Lecture Notes in Physics 771

Percolation Theory for Flow in Porous Media

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Chapter 2
Properties Relevant for Transport and Transport Applications

This chapter describes aspects of percolation theory that can be used in order to predict transport properties of disordered systems. Topics are selected in order to provide a basis for understanding subsequent applications to porous media and are thus not meant to be exhaustive. Still, there will at times be hints to subjects that may have relevance to problems not yet considered within the present framework.

2.1 Exponents Describing Backbone Structure

The structure of the backbone is important to such issues as distributions of arrival times of passive solutes (simply carried along by fluid flow). The resulting dispersion is an inevitable aspect of transport and is frequently of great practical interest. In the soil physics and hydrology literature it is customary to distinguish between "transport" properties (including conduction) and flow properties. In the physics literature all these properties fall under the category of transport.

A number of related properties of the infinite cluster have been investigated in the context of solute dispersion. The mass fractal dimensionality of the backbone cluster is denoted by D_b. This fractal dimensionality has the same fundamental definition as that of percolation clusters generally, but its value lacks the universality of the percolation cluster. In other words the backbone cluster topology can differ significantly depending on whether the percolation model is invasion or random, site or bond and whether the local site or bond probabilities are correlated with each other. The chemical path [1] is the shortest path length between two sites on a large cluster near percolation. Defining chemical path lengths that incorporate the tortuosity of the backbone cluster makes sense in the context of solute transport through porous media, when such solutes are carried passively through percolation structures. The tortuosity of the backbone cluster has been studied since the 1970s. One of the easiest ways to characterize this tortuosity is to give the length of the shortest path, Λ, along the backbone cluster as a function of p and p_c. Stauffer [2] gives this length as follows:

$$\Lambda \propto |p - p_\mathrm{c}|^{-\eta} \qquad (2.1)$$

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with $\eta = 1$ the value of the associated critical exponent (in three dimensions). In fact, the "value" of this exponent has been growing over the last 30 years [3, 4], but any value greater than 0.88 implies that the ratio of the (tortuous) path length to the size of the largest cluster is divergent at $p = p_c$, meaning that the path is infinitely tortuous. Thus the tortuosity, T, may be defined as the ratio Λ/χ, or,

$$T = \left(\frac{\Lambda}{\chi}\right) = |p - p_c|^{\nu - \eta} \tag{2.2}$$

The value of this exponent can be related to the fractal dimensionality, D_{min}, of an optimal chemical path along the backbone by using the defining equation of fractal dimensionality from Mandelbrot [5]. For a path, which is constructed of steps of length ε, the dimensionality is fractal (and larger than 1) if the total length of the path, L, diverges in the limit that ε approaches zero. In particular, D_{min} is given by

$$L(\varepsilon) = \varepsilon^{1 - D_{\text{min}}} \tag{2.3}$$

We can use this expression to relate D_{min} to η. In percolation of course, as the percolation threshold is approached the correlation length, χ, diverges, whereas the individual step lengths (bond dimensions) are constant, but we can simply rescale the picture by reducing the lengths of the individual steps inversely proportionally to the correlation length. This process maintains the physical size of the cluster but increases the detail at which the cluster is drawn, corresponding to Mandelbrot's definition. Thus $\varepsilon \propto \chi^{-1}$ and

$$T \propto \left(|p - p_c|^{\nu}\right)^{1 - D_{\text{min}}} = |p - p_c|^{\nu - \nu D_{\text{min}}} \tag{2.4}$$

which yields $\eta = \nu D_{\text{min}}$.

The mass fractal dimensionality of the backbone cluster D_b [6] appears to be more appropriate in relating the *time of travel* along such a backbone to the linear extent of the cluster. Thus, the time of travel is not simply proportional to the length; it turns out to be even longer than what would be simply predicted by making it proportional to the tortuous length. Further, this time can depend strongly on the type of percolation problem considered.

The argument of Lee et al. [6] follows. For particles entering a backbone cluster at one side of a system, the typical velocity at distance x will scale as $1/n$, where n is the number of bonds at distance x. The number of bonds at distance x is proportional to x^{-1+D_b}. Thus the typical travel time

$$t \propto \int \frac{dx}{v} \propto dx x^{-1+D_b} = x^{D_b} \tag{2.5}$$

Lee et al. [6] do in fact find from simulations in two dimensions that the typical time, t, that a particle takes in traversing a Euclidean distance x scales as the 1.62 power of x, very close to the value of $D_b = 1.6432$ found by Grassberger [7] for the backbone cluster in two dimensions, but nowhere near the value 1.217 for optimal paths (see Table 2.2). Thus a kind of temporal tortuosity factor is given in the

Table 2.1 Fractal dimensionalities associated with chemical path lengths and the backbone percolation cluster in 3D (from Sheppard et al. [4])

Model	D_{min}	D_{b}
Site NTIP	1.37	1.87
Site TIP	1.37	1.86
Bond TIP	1.46	1.46
RP	1.37	1.87
Optimal path	1.43	1.42

Table 2.2 Fractal dimensionalities associated with chemical path lengths and the backbone percolation cluster in 2D (from Sheppard et al. [4])

Model	D_{min}	D_{b}
NTIP	1.1293	1.6422
Site TIP	1.214	1.217
Bond TIP	1.217	1.217
RP	1.1307	1.6432
Optimal paths	1.21	1.21

same form as Eq. (1.59) but with D_{b} substituted for D_{min}. Such a result will have considerable importance for the discussion in Chap. 10.

Sheppard et al. [4] give values for the mass fractal dimensionality of the sample-spanning cluster and the backbone, D_{b}, as well as the fractal dimensionality of the optimal path, D_{min}, in various percolation models. Presenting the basic information from their summary (Tables 2.1 and 2.2) requires defining their acronyms: IP = invasion percolation, TIP = trapping invasion percolation, NTIP = nontrapping invasion percolation, RP = random percolation (the focus here). The difference between trapping invasion percolation and nontrapping invasion percolation is that in the former case the “defending” fluid (defending against the “invading” fluid) is incompressible, meaning that it can be trapped (in finite clusters). In the latter case, the defending fluid can always escape, even if it does not percolate, since it can be compressed to zero volume.

In the present case for our dispersion calculations (Chap. 10) we have used several values of the exponent D_{b}. These values for the fractal dimensionality each lead to distinct values for the exponent η.

2.2 Exponents for Conduction Properties

Consider the site percolation problem introduced in Sect. 1.2 and stipulate for simplicity that all the metallic balls are of the same size and composition. Allow them to be placed on a simple cubic lattice. We have not calculated p_{c} for this lattice but numerical simulations give the result $p_c = 0.3116$. Thus, in an infinite lattice, if fewer than 31.16% of the balls emplaced are conducting and the remainder are insulators, the system will not conduct at all. If $p > p_c$, the system will conduct. Clearly the conductivity of the system must follow a functional form, which vanishes (rather than diverge) at $p = p_c = 0.3116$. The result of percolation theory is that the functional form must be a power law (and the arguments given here justify that), so that what we need to be able to do is predict the exponent.

The most important aspects of this problem treated by percolation theory are probably the connectivity and the tortuosity of the conducting paths; certainly these concepts have been independently (but inconsistently) developed in the porous media communities. Discussions of this topic have occupied a great deal of literature but, as will be seen, the original discussion of Skal and Shklovskii [8] is the simplest introduction, although it does not lead to the most widely accepted result. The following is consistent with the general results of that work.

The electrical conductivity of a system is defined as the ratio of the current per unit area and the applied electrical field. If this ratio is independent of the field (as is normally the case at small field strengths), the system obeys Ohm's law. The current per unit area in the present case involves the current per path and the number of connected paths per unit area. The simplest assumption is that the current for each connected path is identical. Then the number of connected paths per unit cross-sectional area (in three dimensions) is proportional to

$$\chi^{-2} \propto (p - p_c)^{2\nu} \tag{2.6}$$

Since in three dimensions, $\nu = 0.88$, the lowest order estimate of the conductivity is that it should vanish as the $2\nu = 1.76$ power of the difference, $p - p_c$. This suggestion is actually fairly close to observation. But, as we know, the structure of large clusters near the percolation threshold, and by extension also the infinite cluster just above the percolation threshold, is fractal for distances below the correlation length (which of course diverges right at percolation). This fractality produces a tortuosity in the current-carrying path as well. The distance along a connected path, Λ, over a separation equal to the correlation length is actually longer than the correlation length. Λ diverges at the percolation threshold according to [2]

$$\Lambda \propto (p - p_c)^{-\nu D_{\mathrm{min}}} \tag{2.7}$$

Thus, assuming that the resistance of the current-carrying path is just the sum of the resistances of all the metal balls encountered, this resistance per unit system length must actually increase as the percolation threshold is approached, and the increase must be given by the ratio of Λ to χ. This ratio is proportional to $(p - p_c)^{\nu - \nu D_{\mathrm{min}}} = (p - p_c)^{-0.33}$. Here we have used the value for D_{min} for random percolation given in Table 2.1. Such an increase in resistance produces an alteration of the results for the conductivity to

$$\sigma \propto (p - p_c)^{2\nu + (D_{\mathrm{min}}\nu - \nu)} = (p - p_c)^{2.09} \equiv (p - p_c)^{\mu} \tag{2.8}$$

Here the first contribution to the exponent is essentially a result of the connectivity, or separation of the paths along which current can flow, while the second contribution is due to the tortuosity of these paths. The combined exponent is thus the sum of two contributions, $1.76 + 0.33 = 2.09 = \mu$. At the time of the original estimate by Skal and Shklovskii [8], it was thought that $\eta = 1$, which leads to $\mu = 1.88$. Nowadays, μ is known at least as accurately as are the constituents that distinguish μ from 2ν, and more modern publications [9, 10] give $\mu = 2$. As pointed out already by Berkowitz and Balberg [11] the explanation for the discrepancy $\mu = 2$ instead of $\mu = 2.09$ is quite simple. The discussion up until now has omitted the effects on μ of the "blobs," or finite-length parallel paths. But the fact that such blobs become increasingly complex and more numerous in the limit of $p \to p_c$ leads to a reduction in the resistance of the backbone cluster, meaning that μ is reduced from 2.09. The presentation of this argument is meant more to provide extra qualitative understanding than to imply a quantitative inference on the effects of these "blobs" on conductivity.

In two dimensions the Skal and Shklovskii [8] argument would start with $\mu \approx \nu$ rather than 2ν since the relevant current density is defined relative to a perpendicular length (χ) rather than a cross-sectional area (χ^2). Then complications due to a tortuosity would be added. But the exponent μ appears to be smaller in magnitude than ν, making the argument of Skal and Shklovskii [8] more difficult to apply. As Berkowitz and Balberg [11] explain, the structure of the backbone cluster in 2D is different enough to make blobs a more important modification to μ than the tortuosity. As a first approximation to μ one can simply use the exponent for the correlation length, $\nu = 1.33$. Derrida and Vannimenus [12] find that the value of μ in two dimensions is 1.28 and Jerauld et al. [13] find $\mu = 1.27$, while Normand and Herrmann [14] find $\mu = 1.30$. Note that all of these values for μ in two dimensions are not greatly different from the 2D value for ν. Establishing values for μ will have relevance to discussions of Archie's law for the electrical conductivity of porous media. This is why it is important to find the best values for these exponents as well as to determine the conditions under which one expects to observe them. The value for μ in two dimensions (three dimensions) will be assumed here to be 1.3 (2).

In one dimension, the conductivity is either zero (if there are any nonconducting elements at all) or a finite value, implying $\mu = 0$. But μ is, in general, nonuniversal for 1D systems, meaning that, in principle any value of μ can be generated. If there is a variation in the conduction properties of the individual elements (not all resistance values identical), the result $p_c = 1$ implies that the total resistance may be dominated by the resistance of the most resistive element in 1D systems. In that case the conductivity is calculated using extreme value statistics. The choice of the extreme value statistics is determined by the statistics of the individual resistances, making 1D systems highly nonuniversal.

Note that although the concept of conductivity and the discussion of the value of μ were introduced using the example of electrical conduction, the arguments are perfectly general, and the results could be applied to, e.g., the hydraulic conductivity or to air flow as well. What will turn out to differ among these properties is the conditions under which arguments to invoke Eq. (2.8) actually apply.

Berkowitz and Balberg [15] in fact explicitly demonstrated that models of hydraulic conduction yield Eq. (2.8) for the hydraulic conductivity near the percolation threshold, and found values of the exponents compatible with $\mu = 2$ in 3D and $\mu = 1.3$ in 2D, respectively, although they also found results compatible with nonuniversal exponents [16, 17] in certain 3D systems.

One can also use the Einstein relationship [18, 19] between diffusion, D, and conductivity, σ,

$$\sigma = nD \tag{2.9}$$

where n is the number of charge carriers, which is normally assumed to be given by the fraction of sites connected to the infinite cluster, to find

$$D \propto (p - p_{\mathrm{c}})^{\mu-\beta} \tag{2.10}$$

Interestingly enough, as we will find, although other relationships given here are verified, Eq. (2.10) may give inaccurate predictions for solute and gas diffusion in porous media. In fact these two properties are not identical and, although these results may not yet be completely understood, the main discrepancy appears to be due to the ability of solutes to diffuse over thin water films present in otherwise dry pores, while there is ordinarily no equivalent possibility for gases to diffuse through water. It is curious that a simple effective-medium theoretical result [20] yields $D \propto (p - p_{\mathrm{c}})^1$, which is exactly what is observed [21], although it is almost certain that it would be for the wrong reasons. On account of this coincidence, however, and because of the rather close correspondence between effective-medium and percolation theories, the essence of this derivation is repeated here.

The lowest order effective medium approximation for the mean diffusivity, D_{m}, can be obtained via physical arguments [22, 23] or via lattice Green functions [24] as [20]

$$\int_0^\infty \frac{D_{\mathrm{m}} - D}{[(Z/2) - 1]D_{\mathrm{m}} + D} f(D)\,dD = 0 \tag{2.11}$$

Keffer et al. [20] use as a distribution of diffusivities (to describe ultimately the diffusion in zeolites)

$$f(D) = p\delta(D - D_{\mathrm{b}}) + (1-p)\,\delta(D - D_0) \tag{2.12}$$

where D_{b} is a very small value and D_0 is relatively large, and for which these authors define $f \equiv D_{\mathrm{b}}/D_0$. Note that, in an unusual choice, these authors chose to use the symbol p for the low diffusion elements! The solution of Eq. (2.11) using Eq. (2.12) for $f(D)$ is

$$\frac{D_{\mathrm{m}}}{D_0} = \frac{1}{2}\left\{A + \left[A^2 + \frac{4f}{(Z/2) - 1}\right]^{\frac{1}{2}}\right\} \tag{2.13}$$

and

$$A = 1 - p + fp - \frac{f + p - fp}{(Z/2) - 1} \tag{2.14}$$

For $f = 0$ Eq. (2.14) yields

$$\frac{D_{\mathrm{m}}}{D_0} = \frac{[(Z/2)-1]-(Z/2)p}{[(Z/2)-1]} = \frac{(1-p)-(2/Z)}{1-(2/Z)} \tag{2.15}$$

which would seem to yield $p_{\mathrm{c}} = 1 - 2/Z$ and a critical exponent of 1. But given that these authors exchanged the roles of p and $1-p$, the actual result obtained for p_{c} is $Zp_{\mathrm{c}} = 2$, which would be in agreement with the results of percolation theory except that the constant, 2, is more appropriate for 2D, rather than the 3D configurations considered. Note also the conclusion that the critical exponent 1 is unaffected by the transposition of p and $1-p$.

2.3 Summary of Derived Values of Critical Exponents

While most of the entries in Table 2.3 refer to quantities discussed in Chap. 1, it is not presented there because of its inclusion of the conductivity exponent, μ.

Table 2.3

Exponent	$D = 1$	$d = 2$	$d = 3$	$d \geq 6$
α	$\underline{\mathbf{1}}$	$-2/3$	-0.62	$\underline{-1}$
β	$\underline{\mathbf{0}}$	5/36	0.41	$\underline{\mathbf{1}}$
γ	$\underline{\mathbf{1}}$	43/18	1.82	$\underline{\mathbf{1}}$
σ	$\underline{\mathbf{1}}$	$36/91 = 0.396$ $\underline{\mathbf{(0.369)}}$	0.45	$\underline{\mathbf{1/2}}$
τ	$\underline{\mathbf{2}}$	187/91	2.18	$\underline{\mathbf{5/2}}$
ν	$\underline{\mathbf{1}}$	4/3 $\underline{\mathbf{(1.355)}}$	0.88	1/2
μ	Not universal	1.3 $\underline{\mathbf{(1.355)}}$	2.0 ($\underline{\mathbf{1.88)}}$	3

This table was constructed synthesizing the tabulated values for these exponents from Sahimi [18, 19] and Stauffer [2], but using $\mu = 2.0$ in three dimensions [9, 10] and $\mu = 1.3$ in two dimensions [14]. Known values, for which the derivations were described here, are underlined and in bold; if the values obtained here are different from the known values, they are given in parentheses.

2.4 Finite-Size Scaling and Fractal Characteristics

Numerical simulations are a common means to generate values of p_{c} *as well as of critical exponents in percolation theory. But simulations can be performed* only for finite-sized systems. While it is possible to try to extract limiting behavior in the infinite system limit as a means to generate such quantities, a better approach is to generate dependences of, e.g., the conductivity on the system size and use a known transformation to yield the associated dependences on percolation variables. This technique is used often for treating transport problems. For example, quantities like the conductivity, which vanish at the percolation threshold, will diminish with increasing system size until the linear dimension of the system exceeds the correlation length. At larger length scales the system is known to be Euclidean, meaning that the property in question becomes independent of system size. The exception of course is right at the percolation threshold, for which the correlation length is infinite and the scale dependence continues to infinite system size.

Originally it was Fisher [25] who showed how to relate percolation quantities for finite-sized systems to their behavior as a function of $p - p_\mathrm{c}$ in the limit of infinite-sized systems. In particular for a system of finite size L, a percolation quantity, ψ, which obeys an arbitrary power law, $(p - p_\mathrm{c})^{q_0}$, will behave as follows:

$$\psi \propto L^{-\frac{q_0}{\nu}} h\left[\left(\frac{L}{\chi}\right)^{\frac{1}{\nu}}\right] = L^{-\frac{q_0}{\nu}} h\left[L^{\frac{1}{\nu}}\left(p - p_\mathrm{c}\right)\right] \tag{2.16}$$

with h an unknown nonsingular function. Substitute $L = \chi$ into Eq. (2.16) to obtain

$$\psi \propto \left(p - p_\mathrm{c}\right)^{-\nu\frac{-q_0}{\nu}} h[1] = \left(p - p_\mathrm{c}\right)^{q_0} \tag{2.17}$$

Note the similarity of Eq. (2.16) with Eq. (1.8) for the cluster statistics. In particular, the ratio of L to the correlation length enters here because of the fact that systems near the percolation threshold obey fractal geometry (with, e.g., fractal cluster dimensions) only for length scales smaller than the correlation length, χ. For length scales larger than χ the system follows Euclidean geometry. For example, if a system with $p > p_\mathrm{c}$ is smaller than the correlation length, the above finite-size scaling results hold and such transport quantities as a diffusion constant or the conductivity will trend to zero with increasing system size up to a length scale equal to the correlation length. But at larger system sizes, the transport coefficient will not change for any further increase in system size. Only precisely at p_c will the behavior of the transport coefficient continue to diminish indefinitely with increasing system size. But on the way to $p = p_\mathrm{c}$, the transport coefficient has taken on values at each size, which were equal to the transport coefficient at that value of the correlation length. Therefore the first factor in Eq. (2.16) gives the behavior of the variable ψ for the condition $L = \chi$, since the second factor does not change with L for L constrained to equal χ. Thus any such exponent obtained from finite-size simulations (and presented as a function of system size, L) must be multiplied by $-\nu$ to find the value predicted by percolation theory. The similarity of Eq. (2.16) with Eq. (1.8) is a consequence of the relevance to percolation scaling of homogeneous functions, a topic not further considered here, but treated in some detail in the standard references mentioned earlier in the chapter.

2.5 Critical Path Analysis

Although an entire chapter is devoted to critical path analysis (CPA), its introduction here serves to familiarize the reader with its basic concepts. This introduction addresses more general issues, such as effects of the dimensionality of the system, the connectivity of the medium, and the width of a distribution of local conductances, while Chap. 3 treats detailed applications of CPA to systems of experimental relevance.

CPA uses percolation theory to calculate effective conduction properties of a disordered medium. CPA was developed [26–28] to find the limiting resistance value in a random medium with a wide range of local resistances. The initial work was meant to address the electrical conduction problems of impurity conduction systems in crystalline semiconductors as well as amorphous semiconductors, and so topological disorder was included. The present introduction, however, concentrates on lattice models. Because the connectivity of the more highly conductive regions is a critical input into the calculation of effective properties, the fundamental theory of connectivity is an obvious tool to be employed for such a calculation. Then it is not necessary to add connectivity as an afterthought, or to develop alternative methods to quantify connectivity, such as the Euler number [29]. While the latter has an advantage in that it can be used to identify a percolation transition [29], i.e., when the Euler number changes sign the system crosses p_c, its disadvantage is that there is no known relationship between the Euler number and p. Thus there is no way to express $(p - p_c)$ in terms of Euler numbers, making it impossible to use the Euler number to predict any properties given in percolation theory. Two additional advantages of CPA are that it can be applied to any conductance (or conductivity) distribution and that it yields results, which are most accurate (exact) in the limit of large disorder rather than in the limit of a homogeneous system (although in many cases CPA can be formulated to be exact in both limits).

The gist of CPA is that it defines that interconnected network of conductances which has the largest possible value of the smallest, or bottleneck, conductance. This value is called the critical conductance and is found by setting an integral over the conductance distribution equal to the critical percolation probability, p_c. The lower limit of this integral is the critical conductance, and the upper limit is the largest conductance. The analysis can be formulated equivalently in terms of a resistance distribution, for which p_c fixes the upper limit of integration while the lower limit is the smallest resistance in the distribution. In CPA p_c is thus the most important parameter, rather than the critical exponents. The critical percolation probability can vary significantly from system to system. Thus there might be important differences in applying CPA in different systems. Important differences do exist in applying CPA in different dimensions.

2.5.1 Relation of CPA to Extreme Value Statistics in 1D Systems

Consider first the case of 1D systems. In infinite 1D systems the conductivity can always be calculated exactly using what is often called the harmonic mean value of the conductance distribution. This value is related simply to the inverse of the sum of the resistance values since the effective resistance of resistances in series is their sum. For uniform size characteristics (all bonds the same length, for example) the resistance distribution is a perfect proxy for the resistivity distribution as the resistance of any bond is a given constant times its resistivity. For a wide distribution of resistance values, the harmonic mean is dominated by the largest resistance in the system. For a truncated power-law distribution of resistances, $W(R)$ (or equivalently conductances), the harmonic mean conductivity is in fact proportional to the largest resistance value, at least as long as $RW(R)$ is a power of R that is greater than -1. This is simply a property of power-law distributions and may easily be verified by integration (Problem 2.4). Since $p_c = 1$ in one dimension, CPA requires that the lower limit of integration on the conductance distribution be the smallest conductance in the system (or the largest resistance). In other words it is not possible to connect an infinite path which avoids even the smallest conductance. A single missing element will break the path. Thus CPA quickly reaffirms the relevance of the largest resistance to the system conductivity. For a power-law resistance distribution that extends to infinite resistance the conductivity is zero. In general the conductivity in 1D is given by $\sigma = l/R$, with l the system length and R its total resistance.

In finite-length 1D systems, the problem is more interesting. Again, since in 1D $p_c = 1$, the critical conductance g_c is now the smallest actual conductance in the system, rather than the smallest allowed by the distribution. Since it is impossible to avoid even the largest resistance on the path, but this largest resistance can vary from realization to realization, extreme value statistics are implicated in the procedure to find both an ensemble mean conductivity of the system and a distribution of conductivity values as a function of the system length. To find an ensemble mean conductivity it is necessary first to find the dependence on x of the largest expected resistance value, $R_{\max}(x)$ in a system of length x. If $R_{\max}(x)$ is a power of x, then evaluation of the limit of $x/R_{\max}(x)$ for x approaching infinity gives the scaling of the conductivity as a function of length, x. In such cases, the limiting value of $x/R_{\max}(x)$ as x approaches infinity will typically be zero so that an infinite system does not conduct at all. This is the case in the spatially random hopping conduction system considered below. Whenever the system has a nonzero minimum conductance value, however, the typical resistance of a system of length x is proportional to x and the system conductivity is nonzero and well-defined.

The following specific system, r-percolation, is discussed in considerably more detail in Sect. 4.1. Here we only give the briefest summary sufficient to actually perform the calculations. Consider a 1D system with resistances connecting every pair of sites, i and $i+1$, where i denotes the position of a site on a linear chain. Let the separation of the sites $r_{i,i+1}$ be a random variable with uniform probability density, $1/b$, where b is the typical separation of sites. Let the resistance $R_{i,i+1} = R_0 \exp[2r_{i,i+1}/a]$, where $a << b$ and R_0 are constants with units length and resistance, respectively. While the probability of finding an arbitrary site a distance r (within dr) from site i is dr/b, the probability that that site is the nearest neighbor is $(dr/b)\exp(-r/b)$. This probability is normalized over the interval $[0,\infty]$; the nearest neighbor must be somewhere. Now what is the largest likely value of the nearest neighbor distance in a chain of length x? First, the expected number of sites on such a chain is x/b. Thus the number of possible realizations of the nearest neighbor distance is proportional to x/b. This means that the total area under the curve

$\exp(-r/b)/b$ would typically be divided into x/b roughly equal areas, meaning that the largest expected resistance value, $R_{\max} = R_0 \exp[2r_{\max}/a]$, would be found by setting the area under the extreme value distribution between $r_{\max}$ and infinity proportional to b/x,

$$\frac{b}{x} \propto \int_{r_{\max}}^{\infty} \frac{dr}{b} \exp\left[\frac{-r}{b}\right] \tag{2.18}$$

Solution of this integration for $r_{\max}$ in terms of x leads to

$$r_{\max} \propto b \ln\left(\frac{x}{b}\right) \tag{2.19}$$

Substitution into $R_{\max} = R_0 \exp[2r_{\max}/a]$ leads to

$$R_{\max} \propto R_0 \left[\frac{x}{b}\right]^{\frac{2b}{a}} \tag{2.20}$$

with the result that

$$\sigma(x) \propto x^{1-\frac{2b}{a}} \tag{2.21}$$

Equation (2.21), since $b >> a$, leads to a conductivity [30, 31] which is a negative power of the system length and which vanishes in the limit of an infinite chain. In condensed matter applications, where individual resistance values are typically exponential functions of random variables, the only easy way to generate a power-law behavior of the conductivity with system size is to invoke extreme value statistics. The only systems, in which mean-value statistics appear to be relevant, are 1D systems, because of the fact that $p_c = 1$. Thus 1D systems make a very poor starting point for understanding percolation behavior generally. We will find out in the next chapter that, for other reasons, 2D systems make very poor models of 3D porous media.

2.5.2 CPA in Two Dimensions

Next we apply CPA to an idealized conductance distribution on a 2D lattice. An attractive point about 2D systems is the direct relationship there between critical conductance and system conductivity. Consider the elementary relationship between the resistance R and the resistivity ρ for a homogeneous system of length l and cross-sectional area A, in particular $R = \rho l/A$. In two dimensions the analogous relationship is $R = \rho l/z$, where z is the system dimension perpendicular to flow. The particular case of two dimensions, where the sample-dependent property R is equal to the ratio of two lengths times the material property, ρ, is interpreted [32] for the case of disordered systems to imply the equivalence of ρ and R, and thus between the conductance, g, and the conductivity, σ, as well. This makes the system conductivity equal to the critical conductance.

For the bond percolation problem we need the probability density function (pdf) for finding a conductance between two arbitrary nearest neighbor sites with value between g and $g + dg$, called $W(g)$. Normalization of this pdf requires

$$\int_0^\infty W(g)\,dg = 1 \tag{2.22}$$

Consider the case that $W(g)$ is a log uniform distribution of (electrical or hydraulic) resistance values with width 10 orders of magnitude, e.g., from 10^0 to 10^{10} in arbitrary units. Place each conductance at random between two arbitrary nearest neighbor sites on a square lattice. Each site has four nearest neighbors, $z = 4$, and $p_\mathrm{c} = 0.5$. The conductivity of this arrangement is the median conductance value $g = 10^5$ because it is known that emplacement of a fraction 0.5 of the bonds of this lattice guarantees that the system is at the percolation threshold. The median conductance on this lattice is then the smallest conductance value that cannot be avoided by the current, a value which is more generally known as the critical conductance, g_c. g_c is found from

$$\int_{g_\mathrm{c}}^\infty W(g)\,dg = p_\mathrm{c} = 0.5 \tag{2.23}$$

For an infinite square lattice, placement of half the conductances into lattice positions at random guarantees existence of a cluster of interconnected conductances, which just reaches infinite size; choosing that half of the conductance distribution with the largest conductances yields the path of least resistance. If, in a corresponding physical system all bonds have not only the same length, but also the same cross-sectional area, the median conductance value would correspond rigorously to the median conductivity in a distribution of conductivities. Such a picture applies also to media in which the currents are represented numerically in terms of finite difference equations, as long as the medium is divided up into subregions of identical squares. Since the effective conductivity of the medium is known in porous media communities as the upscaled conductivity, then under fairly common conditions we can identify the median of a conductivity distribution with the upscaled conductivity in two dimensions. If the logarithm of K is symmetrically distributed, then the median of the conductivity is also the geometric mean. But the same results do not apply for all 2D systems.

If the same conductances are placed on a triangular lattice, where each point has six nearest neighbors $(Z = 6)$, the dominant conductance value from the distribution is $10^{6.55}$ because p_c is 0.345 and the current avoids the slowest two-thirds of the connections. If the same conductances are placed on a honeycomb lattice, with $z = 3$, the dominant conductance is $g_\mathrm{c} = 10^{3.45}$ because $p_\mathrm{c} = 0.655$ and the current avoids only the slowest one-third of the connections. The corresponding values of the rate-limiting conductances and associated conductivities extend over more than three orders of magnitude in the simplest 2D lattices! In Fig. 2.1 we represent these results pictorially and include as well the range

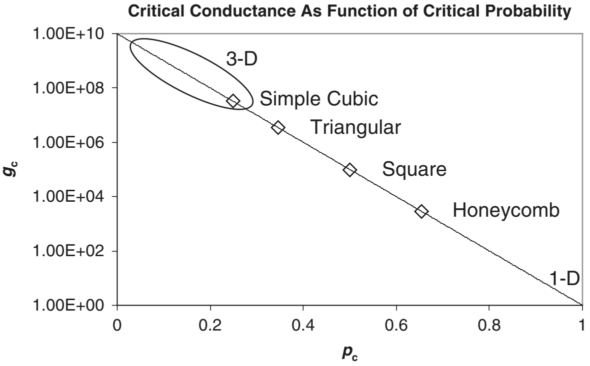

Fig. 2.1 For a log-uniform distribution of conductances the critical (percolating) rate-limiting conductance, g_c, as a function of the critical percolation probability, p_c. Note the rapid diminution of p_c and increase of g_c with increasing dimensionality. Further, if the geometric mean of the distribution is held constant, but the width is increased, all systems to the left of the square lattice will have an increase in K, while all those to the right will experience a decrease

of likely values for g_c in 3D lattices $(p_c \leq 0.2488)$ as well as on a 1D chain (where $p_c = 1$). In 3D the relationship between g_c and system conductivity is more complex, and only in 2D systems can g_c in Fig. 2.1 be interpreted also as the conductivity.

2.5.3 CPA in 3D

In 3D we need to be able to write expressions for the conductivity as well. If only enough resistors are placed on the lattice to guarantee the existence of an infinite cluster ($p = p_c$), then there will be only a single connected path in, say, the x direction over a distance χ in both the y and the z directions. But χ diverges right at the percolation threshold. While this path has the largest rate-limiting conductance value possible for a given network topology and conductance distribution, construction of such a critical path does not optimize the conductivity since the conductivity due to a single conducting path in an infinite cross-sectional area (or perpendicular distance in two dimensions) is zero. However, emplacement of a few smaller conductances into their positions in the network reduces χ rapidly while scarcely diminishing the rate-limiting conductance, allowing the possibility of a general optimization procedure. Such an optimization procedure for a 3D lattice, $d = 3$, is given below. The optimization procedure results in the determination of an optimal value of the conductance, g_{opt}, which is useful as long as g_{opt} is close enough to g_c so that the topology of the conducting paths is described by percolation theory. Nevertheless, the tendency for p_c to be much smaller in 3D than in 2D tends to make the conductivity of 3D systems much higher than in 2D, and we discuss first general tendencies for the conductivity in terms of the dimension of the medium.

2.5.4 Dimensional Dependence and Similarity to Matheron Conjecture

In Fig. 2.1 the dimensional dependence of g_c for the proposed log-uniform distribution of conductance values is clear and strong. In 2D square lattices the critical conductance, 10^5, yields the conductivity and is the geometric mean of the distribution $[(10^0)(10^{10})]^{1/2}$. For 1D systems g_c is the smallest g in the system, while in 3D systems, it is near the large end of the distribution. This dimensional dependence is reminiscent of that in a classical conjecture of Matheron [33]. The relevance of the geometric mean of a conductivity distribution to the 2D upscaled conductivity is not restricted to a log-uniform distribution, but is repeated for log-normal distributions and power law distributions as well, making it possible to compare the result from CPA to a completely different formulation for upscaling K in heterogeneous media. Assume that the logarithm of the hydraulic conductivity is normally distributed,

$$W(K) \propto \exp\left\{-\left[\frac{(\ln(K)-\ln(K_0))^2}{2Var(\ln(K))}\right]\right\} \tag{2.24}$$

where $Var[\ln(K)]$ is the variance of the distribution of $\ln[K]$. Then the lowest order approximation to the hydraulic (or electrical) conductivity is [34]

$$K = K_\mathrm{gm}\exp\left[\left(\frac{1}{2}-\frac{1}{d}\right)Var(\ln(K))\right] = K_0\exp\left[\left(\frac{1}{2}-\frac{1}{d}\right)Var(\ln(K))\right] \tag{2.25}$$

where K_gm, the geometric mean of K, is here equal to K_0, the most likely value of K. In fact, De Wit [34] explains that Eq. (2.25) is essentially a perturbation expansion in the (small parameter) $Var(\ln(K))$. Equation (2.25) also implies that the upscaled conductivity in 2D is equal to the geometric mean or to the median value. Further, the hydraulic conductivity increases with increasing variance in 3D and diminishes with increasing variance in 1D, just as in Fig. 2.1. Since all methods generate the hydraulic conductivity in 1D systems using the inverse of the sum of the resistance values, the two results coincide in 1D as well as in 2D, at least under some circumstances. But in 3D there are some fundamental differences.

In 3D Eq. (2.25) suggests that the conductivity is independent of the properties of the connectivity of the medium as long as $\ln(K)$ is a normally distributed random field. It is known, however, that the connectivity of such fields plays an important role in the upscaling [35–38]. As can be seen from CPA, the tendency for K to increase with diminishing p_c is not restricted to the effects of increasing dimensionality, but includes effects of larger coordination number, Z, as well. Thus increasing the local connectivity reduces p_c and increases K. Further, Eq. (2.25) implies that the conductivity can be represented in terms of the mean value and some parameter describing the variation about the mean. However, it should be apparent from critical path arguments that the important conductance may be far in the tail of the distribution. As mentioned, Eq. (2.25) is not complete: it is believed that in fact Eq. (2.25) represents only the first term in a series [34] of terms proportional to powers of the variance of ln(*K*). Thus the validity of Eq. (2.25) is subject to an important condition on the magnitude of *Var*(ln(*K*)), which must be small. Similarly, even using all the terms in the series is insufficient if the series does not converge, which will be the case for large *Var*(ln(*K*)).

2.5.5 Optimization of the Percolation Network: Contrast Between 2D and 3D

The idea of CPA is actually not best expressed as an upscaling of the conductivity. In particular, in CPA, one seeks an optimization of an expression for the conductivity, which is based on selection of paths with very small values of the maximum resistance and the separation of those paths. Thus we find the dominant conducting paths, the current (or flow) on those paths, and how many such paths per unit area intersect a plane perpendicular to the flow. We cannot restrict our attention precisely to the paths with the smallest possible values of the maximum resistance, since these paths would be precisely at the percolation threshold and then have infinite separation (leading to a zero conductivity). Incorporating some larger resistances reduces the conductances of these paths, but increases their areal density rapidly from zero. The typical separation of these paths is given in terms of the correlation length, χ. The areal density of the relevant paths is thus χ^{-2}. We will then invert an elementary relationship for the resistance of a homogeneous wire $R = \rho l/A$, with $\rho \equiv \sigma^{-1}$ the resistivity, l the length and A the cross-sectional area, to obtain the conductivity from R, l, and A, i.e., $\sigma = l/RA$. A will thus be the square of the correlation length, and l will be the typical separation of maximal resistances on the path. In that expression for the conductivity, however, all the functions must be written in terms of the maximally valued resistance (or minimum conductance) in order to perform an optimization.

The correlation length is defined in terms of $(p - p_c)$; thus we must have a general expression for $(p - p_c)$, which is written in terms of the resistance distribution itself, in order to apply the optimization procedure.

Define

$$F(R) \equiv \int_0^R W(R')\, dR' = p \tag{2.26}$$

Then

$$F(R_c) = \int_0^{R_c} W(R')\, dR' = p_c \tag{2.27}$$

Equations (2.26) and (2.27) can be solved in parallel for $p - p_c$. Define a conductance $g \equiv R^{-1}$ and define l to be the typical separation of the rate-limiting resistances, R. It is then possible to write a relatively simple expression for the conductivity of a 3D network, on which a fraction, p, of bonds with the smallest R values possible, is placed at random,

$$\sigma = \frac{l\left[F\left(g^{-1}\right) - F\left(g_{\mathrm{c}}^{-1}\right)\right]^{2\nu}}{\chi_0^2} g \tag{2.28}$$

In Eq. (2.28) $\chi_0^2[F(g^{-1}) - F(g_{\mathrm{c}}^{-1})]^{-2\nu}$ is the square of the correlation length as a function of the smallest conductance included, g. l is actually the separation of rate-limiting resistances on the dominant, current-carrying path and, as such, would seem to involve only the statistics of the resistance values. If the resistance distribution is discretized in steps of the fundamental constant $\mathrm{e} = 2.718$, then one could write for l,

$$l \approx \chi_0 \left\{ \frac{\int_0^R W(R)\, dR}{\int_{-R/\mathrm{e}^{1/2}}^{\mathrm{e}^{1/2}R} W(R)\, dR} \right\}^{-\frac{1}{3}} \tag{2.29}$$

in three dimensions. Equation (2.29) has a very simple basis actually. Note that the ratio on the right-hand side is just the inverse of the fraction, f, of emplaced resistances which is in the largest discretization class, so that $l^3 f \approx 1$. In this formulation, the distribution of resistances on the percolating cluster is the same as in the medium generally, so that the volume concentration of the largest resistances is easy to obtain from the appropriate bulk distribution, $W(R)$. Note that l in Eq. (2.28) is thus only a very slowly varying function of p, and not a function of $p - p_{\mathrm{c}}$ at all. For this reason optimization of Eq. (2.28) is not complicated by consideration of l. Result Eq. (2.28), however, is not generally agreed on. Several authors identify l with the correlation length $\chi = \chi_0[F(g^{-1}) - F(g_{\mathrm{c}}^{-1})]^{-\nu}$, by arguing that the separation of rate-limiting resistances is topologically constrained, rather than a function of the frequency of occurrence of such resistances. The physical basis for this argument is that, in the vicinity of p_{c} at least, most of the largest resistances are shorted by alternate paths with smaller dominant resistance values, but that, for self-consistency l cannot be larger than χ, otherwise the value of p would have to be changed. This important problem is still not completely settled, with several different perspectives taken in the literature.

If in Eq. (1.83) R is an exponential function of a random variable, such as a site separation ($R \propto \exp(2r/a)$ with a a constant length), then $F(R) - F(R_{\mathrm{c}}) \propto \ln(R/R_{\mathrm{c}}) = \ln(g_{\mathrm{c}}/g)$, but if R is a power of, e.g., a tube radius (for hydraulic conduction), then $F(R) - F(R_{\mathrm{c}}) \propto (R - R_{\mathrm{c}})$ or $g - g_{\mathrm{c}}$ (see the assigned problems). Using Eq. (2.29) for l and optimizing Eq. (2.28) leads to, in the first case,

$$\frac{d\sigma}{dg} = \frac{d}{dg}\left[\frac{l\left[F\left(g^{-1}\right) - F\left(g_{\mathrm{c}}^{-1}\right)\right]^{2\nu}}{\chi_0^2} g\right] = \left[\ln\left(\frac{g_{\mathrm{c}}}{g}\right)\right]^{2\nu} - 2\nu\left[\ln\left(\frac{g_{\mathrm{c}}}{g}\right)\right]^{2\nu-1} = 0 \tag{2.30}$$

Solution of Eq. (2.30) leads immediately to $\ln(g_c/g) = 2\nu$, or $g = g_c \exp(-2\nu)$. Thus the controlling conductance, g, is closely related to the critical value, g_c, and this value of g can also be substituted into $\chi = \chi_0[F(g^{-1}) - F(g_c^{-1})]^{-\nu})$ to generate an expression for σ in Eq. (2.28). Note that choice above of $l \propto \chi$ would yield $g = g_c \exp(-\nu)$, because the exponent 2ν would be replaced by ν. In two dimensions, the factor χ^2 in the denominator is replaced by χ. If l is taken to be proportional to χ, the 2D case becomes special because l/χ has no dependence on the percolation variables, with the conductivity a universal numerical factor (of order unity) times the critical value of the conductance, g_c. This result does appear to be verified [32], and our own simulations agree [39]. Specific results from CPA will be discussed in Chap. 4 and elsewhere.

Note, however, that in many cases it may be possible to apply CPA without using the above optimization if it is desired only to find the ratio of the critical resistance value at two different values of a changing external parameter such as the moisture content, and under the assumption that far from the percolation threshold the topological aspects affecting the optimization will change only slowly with such external parameters. Such cases will also be considered in the chapters on applications.

In hydrogeology one of the most important problems is to be able to predict the effective (hydraulic) conductivity, K_{eff}, of a medium from information regarding the variability of K within the medium. This problem is known as "upscaling the hydraulic conductivity." It is often stated that K_{eff} is bounded by its harmonic and arithmetic mean values. The harmonic mean of a collection of resistance values is the value obtained by configuring them all in series. The arithmetic mean of a collection of resistors is the equivalent resistance value when they are all configured in parallel. Geologists often assert that physicists do not comprehend the complexity of geologic material, which is true, but such an upscaling scheme was obviously developed from the geologic perspective of a subsurface stratified in horizontal geologic units, where horizontal conduction is governed by the arithmetic mean and vertical conduction by the harmonic mean.

Upscaling K in three dimensions as though all resistances were configured in parallel (series) is consistent with assuming that $p_c = 0 (p_c = 1)$. The latter is valid for 1D systems. Thus regarding the bounds of K as being its harmonic and its arithmetic means corresponds to assuming that the critical bond (or volume) fraction for percolation is between 1 and 0, valid for one- and infinite-dimensional systems, respectively. This means that typical guidelines for upscaling state only that the critical percolation probability is a probability, or that conduction takes place in a dimension between one and infinity. In this context we can see what potential improvement in theory exists when a perspective based on percolation theory is adopted. The value of p_c for a given system defines what fraction of the (smallest) individual resistances, which must be considered as connected in series, with the remaining $1 - p_c$ fraction of larger resistances connected in parallel. Any information on connectivity should help to estimate the appropriate value of p_c for a system, guiding the upscaling.

Problems

2.1. Provide the details of the derivation of Eqs. (2.13) and (2.14) for solute diffusion.

2.2. Verify that $p - p_c \propto \ln(g_c/g)$ if $R \propto \exp(2r/a)$, whereas $p - p_c \propto (g - g_c)$ if $R \propto r^{-4}$. Are there any conditions or restrictions on $W(R)$ for the validity of this derivation? Can you name any systems for which these resistance values are appropriate?

2.3. Repeat the optimization procedure for the conductivity if $R \propto r^4$ and $p - p_c \propto g_c - g$. Note that the optimization procedure described in the text (for the exponential case) is unchanged if the conductivity is represented in terms of R rather than in terms of g. However, the optimization procedure in terms of R fails for the case of the power-law dependence of R. Show this explicitly. What does this failure imply?

2.4. Verify that if $W(R) \propto R^{-\alpha}$ between $R_{\min}$ and $R_{\max}$, such that $-2 < \alpha < -1$, the effective resistance of a 1D chain for this choice of $W(R)$ is proportional to $R_{\max}$.

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