oriented chemical engineer. New applications of percolation are still being developed, and in the coming years such applications will find widespread use in many branches of science and technology.

Over the past decade Dietrich Stauffer has greatly contributed to my understanding of percolation theory, disordered systems, and critical phenomena. He has done this through his "referee's reports", e-mail messages, letters, and our collaborations on various problems. Without his constant encouragement and support this book would not have been written. He also read most of the book and offered constructive criticism and very useful suggestions. I am deeply grateful to him. I would also like to thank Ted Davis and Skip Scriven who introduced me to percolation, and Barry Hughes for his many stimulating discussions and fruitful collaboration. Many other people have contributed to my understanding of percolation theory, a list of whom is too long to be given here. I would like to thank all of them.

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Muhammad Sahimi
Los Angeles,
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1
Connectivity as the essential physics of disordered systems

1.0 Introduction

It is a fact of life, which is as challenging to the mind of the scientist as it is frustrating to his or her aspirations, that *nature is disordered*. In nowhere but the theoretician's supermarket can we buy clean, pure, perfectly characterized and geometrically immaculate systems. An engineer works in a world of composites and mixtures (how much more so the biologist). Even the experimentalist who focusses on the purest of subtances, exemplified by carefully grown crystals, can seldom escape the effects of defects, trace impurities, and finite boundaries. There are few concepts in science more elegant to contemplate than an infinite, perfectly periodic crystal lattice, and few systems as remote from experimental reality. We are therefore obliged to come to terms with *disordered structures*; variation in shape and constitution often so ill-characterized that we must deem it to be random if we are to describe it – apparent randomness in the morphology of the system. The morphology of a system has two major aspects: *topology*, the interconnectiveness of individual microscopic elements of the system; and *geometry*, the shape and size of these individual elements.

As if this were not bad news enough, we know that however random the stage upon which the drama of nature is played out, it is also at times very difficult to follow the script. We believe, at least above the quantum mechanical level, in the doctrine of determinism, yet important *continuum* systems exist in which deterministic descriptions are beyond hope. Typical examples are diffusion and Brownian motion where, over certain length scales, we observe an apparent random process, or *disordered dynamics*.

Nature, then, is disordered both in her structure and the processes she supports. Indeed the two types of disorder are often concurrent and

coupled. An example, dear to the heart of the author, is fluid flow through a porous medium where the interplay between the disordered structure of the pore space and the dynamics of fluid motion gives rise to a rich variety of phenomena, some of which will be discussed in this book.

Despite the rather obvious randomness in nature, these topics were, for several decades, familiar to most physicists, engineers, and others only in the form of statistical mechanics, or in the application of such equations as the Boltzmann equation. Research in these fields made remarkable progress by taking advantage of periodic structures. However, as one always has to confront the real world, it became apparent that a statistical physics of disordered systems must be devised to provide methods for deriving macroscopic properties of such systems from laws governing the microscopic world, or alternatively for deducing microscopic properties of such systems from the macroscopic information that can be observed by experimental techniques. Such a statistical physics of disordered systems should take into account the effect of *both* morphology and geometry of the systems. While the role of geometry was already appreciated in the early years of this century, the effect of topology was ignored for many decades, or was treated in an unrealistic manner, simply because it was thought to be too difficult to be taken into account.

A study of the history of science also shows that progress in any research field is not usually made with a constant rate, but rather in a sporadic manner. There are periods when a problem looks so difficult that we do not even know where to start, and periods when some epoch-making discoveries or inventions remove an obstacle to progress and thus enable a great advance. An example is the discovery of a new class of superconducting materials in 1986. Bednorz and Muller (1986) showed that it is possible to have superconductivity in (La, Ba)CuO alloys at temperatures $T_c > 30$K. Subsequently it was shown by Tagaki *et al.* (1987) that the phase $La_{2-x}Ba_xCuO_4$ with $x \sim 0.15$ is responsible for bulk superconductivity with $T_c \sim 35$K. Since then hundreds, and perhaps thousands, of research papers have been written on the subject of high-temperature superconductivity, and the literature on the subject has become very forbidding. The discovery had such an impact on the subject that Bednorz and Muller were honoured with a Noble Prize in physics in 1989. Over the past two decades, statistical physics of disordered systems has been in this rapidly moving stage of progress, partly because standard methods for calculating the average properties of disordered systems have been established from the theoretical side, and also more and more experimental results have been accumulated thanks to many novel experimental techniques. But perhaps the most important reason for the rapid development of the statistical physics of disordered systems is that the role of interconnectivity of the microscopic elements of a disordered system and its effect on the macroscopic properties of the system has been appreciated. This has been possible through the development and application of percolation theory, the subject of this book.

However, this is an applications oriented book written by a chemical engineer, not a book on mathematical or computational methods of a theoretical physicist. As such, the book is necessarily biased.

1.1 What is percolation?

When I was a graduate student, I was living in Minneapolis, Minnesota, and attending the University of Minnesota. Minneapolis is a wonderful city of many lakes and naturally I tried to live near a lake to enjoy the beautiful summer, and to watch little kids skate on the lake during the long winter. The magnificent Mississippi river runs through Minneapolis, dividing the campus of the university into east and west bank sections, and the chemical engineering department where I was a graduate student was on the east bank. I was living in southeast Minneapolis near Lake Calhoun, about eight miles from the campus. Every winter we had many snow storms that would cause temporary closure of many streets in one or both directions for sweeping the snow. Even during the long summer some streets would be closed for repairing the damage caused by the long winter. There are many other types of defects or disorder in the structure of the streets of Minneapolis. There is a big K-Mart store that blocks Nicolete Avenue, one of the most important routes in the city that starts in the downtown area and ends in the suburb in the south. Many railways also cut the streets, and many lakes have created natural blockage for many streets. It often seemed as if the streets were closed at random! Now suppose that we idealize the streets of Minneapolis as the bonds of a very large square network, and block at random some of the streets by a heavy snow, a rail track, a lake, or a store like K-Mart (see Fig. 1.1). As a PhD student of two of the most

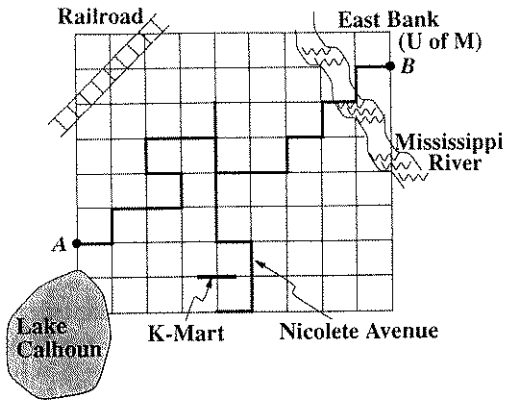

Figure 1.1 *Idealization of streets of Minneapolis.*

accomplished and famous chemical engineering professors in the country in one of the top-ranked departments, I was expected to work on my research topics six days a week, from Monday through Saturday, and many Sundays. I would leave my apartment to go to the department and wonder what fraction of streets of Minneapolis would have to be open to traffic in order for me to reach the department from my apartment. Obviously, if too many streets were closed, I could not reach the department, and therefore would not get anything done. On the other hand, if most streets were open, almost any route would take me to the department. Therefore, there must be a critical value of the fraction of open streets below which I would never reach the department, but above which I could always get to work.

Let us consider another example. Suppose that, instead of representing the streets of Minneapolis, the bonds of the square network of Fig. 1.1 represent resistors. We assign a unit resistance to the open bonds, and an infinite resistance to the closed ones (i.e., the closed bonds are insulators). Suppose also that we impose a unit voltage at point A in Fig. 1.1, and a zero voltage at B. What fraction of the bonds have to have a finite resistance in order for electrical current to flow from A to B? This is an important question because its answer tells us what (volume) fraction of a disordered material, such as carbon black composites that are routinely used in many applications, has to be conducting in order for the composite as a whole to be conducting. The reader can probably see the similarity between the flow of current in the composite and traffic flow in the streets of Minneapolis. As in the first example, if too many bonds are insulating, no macroscopic current will flow from A to B, whereas for a sufficiently large number of resistors one can have electrical current between the two points.

Consider a third example. Imagine that the bonds of the network of Fig. 1.1 are pores of a porous medium, e.g., an underground oil reservoir. In reality, no porous medium looks as regular as the square network, but as an idealization this network serves a useful purpose. Now suppose that the pores are filled with oil, and that there are two wells in the system, one at A and the other at B. We would like to push oil out of this porous medium by injecting water into the system at A (the injection well) and producing oil at B (the production well). Oil and water do not mix with each other, and therefore we assume that each pore is filled with either oil or water. As the water is injected and pushed into the reservoir, it tries to find the *smallest pores* that it can reach and expel the oil from it (why this is so is explained in Chapter 7). In reality, the process is more complex than this, but we ignore all the complications. The expelled oil is produced at well B. What fraction of the pores are filled with water when it reaches the production well at B for the first time (this is called *breakthrough point*)? In other words, we would like to know what fraction of the pores lose their oil, and how much oil is produced at well B at the breakthrough point. This is obviously an important question. In the early 1980s when the price of oil was as high as $40/barrel and the United States suffered a traumatic energy

crisis, intense research was done to answer this and related questions. Even with the relatively cheap oil currently available, intense research is still going on.

Questions such as these are answered by percolation theory. Percolation tells us when a system is *macroscopically* open to a given phenomenon. For example, it can tell us when one can have flow of traffic from one side of a town to its opposite, when electrical current can flow from one side of a composite to the opposite, and how much oil one can extract from an oil reservoir. The point at which the percolation transition between an open system and a closed one takes place for the first time is the *percolation threshold* of the system, and the behavior of the system close to this point is of prime interest and importance. Because a percolation network is created by simply blocking bonds at random, percolation is also useful as a simple model of disordered systems. Moreover, since the main concepts of percolation theory are very simple, writing a computer program for simulating a percolation process is straightforward, and so percolation can also serve as a simple tool for introducing students to computer simulations. Deutscher *et al.* (1983), Bunde and Havlin (1991), Stauffer and Aharony (1992), and Hughes (1993) have emphasized the foundations of percolation theory. This book attempts to summarize some important applications of percolation.

1.2 The scope of the book

Over the past two decades percolation has been applied to modeling a wide variety of phenomena in disordered systems. It is impossible to discuss all such applications in one book. In selecting those applications that are discussed in this book, three criteria were used.

(i) The application is quantitative, in the sense that there is a quantitative agreement between the predictions of percolation and experimental data.
(ii) The problem is of broad interest, or has broad industrial, technological, or scientific importance.
(iii) This author has a clear understanding of the problem and how the application of percolation is made.

Based on these criteria, I selected twelve classes of problems to which percolation has been applied. In discussing each case, it is assumed that the reader already knows the essence of the problem. Stauffer and Aharony (1992) provide an excellent and simple introduction to the percolation concepts. Therefore, Chapter 2 contains only a summary of the main properties that will be used in the rest of this book. Every effort is made to explain the percolation approach in simple terms. In all cases, the predictions are compared with the experimental data to establish the relevance of

percolation concepts and their application to the problem. We also give what we believe are the most relevant references to each subject, or provide the reference to a recent review on the subject.

We finish this chapter by mentioning a few other applications of percolation which, although they do not meet at least one of the above three criteria, represent important and useful applications of percolation theory. The literature cited below and in the subsequent chapters is not necessarily the first or the best work on the subject. It represents what was known to me at the time of writing this book, or what I considered to be the most relevant.

1.3 Applications of percolation that are not discussed in this book

Now that we know what kind of applications of percolation are discussed in this book, let us mention a few other important applications and references to them that will not be discussed here.

1.3.1 Percolation model of galactic structures

It has been shown that the process of star formation may be a percolation process, and that the percolation transition from a disconnected to a connected state plays an important role in the stabilization and control of star formation. For example, for galaxies whose formation can be described by a percolation process, the main feature, namely, the presence of spiral arms, is a consequence of the proximity to the percolation transition. The interested reader should consult Seiden and Schulman (1990) for a review of this interesting application of percolation.

1.3.2 Multicomponent percolation

In all cases that are discussed in this book, the percolation system is essentially a binary mixture of two components. For example, in the above examples one has a two component mixture of open and closed streets, resistors and insulators, and pores filled with oil and water. However, there are many cases in which the system may consist of three or more components. For example, charge transfer salts are random mixtures of a metal M_1 with another metal or element M_2 in which M_1 and M_2 react and produce $M_1^+M_2^-$, if M_1 and M_2 are in close proximity. The reaction is reversible, and can reproduce M_1 and M_2 again. Examples are $Cs_{1-x}Te_x$, $Cs_{1-x}Sb_x$, $Na_{1-x}Sn_x$, and many others. One is interested in the conductivity of this system, which can be treated by a three-component (M_1, M_2, and $M_1^+M_2^-$) percolation model. This and many other applications of multicomponent percolation are discussed by Halley (1983).

1.3.3 Glass transition

It may not be obvious to the reader how the transition between a liquid and glassy state may have anything to do with percolation, since percolation in its fundamental form is a static process, whereas the liquid–glass transition is the result of the system moving away from complete metastable equilibrium. However, it has been shown that percolation can help us understand certain aspects of liquid–glass transition, although this application of percolation remains controversial. Earlier reviews were given by Grest and Cohen (1983) and Zallen (1983). For the most recent reference on the subject see Wittmann *et al.* (1992).

1.3.4 The behavior of supercooled water

A snapshot of liquid water shows that this system, which is a hydrogen-bonded liquid, has the structure of a network above its percolation threshold. However, the network is well above its percolation threshold, and therefore the classic random percolation discussed in the above examples is not applicable to this problem. Instead, a correlated percolation model has been found to explain many unusual properties of supercooled water. For the most recent references on the subject see Stanley *et al.* (1983), Blumberg *et al.* (1984), and Sciortino *et al.* (1990).

1.3.5 Dynamic percolation

In the classical percolation problem the configuration of the system does not change with time. That is, the probability that a bond is open or closed is independent of time. In many situations this description of a disordered system is inadequate since the configuration of the system changes with time. For example, in polymeric ionic conductors above the glass transition temperature, the electrical conductivity is dominated by microscopic motion of the medium. Another example is the problem of oxygen binding to haemoglobin and myoglobin. It is known that the entrance to the haeme pocket is blocked by a number of side chains and thus oxygen could not bind if the side chains were fixed at their equilibrium positions. Because of the dynamic nature of proteins one may expect that a gate would fluctuate between open and closed positions. Thus one has to deal with a diffusion process in a disordered medium whose structure varies with time.

To deal with such problems, various dynamic percolation models in which the probability that a bond or site of a network is open varies with time have been proposed by Druger *et al.* (1985), Harrison and Zwanzig (1985), Sahimi (1986), and Bunde *et al.* (1991); see also Granek and Nitzan (1989, 1990), and Loring (1991). Another type of dynamic percolation was developed by Bunde and coworkers for solid ionic conductors; see Bunde

et al. (1986a, b), Harder *et al.* (1986), and Roman *et al.* (1986). Finally, quite different dynamic percolation models have been suggested for gelation phenomena, and microemulsion systems. They are discussed in Chapters 11 and 12.

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2
Elements of percolation theory

2.0 Introduction

Percolation processes were first developed by Flory (1941) and Stockmayer (1943) to describe how small branching molecules react and form very large macromolecules. This polymerization process may lead to *gelation*, i.e., to the formation of a very large network of molecules connected by chemical bonds, the key concept of percolation theory. However, Flory and Stockmayer developed their theory of gelation for a special kind of network, namely, the Bethe lattice, an endlessly branching structure without any closed loops (see Fig. 2.1). We return to the Flory–Stockmayer theory in Chapter 11.

In the mathematical literature, percolation was introduced by Broadbent and Hammersley (1957). They originally dealt with the concept of the spread of hypothetical fluid particles through a random medium. The terms fluid and medium were viewed as totally general: a fluid can be liquid, vapor, heat flux, electric current, infection, a solar system, and so on. The medium – where the fluid is carried – can be the pore space of rock, an array of trees, or the universe. Generally speaking, the spread of a fluid through a disordered medium involves some random elements, but the underlying mechanism(s) for this might be one of two very different types. In one type, the randomness is ascribed to the *fluid*: the fluid particles decide where to go in the medium. This is the familiar *diffusion process*. In the other type, the randomness is ascribed to the *medium*: the medium dictates the paths of the particles. This was the new situation that was considered by Broadbent and Hammersley (1957). Hence it also demanded its own terminology. It was decided to name it a *percolation process*, since it was thought that the spread of the fluid through the random medium resembled the flow of coffee in a percolator.

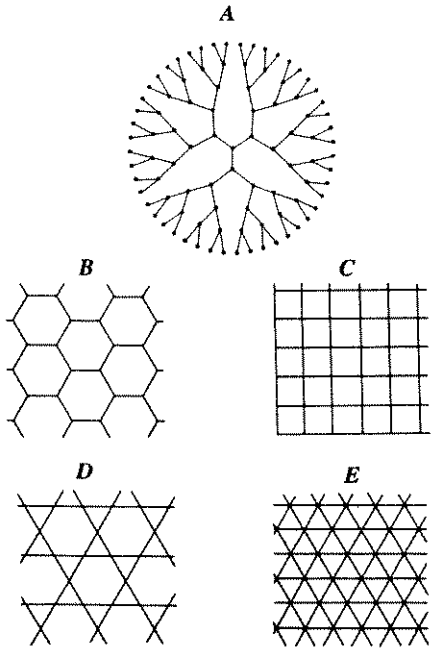

Figure 2.1 *Some regular lattices. (A) The Bethe lattice (Z = 3). (B) The honeycomb lattice (Z = 3). (C) The square lattice (Z = 4). (D) Kagomé lattice (Z = 4). (E) The triangular lattice (Z = 6).*

2.1 Definitions and percolation thresholds

We first discuss percolation processes on regular networks, and then discuss them for random networks and continua. The classical percolation theory centers around two problems. In the *bond percolation problem*, the bonds of the network are either *occupied* (i.e., they are open to flow, diffusion and reaction, they are microscopic conducting elements of a composite, etc.), randomly and independently of each other with probability p, or are *vacant* (i.e., they are closed to flow or current, or have been plugged, they are insulating elements of a composite, etc.) with probability $1 - p$. For a large network, this assignment is equivalent to removing a fraction $1 - p$ of all bonds at random. Two sites are called *connected* if there exists at least one path between them consisting solely of occupied bonds. A set of connected sites bounded by vacant bonds is called a *cluster*. If the network is of very large extent and if p is sufficiently small, the size of any connected cluster is small. But if p is close to 1, the network should be entirely connected, apart from occasional small holes. At some well-defined value of p, there is

a transition in the topological structure of the random network from a macroscopically disconnected structure to a connected one; this value is called the *bond percolation threshold*, p_{cb}. This is the *largest* fraction of occupied bonds below which there is no sample-spanning cluster of occupied bonds.

Similarly, in the *site percolation problem* sites of the network are occupied with probability p and vacant with probability $1 - p$. Two nearest-neighbor sites are called connected if they are both occupied, and connected clusters on the network are again defined in the obvious way. There is a site percolation threshold p_{cs} above which an infinite (sample-spanning) cluster of occupied sites spans the network. We should point out that, depending on a specific application, many variants of bond or site percolation have been developed, some of which will be discussed in this book.

The derivation of the exact values of p_{cb} and p_{cs} has been possible to date only for certain lattices related to the Bethe lattice and for a few two-dimensional lattices. The percolation thresholds of three-dimensional networks have been calculated numerically by Monte Carlo simulations or other techniques. For the Bethe lattice it can be shown that (Fisher and Essam 1961)

$$p_{cb} = p_{cs} = \frac{1}{Z - 1}, \tag{2.1}$$

where Z is the coordination number of the lattice, i.e., the number of bonds connected to the same site. Figure 2.1 shows some regular two-dimensional lattices. We compile the current estimates of p_{cb} and p_{cs} for common two- and three-dimensional lattices in Tables 2.1 and 2.2 respectively. In general, $p_{cb} \leqslant p_{cs}$. These tables show that the product $B_c = Zp_{cb}$ is essentially an invariant of percolation networks. For a d-dimensional system, $B_c \simeq d/(d-1)$. The significance of B_c is discussed below.

Table 2.1 *Currently accepted values of the percolation thresholds of some two-dimensional networks*

Network	Z	p_{cb}	$B_c = Zp_{cb}$	p_{cs}
Honeycomb	3	$1 - 2\sin(\pi/18) \simeq 0.6527$*	1.96	0.6962
Square	4	1/2*	2	0.5927
Kagomé	4	0.522	2.088	0.652
Triangular	6	$2\sin(\pi/18) \simeq 0.3473$*	2.084	1/2*

*Exact result.

Table 2.2 *Currently accepted values of the percolation thresholds of some three-dimensional networks*

Network	Z	p_{cb}	$B_c = Zp_{cb}$	p_{cs}
Diamond	4	0.3886	1.55	0.4299
Simple cubic	6	0.2488	1.49	0.3116
BCC	8	0.1795	1.44	0.2464
FCC	12	0.198	1.43	0.119

2.2 Computer generation of percolation clusters

Generating a percolating lattice by randomly removing sites or bonds, although easy, is often not suitable for practical applications because, in addition to the sample-spanning cluster, this method also generates isolated finite clusters. In most applications one works only with the sample-spanning cluster (or the process of interest starts with a single cluster), and therefore we must first delete all isolated clusters from the system, which is time-consuming. Alternatively, we can use a method, developed by Leath (1976) and Alexandrowicz (1980), that generates only the sample-spanning (or the largest) cluster. In this method one starts with a single occupied site at the center of the lattice, identifies its nearest-neighbor sites and considers them occupied and adds them to the cluster if random numbers $0 < r < 1$, attributed to the neighbors, are less than the fixed value p. The perimeter sites, the nearest-neighbor empty sites of the occupied sites, are found and the process of occupying such sites continues in the same manner. If a selected perimeter site is not occupied, then it remains unoccupied forever. The generalization of this method for generating a cluster of occupied bonds is obvious.

An important task in computer simulations of percolating systems is to count the number of clusters of a given size, or the fraction of occupied sites or bonds that belong to the sample-spanning cluster. For example, during displacement of a fluid A by another immiscible fluid B in a porous medium we may need to know the number of islands or blobs of fluid A of a given size that are completely surrounded by B, which is equivalent to knowing the number of clusters of a given size within the context of a percolation model of fluid displacement in a porous medium (see Chapter 7). An efficient algorithm for doing this was developed by Hoshen and Kopelman (1976). A computer program implementing their method is given by Stauffer and Aharony (1992).

2.3 Percolation quantities

In addition to the percolation thresholds, the topological properties of percolation networks are characterized by several important quantities.

(i) *Percolation probability* $P(p)$. This is the probability that, when the fraction of occupied bonds is p, a given site belongs to the infinite (sample-spanning) cluster of occupied bonds.

(ii) *Accessible fraction* $X^A(p)$. This is that fraction of occupied bonds belonging to the infinite cluster.

(iii) *Backbone fraction* $X^B(p)$. This is the fraction of occupied bonds in the infinite cluster which actually carry flow or current, since some of the bonds in the cluster are dead-end and do not carry any flow. The backbone of a percolating system plays a fundamental role in its transport properties, because the tortuosity of the transport paths is

controlled by the structure of the backbone. We shall discuss the structure of the backbone shortly.

(iv) *Correlation length* $\xi_p(p)$. This is the typical radius of the connected clusters for $p < p_c$, and the length scale over which the random network is macroscopically homogeneous (i.e., the length scale over which the properties of the system are independent of its linear size L) for $p > p_c$. Thus, in any Monte Carlo simulations of percolation we must have $L >> \xi_p$ for the results to be independent of L.

(v) *Average number of clusters of size s (per lattice site)* $n_s(p)$. Since sn_s is the probability that a given site is part of an s-cluster, a mean cluster size $S_p(p)$ can be defined by

$$S_p(p) = \frac{\Sigma_s s^2 n_s}{\Sigma_s s n_s}. \tag{2.2}$$

(vi) *Effective electrical conductivity* g_e. This is the electrical conductivity of a random resistor network in which a fraction p of bonds are conducting and the rest are insulating. Similarly, if a network represents the pore space of a porous medium in which a fraction p of the pores are open to flow or diffusion, an effective diffusivity D_e and a hydrodynamic permeability k can also be defined.

(vii) *Effective elastic modului G*. These are the elastic moduli of the network in which a fraction p of the bonds are elastic elements (e.g., springs), while the rest have no rigidity or stiffness (i.e., they are cut). Figure 2.2 shows

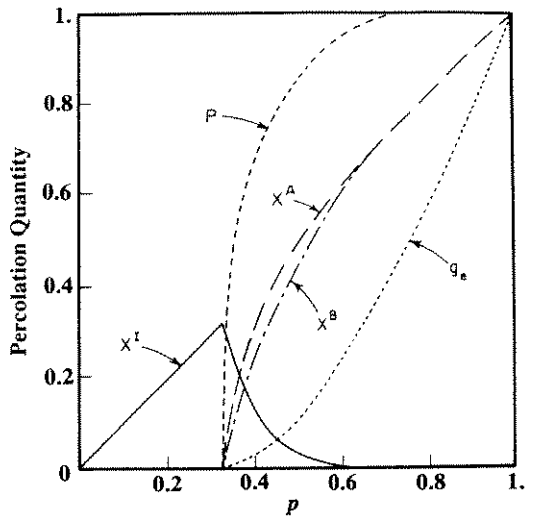

Figure 2.2 *The dependence of some of the percolation quantities on p, the fraction of occupied sites, in site percolation on a simple cubic lattice.*

the typical behavior of some of the percolation properties for a simple cubic network in site percolation, where $X^I(p)$ is the fraction of isolated occupied sites, i.e., $X^I(p) = p - X^A(p)$. The topological properties such as the accessible or backbone fractions are usually calculated by Monte Carlo simulations. For example, Stauffer *et al.* (1982) give a computer program for calculating $X^A(p)$, while Liem and Jan (1988) discuss a method for calculating $X^B(p)$. The transport properties, such as the effective conductivity or the elastic moduli, can be calculated by Monte Carlo simulations or by the analytical approximations discussed in Chapter 5.

2.4 The structure of the backbone at or near percolation threshold

Of particular interest is the structure of the backbone near or at the percolation threshold, since the backbone plays a fundamental role in any transport process in percolating systems. Following Stanley (1977), we can divide the bonds of the backbone into two groups. In one group are those that are in the *blobs*, i.e., the multiply connected part of the backbone. In the second group are the *red bonds*, those that, if cut, would split the backbone into two parts. The reason for calling such bonds red is that in a percolating electrical network they carry all of the current between two blobs, and thus they are the *hottest* bonds in the backbone.

2.5 Universal scaling laws for percolation quantities

The numerical value of every percolation quantity for any p depends on the microscopic details of the system, such as its coordination number. But near the bond or site percolation threshold p_c, most percolation quantities obey scaling laws that are largely insensitive to the network structure and its microscopic details. The quantitative statement of this insensitivity is that, near p_c we have the following scaling laws

$$P(p) \sim (p - p_c)^{\beta_p}, \tag{2.3}$$
$$X^A(p) \sim (p - p_c)^{\beta_p}, \tag{2.4}$$
$$X^B(p) \sim (p - p_c)^{\beta_B}, \tag{2.5}$$
$$\xi_p(p) \sim |p - p_c|^{-\nu_p}, \tag{2.6}$$
$$S_p(p) \sim |p - p_c|^{-\gamma_p}, \tag{2.7}$$
$$g_e(p) \sim (p - p_c)^{\mu}, \tag{2.8}$$
$$G(p) \sim (p - p_c)^{f}. \tag{2.9}$$

The topological exponents β_B, β_p, ν_p and γ_p are completely *universal*, i.e., they are independent of the microscopic details of the system, and depend only

on the dimensionality of the system. Even long, but finite, range correlations do not change this universality, although they do change the value of p_c. The transport exponents μ and f are also largely universal. Later in this chapter we discuss the conditions under which the universality of μ and f may be violated.

The scaling behavior of the effective diffusivity D_e is related to that of $g_e(p)$. According to Einstein's relation, g_e and D_e are related through, $g_e \sim n_e D_e$, where n_e is the density of the electrons. Diffusion can take place both on the sample-spanning cluster as well as the finite clusters. But in most cases, only diffusion on the sample-spanning cluster contributes significantly to the long-time transport properties of the system (the case in which the finite clusters can also contribute significantly is discussed in Chapter 9). In this case, $n_e \sim X^A(p)$, and therefore

$$D_e(p) \sim (p - p_c)^{\mu - \beta_p} \tag{2.10}$$

Similarly, near p_c the permeability k of a percolating network obeys the following scaling law

$$k(p) \sim (p - p_c)^{e}. \tag{2.11}$$

For network models, $e = \mu$. But for percolating continua, e can be significantly different from μ.

Two other transport properties that will be used in this book are as follows. Imagine that in a percolation network a fraction p of bonds are perfect conductors (their resistance is *zero*), while the rest are normal conductors (their resistance is *finite*). Then, *below* p_c only finite clusters of perfect conductors are formed and g_e is finite. As p_c is approached from below, clusters of perfect conductors become larger and g_e increases. Finally, g_e diverges at p_c such that near p_c we have

$$g_e(p) \sim (p_c - p)^{-s}. \tag{2.12}$$

In two dimensions, $\mu = s$, but there is no known relation between s and μ in three dimensions. Similarly, if a fraction p of the bonds are totally *rigid* springs (their spring constant is *infinite*), while the rest are *soft* (their spring constant is *finite*), then the elastic moduli are finite below p_c, but diverge as p_c is approached from below as

$$G \sim (p_c - p)^{-\zeta}. \tag{2.13}$$

The relevance of s and ζ to practical applications is discussed in Chapters 11 and 12. Obviously, when the bonds are elastic springs, one can invent many types of percolation networks by simply changing the force laws that govern the deformation of the springs, and thus the numerical values of the elastic moduli would depend on the type of the force laws that are used. We

show in Chapter 4 that such elastic networks are relevant to modeling of fracture of disordered solids and rock. In Chapters 11 and 12 we demonstrate the relevance of such elastic networks to modeling the viscosity and elastic moduli of polymer networks and other disordered materials.

For large clusters near p_c, $n_s(s)$ obeys the following scaling law

$$n_s \sim s^{-\tau_p} f[(p - p_c)s^{\sigma_p}], \tag{2.14}$$

where τ_p and σ_p are also universal and $f(0)$ is not singular. The geometrical exponents are *not* all independent. For example, one has, $\tau_p = 2 + \beta_p\sigma_p$ and $\nu_p d = \beta_p + 1/\sigma_p = 2\beta_p + \gamma_p$, and in fact knowledge of ν_p and another exponent is sufficient for determining most of the geometrical exponents. Unlike these exponents, the implied prefactors in all of the above scaling laws *do* depend on the type of network, which is why the *numerical* values of percolation quantities depend on the details of the system. If two phenomena are described by two different sets of critical exponents, they are said to belong to two different *universality classes*, in which case the physical laws governing the two phenomena must be fundamentally different. Thus, critical exponents can help one to distinguish between different classes of problems and the physical laws that govern them. An accurate technique for estimating these exponents is the finite-size scaling method discussed below. In Table 2.3 the values of the critical exponents in two and three dimensions are compiled. For comparison, the corresponding values for the Bethe lattices are also given.

Table 2.3 *Currently accepted values of the critical exponents and fractal dimensions for a d-dimensional system. Rational or integer values are exact results*

	$d = 2$	$d = 3$	Bethe lattices
β_p	5/26	0.41	1
β_{BB}	0.48	1.05	2
ν_p	4/3	0.88	1/2
γ_p	43/18	1.82	1
σ_p	36/91	0.45	1/2
τ_p	187/91	2.18	5/2
D_c	91/48	2.52	4
D_{BB}	1.64	1.8	2
$D_{\min}$	1.13	1.34	2
μ	1.3	2.0	3
s	1.3	0.73	0
f	see Chapter 11		
ζ	see Chapter 11		

2.6 Fractals and percolation

For any length scale $L >> \xi_p$, a percolating system is macroscopically homogeneous. But for $L << \xi_p$, the system is *not* homogeneous and the

macroscopic properties of the system depend on L. In this regime, the sample-spanning cluster is on average self-similar, i.e., it looks the same at all length scales up to ξ_p, and its mass M (its total number of bonds or sites) scales with ξ_p as

$$M \sim \xi_p^{D_c}, \tag{2.15}$$

where D_c is called the fractal dimension of the cluster. However, D_c is not a totally new quantity and is given by

$$D_c = d - \frac{\beta_p}{\nu_p}. \tag{2.16}$$

For $L >> \xi_p$, $D_c = d$. Similarly, for $L << \xi_p$, the backbone is a fractal object and its fractal dimension D_{BB} is given by

$$D_{BB} = d - \frac{\beta_B}{\nu_p}. \tag{2.17}$$

Note that if $L < \xi_p$, one should replace ξ_p in (2.15) by L. Note also that ξ_p is divergent at $p = p_c$, so that then the sample-spanning cluster is a fractal object for *any* L.

For $L << \xi_p$, the number of red bonds M_{red} scales with L as, $M_{red} \sim L^{D_{red}}$, and thus D_{red} is the fractal dimension of the set of the red bonds. Coniglio (1981) proved that $D_{red} = 1/\nu_p$. Another important concept is the *minimal* or *chemical* path between two points of a percolation cluster, which is the shortest path between the two points. This concept was first discussed by Alexandrowicz (1980) and Havlin and Nossal (1984). For $L << \xi_p$ the length L_{min} of the path scales with L as

$$L_{min} \sim L^{D_{min}}, \tag{2.18}$$

and therefore D_{min} is the fractal dimension of the minimal path. Chapter 13 shows that the minimal path plays an important role in hopping conductivity of semiconductors. The current values of these fractal dimensions are also listed in Table 2.3.

Once it is established that a system is a fractal, many classical laws of physics have to be significantly modified. For example, Fick's law of diffusion with a constant diffusivity is not appropriate for describing diffusion processes in fractal systems; this is discussed in Chapters 9 and 10.

2.7 Percolation in finite systems and finite-size scaling

So far we have discussed percolation in infinitely large systems. Percolation in finite systems deserves discussion because practical applications usually

involve finite systems. The effect of finite size of the system manifests itself mostly near p_c where ξ_p is large, and thus we need to study its effect in this region. Fisher (1971) investigated the effect of finite size of a thermal system on its critical properties near the critical temperature, and developed a theory for such finite systems, usually called finite-size scaling, which can be adopted for percolation processes. In a finite system, as p_c is approached, ξ_p eventually becomes comparable to the linear size of the network. Therefore, following Fisher (1971), the variations of *any* property P_L of a system of linear size L is written as

$$P_L \sim L^{-x} f(u), \tag{2.19}$$

where, $u = L^{1/\nu_p}(p - p_c) \sim (L/\xi_p)^{1/\nu_p}$, and $f(0)$ is nonsingular. If near p_c and in the limit $L \to \infty$, one has $P_\infty \sim (p - p_c)^\delta$, then one must have $x = \delta/\nu_p$. The finite size of the network also causes a shift in the percolation threshold (Levinshtein *et al.* 1976),

$$p_c - p_c(L) \sim L^{-1/\nu_p}. \tag{2.20}$$

Here p_c is the percolation threshold of the infinite system, and $p_c(L)$ its *effective* value for a finite system of linear size L. Although (2.19) and (2.20) are valid for large values of L, very large systems cannot easily be simulated in practice and therefore an equation such as (2.19) is modified to

$$P_L \sim L^{-x}[a_1 + a_2 g_1(L) + a_2 g_2(L)], \tag{2.21}$$

where g_1 and g_2 are two *correction-to-scaling* terms, particularly important for small and moderate values of L; a_1 and a_2 are constants. For *transport properties* (e.g., conductivity, diffusivity, elastic moduli), $g_1 = (\ln L)^{-1}$, and $g_2 = L^{-1}$ often provide accurate estimates of x (Sahimi and Arbabi 1991). Equation (2.21) also tells us how to estimate the critical exponents: Calculate P_L at p_c for several values of L, and fit the results to (2.21) to estimate x.

2.8 Percolation in random networks and continua

The use of regular networks for investigating various phenomena in disordered systems is popular. But percolation in continua and in topologically random networks, those in which the coordination number varies from site to site, is of great interest. This is because many practical situations deal with such systems. There are at least three ways of realizing percolating continua. For a review of continuum percolation see Balberg (1987); for the most recent references see Alon *et al.* (1991) and Drory *et al.* (1991). In the first method, one has a random distribution of inclusions, such as circles, spheres or ellipses, in an otherwise uniform system, an example of

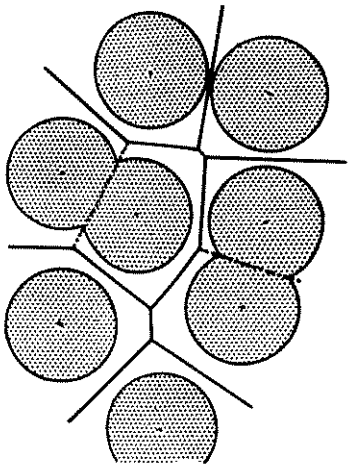

Figure 2.3 *Two-dimensional Swiss cheese model of random continua.*

which is shown in Fig. 2.3. In such systems percolation is defined either as the formation of a sample-spanning cluster of the paths between untouching inclusions, or as the formation of a sample-spanning cluster of touching or overlapping inclusions. In the second method, one divides the space into regular or random polyhedra, a fraction of which is occupied (conducting), while the rest are unoccupied; an example is shown in Fig. 2.4. In the third method, one distributes at random conducting sticks of a given aspect ratio,

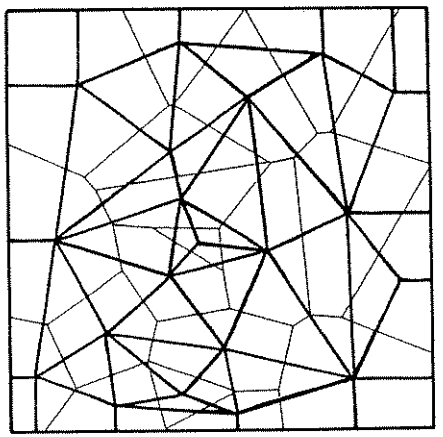

Figure 2.4 *Two-dimensional Voronoi tessellation (thin lines) and Voronoi network (thick lines).*

or plates of a given extent. The last class of disordered continua may be relevant to modeling fracture networks of rock (see Chapter 4).

More formally, one can define percolation in continua as follows. Consider a random and continuous function $h(\mathbf{r})$ at point $\mathbf{r}$, defined for the entire space, with the property that $\langle h(\mathbf{r}) \rangle = \mathbf{0}$, where $\langle . \rangle$ denotes an averaging. We now paint all regions of space for which, $h(\mathbf{r}) < R$ black, where R is a real number, while the rest are white. If R changes from $-\infty$ to $+\infty$, then the volume of the black region can vary from zero to ∞. If R is small, we can only form small black islands. But as R becomes larger, black islands can merge and, finally, at a critical R_c, form a sample-spanning black island. The function $h(\mathbf{r})$ can be thought of as a potential, such that when it reaches a certain level, the system can percolate.

One of the most important discoveries for percolating continua (Scher and Zallen 1970) is that the critical occupied volume fraction ϕ_c, which is defined as

$$\phi_c = p_{cs} f_l, \tag{2.22}$$

where f_l is the filling factor of a lattice when each of its sites is occupied by a sphere in such a way that two nearest-neighbor impermeable spheres touch one another at one point, appears to be an invariant of the system whose value is about 0.45 for $d = 2$ and 0.15–0.17 for $d = 3$. Shante and Kirkpatrick (1971) generalized this idea to permeable spheres, and showed that the average number of bonds per sites B_c at p_c (Tables 2.1 and 2.2) is related to ϕ_c by

$$\phi_c = 1 - \exp(-B_c/8), \tag{2.23}$$

and that the value of B_c for percolating continua is the limiting value of $p_{cs}Z$, when $Z \to \infty$. Accurate estimates of B_c for many systems were obtained by Haan and Zwanzig (1977). If ϕ_c is truly an invariant of continuous systems, then R_c is given by

$$\phi_c = \int_{-\infty}^{R_c} h(\mathbf{r}) dV, \tag{2.24}$$

where V is the volume of the system.

It has been established that the topological critical exponents defined above are the same for lattice and continuous systems (for a review see Balberg 1987). But *transport* (e.g., conduction) in percolating continua can be quite different from that in discrete networks. Consider, for example, the two-dimensional Swiss cheese model, shown in Fig. 2.3, in which circular inclusions (spherical inclusions in three dimensions) are punched at random in an otherwise uniform system. If transport takes place through the channels between the nonoverlapping circles, then the system can be

mapped onto an equivalent percolation problem in a random network made of the *edges* of Voronoi polygons (polyhedra) (Kerstein 1983); see Fig. 2.4. If we construct the *dual* of this network, i.e., connect the centers of the neighbouring polygons (polyhedra), we obtain a Voronoi network, also shown in Fig. 2.4. The *average* coordination number of a Voronoi network is 6 in two dimensions and 15.5 in three dimensions. Kogut and Straley (1979) and Feng *et al.* (1987) used various models and techniques to show that the critical exponents μ_c, e_c, and, f_c, defined for the conductivity, elastic moduli, and permeability of continua, are quite different from μ, e, and f defined above for percolating networks. The reason is that transport in a system such as the Swiss cheese model can be dominated by the narrow necks between the nonoverlapping circles (or spheres). Since the widths of such necks can vary throughout the system, there will be a distribution of local transport properties such as the neck conductance g. If this distribution is singular near $g = 0$, then the universality of μ and other transport exponents can be violated. No such singularities appear in percolation on networks, unless the bond conductances are distributed according to such singular distributions. Feng *et al.* (1987) showed that in a three-dimensional Swiss cheese system $\mu_c \simeq \mu + 1/2$ and $e_c \simeq \mu + 5/2$. For the two-dimensional system $\mu_c = \mu$ and $e_c \simeq \mu + 3/2$.

Jerauld *et al.* (1984) showed that as long as the average coordination number of a random network and the coordination number of a regular network (e.g., the two-dimensional Voronoi and triangular networks) are about the same, many transport properties of the two systems are, for all practical purposes, identical, provided that the same bond conductance distribution is used for both networks. Therefore, in many applications, especially those that involve large-scale computer simulations, a regular network is used as it is much easier to handle. But if we use a random network to represent a disordered continuum, we need the distribution of transport properties of the bonds to closely mimic the properties of the transport paths in the continuum. On the other hand, since the topological exponents are totally universal, we can always use a random or even a regular network to study percolation in a continuum.

2.9 Conclusions

Percolation theory tells us whether a system is macroscopically connected or not. This macroscopic connectivity is of fundamental importance to many phenomena involving disordered media. Moreover, universal scaling laws near the percolation threshold tell us which aspects of a given phenomenon are important in determining its macroscopic properties, and which aspects are not relevant, and therefore we do not have to worry about them.

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