CHAPTER FOUR

The Percolation Model

4.1 INTRODUCTION

Few theoretical techniques are available for dealing with severely disordered systems and stochastic-geometry situations. One of the nicest of these techniques, percolation theory, is the subject of this chapter. The intellectual appeal of the percolation model resides in its almost gamelike mathematical aspects and the fact that it provides a well-defined, transparent, and intuitively satisfying model for spatially random processes. The practical importance of percolation theory resides in its applicability to a broad (and growing) range of physical phenomena. (The reader should look ahead to Table 4.1 for a glimpse of this range, which extends to fields outside of physics.) Amorphous solids, in which the role of topological disorder is of vital importance, provide a natural setting in which unruly geometries abound. In this setting, the ideas of percolation theory can be fruitfully applied.

Percolation theory deals with the effects of varying, in a random system, the richness of interconnections present. From the perspective of condensed-matter physicists (who have been the main ones to adopt this mathematical subject for use in their own discipline), the single most seductive aspect of the percolation model is the presence of a sharp phase transition at which long-range connectivity suddenly appears. It is this percolation transition, which occurs with increasing connectedness or density or occupation or concentration, that makes percolation a natural model for a diversity of phenomena. The percolation transition provides a splendid prototype for second-order phase transitions in general, so that the percolation model is a fine pedagogic instrument for illustrating concepts central to the physics of phase transitions and critical phenomena. Many of these same concepts are useful for amorphous solids.

Two of the most prominent examples of the uses of percolation concepts in amorphous solid-state physics, the glass transition (for atomic motion) and the Anderson transition (for electronic motion), are discussed in the following chapter. Another application (''variable-range hopping'') to electronic trans-
port is also contained in that chapter. Among the illustrative examples introduced in the present chapter is one (the sol → gel transition, see Fig. 4.11) that is a special type of glass transition. For a quick preview of the percolation transition itself, peek ahead to Figs. 4.4 and 4.5.

4.2 AN EXAMPLE: THE VANDALIZED GRID

As an introductory example of a percolation process and the qualitative event called the percolation threshold, consider the gedanken experiment rather fancifully illustrated in Fig. 4.1. A communication network, represented by a very large square-lattice network of interconnections, is attacked by a crazed saboteur who, armed with wire cutters, proceeds to cut the connecting links at random (not a realistic scenario, obviously, but necessary for our purpose here). His aim is to break contact between two well-separated but well-connected communication centers or command posts, represented by the heavy bars which, in Fig. 4.1, form the left and right boundaries of the network. Question: What fraction of the links (or bonds) must be cut in order to isolate the command posts from each other?

This question, which can be given a definite answer by percolation theory, illustrates the central issue at the heart of the percolation model: the existence of a sharp transition at which the long-range connectivity of the system disappears (or, going the other way, appears). This basic transition, which occurs abruptly as the composition of the system—or some generalized density—is varied, constitutes the percolation threshold. At the percolation threshold, significant properties may change qualitatively in a go/no-go manner. In the context of our present example, certainly the question of whether the joint command posts can communicate or not is a yes-or-no matter of some importance.

Other, more simple, physical situations can be discussed in the context of Fig. 4.1. If the square-lattice graph is interpreted, not as a communication grid but instead as an electrical network with the (intact) bonds as unit conductors, the percolation threshold corresponds to the onset/disappearance of electrical conduction between the two bounding electrodes (formerly, the “command posts”). Starting with the wholly occupied network (all conducting bonds present) and then turning the random wire-cutter loose, the current drops as the curve indicated in the lower part of Fig. 4.1 is traversed from right to left. The position of the arrow roughly corresponds to the stage depicted in the upper part of the figure: about 21% of the bonds in the network have been cut, 79% remain uncut. At this stage, current still flows between the electrodes (which are connected externally to a voltage source and an ammeter), although less than initially. Denoting the fraction of uncut bonds remaining as \( p \), \( I(p) \) continues to decrease as \( p \) decreases until a critical bond concentration, denoted as \( p_c \), is reached at which the current \( I \) vanishes. For \( p \) less than \( p_c \), \( I \) is zero (not merely small, but zero!). For \( p < p_c \), there ex-
A third, mechanical, interpretation can be attached to Fig. 4.1, which will also prove relevant. Viewed as a screen, a two-dimensional structural unit, at \( p = 1 \) the structure has its greatest mechanical strength. As structural elements are snipped away and \( p \) decreases, this strength declines until, at \( p_c \), the remainder

Figure 4.1 The randomly cut network as an example of percolation.
of the badly thinned-out screen simply falls apart completely into discrete (finite) bits and pieces.

The existence of a perfectly sharp percolation threshold, a well-defined $p_c$ at which, with decreasing $p$, the joint command posts lose touch with each other or the random resistor network becomes an open circuit or the screen structure disintegrates, has involved a tacit assumption which we now make explicit. When we stated that the lattice of Fig. 4.1 should be understood to be "very large," the quantitative meaning is that the scale length of interest, for example, the distance $L$ between the command posts, greatly exceeds the lattice constant or bond length $a$ of the square lattice: $(L/a) \gg 1$. The connectivity threshold is only mathematically sharp in the limit $(L/a) \to \infty$, an infinite system. For a finite system, repeated experiments such as that of Fig. 4.1 will yield a spread of observed thresholds which bracket $p_c$. (Obviously, for a very small system, our hypothetical randomly snipping saboteur could have significantly good or bad luck, succeeding at a value of $p$ appreciably above or below $p_c$.) Henceforth we will generally assume a very large system; the limit $(L/a) \to \infty$ (the "thermodynamic limit") provides a very good approximation to the cases of interest. Typically, $a$ will be an atomic-scale length and $L$ a macroscopic length.

For the question ("What fraction of the bonds...?") posed at the beginning of this section in connection with Fig. 4.1, the answer provided by percolation theory is $p_c = 0.5$. It is known that $1/2$ is the value of the "percolation threshold for bond percolation on the square lattice." This is a rare case in which an "exact" analytically derived value is available for $p_c$. The percolation threshold is known exactly for a few other two-dimensional lattices, but not for any lattices in three (or higher) dimensions. Note immediately that in one dimension, $p_c = 1$; any nonzero value for the fraction of cut bonds breaks the network into finite sections and destroys long-range connectivity. In $d = 1$ there is no way to "get around" a blockage (as can be done in $d \geq 2$), so no blockages can be tolerated. In effect, there is no percolation in one dimension.

Note also the use of the term bond percolation in the above specification of the percolation threshold for the scenarios envisaged via Fig. 4.1. A lattice (or graph) is composed of sites (vertices, intersections between bonds) and bonds (edges, links, pairwise connections between sites). There are two basic types of percolation processes on lattices: bond percolation and site percolation. In both cases we start (as in Fig. 4.1) with a regular geometric object, a periodic lattice. Now a nongeometric two-state property, which carries the statistical character of the problem (and converts it into a stochastic-geometry situation) is randomly assigned to each site or bond. In bond percolation, such as we have been considering thus far, each bond is either connected (which occurs with probability $p$) or disconnected (which occurs with probability $1 - p$). In place of connected/disconnected, the corresponding terms unblocked/ blocked are often used in order to evoke a fluid-flow image which (as mentioned in the next section) provided the original motivation for the use of the term percolation for the connectivity threshold. The assumption of a completely random system
means that the probability $p$, for every bond, is independent of the state of the neighboring bonds.

In site percolation, each bond is considered to be connected, and it is now the sites which carry the random-connectivity character of the structure. Each site is either connected (unblocked) or disconnected (blocked), with probabilities $p$ and $1 - p$, respectively. Again, $p$ is the same for each site, and is not influenced by the state of the neighboring sites. To convey the concentration-or density-dependence that is an important aspect of most phenomena which can be modeled as site-percolation processes, unblocked and blocked sites are usually referred to as filled and empty sites, respectively. This usage will be adopted.

Just as, in bond percolation, adjacent unblocked bonds are connected to each other, so, in site percolation, adjacent filled sites are connected to each other. Adjacent has an intuitive, nearest-neighbor, meaning here. (For mathematically oriented readers requiring more "rigor": Two bonds are adjacent if they are incident with the same site; two sites are adjacent if they are incident with the same bond.) A set of connected bonds or sites is called a cluster. Thus, in site percolation, two filled sites belong to the same cluster if they are linked by a path of nearest-neighbor connections joining a string of filled sites. Likewise, in bond percolation, two unblocked bonds belong to the same cluster if they are linked by at least one unbroken path of unblocked bonds.

### 4.3 THE PERCOLATION PATH

The term percolation for this class of statistical-geometry model was coined in 1957 by the mathematician J. M. Hammersley, who had in mind the passage of a fluid through a network of channels, with some of the channels (at random) being blocked. A sketch of such a bond-percolation situation, with the channel network idealized as a 2d honeycomb lattice weaving its way through hexagonal "coffee grounds," is shown in Fig. 4.2. A map of the network is shown in the lower part of the figure, with the unblocked bonds represented by heavy lines and several clusters labeled. One cluster has been labeled as a possible percolation path, as explained below. Bond-percolation processes can thus be viewed in terms of the flow of some generalized "fluid" through a medium represented by interconnecting pipes, some of which are valved shut as shown in Fig. 4.3b. Such a "plumbing analogy" can similarly be constructed for site percolation, as indicated in Fig. 4.3a. Now the valves are placed at the joints (intersections), rather than in the pipes, of the plumbing network. It is clear from this that a combined percolation process can be considered which corresponds to valves placed both in the pipes and at the joints. This is called, not surprisingly, site-bond percolation, and is an example of an interesting and useful generalization of "conventional" percolation theory. Several such generalizations will be touched upon in this chapter, usually (as here) quite briefly. One in particular,
Figure 4.2  The percolation of a fluid through a porous medium that is modeled as a network of interconnected channels (some of which are blocked, at random) constitutes a bond-percolation process. The unblocked channels in this example play a role analogous to that played by the uncut wires in Fig. 4.1. The connectivity map shown in the lower part of the figure corresponds to the array of blockages shown in the upper diagram. In the latter, liquid is shown in the channels which belong to the percolation path.
continuum percolation, is especially important in its application to amorphous solids, and will be developed more fully.

The most striking aspect of a percolation phenomenon is the dramatic change that occurs in the connectivity of the system at the percolation threshold. Our introduction of this sharp transition, given in the previous section in the context of Fig. 4.1, was slightly unorthodox. There we started with an extended connected network and proceeded to progressively dilute it, in a random manner, until it fell apart (at $p_c$) into finite fragments. In other words, we traversed Fig. 4.1b from right to left, in the direction of increasing dilution or decreasing concentration. The more usual visualization of the percolation threshold views the process as "proceeding" in the other direction, that of increasing concentration, i.e., from left to right in Fig. 4.1b: we increase the probability $p$ that a bond, chosen at random, is unblocked, from $p = 0$ through $p = p_c$ to $p = 1$. Since there is no a priori time bias built into percolation, "directionality" in this sense is simply a matter of custom and both viewpoints are obviously equally good. It is useful to compare the two way of approaching $p_c$, and this can easily be done with the aid of an illustrated case such as that shown in Fig. 4.4.
Figure 4.4 portrays a portion of a square lattice upon which a site-percolation process has been superimposed. The three frames represent the same region of the lattice at three different concentrations: The fraction of filled sites \( p \) grows from 0.25 to 0.50 to 0.75 in going from Fig. 4.4a to 4.4b to 4.4c. Filled sites are shown as heavy dots, nearest-neighbor filled sites (which are connected, i.e., belong to the same linked cluster) are shown joined by heavy lines, and several cluster sizes are indicated.

The three panels of Fig. 4.4 can be thought of as the middle three frames of a five-frame sequence spaced at equal \( \Delta p = 0.25 \) intervals. The frame preceding \( (a) \) is the completely empty lattice, the low-density limit corresponding to \( p = 0 \), while that following \( (c) \) is the high-density \( p = 1 \) limit in which every site is filled and connected with every other site in one giant cluster which completely fills the lattice. The latter situation is the site-percolation analog of the fully connected bond-percolation situation which was the starting point for the treatment of Fig. 4.1. As indicated there, beginning at \( p = 1 \) and then progressively diluting the giant cluster (cutting bonds in bond percolation, removing filled sites in site percolation) first introduces small holes, then thins out the giant cluster and renders it more and more ragged, and eventually destroys its long-range connectivity by breaking it up into finite pieces. Now let us, as promised, view the process the other way, from top to bottom in Fig. 4.4.

For \( p \ll 1 \), the low-concentration regime, nearly all of the filled sites occur as isolated singlets, clusters of size one. Choosing a site at random, the chance of it being a filled site is \( p \). Suppose that we have landed on a filled site; what is the likelihood that it belongs to a cluster of size \( 2^k \)? Since there are four nearest neighbors in the square lattice, and since \( p \ll 1 \), the chance of this being the case is \( 4p \), which is negligible. By similarly counting the possibilities, the probability of a given filled site belonging to a cluster of size \( 3 \) is \( 18p^2 \) for the square lattice, which is even more negligible in the small-\( p \) limit. Put another way, at low concentrations the probability of encountering a cluster of size \( s \) is of the order of \( p^s \). Thus the cluster-size distribution, in the \( p \to 0 \) low-density limit, is sharply peaked at \( s = 1 \) and falls off exponentially with increasing \( s \). Henceforth, \( s \) will be used to denote cluster size.

The cluster-size distribution is typically expressed as a discrete function \( n(s) \), defined at \( s = 1, 2, 3, 4, \ldots \), where \( n(s) \) is normalized per site, that is, \( n(s) \) is the number of clusters of size \( s \) divided by the total number of sites in the system (for a large system, of course). Away from \( p = 0 \), it is not so easy to specify \( n(s) \) analytically. [For site percolation on the square lattice, the previous paragraph showed that, for \( p \approx 0 \), \( n(s) = p, 4p^2, 18p^3 \), for \( s = 1, 2, 3 \). These are approximations expressed "to lowest order in \( p \)," quite accurate for \( p \) less than 0.1, but "exact" only in the \( p \to 0 \) limit.] Nevertheless, for many lattices of interest, \( n(s) \) is reasonably well known over the full concentration range as a result of computer simulations. For the moment, we are not concerned with quantitative aspects of the evolution of \( n(s) \) with increasing \( p \), but are interested instead in the qualitative change that takes place at the per-
colation threshold. Thus we may discuss what happens, as we move away from $p \approx 0$, qualitatively.

As $p$ increases, the proportion of filled sites belonging to $s \geq 2$ clusters increases, since the probability of continuing a cluster—by finding an adjacent filled site—becomes larger. The mean cluster size, which we will denote as $s_{av}$, grows. Since the number of sites occurring in clusters of size $s$ is proportional to $s n(s)$, then the site-weighted average cluster size is given by

$$s_{av} = \frac{\sum_{s=1}^{\infty} s^2 n(s)}{\sum_{s=1}^{\infty} s n(s)}.$$ (4.1)
The sum in the denominator of this expression is proportional to the total number of filled sites. [In fact, since the proportionality constant contained in \( n(s) \) is the reciprocal of the total number of sites in the system, this sum is simply equal to \( p \).] The numerator is a corresponding sum in which each filled site is weighted by the size of the cluster to which it belongs. In other words, if we choose a filled site at random and note down its \( s \) value, the average value characterizing the resulting list of numbers is \( s_{av} \).

\( s_{av} \) starts out (for small \( p \)) at unity, reflecting the total dominance of singlet clusters at low concentrations. As \( p \) increases, so does \( s_{av} \). Consulting Fig. 4.4, our illustrative example examining site percolation on the square lattice, panel \( a \) represents a typical configuration for \( p = 0.25 \). (It was constructed with the aid of a random number generator, the computer equivalent of a coin-tossing sequence.) With 25% of the sites filled, the mean cluster size, as defined above, is about 3.5. Singlets still account for nearly a third of the filled sites, but appreciable numbers of larger clusters now appear.

Increasing \( p \) to 0.5 has the effect indicated in Fig. 4.4\( b \), which is one possible evolution developed out of Fig. 4.4\( a \) by the (random) filling in of one-third of the remaining empty sites. Clusters have grown larger, and some have joined together to form quite large clusters. \( s_{av} \) has now reached a value well in excess of 20, and this quantity is now increasing, as \( p \) increases, very rapidly indeed.

Although the situation depicted in Fig. 4.4\( b \) has come a long way from the situations obtaining at small concentrations, in one extremely crucial respect the situation has not changed from that of Fig. 4.4\( a \) or even from the singlets-only low-concentration limit: All clusters are finite in size. Before examining this statement further, let us look at Fig. 4.4\( c \), in which the concentration has been increased again (by randomly occupying half of the empty sites remaining in Fig. 4.4\( b \)) to \( p = 0.75 \).

In Fig. 4.4\( c \) we observe a large cluster which extends across the entire sample (from the top edge to the bottom, from left to right). This extended cluster is called a spanning cluster for the finite sample at hand. For \( p = 0.75 \), such a spanning cluster persists as the lattice sample grows indefinitely large. This infinitely extended or unbounded cluster is called the percolation cluster or percolation path. Note that although the percolation cluster is infinite in size (\( s \rightarrow \infty \)), it does not fill the entire lattice (except, of course, at \( p = 1 \), the high-density limit). Instead it coexists with finite clusters and islands of empty sites.

The critical event in the connectivity has occurred between 4.4\( b \) and 4.4\( c \), at a composition between \( p = 0.5 \) and \( p = 0.75 \). If a sequence of frames such as that shown in the figure were executed using a very large lattice size and very small density increments (equivalent to what is done in some Monte Carlo computer simulations of percolation), the percolation path would first be observed at \( p = 0.59 \), which is the critical concentration \( p_c \) for site percolation on the square lattice. With increasing concentration, the percolation threshold \( p_c \) marks the appearance of the unbounded, lattice-spanning, percolation cluster. It signals the point at which the system of interconnections has thickened sufficiently for a connected network to propagate indefinitely.
The above statement is the standard one used for defining the threshold. Clearly, it is equivalent to the approach taken earlier (Fig. 4.1) in which we watched the infinite network dissolve and disappear as the system of interconnections was thinned out. The discussion of Fig. 4.1 was for a bond-percolation case, while that given for Fig. 4.4 is for site percolation, but it is easy to see how the analogous quantities (cluster size, percolation path, percolation threshold $p_c$) carry over between the two cases.

Above $p_c$, the percolation path exists; below $p_c$, it does not. From $p = p_c$ to

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**Figure 4.5** The behavior, as a function of the fraction ($p$) of filled bonds, of key properties that characterize bond percolation on the square lattice in two dimensions. The percolation probability $P(p)$ and the average cluster size $s_{av}(p)$ are results of computer studies carried out by Nakanishi (1980); the random-network conductivity $\sigma$ is from the work of Kirkpatrick (1973); and the curve shown for the mean spanning length is schematic.
\( \frac{dP}{dp} \) differs strikingly from \( \frac{d\sigma}{dP} \) above \( p_c \). The percolation probability vanishes (i.e., \( P \) is not merely small, but is identically zero) until the concentration of connections reaches \( p_c \), then it rises very steeply. Eventually \( P(p) \) approaches \( p \) as \( p \) approaches 1; the infinite cluster consumes the finite ones. Several other curves, representing functions to be described below, are displayed in Fig. 4.5. All of these do something special ("exhibit singularities") at the percolation threshold. But the percolation probability \( P(p) \) is really the key function characterizing a percolation process. It marks the qualitative change at \( p_c \), as the opportunity for long-range connectivity goes from nothing to something, and it provides the principal measure of the growth in volume of the extended network as the concentration increases beyond \( p \).

### 4.4 Applications to Phase Transitions

The qualitative shape of the \( P(p) \) curve of Fig. 4.5 evokes, for condensed-matter physicists, the image of a phase transition. It has the look of the behavior of the "order parameter" in a second-order thermodynamic transition, which goes to zero rapidly, but continuously, as the transition temperature is approached. In fact, the percolation model serves as a splendid paradigm for the theory of critical phenomena, which is concerned with the properties of a system near its transition point. Analogies between percolation and, for example, the traditional models for magnetic transitions will be drawn later in this section and the next.

The curve labeled \( \sigma(p) \) in Fig. 4.5 relates directly to our original example of Fig. 4.1. It sketches the behavior of the macroscopic conductance of the randomly diluted resistor network, and simply mirrors the current-versus-concentration curve of Fig. 4.1. Like \( P(p) \), \( \sigma(p) \) is zero for \( p < p_c \), and increases monotonically above \( p_c \). However, one is immediately struck by the dramatic difference in the behavior of these two functions near the percolation threshold. Just above \( p_c \), \( P \) rises very steeply. Right at threshold, in fact, it rises with infinite slope (i.e., \( dP/dp \) becomes arbitrarily large as \( p - p_c \) is chosen to be arbitrarily small). The conductance, on the other hand, shows a very soft rise: its initial slope is zero at threshold (\( d\sigma/dP \) approaches zero as \( p - p_c \) goes to zero).

The striking difference between the way that the percolation probability and the resistor-network conductivity "take off" above \( p_c \) illustrates an aspect belonging to the realm of critical phenomena, the topic which focuses on the
region very close \(|p - p_c| \ll 1\) to the critical point. Behavior in this regime is controlled by the ubiquitous quantities known as critical exponents, such as those we have met earlier in connection with polymers and random walks. Critical exponents for percolation processes, and a comparison to those which are standard in magnetic phase transitions, will be discussed in the following section. In the meantime, it is not hard to understand the physical reason for the contrast between the near-threshold behavior of \(P\) and \(\sigma\). (With the benefit of hindsight, it is easy to say this. Historically, however, the point mentioned in the next paragraph suffered a substantial time delay prior to its appreciation.)

The explosive growth in \(P\) reflects the rapidity with which finite clusters link up with the infinite one as the concentration exceeds \(p_c\). Consider a finite cluster which, with the addition of one unblocked bond (or filled site, the argument applies to site percolation as well as bond percolation), joins up with the previously formed percolation path. Since it now is connected to, and forms part of, the infinite cluster, it contributes to the percolation probability \(P(p)\). But from the point of view of macroscopic current flow, the new bonds add nothing in the way of a new parallel path for current to pass through because they form a cul-de-sac on the original extended network. They do not lead anywhere ("no outlet") and thus they do not contribute to \(\sigma(p)\). Just above threshold, such dead ends dominate the percolation path, and only a negligible fraction of it (which constitutes its skeleton or "backbone") contributes to the conductivity. This is the explanation for the slow start in \(\sigma(p)\) just above \(p_c\). As \(p\) increases, so does the portion of the percolation path which participates in conductivity until, at \(p \to 1\), all of it contributes.

Another way of saying what is said in the previous paragraph is that near threshold, the impedance of the extended network is enormous. When it first appears, the percolation path is terrifically tortuous. It is so lacy and stringy in character that distinct parallel paths available for supporting current are extremely scarce. It turns out that this tenuous nature of the infinite cluster, when it appears at \(p_c\), can be characterized by a fractal dimensionality which is somewhat smaller than the space dimensionality of the percolation process being considered. This fractal dimensionality is related to the critical exponents controlling the properties of a percolating system near its critical point, and its discussion is included in the next section.

The percolation transition, which takes place as the occupation or concentration or density is varied in a disordered system, makes percolation a natural model for describing a diversity of phenomena. Table 4.1 lists some 15 different physical (also chemical and biological) situations to which percolation ideas have been applied. Nearly half of these refer to macroscopic phenomena, the rest to microscopic phenomena. The macroscopic/microscopic demarcation is easy to spot in the center of the table, since the two extreme cases have deliberately been placed in juxtaposition in order to dramatize the diversity. The astrophysical application concerns the propagation of star formation by supernovae, and the percolation transition occurs as a function of interstellar gas density. The particle physics application concerns the confinement (or lack
Table 4.1 Applications of percolation theory

<table>
<thead>
<tr>
<th>Phenomenon or System</th>
<th>Transition</th>
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<tbody>
<tr>
<td>Flow of liquid in a porous medium</td>
<td>Local/extended wetting</td>
</tr>
<tr>
<td>Spread of disease in a population</td>
<td>Containment/epidemic</td>
</tr>
<tr>
<td>Communication or resistor networks</td>
<td>Disconnected/connected</td>
</tr>
<tr>
<td>Conductor-insulator composite materials</td>
<td>Insulator/metal</td>
</tr>
<tr>
<td>Composite superconductor-metal materials</td>
<td>Normal/superconducting</td>
</tr>
<tr>
<td>Discontinuous metal films</td>
<td>Insulator/metal</td>
</tr>
<tr>
<td>Stochastic star formation in spiral galaxies</td>
<td>Nonpropagation/propagation</td>
</tr>
<tr>
<td>Quarks in nuclear matter</td>
<td>Confinement/nonconfinement</td>
</tr>
<tr>
<td>Thin helium films on surfaces</td>
<td>Normal/superfluid</td>
</tr>
<tr>
<td>Metal-atom dispersions in insulators</td>
<td>Insulator/metal</td>
</tr>
<tr>
<td>Dilute magnets</td>
<td>Para/ferromagnetic</td>
</tr>
<tr>
<td>Polymer gelation, vulcanization</td>
<td>Liquid/gel</td>
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<tr>
<td>The glass transition</td>
<td>Liquid/glass</td>
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<tr>
<td>Mobility edge in amorphous semiconductors</td>
<td>Localized/extended states</td>
</tr>
<tr>
<td>Variable-range hopping in amorphous semiconductors</td>
<td>Resistor-network analog</td>
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</tbody>
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thereof) of quarks in nucleons, and the relevant density is that of nuclear matter in the cores of neutron stars. Note that the characteristic length scales in these two examples differ by a factor of $10^{35}(!)$: the characteristic galactic dimension is of the order of $10^{22}$ cm, while the nucleon dimension is of the order $10^{-13}$ cm.

The applications of percolation to amorphous solids appear in the lower part of the table. Notable among these are the connection of percolation to the localization of electrons (the mobility edge, or Anderson transition, in amorphous semiconductors) and of atoms (the glass transition itself). The characteristic length scales in these condensed-matter contexts range from atomic dimensions upward, typically $10^{-8}$ to $10^{-2}$ cm. The Anderson and glass transitions are individually discussed in the following chapter; some of the other entries in Table 4.1 are more briefly treated here.

Figure 4.6 illustrates two of the situations mentioned in the table. One of these is a macroscopic example, the other, microscopic; one involves bond percolation, the other, site percolation. Although one phenomenon is essentially two dimensional in character and the other is three dimensional, for clarity, both have been represented as occurring in two dimensions (using the easy-to-draw square lattice).

Having mentioned length scales appropriate to galaxies and quarks, it may be reassuring to first consider the human-scale enterprise sketched in Fig. 4.6a. This figure is meant to illustrate the second entry in Table 4.1: the propagation of a disease (or a rumor, or an idea, etc.) through a susceptible population. Imagine a uniformly planted orchard which is composed of a species of fruit tree that is subject to a certain highly contagious blight. Assume that we know the function, call it $p(r)$, which gives the probability of a diseased tree infecting a neighboring healthy tree located a distance $r$ away. Given this func-
tion, and the natural wish of the farmer to maximize his yield by planting the largest practical number of trees on the available acreage, we can present the following problem: What is the highest density permissible for the planting which avoids the risk of blight-induced wipeout? We assume that a few widely scattered individuals will inevitably develop the disease, and define a wipeout as an event in which a single sick tree produces an epidemic that spreads throughout the orchard, destroying a finite fraction of the entire tree population.
It is evident that the percolation model answers the problem posed here in the following way: The orchard lattice constant $a$ must be chosen large enough to ensure that $p(a) < p_c$. The spacing must exceed the critical distance $r_c$ for which, as sketched in Fig. 4.6a, $p(r)$ falls below $p_c$. Thus the percolation solution is to take $a \geq r_c$. Contamination is now confined to a finite cluster surrounding the initially infected tree.

At first glance it perhaps might seem that the situation described is one corresponding to site percolation, but this is not so. This is a bond-percolation process. The "fluid" is the disease, and its "flow" occurs along the bonds between neighboring trees. Although the simplest percolation model considers only nearest-neighbor bonds, it is relatively straightforward to construct the generalization which includes more distant neighbors. Such a long-range-interaction model would make more realistic use of the interaction function $p(r)$ of Fig. 4.6b, invoking its value not only at $r = a$ but also at $r = a\sqrt{2}$, $r = 2a$, $r = a\sqrt{5}$, $r = a\sqrt{8}$, etc. By not neglecting the small possibility for the disease to leap-frog over nearest neighbors to infect a more distant tree, a better estimate for the epidemic-avoiding lattice constant would be obtained (it would be slightly larger than the first estimate).

In a related example, experience with forest fires (in hot, dry weather) shows that the nearest-neighbor spacing in most woods is appreciably smaller than the $r_c$ corresponding to the $p(r)$ appropriate for describing the spread of the fire from a burning tree to a fresh one. Thus forest fires, if not caught very early, are almost certain to propagate. One technique for fighting such fires is to attempt to surround it with a ring of burnt-out land (cleared by the use of backfires) of width $w$ which is large enough so that $p(w) \ll 1$. Note that the connection between forest fires and phase transitions is by no means as fanciful as might seem at first sight. The phenomenon involves the nucleation and growth of a new phase (burnt-out land) within an old one (virgin forest), occurring in a process which is, rather manifestly, exothermic.

In these examples, the objects (trees) which define the sites of the lattice, although alive, are immobile. Nearest neighbors remain nearest neighbors, second neighbors remain second neighbors; the topology of the system is time-independent. This static character is characteristic of "pure" percolation; the medium is spatially stochastic, but does not fluctuate with time. Suppose we attempt to analyze the spread of disease among a population composed of individuals that are not sedentary (e.g., trees) but are highly mobile (e.g., people). Now we must contend with the fact that people change partners: the set of other individuals who are nearest neighbors of any particular individual changes with time. Thus the study, for example, of the spread of Asian flu in Manhattan involves, not only percolation, but also diffusion. There is no static lattice, but only one which is constantly reconstructing (old bonds are broken, new ones formed) with the passage of time. The distinction here is one which should by now be familiar; it is the same as that which distinguishes a liquid from an amorphous solid. This aspect is one of those which complicate the analysis of the glass transition, as discussed in Chapter Five.
In moving on to Fig. 4.6b, we reenter more familiar territory in solid-state physics in order to establish an analogy between percolation and magnetism. Figure 4.6b schematically represents the case labeled “dilute magnets” in Table 4.1. Consider a ferromagnetic crystal which is diluted by the random substitution of nonmagnetic atoms for magnetic ones. Assuming nearest-neighbor exchange interactions only and spin-½ magnetic ions (the “Lenz-Ising model”), the spin Hamiltonian is then \( -J \sum_{i,j} S_z(i)S_z(j) \). \( S_z(i) \) is the z-component of the spin at site \( i \) occupied by a magnetic ion, and can take on values +½ and −½. \( J \) is the nearest-neighbor exchange integral, and the sum extends over all pairs \((i,j)\) of sites which are nearest neighbors and for which both sites are occupied by magnetic ions. The fraction of magnetic ions is \( p \), of nonmagnetic ions, \( 1 - p \).

Let us look at the magnetic character of the system at zero temperature, as the dilution \((1 - p)\) is varied. At \( T = 0 \), all adjacent spins must be aligned parallel, so that the undiluted \((p = 1)\) pure system is a ferromagnet with all spins parallel and all sites contributing to the macroscopic magnetization \( M \). As \( p \) decreases with the addition of nonmagnetic ions, \( M \) also decreases. When \( p \) falls below \( p_c \), the site-percolation threshold for the lattice, \( M \) vanishes. The reason for this is clear, as illustrated in Fig. 4.6b. Although plenty of spins are still present, for \( p < p_c \) there can be no macroscopically extended cluster of exchange-coupled spins. All of the magnetic ions now occur in finite clusters, and although within each cluster all spins are coupled and they must either all be up \((S_z = +\frac{1}{2})\) or all down \((S_z = -\frac{1}{2})\), the separate clusters can independently be either up or down so that the net magnetization cancels out on a macroscopic scale. There is no longer a spontaneous magnetization; the heavily diluted system is paramagnetic, not ferromagnetic.

Percolation theory thus provides the critical concentration of magnetic ions necessary for the appearance (at \( T = 0 \)) of magnetic order. The critical composition corresponds to the site-percolation threshold. This is a site process rather than a bond one because the coupling, although it obviously “travels” along nearest-neighbor bonds, only exists for adjacent sites occupied by

<table>
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<td>Unblocked-bond probability ( p )</td>
<td>Exchange-interaction coupling ((J/kT))</td>
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<td>Percolation threshold ( p_c )</td>
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magnetic ions. If two spins occupy nearest-neighbor sites, their coupling, at zero temperature, is certain. From this discussion, the composition-dependent magnetization $M(p)$ would be expected to mimic $P(p)$. Evidence for this general behavior has been found in some ferromagnetic alloys, although usually not simple $A_pB_{1-p}$ binaries as assumed here. Note that the critical concentration depends only on the lattice and on the assumption of nearest-neighbor-only coupling. The same result obtains in the Heisenberg model as in the Ising model for ferromagnetism $[-JS(i) \cdot S(j)$ for the coupling, instead of $-JS_x(i)S_x(j)$], for spin greater than $\frac{1}{2}$, and even for dilute antiferromagnets ($J < 0$).

The above connection between models for dilute magnets at $T = 0$ and the percolation model is quite close. There exists another connection, not quite as close but much more significant, between percolation and the thermodynamic paramagnetic/ferromagnetic transition at finite temperature. This analogy is important because it connects percolation theory to a vast body of theory that has been developed for thermal phase transitions and critical phenomena. The magnetic case is the prototype of a second-order thermodynamic transition, and some key elements of the analogy to percolation are indicated in Table 4.2.

In the dilute-magnet case, we were concerned with the behavior of the system as we varied the composition ($p$) at fixed temperature ($T = 0$). Now we are interested in varying the temperature for a system of fixed composition ($p = 1$, the pure ferromagnet). At zero temperature, the parallel alignment of adjacent spins is mandated by the nearest-neighbor exchange coupling. When we "turn on" temperature to a finite value, parallel alignment of adjacent spins is no longer fully obligatory because the nonvanishing Boltzmann factor $\exp(-J/kT)$ permits the occurrence of low-energy configurations in which a few spins are flipped. Eventually, at very high temperature ($kT \gg J$), adjacent spins decouple completely as the Boltzmann factor approaches unity and the exchange-induced bias in favor of parallel spins disappears. In between, at a critical temperature $T_c$, which is of order $J/k$, the solid ceases to be a ferromagnet.

The situation described in the previous paragraph resembles a bond-percolation process, with temperature playing the part (as the agent active in bond scission) of the "little man with the shears" in Fig. 4.1. The "fluid" flowing along the bonds is the control or influence exerted by the alignment of one spin on that of its neighbor. At $T = 0$ this control is complete; at $T \to \infty$, it is nonexistent. In order for any spin to have a chance of propagating information about its alignment over a macroscopic distance (i.e., belong to the infinite cluster, or macroscopic magnetization), the "influence" must, in some sense, exceed the bond-percolation threshold. As indicated in Table 4.2, the dimensionless ratio which plays a role analogous to that of $p$ is $(J/kT)$, which is a measure of the exchange-interaction coupling between neighboring spins. The bond-probability/coupling-constant analogy is made closer by considering, instead of $(J/kT)$, a function of this ratio such as the complement of the Boltzmann factor: $1 - \exp(-J/kT)$. Such a form for the coupling strength
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4.5 CLOSE TO THRESHOLD: CRITICAL EXPONENTS, SCALING, AND FRACTALS

Of the four percolation functions that have been exhibited in Fig. 4.5 for the case of bond percolation on the two-dimensional square lattice, the two which

goes from unity at \( T = 0 \) to zero at \( T \to \infty \), making the correspondence to \( p \) closer.

While the connection between site percolation and the variable-composition magnetic alloy case of Fig. 4.6b is really quite close, the analogy between bond percolation and the thermodynamic ferromagnetic/paramagnetic transition is looser. This will be evident when the critical exponents for percolation and magnetism are compared in the next section; they are not the same. Nevertheless, the correspondences indicated in Table 4.2 provide an invaluable mapping of the percolation model onto the classic model of a continuous (second-order) phase transition. Many readers already familiar with the magnetic case can use Table 4.2 to ease this introduction to percolation theory. For others, a left-to-right reading of the table may be of interest, because magnetism is more subtle than the inherently geometric percolation model. As stated at the outset of this chapter, percolation provides a reasonably painless introduction to the field of phase transitions and critical phenomena.

The first three correspondences listed in Table 4.2 have already been discussed, and most of the others will be discussed in the following section. Because it allows us to hark back to a structural aspect of the percolation transition which was noted earlier in connection with Fig. 4.1, we close the present section with an explanation of the next-to-last entry in Table 4.2. The analogy pointed out here also connects the paramagnet/ferromagnet transition to the insulator/metal transition that occurs so frequently, in different guises, in Table 4.1 as an intuitively natural application of percolation. In discussing Fig. 4.1, we observed that the same dilution at which the mesh screen ceased to function electrically as a macroscopically conducting network, it also ceased to function elastically (it fell apart). Indeed, this indicated connection between electrical conductance and elastic stiffness is demonstrated in Table 4.2 for a magnetic counterpart of mechanical rigidity, the “exchange stiffness” \( A \). \( A \) is essentially a magnetic elastic constant; it is a measure of the stiffness of the direction of the magnetization \( M \) against tilt away from its stable direction. This magnetic stiffness coefficient is the analog, in the magnetic case, of the resistor-network conductivity in percolation. The analogy between conductance and spin-tilt stiffness, stated here simply as a plausible pronouncement in view of the simultaneous disappearance of electricity and rigidity in the gedanken scenario of Fig. 4.1, can be justified mathematically by a one-to-one correspondence in form between Kirchhoff’s laws for the voltage drops in the resistor-network case and the equations governing spin directions in the magnetic case. An analogy to an actual elastic stiffness will appear in Section 4.6 in connection with polymer gels.
have been discussed thus far, the percolation probability \( P(p) \) and the resistor-network conductivity \( \sigma(p) \), are functions which take off from zero at the percolation threshold \( p_c \), and which then grow monotonically to a finite maximum value at \( p = 1 \). Both \( P \) and \( \sigma \) vanish throughout the low-density regime \( 0 < p < p_c \). The other two functions shown in the figure behave in an entirely different way. For them the region of primary interest is below \( p_c \), where they provide advance warning of the impending event. Both are finite at \( p = 0 \), grow monotonically and with increasing slope as \( p \) increases, and increase without bound as \( p \) approaches \( p_c \).

The two quantities which diverge as the density draws near to \( p_c \) are the mean cluster size \( s_{av}(p) \) and the mean spanning length \( l_{av}(p) \). \( s_{av} \) was defined earlier, via Eq. (4.1), in Section 4.3. It starts out at \( s_{av}(p \approx 0) = 1 \) in the singlet-dominated low-density limit, grows as \( p \) increases, becomes very large as \( p \rightarrow p_c \) as very large clusters form, and finally becomes infinite at \( p = p_c \) with the emergence of the infinite cluster.

Whereas \( s \), the number of connected sites or bonds, provides the natural measure of the content or volume or "mass" of a given cluster, \( l \) (as yet undefined) provides a measure of the cluster's characteristic linear dimension. \( l \) and \( s \) are separate and distinct attributes. Most notably, because of the subtlety and complexity of the question of cluster shape for the large clusters that occur close to threshold, we shall find that the conventionally expected relationship \( s \sim l^d \) (\( d \) is the spatial dimensionality) does not hold as \( l, s \rightarrow \infty \).

There are several possible choices for the characteristic length, such as the average or the rms distance from the center of gravity of the cluster. Since they are all essentially equivalent (same order of magnitude, same scaling behavior), it is simplest to take \( l \) to be the spanning diameter or spanning length of the cluster. The spanning length is defined as the maximum separation of two sites (or bond centers, for bond percolation) in the cluster:

\[
l = \max \{|r_i - r_j| \}_{i,j \text{ in cluster}}.
\]

(4.2)

For a given \( p \), the characteristic length obtained by averaging \( l \) over all clusters is the mean spanning length \( l_{av}(p) \). This quantity plays a part, in percolation, analogous to that played by the correlation length \( \xi \) in phase transitions. Both provide length scales which correspond to the graininess of the system. This graininess, very fine far away from the percolation threshold or phase transition, coarsens dramatically as the transition is approached.

In a magnetic phase transition, the function whose characteristic length is specified by \( \xi \) is the spin-spin correlation function. The corresponding function in percolation theory, for which \( l_{av} \) sets the scale, is the pair connectedness \( g(r) \). \( g(r) \) is the probability that two sites \( i \) and \( j \), separated by the distance \( r = |r_i - r_j| \), belong to the same cluster. From what we know thus far, we may immediately deduce the asymptotic limit for \( g(r) \) as \( r \rightarrow \infty \). If the concentration of filled sites is less than the percolation threshold, then the asymptotic value \( g(\infty) \) is zero since all clusters are finite, and there is no chance whatever of two infinitely separated sites being connected. But if the concentration exceeds \( p_c \), a
pair of widely separated sites will be connected to each other if both of them belong to the infinite cluster. Since both must belong, the \( r \to \infty \) limit of \( g(r) \) must be the square of the percolation probability \( P \):

\[
\lim_{r \to \infty} g(r) = [P(p)]^2. \tag{4.3}
\]

While the above relation follows directly (i.e., is "derived") from the definitions of \( g(r) \) and \( P(p) \), the following statement appeals to higher authority. Like many other statements presented in this chapter about the behavior of various functions which describe percolation, it is asserted as an experimental fact! (The experiments referred to are, for the most part, Monte Carlo simulations of site or bond percolation on various lattices in two and three dimensions. In addition to such computer experiments, some more traditional laboratory experiments have been carried out for both site and bond versions of random resistor networks.) The approach of \( g(r) \) to its limiting value at large \( r \) occurs exponentially, with a characteristic decay length \( l_0 \), which differs from \( l_{av} \) only by a numerical factor of order unity:

\[
r \to \infty : \quad g(r) - [P(p)]^2 \sim \exp(-r/l_0). \tag{4.4}
\]

Although the asymptotic behavior expressed in Eq. (4.4) should be regarded, along with many of the other mathematical relations discussed for percolation, as empirically established, and although it is really extremely dangerous to attempt to generalize from behavior in one dimension, it is nevertheless instructive to reproduce a simple argument for 1d which was noted by Kirkpatrick (1979). For a 1d chain in which unblocked bonds occur with probability \( p \), the probability \( g(r) \) that two sites separated by distance \( r \) (with \( r = na \), where \( a \) is the lattice constant and \( n \) is the number of bonds) are connected is just \( p^n \). Hence \( g(r) \) can be written as \( p^{(r/a)} \), which in turn is \( \exp[(r/a) \ln p] \), which in turn is \( \exp(-r/l_0) \) with the decay length \( l_0 \) given by \( a/(\ln p) \). In 1d, \( g(r) \) decays exponentially, not only for large \( r \) (as in \( d > 1 \)), but for all \( r \). It also asymptotes to zero for all \( p \), since \( p_c = 1 \). Note that \( l_0 \to \infty \) as \( p \to p_c \). This important aspect of the 1d behavior is also true in higher dimensions; the correlation length diverges as the percolation threshold is approached [as shown for \( l_{av}(p) \) in Fig. 4.5].

The below-threshold regime of the asymptotic form of the pair connectedness, as contained in Eq. (4.4), is important enough to warrant a mild redundancy in the form of a separate, explicit equation:

\[
p < p_c, \quad r \to \infty : \quad g(r) \sim \exp(-r/l_0). \tag{4.5}
\]

As discussed in the previous paragraph and displayed in Fig. 4.5, the decay length \( l_0 \) (\( \approx \) the mean cluster-spanning length \( l_{av} \)) depends sensitively on density. The significance of Eq. (4.5) is the association between localization \( (p < p_c, \text{ all clusters finite}) \) and a spatial dependence showing an exponential fall off at large distances. These two concepts will prove to be essentially synonymous, as will be seen in the discussion of disorder-induced localization of electron wave functions.
The preceding discussion of $l_{\text{av}}$ and $g(r)$ presents some parallelisms to features that appeared previously in connection with glass structure. The pair connectedness in percolation processes resembles the pair-correlation function [which we have usually called the radial distribution function RDF$(r)$] that is used to characterize the structure of amorphous solids. Specifically, $g(r)$ is analogous to the reduced radial distribution function $G(r) = 4\pi r [n(r) - n_0]$, which was shown in Fig. 2.22 for the case of a metallic glass. Both $g(r)$ and $G(r)$ damp out beyond a characteristic distance. (For $g(r)$, the characteristic radius is a measure of the typical linear dimension of a cluster ($\approx l_{\text{av}}$). For $G(r)$, it is a measure of the range of the short-range order.

A connection with polymer structure also presents itself. The mean spanning length $l_{\text{av}}$ plays the part for percolation clusters which $R_{\text{rms}}$, the configuration-averaged end-to-end length, plays for polymers and self-avoiding walks. Later on in this section, the percolation/polymer comparison will be analyzed in terms of the asymptotic scaling behavior and fractal dimensionalities of percolation clusters and polymer coils.

Although other characteristic functions for percolation can be introduced, the four displayed in Fig. 4.5 are probably the most basic. They suffice to illustrate the main features. Two of the functions, $s_{\text{av}}(p)$ and $l_{\text{av}}(p)$, describe geometric aspects of the growth of the clusters below the percolation threshold. These quantities are finite below $p_c$ and infinite above $p_c$. They may be regarded as being complementary to the quantities $P(p)$ and $\sigma(p)$, which vanish below $p_c$ and are finite above $p_c$. $P$ and $\sigma$ describe different measures of the filling out of the percolation path above threshold.

It should be noted that, although $s_{\text{av}}$ and $l_{\text{av}}$ as defined here (averaged over all clusters) remain infinite above $p_c$ because of the presence of the infinite cluster, they are sometimes defined to exclude the latter. Above $p_c$ they then characterize the finite clusters which coexist with the infinite one, falling off sharply from $p = p_c$ to $p = 1$ in a way which is roughly a mirror image of their behavior between 0 and $p_c$. Near $p = 1$, this definition of $s_{\text{av}}$ and $l_{\text{av}}$ describes the geometry of the holes or "pores" in the "sponge" formed by the extended cluster. This version of $s_{\text{av}}$ and $l_{\text{av}}$ (which lacks the nice "complementarity" aspect, noted above, vis-à-vis $P$ and $\sigma$) will not be considered further. Our attitude is that the main value of $s_{\text{av}}$ and $l_{\text{av}}$ resides in what they tell us about the localization of the clusters below $p_c$. Once the percolation path appears, it absorbs our interest. Our attention then shifts to $P$ and $\sigma$, which describe the macroscopically extended (delocalized) cluster.

We now focus down on the important region very close to the percolation threshold, the critical region in which $|p - p_c| \ll 1$. In this regime, the percolation functions are observed to obey power-law dependences on the distance-from-threshold $p - p_c$. For the divergence of the average size and linear dimension of the clusters as $p_c$ is approached from below,

$$\left(p_c - p\right) \to 0: \quad s_{\text{av}} \sim \frac{1}{(p_c - p)^\gamma} ,$$  \hspace{1cm} (4.6)
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\[ l_{av} \sim \frac{1}{(p_c - \rho)^\tau} \]  

(4.7)

For the initial increase in the content and conductivity of the percolation path,

\[(p - p_c) \to 0: \quad P \sim (p - p_c)^\beta, \]  

(4.8)

\[ \sigma \sim (p - p_c)^t \]  

(4.9)

In Eqs. (4.6)-(4.9), the exponents \( \gamma, \nu, \beta, \) and \( t \) are found to be, for lattices in two and three dimensions, positive numbers that are \textit{not} integers. The experimentally observed exponents are presented in Table 4.3.

Now as we will find in the following section, the percolation threshold \( p_c \) is a quantity which varies greatly from lattice to lattice. (To quote a three-dimensional demonstration of \( p_c \)’s variability, the critical concentration for site percolation on the diamond lattice is more than double that for the fcc lattice.) The remarkable feature of the power-law dependences of Eqs (4.6)-(4.9) is that \textit{these exponents do not depend on the details of lattice geometry, they are the same for all lattices of the same dimensionality.}

Called critical exponents because they govern the scaling behavior (power-law dependences) in the critical region, these quantities are examples of \textit{dimensional invariants}. Each exponent has a fixed value for a given dimensionality \( d \), without regard to the specific nature of the short-range structure. The values for lattices in two and in three dimensions are shown in Table 4.3 in the columns headed \( d = 2 \) and \( d = 3 \), respectively. The column headed \( d \geq 6 \) has a special significance which is mentioned at the end of this section.

\begin{table}[h]
\centering
\caption{Critical exponents controlling the near-threshold scaling behavior of key quantities in percolation$^a$}
\begin{tabular}{llll}
\hline
Functional Form close to \( p = p_c \) & Exponent & \( d = 2 \) & \( d = 3 \) & \( d \geq 6 \) \\
\hline
\( P(p) \sim (p - p_c)^\beta \) & \( \beta \) & 0.14 & 0.40 & 1 \\
\hline
\( \sigma(p) \sim (p - p_c)^t \) & \( t \) & 1.1 & 1.65 & 3 \\
\hline
\( s_{av}(p) \sim (p_c - p)^{-\gamma} \) & \( \gamma \) & 2.4 & 1.7 & 1 \\
\hline
\( l_{av}(p) \sim (p_c - p)^{-\nu} \) & \( \nu \) & 1.35 & 0.85 & \( \frac{3}{2} \) \\
\hline
\( s \to \infty: n(s) \sim s^{-\tau} \) & \( \tau \) & 2.06 & 2.2 & \( 2\frac{1}{2} \) \\
\hline
\( s \to \infty: l(s) \sim s^{(1/\nu)} \) & \( f \) & 1.9 & 2.6 & 4 \\
\hline
\hline
Magnetism & & & & \\
\hline
\( M(T) \sim (T_c - T)^\beta \) & \( \beta \) & 0.125 & 0.32 & \( \frac{3}{2} \) \\
\hline
\( \partial M/\partial H \sim (T - T_c)^{-\gamma} \) & \( \gamma \) & 1.75 & 1.24 & 1 \\
\hline
\( \xi(T) \sim (T - T_c)^{-\nu} \) & \( \nu \) & 1.0 & 0.63 & \( \frac{3}{2} \) \\
\hline
\end{tabular}
\end{table}

$^a$For three exponents, the analogies to the corresponding quantities in magnetism are shown in the lower part of the table.
The impressive generality of the critical exponents has been given an impressive name in the field of phase transitions, in which such exponents have long been known and appreciated. It is called "universality." The Greek symbols used for the percolation exponents have been chosen to correspond to those which have become traditional for phase transitions. For example, the exponent $\nu$, which describes the near-threshold divergence of the mean cluster diameter, is named in correspondence with the exponent that describes the divergence of the correlation length near a second-order transition. Magnetic analogies for $\beta$, $\gamma$, and $\nu$ are indicated in the last three rows of Table 4.3. The analogies for the correlation-length exponent $\nu$ and the order-parameter exponent $\beta$ are straightforward, but the correspondence of the cluster-size exponent $\gamma$ to the exponent which describes the response function (susceptibility $\partial M/\partial H$) of the magnetic system is more subtle and will not be discussed here.

No distinction between site percolation and bond percolation has been made in the table. This is a further tribute to the generality of the critical exponents: For the same dimensionality, they are observed to be the same for bond processes as for site processes. In the jargon of phase transitions, site percolation and bond percolation are said to belong to the same "universality class."

In Eqs. (4.6)-(4.9), the exponents have been defined, for convenience as well as for concordance with tradition, so that their values are all positive numbers. Of course, exponents which describe properties that diverge as a function of the distance-to-threshold $|p - p_c|$, such as $s_{av}$ and $l_{av}$, are inherently negative, while those which describe properties that grow from zero upon passing threshold (e.g., $P$, $\sigma$) are inherently positive. With respect to the latter two, the numerical magnitude of the exponent has an important bearing on the qualitative behavior near threshold. It is quite noticeable, in Fig. 4.5, that $P(p)$ and $\sigma(p)$ begin their growth in completely different ways. While the ascent of $P(p)$ is extremely steep, that of $\sigma(p)$ is extremely gentle. More precisely, at $p_c$, $P(p)$ starts out with infinite slope while $\sigma(p)$ starts out with zero slope. Both features follow from the form of Eqs. (4.8) and (4.9) and from the fact (Table 4.3) that $\beta < 1$ while $t > 1$. Note that the behavior of the percolation probability is that expected for an order parameter in a second-order phase transition: at $p_c$, $P(p)$ is continuous while $dP/dp$ is discontinuous.

The exponent $\tau$, defined and tabulated in the fifth row of Table 4.3, is a bit different from those which have been discussed thus far. Instead of describing the asymptotic behavior of some function as $|p - p_c| \to 0$, $\tau$ describes the behavior, at $p = p_c$, of the cluster-size distribution in the asymptotic limit of large cluster size,

$$ p = p_c, \quad s \to \infty : \quad n(s) \sim s^{-\tau}. \quad (4.10) $$

We introduce this exponent because it will allow us to make contact with the concept of fractal dimensions in the context of the percolation model, as we have done earlier in the context of random walks and polymer structure.

Before going ahead with the discussion of Eq. (4.10), we must take care to emphasize that this relatively gradual power-law falloff in $n(s)$ appears only at
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$p_c$. Throughout the entire range below threshold, for each value of $p$ the large-$s$ falloff in $n(s)$ is much more rapid:

$$p < p_c, \quad s \to \infty: \quad n(s) \sim \exp[-\text{const.} \times s]. \quad (4.11)$$

This exponential decay of the frequency of occurrence as a function of cluster size is the asymptotic behavior appropriate to a regime in which localization (all clusters finite) applies, and was met previously in Eq. (4.5) for the pair connectedness. The constant in Eq. (4.11) is fixed for fixed $p$, but clearly changes when $p$ changes. Incidentally, the pair connectedness $g(r)$ also exhibits a property analogous to Eq. (4.10): Right at $p_c$, with the correlation length $l_0$ of Eq. (4.5) having gone out of sight, $g(r)$ has a power-law decay at large $r$ with its own characteristic exponent (which will go, mercifully, unmentioned; it is all too easy to let these exponents proliferate!).

The exponent $\tau$ must be a number lying between 2 and 3. To see this, look at the sums in the denominator and numerator of Eq. (4.1). The contribution of large clusters to these sums may be replaced by an integral from $s_0$ to infinity, where $s_0$ is a cluster size large enough for the asymptotic form given by Eq. (4.10) to be accurately obeyed for $s > s_0$. The large-cluster contribution to $\Sigma n(s)$ is then $\int_{s_0}^{\infty} n(s)ds$, which is proportional to $\int_{s_0}^{\infty} s^{-\tau+1} ds$. This integral must be finite, because $\Sigma n(s)$ is equal to $p$ (here, actually, $p_c$, since we are discussing the situation at the critical concentration). For this integral to be finite, it is necessary that $\tau > 2$. In similar fashion, the condition $\tau < 3$ can be derived from the form of the integral that measures the large-cluster contribution to the numerator of Eq. (4.1), taken together with the knowledge that $s_{av}$ diverges at $p_c$.

Enter now the sixth, and last, of the critical exponents which we will discuss for the percolation model. This one is especially interesting because it says something about the wild and peculiar geometry of the infinite cluster when it makes its debut at $p_c$. To appreciate the need for such a measure of the special geometric character of the percolation path, we may pause to look at the large cluster shown in Fig. 4.7.

This figure displays a typical cluster observed in a careful computer study (Leath and Reich, 1978) of site percolation of the 2d triangular lattice. The concentration of filled sites is $p = 0.48$, just below threshold ($p_c = 1/2$), and this particular cluster contains $s = 4741$ filled sites (shown as solid dots). Also shown in the figure (as open circles) are the surrounding empty sites which block continuation of the cluster. The blocking sites are said to form the boundary, and the number of empty sites comprising it is denoted by $t$. (This usage will appear only in this paragraph and the next, so there should be no confusion with the conductivity exponent $t$.) For this cluster, $t = 5102$.

Now we normally ("normality" being defined, geometrically, by Euclid) think of a $d$-dimensional object as being bounded by a $(d - 1)$-dimensional surface, and we normally expect the surface/volume ratio to go to zero as the size of the object goes to infinity. This does not happen for percolation clusters near threshold. Let us look at the ratio $t/s$ which, for want of a better alternative, we
Figure 4.7 A large cluster observed just below the percolation threshold by Leath and Reich (1978) in a computer study of site percolation on the triangular lattice. The dots are filled sites belonging to the cluster, while the open circles are the blocking open sites at the boundary.
4.5 CRITICAL EXACTNENTS, SCALING, AND FRACTALS

take to be the surface/volume ratio for a cluster. For the sizable cluster of Fig. 4.7, this ratio is not small; \( t \) is actually larger than \( s \). As \( s \) increases, \( t/s \) is found to approach a limiting value of order unity, and indeed it can be rigorously shown that \( \lim_{s \to \infty} (t/s) \) is exactly given by \( (1 - p_c) p_c \). (This ratio happens to be exactly unity for site percolation on the triangular lattice, which explains why \( t = s \) for the example shown in Fig. 4.7.) Thus the surface-to-volume relationship for large clusters is an unexpected one. To quote Mandelbrot (1977), these quantitative observations bear out the qualitative appearance of the large clusters as being "all skin and no flesh."

Although symptomatic of something unusual about the dimensionality of the large clusters, the property described above is, by itself, inconclusive. After all, Swiss cheese is a familiar example of an entity for which the surface area (of the internal voids) is proportional to the volume of the sample. Another three-dimensional example, more apt in relation to near-threshold percolation, is that of a sponge. More meaningful is the demonstration of a fractal dimensionality, different from the space dimensionality, for the very large clusters. This demonstration follows.

It is borne out by experiment that for large clusters, the average relationship between the cluster size \( s \) and the spanning length \( l \) is well described by a power law,

\[
\rho = \rho_c, \quad s \to \infty: \quad s \sim l^d,
\]

or

\[
l(s) \sim s^{(d/f)}, \quad (4.12)
\]

Relation (4.12) links a length dimension \( l \) with a measure of content or volume \( s \), and the exponent that normally appears in such a relation [in the place where \( f \) appears in Eq. (4.12)] is the space dimensionality \( d \). But \( f \) (the sixth and final critical exponent to be identified here) does not coincide with \( d \) for large percolation clusters. Instead, it is found to be smaller than \( d \): \( f \) is approximately 1.9 in two dimensions, 2.6 in three dimensions.

From the definition of \( f \) in Eq. (4.12), and from the discussion of fractal dimensions given in Section 3.2.5, it is quite natural to interpret \( f \) as a fractal dimensionality which characterizes the very large clusters (and, thereby, the percolation path itself very close to \( p_c \)) which occur close to threshold. \( f \) provides a quantitative measure of a very interesting quality, evident in a glance at Fig. 4.7, which is possessed by the nearly percolating large clusters and which has already been briefly alluded to ("all skin and no flesh"). It is the feature that underlies the disparity between the content and the conductivity of the percolation path just above threshold (i.e., the \( P/\sigma \) dichotomy of Fig. 4.5, with \( \beta < 1 \) and \( t > 1 \)).

The key quality in question, a basic attribute of the large clusters, is their wispy, tenuous, insubstantial character. This quality evokes many nice adjectives, including (in addition to the three already mentioned): lacy, stringy, sparse, ragged, airy, rarefied, ramified, and ethereal. Many of these terms
have been applied to percolation clusters in the physics literature. Our favorites for this purpose are diaphonous and, especially, *gossamer*. Alas, physicists must eventually abandon verbal niceties for mathematical ones, and the fractal dimensionality $f$ is the quantity which captures the quality of flimsiness inherent in the large clusters near threshold. More aptly, it is the difference $d - f$, the amount by which the cluster fractal dimensionality falls short of the space dimensionality (and thereby fails to fill $d$-space), that provides the best measure of "gossameriness." It gives an answer to the question, How wispy is it? The dimensionality deficit $d - f$ is called by mathematicians the "Hausdorff codimension." For an ordinary, substantial, $d$-dimensional object (such as the percolation path away from the critical region, say $p - p_c > 0.05$), $f$ equals $d$ and the deficit vanishes.

There exists, and it is instructive to deduce it, a connection between $f$, the exponent governing the linear dimension $l(s)$ of large clusters of size $s$, and $\tau$, the exponent governing the frequency of occurrence $n(s)$ of such clusters. The following argument, much simpler than others used for this purpose, was first proposed by Harrison, Bishop, and Quinn (1978). The argument is phrased in a way to apply, in general fashion, to dimensionality $d$, an approach frequently adopted in this book.

Consider a large $d$-dimensional box of side $L$. For a cluster to span this box (reach from one face to the opposite one), it needs to be of size $s(L) - L$, for larger. The probability of finding such a cluster is proportional to

$$L^d \int_{s(L)}^{\infty} n(s) ds \sim L^d \left[ L^f \right]^{-\tau + 1} \sim L^d - f(\tau - 1).$$

(4.13)

The factor of $L^d$ in Eq. (4.13) is proportional to the total number of sites in the box. [Recall that $n(s)$ is a normalized quantity specifying the frequency of occurrence per site.] The integral is proportional to that portion of the cluster-size distribution corresponding to clusters larger than $s(L)$, the box-spanning size.

Now let $L$ go to infinity. Since Eq. (4.13) represents a probability and therefore is finite, the exponent of $L$ cannot be positive. Since we are at the percolation threshold (let us cheat slightly and assume that we are very slightly above $p_c$), we may expect the probability of occurrence of a spanning cluster to remain nonzero as $L \to \infty$. Hence the exponent is not negative. It must, therefore, be zero, and setting it to zero yields

$$f = \frac{d}{\tau - 1}$$

(4.14)

This is the desired connection between $f$ and $\tau$; it is seen to include the space dimensionality $d$. Since we have seen that $\tau$ is larger than 2, it follows that $f$ is smaller than $d$. 


4.5 CRITICAL EXPONENTS, SCALING, AND FRACTALS

A relation such as Eq. (4.14), which connects two critical exponents (here, \( f \) and \( \tau \)), is known as a scaling law. Similar scaling laws appear in percolation theory as in the theory of phase transitions (Stanley, 1980). One very important example of such an interdependence among exponents, the Josephson scaling law, will appear below [as Eq. (4.17)] in connection with the critical dimensionality \( d = 6 \) for percolation processes. Other scaling laws will not be explicitly mentioned, except to state, without proof, that they can be used to recast the result for \( f \) [Eq. (4.14)] in terms of the other exponents introduced earlier,

\[
\begin{align*}
f &= d - (\beta/\nu) \\
f &= \frac{d + (\gamma/\nu)}{2}
\end{align*}
\] (4.15) (4.16)

It is evident from Eqs. (4.14)-(4.16) that there are scaling laws in sufficient supply to ensure that only two of the critical exponents can be independently set.

Equation (4.15) is nice because it exhibits a remarkably simple result \((\beta/\nu)\) for the dimensionality deficit \( d - f \), our measure of the large-cluster wispiness at \( p_c \). Even more interesting is Eq. (4.16). First note that, from Table 4.3, the ratio \((\gamma/\nu)\) is rather insensitive to dimensionality—it stays close to 2. So Eq. (4.16) may be approximated by \( f = (d + 2)/2 \). This reminds us of something. Recall Eq. (3.14) for the exponent governing the characteristic radius \( (R_{\text{rms}} \sim N^p) \) of \( d \)-dimensional self-avoiding walks: \((1/\nu_{\text{SAW}}) = (d + 2)/3 \). The similarity suggests a connection, and there is one, since in Section 3.2.5 we saw that the fractal dimension for large SAWs is given by \((1/\nu_{\text{SAW}})\). Having noted this, it is then straightforward to proceed to write down the correspondences which form an attractive analogy between the properties of percolation clusters and of polymer configurations:

<table>
<thead>
<tr>
<th>Percolation</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic length scale</td>
<td>( l )</td>
</tr>
<tr>
<td>Characteristic size or &quot;volume&quot;</td>
<td>( s )</td>
</tr>
<tr>
<td>Asymptotic (scaling) regime</td>
<td>( s \to \infty )</td>
</tr>
</tbody>
</table>

Having arrived, via the unusual route of fractals, at the analogy between percolation and random flights, and having a partiality toward Cole Porter (1935, "Just One of Those Things"), the author cannot resist the temptation to compare the "gossamer wing" of Fig. 4.7 with the "fabulous flight" of Fig. 3.13. For a large near-threshold cluster in a percolation process occurring in two dimensions, the fractal dimension \( (f = 1.9) \) is intermediate between that of a Brownian-motion random flight \( (f = 2, \text{Fig. 3.13}) \) and that of a self-avoiding random flight on a 2d lattice \( (f = 4/3, \text{Fig. 3.16}) \).

We close this section by finally coming to grips with the mysterious fifth column of Table 4.3. This column, labeled \( d \geq 6 \), provides a bridge to a topic...
covered in the next section. The exponents listed here correspond to the critical exponents that appear in a mean-field theory for percolation, a theory which is the percolation counterpart of the Weiss molecular-field theory for ferromagnetism or the Flory-Fisher theory for polymer configurations. For percolation, mean-field theory corresponds to the theory of a cascade process on a Bethe lattice (these terms are defined in the next section). Now for phase transitions, it is known that there exists a *marginal dimensionality* $d^*$ such that the critical exponents take on their "classical" (mean field) values for $d \geq d^*$. Though the justification for this is beyond the scope of this book, a rough argument for its plausibility is contained in the observation that the higher the dimensionality, the larger is the number of neighbors with which each site is in touch, and thus the closer is its environment to an average (i.e., mean field) environment. Another way to say this: If $d$ is sufficiently large, then no essential mistake is made by assuming that *every site is an average site*. Conditions are such that spatial fluctuations are unimportant. [It is interesting to note that the coordination number $z_{cp}(d)$ for a close-packed lattice in $d$ dimensions is known up to $d = 8$. The number of nearest neighbors goes up much more rapidly than $d$: $z_{cp} = 2, 6, 12, 24, 40, 72, 126, 240$ for $d = 1$ through $d = 8$, respectively.] For magnetism, $d^* = 4$; in four or more dimensions the exponents are the mean-field ones given in the lower right of Table 4.3. The question arises: What is $d^*$ for percolation?

The answer to this was given by Toulouse in 1974, who reasoned that the Bethe-lattice values of the percolation exponents (see the next section) were indeed mean-field values, and to this added the observation that $d^*$ is the value of $d$ for which the Josephson scaling law is satisfied when $\beta, \gamma, \nu$ have their mean-field values ($1, 1, \frac{1}{2}$, respectively). The Josephson is a particularly important scaling law because it connects the key exponents and [like Eq. (4.14)] contains the dimensionality:

$$2\beta + \gamma = \nu d.$$  \hspace{1cm} (4.17)

Equation (4.17) is satisfied for $d \leq d^*$; it fails for $d > d^*$ where $\beta, \gamma, \nu$ retain their mean-field values, independent of dimensionality. Plugging these values into Eq. (4.17) yields $d^* = 6$ for percolation.

Toulouse quietly proposed $d^* = 6$ as a "nonimplausible conjecture" for the marginal dimensionality for percolation, and this nice idea was neatly confirmed by Kirkpatrick (1976) in a classic computer study of percolation in higher dimensions. The important part played in percolation theory by Monte Carlo computer calculations has already been emphasized several times; indeed, it can hardly be overemphasized. Dimensionalities higher than three present no special problems for such "computer experiments," that to say, no problems other than the usual ones of machine speed, memory, and, of course, cost. (Note that Kirkpatrick did this work at IBM, where these problems are less severe than elsewhere). By analyzing the observed near-threshold behavior for site percolation on simple cubic lattices in $d = 2$ through $d = 6,$
Kirkpatrick was able to show that the critical exponents do indeed attain their mean-field values at \( d = 6 \). This established the validity of a marginal dimensionality for percolation, \( d^* = 6 \), further strengthening the analogy to the theory of second-order phase transitions.

By this time, noninteger dimensionalities should be rather familiar objects; such generalizations, strange at first, are simply a matter of getting accustomed to. (Then, going perhaps too far in the other direction, they are taken for granted!) One of the most important uses of the concept of dimensionality as a continuous variable, in condensed matter physics, is as an expansion parameter in the theory of phase transitions. The basic idea, which invokes the marginal dimensionality discussed above, is a form of perturbation theory. A pioneering 1972 paper, by Wilson and Fisher, was called “Critical Exponents in 3.99 Dimensions.” For magnetic phase transitions, the question of critical exponents is a solved problem in \( d^* = 4 \) dimensions, where mean-field theory applies. If we are interested in \( d \) dimensions (say, \( d = 3 \)), the program is to obtain each quantity as a power-series expansion about the known \( (d = 4) \) regime, using \( (4 - d) \) as the expansion parameter. The technique used to calculate the expansion is called renormalization group theory (see Section 4.8), and the approximation works when \( (4 - d) \) is small.

This approach is sometimes referred to as the “epsilon expansion,” where epsilon refers to the parameter of smallness \( \epsilon = d^* - d \). It has been applied to percolation, for which \( \epsilon = 6 - d \). For percolation processes, physically realizable dimensionalities (\( d = 3 \) and \( d = 2 \)) are much further away from the “solved” dimensionality \( (d^* = 6) \) than is the case for magnetism \( (d^* = 4) \). This is the reason that the critical exponents for percolation in three and in two dimensions deviate much more markedly from their mean-field values (see Table 4.3) than do the corresponding exponents in magnetic phase transitions.

The unifying concept of universality was already mentioned. For the percolation critical exponents which have been introduced and collected in Table 4.3, namely \( \beta, \gamma, \nu, \tau \), and \( f \), universality means the applicability of the value of a given exponent to the near-threshold behavior of all site or bond percolation processes on all lattices of a given dimensionality. The scaling laws, the relationships between exponents, of which Eq. (4.17) is a beautiful example, are even more universal than the exponents themselves because they cut across different dimensionalities. The high degree of universality exhibited by the scaling laws is well exemplified by the validity (within experimental error) of Eq. (4.17) to all six sets of \( (\beta, \gamma, \nu, d) \) values contained in Table 4.3, both those for percolation and those for magnetism. This is so even though percolation and magnetism belong to different universality classes, have different values for the exponents.

From the height of generality epitomized by the Josephson scaling law of Eq. (4.17), we are about to proceed to the other extreme in a treatment of the position \( (p_c) \) of the critical point. The percolation threshold is a thoroughly nonuniversal, but enormously important, parameter of percolation phenomena,
and its dependence upon local structure is described in the next section. First, however, we show in Fig. 4.8 a diagram which is a fitting concluader for the present section.

The x axis in Fig. 4.8 is dimensionality $d$. Plotted against it are the values of critical exponents for percolation, as introduced in this section. (The quantity $\phi_c$ included in the figure is not an exponent, but a different type of dimensional invariant to be discussed in Section 4.7.) There are three main messages:

1. Each of the quantities plotted has a well-defined value for a given dimensionality (dimensional invariance, the universality aspect).
2. They show a quite systematic variation from $d = 2$ to $d = 6$. 

Figure 4.8  The dimensionality dependence of the critical exponents for percolation. The meaning of the exponents $\beta$, $\gamma$, $\nu$, $f$, and $t$ are given in Table 4.3; while $\phi_c$ is the critical volume fraction of Section 4.7.
3. For $d \geq 6$, mean-field theory is "exact" for the values of the percolation exponents.

The smooth curves that have been "eyeballed" through the experimental points are given in the spirit of the notion of dimensionality as a continuous variable.

### 4.6 TREES, GELS, AND MEAN FIELDS

Figure 4.9 displays four of the most basic two-dimensional lattices, the triangular, square, kagomé, and honeycomb lattices, along with their respective percolation thresholds. (The fifth structure illustrated, part of a Bethe lattice, will be discussed shortly.) All of these are "regular" lattices, every site has the same coordination $z$ as every other site. They are also very symmetric structures, every site (or bond) is equivalent to every other side (or bond). Because of the high symmetry and simplicity of these lattices, it has been possible to analytically derive exact values for thresholds in several cases. Those $p_c$ values that are known exactly are the ones given in Fig. 4.9 to four significant figures, namely, the critical concentrations for bond percolation on the triangular, square, and honeycomb lattices, and for site percolation on the triangular and kagomé lattices. Two of the five numerical values so quoted correspond simply to $p_c = \frac{1}{2}$, a third corresponds to the solution of $3p_c - p_c^2 = 1$, and the other two correspond to the complement ($p_c = 1 - p_c$) of the latter solution.

The detailed arguments that are used to deduce the above exact values will not be given here, since they cannot be extended to less symmetric lattices. Also, no exact results for $p_c$ are known for lattices in three (or more) dimensions. However, the general type of reasoning involved in the derivations of $p_c$ for the four 2d lattices can be nicely illustrated by a pretty application to an electrical-network setting (Thouless, 1979). The basic idea exploited for the two-dimensional derivations is the notion of special relationships between pairs of lattices. The duality relationship between the triangular and the honeycomb lattices was illustrated earlier in Fig. 2-10; two lattices are duals of each other if (sites, bonds, cells) of one can be mapped in one-to-one correspondence to (cells, bonds, sites) of the other. The dual of a square lattice is another square lattice, and this self-duality property is the key to the argument now sketched.

Consider a resistor network arranged as a square lattice with the place of each bond being taken by a conductor with conductance equal to either zero (perfect insulator) or to one (normal metal) or to infinity (superconductor). (As discussed in Section 4.8, this three-species situation corresponds to a problem in polychromatic percolation.) For such a planar resistor network, a dual resistor network may be constructed by replacing each bond conductance by the intersecting bond of the dual lattice, with the new conductance having a value given by the reciprocal of the old. This transformation converts the original lattice into its dual and transforms electrical elements so that insulators be-
Figure 4.9 Four two-dimensional lattices and their percolation thresholds. Also shown is the threefold-coordinated Bethe lattice, whose dimensionality is effectively infinite.
come superconductors, superconductors become insulators, and unit conductors become unit conductors. It can be shown (Straley, 1977) that the conductivity of the dual network is the reciprocal of that of the original network. Suppose a square-lattice random-resistor network has unit conductors present with probability \( p \) and both insulators and superconductors present with equal probability \( \frac{1}{2}(1 - p) \). Since the square lattice is self-dual and since the composition in terms of electrical elements is unchanged, the transformed network is macroscopically indistinguishable from the original one. Since its conductivity equals the reciprocal of that of the original network, it therefore follows that the network described has unit conductance.

Turn back briefly to glance at Fig. 4.1. It happens that the square lattice was used to illustrate the resistor network under siege by the little man with the shears. That little man is, of course, in the process of effectively replacing unit conductors by insulators, thereby reducing the conductivity of the network. What has just been demonstrated is that the influence of the shearer (on the conductivity of the system) may be exactly neutralized by a second little man who randomly replaces unit conductors by superconductors at the same rate as the shearer replaces other conductors by insulators.

Having broached the idea of a random network containing superconducting links, we should briefly note that the conductivity-versus-composition curve of a network composed of normal conductors and superconductors would resemble, not the \( \sigma(p) \) curve of Fig. 4.5, but instead the \( s_{av}(p) \) and \( l_{av}(p) \) curves. Starting out with finite conductivity when all links are normal (\( p = 0 \)), the conductivity increases when some links are made superconducting (\( p > 0 \)), and becomes infinite when the superconducting fraction exceeds \( p_c \) and the superconducting links percolate. Moreover, the reciprocity theorem mentioned above for dual pairs of electrical networks provides an immediate result for the critical exponent describing the divergence of the conductivity of such a normal/superconductor resistor network as \( p_c \) is approached: At least in two dimensions, that exponent must be \( -t \).

An inventory of lattices for which \( p_c \) values are known is given in Table 4.4. The threshold concentrations for bond percolation and for site percolation are shown in the third and fourth columns of the table. The main message evident from a glance at these data is the large variation from lattice to lattice, the sensitivity of \( p_c \) to local structure. For the two-dimensional lattices listed, the \( p_c \) values extend from 0.35 to 0.70; for the three-dimensional lattices, \( p_c \) spans the range from 0.12 to 0.43. As emphasized earlier, the percolation threshold is by no means a dimensional invariant.

Systematic behavior is quite discernible in the table. The coordination number \( z \) is included in the table as a measure of lattice connectivity, and it is easy to see the correlation between increasing connectivity and decreasing \( p_c \). The more highly connected a lattice is, the lower is the concentration of filled sites (or unblocked bonds) needed for the formation of the infinite cluster. Similarly, because lattices in higher dimensions are more highly connected than those in lower dimensions, the trend is to decreasing \( p_c \) with increasing \( d \).
Table 4.4 Critical concentrations for bond ($p_c^{\text{bond}}$) and site ($p_c^{\text{site}}$) percolation on a variety of lattices.\(^a\)

<table>
<thead>
<tr>
<th>Dimensionality $d$</th>
<th>Lattice or Structure</th>
<th>$p_c^{\text{bond}}$</th>
<th>$p_c^{\text{site}}$</th>
<th>Coordination $z$</th>
<th>Filling Factor $v$</th>
<th>$z v p_c^{\text{bond}}$</th>
<th>$v p_c^{\text{site}} = \phi_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chain</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Triangular</td>
<td>0.3473</td>
<td>0.5000</td>
<td>6</td>
<td>0.9069</td>
<td>2.08</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>Square</td>
<td>0.5000</td>
<td>0.593</td>
<td>4</td>
<td>0.7854</td>
<td>2.00</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>Kagomé</td>
<td>0.45</td>
<td>0.6527</td>
<td>4</td>
<td>0.6802</td>
<td>1.80</td>
<td>0.44</td>
</tr>
<tr>
<td>2</td>
<td>Honeycomb</td>
<td>0.6527</td>
<td>0.698</td>
<td>3</td>
<td>0.6046</td>
<td>1.96</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>fcc</td>
<td>0.119</td>
<td>0.198</td>
<td>12</td>
<td>0.7405</td>
<td>1.43</td>
<td>0.147</td>
</tr>
<tr>
<td>3</td>
<td>bcc</td>
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<td>0.245</td>
<td>8</td>
<td>0.6802</td>
<td>1.43</td>
<td>0.167</td>
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<tr>
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<td>sc</td>
<td>0.247</td>
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<td>0.5236</td>
<td>1.48</td>
<td>0.163</td>
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<td>Diamond</td>
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<td>0.428</td>
<td>4</td>
<td>0.3401</td>
<td>1.55</td>
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<tr>
<td>3</td>
<td>rcp</td>
<td>[0.27](^b)</td>
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</tr>
<tr>
<td>4</td>
<td>sc</td>
<td>0.160</td>
<td>0.197</td>
<td>8</td>
<td>0.3084</td>
<td>1.3</td>
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<tr>
<td>4</td>
<td>fcc</td>
<td>0.098</td>
<td></td>
<td>24</td>
<td>0.6169</td>
<td>0.600</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>sc</td>
<td>0.118</td>
<td>0.141</td>
<td>10</td>
<td>0.1645</td>
<td>1.2</td>
<td>0.023</td>
</tr>
<tr>
<td>5</td>
<td>fcc</td>
<td>0.054</td>
<td></td>
<td>40</td>
<td>0.4653</td>
<td></td>
<td>0.025</td>
</tr>
<tr>
<td>6</td>
<td>sc</td>
<td>0.094</td>
<td>0.107</td>
<td>12</td>
<td>0.0807</td>
<td>1.1</td>
<td>0.009</td>
</tr>
</tbody>
</table>

\(^a\)The last two columns indicate a pair of approximate dimensional invariants that are useful in unifying threshold data for different lattices.

\(^b\)Results of experiments of the type shown in Fig. 4.13.
Another point made by Table 4.4 is that bond percolation occurs more readily than site percolation; for a given lattice $p_{c}^{\text{bond}} < p_{c}^{\text{site}}$. One way to view the reason for this may be illustrated in terms of the square lattice shown in Fig. 4.9. While a site on this lattice is adjacent to four other sites, a bond is seen to touch six other bonds. In general, while a site has $z$ nearest-neighbor sites, a bond has $2(z - 1)$ nearest-neighbor bonds. In this way a given lattice presents a richer connectivity to a bond process than it does to a site process, which is why bond percolation is "easier" than site percolation.

The statement $p_{c}^{\text{bond}} < p_{c}^{\text{site}}$ is violated by the equality of the two thresholds given in the first row of Table 4.4, but this exception is not very interesting since the one-dimensional lattice (included in the table for completeness) lacks percolation anyway because $p_{c} = 1$. More significant is the $p_{c}^{\text{bond}} = p_{c}^{\text{site}}$ situation shown on the right of Fig. 4.9. This will now be discussed, but first a few comments about the other material contained in the table. The last row among the 3d entries refers to results obtained for the random close-packed lattice, and will be discussed in the next section (as will the rows for $d > 3$). The last three columns relate to efforts to find approximate dimensional invariants ("almost-invariants") related to the position of the percolation threshold, and are also discussed in Section 4.7.

The structure shown at the right of Fig. 4.9 represents a part of an infinite network of a type known as a Bethe lattice. The finite portion shown in the figure is an example of a Cayley tree, a graph containing no closed loops (= no cycles = no circuits). A Bethe lattice is defined as an infinite, regular, Cayley tree.

A Bethe lattice is not a lattice in a conventional sense. Obviously it is not periodic, but this lack is unimportant. The continuous random networks of Chapter Three are not periodic, but they are statistically well-defined lattices possessing the crucial property of being uniform in the large—macroscopically homogeneous. This physically essential property of macroscopic homogeneity is dispensed with by a Bethe lattice in spectacular fashion. The prohibition against closed loops enforces an endlessly increasing density as the structure is extended. The small portion of a $z = 3$ Bethe lattice that is shown in Fig. 4.9 in a two-dimensional setting already exhibits serious crowding at the boundary. (Among the criteria set down in Chapter Two for continuous random networks was the requirement that the surface density of dangling bonds remain constant as the lattice is extended. For a Bethe lattice that surface density is not merely inconstant, it grows without limit!)

The crowding problem can be alleviated, but it cannot be removed, by setting the Bethe lattice in a space of higher dimensions. A Bethe lattice in three dimensions also suffers from a density that diverges with size, as is nicely demonstrated by the drawing reproduced as Fig. 4.10. (The wintry plant represented in Marianne Lehmann's graceful ink drawing actually corresponds fairly well in structure to a $z = 3$ Cayley tree.) A given severity of crowding is reached at a larger sample size in three dimensions than in two, but the problem is only postponed, not eliminated. Similarly, in still higher dimensions the regions of unbearable density are pushed further out (delaying the Malthusian
catastrophe), but eventually the branching process overwhelms the available space. This property of unbounded density persists in a space of any finite dimensionality $d$, because the number of branches in a tree of radius $r$ grows exponentially with $r$, while the available space grows only as $r^d$. The mathematical statement is that a Bethe lattice "cannot be embedded in any finite-dimensional space."

The upshot of these considerations is that a Bethe lattice may legitimately be regarded as the equivalent of a conventional lattice in a space of infinite dimensionality. If this is so then it follows, using reasoning taken over from the theory of phase transitions and discussed in the previous section, that the percolation properties of such a lattice constitute the equivalent of mean-field behavior for percolation processes. It then becomes of interest to determine that behavior. Happily, it turns out that the absence of closed loops simplifies life so enormously (only one path connects any two points) that it is possible to derive explicit equations which determine $p_c$ and $P(p)$ for a Bethe lattice.

For all its apparent peculiarity, a Bethe lattice is actually the natural geometric framework for the description of some quite familiar phenomena (e.g., chain reactions, avalanche showers) which come under the heading of cascade processes. Realizing this permits us to write down the percolation threshold almost "by inspection." Think of a species in which each individual gives birth
during its lifetime to two offspring, each of which has a probability \( p \) of surviving long enough to undergo reproduction itself. If \( p \) is less than \( \frac{1}{2} \) the species is doomed, it faces certain extinction as the average number of offspring per parent \( (= 2p) \) is less than one. If \( p \) exceeds \( \frac{1}{2} \) the species should be viable; a single individual has a nonzero chance of producing an immortal dynasty. These statements solve for \( p_c \) on the \( z = 3 \) Bethe lattice. A living individual corresponds to an unblocked bond, and the number of surviving-to-reproduction offspring (0 or 1 or 2 in this case) corresponds to the number of unblocked bonds which appear at the next fork. An immortal dynasty corresponds to an infinite cluster. Essentially the same analogy applies to site percolation.

For a Bethe lattice with coordination \( z \), each fork presents \( z - 1 \) independent opportunities for continuation. (The continuations are completely independent because, once embarked upon, their paths never cross. This powerful simplification is not available for ordinary lattices, in which the presence of closed loops permits innumerable crossings.) For the average number of realized continuations per fork to exceed unity (the prerequisite for percolation), \((z - 1)p > 1\). This condition applies equally to bond processes and site processes. In general, therefore, \( p_c = 1/(z - 1) \) is the value of the percolation threshold on a \( z \)-coordinated Bethe lattice. A more formal (but less enlightening) demonstration of this result is contained in the following derivation for the full percolation probability \( P(p) \).

Assume that, following a path of unblocked bonds on a Bethe lattice with coordination \( z \), we arrive at a given vertex (site) and are faced with \( z - 1 \) new bonds, each of which initiates a branch. For a bond process on such a tree lattice, with \( p \) the fraction of bonds being unblocked, let \( R(p) \) denote the probability that a branch is restricted to a finite size (i.e., is a dead end). For a branch to be finite, either the first bond of the branch is blocked (which happens with probability \( 1 - p \)), or, if it is unblocked (probability \( p \)), then all of the \( z - 1 \) branches which lead out from the far end of the first bond must be dead-ended. But the probability of the latter event, \( z - 1 \) independent branches being finite, is \( R^{z-1} \). Therefore

\[
R = 1 - p + pR^{z-1}. \tag{4.18}
\]

Equation (4.18) determines \( R(p) \). It also determines \( p_c \) (for readers requiring a more mathematical argument than that already given). For \( p \) less than \( 1/(z - 1) \), \( R = 1 \) is the smallest positive root of Eq. (4.18). \( R = 1 \) means that there is no chance of finding a branch which is not finite, i.e., no percolation. For \( p \) larger than \( 1/(z - 1) \), Eq. (4.18) possesses a positive root smaller than unity, which permits percolation. Hence, \( (z - 1)^{-1} \) is confirmed as the percolation threshold.

We wish to know \( P(p) \), the probability that a randomly chosen bond belongs to an infinite cluster. For it to do so, the bond must be unblocked (probability \( p \)) and at least one of the branches that lead outward from the two ends of the bond must be infinite. Now there are \( 2(z - 1) \) outward-bound branches, and the chance of their all being blocked is simply \( R^{2z-2} \). Thus the probability
THE PERCOLATION MODEL

is \( 1 - R^{2z-2} \) that at least one branch is unblocked. Therefore the percolation probability is given by

\[
P(p) = p(1 - R^{2z-2}).
\]

(4.19)

Knowing \( R(p) \) from Eq. (4.18), we have determined \( P(p) \).

For concreteness, consider the simplest Bethe lattice, the \( z = 3 \) case illustrated in Fig. 4.9. [The \( z = 2 \) case corresponds to the linear chain, a nonpercolating situation with \( p_c = (z - 1)^{-1} = 1. \)] Equation (4.18) becomes a simple quadratic equation, which has the solution \( R = (1 - \rho)/\rho \) for \( \rho > p_c = \frac{1}{2} \). Substituting this for \( R \) in Eq. (4.19) yields for the percolation probability \( P = p(1 - R^4) = p[1 - (1 - \rho)^4 \rho^{-1}], \) for \( \rho > \frac{1}{2} \).

Note that, for the closed-form solution available for this example, \( P(p) \) rises from zero with finite slope at \( \rho = p_c \). This corresponds to \( \beta = 1 \) in \( P \sim (\rho - p_c)^\beta \). This result, which obtains in general for percolation on trees, constitutes the mean-field value for this exponent. It was the value entered in the \( d \geq 6 \) column of Table 4.3. The other entries in that column also represent results derived for these "infinite-dimensional" entities, Bethe lattices.

The analysis of site percolation on a Bethe lattice is quite similar. In fact the equation for the site analog of \( R \) is identical to Eq. (4.18) for the bond case, showing that \( p_c \) is indeed the same for site processes on a tree as for bond processes. However, the functional form of \( P(p) \) is different in the site case, because the site analog of Eq. (4.19) replaces the power \( 2z - 2 \) (the number of bonds adjacent to one bond) by \( z \) (the number of sites adjacent to one site). Thus the percolation probability for site percolation on, for example, the \( z = 3 \) tree is \( p[1 - (1 - \rho)^3 \rho^{-3}] \). Note that, throughout \( p_c < \rho < 1, \ P_{site}(\rho) < P_{bond}(\rho) \); though their percolation thresholds are equal, it remains true that bond percolation is "easier" than site percolation.

It is worthwhile to pause momentarily to take note of the structure of Eq. (4.18). When we set about the task of constructing an expression for the quantity \( R(p) \), which was done on route to a determination of the order parameter \( P(p) \), we found that the resulting expression—the right-hand side of Eq. (4.18)—itself contained \( R \). This self-consistent structure is characteristic of mean-field theories. Such an implicit equation [of which genre Eq. (4.18) is a very simple example] determines, for example, the Weiss molecular field in the mean-field theory of magnetic phase transitions.

Figure 4.11 portrays an idealized version of a class of physicochemical phenomena which provides a fine vehicle for the interplay of percolation ideas, most notably the competition between the percolation model and its mean-field (Bethe-lattice) counterpart with respect to suitability for the description of a subtle and complex experimental situation. It also represents an application of percolation ideas which anticipated, by about 15 years, Hammersley's explicit formulation of "the percolation problem." This historical aspect will be briefly described below.

When sodium metasilicate—\( \text{Na}_2\text{SiO}_3 \)—is dissolved in water (forming "waterglass"), the dissolution may be considered to proceed via the reaction
Na₂SiO₃ + 3H₂O ⇌ 2NaOH + H₄SiO₄. The second product, more appropriately written in the form Si(OH)₄, is called monosilicic acid and is a tetrahedral molecule consisting of a silicon atom bonded to four OH groups. For pictorial convenience, Si(OH)₄ tetrahedra are schematically represented in Fig. 4.11 as planar (square) units. In the solution, two molecules of monosilicic acid may combine to form a larger molecule represented at the upper right of Fig. 4.11. Two OH groups on nearby Si(OH)₄ molecules have reacted to form a Si—O—Si bridge, with the release of a water molecule. (No H₂O molecules are shown in Fig. 4.11; the aqueous solvent is simply understood to be present and to occupy the "empty space" which separates the silicic molecules shown.)

This polymerization reaction can continue, building up larger molecules as indicated in the figure. Each initial Si(OH)₄ "monomer" can form as many as four "reacted bonds," oxygen bridges to silicon atoms originating from other molecules. Although in actual fact the polymerization process is known to occur through the mediation of ionic variants of these species, and not through the simple combining of uncharged silicic acid molecules, the picture painted in Fig. 4.11 captures the essential feature of this condensation phenomenon. Because of the stability of the silicon–oxygen bond, we may view this particular condensation process as essentially irreversible: Once the Si—O—Si cross-links form, they remain.
What comes next has certainly been guessed by the reader. As the reaction goes on and more cross-links form, larger and larger molecules appear. Eventually, and abruptly, at a critical stage in the condensation process, an "infinitely extended" molecule appears, a huge molecule whose extent is limited only by the size of the vessel in which the reaction is taking place. The macroscopically extended 3d-network molecule is called the gel macromolecule, the process of its formation is called gelation, and its abrupt appearance is called the sol–gel transition or the gel point. The term sol applies to the solution containing only finite molecules, while the term gel applies to the system containing the extended network.

In the sol phase, only atomic-scale molecules are present, and the material is a quite conventional liquid. Its viscosity increases as the sol–gel transition is approached, and close to the transition this physical parameter goes through the roof (becomes unmeasurably large) as many physical properties change spectacularly. Above the transition, with the gel present, the system is no longer liquid. The material can now resist shear stresses, and it deforms elastically like an isotropic solid. The system is now neither a conventional solid nor a conventional liquid, since an extended and continuous solid component (the gel macromolecule) is microscopically coexistent with a liquid component (some sol remains and is intimately intermixed with the gel, above the sol–gel transition). This complexity makes it difficult to give a clear definition of a gel, a point which has been aptly described by Henisch (1970): "A gel, for instance, has been defined as a 'two-component system of a semisolid nature, rich in liquid,' and no one is likely to entertain illusions about the rigor of such a definition."

For us the essential point to keep in mind about a gel is that, despite its complexity, it clearly contains a solid component provided by the three-dimensional covalently bonded framework that comprises the gel macromolecule. Solidity is manifested by the appearance of mechanical rigidity at the gel point. The rigidity increases as cross-linking continues beyond that point. The material which results from the specific condensation reaction described above and illustrated in Fig. 4.11 is called silica hydrogel. With the solvent still present (a "swollen" gel) so that the material is mostly water, silica hydrogel is a soft solid easily cut with a knife. With the solvent largely removed (a "dry" gel), the material is a brittle solid which is the familiar desiccant known as silica gel.

Silica gel is an amorphous solid, a not-too-distant relative of fused silica. It differs from the SiO₂ crn structure of Section 2.4.5 in that not all oxygens are bridging (Si—O—Si) but many are dead-ended in hydroxyl groups (Si—OH). It is also evident that silica gel is much less dense than silica. It is very porous (a property important for the application of dry gels as catalysts), with pore sizes on the order of 20–100 Å in diameter. One way to visualize the structure of silica gel is as a kind of highly diluted, loosely connected, continuous random network. (A related material, in a sense intermediate between fused silica and silica gel, is Vycor glass, a porous glass formed by dissolving away the soluble phase of an initially two-phase borosilicate glass. The pores
in Vycor are coarser than in silica gel, and there is a sharper distinction between the “empty space” of the pores and the surrounding sponge of “bulk material”—which is close in structure to a standard, dense, SiO₂-type crn.)

One way to phrase the difference between the three-dimensional random network of silica gel and that of fused silica is in terms of their respective ring statistics. It is clear that, whatever the quantitative details, the low density and fine-grained microporosity of silica gel means that its network structure must be deficient in small rings relative to the network of SiO₂ glass.

A connection between percolation and the sol→gel transition was appreciated early on (Frisch and Hammersley, 1963), but was first analyzed in depth in a pair of independent 1976 papers by de Gennes and Stauffer. This connection is laid out in Table 4.5, which is reasonably self-explanatory.

<table>
<thead>
<tr>
<th>Percolation</th>
<th>Gelation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percolation threshold</td>
<td>Gel point</td>
</tr>
<tr>
<td>Connected (unblocked) bond</td>
<td>Formed crosslinking chemical bond</td>
</tr>
<tr>
<td>Bond-connectedness probability $p$</td>
<td>Fraction of formed crosslinks</td>
</tr>
<tr>
<td>Finite cluster</td>
<td>Sol molecule</td>
</tr>
<tr>
<td>Mean cluster size $s_{av}$</td>
<td>Average molecular weight</td>
</tr>
<tr>
<td>Infinite cluster</td>
<td>Gel macromolecule</td>
</tr>
<tr>
<td>Percolation probability $P$</td>
<td>Gel fraction $G$</td>
</tr>
<tr>
<td>Coordination number $z$</td>
<td>Functionality $z$</td>
</tr>
<tr>
<td>Resistor-network conductivity</td>
<td>Elastic shear modulus</td>
</tr>
<tr>
<td>Bethe-lattice approximation</td>
<td>Flory-Stockmayer theory</td>
</tr>
</tbody>
</table>

Flory–Stockmayer theory (henceforth, FS theory) is the standard theory used in physical chemistry to describe the sol→gel phase transition and the molecular size distributions which accompany it. It dates from a series of classic papers written by Flory in 1941 and Stockmayer in 1943. The basic assumption of the theory is that gelation may be modeled as a branching process; FS theory is essentially a theory of dendritic polymerization.
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Figure 4.12  Schematic of a trifunctionally branched molecule (after Flory, 1941).

Figure 4.12 is from the first of Flory's three 1941 papers. It shows the skeleton of a possible molecule formed by the condensation of "trifunctional monomers" ($z = 3$). We immediately recognize this as one of the many possible bond clusters on a $z = 3$ Bethe lattice (compare Fig. 4.12 to Fig. 4.9e). FS theory assumes that all molecules created by the reacting monomers have such a treelike form. Flory's formulation of the condensation reaction as a branching process, and his quest for a quantitative theory which would account for "the existence of a sharply-defined gel point...which occurs when a critical number of intermolecular linkages has been exceeded," led him to derive a key connection between the critical "extent of reaction" (at which gelation occurs) and the functionality $z$ of the reacting monomers. This key relation is, in effect, $p_c = 1/(z - 1)$; we have already met it as the value of the percolation threshold on a $z$-coordinated Bethe lattice. The Flory-Stockmayer theory of gelation is equivalent to the exact solution of the percolation problem on a Bethe lattice. Of course, percolation theory "was not around" in 1941. Yet gelation really provided the first application of percolation ideas to a phase transition, well in advance of the formal (and "official") introduction of the topic by Hammersley in 1956. Here is a good example of the physicist's/chemist's pragmatic invention of the mathematical machinery needed for the task at hand.

The correspondence between gelation and percolation seems irresistible. Consider the following quote: "We seek the answer to the question: Under what conditions is there a finite probability that an element of the structure, selected at random, occurs as part of an infinite network?" Evidently the question phrased here makes an inquiry about the percolation probability $P(p)$. But these lines are, in fact, from the beginning of the gelation chapter of Flory's 1953 classic on polymer chemistry!

FS theory is successful in several respects. It predicts a sharp gel point, as is observed experimentally, and the critical extent of reaction at which it occurs is given reasonably well by the FS value $p_c = 1/(z - 1)$. The very steep
viscosity increase just prior to the gel point is also naturally explained, because the weight-averaged molecular weight diverges here [for a Bethe lattice $s_{av} \sim (p_c - p)^{-1}$, as shown on the right of Table 4.3] and viscosity is known to be closely tied to average molecular weight. Measurements of viscosity as a function of extent of reaction yield results which resemble the $s_{av}(p)$ curve of Fig. 4.5.

But there is an obvious problem. We have seen that percolation theory developed for a Bethe lattice constitutes a mean-field theory which should not work in dimensionalities lower than six. One way to see the problem is to note the fractal dimensionality of four (for large clusters near $p_c$) listed for Bethe-lattice percolation on the right of Table 4.3. This has the interpretation $l(s) \sim s^{1/4}$ for the radius $l(s)$ of clusters of size $s$ as $s \to \infty$. In three dimensions, the average density of large clusters would then go as $(s/l^3) \sim s^{1/4}$, increasing without limit as $s$ increases! This unphysical result (the density “blows up” for large clusters) reflects the overcrowding problem inherent in a ring-free branching structure. Inevitable overcrowding was evident in Figs. 4.9e and 4.10, somewhat disguised in Fig. 4.12.

The classical FS theory can therefore be considered to be “only” an important first approximation to gelation in three dimensions. The assumption of the FS theory which, on the one hand, allows it to be solved exactly (equivalent to Bethe-lattice percolation) and, on the other hand, sets limits to its realism and applicability to experiment, is the absence of closed rings. This prohibition against closed loops or cycles of bonds (one such ring was included in Fig. 4.11, at the lower left) is probably not serious at early stages in the condensation reaction, but must become important at later stages. The gel macromolecule itself possesses a network structure with a great many rings, as attested to by its observed rigidity. Thus, the treelike picture inherent in the classical theory has difficulty in squaring with the gelation process near the gel point and above it.

A model of gelation which automatically includes the presence of rings is bond percolation on a three-dimensional lattice. Each lattice site is considered to be occupied by a monomer, and each monomer may react with—and establish a covalent bond to—one of its $z$ nearest neighbors.

Let us compare some of the predictions of the classical FS model with the corresponding predictions of a lattice bond-percolation model for $z = 4$, the functionality appropriate to the case of silicic acid gelation represented in Fig. 4.11. Qualitatively, the predictions are similar, since percolation underlies both theories. Each predicts a sharp gel point, a diverging average molecular weight (and, thereby, a diverging viscosity) below $p_c$, and an increasing elastic rigidity above $p_c$. Quantitatively, there are definite differences. The critical extent of reaction in the FS model is $p_c = 1/(z - 1) = 1/3$. Taking a diamond structure as the three-dimensional, four-coordinated lattice for the lattice-percolation model, $p_c = 0.39$. More significant are the differences in the critical exponents. The gel fraction increases near threshold as $(p - p_c)^{0.4}$ in the lattice model, much faster than the linear $(p - p_c)$ increase predicted by the FS theory. Similarly, the divergence of the average molecular weight as the
sol→gel transition is approached is more rapid for the 3d-lattice model than for the FS model (compare values for \( \gamma \) in Table 4.3). Experimental determinations of these gelation exponents are very difficult, and unfortunately it appears that no definitive test of the differing predictions is yet available.

Just as Bethe-lattice percolation, the classical FS theory of gelation can be criticized as a physical model on the grounds of its failure to take into account the undoubted occurrence of closed rings when large molecular structures are formed (a serious criticism at and above \( p_c \)), so also 3d-lattice percolation model has difficulties of its own. Obviously, real monomers in solution are not arranged on a regular lattice. More seriously, where are the solvent molecules in this model? As specified above, the lattice-percolation model is really a model for gelation in the absence of solvent. A more realistic model, which incorporates solvent molecules, is based on the generalization known as site-bond percolation (discussed in Section 4.8). Critical exponents for site-bond percolation have been shown to be the same as for ordinary percolation.

Earlier, when we introduced the analogy between percolation and magnetism that is expressed in Table 4.2, we noted there a correspondence between the resistor-network conductivity \( \sigma \) of the percolation model and a magnetic ("exchange-stiffness") version of an elastic constant which applies to spin waves in the ferromagnet. At that time a promise was made to deliver a connection between \( \sigma \) and a bona fide mechanical elastic constant. The time has come. This conductivity-rigidity connection was evident in a qualitative way when Fig. 4.1 was discussed (the screen falls apart at the same moment that conductivity ceases). The quantitative argument, given here for a gel, is due to de Gennes (1976, 1979). In a gelation process, the elastic shear modulus vanishes for the sol (a liquid), begins to grow at the sol→gel transition, and continues to increase as the cross-linking increases in the gel (solid) phase. What will now be shown is that the behavior of the elastic modulus, as a function of the cross-linking concentration, is the same as that shown for \( \sigma(\rho) \) in Fig. 4.5.

We consider a lattice model with monomers at all sites and with some fraction \( p (> p_{\text{bond}}) \) of the mathematical bonds between nearest-neighbor sites corresponding to formed (reacted) chemical bonds between monomers. The elastic energy of this gel network may be written as

\[
E_{\text{elastic}} = \frac{1}{2} \sum_{ij} k_{ij} (u_i - u_j)^2. \tag{4.20}
\]

Here \( u_i \) is the displacement of monomer \( i \) from its equilibrium position at lattice site \( i \), and \( k_{ij} \) is the force constant of bond \( ij \). [To simplify the expression, the subscript specifying the Cartesian component of \( u \) is omitted.] The sum in Eq. (4.20) should be interpreted as extending over the three orthogonal components. The spring constant \( k_{ij} \) is taken equal to \( k \) if bond \( ij \) is connected (probability \( p \)); otherwise (probability \( 1 - p \)), \( k_{ij} \) is zero.

For monomer \( i \) to be in equilibrium, the forces exerted upon it by the bonds joining it to its neighbors must cancel to zero,
Now consider an electrical network that is isomorphic to the gel network, having a bond conductance $g_{ij}$ equal to $g$ when the force constant $k_{ij}$ of the corresponding gel bond is $k$, and equal to zero when $k_{ij}$ is zero. When subject to an applied voltage drop, the equilibrium voltage $v_i$ at each node (site) $i$ must satisfy the requirement (Kirchhoff's law) that there be no net current into the node,

$$\sum_j g_{ij} (v_i - v_j) = 0. \quad (4.22)$$

The equivalence between Eqs. (4.22) and (4.21) provides the sought-for correspondence, on a microscopic level. Macroscopically, the consequence of the bond conductances in the electrical case is the conductivity, while in the gel-network case the bond springs result in the elastic moduli.

An amorphous solid, being isotropic, possesses only two independent elastic moduli. One of these may be chosen to be the inverse compressibility or bulk modulus $B = -V(\partial P/\partial V)$, which is a measure of the elastic stiffness against volume decrease enforced by hydrostatic pressure. The other is the shear modulus which is a measure of the stiffness against volume-conserving change in shape. In interpreting the conclusion of the previous paragraph, we must bear in mind that the lattice bond-percolation model for gelation leaves out the solvent molecules. Below the gel point, in the sol phase, the material is a liquid. Its shear modulus, by definition, is zero. But the bulk modulus is finite; the solvent molecules are not infinitely compressible. Therefore, the correspondence to the resistor-network conductivity really applies closely only to the shear modulus, the measure of the elastic stiffness against shear, the rigidity which opposes distortion.

We conclude, therefore, that the elastic shear modulus of a gel should depend upon the fraction of formed cross-links in exactly the same way as the conductivity of a random-resistor network depends upon the fraction of conducting bonds. The functional form should closely resemble the $\sigma(p)$ curve of Fig. 4.5, starting from zero at the gel point and increasing gently beyond that. In particular, close to the gelation threshold, the shear modulus should increase as $(p - p_c)^t$, with $t$ being the $d = 3$ conductivity exponent of Table 4.3. This prediction of the 3d-lattice percolation theory of gelation is indeed borne out experimentally. Note that the observed discrepancy between the slow increase in the elastic rigidity and the swift increase in the gel fraction has the same root cause as the corresponding discrepancy between $\sigma(p)$ and $P(p)$. Cross-links which belong to the gel macromolecule but which lead to dead-ended or dangling molecules do not contribute to the solid's shear stiffness. Only the backbone of the percolation path (that is, the infinite cluster with all loose ends removed) supports the electric current in the resistor-network case or the elastic rigidity in the mechanical-network case.

It should by now be quite clear that connections or correspondences or parallels or analogies, such as those given in Tables 4.2 and 4.5 of this chapter,
are very instructive and helpful in providing insight. Such mappings of different fields onto each other are, of course, part of an old tradition in physics. Percolation provides particularly nice examples of such mappings. The connection to magnetic phase transitions (Table 4.2) has imbued percolation with much of the elegant and powerful machinery (scaling, universality, renormalization) which pervades phase-transition theory. Similarly, the correspondence between percolation and the theory of gelation has allowed the latter to take advantage of, for example, the results of the extensive computer simulations that have been used to determine the exponent $t$ for random resistor networks. Putting two and two together (magnetism $\rightarrow$ gelation connection, via percolation), it is also true that phase-transition concepts such as scaling apply to the sol $\rightarrow$ gel transition.

The sol $\rightarrow$ gel transition can be viewed, in the context of the concept of network dimensionality which was introduced in Section 3.1.1, as a transition between a zero-dimensional-network situation and a three-dimensional-network situation. In the gelation process that produces silica gel, the initial liquid state contains atomic-scale (0d-network) molecules such as Si(OH)$_4$, while the final solid state is supported by a 3d-network macromolecule akin to the SiO$_2$ random network. This 0d $\rightarrow$ 3d feature accompanies percolation processes in three dimensions. (In general, in $d$ dimensions, 0d-network elements merge to form a $d$-dimensional connected network at the percolation threshold.)

There is another type of chemical cross-linking process, called vulcanization, which essentially a 1d $\rightarrow$ 3d connectivity transition.

In vulcanization, a dense melt made up of individual, flexible, organic polymer chains is transformed, by the action of a cross-linking agent, into a single giant molecule. Thus the process resembles gelation except that the initial building blocks are 1d-network molecules rather than 0d-network molecules. Chemically, the prototype vulcanization process involves a cross-linking mechanism which is not very different from that indicated in Fig. 4.11 for our gelation example. Representing the fourth column of the Periodic Table we now have, instead of silicon, the carbon atoms of the hydrocarbon polymer chains. From column six, in the role of the twofold-coordinated bridging oxygens of Fig. 4.11, we now have bridging sulfur atoms contributed by a sulfur-containing species added to the polymer melt. C$-S-C$ cross-links between chains play the part that corresponds (in Fig. 4.11) to the Si$-O-Si$ cross-links between monomers.

Each of the $N$ carbons of the chain backbone provides an opportunity (with probability $p$) for cross-linking, so that for each chain the effective coordination number $z$ equals $N$ for this very nonstandard percolation problem. Because the chains are long and $N >> 1$, the effective coordination number is enormous, rings are unimportant, and FS theory is valid: $p_c = 1/(z - 1) = 1/N$. Critical cross-linking occurs when there is, on average, one cross-link per chain (the equivalent of one offspring per parent in a cascade process).

The above result, namely a very small $p_c$ for an assembly of long chains, is relevant to the structure of the chalcogenide glass Se$_{1-x-y}$As$_x$Ge$_y$, which was
schematically sketched in Fig. 3.7. Ge and As atoms in this system provide, in effect, cross-linking points for chains of Se atoms, and we see that only a very small concentration \((x + y = N^{-1})\) of such cross-linking atoms need be present to stitch together a 3d-network macromolecule. This point has practical importance in the use of these materials as photoconductors, as will be mentioned in Chapter Six.

4.7 CONTINUUM PERCOLATION AND THE CRITICAL VOLUME FRACTION

Along with its relevance to a rich variety of physical phenomena, the percolation model possesses a transparency that gives it great educational value. Figure 4.13 illustrates a homey experiment which is beginning to find its way into undergraduate laboratories as a pedagogic device for conveying ideas about phase transitions and critical phenomena. The procedure is typically as follows. Crumpled aluminum foil is pressed into the bottom of a glass beaker and is electrically connected to a battery. A mixture of small plastic and

![Diagram of the experiment](image)

**Figure 4.13** The experiment carried out by Fitzpatrick, Malt, and Spaepen (1974) as part of a freshman physics course at Harvard. Aspects simultaneously present in this simple arrangement include random close packing, percolation, and random-resistor network.
metallic balls of equal size is now poured into the beaker and "pressed down and shaken together" (following Section 2.4) in the ancient recipe for random close packing. A second crumpled-foil electrode is pressed onto the top of the mixture, and the circuit is completed through an ammeter to the other side of the battery. The current, if any, that is flowing in the circuit is measured by the ammeter and recorded.

The above experiment associates a value of electric current \( I \) with another number that specifies the overall composition of the system, the mix of conducting (metal) and nonconducting (plastic) balls. We may choose, as the composition parameter \( p \), the fraction of the balls in the beaker which are metallic. The procedure described above determines, say, the current \( I_1 \) that corresponds to composition \( p_1 \). The beaker is now emptied and refilled with a different metal/(metal-plus-plastic) mix \( p_2 \), and the current \( I_2 \) is measured. A series of such measurements, repeated with different mixtures in the beaker, maps out a function \( I(p) \). Question: What is the form of \( I(p) \) and, in particular, what is the critical composition—the minimum fraction of metal balls needed to support across-the-beaker conductivity—that separates the setups for which current flows from those for which no current is seen?

The experimental situation of Fig. 4.13 simultaneously incorporates several distinct aspects: random resistor network, percolation, and an underlying structure which is topologically disordered. We recognize the particular form of topological disorder that is present here, i.e., that which characterizes the array of spheres within the beaker, as the random close-packed structure which was described in Chapter Two in connection with the atomic-scale structure of amorphous metals. The aspect of underlying topological disorder is very important. It distinguishes this percolation process from all of those that have been discussed thus far.

In conventional percolation on a lattice, the structural starting point is that most regular of geometric objects—a periodic lattice. Disorder is introduced by superimposing on the sites or bonds of such a lattice a randomly assigned two-state property (filled/empty or unblocked/blocked). The bimodal statistical variable, imposed on a regular geometry, results in a stochastic-geometry situation. (Incidentally, the use of the term stochastic geometry dates back at least as far as the 1963 review on percolation by Frisch and Hammersley.) But the situation depicted in Fig. 4.13 represents a higher order of stochastic geometry because the disorder-generating statistical variable (metal/insulator) is superimposed on a structure that is itself topologically disordered.

If the balls of Fig. 4.13 had been arranged, not in random close packing, but, for example, in a face-centered-cubic crystalline array, then the answer to the question asked about the critical composition (metal-ball fraction) for current flow could have been plucked from the fourth column of Table 4.4: \( p_{\text{site}}^{\text{site}} \) (fcc) = 0.198. But how do we handle the analogous site-percolation problem on a noncrystalline lattice such as rcp? Or deal with situations in which no underlying lattice whatever may be defined? A pragmatic approach to this
problem invokes a stochastic-geometry construct (Scher and Zallen, 1970) which has come to be called the critical volume fraction for site percolation.

The notion of critical volume fraction is most simply defined in the context of a specific example. Figure 4.14 shows the situation for site percolation on the 2d honeycomb lattice. With each lattice site we associate a circle of radius equal to half the nearest-neighbor separation. In Fig. 4.14, open circles surround empty sites, shaded circles surround filled sites, and clusters of connected sites are indicated by the heavy lines joining adjacent filled sites. Now while $p$ is the fraction of the circles that are shown shaded in Fig. 4.14, the volume fraction $\phi$ is defined as the fraction of space that is taken up by the filled (shaded) circles. The relationship between $\phi$ and $p$ is dictated by simple geometry: $\phi = v p$, where $v$ is the filling factor for the lattice, the fraction of space occupied by all of the circles of Fig. 4.14. The critical volume fraction $\phi_c$ is the value of $\phi$ which applies at the site-percolation threshold: $\phi_c = vp_{\text{site}}$.

For the two-dimensional example of Fig. 4.14, the volume fraction is, of course, an area fraction. The term "volume fraction" should be interpreted as appropriate to the dimensionality at hand. ("Space fraction" or "content fraction" are alternatives that could be used to avoid a 3d connotation, but these terms are less transparent than volume fraction.) In general, for the simple (connections only between nearest neighbors) lattice $j$ in $d$ dimensions, the critical volume fraction is $\phi_c(j,d) = v(j,d)p_c(j,d)$, where $p_c(j,d)$ is the site-percolation threshold and $v(j,d)$ is the filling factor of the lattice corresponding to the packing of equal, touching, nonoverlapping, $d$-dimensional spheres centered on the lattice sites.

Thus far, for site percolation on any given lattice, all we have done is to convert the percolation threshold from a critical site-occupation probability $p_c$.

Figure 4.14 Illustration of the idea of the critical volume fraction for percolation, in the context of the two-dimensional honeycomb lattice. Shaded circles indicate filled sites, open circles indicate empty sites, and linked clusters are shown connected by heavy lines (Scher and Zallen, 1970).
to a critical volume fraction $\phi_c$. What have we gained by this? The benefit that results may be seen by comparing the second and eighth columns of Table 4.4, which list $\rho_c$ and $\phi_c$ values for various 2d and 3d lattices. While the variability ("nonuniversality") of $\rho_c$ from lattice to lattice has already been remarked upon, what we find for $\phi_c$ is, for all lattices of the same dimensionality, a remarkable insensitivity to lattice structure. In the notation of the previous paragraph, $v(j,d)p_c(j,d) \approx \phi_c(d)$, the lattice-specifying index $j$ may be dropped, to good approximation, from $\phi_c$. To within a few percent, the critical volume fraction is 0.45 in two dimensions, 0.16 in three dimensions.

The critical volume fraction constitutes an approximate dimensional invariant for the threshold in site-percolation processes. As such it is an extremely valuable construct, useful in a wide variety of applications. One such application is the experiment which has concerned us here, that pictured in Fig. 4.13. We can now answer the question posed earlier. For the random packings typical of such experiments, the filling factor $v$ is close to 0.60 (somewhat lower than the optimum rep value of 0.637 discussed in Chapter Two). Using $\phi_c(d = 3) = 0.16$ in conjunction with $v = 0.6$, we obtain $\rho_c = 0.27$, predicting that current flow occurs when the fraction of metal balls in the mixture exceeds 27%. This is what is observed. Above this threshold, the current-versus-composition characteristic follows a curve similar to $\sigma(p)$ of Fig. 4.5.

A microscopic counterpart of the basic situation portrayed in Fig. 4.13 is provided by a class of solids, usually prepared in thin-film form at low temperature, that are atomically mixed dispersions of alkali atoms in rare-gas solids. Examples are $\text{Rb}_x\text{Kr}_{1-x}$ and $\text{Cs}_x\text{Xe}_{1-x}$. These alloys behave as "paradigms of percolative processes on an atomic scale" (Phelps and Flynn, 1976). The insulator→metal transition in these solids occurs, as a function of composition, when the proportion ($x$) of alkali atoms corresponds to an alkali-atom volume fraction of 16% ($= \phi_c$).

Many macroscopic two-phase systems are controlled by the critical volume fraction for percolation. One example is the required quantity of photoconducting material which, when dispersed in an insulating "binder," is adequate for the composite material to exhibit photoconductivity. Another example is the composition at which the normal→superconducting transition occurs for a disordered system consisting of Nb$_3$Sn filaments embedded in a copper matrix. In such systems the stochastic geometry resembles a situation (glance ahead briefly to Fig. 4.16) that may be characterized by the expression percolation on a continuum, which we are nearly ready to discuss.

The empirical basis for $\phi_c$, the observed near-constancy of $v\rho_c^{\text{site}}$ as exhibited by the numerical values in the last column of Table 4.4, is given a graphic setting in Fig. 4.15a for the three-dimensional case. The reciprocal $\rho_c^{-1}$ of the site-percolation threshold is shown plotted against the lattice packing fraction or filling factor $v$. The slope of the straight line is $\phi_c^{-1}$. Shown in Fig. 4.15b is an analogous plot for a different dimensional invariant (also, as $\phi_c$, an approximate one) that was noticed early in the game for bond percolation and for which numerical evidence was included in the next-to-last column of
Figure 4.15  Two empirical correlations between percolation threshold and lattice connectivity for various three-dimensional structures. For site percolation, the correlation between the reciprocal of the percolation threshold and the lattice packing fraction (or filling factor) is shown in $a$. For bond percolation, the correlation between the reciprocal of the threshold and the lattice coordination is shown in $b$. The correlation demonstrated in $a$ provides an empirical basis for the usefulness of the approximate dimensional invariant known as the critical volume fraction.
Table 4.4. Plotted here, for 3d lattices, is the reciprocal of the bond-percolation threshold as a function of the lattice coordination \( z \). The significance of the straight line in this plot is that \( zp_c^{\text{bond}} \) is a dimensional near-invariant applicable to bond processes. In three dimensions, for regular lattices with nearest-neighbor bonds, \( zp_c^{\text{bond}} \) is close to 1.5. This may be paraphrased as follows: At the bond-percolation threshold for 3d lattices, an average site sees one-and-a-half unblocked bonds.

Although the sensitivity of the value of the percolation threshold to the specifics of the lattice structure has been repeatedly pointed out, we now have found that there exists, for both site percolation and bond percolation, a restatement of the threshold which, to a useful level of accuracy, is independent of the details of lattice geometry. For site percolation, that determinant of the composition at threshold is the critical volume fraction \( \phi_c \); for bond percolation, it is the critical bond number \( zp_c \)—the critical value of the average number of connected bonds per site. These constructs restore a respectable degree of universality to the position of the percolation threshold.

Note a highly suggestive parallelism of form between the two parts of Fig. 4.15. In each instance, a measure of the ease of percolation (the inverse threshold) is seen to be proportional to a measure of the connectivity of the structure. For bond percolation, that measure of connectivity is our familiar standard for this purpose, the coordination number \( z \). But for site percolation, \( z \) is replaced by \( v \), the filling factor based on the packing of equal spheres. For site-percolation processes, the proper measure of connectivity is the efficiency with which the structure (viewed as a packing) fills space. This distinction between bond and site percolation is analogous to the graph/froth or crn/rcp dichotomy of Chapter Two. On an atomic-scale bonding level, \( z \) is the proper measure of connectivity for covalent solids, while \( v \) is the measure of choice for metals.

These dimensional invariants, useful in \( d = 2 \) and \( d = 3 \), may also be estimated for dimensionalties up to \( d = 6 \) by virtue of computer experiments on the \( d > 3 \) counterparts of simple cubic lattices ("hypercubic" lattices). The data are given in Table 4.4, and \( \phi_c(d) \) was given earlier in Fig. 4.8 along with those more traditional dimensional invariants, the critical exponents.

Enter now the unruly geometry of Fig. 4.16, and the topic of continuum percolation. (Another example of this genre will appear, as Fig. 5.15, in the discussion of electron states in amorphous semiconductors.) There is no lattice, no discrete structure, which serves as a substrate for the disorder shown here. Yet we are interested in the connectivity properties (e.g., Does black percolate left-to-right in Fig. 4.16?); hence, we are dealing with percolation on a continuum. One reason for having hope in the face of such a wild scene as that of Fig. 4.16 is the percolation criterion provided by the critical volume fraction, because this concept dispenses with the need for a lattice! Where \( p_c \) is the occupation fraction for a discrete set of locations (the lattice sites), \( \phi_c \) is the occupation fraction for a continuous set (spatial positions). In addition to the empirical justification of \( \phi_c(d = 3) = 0.16 \) provided by Fig. 4.15a, computer
Figure 4.16 Sample geometry in the electrical experiments of Smith and Lobb (1979). The stochastic-geometry conductor-insulator films were photolithographically generated from laser speckle patterns. In a, which shows a small section of a speckled film, the black areas are metal. In b, the cross-hatched regions are thick metal contacts.

simulations of continuum percolation (Webman, Jortner, and Cohen, 1976) support the same result.

The two-dimensional pattern that appears in Fig. 4.16 was generated from a laser speckle pattern by a photographic procedure (Smith and Lobb, 1979). In this experiment, green light from an argon laser ($\lambda = 5145$ Å) was incident upon a diffusely scattering surface, and the speckle pattern formed by the scattered light was recorded on high-contrast film. The developed film shows no gray scale; it contains a pattern of clear regions and opaque regions whose
relative area fractions depend on the laser intensity and the exposure time. Using the developed film as a mask for contact printing, the pattern was then photolithographically reproduced as a vapor-deposited metal thin film on a glass slide. In the small sample of a typical pattern that is shown in Fig. 4.16, the black areas are metal; they correspond to the dark parts (light intensity below a cutoff level determined by film exposure) of the original speckle pattern.

Figure 4.17 shows the results of electrical measurements on a series of films made in this way. Current was measured between opposite edges of each film, using thin-film electrodes indicated by cross-hatching in Fig. 4.16b. In Fig. 4.17, normalized conductivity $\sigma/\sigma_0$ is plotted against area fraction $\phi$. ($\phi$ was determined by measuring the optical transmission of the film). The $\sigma(\phi)$ curve, between threshold and full coverage, is not badly approximated by a linear behavior. The reason for this is that the critical exponent $t$ in $\sigma \sim (\phi -
4.8 GENERALIZATIONS AND RENORMALIZATIONS

$\phi_c$ is close to unity: $t$ is about 1.2–1.3 for the data of Fig. 4.17. This is not significantly different from the value (based on computer experiments for random-resistor networks on two-dimensional lattices) listed earlier in Table 4.3: $t(d = 2) = 1.1$. Critical exponents for continuum percolation seem to be similar to those for conventional (lattice) percolation.

Although the critical volume fraction for site percolation on 2d lattices is $\phi_s(2d) = 0.45$, it will be shown in the next chapter (Section 5.6) that for 2d continuum percolation in systems characterized by black/white symmetry, $\phi_c$ is $\frac{1}{2}$. This symmetry is not present in Fig. 4.16 (black regions tend to be concave with cuspy exteriors, white regions tend to be convex with rounded exteriors), which is why $\phi_c$ is different from $\frac{1}{2}$ in Fig. 4.17.

4.8 GENERALIZATIONS AND RENORMALIZATIONS

Continuum percolation, as discussed in the previous section, is an example of a generalization of conventional or classical percolation theory—one that happens to provide (via the critical volume fraction) an extremely useful extension to situations in which the geometry is quite irregular. In this section, several other generalizations of percolation are discussed. While many such generalizations are imaginable, those mentioned here are ones with high applicability to physical systems. In addition, the powerful theoretical technique known as the renormalization group is illustrated in this section in a percolation context.

Probably the simplest generalization of classical percolation is site-bond percolation, in which both sites and bonds on a lattice are randomly occupied (unblocked, connected) with probabilities $p_{\text{site}}$ and $p_{\text{bond}}$, respectively. First proposed by Frisch and Hammersley in 1963, this hybrid model was not extensively developed until 15 years later when Stanley and others adopted it as a model for gelation. In the plumbing analogy of Fig. 4.3, a site–bond percolation process has valves placed both at the joints and within the pipes of the flow network.

In the last section’s treatment of bond percolation as a model for gelation, monomer molecules occupied all of the sites of a lattice, and reacted chemical bonds between adjacent monomers were present with probability $p_{\text{bond}}$. The shortcoming of this pure bond-percolation model is its failure to include the solvent molecules, whose presence has the effect of diluting the concentration of reactant monomer molecules. Such effects of random dilution are readily treated by percolation theory, and the remedy prescribed in this instance is to have each lattice site occupied by either a monomer molecule (with probability $p_{\text{site}}$) or an inert molecule (with probability $1 - p_{\text{site}}$). In this system, connected clusters (condensation-reaction products) consist of continuous sequences of occupied sites (monomers) linked by occupied (reacted) bonds. Thus, site-bond percolation is a very natural model for gelation.

With both sites and bonds occupied at random (but with, in general, different probabilities: $p_{\text{site}} \neq p_{\text{bond}}$), there will occur occupied bonds which have
either or both endpoint sites empty. In a model for gelation, occupied bonds of this type are unphysical; they do not represent reacted chemical bonds, which must join pairs of monomers (both endpoint sites filled). Fortunately, such bonds do not contribute to cluster connectivity since they are either dead-ended (one endpoint site empty) or completely isolated (both endpoints empty). Therefore, they do not influence such matters as the presence or absence of an infinite cluster (gel macromolecule), and they do not spoil the model. But the presence of some occupied but unphysical bonds means that the proper measure of cluster size is the number of sites it contains rather than the number of bonds. Occupied sites, even if isolated (solitary singlets) or dead-ended (on the "outside surface" of a cluster), retain their ability to represent monomer molecules in a physical model.

In a site–bond percolation process, the composition of the system is specified by two independent variables, $p^\text{site}$ and $p^\text{bond}$. For a percolation path to occur, both $p^\text{site}$ and $p^\text{bond}$ must be large. How large each must be depends on the other; they are interdependent. Figure 4.18 displays, for site–bond percolation on the square lattice, the large-$p$ high-density portion of the phase

![Phase diagram](image)

**Figure 4.18** Phase diagram for site–bond percolation on the square lattice. The solid line separates the percolating regime (labeled "gel") from the nonpercolating regime (labeled "sol") (after Agrawal, Redner, Reynolds, and Stanley, 1979).
diagram in \((\rho \text{site}, \rho \text{bond})\) composition space (Agrawal et al., 1979). The solid line is the phase boundary that separates the percolating regime (labeled "gel" in the figure) from the nonpercolating regime (labeled "sol"). For compositions in the "gel" region, an infinite cluster occurs; for compositions in the "sol" region, all clusters are finite.

The upper border of Fig. 4.18 is the line along which \(\rho \text{site}\) is unity while \(\rho \text{bond}\) varies. This horizontal line represents those situations in which all sites are connected, but only some bonds are. It corresponds to pure bond percolation, and the sol\(\rightarrow\)gel transition line intercepts it at \((\rho \text{site}, \rho \text{bond}) = (1, \rho_c \text{bond})\), the bond-percolation threshold. Similarly, the right-hand boundary of the figure represents pure site percolation, and this vertical line is intercepted by the sol\(\rightarrow\)gel phase boundary at the site-percolation threshold \((\rho_c \text{site}, 1)\). The fact that the two points which represent the thresholds for the two "pure" limiting cases are connected by a smooth and continuous phase-transition curve, the locus of percolation thresholds that comprises the sol\(\rightarrow\)gel boundary of Fig. 4.18, has a special significance discussed below.

Figure 4.19 contains two diagrams, both of which, like Fig. 4.18, show the two-dimensional \((\rho \text{site}, \rho \text{bond})\) composition field for site–bond percolation on the square lattice. (Unlike Fig. 4.18, \(\rho \text{site}\) is plotted horizontally and \(\rho \text{bond}\) vertically in Fig. 4.19. Also, the full field is shown in each diagram of Fig. 4.19, not just the part near the transition line.) Both diagrams, published independently and near simultaneously by Shapiro (1979) and by Nakanishi and Reynolds (1979), represent the renormalization-group flow diagram for site–bond percolation. Although any attempt at a proper development of renormalization-group theory is well beyond the scope of this book, percolation provides so fine an illustration of such a flow diagram that it deserves to be mentioned. Also, as with other concepts in the theory of phase transitions, the percolation model serves as a lucid setting for displaying the ideas of the renormalization group. Before discussing Fig. 4.19, a simpler example is now presented for the renormalization-group concepts of flow diagram and fixed point.

The basic idea of the renormalization group is that of a continuous family of transformations on the length scale of the system. Consider a political analogy. Let Fig. 4.20a represent a small portion of the two-dimensional political map of the United States. There are 81 voters in this region, and we assume total two-party dominance, with all individuals voting either for the Democratic (d) or Republican (R) candidate. In the election indicated in the figure, the Republicans have carried the region 48 to 33, that is, with about 59% of the vote. Using the Republican fraction to specify the composition \(\rho\) of the system, \(\rho = (48/81) = 0.59\).

Now suppose that this same region contains nine election districts of equal size (nine voters), as shown in Fig. 4.20b. On the district level, the Republicans have taken the region seven districts to two. Viewed on this scale, in which the smallest discernible unit is an election district (with each district credited, in winner-take-all fashion, to the party having the majority of votes...
Figure 4.19 Two representations of the renormalization-group flow diagram for site-bond percolation on the square lattice. Diagrams a and b are, respectively, from the work of Nakanishi and Reynolds (1979) and Shapiro (1979).
within it), the political map of the region looks like Fig. 4.20c, and the composition of the system is now \( p' = (7/9) = 0.78 \). In going from \( a \) to \( e \) in Fig. 4.20, the unit of length has dilated by a factor of \( b = 3 \), and the original composition \( p \) has been "renormalized" via this scale transformation to the value \( p' \). In general, \( p' \) depends on both \( p \) and \( b \): \( p' = p'(p, b) \). The scale factor \( b \) can be expressed as \( N^{(1d)} \), where \( N \) is the number of original units that transform into one elementary unit of the renormalized system and \( d \) is the dimensionality. For our example, \( N = 9 \) and \( d = 2 \).

This process can be repeated, as indicated in Fig. 4.20d. Assume that nine election districts make up one county, and award each county to the party that carries the majority of its nine districts. In our sample region, which contains only a single county, the renormalized composition after a second \( b = 3 \) scale transformation to the county level is \( p'' = (1/1) = 1 \). In a much larger area, \( p'' \) would not be unity but, say, \( p'' = 0.97 \). Thus, in the two stages of scale transformation which have been carried out, \( p \) has gone from 0.59 at the voter level to 0.78 at the district level to 0.97 at the county level. For the renormalization function \( p'(p, b) \): \( p'(p = 0.59, b = 3) = 0.78 \) and \( p'(p = 0.78, b = 3) = 0.97 \).

The bottom panel of Fig. 4.20 graphically places these compositions on a linear composition field. The effect of successive scale transformations is to generate a flow diagram in composition (or density) space. For \( p > \frac{1}{2} \), as in our example, the composition flows to the right (appropriately enough for a Republican victory) in Fig. 4.20e, approaching the \( p = 1 \) high-density limit. For \( p < \frac{1}{2} \), the flow is to the left, toward the \( p = 0 \) low-density limit. There are three special points in this flow field in composition space, each of which corresponds to a composition or density that remains invariant under scale transformation. These are the renormalization-group fixed points, points in parameter space that correspond to states of the system which, in some sense, "look the same" at all scales of length. (The concept of self-similarity, discussed in Section 3.2.5 in connection with Brownian motion and Fig. 3.13, is also useful here.) Of the three fixed points in Fig. 4.20e, two of these are relatively uninteresting. These are the two "sinks" of the flow, the endpoints at \( p = 0 \) (the completely empty limit) and at \( p = 1 \) (the completely filled limit). These are "stable" or "homogeneous" fixed points; renormalization drives compositions toward these "pure" limits in which the minority component entirely disappears. In our political analogy, renormalization to large units tends to produce unanimity. American presidential elections under the electoral college system are one-stage renormalizations from the voter level to the state level (\( N \approx 10^6 \)), and reasonably close popular-vote results (say, \( p = 0.45 \) or \( p = 0.55 \)) are often transformed into electoral-college "landslides" (\( p' < 0.1 \) or \( p' > 0.9 \)).

The key point in the flow field is the "source" of the flow, the unstable fixed point at \( p = \frac{1}{2} \). This corresponds to a phase transition of the system. It separates the regions of the phase diagram that scale toward different single-component limits. Critical phenomena, in renormalization-group theory, are
Figure 4.20  A political analogy which exhibits renormalization-group concepts.
controlled by the properties of the flow diagram in the immediate neighborhood of the unstable fixed point.

In Fig. 4.20, the criterion for deciding the state (R or d) of the renormalized element in ε is based on majority rule applied to the corresponding cell of elements of the original system in b. For percolation, the criterion for deciding the state (occupied or empty) of the renormalized element is based on whether or not the corresponding cell of the original system percolates, that is, exhibits connectivity between two opposite faces (in d = 3) or edges (in d = 2). There are some subtleties and ambiguities in implementing this "spanning-cluster" criterion when the scaling factor b is small, but for large b (b ≫ 1) all reasonable criteria converge to the same limit.

We can now interpret Fig. 4.19, which shows two different renormalization-group implementations (both for b = 2) for percolation on the square lattice. Unlike the one-dimensional flow diagram of Fig. 4.20e, the flow diagram for site-bond percolation occurs in the plane (x, y) = (ρ_{site}, ρ_{bond}). The two sets of results in Fig. 4.19 agree well with each other, although they are presented in two somewhat different formats. Figure 4.19a shows the direction of flow throughout the phase diagram, while Fig. 4.19b shows a set of distinct trajectories. Their results along the lines ρ_{bond} = 1 and ρ_{site} = 1 may be used to gauge the accuracy of these calculations. The known thresholds (Table 4.4) for the square lattice are ρ_{site} = 0.593 and ρ_{bond} = 0.500. By comparison, the estimates for ρ_{site} are 0.57 and 0.63, and for ρ_{bond} are 0.51 and 0.52, for Figs. 4.19a and 4.19b, respectively.

Like the political flow diagram of Fig. 4.20e, the percolation flow diagram of Fig. 4.19 contains two homogeneous fixed points and one critical fixed point. The homogeneous fixed points occur at compositions (0,0) and (1,1), corresponding to the dull cases in which all bonds and sites are empty or occupied, respectively. The critical fixed point occurs at (ρ_{site}, ρ_{bond}) = (0.90, 0.59). Viewing the flow diagram as a drainage pattern on an actual terrain, the critical fixed point is a saddle point, the low point in a ridge line that connects the percolation thresholds for pure site percolation (ρ_{site}, 1) and pure bond percolation (1, ρ_{bond}). This ridge line is the continental divide of the terrain. The watershed lying to the south and west of this line drains to the empty lattice fixed point at (0,0); the watershed lying to the north and east drains to the fully occupied fixed point at (1,1). The southwest watershed corresponds, of course, to the nonpercolating region of phase space; compositions in this region renormalize under rescaling to lower and lower density. The northeast watershed corresponds to the percolating regime, embracing all (ρ_{site}, ρ_{bond}) values that renormalize toward the high-density limit. Just as in the political case, the scaling-induced flow is away from criticality (away from the phase-boundary ridge line in Fig. 4.19, away from the point representing a 50-50 vote split in Fig. 4.20).

In our discussion of scaling behavior in Sec. 4.5, the statement that site-percolation processes and bond-percolation processes both belong to the same universality class (have the same critical exponents) was asserted as empirically
established, as based on experiment. With regard to this important point there is special significance in the demonstration, via Fig. 4.19, that the critical fixed points for the two basic types of percolation processes are both controlled by (renormalize to, flow into) the same critical fixed point in the phase space for the hybrid process. This demonstration augments the empirical evidence with a degree of theoretical underpinning: In the context of renormalization-group theory, its interpretation assigns site percolation and bond percolation to the same universality class.

The approach exemplified by Figs. 4.19 and 4.20 is called direct or real-space renormalization. A picturesque way to express the underlying viewpoint of this approach is in terms of a declaration that captures the philosophy of the renormalization-group theory of phase transitions: At the critical point, all scales of length coexist. The characteristic length for the system goes to infinity, becoming arbitrarily large (macroscopic) with respect to atomic-scale lengths. For magnetic phase transitions, the measure of the diverging length scale is the correlation length $\xi$. For percolation, the diverging length scale is set by the connectedness length $\xi_{\text{av}}$. The presence of a diverging length scale is what makes it possible to apply to percolation the elegant program of real-space renormalization.

There is another form of renormalization-group theory, one which operates on the Hamiltonian constructed for the statistical mechanics of the physical system at hand. This is the form which yields the “$\epsilon$ expansion,” in which the results of mean-field theory (valid for $d = d^*$, the marginal dimensionality) are expanded in a power series in $\epsilon = d - d^*$. The epsilon expansion explicitly exhibits the renormalization group as a next stage, beyond mean-field theory, in the development of the theory of phase transitions.

For completeness, it is worthwhile to point out that there exists, for the percolation model, such a Hamiltonian (or momentum-space) formulation of the renormalization group. The basis is essentially the percolation→magnetism analogy given previously in Table 4.2. A generalization of the Lenz-Ising model for magnetism, known as the “$s$-state Potts model,” generates bond percolation as a particular limiting case.

Though it might seem an unlikely match, it happens that the combination of the elegant ideas of renormalization-group analysis with the brute-force methods of computer simulations results in a rather productive marriage. Figure 4.21 shows a set of Monte Carlo calculations (Kirkpatrick, 1979) for bond percolation on the three-dimensional simple cubic lattice. The horizontal axis shows $p$, the fraction of bonds that are connected in a sample cube containing $b^3$ bonds. Plotted along the vertical axis is the fraction $p'$ of such samples that percolate (have opposite faces connected). Five such “experimental” curves are shown in Fig. 4.21, each of which corresponds to a given cube size $b^3$. The five values for the cube edge $b$ are $b = 10, 20, 30, 50,$ and $80$, and each data point shown represents a large number of cases that ranges from $20,000$ for $b = 10$ to $500$ for $b = 80$.

Naturally, in the limit $b \rightarrow \infty$, the function $p'(p)$ becomes a step function
that jumps abruptly from \( p' = 0 \) to \( p' = 1 \) at the percolation threshold \( p = p_c \). For finite \( b \), the transition from \( p' \approx 0 \) to \( p' \approx 1 \) is smeared out over a finite range of \( p \). Now in the spirit of the renormalization group, we interpret \( p'(p, b) \) as the renormalized probability corresponding to an initial probability \( p \) and a lattice rescaling by a scale factor \( b \). Then, for a given \( b \), a critical fixed point \( p^*(b) \) is determined by finding the value of \( p \) that transforms into itself under that rescaling

\[
p'(p^*, b) = p^*.
\]  

The solution of Eq. (4.23), for each value of \( b \), may be obtained graphically from Fig. 4.21 by locating the intersection of the curve \( p'(p) \) with the straight line \( p' = p \). We see that, though \( p^*(b) \) slightly underestimates \( p_c \) (which is
0.247 for bond percolation on the sc lattice, \( p^* \) closely approximates \( p_c \) even for \( b \) as small as 10. By \( b = 80 \), \( p^* \) is within 0.001 of \( p^* (\infty) = p_c \).

Besides providing an alternate route to \( p_c \), a computer-experiment implementation of the renormalization-group philosophy also yields accurate information about the correlation-length exponent \( \nu \). In terms of the rescaled bond-connectedness probability \( p' (p, b) \) illustrated in Fig. 4.21, the news about \( \nu \) is contained in the steepness of each curve near \( p^* \). If, for a scale factor \( b \), the slope at \( p = p^* \) is denoted by \( (dp'/dp)_{p^*} \) it is a result of scaling theory that \( \nu \) is given by

\[
\nu = \frac{\ln b}{\ln (dp'/dp)_{p^*}} \tag{4.24}
\]

We present a rough argument for the plausibility of Eq. (4.24). Let \( l - (\Delta p)^{-\nu} \) and \( l' - (\Delta p')^{-\nu} \) denote the connectedness lengths \( l \) and \( l' \) in the initial and rescaled systems, respectively. \( \Delta p \equiv p - p_c \) and \( \Delta p' \equiv p' - p_c \) denote the initial and rescaled distance from threshold, which is assumed to be small. Since \( (l/l') = b \) because the rescaled unit of length is \( b \) times the original unit, then \( (\Delta p'/\Delta p)^{\nu} = b \). Interpreting \( \Delta p'/\Delta p \) as \( dp'/dp \) at \( p = p^* \approx p_c \), and solving for \( \nu \) yields Eq. (4.24).

Figure 4.22 shows the determination of \( \nu \) according to the scaling-law expectation expressed in Eq. (4.24) and the numerical data shown in Fig. 4.21. The slope of \( p'(p) \) near \( p_c \) is plotted against \( b \) on a log-log plot. The straight line that closely fits these data corresponds to a value of \( \nu = 0.85 \) for the connectedness-length critical exponent in three dimensions.

The bond-percolation computer experiments whose results yield the data displayed in Figs. 4.21 and 4.22 provide a straightforward and concrete realization for renormalization-group concepts. It is similarly straightforward to obtain analogous results for site percolation. Here, a block of \( b^3 \) sites on the original lattice would transform into a single site on the rescaled lattice. The renormalized probability \( p' = p'(p, b) \) would now state the probability for that site to be occupied, given \( p \) as the occupation probability on the initial lattice. This situation closely resembles the magnetic "site-spin→block-spin" transformation that was introduced by Kadanoff in 1966 in the theoretical development that provided the intuitive conceptual precursor of the formal renormalization-group approach to phase transitions.

We close with a few final generalizations of percolation theory. Figure 4.23 illustrates two such generalizations: polychromatic percolation (Zallen, 1977) and extended-range percolation (Domb and Dalton, 1966). Conventional percolation is a problem in black and white. The statistically assigned state function takes on either of just two values (e.g., filled or empty), and our attention is in fact normally focused on only one (e.g., the filled sites) of the two species present. In polychromatic percolation, the state function is permitted to take on three or more discrete values. In polychromatic site percolation, each site is occupied by a "particle" of some color, and adjacent sites are connected if
they are occupied by particles of the same color. Similarly, in polychromatic bond percolation, each bond is permeable to a "fluid" of some color, and adjacent bonds of (permeable to the fluid of) the same color are linked.

Figure 4.23 represents a site-percolation process with three species (colors) present, i.e., trichromatic site percolation. The three states or particle types are denoted by solid circles, open squares, and crosses, and are present here in concentrations of roughly 45%, 45%, and 10%, respectively. Since $p_{c \text{ site}}$ is 0.59 for the square lattice, none of the species percolate. Polychromatic percolation becomes interesting when it is possible for two or more species to
simultaneously percolate. This cannot happen for standard site percolation in two dimensions, since $p_c$ is never less than $\frac{1}{2}$. For site percolation in two dimensions, an unbounded black sponge cannot coexist with a white one. But in three (or higher) dimensions, $p_c$ can be quite small and several sponges (infinite clusters) of different colors can coexist. Thus, for site percolation on the $d = 3$ sc lattice, with $p_c = 0.31$, both the circles and the squares (with $p = 0.45$) would percolate, forming a pair of extended and intertwined sponges.

Such interleaving three-dimensional percolation paths are hard to show in a two-dimensional illustration. Fortunately, there is another route to a multiple percolation situation that is much easier to illustrate. The basic prerequisite for a low threshold is a high connectivity. While connectivity increases with increasing dimensionality, high connectivity can also be achieved for lattices of low dimensionality by dropping the limitation (adhered to up to this point) to simple lattices with bonds only between nearest-neighbor sites. By adding direct connections beyond nearest neighbors, we can encounter quite low percolation thresholds in three dimensions—and even in two.

Multiple percolation via increased range of interaction in two dimensions is demonstrated in Fig. 4.23. While $z = 4$ and $p_c = 0.59$ for the simple square lattice shown in the upper half of the figure, extending the interaction range to next-nearest neighbors increases $z$ to 8 and lowers the site-percolation threshold to $p_c = 0.41$. While, for the configuration shown, none of the species
percolate on the simple lattice, both the circles and the squares percolate \( (p > p_c) \) on the more highly connected lattice shown in the lower half of Fig. 4.23.

A simple setting for envisioning polychromatic percolation is a resistor network composed of three types of connectors: perfect insulators, unit conductors, and superconductors, present with probabilities \( p_0, p_1 \) and \( p_\infty \), respectively. Depending upon the values of these probabilities, the macroscopic network is either insulating, conducting, or superconducting. If \( p_\infty \) exceeds \( p_c \), the system is superconducting, whatever the values of \( p_0 \) and \( p_1 \). If \( p_1 \) exceeds \( p_c \) while \( p_\infty \) does not, the system is a normal conductor. It is also normally conducting if the combined network of conductors and superconductors percolates, even though neither component percolates on its own: \( p_1 < p_c, p_\infty < p_c \), but \( p_1 + p_\infty > p_c \). Only if the union of conductors and superconductors fails to percolate \( (p_1 + p_\infty < p_c \) or, equivalently, \( p_0 > 1 - p_c \)) is the system insulating. These conditions carve up the composition field into three regimes which constitute the phase diagram for this polychromatic percolation system.

The last generalization of percolation that will be mentioned now to close this chapter is one which will be useful, in the following chapter, in the treatment of the free-volume theory of the glass transition. It is called high-density percolation (Reich and Leath, 1978, Cohen and Grest, 1979). In the site-percolation version, each site is occupied \( (p) \) or not \( (1 - p) \) as usual, but an occupied site is considered to belong to a cluster only if it is adjacent to \( m \) or more occupied sites. Thus, isolated \( (m = 0) \) filled sites are ignored. If \( m \) is chosen to be 1, the situation remains essentially similar to standard site percolation. For values of \( m \) lying between \( m = 2 \) and \( m = z \), high-density percolation yields a percolation process that focuses on the appearance of dense, well-connected clusters. For \( m = 2, p_c \) is the same as for standard \((m = 1)\) percolation, since only the inessential dangling bonds at the outskirts of the infinite cluster are eliminated by the \( m = 2 \) requirement. But for \( m \geq 3 \), the percolation threshold is shifted to higher densities. Critical exponents remain the same as for ordinary percolation.

REFERENCES

Porter, C., 1935, lyrics* from the song "Just One of Those Things" from the musical comedy *Jubilee*:

> It was just one of those nights,
> just one of those fabulous flights,
> a trip to the moon on gossamer wings,
> just one of those things.


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