

Chapter 2

Properties Relevant for Transport and Transport Applications

This chapter describes aspects of percolation theory that can be used to predict transport properties of disordered systems. Topics are selected 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 [30] is the shortest path length between two sites on a large cluster near percolation. Defining travel lengths and times that incorporate measures of 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. Although later works showed the need to generate greater breadth of classification, the initial way to characterize this tortuosity was to give the length of the shortest

path, Λ , along the backbone cluster as a function of p and p_c . Stauffer [39] gives this length as follows,

$$\Lambda \propto |p - p_c|^{-\eta} \quad (2.1)$$

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 [15, 36], 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 becomes infinitely tortuous at the percolation threshold. Thus the tortuosity, T , may be defined as the ratio Λ/χ , or,

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

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 [25]. For a path 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

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

We can use this expression to relate D_{\min} to η . 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

$$T \propto (|p - p_c|^\nu)^{1-D_{\min}} = |p - p_c|^{\nu-\nu D_{\min}} \quad (2.4)$$

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

The mass fractal dimensionality of the backbone cluster, D_b [24], 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. [24] is as follows. For particles entering a backbone cluster at one side of a system, the typical velocity v 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 is

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

Lee et al. [24] 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

Table 2.1 Fractal dimensionalities associated with chemical path lengths and the backbone percolation cluster in three dimensions (from [36])

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 two dimensions (from [36])

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

power of x , very close to the value of $D_b = 1.6432$ found by Grassberger [14] 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 same form as Eq. (2.4) but with D_b substituted for D_{\min} . Such a result will have considerable importance for the discussion in Chap. 11.

Sheppard et al. [36] 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 = non-trapping invasion percolation, and RP = random percolation (the focus here). The difference between trapping invasion percolation and non-trapping 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. 11) 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 diverges) 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); what we need 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, concepts which 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 [38] 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 both 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

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

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 $p - p_c$. This suggestion is actually fairly close to observation. But the structure of large clusters near the percolation threshold, and by extension the infinite cluster just above the percolation threshold, is fractal for distances below the correlation length (which of course diverges 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. Specifically, Λ diverges at the percolation threshold according to [39]

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

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, with the increase given by the ratio Λ/χ . This ratio is proportional to $(p - p_c)^{\nu - \nu D_{\min}} = (p - p_c)^{-0.33}$ (using the value for D_{\min} for random percolation, Table 2.1). Such an increase in resistance alters the conductivity to

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

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 [38], 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 [7, 13] give $\mu = 2$. As pointed out by Berkowitz and Balberg [5], 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 numerous in the limit of $p \rightarrow p_c$ 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 [38] argument would start with $\mu \approx \nu$ rather than 2ν , because 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 [38] more difficult to apply. As Berkowitz and Balberg [5] 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 [8] find that the value of μ in two dimensions is 1.28, while Jerauld et al. [19] find $\mu = 1.27$, and Normand and Herrmann [29] find $\mu = 1.30$. But none of these values for μ in two dimensions differs much from the two-dimensional value for ν . Establishing values for μ will have relevance to (for example) 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 (2.0).

In one dimension, the conductivity is either zero (if there are any non-conducting elements at all), or a finite value, implying $\mu = 0$. But generally μ is non-universal for one-dimensional 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 one dimensional systems. In that case the conductivity is calculated using extreme value statistics. The choice of the extreme value statistic is determined by the statistics of the individual resistances, making one-dimensional systems highly non-universal.

Although the concept of conductivity and the discussion of the value of μ were introduced in the context of electrical conduction, the arguments are perfectly general, and the results could instead be applied to, e.g., the hydraulic conductivity or to air flow. 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 [4] 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. However, they also found results compatible with non-universal exponents [10, 35] in certain 3d systems.

The Einstein relationship [32] relates diffusion, D , and conductivity, σ , via the number of charge carriers n :

$$\sigma = nD \quad (2.9)$$

where we assume that n is given by the fraction of sites connected to the infinite cluster. From this relationship we find

$$D \propto (p - p_c)^{\mu - \beta} \quad (2.10)$$

The following summary is from ben-Avraham and Havlin [2], and will be important when we address diffusion in Chap. 7. The average diffusion constant near and above the percolation threshold and at very long times, for which the root mean square excursion $R = [\langle R^2(t) \rangle]^{0.5}$ of the walks not restricted to the incipient infinite cluster is much larger than the percolation correlation length, is

$$D(t \rightarrow \infty, p) \sim (p - p_c)^\mu \quad (2.11)$$

Equation (2.11) includes diffusion in all clusters of the system unrestrictedly. We will show that experimental results conform to Eq. (2.11).

Meanwhile, at the percolation threshold the average diffusion constant follows

$$D(t, p_c) \sim t^{(2-d_w)/d_w} \quad (2.12)$$

where d_w is the random walk fractal dimension. And finally, below the threshold we find

$$D(t \rightarrow \infty, p) \sim t^{-1} (p_c - p)^{-2v + \beta} \quad (2.13)$$

For the restricted ensemble, consisting of only the incipient infinite cluster, Eqs. (2.11) and (2.13) change to

$$D(t \rightarrow \infty, p) \sim (p - p_c)^{\mu - \beta}, \quad p > p_c \quad (2.14)$$

and

$$D(t \rightarrow \infty, p) \sim t^{-1} (p_c - p)^{-2v}, \quad p < p_c \quad (2.15)$$

but Eq. (2.12) remains the same. Curiously, a simple effective-medium theoretical result [20] yields $D \propto (p - p_c)^1$, which has been alleged (as $p(p - p_c)$) to occur in soils [27]. However, typical conditions in porous media make it very difficult to distinguish the Moldrup et al. [27] result from universal scaling predictions, and we argue (Chap. 7) that overall the relevance of universal scaling is best supported. Nevertheless, both on account of this coincidence, and because in fact the effective-medium relationship does hold for $p - p_c > 0.8$, the essence of the Keffer et al. [20] derivation is repeated here.

The lowest order effective medium approximation for the mean diffusivity, D_m , can be obtained via physical arguments [21, 22] or via lattice Green functions [33] as [20]

$$\int_0^\infty \frac{D_m - D}{(\frac{Z}{2} - 1)D_m + D} f(D) dD = 0 \quad (2.16)$$

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

$$f(D) = p\delta(D - D_b) + (1 - p)\delta(D - D_0) \quad (2.17)$$

where D_b is a very small value and D_0 is relatively large, and for which these authors define $f \equiv D_b/D_0$. We caution that these authors made the unusual (and confusing) choice to use the symbol p for the low diffusion elements! The solution of Eq. (2.16) using Eq. (2.17) for $f(D)$ is,

$$\frac{D_m}{D_0} = \frac{1}{2} \left\{ A + \left[A^2 + \frac{4f}{\frac{Z}{2} - 1} \right]^{\frac{1}{2}} \right\} \quad (2.18)$$

where

$$A = 1 - p + fp - \frac{f + p - fp}{\frac{Z}{2} - 1} \quad (2.19)$$

For the case $f = 0$, Eq. (2.19) yields

$$\frac{D_m}{D_0} = \frac{(\frac{Z}{2} - 1) - (\frac{Z}{2})p}{(\frac{Z}{2} - 1)} = \frac{(1 - p) - \frac{2}{Z}}{1 - \frac{2}{Z}} \quad (2.20)$$

which would seem to yield $p_c = 1 - 2/Z$ and a critical exponent of 1. But in another confusing choice these authors exchanged the roles of p and $1 - p$, so the actual result obtained for p_c is $Zp_c = 2$. This would be in agreement with the results of percolation theory except that the constant, 2, is more appropriate for two-dimensions, rather than for the three-dimensional configurations considered. With the transposition noted, Eq. (2.20) becomes $D_m/D_0 = (p - p_c)/(1 - p_c)$! Note also that the conclusion that the critical exponent is 1 is unaffected by the transposition of p and $1 - p$.

In this third edition we will show that nearly all diffusion results in porous media actually conform to Eq. (2.11), eliminating a significant uncertainty in earlier editions.

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 was constructed synthesizing the tabulated values for these exponents from Sahimi [32] and Stauffer [39], but using $\mu = 2.0$ in three dimensions [7, 13] and $\mu = 1.3$ in two dimensions [29]. 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.

Table 2.3 Values of critical exponents

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

2.4 Finite-Size Scaling and Fractal Characteristics

Numerical simulations are a common means to generate values of both p_c and 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, then use a known transformation to yield the associated dependences on percolation variables. This technique is often used for treating transport problems. For example, quantities like the conductivity, which vanishes 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 [11] who showed how to relate percolation quantities for finite sized systems to their behavior as a function of $p - p_c$ 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 $(p - p_c)^{q_0}$, will behave as

$$\psi \propto L^{-\frac{q_0}{\nu}} h \left[\left(\frac{L}{\chi} \right)^{\frac{1}{\nu}} \right] = L^{-\frac{q_0}{\nu}} h \left(L^{\frac{1}{\nu}} (p - p_c) \right) \quad (2.21)$$

with h an unknown non-singular function. Substitute $L = \chi$ into Eq. (2.21) to obtain,

$$\psi \propto (p - p_c)^{-\nu \frac{-q_0}{\nu}} h[1] = (p - p_c)^{q_0} \quad (2.22)$$

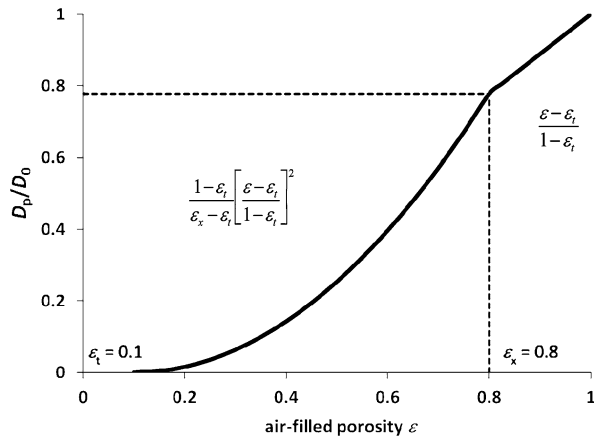
Note that Eq. (2.21) is similar to Eq. (1.8) for the cluster statistics. In particular, the ratio of L to the correlation length enters here, because systems near the percolation threshold obey fractal geometry (with e.g., fractal cluster dimensions) only for length scales smaller than the correlation length. For length scales larger than χ the system follows Euclidean geometry. For example, if a system with $p > p_c$ is smaller than the correlation length, the above finite-size scaling results hold, and transport

quantities (e.g., diffusion constant or 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 remain constant with 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 $p = p_c$, 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. (2.21) gives the behavior of the variable ψ for the condition $L = \chi$, since the second factor does not change with L where L is 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. (2.21) to Eq. (1.8) is a consequence of the relevance to percolation scaling of homogeneous functions, a topic not considered here but treated in the standard references mentioned earlier in this chapter.

2.5 Scaling Far from the Threshold

In most applications in this book we can restrict our attention either to critical path analysis (Sect. 2.6) or the asymptotic results from percolation theory above. But we will see that in the case of the thermal conductivity, measurements are taken so far from the percolation threshold that the asymptotic results no longer apply. In addition, we will find that for the gas diffusion, the normalization factor used in the reporting of the data is determined at porosity 1, also so far from the threshold that a roughly 30 % inconsistency in a purely numerical factor is introduced. Both of these difficulties are removed if we refer back to Kirkpatrick [22]. There it was determined that the percolation scaling of $(p - p_c)$ was most accurate to about $p = 0.8 \equiv \varepsilon_x$. Above this value of p , he showed that a linear dependence in $p - p_c$ was superior, a result that derived from effective medium theories and given in Eq. (2.25). We show what form of the conductivity results in Fig. 2.1. Note that for electrical conductivity, solute and gas diffusion, and air permeability, the largest value of p ever investigated is equal to the porosity, which is typically no greater than 0.6, meaning that the complication is never observed directly. However, in the case of the thermal conductivity, where the solid portion of the medium is at least as conducting as the water, the typical case of $\varphi = 0.4$ means that the observed moisture dependence investigates values of p between 0.6 and 1. This means that the cross-over from the quadratic to the linear dependence will show up in the middle of the range of investigated values. Note that the prefactor, $(1 - \varepsilon_t)(\varepsilon_x - \varepsilon_t)$, in the percolation scaling term is about 1.28 for the typical value of $\varepsilon_t = 0.1\varphi$. At the time of Kirkpatrick's analysis, the scaling exponent μ appeared to take on the value of 1.6. It is now known to be 2. This change in exponent value would force the cross-over to take place at a somewhat lower value of ε , requiring a numerical constant somewhat larger than 1.28. Since these changes would be relatively small, however, we have deferred any investigation to a later time.

Fig. 2.1 Actual conductivity in three dimensions as a function of p , as compared with the assumption of the validity of percolation scaling. The sharp cross-over at $p = 0.8$ is an artifact of the need to choose the effective-medium result (Eq. (2.20)) for $p > 0.8$ and percolation scaling (Eq. (2.11)) for $p < 0.8$. In actuality we expect a smoother cross-over



2.6 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. 5 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 [1, 12, 31] 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 [28]. While the latter has an advantage in that it can be used to identify a percolation transition [28], 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 critical path analysis 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 critical path analysis can be formulated to be exact in both limits).

The gist of critical path analysis is that it defines that interconnected network of conductances which has the largest possible value of the smallest, or bottleneck,

conductance. This value, called the critical conductance, 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 critical path analysis 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 critical path analysis in different systems. Important differences do exist in applying critical path analysis in different dimensions.

2.6.1 Relation of Critical Path Analysis to Extreme Value Statistics in 1D Systems

Consider first the case of one-dimensional systems. In infinite one-dimensional 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 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, because the resistance of any bond is some 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, $W(R)$, 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, critical path analysis 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 critical path analysis 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 one-dimensional systems, the problem is more interesting. Again, since in 1D we have $p_c = 1$, 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 non-zero minimum conductance value, however, the typical resistance of a system of length x is proportional to x , and the system conductivity is non-zero 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 one-dimensional 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 $a \ll b$ 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 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 :

$$\frac{b}{x} \propto \int_{r_{\max}}^{\infty} \frac{dr}{b} \exp\left[\frac{-r}{b}\right] \quad (2.23)$$

Solution of this integration for r_{\max} in terms of x gives

$$r_{\max} \propto b \ln\left(\frac{x}{b}\right) \quad (2.24)$$

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

$$R_{\max} \propto R_0 \left[\frac{x}{b}\right]^{\frac{2b}{a}} \quad (2.25)$$

with the result that

$$\sigma(x) \propto x^{1-2b/a} \quad (2.26)$$

Because $b \gg a$, Eq. (2.26) leads to a conductivity which is a negative power of the system length and which vanishes in the limit of an infinite chain [6, 16, 17]. 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 one-dimensional systems, because of the fact that $p_c = 1$. Thus one-dimensional systems make a very poor starting point for understanding percolation behavior generally. In the next chapter we will also see (for different reasons) that two-dimensional systems make very poor models of 3d porous media.

2.6.2 Critical Path Analysis in 2D

Now we apply critical path analysis to an idealized conductance distribution on a two-dimensional lattice. An attractive aspect of 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 : $R = \rho l/A$. 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 [40] 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), denoted $W(g)$, for finding a conductance between two arbitrary nearest neighbor sites with value between g and $g + dg$. Normalization of this pdf requires,

$$\int_0^\infty W(g)dg = 1 \quad (2.27)$$

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 for the square lattice we know that $p_c = 0.5$. 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 . That is, the value of g_c is found from

$$\int_{g_c}^\infty W(g)dg = p_c = 0.5 \quad (2.28)$$

For an infinite square lattice, placement of 1/2 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

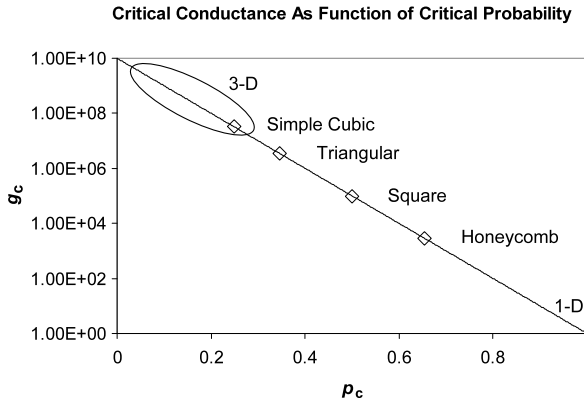


Fig. 2.2 For a log-uniform distribution of conductances the critical (percolating) rate-limiting conductance, g_c , as a function of the critical percolation probability, p_c . Note the rapid diminution of p_c and increase of g_c with increasing dimensionality. Further, if the geometric mean of the distribution 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

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 sub-regions 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.

These results do not apply for all two-dimensional 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 2/3 of the connections. If the same conductances are placed on a honeycomb lattice, with $Z = 3$, the dominant conductance is $g_c = 10^{3.45}$, because $p_c = 0.655$ and the current avoids only the slowest 1/3 of the connections. Thus in our example, the values of the rate limiting conductances and associated conductivities extend over more than three orders of magnitude in the simplest two dimensional lattices (2D)! In Fig. 2.2 we represent these results pictorially, indicating also the range 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. 2.2 also be interpreted as the conductivity.

2.6.3 Critical Path Analysis in 3D

In three dimensions 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 exis-

tence 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 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 three-dimensional lattice 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.

2.6.4 Dimensional Dependence and Similarity to Matheron Conjecture

In Fig. 2.2 the dimensional dependence of g_c for the proposed log-uniform distribution of conductance values is clear and strong. In two-dimensional 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 one dimensional 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 [26]. 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 critical path analysis to a completely different formulation for upscaling K in heterogeneous media. Assume that the logarithm of the hydraulic conductivity is normally distributed,

$$W(K) \propto \exp \left\{ - \left[\frac{(\log(K) - \log(K_0))^2}{2 \text{Var}(\log(K))} \right] \right\} \quad (2.29)$$

where $\text{Var}[\log(K)]$ is the variance of the distribution of $\log[K]$. Then the lowest order approximation to the hydraulic (or electrical) conductivity is [9]

$$K = K_{\text{gm}} \exp \left[\left(\frac{1}{2} - \frac{1}{d} \right) \text{Var}(\log(K)) \right] = K_0 \exp \left[\left(\frac{1}{2} - \frac{1}{d} \right) \text{Var}(\log(K)) \right] \quad (2.30)$$

where K_{gm} , the geometric mean of K , is here equal to K_0 , the most likely value of K . In fact, De Wit [9] explains that Eq. (2.30) is essentially a perturbation expansion in the (small parameter) $\text{Var}(\log(K))$. Equation (2.30) 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. 2.2. Since all methods generate the hydraulic conductivity in 1-dimensional 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. (2.30) suggests that the conductivity is independent of the properties of the connectivity of the medium as long as $\log(K)$ is a normally distributed random field. It is known, however, that the connectivity of such fields plays an important role in the upscaling [3, 23, 34, 41]. As can be seen from critical path analysis, 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 as well. Thus increasing the local connectivity reduces p_c and increases K . Further, Eq. (2.30) 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. (2.30) is not complete: it is believed that Eq. (2.30) represents only the first term in a series [9] of terms proportional to powers of the variance of $\log(K)$. Thus the validity of Eq. (2.30) is subject to an important condition on the magnitude of $\text{Var}(\log(K))$, 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 $\text{Var}(\log(K))$.

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

The idea of critical path analysis is actually not best expressed as an upscaling of the conductivity. In particular, in critical path analysis, 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,

$$F(R) \equiv \int_0^R W(R') dR' = p \quad (2.31)$$

Then,

$$F(R_c) = \int_0^{R_c} W(R') dR' = p_c \quad (2.32)$$

Equations (2.31) and (2.32) can be solved in parallel for $p - p_c$. Define a conductance $g \equiv R^{-1}$ and 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 three dimensional network, on which a fraction, p , of bonds with the smallest R values possible, is placed at random,

$$\sigma = \frac{l[F(g^{-1}) - F(g_c^{-1})]^{2\nu}}{\chi_0^2} g \quad (2.33)$$

In Eq. (2.33) the factor $[F(g^{-1}) - F(g_c^{-1})]^{2\nu}$ arises from the square of the correlation length in the denominator. Equation (2.33) is, for heterogeneous systems, again equivalent to the result in elementary physics texts 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. In Eq. (2.33) $\chi_0^2[F(g^{-1}) - F(g_c^{-1})]^{-2\nu}$ 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 $e = 2.718$, then one could write for l ,

$$l \approx \chi_0 \left\{ \frac{\int_0^R W(R) dR}{\int_{-R/e^{1/2}}^{e^{1/2}R} W(R) dR} \right\}^{-\frac{1}{3}} \quad (2.34)$$

in three dimensions. Equation (2.34) actually has a very simple basis. 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. (2.33) is thus only a very slowly varying function of p , and not a function of $p - p_c$ at all. For

this reason optimization of Eq. (2.33) is not complicated by consideration of l . Result Eq. (2.33), however, is not generally agreed on. Several authors identify l with the correlation length $\chi = \chi_0[F(g^{-1}) - F(g_c^{-1})]^{-\nu}$, 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, including an important contribution from a soil physicist [37].

If in Eqs. (2.31) and (2.32) 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 $F(R) - F(R_c) \propto \ln(R/R_c) = \ln(g_c/g)$, but if R is a power of, e.g., a tube radius (for hydraulic conduction), then $F(R) - F(R_c) \propto (R - R_c)$ or $g - g_c$ (see the assigned problems). Using Eq. (2.34) for l and optimizing Eq. (2.33) leads, in the first case, to [12]

$$\frac{d\sigma}{dg} = \frac{d}{dg} \left[\frac{l[F(g^{-1}) - F(g_c^{-1})]^{2\nu}}{\chi_0^2} g \right] = \left[\ln\left(\frac{g_c}{g}\right) \right]^{2\nu} - 2\nu \left[\ln\left(\frac{g_c}{g}\right) \right]^{2\nu-1} = 0 \quad (2.35)$$

Solution of Eq. (2.35) yields $\ln(g_c/g) = 2\nu$, 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. (2.33). 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 two-dimensional 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 [40], and our own simulations agree [18]. Specific results from critical path analysis will be discussed in Chap. 5 and elsewhere.

Note, however, that in many cases it may be possible to apply critical path analysis 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. Predominantly 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 one-dimensional 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.

2.7 Summary

In predicting transport properties of porous media it is necessary to be able to distinguish the roles of the medium and the fluids within the medium. Likewise, it is essential to be able to calculate inputs from both geometry (e.g., pore size distributions) and topology (specifically fluid connectivity within the pore space). In the framework of this book we can make the following generalizations:

- (1) Values of the effective hydraulic conductivity K are strongly affected by the local resistance distribution (obtained at the pore-scale from the pore-size distribution), both at complete saturation, and as a function of saturation.
- (2) All other conduction parameters are dominated by fluid connectivity issues, leading to the relevance of universal scaling of percolation for saturation dependences.
- (3) When conductance distributions are important, i.e., for K , its effective value is best calculated in critical path analysis. Beyond its aesthetic appeal and greater accuracy of prediction, critical path analysis has the additional advantage of providing a physical interpretation for the “irreducible” moisture content, being mathematically consistent with scaling approaches, and thus allowing parameters to have consistent values across different properties, whether pore-size dominated, or fluid-connectivity dominated.

Problems

- 2.1 Provide the details of the derivation of Eq. (2.18) and Eq. (2.20) 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} .

References

1. Ambegaokar, V.N., Halperin, B.I., Langer, J.S.: Hopping conductivity in disordered systems. *Phys. Rev. B* **4**, 2612–2621 (1971)
2. ben-Avraham, D., Havlin, S.: *Diffusion and Reactions in Fractals and Disordered Systems*. Cambridge University Press, New York (2000)
3. Batchelor, G.K.: Transport properties of two-phase materials with stochastic structure. *Annu. Rev. Fluid Mech.* **6**, 227–255 (1974). doi:[10.1146/annurev.fl.06.010174.001303](https://doi.org/10.1146/annurev.fl.06.010174.001303)
4. Berkowitz, B., Balberg, I.: Percolation approach to the problem of hydraulic conductivity in porous media. *Transp. Porous Media* **9**, 275–286 (1992)
5. Berkowitz, B., Balberg, I.: Percolation theory and its application to groundwater hydrology. *Water Resour. Res.* **29**, 775–794 (1993)
6. Bernasconi, J., Schneider, W.R.: Classical hopping conduction in random one-dimensional systems—non-universal limit-theorems and quasi-localization effects. *Phys. Rev. Lett.* **47**, 1643–1647 (1981)
7. Clerc, J.P., Podolskiy, V.A., Sarychev, A.K.: Precise determination of the conductivity exponent of 3D percolation using exact numerical renormalization. *Eur. Phys. J. B* **15**, 507–516 (2000)
8. Derrida, B., Vannimenus, J.: A transfer matrix approach to random resistor networks. *J. Phys. A, Math. Gen.* **13**, L557–L564 (1982)
9. De Wit, A.: Correlation structure dependence of the effective permeability of heterogeneous porous media. *Phys. Fluids* **7**(11), 2553–2662 (1995)
10. Feng, S., Halperin, B.I., Sen, P.N.: Transport properties of continuum systems near the percolation threshold. *Phys. Rev. B* **35**, 197 (1987)
11. Fisher, M.E.: The theory of critical point singularities. In: Green, M.S. (ed.) *Critical Phenomena*, Proc. 1970 Enrico Fermi Internat. Sch. Phys., Course No. 51, Varenna, Italy, pp. 1–99. Academic Press, New York (1971)
12. Friedman, L., Pollak, M.: The Hall effect in the variable-range hopping system. *Philos. Mag. B* **44**, 487–507 (1981)
13. Gingold, D.B., Lobb, C.J.: Percolative conduction in three dimensions. *Phys. Rev. B* **42**(13), 8220–8224 (1990)
14. Grassberger, P.: Conductivity exponent and backbone dimension in 2-d percolation. *Physica A* **262**, 251–263 (1999)
15. Herrmann, H.J., Stanley, H.E.: The fractal dimension of the minimum path in two-dimensional and three-dimensional percolation. *J. Phys. A* **21**, L829–L833 (1988)

16. Hunt, A.: One-dimensional hopping conductivity calculations. *Philos. Mag. B* **64**, 327–334 (1991)
17. Hunt, A.: A general treatment of 1-dimensional hopping conduction. *Solid State Commun.* **86**, 765–768 (1993)
18. Hunt, A.G.: Applications of percolation theory to porous media with distributed local conductances. *Adv. Water Resour.* **24**(3,4), 279–307 (2001)
19. Jerauld, G.R., Hatfield, J.C., Scriven, L.E., Davis, H.T.: Percolation and conduction on Voronoi and triangular networks: a case study in topological disorder. *J. Phys. C* **17**, 1519–1529 (1984)
20. Keffer, D., McCormick, A.V., Davis, H.T.: Diffusion and percolation on zeolite sorption lattices. *J. Phys. Chem. US* **100**, 967–973 (1996)
21. Kirkpatrick, S.: *Phys. Rev. Lett.* **27**, 1722 (1971)
22. Kirkpatrick, S.: Percolation and conduction. *Rev. Mod. Phys.* **45**, 574–588 (1973)
23. Knudby, C., Carrera, J., Bumgardner, J.D., Fogg, G.E.: Binary upscaling—the role of connectivity and a new formula. *Adv. Water Resour.* **29**, 590–604 (2006)
24. Lee, Y., Andrade, J.S., Buldyrev, S.V., Dokholoyan, N.V., Havlin, S., King, P.R., Paul, G., Stanley, H.E.: Traveling time and traveling length in critical percolation clusters. *Phys. Rev. E* **60**(3), 3425–3428 (1999)
25. Mandelbrot, B.B.: *The Fractal Geometry of Nature*. Freeman, San Francisco (1983), 468 pp.
26. Matheron, G.: *Éléments Pour Une Théorie des Milieux Poreux*. Masson et Cie, Paris (1967)
27. Moldrup, P., Olesen, T., Komatsu, T., Schjoning, P., Rolston, D.E.: Tortuosity, diffusivity, and permeability in the soil liquid and gaseous phases. *Soil Sci. Soc. Am. J.* **65**, 613–623 (2001)
28. Neuweiler, I., Vogel, H.-J.: Upscaling for unsaturated flow for non-Gaussian heterogeneous porous media. *Water Resour. Res.* **43**, W03443 (2007)
29. Normand, J.-M., Herrmann, H.J.: Precise numerical determination of the superconducting exponent of percolation in three dimensions. *Int. J. Mod. Phys. C* **1**, 207–214 (1990)
30. Pike, R., Stanley, H.E.: Order propagation near the percolation threshold. *J. Phys. A* **14**, L169–L177 (1981)
31. Pollak, M.: A percolation treatment of dc hopping conduction. *J. Non-Cryst. Solids* **11**, 1–24 (1972). doi:[10.1016/0022-3093\(72\)90304-3](https://doi.org/10.1016/0022-3093(72)90304-3)
32. Sahimi, M.: Flow phenomena in rocks—from continuum models to fractals, percolation, cellular automata, and simulated annealing. *Rev. Mod. Phys.* **65**(4), 1393–1534 (1993)
33. Sahimi, M., Hughes, B.D., Scriven, L.E., Davis, H.T.: Real-space renormalization and effective-medium approximation to the percolation conduction problem. *Phys. Rev. B* **28**, 307–311 (1983)
34. Sanchez-Villa, X., Carrera, J., Girardi, J.P.: Scale effects in transmissivity. *J. Hydrol.* **183**, 1–22 (1996)
35. Sen, P.N., Roberts, J.N., Halperin, B.I.: Non-universal critical exponents for transport in percolating systems with a distribution of bond strengths. *Phys. Rev. B* **32**, 3306–3308 (1985)
36. Sheppard, A.P., Knackstedt, M.A., Pinczewski, W.V., Sahimi, M.: Invasion percolation: new algorithms and universality classes. *J. Phys. A, Math. Gen.* **32**, L521–L529 (1999)
37. Skaggs, T.H.: Effects of finite system size and finite heterogeneity on the conductivity of broadly distributed resistor networks. *Physica B* **338**, 266–269 (2003)
38. Skal, A.S., Shklovskii, B.I.: Topology of an infinite cluster in the theory of percolation and its relationship to the theory of hopping conduction. *Sov. Phys. Semicond.* **8**, 1029–1032 (1975)
39. Stauffer, D.: Scaling theory of percolation clusters. *Phys. Rep.* **54**, 1–74 (1979)
40. Stauffer, D., Aharony, A.: *Introduction to Percolation Theory*, 2nd edn. Taylor and Francis, London (1994)
41. Torquato, S.: *Random Heterogeneous Materials*. Springer, Berlin (2002)

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