is of course longer. With this understanding of the flow network geometry, it is now

possible to consider the quantitative relationship between the possible flow and the probability of finding an open bond.

If the permeability of each bond in a network is known, then by use of Kirchhoff's law for each closed loop (which requires that the algebraic sum of the fluxes at each junction equal zero), the calculation of the overall system permeability, K, in a finite system is straightforward (Balberg, 1986b; Berkowitz and Balberg, 1992). The value of K depends only on the connectivity of the system (i.e., on the bond occupation p), the radii of the individual bonds, and the specific randomization of the given case. This approach can be generalized to other types of networks, and is thus useful for computer simulations of finite model systems. However, while providing a complete solution, it has two major drawbacks. The first is that it is necessary to know all the details of the system, and the second is that, even if all of this information is available, it will always be limited to finite (and thus relatively small) systems. As such, the statistics used in the simulations may yield very poor accuracy in the results, considering the larger system that the model tries to simulate.

Analysis of pores in rocks and soils requires an approach that circumvents these drawbacks; this is where the universality of percolation theory becomes helpful. Similar to power laws given by (4) and (7), scaling arguments indicate that the critical behavior of the permeability K of an infinite system is defined by

$$K \propto (p - p_c)^{\kappa} \tag{9}$$

which is determined by the exponents ζ_κ and ν according to

$$\kappa = \zeta_\kappa + (d - 2)\nu. \tag{10}$$

Conveniently, ζ_κ and ν can be determined in simple systems, and then used to predict the behavior of systems for which no, or very few (usually global) details are known. However, in order to have an equal sign in Equation (9), many more details are required, so that one must resort to finite procedures such as those outlined above using Kirchhoff's law. Thus one of the main contributions of percolation theory lies in its ability to predict the value of κ. Since, as pointed out above, ν can be determined analytically (for two-dimensional systems) using a simple lattice model, the quantity that still remains to be found, which is closely related to the flow problem, is ζ_κ. Techniques for estimating ζ_κ, based on considerations of the link structure, are discussed by Berkowitz and Balberg (1993).

2.4. CONTINUUM PERCOLATION

It is apparent that lattice systems, in general, are the exception rather than the rule among systems in which the connectivity determines the behavior of a system. Most real systems possess a much less "ordered" network, and a distribution of local bond permeability values. This is of course the case in many geological porous media

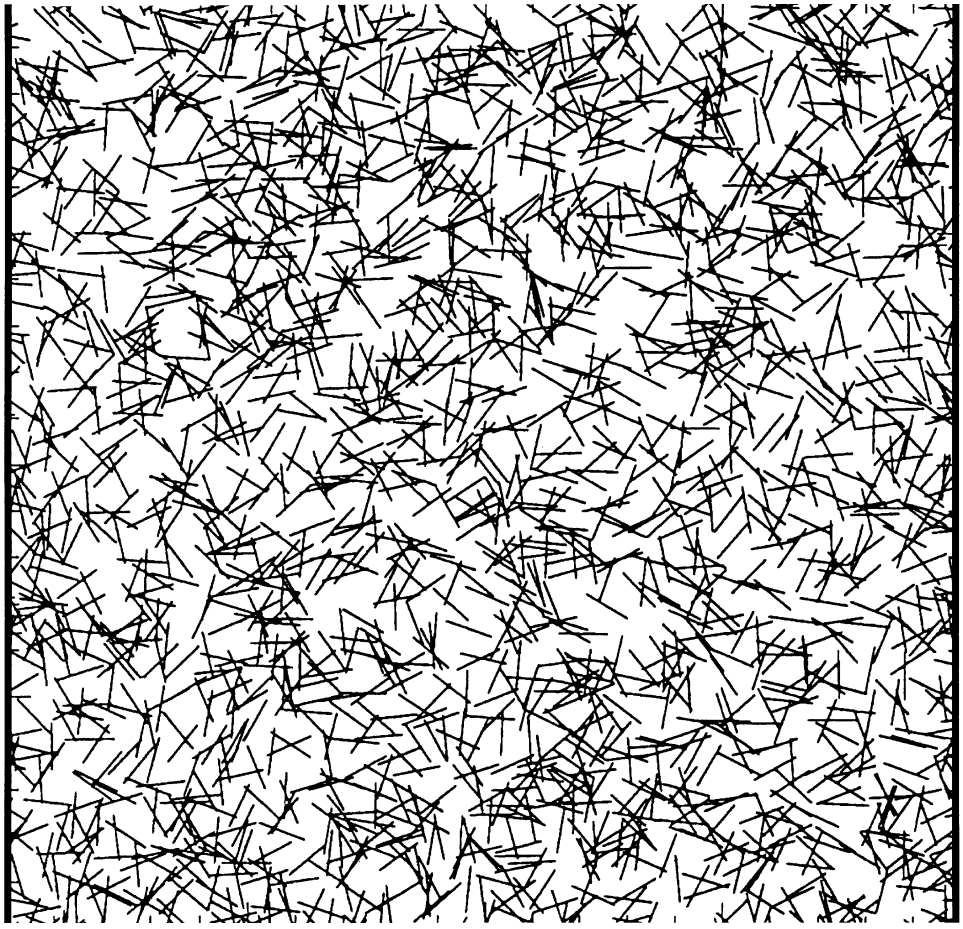

Figure 3. An illustration of a continuum model. The line segments may be considered to be fractures or channels which can conduct a fluid. This system is characterized by the number of segments in its finite version, and by the number of bonds per segment in its infinite version. The network shown here is just above the percolation threshold (after Berkowitz and Balberg, 1993).

such as fractured rocks. As an example, Figure 3 illustrates a computer-generated sample of randomly-aligned line segments. This can be envisioned as an aerial photograph or a cross-section of fractures or cracks in a formation, or a system of natural channels. Percolation in such systems is called continuum percolation (e.g., Halperin et al., 1985; Balberg, 1987), and the mathematics used to describe it are similar, but not identical to, what we have presented thus far. The conspicuous features that distinguish continuum percolation networks from lattice networks are (i) the variable number of possible connecting bonds per site (or object), (ii) the variation of the bond length, and (iii) the local variation in the bond direction. We consider these aspects below.

The first question we ask pertains to the quantity that should be used here, instead of p, so that a "proximity" parameter such as $p - p_c$ can be defined. To answer this question, reconsider now the sites and bonds in Figure 1c. In this lattice structure, each site has z (= 4 in this figure) possible bonds. If a fraction p of these bonds is open, the average number of bonds per site is $B = pz$. The percolation threshold, or the critical number of bonds per site, can then be defined by $B_c = p_c z$. Hence, since z is a constant, $B - B_c$ is as good a proximity parameter as $p - p_c$. We can now return to the continuum percolation model of Figure 3 and ask what the average B (i.e., number of intersecting segments per line segment, or fracture) is, and then compute any physical property as a function of $B - B_c$. It has been assumed then, from the universality applicable to the various lattice systems, that all the results previously derived for lattice percolation are also applicable to such continuum systems, except that here the well-defined $B - B_c$ is used instead of the lattice parameter $p - p_c$.

To show that Equation (1) describes the same critical behavior as the other critical behaviors given above, i.e., that (up to a proportionality factor) $N - N_c$ is the same proximity parameter as $p - p_c$ and $B - B_c$, the concept of the excluded volume is now introduced (Balberg et al., 1984). The excluded volume (or area, in a two-dimensional system) is defined as the volume around an object in which the center of another object must be in order for them to overlap. For example, for spheres or cubes of volume V, the excluded volume, V_{ex}, is simply given by $V_{\text{ex}} = 8V$. In cases where the excluded volume is different for two given objects or two given intersections, the average excluded volume, $\langle V_{\text{ex}} \rangle$, must be used. A simple example of such a case is that of "sticks", or fractures, as shown in Figure 3. If all the fractures are of length l_0, and there is an angle of $\theta_i - \theta_j$ between two of them, the corresponding excluded "volume" (area) is $A = l_0^2 \sin|\theta_i - \theta_j|$. If θ_i and θ_j are randomly and uniformly distributed between $-\pi/2$ and $\pi/2$, the average excluded "volume" is $(2/\pi)l_0^2$ (Balberg et al., 1984). Now the number of objects whose centers lie within the average excluded volume is $\rho\langle V_{\text{ex}} \rangle$, where ρ is the density of objects in the system. But this is also the average number of objects that overlap, or are bound, to a given object (i.e., B). Thus

$$B - B_c = (\rho - \rho_c)\langle V_{\text{ex}} \rangle. \tag{11}$$

For a finite system (lattices or continuum), $(N - N_c) \propto (\rho - \rho_c)$, and Equation (1) can be used. However, for infinite systems (for which percolation theory gives accurate results), $p - p_c$ and $B - B_c$ should be used, respectively.

Comparison of Figures 1c and 3 reveals another significant difference between lattice models and real systems. While the length of each bond is the same in Figure 1, the flow in the "equal length fractures" in Figure 3 takes place along segments of different length. Thus, there is a distribution of flow segments, and a distribution of local hydraulic conductivity (k) values. The question of interest is whether this situation affects the values of ζ_κ that were derived for models in which it was assumed that k is the same for all elements through which fluid flow occurs.

Since the percolation theory predictions are accurate close to the threshold (i.e., when ξ is very large in comparison with the details of the system), a "well-behaved" distribution of k values (e.g., Gaussian) will manifest itself by average parameters, so that ζ_κ is the same as for lattices. The situation appears to be quite different, however, if the distribution of k values diverges as $k \to 0$. Under such conditions, the decrease in K as the percolation threshold is approached from above is due not only to the decreasing number of flow paths, as in the lattice, but also to the fact that the participating paths consist of elements with smaller and smaller k values (unlike the lattice case). Such a distribution may yield a ζ_κ value that is different from that of the non-diverging k value distributions. The behavior associated with these different values is known as the "non-universal" behavior.

Historically, one of the fundamental results in continuum percolation involves the relationship between the percolation threshold, ρ_c (i.e., some critical object density) and porosity. For a system of non-overlapping spheres, wherein spheres touch each other at single points, and the spheres are the "conducting pores", it is clear that $\phi_c = \rho_c V$, where ϕ_c is the critical volume fraction that is occupied by spheres, and V is the volume of each sphere. This quantity has been found to be dimensionally invariant (i.e., insensitive to lattice structure). Generalizing this concept to permeable spheres (i.e., pores), it was shown (Shante and Kirkpatrick, 1971) that the average critical number of bonds per site (which is sometimes called the "average coordination number"), denoted B_c, is related to the critical fractional pore volume ϕ_c by

$$\phi_c = 1 - \exp(-B_c/8). \tag{12}$$

It has been further shown that B_c is an invariant for groups of convex objects (Balberg et al., 1984). The value of having information on the average number of intersections of a pore with its neighbors is that it provides information on the general average topological structure of a porous medium.

The concept of the excluded volume has been useful in developing general empirical rules for the dependence of the percolation threshold ρ_c on the geometry of the objects (i.e., pore shapes) making up the system, as well as on the macroscopic properties, such as anisotropy, of the system (Balberg et al., 1984). More recently, exact analytical calculations have been presented for the same purpose (Drory et al., 1991). This concept, which accounts for "interactions" (i.e., intersections) between objects is simply connected to B_c, for permeable objects, by the relation

$$B_c = \rho_c \langle V_{\text{ex}} \rangle \tag{13}$$

where $\langle V_{\text{ex}} \rangle$ is the average of the excluded volumes of the objects (see also Equation 11). Balberg (1986a) then generalized Equation (12) to

$$\phi_c = 1 - \exp[-(B_c V / \langle V_{\text{ex}} \rangle)] \tag{14}$$

for systems comprised of permeable convex objects of any kind. The relevance of the excluded volume concept to practical systems of interest in porous media problems is clear when considering that Equations (13) and (14) yield the critical porosity applicable to porous media. For example, these equations, through their dependency on V and V_{ex}, allow determination of critical porosities for a variety of systems, and can account for the fact that, in certain types of rocks, flow is present although porosity is close to zero (if pores are considered to be thin and sheet-like, i.e., there is a small $V/\langle V_{\text{ex}}\rangle$ ratio).

In fact, Equation (14) follows from the more fundamental relationship between critical porosity and excluded volume (Balberg, 1986a), which, for an infinite system, is given by

$$\phi_c = 1 - \exp(-\rho_c V). \tag{15}$$

Relationships between ρ_c and ϕ_c can be derived from these expressions. In the case of spherical pores, for example, it is well-known (Balberg, 1987) that $\rho_c V_{\text{ex}} = 2.8$, $V_{\text{ex}}/V = 8$ and $\phi_c \approx 0.29$.

Another aspect of interest in random networks is the relationship between the percolation correlation length, ξ, and the size of a REV (representative elementary volume). The general physical significance of ξ (which characterizes the average distance over which two sites are connected; see Equation 7) is that only for length scales $L \gg \xi$ is the system macroscopically homogeneous. Thus, the correlation length is in a sense the basic macroscopic building block of the system. The REV of a porous medium, associated with, for example, permeability, is defined by a scale at which permeability fluctuations become negligible. As known from the density dependence of ξ (Equation 7), and shown by, for example, Robinson (1983) and Charlaix et al. (1987), for a fracture network, the correlation length decreases as the fracture density increases; thus, the REV size also decreases.

A natural question to ask is whether various porous media, and networks of fractures and soil cracks, have a fractal structure. Fractal properties have been identified for various porous materials, such as sandstone (e.g., Katz and Thompson, 1985), as well as for patterns of fracture and crack networks (e.g., Barton, 1995). Study of fractal (and multifractal) properties of soils is also now receiving attention, as is the problem of developing numerical methods for generation of realistic fractal porous media.

This necessarily brief review has presented a few of the highlights of what percolation theory has to offer to a mathematical treatment of porous media. The theory offers a perspective on disordered systems that more conventional methods clearly cannot match. Moreover, as will be seen below, this framework has provided the basis for development of other, complementary, variants of percolation theory. While the proximity of real porous rocks and soils to percolation thresholds is a matter of question, the theory is flexible, being suited to working with discrete pore and fracture system geometries, as well as a variety of flow and transport phenomena.

3. Percolation Theory and Network Models of Porous Media

In this section, we give a brief history of the network model, trace the merging of network models with percolation theory, and give some of the highlights of their co-evolution.

3.1. Early network models

Early conceptualizations of pore space topology involved considering bundles of capillary tubes of varying radius (Figure 4a; see, e.g., Bear, 1972, for a review). Due to the topological simplicity, essentially all flow properties of such systems can be treated analytically, and numerous flow and transport phenomena can be simulated successfully. However, such models neglect the fundamental topological randomness of porous media. Analyses of pore structures indicate that the pore space is characterized by a wide distribution of channel sizes, and that random networks more closely represent actual systems of pores (e.g., Doyen, 1988). The network model of porous media was developed by Fatt (1956a,b,c), who found inadequate the existing conceptual models of his time, the bundle of parallel tubes and the sphere pack. He argued that the sphere pack was still too complex for a complete analysis, and the equations developed from it (such as the Kozeny-Carmen equation) still had empirical coefficients. Meanwhile, the parallel tube model was conceptually inadequate, structurally anisotropic, and it also needed to be adjusted via empirical coefficients. Fatt (1956a) proposed a regular 2D lattice of tubes with randomly assigned radii (Figure 4b), arguing that it was simple enough to be analyzed, yet displayed enough of the complex behavior of porous media to be useful.

Fatt (1956a) developed a drainage algorithm that starts with the network tubes completely filled with the wetting fluid (typically water in the case of unsaturated soil). As the capillary pressure is increased, air surrounding the network moves into the largest tubes along the interface, which becomes larger and more complex as more tubes drain. The pressure can be plotted against the proportion of the network that is still water-filled to yield a drainage curve. Computer facilities at the time were limited, so the drainage algorithm used paper and pencil accounting. Fatt (1956a) compared drainage curves generated by draining different lattices (square, triangular, honeycomb, double-hexagonal and bundle-of-tubes) with various pore size distributions, and noted that differences between lattices were minor compared to differences between pore size distributions. He found that the drainage curves gave better predictions of the pore size distribution as the lattice connectivity z increased. Finally, he derived a method for correcting the measured pore size distribution to account for network effects such as the percolation threshold. In subsequent papers, Fatt (1956b,c) measured relative permeability (unsaturated hydraulic conductivity) of physical networks built of electrical resistors as they were being "desorbed" following the algorithm developed in the first paper.

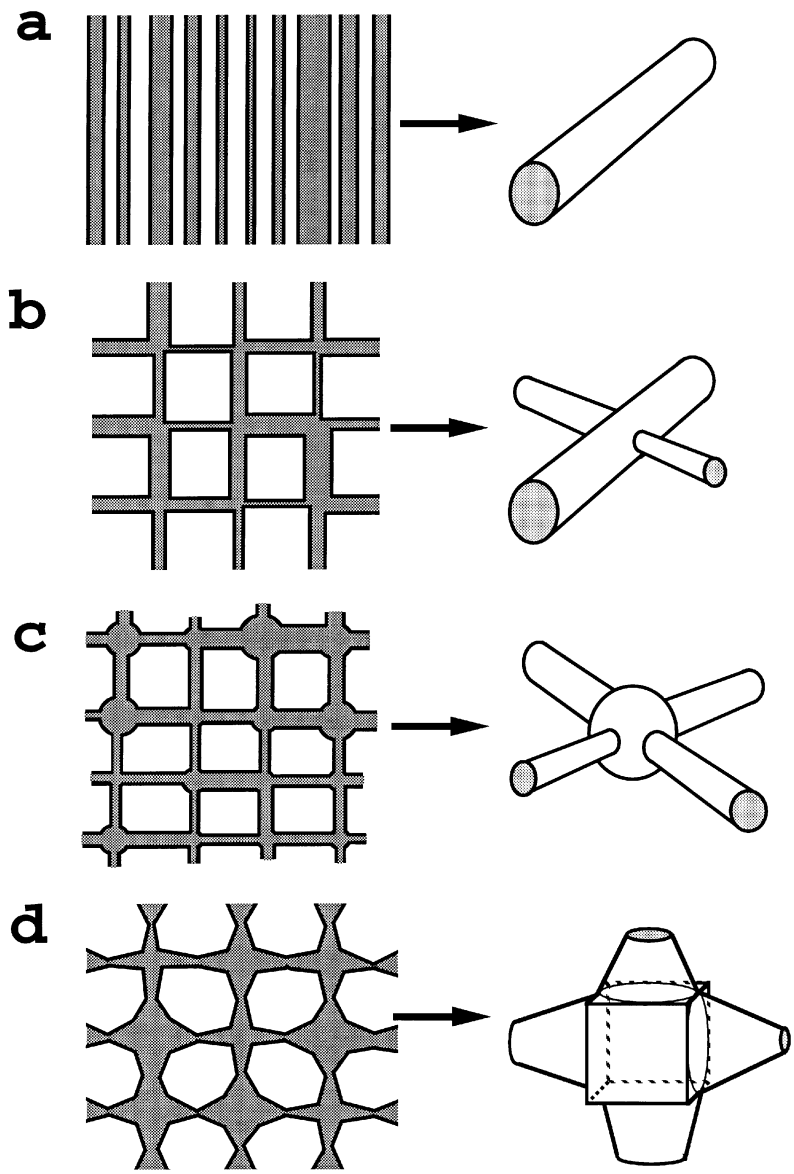

Figure 4. Evolution of pore space models. (a): parallel tubes, (b): tube network of Fatt (1956), (c): ball-and-stick network of Chandler et al. (1982) and Koplik (1982), (d): 2D version of Toledo et al.'s (1989) biconical pore network.

Several aspects of Fatt's (1956a) work are related to percolation theory, and many are still important today. While recognizing that real porous media are 3D, he chose to work in 2D because it was simpler. The differences between 2D and 3D networks were not well understood until at least 1977 (Chatzis and Dullien),

and even today much important work is still done on 2D networks. Based on observations of thin sections of sandstones, Fatt (1956a) made the assumption that the length of a tube is inversely proportional to its radius. Interestingly, the opposite assumption (length is proportional to radius), mistakenly attributed to Fatt (1956a) by Mualem (1976), is incorporated into the widely used Mualem-van Genuchten formulation (van Genuchten, 1980) for unsaturated flow. Fatt's (1956a) drainage algorithm, in a different guise, is virtually identical to a computational algorithm suggested by Hammersley (1963), and the invasion percolation algorithm proposed by Wilkinson and Willemsen in 1983 (see discussion below). Finally, Fatt (1956a) assumed that, since the contact angle is 0° (perfect wetting), water can drain from "trapped" pores via thin films. This assumption was controversial at the time (Rose et al., 1956) and is still under discussion today (e.g., Blunt et al., 1992; Blunt and Scher, 1995): depending on how trapping is handled, a variety of behaviors can be seen (see Section 3.3).

Advances in network modeling were slow from Fatt (1956a,b,c) through the 1970s, at least partly because computer resources were limited. Most of the modeling was done in the field of petroleum engineering, both because this was its field of origin, and because petroleum engineers had easier access to computers than, for example, agricultural scientists. The first computer-based network modeling was apparently done on Illiac by Rose et al. (1956), who eventually studied 3D lattices with at least 1728 nodes (Rose, 1957). Ksenzhek (1963) examined the effect of the size of a 3D lattice on the drainage curve, and noted that lattices show a breakthrough or bubbling pressure similar to real porous media. Nicholson (1968) used a physical 3D network to study sorption and desorption isotherms, and remarked that the presence of a network enhances hysteresis. Torelli and Scheidegger (1971) referred to concepts from percolation theory and developed a network of uniform diameter tubes for modeling dispersion; Torelli (1972) extended their work for lattices with unequal tube diameters. Simon and Kelsey (1971, 1972) used networks to simulate a waterflood (water displacing oil in an oil reservoir to enhance oil recovery) and calculated its efficiency. Networks were also used to interpret mercury porosimetry experiments (Androutsopoulos and Mann, 1979) and to explain, at a pore scale, low oil recovery following a waterflood (Mann et al., 1981).

Broadbent and Hammersley's (1957) seminal paper on percolation theory specifically referred to porous media, but percolation theory came slowly to the attention of hydrologists and soil scientists. In 1977, Levine et al. regretted that "[percolation] theory has dealt mainly with abstract objects, such as bonds, sites and clusters, and few direct applications have been made to flow through a porous medium." The first general application of percolation theory (without network models) in a journal read by hydrologists and soil physicists may be Golden's 1980 article, which proposed using percolation mathematics both to predict unsaturated hydraulic conductivity and to provide a more powerful language for discussing hysteresis via domain concepts (e.g., Topp, 1971; Mualem and Dagan, 1975, and references therein).

Some of the earliest work connecting percolation theory and porous media involves the phenomenon of oil blob creation and mobilization (Larson et al., 1977). While this is not ordinarily of interest to soil scientists, we include it for its applicability to soil pollution remediation as well as its historical interest. Oil is often extracted using a waterflood, in which water is pumped into a series of injection wells and the oil driven to and withdrawn from extraction wells. In the process, blobs of oil are surrounded by water and so disconnected from the rest of the oil (Chatzis et al., 1983). These blobs tend to stay in place, decreasing the amount of oil that is recovered. Since large blobs are more readily swept along by flowing water than small ones (Ng and Payatakes, 1980; Dias and Payatakes, 1986), the expected blob size distribution is of some interest. It turns out that the size distribution, which depends on the connectivity of the pore space, can be predicted using cluster size distributions given by percolation theory (Larson et al., 1977).

The year 1977 saw, in journals occasionally read by porous media scientists, the first solid links between percolation theory and network models. Chatzis and Dullien (1977) stated that "penetration of the non-wetting phase into a network of pores is closely analogous to the 'bond' problem of percolation theory," while Levine et al. (1977) noted that Fatt's (1956a) network model was similar to a computational method described by Hammersley (1963), and so it could, if sufficiently large, be used to calculate percolation probabilities. Chatzis and Dullien (1977) explicitly opened discussion on some of the assumptions of Fatt's (1956a) model, and implicitly made the connection that pore throats or constrictions are like the bonds in percolation theory, while pore intersections or pore bodies are like sites. The analogy between percolation on the one hand, and porous media processes on the other, has since proven to be a very fruitful one, and yet, from the perspective of 1977, it is not obvious that it should be so. There are many kinds of percolation and porous medium processes, and the percolation process most analogous to the drainage studied by Chatzis and Dullien (invasion percolation) had not even been invented in 1977. We will not formally justify the analogy in this review, but will simply point out that it is a natural one to make, given that each is based on discrete units (pore, sites) and events (emptying, draining) that display on the aggregate scale complex behaviors that are not apparent at the scale of the individual units.

Chatzis and Dullien's (1977) article set the standard for much of the network modeling that followed, so it is worth examining in more detail. They pointed out, for example, the until then universal assumption that the pore intersections do not have any volume of their own: in fact, most researchers nowadays attribute the majority of the porosity to the pore bodies. They recalled the topological principle that bicontinua (for our purposes, two continuous phases such as water and air) cannot exist in two dimensions, so 3D simulations are necessary to reproduce phenomena accurately. In addition, they pointed out that for a given coordination number, both the percolation threshold and the pore accessibility function are different in 2D and 3D. (Studies on the transition from 2D to 3D were published

by Silliman (1990), and will be discussed in Section 4.) Chatzis and Dullien (1977) noted that the assumption that pore sizes are randomly distributed within the network had never been justified; we will revisit this assumption in Section 4 of this review. They showed that neither constant tube length, tube length proportional to tube radius, nor tube length inversely proportional to tube radius gave good agreement with experiment, and proposed that networks use tubes with bulges in the middle. They demonstrated graphically that a minimum size network, of the order of 40×40 in 2D and $20 \times 20 \times 20$ in 3D, was required to give results that reasonably approximated an infinite lattice. Finally, they noted that lower coordination, z, gave later breakthrough, and coordination around 20 gave results close to the bundle of tubes model; from this, they raised the important question, how can one determine z for a given porous medium?

In a later article, Chatzis and Dullien (1981) pointed out that drainage and imbibition were inherently different processes, in that drainage was controlled by the pore throat radii, while imbibition was controlled by the pore body radii. This has interesting implications in terms of percolation theory, as it suggests that drainage is a bond percolation process, while imbibition is site percolation (see, e.g., Lane et al., 1986). Upon further consideration, however, it is clear that a necessary, but not sufficient, condition for this conclusion to be true is that the bonds and sites must each be independently and randomly distributed throughout the medium. In contrast, measurements of pore structure indicate that a correlation exists between the size of a pore body and the adjacent pore throat radii; at the very least, the radius of a pore throat must be smaller than the smallest of the two adjacent pore bodies. As a consequence, Dullien and coworkers (e.g., Diaz et al., 1987; Kantzas and Chatzis, 1988; Ioannidis and Chatzis, 1993) have since incorporated such a correlation between the size of neighboring pore bonds and sites along with a random distribution of site sizes across the network, resulting in a 'bond-correlated site percolation'. Drainage can then be treated as a site percolation problem, due to the assumption of randomly distributed site sizes, but the actual drainage process is controlled by the size of the bonds connecting neighboring sites. This modeling approach contributed substantially to the good agreement obtained between model predictions and experimental measurements.

While some researchers continued to use Fatt's convention of intersections having no volume, after Chatzis and Dullien (1977) most started giving pore bodies both size and volume. This practice was "formalized" by Koplik's (1982) paper on flow through networks, in which he justified the assumption that most of the resistance to flow is in the narrow bonds, with the wider pore bodies contributing relatively little resistance. A companion paper by Chandler et al. (1982) formalized the convention for drainage; the two together had the effect of popularizing the "ball-and-stick" model (Figure 4c) which is still widely used today.

The 1980s and early 1990s have seen an enormous increase in research using network models linked with percolation theory. Following the lead of Fatt (1956a,b,c), research focused mainly on relative permeability (also called unsaturated hydraulic

conductivity), and drainage and rewetting (porosimetry, immiscible displacement). A third active area of research, growing out of the discussion between Fatt (1956a,b,c) and Rose et al. (1956), was on the nature of the actual pore-scale events, while a fourth area examined the structure of the porous medium itself. A final area of research concerns random walks and dispersion.

3.2. PERMEABILITY

The calculation of the relative permeability of a porous medium solely from its pore size distribution has been elusive, with statistical (e.g., Marshall, 1958) and network (e.g., Farrell and Larson, 1972) approaches meeting only limited success. An analogous problem exists in percolation theory: how does the conductivity of a lattice change as bonds or sites are eliminated? As with Fatt (1956b), the problem is commonly statistically mapped onto an electrical resistance analog; the conductivity is then solved for, either with real resistance models or via Monte Carlo simulations (see Section 2). Kirkpatrick (1971, 1973) derived an effective medium theory (EMT) that gave good unsaturated conductivity estimates, using as inputs the distribution function of conductors (derivable from pore size) and the coordination number of the medium; this approach enjoys widespread use. Larson et al. (1981) used Bethe lattices to derive expressions for two phase flow. Heiba et al. (1982, 1984) presented an elegant combination of statistical and percolation approaches that gave relative permeability for two- and three-phase flow. Because of the extensive computer time and detailed knowledge of the pore structure that are required, reliable estimates of saturated and relative permeability of individual porous media are rare.

3.3. POROSIMETRY

Porosimetry, the characterization of a pore size distribution via drainage and imbibition pressure-saturation relationships, is a natural research area for both percolation theory and network models. In percolation theory, the concept of invasion percolation was developed (Lenormand and Bories, 1980; Wilkinson and Willemsen, 1983) to model the processes of drainage and imbibition. Invasion percolation is applicable when considering how sites and bonds become filled, or occupied, by a fluid continuum that penetrates (i.e., invades) the network from a well defined source. In these instances, it is important to distinguish between a site or bond which is ‘allowed’ (‘open’), and one that is actually ‘occupied’ by the invading fluid. For example, in the case of a nonwetting fluid invading a pore network (i.e., drainage), pores that allow penetration may not actually become occupied, if the paths leading to these pores contain pores that are too small to be penetrated at the prevailing capillary pressure. Hence, this class of problems requires that we distinguish between allowed and occupied sites and bonds, and modify our percolation theory framework accordingly.

Invasion and ordinary percolation are similar in that probabilities are assigned to the sites or bonds randomly and independently. However, in invasion percolation, unlike ordinary percolation, a (for example) unoccupied site (where we now distinguish between ‘open’ and ‘occupied’) with no occupied neighbors cannot become occupied; rather, unoccupied sites are “invaded” by neighboring occupied sites (Figure 5). To put it another way, all occupied sites are ultimately connected to each other through the occupation source, typically a side (of a 2D lattice) or face (of a 3D lattice) from which the "invasion” spreads, like air moving into soil pores through the soil surface during drainage. Each individual invasion changes the interface; after each invasion, the new interface is scanned for the site or bond with the lowest probability, which will be invaded next. This makes occupation (of sites or bonds) subject to two rules: first, the probability must be correct (as in ordinary percolation), and second, there must be a continuous pathway of occupied sites or bonds, from the invasion source to the site or bond under consideration. Wilkinson and Willemsen (1983) explicitly linked invasion percolation to slow capillary processes in porous media, and clearly the analogy with porous media is strengthened by this new variant. Following some initial doubts, it became clear (Wilkinson and Barsony, 1984) that invasion percolation is in the same universality class as ordinary percolation: most of the mathematical reasoning and results developed with ordinary percolation, such as the fractal dimension of the percolating cluster, therefore apply to invasion percolation as well.

With invasion percolation came the concept of trapping (Lenormand and Bories, 1980; Wilkinson and Willemsen, 1983): once a cluster of unoccupied sites is surrounded by occupied sites, it is “trapped” and the sites cannot be invaded. This procedure, illustrated in Figure 5, is very sensitive to the order in which events occur: one invasion can trap a large cluster of otherwise allowed sites. To extend the analogy with porous media, trapping means that the fluids are incompressible and no thin film flow is allowed, so once a cluster of water-filled pores (for example) is surrounded by air during drainage, the water cannot escape and so air cannot displace it. This is in contrast to Fatt’s (1956a) network model. It turns out that trapping assumes greater importance in 2D than in 3D models (Dias and Wilkinson, 1986), and so it can often be ignored in 3D work.

An extensive body of work exists on wettability of the medium and its effect on fluid migration and distribution. In the context of invasion processes, in particular, it is important to recognize the key role of the wetting phase (e.g., Blunt et al., 1992; Blunt and Scher, 1995; see also Section 3.4). For example, experimental evidence demonstrates the mobility of the wetting phase, especially along crevices and pore edges (e.g., Dullien et al., 1989; Dong and Chatzis, 1995). As a consequence, for example, in a controlled infiltration process which proceeds sufficiently slowly (e.g., using pressure or pump controls), individual pores are occupied (invaded) independently of the presence of other pores in the path of the fluid. Cieplak and Robbins (1990) and Koiller et al. (1992) noticed that, during drainage, there is a transition from a fractal front to a relatively smooth front at some critical contact

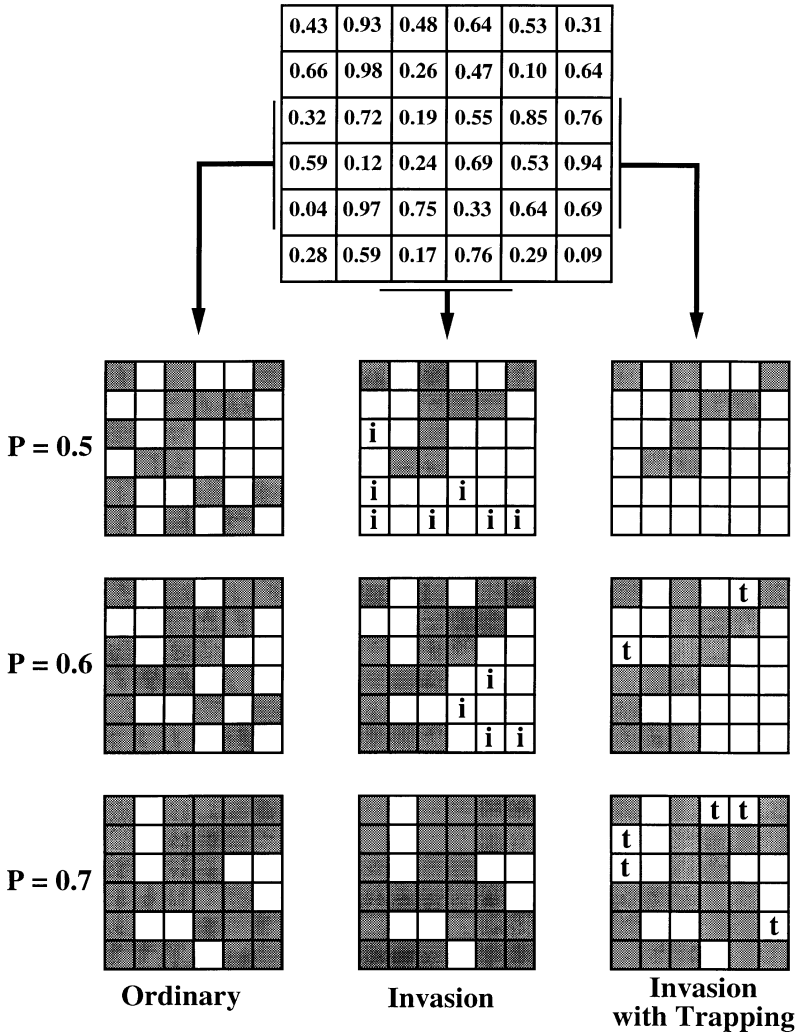

Figure 5. A comparison of ordinary percolation, invasion percolation, and invasion percolation with trapping. Invasion is from the top, and occupied sites are shaded. Numbers in the boxes at the top denote the invasion probabilities of the individual sites, while numbers down the side refer to the current occupation probability of the system. Sites marked with an "i" are invadable (sufficiently low probability) but inaccessible. Sites marked with a "t" are invadable and accessible, but trapped. As the occupation probability p increases, differences between ordinary and invasion percolation decrease, while differences between invasion percolation with and without trapping increase.

angle whose value is dependent on the porosity. Sutanto (1991) has done some elegant network modeling in conjunction with cryo-SEM examinations of fluid distributions to examine the effects on slow displacement when the medium is mixed-wet (randomly distributed oil-wet and water-wet surfaces, as often happens in oil reservoirs); this work may be useful to investigators working with hydropho-

bic soils or organic pollutants in soils rich in organic matter. In general, a variety of fluid migration and distribution behaviors can be seen, depending on how pore geometry and topology, fluid and matrix properties, and boundary conditions (such as invasion rate) affect trapping processes.

In terms of network modeling, invasion percolation had been used before it was so named (e.g., Fatt, 1956a; Chandler et al., 1982), and it continued to be the primary conceptual model for drainage and imbibition. Chatzis and Dullien (1985) used 2D and 3D networks to model mercury intrusion from a sandstone sample and to estimate the relative permeability curve. They obtained good agreement between measured and simulated values when using cubic ($z = 6$) and tetrahedral ($z = 4$) 3D lattices. More recently, effort has focused on modeling displacement in structured rather than random media, and in the presence of other forces besides capillarity. These will be discussed in Section 4 of this review.

The interpretation of mercury porosimetry data in light of percolation concepts has been an active field of research, going back to Fatt's (1956a) attempts to reconstruct the pore size distribution from his simulated drainage curves. More modern research along this line is presented by Yanuka (1989a,b) and Zhou and Stenby (1993). Yanuka (1989a,b) used pore size distributions for a variety of porous media, together with percolation theory, to calculate capillary pressure curves for both drainage and imbibition (i.e., hysteresis loops). These predictions compared favorably with available experimental data. A difficulty in this field of research is that many factors are involved: the sample size, the coordination number, and the degree of non-randomness (among other factors) all affect the retention curve obtained from a given pore size distribution.

Mercury porosimetry is usually performed using injection to predetermined pressures, followed by measurement of the volume of mercury injection. Such a system yields discrete pressure versus saturation points which are often translated into a smooth pore size distribution (Washburn, 1921). However, slow continuous mercury injection, with a constant rate pressure increase and continuous monitoring, reveals (Figure 6a) (Thompson et al., 1987) a "devil's staircase" (Mandelbrot, 1983) of electrical resistance through the mercury, rather than a smooth curve, indicating that the processes at work are not as smooth or continuous as our presentation of the data.

When slow, constant rate *volume* injection is used, with a continuous recording of the resulting pressure, the response (Figure 6b) (Yuan and Swanson, 1986) is not so much a curve or staircase, as a jumble. The pressure alternately rises, as the advancing mercury menisci are forced into narrow pore throats, then falls, as the mercury enters a wider pore body, retracting mercury that was advancing into tighter throats, as a new equilibrium is found. In other words, this sort of porosimetry can be used to evaluate sizes of individual pores, and to distinguish pore throat volume from pore body volume. Toledo et al. (1989) performed careful network simulations that reproduced this more complex "devil's jumble," showing how detailed information on the sample's pore structure could be extracted from

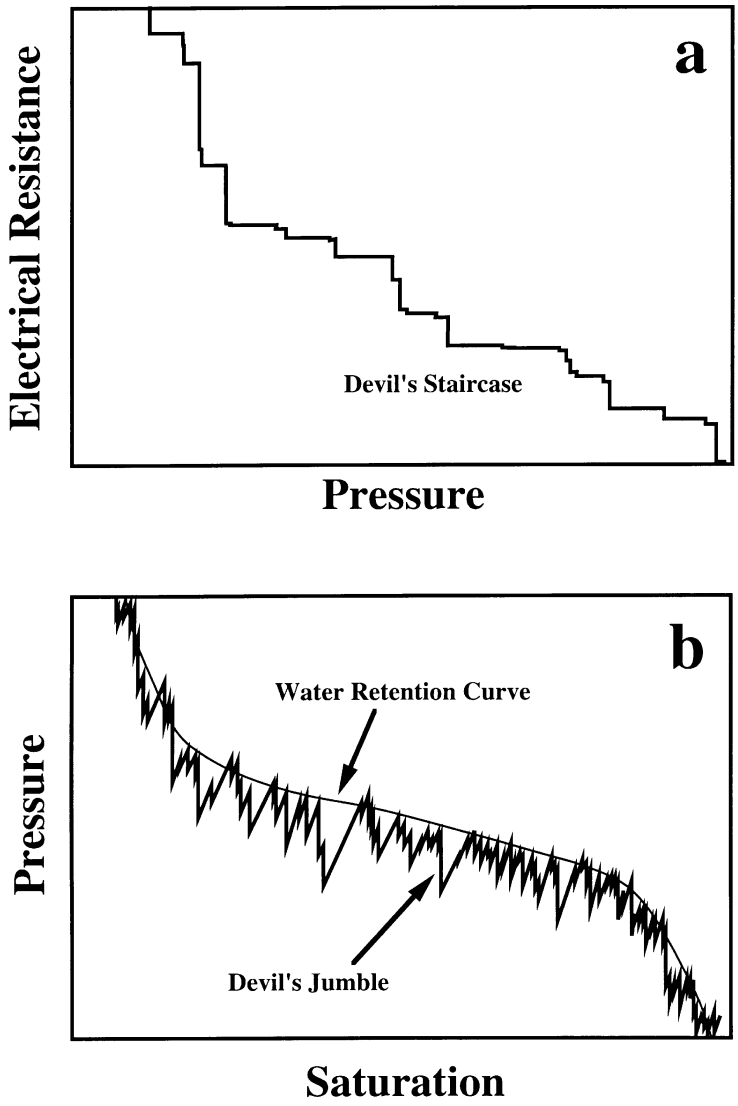

Figure 6. (a): A "devil's staircase" of electrical resistance through the mercury during pressure-controlled mercury porosimetry (after Thompson et al., 1987), (b): A "devil's jumble" of pressure during volume-controlled porosimetry (after Toledo et al., 1989).

this new porosimetry method. Toledo et al.'s (1989) model is also important because it shows a clear advantage of biconical pore throats (Figure 4d) over the earlier ball-and-stick (Figure 4c) network model. Biconical throats (two cone sections sharing the same center axis and overlapping near their points) were used both to capture the converging-diverging nature of real pores, and because the cylindrical

tubes in the ball-and-stick model wrongly imply the presence of a stable interface between connected pore bodies.

3.4. PORE-SCALE EVENTS

Attempts to model macroscopic behavior based on pore-scale events must necessarily have a clear understanding of those events. While Fatt (1956a,b) had essentially three events – complete replacement of one fluid by another (e.g., water by air), drainage via thin film flow, and steady-state flow – the list has continued to expand. Mohanty et al. (1980) modeled the phenomenon of choke-off (Figure 7), in which the wetting fluid builds up at the narrow point of a pore throat, then spontaneously coalesces to divide the non-wetting phase (oil in their case) in two. This is similar to ordinary (non-invasion) bond percolation, in that it is the bonds that are cut, and since the water is supplied by thin film flow, the cut bonds need not be part of a visible or coherent front. Lenormand (1987) demonstrated a phenomenon he called compact cluster growth, in which a choke-off appears to trigger neighboring choke-offs, forming a saturated cluster ahead of the "wetting front". While this occurs primarily in micromodels with square tube-like pores, it may also apply to porous media in which small pores are clustered together. Yuan and Swanson's (1986) and Toledo et al.'s (1989) porosimetry work, cited above, nicely illustrates the existence of two distinct types of pore-scale displacements: reversible, as in mercury advancing into a converging throat, and irreversible, such as a large pore body suddenly being filled with mercury. This latter event is often referred to as a Haines jump, after the soil scientist who first noticed that drainage can occur as discrete events (Haines, 1930).

Pore level events are still under discussion, and new ones are added for both theoretical reasons and in response to poor agreement between model and reality. Blunt et al. (1992) show schematically how the trapping rules first proposed by Rose et al. (1956) could potentially result in near-zero permeability, and thereby propose a distinction between trapping in pore throats, and trapping in pore bodies. Prat (1993), modeling drying of a porous medium via evaporation, found that the drying patterns produced by invasion percolation with trapping did not reflect the fact that drying was both driven and limited by diffusion. The trapping rule would not dry water-filled clusters once they were surrounded, but Prat (1993) recognized that the physics of the situation required that wetting fluid be transported through the non-wetting phase. Transport was also limited by diffusion, necessitating the calculation of the moisture gradient at each time step to account for different evaporation rates at different distances from the "outside edge" of the medium. More recently, Blunt and Scher (1995) provide a detailed investigation of wetting behavior at the pore scale, accounting for competing flow in the centers of the pore spaces and along crevices, and compare predictions of residual saturations based on percolation theory.

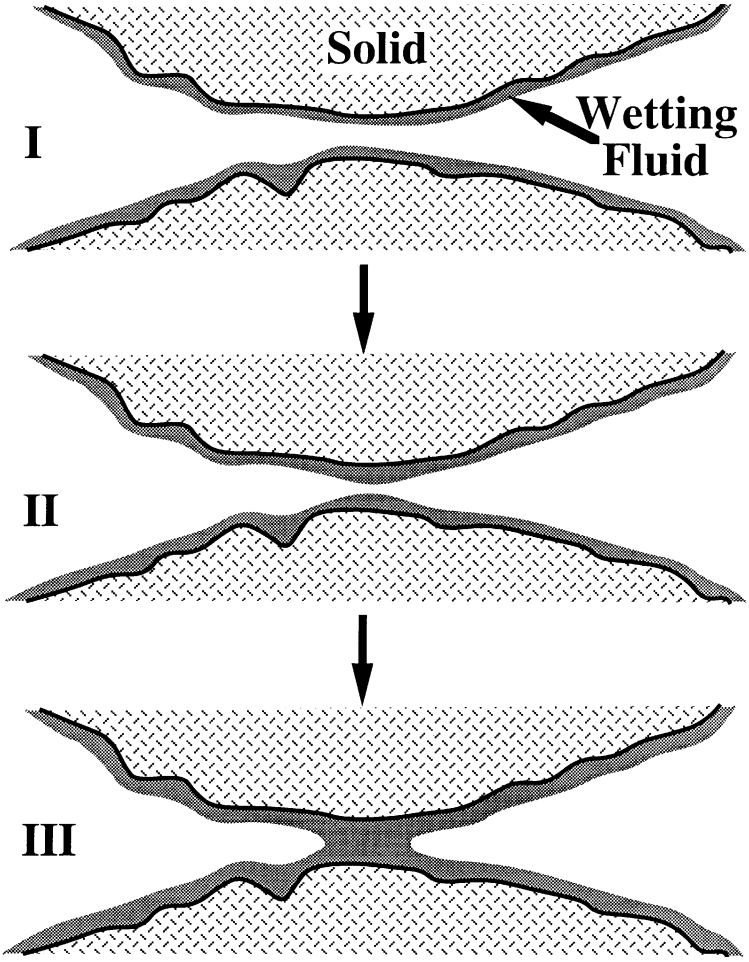

Figure 7. "Choke-off" of a pore throat by the wetting fluid (after Mohanty et al., 1980). As the film of wetting fluid thickens (II), the portion of the film at the throat becomes unstable and collapses (III), blocking the pore to passage of non-wetting fluid.

3.5. PORE STRUCTURE

All of the network modeling discussed above was done on regular lattices with a fairly limited range of coordination numbers, and the critical reader may wonder whether this is applicable to natural porous media, with their chaotic structure and microscopic pores whose connections defy study. Mohanty et al. (1980) pointed out that, in principle, a porous medium could be completely mapped onto a network, i.e. reconstructed symbolically in terms of connections, body radii and throat radii. However, there are two somewhat arbitrary limits to the mapping (Mohanty et al., 1980): the size of the smallest pore one was willing to map, and the definition one used to define individual "pores". They argued that statistical mapping, i.e.

determination of the pore size distribution and other functions, then “decorating” a lattice of the correct coordination number by assigning values drawn at random from the distribution, was therefore more practical than direct mapping. Some assumptions and problems involved in this move from direct to statistical mapping will be discussed in Section 4.

Direct mapping will yield an irregular lattice, whereas statistical mapping, for the sake of convenience, is done on regular lattices. Winterfeld et al. (1981) performed extensive Monte Carlo experiments and found that percolation and conduction properties of 2D Voronoi tesselations (Figure 2d) were essentially identical to properties of hexagonal lattices. Their work was expanded and extended to 3D by Jerauld et al. (1984a,b), who examined backbones and percolation exponents of Voronoi and regular 2D and 3D systems. They found that regular and irregular lattices behave essentially identically as long as they have identical coordination numbers. The equivalence of regular and disordered systems formally justifies application of work on regular lattices to real porous media. With respect to coordination, work by Lin and Cohen (1982), Chatzis et al., (1983) and Yanuka et al. (1984) has shown that sandstones have coordination numbers in the range of 4–8. The coordination number applicable to soil is a more complex matter, however, and discussion is deferred to Section 4.

In a related study, Gladden et al. (1995) demonstrated how spatial heterogeneities in pore size distributions can be characterized by use of nuclear magnetic resonance imaging, and used percolation theory to quantify pore cluster sizes and proximity to the percolation threshold. Analysis of "homogeneous” porous catalyst support pellets indicated wide variability in these properties. Detailed, quantitative understanding of pore structure can also be achieved by reconstruction of 3D pore spaces from 2D serial section measurements of porous materials (e.g., Kwiecien et al., 1990 and references therein; Adler, 1994). In addition, extremely detailed images of the microstructure of porous rocks have been obtained using high resolution microtomography (e.g., Auzerais et al., 1996). While these methods are useful complements to percolation theory and network modeling in the study of soils and other porous media, discussion of them is beyond the scope of this review.

3.6. DISPERSION

A detailed analysis of dispersion phenomena in porous media using network models and percolation theory is presented by Sahimi (1984, 1987) and Sahimi and Imdakm (1988). Sahimi (1987) derives a set of relationships relevant to geometrical and hydraulic characteristics of capillary tube networks and uses them to establish various expressions for describing dispersion of contaminants under various conditions and assumptions, near the percolation threshold. In particular, the relationship between mean square particle displacement and time yields different exponents, depending on the flow conditions (e.g., as characterized by the Péclet number Pé $\equiv vl/D$, where v is mean fluid velocity, l is the characteristic length (roughly, the

mean pore size), and D is the diffusion coefficient. This dimensionless number gives the ratio of advective to diffusive forces.). Additional discussion of these relationships is given by Berkowitz and Braester (1991) and Yanuka (1992).

A detailed study of dispersion processes in porous media was then presented by Sahimi and Imdakm (1988), who incorporated several earlier sets of results (given as references), and employed intensive Monte Carlo numerical simulation and particle (solute) tracking in random capillary networks. Random networks were constructed (in both two and three dimensions) by removing segments from an orthogonal lattice network, according to various criteria. They showed that, as the percolation threshold is approached from above, particle (solute) transport, as characterized by mean square displacement, behaves in an anomalous manner. The dispersion coefficient is not constant, so the conventional advection-dispersion equation (e.g., Bear, 1972) cannot be applied. Rather, solute transport is found to be scale-dependent, on either length or time, with exponents varying for the flow and transport processes considered (i.e., proximity to percolation threshold; Péclet number indicating either diffusive or advective domination; consideration of diffusive transport into dead-end and stagnant regions). This framework provides an important perspective for understanding anomalous dispersion, which is usually only attributed to long-range spatial correlations in the permeability field.

Using similar random networks, Koplik et al. (1988) considered a full distribution of particle transit times (i.e., times required for particles to advance through a given length of the system), and derived relationships for higher order moments (i.e., in addition to mean and variance) of the particle displacements. Their formulation takes into account advective transport through the backbone and diffusive transport into dead ends and stagnant regions. They developed a computational approach which allows determination of transit time distributions of the particles, as a function of the macroscopic (mean) fluid velocity. Numerical calculations were in good agreement with analytical predictions of percolation theory.

The agreements between these theoretical and numerical results indicate that percolation models can be of use in understanding detailed transport phenomena in porous and fractured formations. For example, the results illustrating the non-Fickian (anomalous) nature of dispersion in such systems can be applied to explain the now well-known scale-dependency of the dispersion coefficient in the advection-dispersion equation. It should also be pointed out that networks of the type considered in these studies (i.e., near the percolation threshold) are fractal in nature (see Section 2). Thus these results, which have been derived for physically-based flow systems, add considerable theoretical and quantitative support to expressions developed by, for example, Ross (1986), Wheatcraft and Tyler (1988), and Cushman (1991), which attribute the scale-dependency of the dispersion coefficient to fractal paths.

4. Percolation Theory and Soils: Assumptions, Problems and Variations

Throughout much of the preceding discussion of percolation theory and network models, we have maintained several assumptions which now require further examination. These assumptions fall into two classes, namely medium effects and fluid effects. They will be discussed in turn.

4.1. MEDIUM EFFECTS: LARGE-SCALE STRUCTURE

Percolation theory assumes that the medium is infinite, stationary (roughly, the statistical properties do not vary with location), and random (in the sense that occupation probabilities or pore sizes are assigned randomly and independently). Soils and other geological porous media do not strictly meet any of these assumptions. The deviation from infinity is obvious, although at the pore scale many geological formations are large enough that extension of results to infinity seems reasonable. Since many investigations of percolation theory are based on Monte Carlo experimentation, the effect of the size of the problem domain has been examined. As mentioned in Section 3, Chatzis and Dullien (1977) showed how the apparent percolation threshold changes as a function of sample depth. Their results are representative of the well-established (Stauffer and Aharony, 1992) finite-size scaling effects of percolation. Chandler et al. (1982) found that, in two dimensions, the residual (trapped) saturation increases as the lattice width increases, although it is invariant with lattice length provided the length exceeds the width. Wilkinson and Willemsen (1983) noted that residual saturation is invariant with lattice size on a cubic lattice in three dimensions.

A less obvious effect of non-infinite media is the effect of the shape of the medium, that is, whether it is wide or narrow with respect to the direction of percolation. A soil horizon or geological formation, for example, might extend for kilometers in two dimensions, but only be several centimeters thick in the third. Ewing and Gupta (1993a) examined this issue using site invasion percolation on a cubic lattice, and examined effects of the lattice size and shape on the percolation threshold, the degree of saturation at breakthrough and the degree of residual saturation. Lattices that were wider than they were long in the direction of the invasion under-estimated the percolation threshold, while lattices that were longer in the invasion direction than they were wide, over-estimated the threshold (Figure 8). Interestingly, the percolation threshold was constant for lattices that were of equal size in all three dimensions. Wilkinson and Willemsen's (1983) assertion of invariant residual saturation in three dimensions was shown to be a simplification: where the lattice width exceeds the length, residual saturation is invariant with width but increases asymptotically with length. This behavior has also been seen by Hirsch and Thompson (1994).

In a related study, Silliman (1990) used percolation theory and Monte Carlo simulations to analyze finite cubic domain-type lattices. He demonstrated that

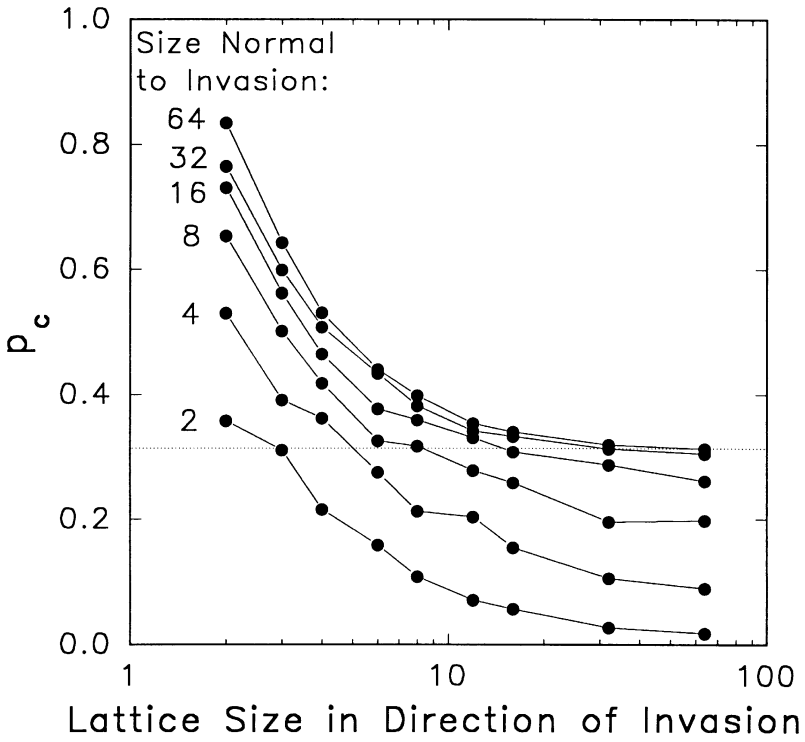

Figure 8. Site percolation thresholds on a cubic lattice as a function of lattice size, both in the direction of the invasion and normal to the direction of invasion. The threshold is essentially constant for cubes (adapted from Ewing and Gupta, 1993a).

lattice geometry and domain discretization can significantly influence the mean critical probability within a discretized random field. In particular, it is shown that refined discretization of a lattice in the horizontal direction cannot compensate for information lost when reducing the vertical discretization of the lattice, due to the variability in connectivity (and therefore hydraulic conductivity) properties between two- and three-dimensional systems. This result is also supported by recalling well-known percolation results which show, for example, that the critical (site) percolation probability for a three-dimensional cubic system (p_c = 0.312) is considerably smaller than that for a two-dimensional square system (p_c = 0.593). This observation has important implications in terms of numerical modeling of hydrological systems, where complex three-dimensional flow domains are often reduced in their dimensionality for the sake of simplicity.

Another aspect of structure at a large scale is layering, which may be considered a special case of anisotropy. Soils and geological media in general tend to be layered, while percolation theory in its basic form assumes that the medium is equally random at all points. However, several investigators have performed network modeling of layered media. Ferrand and Celia (1992) simulated drainage in lattices

composed of both coarse and fine media. The proportion of fine material was varied from 29% to 59%, and at each proportion layered media were compared to random media. In general, as the proportion of fine material increased, they saw an increased difference between the drainage curves from layered and random media. Effects of the number of layers, and the relative heterogeneity within and between layers, were not considered in this study. Hansen et al. (1993) studied conductivity both parallel and perpendicular to layering, assuming each layer to be internally uniform and therefore treatable as a site with a known probability p. They found that conductivity parallel to the layering could be predicted by effective medium techniques (Kirkpatrick, 1971, 1973) with an error of 10% or less. However, conductivity perpendicular to the layering was more complex (albeit one-dimensional), and could only be explained by percolation theory.

While layering is the most obvious form of non-stationarity encountered in soils, other forms may also appear. For example, rather than having discrete layers, the medium may become continuously finer or less porous with depth, or the correlation length may increase with depth. These effects have not been investigated, although we note here that fining downward has some effects similar to those of gravity, discussed below. A recent study by Friedman and Seaton (1996) considers anisotropic lattices, and finds that permeability and diffusive properties depend strongly on anisotropy induced by directionally different coordination numbers, and by anisotropic pore size distributions.

4.2. Medium effects: pore-scale correlations

Soils and geological porous media tend to be non-random at the scale of individual pores or local pore domains. The most commonly studied non-randomness at this level is correlation in the sizes of neighboring pores. In percolation theory, it is assumed that each site is assigned a state independently of its neighbors (Section 2), although some aspects of anisotropy have been considered (see the discussion preceding Equation (15), and Balberg and Binenbaum (1985)). This assumption was implicitly included in the statistical mapping concept of Mohanty et al. (1980). Some researchers working in percolation in porous media (e.g., Chatzis and Dullien, 1982; Wardlaw et al., 1987; Bryant et al., 1993) have noted that this assumption does not apply to their materials: pore throats are often correlated with the size of the pore bodies to which they connect. This observation has led to the development of models that use some form of correlation between bonds and/or sites (e.g., Diaz et al., 1987; Kantzas and Chatzis, 1988; Ioannidis and Chatzis, 1993; as discussed in Section 3.1).

As pointed out by Jerauld and Salter (1990), there are several possible forms of correlation, such as correlation between pore bodies and the throats that connect them, correlation between adjacent bodies only, and correlation between neighboring throats only. Wardlaw, Laidlaw and coworkers tried several variations: Li et al. (1986) and Wardlaw et al. (1987) used throats whose diameter was a function of

the two pore bodies it connected, while Maier and Laidlaw (1990) had the throat diameter equal to the diameter of the smallest connecting site. Yanuka et al. (1986) and Diaz et al. (1987) employed similar approaches. Correlation tends to decrease both the percolation threshold and the amount of residual non-wetting phase following imbibition. In general, correlated networks are better than uncorrelated networks in yielding drainage curves that resemble curves from real porous media (usually sandstone). The same results might be obtained by using networks with higher coordination, but since sandstone probably has coordination in the range of 4-8 (Lin and Cohen, 1982; Chatzis et al., 1983; Yanuka et al., 1984), increasing the coordination of the lattice beyond this range is not a realistic alternative. At present, however, it is not clear to what extent correlated networks still obey the scaling laws followed by random networks.

Correlation between throat sizes and/or pore body sizes in soils is likely both longer range and more complex than the simple methods used above. One approach to dealing with this long range corrrelation is to use pore domains (groups of interconnected pores that are considered as single units) rather than individual pores as the units operated upon (Kueper and McWhorter, 1992; Ewing and Gupta, 1993a; Yortsos et al., 1993), which allows network approaches to be scaled up from the pore level. A difficulty with this method, however, is that coordination numbers are even more difficult to measure experimentally for domains than for individual pores. Some insight may be provided by an interesting study in long range correlation conducted by Renault (1991), who used random fields to assign probabilities to sites and bonds, rather than assigning them independently. As the correlation length was increased from 0 to 5 node spacings, the percolation threshold fell, consistent with the studies cited above. What was remarkable was that the thresholds for cubic lattices with site percolation, cubic lattices with bond percolation, and tetrahedral lattices with bond percolation all converged to the same range – approximately 0.15. Renault (1991) explained this by introducing the concept of blob percolation, since percolation now occurred through blobs of related sites or bonds. A follow-up study of accessibility characteristics of random field lattices was published by Ioannidis et al. (1993).

During blob percolation in a random field correlated lattice, it is the coordination of the blobs that determines the percolation threshold, so changing how the blobs are constructed should change the threshold. Ewing and Gupta (1993b) point out that Renault's (1991) percolation threshold of approximately 0.15 is near the expected value for site percolation on a 3D Voronoi lattice (0.145, cf. Jerauld et al., 1984b), which has a coordination number of approximately 15.54 (Meijering, 1953), and suggest that the blobs have the same connectivity structure as Voronoi polyhedra. A percolation threshold of approximately 0.31 would presumably be obtained using Ferrand and Celia's (1992) "random heterogeneity" method, which simply generates cubic blobs. If soil properties are structured like random fields, perhaps they can be better modeled using domains structured as Voronoi polyhedra or, rather

more conveniently, tetrakaidecahedra (the union of a cube and an octahedron, with $z = 14$) (Jerauld et al., 1984b).

Correlation affects permeability as well as drainage and imbibition. In an elaborate simulation study, Jerauld and Salter (1990) found that, as the degree of correlation between nearby throats increased, wetting phase saturated permeability and non-wetting phase relative permeability increased. An explanation for this increase in saturated permeability with increased correlation can be found in Ambegaokar et al.'s (1971) model of hopping conductivity, which holds that flow through a random medium is dominated by a few pathways of high conductivity. Correlation appears to increase the probability and/or the conductance of these individual pathways (Jerauld and Salter, 1990). Interestingly, correlation in size between nearby pores in sandstones has also been observed to affect miscible dispersion (Bretz et al., 1988). This kind of small-scale property affecting larger scale behavior is typical in percolation-type studies, and suggests that even pore-scale structure might be worth examining in otherwise "structureless" soils.

A different type of fine scale non-randomness was mentioned by Ewing and Gupta (1993a). They suggested that, in a random medium with a wide pore size distribution, the coordination number could be a function of pore size, with larger pores having higher coordination. This makes pore-scale percolation studies more difficult: how can percolation scaling laws be used when z is a function of p? They argued that, in structured soils, coordination numbers in the thousands are possible, because of the presence of (for example) clay skins and macropores. They also noted that in soils, the aspect ratio of pores could be linked to pore size, since pores in clay tend to be flatter than pores between sand grains. This line of reasoning can be extended further: for example, clay regions in soils may be more prevalent than silt or sand regions, suggesting that the degree of clustering of pores of similar size, and even the shape of the clusters, may also be functions of pore size. Furthermore, contact angle may be different in pores whose walls are coated with organic matter; if these pores tend to be clustered spatially or by pore size, this would further affect fluid occupancy and thus the percolation threshold. Such size-based characteristics represent a second major drawback to Mohanty et al.'s (1980) statistical mapping. Detailed examinations of structured soils are needed to help determine to what extent statistical mapping is valid in soils.

Moving beyond the blob-type correlation of Renault (1991), Ewing and Gupta (1993b) considered different types of pore clustering. They clustered pore domains with similar sized pores into different shapes such as line and plane segments, and examined the effects of the size of these clusters, the proportion of the medium occupied by the clusters, and the internal homogeneity of the clusters. Increased cluster length, fraction and homogeneity lowered both the percolation threshold and the residual saturation. Of the various cluster shapes examined, linear-type clusters were the most efficient at lowering the percolation threshold or increasing permeability. This agrees with the experience of soil physicists over the last decade, that linking soil morphology to hydraulic properties might most profitably concentrate

on long structures (macropores) rather than on blob-type clusters (fabric). Related current work in this direction involves disk- or sphere-shaped objects considered as pores rather than assemblages of pore domains (e.g., Berkowitz and Balberg, 1992). These "inverted Swiss cheese" (or "inverted random void") constructions are an extension of the continuum "Swiss cheese" (or "random void") models (e.g., Halperin et al., 1985), using the spheres, disks, or other shapes as the permeable rather than the impermeable phase.

In summary, soils are structured in many different ways, making them different from the infinite, random medium postulated by percolation theory. Some of these differences (e.g., bond-correlated sites) have been recognized and studied for years, though not always with the intention of applying percolation laws to them. Other differences, such as large-scale correlations, anisotropies and pore-size dependence of other properties, are relatively new in the literature. Here, as with most areas of soil structure research, even the basics have not been universally agreed upon, let alone their effects on the percolation properties of the resulting medium. This suggests that there is considerable opportunity for further research.

4.3. FLUID EFFECTS: VISCOSITY

The structural considerations mentioned above all stem from properties of the medium; we will now consider fluid-based effects. Factors such as viscosity and gravity can complicate an already sufficiently complex capillary-driven flow process. We will discuss these factors in turn.

Wilkinson and Willemsen (1983) described invasion percolation as applicable to imbibition that proceeded at a constant flow rate, rather than at a constant pressure. In addition, the process must be slow, allowing capillary forces to dominate over viscous forces. Drainage and imbibition are closest to being invasion percolation-like processes at low capillary numbers (Chatzis and Morrow, 1981; Lenormand et al., 1988), where the capillary number $Ca \equiv \mu v/\sigma$, for viscosity μ, velocity v and interfacial tension σ. When we are dealing with the combination of immiscible fluids at constant densities, high capillary numbers (for example, $Ca > 10^{-4}$), and viscosity ratios $M < 1.0$ ($M \equiv \mu_i/\mu_d$, where subscripts i and d refer to the invader and defender phases, respectively), viscous fingering (Figure 9a) can result.

A full description of the physics of viscous fingering is beyond the scope of this review; readers are referred to reviews by Saffman (1986) and Homsy (1987) for details. Briefly, the fingering comes about because, when viscous forces are non-trivial, they affect "decisions" at the pore scale. To illustrate, suppose we have a one meter square, horizontal sand layer through which oil is flowing. Ignoring diffusion, the oil flows steadily along streamlines, with the local speed determined by the local geometry. Assuming that the sand is relatively homogeneous, a front of a different colored oil with otherwise identical properties would move relatively stably, with distinct fingers (or 'tongues') advancing at different rates according to local flow. Now suppose we start injecting air (negligible viscosity) instead of oil. A tongue

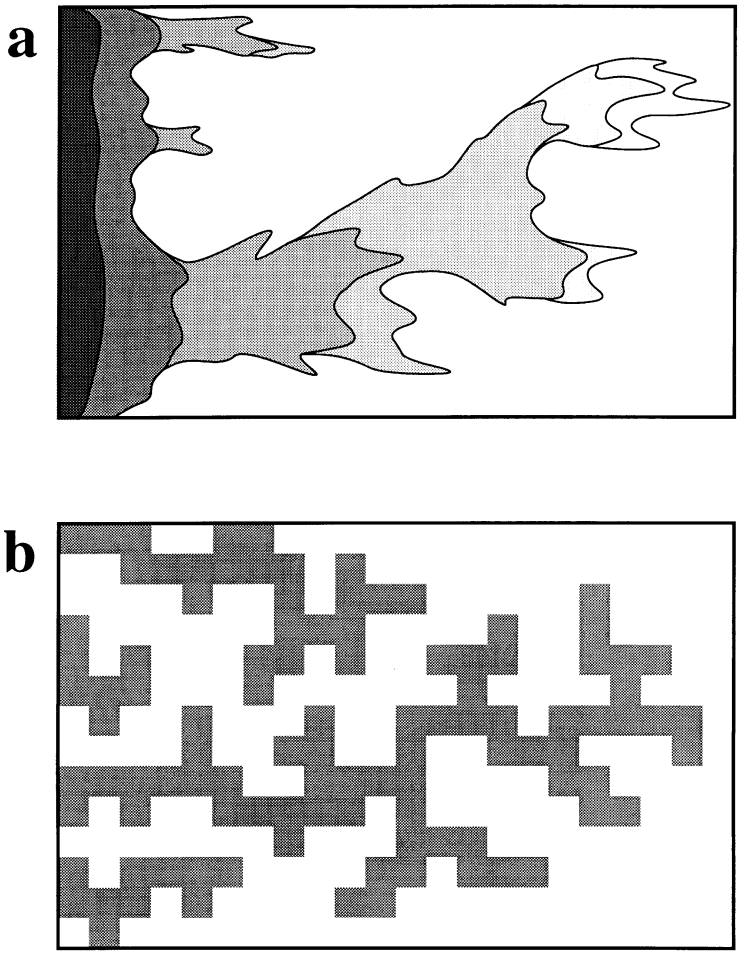

Figure 9. (a): Viscous fingering. Earlier times are shown with darker fluid. (b): Diffusion-limited aggregation (DLA), with the seed being the left side. In both cases, the interface moves from left to right.

of air that advances ahead of the front due to some local perturbation will then have less resistance between it and the far end of the sand layer, so it will advance further. At each instant, decisions at each point along the interface are determined by the total resistance between that point and the end of the streamline. This results in many individual tongues advancing rather than a single front, although where the medium is narrow normal to the flow direction, a single tongue of air will dominate (Figure 9a).

Paterson (1984) made the interesting observation that viscous fingering resembles DLA or diffusion-limited aggregation patterns (Figure 9b) (Witten and Sander, 1983), which have fractal dimension of approximately 1.70 in 2D and 2.50 in 3D. DLA can be simulated by making a "seed", which can be a point, a line, or some

other shape. “Sticky” particles are then released nearby and diffuse freely until they touch the seed, whereupon they stick to it and become part of it. The resulting shape is dendritic (Figure 9b). Paterson’s (1984) article connected a real-world phenomenon to a particular fractal type, and called the attention of physicists to a problem that previously had occupied only a few specialists in porous media, fluid dynamics, and petroleum engineering. The opposite process, anti-DLA or diffusion-limited annihilation (Meakin and Deutch, 1986), has anti-particles diffuse into a domain fully occupied by particles. Each anti-particle diffuses freely until it reaches an occupied site, wherein both particle and anti-particle are removed from the domain. Anti-DLA results in a stably expanding front similar to the Eden growth model (Eden, 1961).

If we increase the interfacial tension in the example above, we see that it tends to decrease the surface area of the interface, and so rounds and diminishes the advancing finger. Thus, there could be three flow regimes in our example above: capillary fingering, viscous fingering and stable displacement. Such a classification was developed in an elegant combination of simulations and experiments by Lenormand et al. (1988), who developed a “phase diagram" showing which locations on the M, Ca plane correspond to which flow regime. These regimes also correspond to the statistical models of invasion percolation, DLA and anti-DLA. In addition to documenting and locating these regimes in the phase diagram, Lenormand et al. (1988) also showed that the boundaries are not sudden: one regime changes continuously into the next, in both form and (apparently) fractal dimension. The original research was conducted using only drainage; subsequent work (Lenormand, 1990) extends the approach to imbibition, and considers the influence of the aspect ratio and the width of the pore size distribution.

Lenormand and coworkers’ (1988, 1990) experiments and simulations used regular lattices in 2D, and correlated or structured media were never considered. In addition, inertial and buoyancy effects were avoided. Nonetheless, the experiments provide a useful framework for future work, and show that interesting deviations from pure invasion percolation commonly arise in porous media. It remains to be seen whether accessibility, scaling exponents, and other concepts from percolation theory can be applied to flow that is not strictly percolation-like. Initial work on continuously blending the different statistical models, in two dimensions, has been published by Sahimi and Yortsos (1985), Leclerc and Neale (1988) and Kiriakidis et al. (1990, 1991).

Viscous fingering represents an extreme that does not normally occur in soils, since air, the low-viscosity fluid in soils, does not displace water at a rate sufficiently high to put the flow into the viscous fingering regime. More relevant in soils is the consideration that not all flow takes place at very low capillary numbers, so viscosity can affect flow even when viscous fingering does not occur. The effect of viscosity during infiltration in soils is actually to stabilize the front: due to the viscosity of water, medium-sized pores near the soil surface may imbibe water sooner than smaller pores deeper down. In Lenormand et al.’s (1988) phase diagram, this is the

anti-DLA (stable interface) regime. This is one of the reasons why percolation-like water-air interfaces are not seen in soils; a second reason is discussed below.

4.4. FLUID EFFECTS: BUOYANCY

Another factor that can complicate immiscible fluid displacement is the effect of gravity. More strictly, this effect can be called a buoyancy effect, as it depends on the relative densities of the fluids involved. Simulations that have modeled drainage or imbibition as a percolation process have, as a rule, ignored gravity (e.g., Fatt, 1956a,b,c; Chatzis and Dullien, 1985), meaning they resemble slow imbibition or drainage in a zero gravity environment. These systems correspond exactly to the original model of invasion percolation. If, on the other hand, gravity is allowed, the pore radius at which a given pore can be invaded is a function of the pore's location in the gravity field.

The related subset of percolation theory is gradient percolation (e.g., Rosso et al., 1986). The situation is analogous to the microscopic wetting pattern above a static water table: as one moves farther above the water table, the radius of the largest water-filled pore becomes smaller. Clearly, in the case of soil, buoyancy forces will tend to stabilize a downward moving drying front (since air is less dense than water) and destabilize a downward moving wetting front. Wilkinson (1986) examined analytically how such a case would impact percolation mathematics in 3D, with particular emphasis on effects on the correlation length. Ioannidis et al. (1996) examined the interacting effects of buoyancy forces and medium structure, using a macroscopic or domain percolation approach. They noted that the buoyancy forces become non-negligible within the individual domains as a function of both the fluid density difference, and the size of the domains. Birovljev et al. (1991) used both simulations and experiments to examine the 2D case, varying the effect of gravity by tilting their 2D micromodel. More recent experiments and simulations were performed by Frette et al. (1992), Prat (1993) and Hirsch and Thompson (1995).

Under certain circumstances, a different form of fingering known as gravity fingering can emerge (Glass et al., 1989a,b; Hillel, 1993). This fingering is reminiscent of viscous fingering, but differs in that branching and rejoining rarely happen once the fingers are formed. Stability analyses (Saffman and Taylor, 1958; Raats, 1973; Parlange and Hill, 1976; Glass et al., 1989a) indicate that finger formation is favored when gravity effects are greater than capillary effects, when the medium has saturation and/or conductivity increasing with depth, and under various other criteria. The fingers do not appear percolation-like, yet both this process and its "inverse" (a low density fluid migrating upward through a higher density fluid) can be simulated using an invasion percolation algorithm that includes gravity (Frette et al., 1992). This suggests that stochastic growth models might readily be adapted to handle gravity fingering as well as the other phenomena mentioned earlier. Moreover, Lenormand et al.'s (1988) phase diagram might be extended

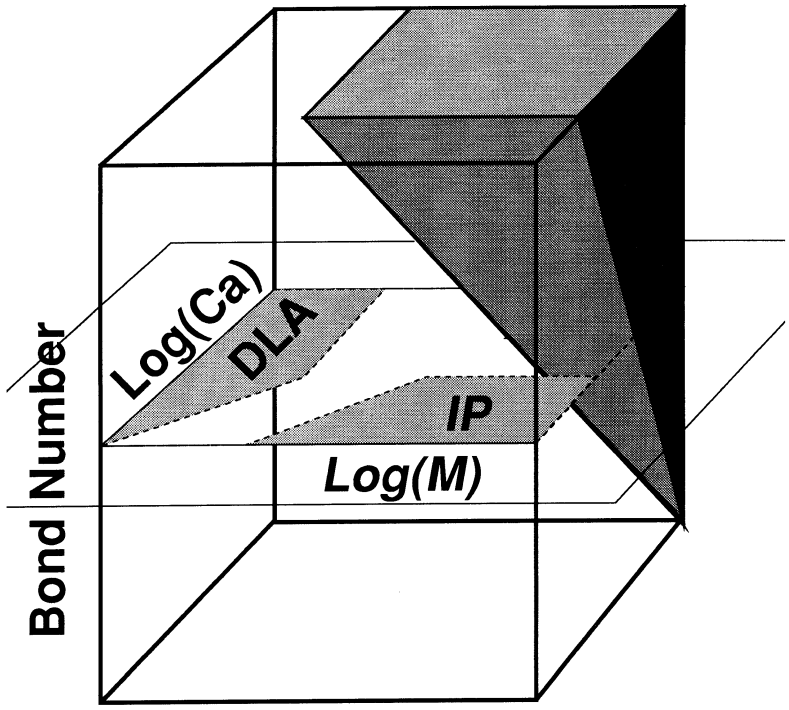

Figure 10. Proposed extension of the phase diagram of Lenormand et al. (1988) to account for gravity effects. The shaded regions indicate conditions of applicability of invasion percolation, DLA and anti-DLA (stable growth) models. By convention, positive values of Bo stabilize the front, and negative values destabilize it.

from a 2D model to a 3D phase space encompassing Ca, M and Bo (Figure 10). The Bond number, Bo, gives the ratio of gravity to capillary forces, and is defined by $Bo \equiv gl^2\Delta\rho/\sigma$, where g is gravitational acceleration, l is the characteristic pore size, $\Delta\rho$ is the fluid density difference and σ is the interfacial tension. This third dimension would make the diagram more applicable to situations commonly encountered in soils.

5. Some Recent Work Relating Percolation Theory and Network Models to Soils

Several recent works have appeared that concern percolation theory and soils, involving pore continuity, porous media basics and issues of flow and transport. Some of these studies used percolation theory directly, while others used pore-scale network modeling without explicit reference to percolation theory. For example, at least four articles have appeared in the soils literature that use network models but have not connected with relevant aspects of percolation theory: Cox (1983), studying drainage, Ewing and Gupta (1994), modeling clogging of pores during

surface sealing, and Steele and Nieber (1994a,b), examining diffusion of gases at different water contents.

A study of pores in cracking clay soils by Scott et al. (1988a,b) analyzed the numerical and topological density of cracks by making serial sections through a resin-impregnated clay and following individual cracks as they branched and merged. The two soils studied had numerical densities (number of discrete crack networks) of approximately 34 cm^{-3} and 75 cm^{-3}, and topological densities (number of closed loops in the networks) of approximately 300 cm^{-3} and 195 cm^{-3}. However, this study left unanswered the question of most interest to workers in flow and transport: was there at least one crack network that spanned the entire sample? A familiarity with percolation theory might have suggested this question, along with the related issue of network size distribution. Also, using continuum percolation, it would have been possible to estimate the percolation threshold for the crack types represented; analysis of cluster sizes might also have shown whether cracks were randomly placed or preferentially connected.

Fracture networks in geological formations have been analyzed extensively (e.g., Berkowitz, 1994), and while such fracture networks are different in nature than cracks in soil structures, the same conceptual approaches can be applicable. Various geometrical and connectivity characteristics, as well as flow and transport properties, of fracture networks, have been analyzed in terms of percolation theory. The concept of the average number of intersections per fracture, and the critical percolation density, have been used as a measure of connectivity in random fracture geometries (e.g., Robinson, 1983, 1984; Charlaix et al., 1984). Moreover, Balberg (1986b) and Berkowitz (1995) have shown that general connectivity and power law relationships (of the form of Equation 1) characterize the density of fractures and average number of intersections per fracture necessary to ensure network connectivity, the likelihood of a fractured formation being hydraulically connected, and the size and extent of fracture clusters.

A related issue is the accessibility, to microorganisms of different sizes, of pores inside aggregates. Glasbey et al. (1991) approached this problem by synthesizing 3D images using an overlapping spheres model: spheres corresponding to a predetermined size distribution (representing soil solids) were synthesized inside a large 3D domain. Depending on the final porosity, the remaining pore space was more or less connected and continuous. This scenario corresponds to the continuum or "Swiss-cheese" model of percolation (Halperin et al., 1985; Feng et al., 1987), and has also been studied in sintering experiments (see, e.g., Pathak et al., 1982 and references therein). Exact relationships are available, at least for uniform sphere sizes. In addition, the percolation threshold and the point at which the pore space first becomes disconnected are useful percolation concepts in this context.

An innovative use of percolation theory was recently proposed by Luxmoore and Ferrand (1993), who had observed in several previous studies that macropore flow during rain events was composed of a mixture of "old" water already present in the soil matrix, and "new," just infiltrated water. Considering the soil to be composed

of macropores, mesopores and micropores, they hypothesized that chemicals held in the mesopores between rain events were somehow moving into the macropores. Mass flow seemed an unlikely explanation, leaving diffusion as the only available mechanism. Using percolation theory, they estimated the surface area connecting the mesopore and macropore domains, and found that diffusion during macropore flow was not sufficient to explain the mixing. Consideration of percolation theory led them to a third hypothesis, that mesopore regions were connected by macropore links, like a blob and link model of a percolation backbone (Stanley, 1977). Between rains, the soil dried to the point that the macropore links desaturated, and mesopore water equilibrated with the soil solution. When rain fell again, the macropores reconnected with the mesopore blobs, carrying with them the mesopore water, and thus mixing “old” and “new" water. This work is continuing, emphasizing characterization of soil heterogeneity across many scales with an eye to building more realistic percolation models (Homer et al., 1994).

The analogy between drainage and invasion percolation suggests a further analogy between bubbling pressure (defined as the pressure at which the soil drains to the point that air can pass through the entire sample) and the percolation threshold. Katz and Thompson (1986) and Thompson et al. (1987) examined this analogy both empirically (using mercury porosimetry) and theoretically, and derived an equation for saturated permeability which applies to a wide variety of porous rocks. Their equation, $k = (r^2(\sigma/\sigma_0))/226$, relates conductivity to the pore radius r that corresponds to the bubbling pressure. Structural effects are handled in the σ/σ_0 or formation factor term, given by the ratio of the electrical conductivity of the medium when saturated with an electrically conducting fluid to the conductivity of the fluid itself. Interestingly, Katz and Thompson’s (1986) work relates the percolation threshold to the inflection point on the drainage curve; this has implications for any attempt to derive bubbling pressure from drainage data. A recent application of the Katz and Thompson (1986) approach to clay-bearing sedimentary rock (Korvin, 1992) implies that the 3D percolation conductivity exponent t changes continuously from the lattice value 2.0 to a continuum value of 4.4 (Halperin et al., 1985) as the texture moves from coarse sand to shale.

The relationship between bubbling pressure and conductivity shows up elsewhere as well (e.g., Wang and Narasimhan, 1992), but has not always been recognized as such. For example, it appears in the data of Laliberte and Brooks (1967), but was only recently recognized as such (Ewing and Gupta, 1993b). Baver (1938) proposed an equation for predicting saturated conductivity based on the inflection point in the water characteristic curve. The equation for relative air permeability derived by Brooks and Corey (1964) uses a proximity parameter similar to the standard percolation theory form $(p - p_c)$ (see Equation 9), and air (being the non-wetting fluid) corresponds well to the invading fluid in invasion percolation.

The unsaturated conductivity (relative permeability) functions of Brooks and Corey (1964), Bouwer (1966), Campbell (1974) and van Genuchten (1980) also use bubbling pressure as an input parameter. However, these relationships use a

proximity parameter quite different from the $(p - p_c)$ form typical of percolation theory. This may be because the percolation equations are most accurate close to the percolation threshold, while the water retention and conductivity function cover a much wider range. At the dry end, for example, thin films (see Toledo et al., 1990) dominate conductivity; Dullien et al. (1989), working with SEM and residual saturations as low as 1%, argue that residual saturation is due to surface roughness. On the other hand, water forms a continuous phase through virtually the entire range of the retention and conductivity functions, in contrast to the assumptions of percolation theory, indicating that percolation theory may not be appropriate for these functions.

The analogy between bubbling pressure and the percolation threshold is most useful in unstructured media or samples above the REV, and where buoyancy effects are minimal. Unfortunately these two considerations clash in most agricultural soils: the REV in a structured soil may be large, at which scale gravity is likely to be non-negligible (Blunt et al., 1992).

6. Concluding Remarks

This review has been written with two principle objectives. The first was to provide a useful summary and reference work for soil scientists wanting to learn more about percolation theory and network models, and their application to soils. The second was to expose some of the many remaining issues and challenges in this field. These challenges are discussed throughout the review, and include the development of critical relations for media that in some ways resemble both lattices and continua (Section 2), relevant pore scale events (Section 3), the statistical properties of structured soils, and the applicability of various statistical and network models to different flow regimes (Sections 4 and 5).

Percolation may be considered as representing one of several statistical theories that is applicable for calculating macroscopic, or 'large-scale' properties. Depending on the properties of the one or more fluid (and/or gas) phases present in the medium, the geometrical randomness of the medium itself, and the coupling between fluid and medium properties, any of several statistical theories may be applicable, including, in different ranges, percolation, DLA, anti-DLA and gradient percolation, as well as effective medium theories. In terms of medium geometry, standard percolation theory can be reasonably applied to poorly connected and cracked soils and fractured rock; invasion percolation and its variants can be usefully applied to model a range of multiphase displacement mechanisms. From the many examples discussed above, it should be clear the challenge is not to force non-percolation processes into the percolation mold, but rather to develop statistical models that can represent the entire continuum, and to clarify the linkage between statistical and physical models. In addition, since the statistical models appear to be linked, it remains to determine what percolation theory can contribute

to the ensemble (e.g., the concept of universality), as well as what other statistical models can contribute to percolation.

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