REVIEWS OF MODERN PHYSICS VOLUME 45, NUMBER 4 OCTOBER 1973

Percolation and Conduction

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(Received 21 March 1973)

Extensions of percolation theory to treat transport are described. Resistor networks, from which resistors are removed at random, provide the natural generalization of the lattice models for which percolation thresholds and percolation probabilities have previously been considered. The normalized conductance, G, of such networks proves to be a sharply defined quantity with a characteristic concentration dependence near threshold which appears sensitive only to dimensionality. Numerical results are presented for several families of $3D$ and $2D$ network models. Except close to threshold, the models based on bond percolation are accurately described by a simple effective medium theory, which can also treat continuous media or situations less drastic than the percolation models, for example, materials in which local conductivity has a continuous distribution of values. The present calculations provide the first quantitative test of this theory. A "Green's function" derivation of the effective medium theory, which makes contact with similar treatments of disordered alloys, is presented. Finally, a general expression for the conductance of a percolation model is obtained which relates G to the spin-stiffness coefficient, D, of an appropriately defined model dilute ferromagnet. We use this relationship to argue that the "percolation channels" through which the current flows above threshold must be regarded as three dimensional.

CONTENTS

I. INTRODUCTION

This paper concerns itself with theories of, and models for transport in inhomogeneous conductors, especially those exhibiting a percolation threshold. Possible examples of such systems could be compacted mixtures of conducting and nonconducting materials or homogeneous two-phase systems in which one phase is much more conductive. In addition, the numerical methods and most of the analytic results presented can also be used to study materials with more modest inhomogeneities. However, in this paper we shall focus attention on the percolation limit, partly because of its inherent interest, and partly because it provides the strictest test of any analytic theory of the effects of inhomogeneities and permits a clear statement of the limits of viability of such theories.

Percolation thresholds were first studied formally by Broadbent and Hammersley (1957) [see also Hammersley (1957)], who introduced lattice models for the flow of a fluid through a static random medium, and showed rigorously that no fluid will flow if the concentration of active medium is smaller than some nonzero threshold value. They also introduced the notion of a percolation probability, which is the likelihood that any given region of the medium is sufficiently well connected to the rest to be available for conduction. This work, its generalizations, and some experimental evidence of percolation thresholds in classical systems are summarized in Sec. II. For more detail, the reader is referred to the available review papers (see, e.g., Frisch and Hammersley, 1963; Fisher, 1964; Shante and Kirkpatrick, 1971; Essam, 1973).

A major cause of recent interest (Shante and Kirkpatrick) in percolation theory has been the suggestion, due to several workers, that percolation effects may play a role in the metal–semiconductor transitions seen in some disordered systems, or in the unusually low mobilities associated with free carriers in amorphous materials. The "semiclassical" arguments by which the connection to percolation theory may perhaps be made for these obviously quantum-mechanical systems are also reviewed in Sec. II.

In an elegant table-top experiment, Last and Thouless (1971) recently demonstrated that the theory reviewed in the above references is incomplete, as it does not describe transport processes near threshold. In Sec. III, a class of random resistor networks is introduced and shown to be capable of simulating the details of transport in mixtures, both near and far from a percolation threshold. In addition, the network models prove amenable to both numerical (Monte Carlo) and analytical study. We feel that such resistor networks provide the natural extension to treat transport processes of the existing lattice models for percolation.

Numerical results obtained over a wide range of concentrations in three simple network models are presented in Sec. IV. Near threshold, a similar power law dependence of the network conductivity upon concentration is found in all three models. We argue that this behavior should be a general feature of transport near a percolation threshold in continuous media as well.

The conductivity far from threshold is sensitive to details of the model considered. In Sec. V we develop a self-consistent effective medium theory which gives good agreement with the Monte Carlo data far from threshold and can be generalized to treat transport processes more complex than our simplified percolation models.

Two derivations of this theory are given in Sec. V. The first is essentially an extension of an old theory of conduction in mixtures (Bruggeman, 1935; Landauer, 1952), while the second is more formal, and makes contact with self-consistent treatments used in the study of alloys (Soven, 1967; Velický, 1968). The effective medium transport theory is applicable to an extremely wide class of systems. The Monte Carlo data reported here provides the first quantitative confirmation of its accuracy. From the formal treatment we obtain estimates of the conditions under which this simple theory will be valid.

We have also obtained a general expression for the conductivity at arbitrary concentrations for one of the resistor network models studied, using a response function analysis recently developed by Brenig *et al.* (1971) to treat hopping conduction among localized states. Although this result, described in Sec. VI, does not seem too useful for explicit calculation, it does give some insight into the nature of transport in the critical region, and permits us to establish a connection between the present calculations and certain properties of simple models of disordered magnetic materials.

In Sec. VII we comment briefly on the applicability of both the specific numerical results for the conductivity, and the effective medium theory for conductivity and more complex transport coefficients to real systems exhibiting a metal–semiconductor transition.

Several preliminary descriptions (Kirkpatrick, 1971, 1972a) and partial reports (Kirkpatrick, 1973b) of this material have now appeared. A second paper is in preparation, in which the results of this paper are used to study the role of the percolation threshold in hopping conduction, and to provide a microscopic theory of the prefactor terms in the conductivity. A summary of the latter work is found in Kirkpatrick (1973b).

II. BACKGROUND

Observations of conduction thresholds in mixtures of conducting and nonconducting materials are scattered throughout the literature of materials science. Gurland (1966), for example, studying compacted mixtures of silver balls and Bakelite powder, reports a pronounced threshold when 30% by volume of the compact is metallic. [The later work of Malliaris and Turner (1971) has shown that the value of the threshold concentration is sensitive to preparation methods.]

Microscopic examination of these compacts shows that all dimensions of the conducting regions are much greater than the room-temperature mean free path of conduction electrons in a metal such as Ag. Therefore, when metallic, these are essentially classical systems, as far as the effects of disorder on transport are concerned. The electrons can be treated as a fluid subject to the constraints of classical electrostatics, while disorder enters through the contorted boundary conditions which the equilibrium current distribution must satisfy.

The first mathematical formulation of the classical threshold was that of Broadbent and Hammersley (1957). They introduced a simplified "lattice percolation" model for the flow of a fluid through a porous medium and were able to show rigorously that their model possessed a threshold. This model requires fluid to flow through the "bonds" which connect nearest neighbors in a regular lattice of "sites." Disorder may be introduced in a variety of ways. The most common statistical assumptions are known as the "bond percolation" and "site percolation" models (Frisch and Hammersley, 1963; Fisher, 1964; Shante and Kirkpatrick, 1971; Essam, 1973). In the first, some known fraction of the bonds, distributed at random, are missing from the lattice, and fluid cannot flow through them. In the second, a known fraction of sites are assumed to be missing. The absence of a site implies that no current can flow through any of the bonds which join that site to its neighbors.

Detailed studies of percolation on lattices have been carried out by both numerical (Dean and Bird, 1966, 1967) and analytical (Erdös and Rényi, 1960; Fisher and Essam, 1961) techniques. The analytical results available apply only to rather special models. The Monte Carlo studies of Dean and Bird, using the site percolation model, encompass all the common 3*D* and 2*D* lattices. This work is not widely known, but its extensive tabulations of cluster properties appear to be quite accurate and should be useful in the quantitative description of many local properties of random systems.

A general picture of what might be called the topological aspects of a percolation threshold has emerged from the work of Dean and Bird, Erdös and Rényi and Fisher and Essam and other studies (Shante and Kirkpatrick, 1971). To illustrate this picture, we shall describe the stages of site percolation on a lattice which contains N sites, with N a large number. Quantities relevant to percolation are defined in the limit $N\rightarrow\infty$, and will depend upon x, the concentration of "allowed" sites, and the geometry of the lattice.

When the concentration is low ($x\ll x_c$), the allowed sites occur singly or in small isolated clusters of adjacent allowed sites. As x increases, larger clusters occur, and the mean size of a cluster increases monotonically. As x approaches x_c from below, the larger clusters begin to merge, creating a few extremely large clusters, so that in the limit $N\rightarrow\infty$ the mean cluster size diverges at x_c. For any finite N this implies that there is a completed path of adjacent allowed sites crossing the system, and thus macroscopic flow through the system becomes possible.

As soon as $x>x_c$ it appears [although no rigorous

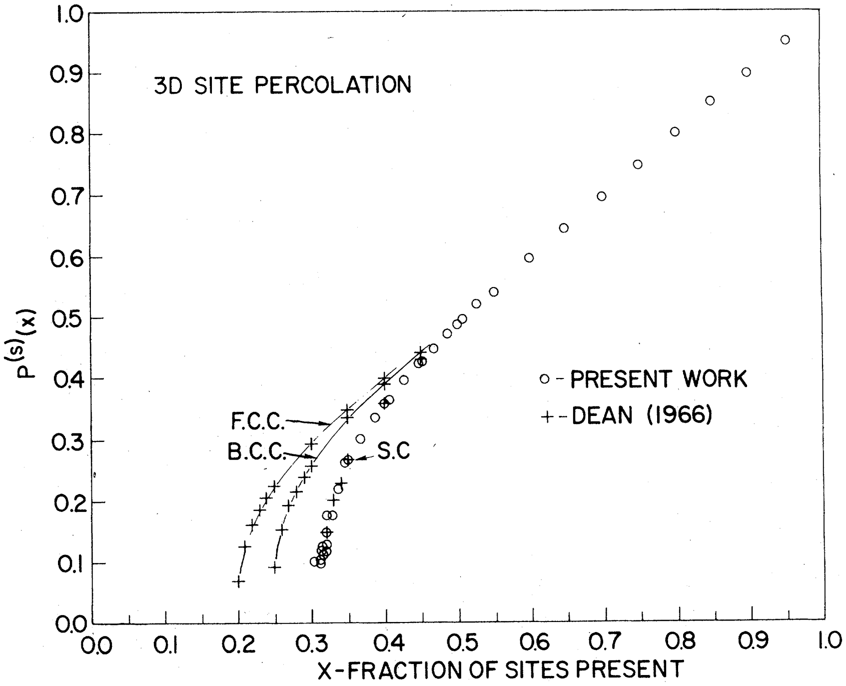

FIG. 1. Site percolation probability, $P^{(s)}(x)$, for three different $3D$ lattices, plotted as a function of the fraction of sites present. Circles represent Monte Carlo data obtained (Kirkpatrick, 1973a) on $3D$ simple cubic (sc) $30\times30\times30$ site networks. Crosses indicate Dean and Bird's (1966, 1967) calculations for sc, body-centered cubic (bcc), and face-centered cubic (fcc) lattices. Each cross represents an average over data from twenty networks of approximately 60 000 sites each. Threshold concentrations, those values of x_c for which the power law form (2.1) was best satisfied, were: (sc) 0.312 ± 0.002; (bcc) 0.248 ± 0.003; (fcc) 0.200 ± 0.002.

proof exists (Shante and Kirkpatrick, 1971)] that if N is sufficiently large only one large cluster remains, along with many small ones. The ratio of the number of sites in this "infinite cluster" to the number of sites in the lattice tends to a sharply defined function of x when N is made very large with $x>x_c$ held constant (Broadbent and Hammersley, 1957; Hammersley, 1957). This ratio, which we shall term the "site percolation probability" $P^{(s)}(x)$, proves to be a natural quantity to use in discussing transport, since it is the fraction of the volume of the system in which dc conduction is possible. However, we caution that our definition of $P(x)$ differs by a factor of x from the definition customary in the mathematical literature.

As x increases above x_c, the infinite cluster grows rapidly, absorbing smaller clusters. Correspondingly, $P^{(s)}(x)$ rises sharply from zero just above threshold, and goes asymptotically to x when $x\gg x_c$, and isolated clusters become rare. The numerical results of Dean and Bird (1966, 1967) and Kirkpatrick (1973a) for $P^{(s)}(x)$ on three common $3D$ lattices, which demonstrate this behavior, are displayed in Fig. 1. $P^{(s)}(x)$ near threshold can be characterized by a simple power law,

$$P^{(s)}(x)\propto(x-x_c)^s, \qquad (2.1)$$

where s is approximately the same for all three lattices (Kirkpatrick, 1973a)

$$0.3\leq s\leq 0.4. \qquad (2.2)$$

Thresholds of this type are not restricted to nearest-neighbor percolation on regular lattices, or even to lattices at all. The threshold also occurs for models in which sites several lattice constants apart are considered to be connected (Shante and Kirkpatrick, 1971). For the bond percolation model, the mean number n_c of allowed bonds per site on the lattice at threshold proves to be an invariant property, determined almost entirely by dimensionality and insensitive to the details of the lattice studied. The relation (cf. Vyssotsky *et al.*, 1961; Ziman, 1968)

$$n_c\approx d/(d-1) \qquad (2.3)$$

is satisfied to within a few percent for all common $2D$ and $3D$ lattices (Shante and Kirkpatrick, 1971). This general rule must be at least approximately valid for lattices lacking perfect translational symmetry.

A similar invariant construction has been used to link site percolation to the properties of continuous materials. By associating an allowed volume with each allowed site (the volume of a sphere with radius equal to half the nearest-neighbor separation), Scher and Zallen (1970) showed that the values of x_c found for site percolation on various lattices correspond to an allowed region which is 0.15 of the volume of the system in $3D$, and 0.45 in $2D$. This result is accurate to a few percent.

These numbers are not immediately relevant to the problem of predicting threshold concentrations for percolation in a continuous medium. The allowed volume in Scher and Zallen's construction consists of non-overlapping spheres (or circles) whose centers are constrained to lie on a regular lattice, and bears little resemblance to the metallic portion of the compacts studied by Gurland (1966) and Malliaris and Turner

(1971). A continuum percolation model in which the allowed volume consists of identical spheres (or circles in $2D$) permitted to overlap, with centers distributed at random, has been studied numerically. The threshold volume fraction, v_c, for this model (Shante and Kirkpatrick, 1971) is 0.29 in $3D$ and 0.68 in $2D$. Finally, we argue in the following section that $v_c=0.25$ in $3D$ and $V_c=0.5$ in $2D$[1] may be the best estimate of the threshold concentration for a compact whose metallic and nonmetallic regions have, on the average, similar shapes. The threshold concentrations for most real compacted mixtures should fall within the range of these three estimates.

Abeles and Hanak (1970) have reported $3D$ composite materials with thresholds at much higher metallic concentrations, e.g., with v_c greater than 0.5. For this to occur there must be a high degree of asymmetry between the characteristic shapes of the conducting and the nonconducting regions. Consequently the results of this paper will require modification before they can be applied to such systems.

Several authors (Ziman, 1968; Eggarter and Cohen, 1970; 1971; Zallen and Scher, 1971) have appealed to percolation theory in order to describe the electronic states of systems which are disordered on a scale too small to permit macroscopic treatment. The most complete exposition of this line of argument is that of Eggarter (1972). He considers the motion of an electron injected into dilute He vapor, treating the He atoms as a gas of massive hard spheres, and replacing the hard sphere potentials by a position- and energy-dependent effective potential, $V(x, E)$, calculated in a low-density approximation. The effective density of scatterers, and consequently the effective potential, fluctuates from point to point, but only on a scale sufficiently long for the electron's response to it to be essentially classical. Eggarter and Cohen (1970, 1971) and Eggarter (1972) define such a local density, felt near a given point by an electron with energy E, by averaging over a surrounding sampling region whose radius is approximately the deBroglie wavelength $L=h(2/mE)^{1/2}$.

This effective potential may be used for two types of calculation. The density of states is given to a good approximation by Eqs. (21) and (26) of Eggarter (1972) as the spatial average,

$$\rho(E)=\int d^3x\rho^{(0)}[E-V(x,E)], \tag{2.4}$$

where $\rho^{(0)}(E)$ is the density of states in the absence of any scatterers. Equation (2.4) and the arguments outlined above have been used to predict the form of the tail in the density of states for several simple systems. The results are in excellent agreement with accurate numerical calculations performed for a model tight-binding band in the presence of a high concentration of short-ranged repulsive scatterers (Kirkpatrick, 1972b).

The second application is to transport. The effective potential has been smoothed sufficiently that an electron's wave function will be extremely small in the classically forbidden region where $V(x, E)>E$, and the electron will be largely confined to the allowed regions. Thus when $v(E)$, the fraction of the material which is classically allowed to an electron with energy E, exceeds the critical value for percolation, v_c, conduction becomes possible. Eggarter and Cohen determine a mobility edge, E_c, by

$$v(E_c)=v_c. \tag{2.5}$$

Using Eq. (2.5) and an approximate calculation of the mobility near E_c, they were able to give a good account of the electron mobility as it decreases by 5 orders of magnitude with increasing He vapor density.

Thus, the achievements of percolation theory up to 1971 are essentially twofold. The percolation threshold has been shown to be a very general phenomenon, relevant to systems without underlying regular structure, as well as to the lattice models on which numerical work has been done. General features of the percolation probability have also been observed, in particular its appearance near threshold.

However, the connection between $P(x)$ and the conductivity of a system remains unclear. This was demonstrated very effectively by Last and Thouless (1971), who measured the conductivity of a piece of conducting paper as holes were punched in it at random with approximately the statistics of site percolation. The conductivity as a function of the fraction of the paper remaining was observed to go to zero with zero slope at approximately the critical concentration for $2D$ site percolation. Thus the threshold is correctly predicted by x_c, but the form of the conductivity near threshold cannot come from $P(x)$ alone, since $P(x)$ (see Fig. 1) has infinite slope at threshold. [The data of Fig. 1 describe a $3D$ model. While the exponent s in Eq. (2.1) has not been accurately determined for any $2D$ models, there exist general arguments which require that $s(2D)\leq 0.5$, and the available numerical data on $P(x)$ (Frisch *et al.*, 1962) suggests that $s(2D)<s(3D)$.]

In the following sections we introduce and analyze an extension of the basic percolation lattice model which makes it possible to consider conduction in the presence of randomly distributed excluded volumes in three as well as two dimensions, and under a variety of statistical constraints. In terms of this model, it is possible to define a percolation conductance, $G(x)$, which appears to be of general use in describing transport near a percolation threshold.

III. RESISTOR NETWORK MODELS

Let us suppose that we know the detailed spatial arrangement of the conducting and the nonconducting materials in a composite system such as one of the mixtures studied by Gurland (1966) or Malliaris and Turner (1971). If all dimensions of the conducting regions are large with respect to electronic mean free

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[1] This estimate of the $2D$ case has also been obtained, by a different line of reasoning, by Zallen and Scher (1971).

paths, a local conductivity, $\sigma(r)$, can usefully be defined by the bulk value of the conductivity for the material found at the point r. We could then seek to calculate the conductivity of the composite material, and determine to what extent this can be related to simple statistical characterizations of the distribution of $\sigma(r)$'s in the material.

The random arrangement of the material modifies the conductivity of a sample in several ways. As noted in the preceding section, isolated conducting regions cannot contribute to transport, so that only the connected part of the conducting material, a fraction $P(x)$ of the whole, is of interest. Let us suppose that the connected region were arranged in regular layers parallel to the applied field. This is clearly the optimal arrangement and results in the ratio of the conductivity of the composite to the bulk conductivity of the metallic part being equal to $P(x)$, an upper bound. Near threshold in the actual composite, as Last and Thouless (1971) have noted, this bound cannot be achieved, since much of the connected part should consist of useless dead ends, and the current will flow predominantely through a fraction of the sample which is significantly less than $P(x)$. Even when dead ends are not a problem, as for example when the insulating regions are small and isolated, the effects of the local fields necessary to guide the current around obstacles must be considered. This contribution is stressed in the effective medium treatments (Bruggeman, 1935; Landauer, 1952) which have been applied to this problem (see Sec. V).

Given $\sigma(r)$, we can treat both effects exactly by solving the usual equations of electrostatics,

$$j(r)=\sigma(r)\nabla V(r),$$
$$\nabla\cdot j(r)=0 \qquad (3.1)$$

for the voltage, $V(r)$, and current, $j(r)$, which result when a field is applied across the sample. Equations (3.1) may be solved to any desired accuracy using a finite difference approximation. By introducing a regular cubic mesh of points $\{r_i\}$, with spacing Δr, one obtains a system of linear equations for the voltages $V_i=V(r_i)$,

$$\textstyle\sum_j g_{ij}(V_i-V_j)=0 \qquad (3.2)$$

for all r_i not at a surface, with

$$g_{ij}=\Delta r\sigma[(r_i+r_j)/2], \qquad (3.3)$$

and i, j neighboring sites on the mesh.

A natural lattice idealization of this problem is based on the observation (Kirkpatrick, 1971) that Eq. (3.2) is identical to the Kirchoff current law for a regular network of random-valued conductances g_{ij}, with V_i denoting the voltage at the ith node. In this paper we shall construct and study several classes of random resistor networks in which g_{ij} is restricted to one of the two values, 0 or 1. The networks are interesting in their own right, since clearly they will exhibit a percolation threshold, and they can be related to real composite materials by analogy to Eqs. (3.1)–(3.3). Since a cubic mesh is both necessary and sufficient for the finite-difference expansion [see, e.g., Godunov and Ryabenki (1964)] of Eq. (3.1), we shall consider only 3*D* simple cubic and 2*D* square networks. The consequences of various assumptions about the statistical distribution and spatial correlation of the g_{ij} have been explored, in an attempt to learn which features of the conductivity are insensitive to such details. Three different percolation models will be distinguished:

(A) The *bond percolation model* is the simplest case. A fraction of the bonds are chosen at random and "removed," i.e., assigned the conductance $g_{ij}=0$. In numerical calculations, this is done by assigning to each bond a random number uniformly distributed between 0 and 1, then removing all bonds whose numbers fall into a selected interval. All properties are studied as a function of p, the fraction of bonds which remain. By the arguments used in deriving Eqs. (3.1)–(3.3) we see that p corresponds to the fraction of the volume which is conducting.

(B) In the *site percolation model*, we assign a random number to each node, or site, in the network, in order to select a fraction of the sites to be removed from the network. In this paper we shall use x to denote the fraction of sites present, as distinguished from p, the fraction of bonds present. Removal of a site means that all bonds from that site to its neighbors are assigned $g_{ij}=0$. In this model there is a strong spatial correlation in the presence or absence of nearby bonds, since if a bond is absent, so are all of the bonds joined to it at one or both of its endpoints.

(C) A *correlated bond percolation model* may be defined as follows: Each site is assigned a random number, E_i, uniformly distributed between -1 and $+1$. Random numbers E_{ij} for the bonds are calculated from the numbers characterizing the sites by the rule

$$E_{ij}=\tfrac{1}{2}(|E_i|+|E_j|+|E_i-E_j|). \qquad (3.4)$$

Finally, all bonds with E_{ij} greater than some selected limit are removed. There is a statistical correlation between bonds in this model which is quite different from that found in the site percolation model. A bond, g_{ij}, is present only if E_{ij} is sufficiently small, which implies that $|E_i|$ and $|E_j|$ are also small. Thus, if a bond is present, its neighbors have a greater than average probability of also being present. In this model the bonds remaining in the network are clustered together, in contrast to the site percolation model in which the missing bonds cluster.

In treating the properties of simple mixtures it is usually assumed that the conducting and nonconducting regions can and should be treated on an equal footing (Bruggeman, 1935; Landauer, 1952). That is, interchanging the conducting and nonconducting regions in a sample with a fraction x of its volume conducting should yield an equally plausible sample with conducting fraction $1-x$. The bond percolation model also has this symmetry between bonds present and bonds missing. Therefore its threshold concentration provides our best estimate for the critical volume fraction of a random mixture, if we identify, following Eqs. (3.1)–(3.3), bond concentration with volume fraction. The critical concentrations for bond percolation on cubic lattices, 0.5 in $2D$ and 0.25 in $3D$, provide the estimates of v_c cited in Sec. II.

IV. NUMERICAL STUDIES

In the numerical studies reported below, the networks have a finite number of sites. Dimensions of the networks from which particular sets of data were obtained are indicated in the appropriate figure captions. The conductivity of each random network was obtained by setting the voltage at each node on one end surface of the cubic mesh equal to zero, assigning a constant voltage to all the nodes on the opposite end, and solving Eq. (3.3) on a computer to obtain the current flow between them. Cyclic boundary conditions are imposed by connecting pairs of mesh points on the opposite free faces through an extra layer of random conductances. Thus the samples are essentially infinite in the directions perpendicular to the applied voltage. For the analytic methods discussed in the following sections we shall assume that the sample is infinite. Since the mesh is cubic, the conductivity is isotropic. For convenience we shall always calculate it along a cubic axis.

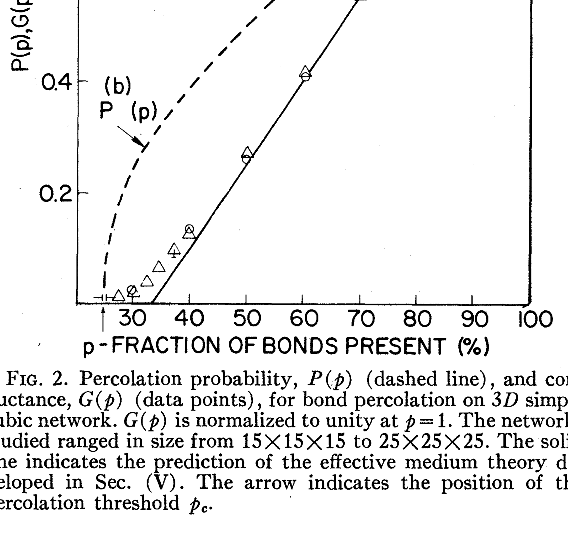

FIG. 2. Percolation probability, $P(p)$ (dashed line), and conductance, $G(p)$ (data points), for bond percolation on $3D$ simple cubic network. $G(p)$ is normalized to unity at $p=1$. The networks studied ranged in size from 15×15×15 to 25×25×25. The solid line indicates the prediction of the effective medium theory developed in Sec. (V). The arrow indicates the position of the percolation threshold p_c.

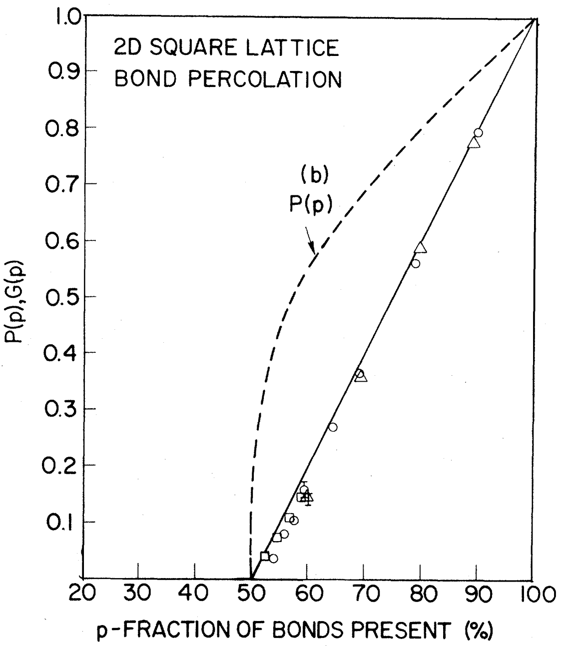

FIG. 3. Results for bond percolation on 50×50 site $2D$ square networks. Labelling conventions same as in Fig. 2. The threshold concentration for this lattice is $p_c=\frac{1}{2}$, an exact result.

Conductance data for the bond percolation model are presented in Figs. 2 ($3D$ model) and 3 ($2D$). The conductance $G(x)$, normalized so that $G(1)=1$, is plotted as a function of the bond fraction, p. For comparison, $P^{(b)}(p)$, the percolation probability in the bond problem, has been sketched in, following the numerical results of Frisch, Hammersley, and Welsh (1962). In Fig. 2, the two quantities appear to have the same threshold concentrations, with an uncertainty of less than 0.01, but the difference in their concentration dependences near threshold is unmistakable, in agreement with Last and Thouless's (1971) observation. Two domains of concentration are apparent in Fig. 2—a critical region in which $G(p)$ increases from zero with initially zero slope, and a high concentration regime in which the concentration dependence appears simpler. The effective medium theory to be described in Sec. V (solid line) gives a very accurate prediction of $G(p)$ in the high concentration regime for this model.

Variations in $G(p)$ among samples with the same concentration were more severe in $2D$ than in $3D$, so only the simplest possible $2D$ model, the bond percolation model, was studied. The data for all samples studied are plotted in Fig. 3. Again, $P(p)$ and $G(p)$ appear to have the same threshold, but the critical region for the $2D$ model seems to be confined to too small a range of concentrations for accurate numerical study. As in the preceding case, the effective medium theory (solid line) is in good agreement with the data far from p_c.

Data obtained on the $3D$ site percolation model are plotted against the fraction of sites present in Fig. 4.

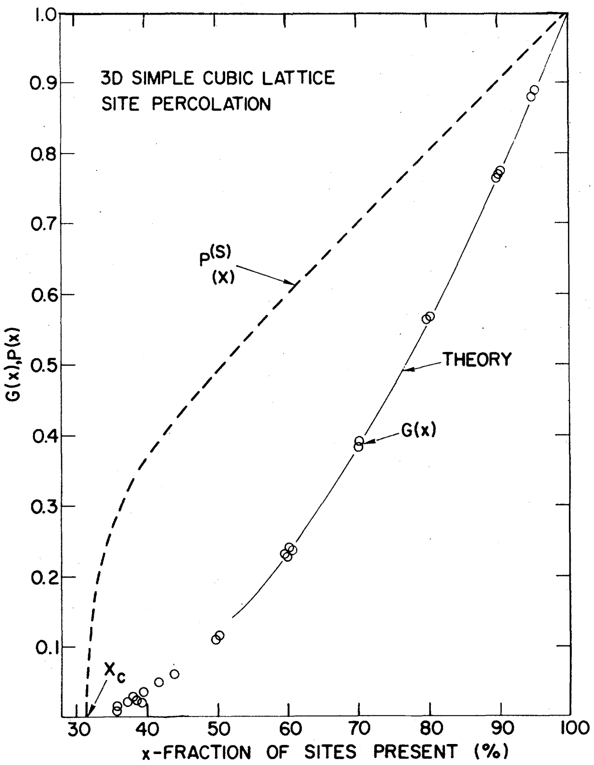

Fig. 4. Percolation probability and conductance data for site percolation on 20×20×20 site simple cubic networks, plotted against the fraction of sites present. The solid line labelled THEORY is the "low-density" (of missing sites) approximation (6.22).

Again the onset of conduction occurs with zero first derivative, but the high concentration region of Fig. 4 looks much droopier than the same region in Fig. 2. In its concave appearance, Fig. 4 is similar to the experimental results of Last and Thouless, who simulated site percolation in the way they punched their holes. Recently, Adler *et al.* (1973) have studied the conductivity of the site percolation model by both numerical and analog (real resistors) means. Their results appear to agree with Fig. 4. The differences between the bond and site models are much less apparent if G for the site model is plotted as a function of the fraction of bonds present, as in Fig. 5. In this model, the fraction of bonds present is the square of the fraction of sites present, since a bond is present only if the sites at both ends are present.

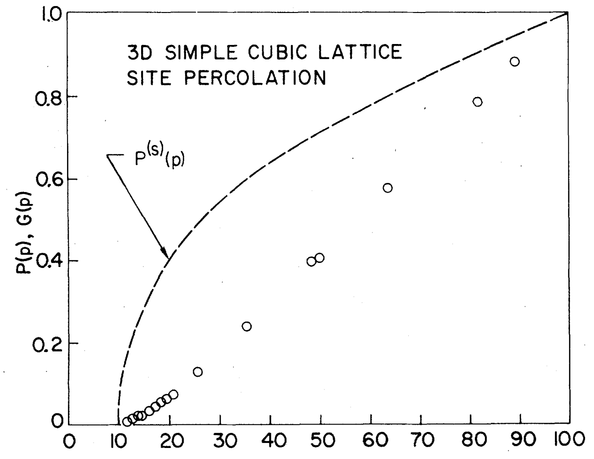

Fig. 5. Site percolation data, plotted against p, the fraction of bonds present, rather than x, the fraction of sites present.

$G(p)$ for the correlated bond percolation model, plotted in Fig. 6, closely resembles the results for the site model of Fig. 5, despite the different character of the statistical correlations between bonds in the two models. The threshold concentration for the correlated bond model was found to be $p_c = 0.103 \pm 0.1$ (by looking for the appearance of the first completed path, in ten 30×30 samples), but no data on the percolation probability is available.

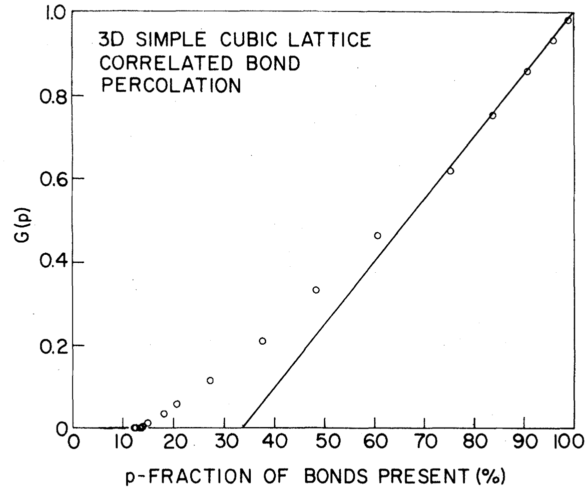

Fig. 6. Conductance of 25×25×25 site correlated bond percolation networks, prepared as described in the text for model C. There are no data available on the percolation probability. The solid line, as in Fig. 2, represents the effective medium theory prediction.

The conductances observed for the three models differ considerably in the high concentration regime. The correlated bond model data have the same slope near $p=1$ as does the simple bond percolation model, and hence agrees with the prediction of the effective medium theory. However, as p decreases $G(p)$ for the correlated bond percolation model curves upwards, lying above the effective medium result. The site percolation model results (Fig. 5) have a smaller initial slope than is seen in Figs. 2 and 6. Explanations for these differences are obtained in the next two sections.

Near threshold, the curves in Figs. 2, 5, and 6 are strikingly similar. For all three cases, a power law form,

$$G(p) \propto (p - p_c)^t, \qquad (4.1)$$

was observed to hold over a range of concentrations extending 0.2 or more above the respective threshold concentrations. The values of t found for the three models were mutually consistent:

$$\begin{aligned} t&=1.6\pm0.1 && \text{(bond percolation)}\\ t&=1.5\pm0.2 && \text{(site and correlated bond percolation).} \end{aligned} \tag{4.2}$$

As is commonly found in the study of critical phenomena, these different $3D$ models all have similar behavior sufficiently close to the critical concentration. The dimensionality of the system appears more important than the details of the lattice or cluster statistics. Although results for a $2D$ model (Fig. 3) may have been flawed by the use of too small a sample, the exponent appears to lie between 1 and 1.3.

In Sec. II we noted that the threshold condition for bond percolation can be stated in a form which is invariant for $3D$ lattices with arbitrary coordination number, z: The mean number of bonds present at any site of the network $n_c=zp_c=1.5$ at threshold. We shall now construct a similar invariant for the correlated bond percolation problem (model C), and use it to relate G and p_c for this model to the corresponding properties of the bond percolation model.

For a given realization of model C, we need only consider the sites with energies $|E_i|\leq\Delta$, where Δ is a cutoff energy, since according to Eq. (3.4) only these sites can be part of the network of bonds selected by the criterion $E_{ij}\leq\Delta$. Thus only a fraction, Δ, of the sites are relevant, and the number of bonds open at each relevant site is given by

$$n(\Delta)=zp(\Delta)/\Delta, \tag{4.3}$$

where for the correlated bond model,

$$p(\Delta)=3\Delta^2/4, \quad \text{if} \quad \Delta\leq1. \tag{4.4}$$

Thus on the simple cubic lattice, we have

$$n(\Delta)=9\Delta/2. \tag{4.5}$$

Setting $n_c=1.5$ in Eq. (4.5) we find $\Delta_c=\frac{1}{3}$, and $p_c=\frac{1}{12}$, in reasonable agreement with the numerical results, $\Delta_c=0.39$ and $p_c=0.103\pm0.01$. Thus $n(\Delta)$, when defined with respect to the relevant portion of the lattice only, may be an invariant of this generalized bond percolation problem.

The results for $G(p)$ can also be rephrased in terms of n and n_c. For model A, the data were fitted by the expression $G(p)\approx3.2(p-p_c)^{1.6}$, which is equivalent to $0.18(n-n_c)^{1.6}$. The corresponding result for model C can be transformed, using Eq. (4.5), into $G(n)\approx0.12(n-n_c)^{1.6}$, if we assume that the same exponent applies. There is a simple explanation for the difference in coefficients. Since only $\Delta_c=0.39$ of the sites participate in the correlated bond network near threshold, the mean distance between relevant sites exceeds the nearest-neighbor distance. This scale change should reduce the bulk conductivity of model C by a factor of $l/L=(0.39)^{1/3}=0.7$, which is in good agreement with the actual ratio, $\frac{2}{3}$, of the two coefficients. Therefore we propose that

$$G(n)\approx0.18(n-n_c)^{1.6}/L \tag{4.6}$$

will be a general result for all sorts of bond percolation near threshold, accurate to perhaps 20%. This expression proves useful in the treatment of hopping conduction (Kirkpatrick, 1973b).

The exponents quoted in Eqs. (4.2) were obtained from the slopes of log–log plots of $G(p)$ versus $(p-p_c)$. The errors given are subjective confidence limits, and reflect the effects on such plots of fluctuations in the data and uncertainties of a percent or so in the value of p_c. (The latter uncertainty is a problem in $3D$ only; for bond percolation on the $2D$ square network, $p_c=\frac{1}{2}$ is an exact result.)

The percolation model data of Figs. 2–6, for networks in which $g_{ij}=1$ or 0, were obtained by a limiting process of solving first for the voltages in a network in which $g_{ij}=1$ or α, with α typically $\frac{1}{2}$, then using that solution as a starting point for solving the same network with $\alpha=\frac{1}{4}$, and so forth until α was made small enough that no further changes in the conductance occurred. From six to eight steps were required to reach $\alpha=10^{-5}$, which was usually taken to be zero. Changes in $G(x)$ resulting from further decreases in α were estimated or observed to be less than 0.01 in all cases.

At each step Eqs. (3.2) were solved by direct iteration of the inverted form,

$$V_i=\sum_j g_{ij}\,V_j/\sum_j g_{ij}. \tag{4.7}$$

No attempt at over- or under-relaxation was made. For the $2D$ cases, where convertence proved to be much slower, an implicit iterative algorithm due to Stone (1968) gave a slight improvement.[2] In all cases it proved desirable to do the calculation in double precision arithmetic. Solution of a $3D$ network of $15\times15\times15$ sites, using 50 iterations, on an IBM 360–65 computer required about 5 sec.

V. ANALYTIC RESULTS: EFFECTIVE MEDIUM TREATMENT

Outside the critical region, one can obtain an accurate analytic calculation of G, at least for the two bond percolation models. The effective medium theory that we shall develop in this section is, in some of its guises, quite ancient, yet it has features in common with the most recent theories of excitations in substitutional alloys. We shall begin by giving a derivation of this result that follows the lines of the classical theory of

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[2] Stone's method normally provides a factor of 50 to 100 improvement in computational efficiency over direct relaxation schemes in solving finite-difference transport equations in complicated finite systems. The cyclic boundary conditions employed here apparently nullify this advantage.

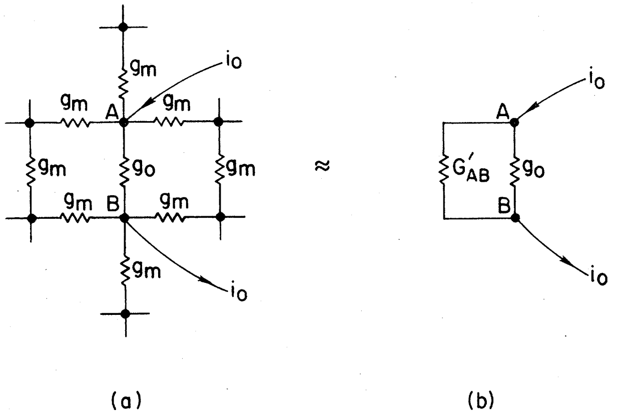

FIG. 7. Constructions used in calculating the voltage induced across one conductance, g_0, surrounded by a uniform medium.

conduction in mixtures (cf. Bruggeman, 1935; Landauer, 1952; Brown, 1956; Kerner, 1956).[3]

The distribution of potentials in a random resistor network to which a voltage has been applied along one axis may be regarded as due to both an "external field" which increases the voltages by a constant amount per row of nodes, and a fluctuating "local field," whose average over any sufficiently large region will be zero. We shall represent the average effects of the random resistors by an effective medium, defined as that medium in which the total field inside is equal to the external field. Such a medium must be homogeneous. For simplicity we shall consider it to be made up of a set of equal conductances, g_m, connecting nearest neighbors on the cubic mesh. As the criterion to fix g_m, we require that the extra voltages induced; i.e., the local fields, when individual conductances g_{ij} replace g_m, in this medium should average to zero.

Consider one conductance oriented along the external field, surrounded by the effective medium [Fig. 7(a)], and having the value $g_{AB}=g_0$. The solution of the network equations (3.2) in the presence of g_{AB} which reduces to a uniform field far from g_{AB} is constructed by superposition. To the uniform field solution, in which the voltages increase by a constant amount, V_m, per row, we add the effects of a fictitious current, i_0, introduced at A [in Fig. 7(a)] and extracted at B. Since the uniform solution fails to satisfy current conservation at A and B, the magnitude of i_0 is chosen to correct for this:

$$V_m(g_m-g_0)=i_0. \qquad (5.1)$$

The extra voltage, V_0, induced between A and B, can be calculated if we know the conductance G_{AB}' of the network between points A and B when g_{AB} is absent [see Fig. 7(b)]:

$$V_0=i_0/(g_0+G_{AB}'). \qquad (5.2)$$

Calculation of G_{AB}' is a classic student problem. We first obtain the conductance G_{AB} between A and B in the uniform effective medium, since $G_{AB}=G_{AB}'+g_m$. A symmetry argument is useful: Express the current distribution in Fig. 7(a) with $g_0=g_m$ as the sum of two contributions, a current i_0, introduced at A and extracted at a very large distance in all directions, and an equal current, introduced at infinity and extracted at B. In each case, the current flowing through each of the z equivalent bonds at the point where the current enters is i_0/z, so that a total current of $2i_0/z$ flows through the AB bond. This determines the voltage developed across AB, and from that follows the result, $G_{AB}=(z/2)g_m$, or $G_{AB}'=(z/2-1)g_m$. Using Eqs. (5.1) and (5.2), we obtain

$$V_0=V_m(g_m-g_0)/[g_0+(z/2-1)g_m], \qquad (5.3)$$

valid in both $2D$ and $3D$.

If the value of a bond, g_{ij}, is distributed according to a probability distribution $f(g)$ (which may be either continuous or discrete), the requirement that the average of V_0 vanish gives a condition determining g_m:

$$\int dgf(g)(g_m-g)/[g+(z/2-1)g_m]=0. \qquad (5.4)$$

For a binary distribution, we have

$$f(g)=p\delta(g-1)+(1-p)\delta(g-\alpha); \qquad (5.5)$$

as is appropriate to the percolation network models, Eq. (5.4) reduces to a quadratic equation for g_m:

$$(z/2-1)g_m^2+\{(z/2)p-1+\alpha[z/2(1-p)-1]\}g_m-\alpha=0. \qquad (5.6)$$

The relevant root of Eq. (5.6)

$$g_m=\{(z/2)p-1+\alpha[z/2(1-p)-1]\}/(z-2)+(\{(\tfrac{1}{2}z)p-1+\alpha[\tfrac{1}{2}z(1-p)-1]\}^2+2(z-2)\alpha)^{1/2}(z-2)^{-1} \qquad (5.7)$$

has a simple limiting form when $\alpha\to 0$:

$$g_m(\alpha=0)=1-(1-p)/(1-2/z), \qquad (5.8)$$

a straight line[4] in which g_m goes to zero when $p=2/z$. Equation (5.8) is the prediction plotted in Figs. 2, 3, and 6.

The numerical results of the preceding section show that the effective medium theory (5.8) is surprisingly accurate for the bond percolation model (Figs. 2 and 3), and for the correlated bond model (Fig. 5) when $p\gtrsim 80\%$. Furthermore, it was shown in Kirkpatrick (1971) to be accurate to within a few percent at all

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[3] Two useful references for further reading in the classical transport literature are Krumhansl (1973) which has references to work on other-than-electrical problems, and Miller (1969) which has a variational calculation to determine when the volume fraction is the dominant parameter in transport.

[4] The existence of this percolationlike solution to the effective medium theory was first pointed out in the context of the continuum problem by Landauer (1971).

concentrations whenever $\alpha \gtrsim 0.1$ for the bond percolation model. However, for the site percolation model (Fig. 5), it gives the wrong slope at high concentration (small concentrations of missing sites). To see why this is so, we shall cast the resistor network problem into a slightly more formal notation, and re-derive Eq. (5.4) by what amounts to a Green's function theory of resistor networks. Some interesting connections between the network problem and other well-known problems in disordered materials emerge from this analysis.

Rewriting Eq. (3.2) as a matrix equation, we obtain

$$\mathbf{W}\mathbf{V}=\mathbf{S}, \qquad (5.9)$$

where $\mathbf{V}$ is a vector of node voltages, expressed in a bra-and-ket notation as

$$\mathbf{V}=\sum_{i} | i\rangle V_i, \qquad (5.10)$$

while

$$\mathbf{W}=\sum_{ij} | i\rangle(\delta_{ij}\sum_{k} g_{ik}-g_{ij})\langle j | \qquad (5.11)$$

and $\mathbf{S}$ is zero, except at the two ends of the sample. The voltages and subsequently the current flow can be obtained if we can solve

$$\mathbf{V}=\mathbf{W}^{-1}\mathbf{S} \qquad (5.12)$$

so $\langle\mathbf{W}^{-1}\rangle$ contains the information necessary to determine the average conductivity.

To calculate $\mathbf{W}^{-1}$, we separate $\mathbf{W}$ into a homogeneous part, $\mathbf{W}_m$, whose inverse is presumed known, and a fluctuating part, which we may expand whenever $\mathbf{W}_m$ is, in some sense, not too small:

$$\mathbf{W}=\mathbf{W}_m-\delta\mathbf{W}, \qquad (5.13)$$

where

$$\mathbf{W}_m=\sum_{ij} | i\rangle g_m(z\delta_{ij}-\Delta_{ij})\langle j |, \qquad (5.14)$$

and Δ_{ij} is unity if sites i and j are nearest neighbors, zero otherwise. The normalized conductivity of the uniform medium characterized by $\mathbf{W}_m$ is g_m.

It proves useful to separate $\delta\mathbf{W}$ into contributions from different bonds (ij),

$$\delta\mathbf{W}=\sum_{(ij)}\delta\mathbf{w}_{ij}, \qquad (5.15)$$

where the contribution of the bond (ij) is

$$\delta\mathbf{w}_{ij}=(g_m-g_{ij})(| i\rangle\langle i |+| j\rangle\langle j | \\ -| i\rangle\langle j |-| j\rangle\langle i |). \qquad (5.16)$$

Although $\delta\mathbf{w}_{ij}$ has four matrix elements in Eq. (5.15), it only affects the difference in voltage between nodes $| i\rangle$ and $| j\rangle$. To show this, we factor Eq. (5.16) into

$$\delta\mathbf{w}_{ij}=\delta w_{ij}\mathbf{P}_{ij}, \qquad (5.17)$$

where

$$\delta w_{ij}=2(g_m-g_{ij}), \qquad (5.18)$$

and $\mathbf{P}_{ij}$ is a projection operator for the ijth bond:

$$\mathbf{P}_{ij}=\tfrac{1}{2}(| i\rangle-| j\rangle)(\langle i |-\langle j |). \qquad (5.19)$$

These definitions are useful in evaluating the series expansion for $\mathbf{W}^{-1}$,

$$\mathbf{W}^{-1}=\mathbf{W}_m^{-1}\sum_{n=0}^{\infty}[(\sum_{(ij)}\delta w_{ij}\mathbf{P}_{ij})\mathbf{W}_m^{-1}]^n, \qquad (5.20)$$

since all terms involving repeated powers of a given δw_{ij} can be simplified and collected by introducing a *t*-matrix (Edwards, 1961), $\mathbf{t}_{ij}$, for the bonds:

$$\mathbf{t}_{ij}=\mathbf{P}_{ij}\delta w_{ij}/(1-\delta w_{ij}F_{ij}), \qquad (5.21)$$

involving only the matrix element of $\mathbf{W}_m^{-1}$ which is projected out by $\mathbf{P}_{ij}$:

$$F_{ij}=\tfrac{1}{2}(\langle i |-\langle j |)\mathbf{W}_m^{-1}(| i\rangle-| j\rangle). \qquad (5.22)$$

The series (5.20) is resumed in terms of the $\mathbf{t}_{ij}$'s by standard methods

$$\mathbf{W}^{-1}=\mathbf{W}_m^{-1}+\mathbf{W}_m^{-1}\sum_{(ij)}\mathbf{t}_{ij}\mathbf{W}_m^{-1}+\mathbf{W}_m^{-1}\sum_{(ij)}\mathbf{t}_{ij}\mathbf{W}_m^{-1} \\ \times\sum_{(kl)\neq(ij)}\mathbf{t}_{kl}\mathbf{W}_m^{-1}+\cdots. \qquad (5.23)$$

From the sum (5.23) we see that the "best" choice of g_m is that which makes

$$\langle t_{ij}\rangle=0; \qquad (5.24)$$

since then $\langle\mathbf{W}^{-1}\rangle$ is given by $\mathbf{W}_m^{-1}$, with corrections of $\langle\mathbf{t}_{ij}\mathbf{t}_{kl}\rangle$ or higher order, and g_m will be a good approximation for $G(x)$, suitably normalized.

In general, matrix elements of $\mathbf{W}_m^{-1}$ can only be expressed in terms of exotic integrals (Morita and Horiguchi, 1971), but the F_{ij} needed here is an exception. By taking the $\langle i|\ |i\rangle$ matrix element of the equation $\mathbf{W}_m^{-1}\mathbf{W}_m=1$, using Eq. (5.14), we obtain

$$z\langle i \mid W_m^{-1} \mid i\rangle-\sum_{k}\Delta_{ik}\langle i \mid W_m^{-1} \mid k\rangle=1. \qquad (5.25)$$

Since W_m^{-1} is real, we have

$$\langle i \mid W_m^{-1} \mid j\rangle=\langle j \mid W_m^{-1} \mid i\rangle, \qquad (5.26)$$

which, with translational invariance and cubic point symmetry, implies that all matrix elements of W_m^{-1} between nearest neighbors are equal. Thus for i, j adjacent, we have

$$F_{ij}=\langle i \mid W_m^{-1} \mid i\rangle-\langle i \mid W_m^{-1} \mid j\rangle, \qquad (5.27)$$

$$=1/(zg_m). \qquad (5.28)$$

Therefore, we have

$$\mathbf{t}_{ij}=\mathbf{P}_{ij}zg_m(g_m-g_{ij})/[g_{ij}+(z/2-1)g_m], \qquad (5.29)$$

and the equation $\langle\mathbf{t}_{ij}\rangle=0$ [Eq. (5.24)] is equivalent to Eq. (5.4).

Study of higher-order contributions to $\mathbf{W}^{-1}$ explains why the effective medium theory works so well for the bond percolation model. As long as there is no correlation between bonds, we have

$$\langle\mathbf{t}_{ij}\mathbf{t}_{kl}\rangle=\langle\mathbf{t}_{ij}\rangle\langle\mathbf{t}_{kl}\rangle=0, \qquad (5.30)$$

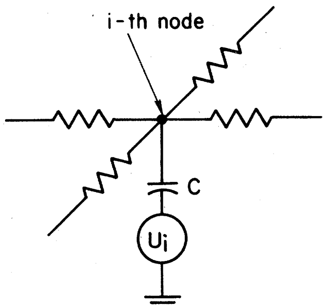

FIG. 8. Alternating current modification of the basic resistor network model, in which each node is connected through a capacitance C to an external potential U_i which may vary in time and position.

whenever $(ij)\neq(kl)$. Just as in the simplest models of electrons in disordered alloys, the first contribution to $\langle \mathbf{W}^{-1}\rangle$ comes from terms involving $\langle t^4\rangle$, and is proportional to $(1-p)^2$. For the correlated bond model (Fig. 5), Eq. (5.30) fails by a small amount, and the first corrections to $\langle \mathbf{W}^{-1}\rangle$ are of order $\langle t^2\rangle$, but again proportional to $(1-p)^2$.

For the site percolation model, corrections of order $\langle t^2\rangle$ are also found, but they are proportional to $(1-p)$, since defects, even in lowest order, involve the removal of z neighboring bonds. Thus the slope of $G(p)$ near $p=1$ in Fig. 5 disagrees with the effective medium theory result. In order to include all effects of order $(1-p)$ in a calculation of $\langle \mathbf{W}^{-1}\rangle$ for this problem, it is necessary to deal with t-matrices describing the scattering from absent sites, rather than the $\mathbf{t}_{ij}$'s. While this can be done (Izyumov, 1966), the structure of the resulting approximations to $\langle \mathbf{W}^{-1}\rangle$ is more complex, and $G(x)$ can no longer be obtained "by inspection", i.e., by exhibiting g_m. In the next section, we shall derive a general expression for $G(x)$, valid in the critical region as well as outside, and then reconsider the site percolation problem.

VI. GENERAL EXPRESSION FOR $G(x)$; RELATION OF RESISTOR NETWORKS TO DISORDERED FERROMAGNETS

Explicit expressions for $G(x)$ in terms of certain general properties of the operator $\langle \mathbf{W}^{-1}\rangle$ will now be derived. The procedure used is to solve an ac generalization of the network problem at a finite frequency ω, then take the limit $\omega\rightarrow 0$. The ac system to be solved is somewhat arbitrary, as it need only reduce to the resistor network of interest in the limit $\omega\rightarrow 0$. Our ac generalization is similar to a construction suggested by Pollak for treating ac hopping conduction. The derivation of a general expression for $G(x)$ follows rather closely the treatment of hopping conduction by Brenig *et al.* (1971), but special simplifications are possible for the percolation models studied here. In addition, the analysis reveals an interesting connection between conduction in these resistor networks and the propagation of spin excitations in certain dilute magnetic systems[5] (Kirkpatrick, 1973a). We shall exploit this connection to obtain some insight into the topology of the "infinite cluster" through which the current flows.

Kirchoff's law, the basis of the network equations (3.2), is simply the requirement that charge ρ is neither created nor destroyed at the nodes:

$$d\boldsymbol{\rho}(t)/dt=\mathbf{W}\mathbf{V}=0. \qquad (6.1)$$

We will make Eqs. (3.2) into an ac problem by modifying the network so that $\dot{\rho}\neq 0$. A construction with this effect is sketched in Fig. 8. At each vertex is added a capacitive shunt C and an external voltage generator, U_i, which may be thought of as due to an ac external field, and

$$d\rho_i(t)/dt=Cd(V_i-U_i)/dt. \qquad (6.2)$$

We shall assume that the driving field has only one Fourier component, i.e.,

$$U_i(t)\propto U(k,\omega)\exp(ik\cdot r_i-i\omega t), \qquad (6.3\text{a})$$

or

$$\mathbf{U}=|k\rangle U(k,\omega)\exp(-i\omega t), \qquad (6.3\text{b})$$

where

$$\langle i\,|\,k\rangle=(N)^{-1/2}\exp(-k\cdot r_i), \qquad (6.4)$$

and N is the number of sites in the lattice. The Fourier transform of the network equations becomes

$$\mathbf{W}\mathbf{V}=-i\omega C(\mathbf{V}-\mathbf{U})+\mathbf{S}, \qquad (6.5)$$

which is formally equivalent to the kinetic equations governing hopping conduction. In the limit $\omega\rightarrow 0$, the original equations (3.2) are recovered. Henceforth we shall take the limit of a large sample and disregard $\mathbf{S}$.

If we define a response function L, relating the induced charge to the external potential U, by

$$\delta\rho(k,\omega)=L(k,\omega)U(k,\omega), \qquad (6.6)$$

then a standard result of linear response theory (Kadanoff and Martin, 1963), requiring only that this response be causal, relates the conductivity to L:

$$G=\lim_{\omega\to 0}\lim_{k\to 0} i\omega L(k,\omega)/k^2. \qquad (6.7)$$

L can be identified by solving Eq. (6.5) for V, and using Eqs. (6.1) or (6.2):

$$L(k,\omega)=C\langle k\,|\,\mathbf{W}/(\mathbf{W}+i\omega C)\,|\,k\rangle. \qquad (6.8)$$

From Eq. (6.7) and the real part of Eq. (6.8), the dissipative part of the conductance is obtained

$$G=\lim_{\omega\to 0}\lim_{k\to 0}(\omega^2C^2/k^2)\langle k\,|\,\mathbf{W}/(\mathbf{W}^2+\omega^2C^2)\,|\,k\rangle. \qquad (6.9)$$

Equation (6.9) may be evaluated formally by introducing a set of exact eigenvectors, $|\alpha\rangle$, of the con-

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[5] This connection has been independently noticed by Last and Thouless (private communication) and is alluded to briefly in Last (1972).

ductance matrix W:

$$\mathbf{W}\mid\alpha\rangle=\lambda_\alpha\mid\alpha\rangle, \tag{6.10}$$

in terms of which Eq. (6.9) becomes

$$G=\lim_{\omega\to0}\lim_{k\to0}(\omega^2C^2/k^2)\times\sum_\alpha\mid\langle k\mid\alpha\rangle\mid^2\lambda_\alpha/(\lambda_\alpha^2+\omega^2C^2). \tag{6.11}$$

Some of the eigenfunctions of $\mathbf{W}$ will be localized with nonvanishing values of λ_α and an overlap matrix element $\mid\langle k\mid\alpha\rangle\mid^2$ of order k^2 or smaller. Taking the limit $k\to0$ in Eq. (6.11) leaves a quantity proportional to ω^2 for the contribution of such states. Only extended eigenfunctions of $\mathbf{W}$ with small eigenvalues contribute to G in the dc limit. From the structure of $\mathbf{W}$ one can show (Brenig *et al.*, 1971) that there are eigenstates near the bottom of the spectrum for which k becomes a good quantum number, and that such eigenfunctions may be expanded in powers of k:

$$\langle i\mid\psi_k\rangle=\exp(ik\cdot r_i)[V^0(i)+k\cdot V^1(i)+\mathcal{O}(k^2)]. \tag{6.12}$$

The eigenvalue associated with a state such as (6.12) will be dominated by a term proportional to $(ka)^2$, where a is the distance between adjacent nodes:

$$\lambda_k=Dk^2a^2+\mathcal{O}(k^3). \tag{6.13}$$

Inserting Eqs. (6.12) and (6.13) into Eq. (6.11) yields, upon taking the two limits,

$$G=a^2D\mid\sum_i V^0(i)\mid^2. \tag{6.14}$$

For the percolation conduction networks studied here the sum in Eq. (6.14) can be evaluated. [In the more complicated hopping conduction problem (Brenig *et al.*, 1971), it cannot, in general.] The eigenvectors ψ_k, as $k\to0$, are just uniform shifts of the voltages on all sites of the infinite cluster. Thus $V^0(i)$ is constant on those sites, and zero elsewhere, and normalization implies that

$$\mid\sum_i V^0(i)\mid^2=P^{(s)}, \tag{6.15}$$

where $P^{(s)}$ is the fraction of the sites in the material which lie in the infinite cluster. Thus Eq. (6.14) becomes

$$G=a^2DP^{(s)}. \tag{6.16}$$

$P^{(s)}$ for the site percolation problem was plotted in Fig. 1. When most of the sites are present, $P^{(s)}$ is approximately equal to the fraction of sites remaining in the sample. $P^{(s)}$ for the bond percolation models A and C has a different form, since sites are not separated from the infinite cluster until bonds on all sides have independently been removed. For model A, the simple bond percolation model, where P is the fraction of bonds present, the leading terms in $P^{(s)}$ are

$$P^{(s)}(p)=1-(1-p)^6-6p(1-p)^{10}-\cdots(3D\text{ bond percolation, SIMPLE CUBIC lattice}). \tag{6.17}$$

If $p\gtrsim0.7$, Eq. (6.17) is close to unity, and $G(p)$ is simply proportional to $D(p)$.

We can gain some feeling for the nature of D by showing that the spin excitations of a simple class of random magnetic systems are simply related to the eigenstates of $\mathbf{W}$. That is, the spin stiffness of such systems is proportional to D.

Suppose that a spin S_i is located at each node of the regular network and that the interaction energy of two spins is $J_{ij}\mathbf{S}_i\cdot\mathbf{S}_i$. The equations of motion for a spin-lowering operator, in linearized form,

$$idS_i^-(t)/dt=2S\sum_j J_{ij}[S_i^-(t)-S_j^-(t)], \tag{6.18}$$

are essentially identical to the time-dependent form Eq. (6.1) of the network equations (3.2), if each conductance g_{ij} is equal to $2SJ_{ij}$. The low-lying spin wave modes given by Eq. (6.18) have energies

$$E(k)=Dk^2a^2, \tag{6.19}$$

where D is the quantity defined by Eq. (6.13), once this identification is made. Equation (6.19) is a common definition of a spin-stiffness coefficient.

The site percolation model, model B, corresponds in the above sense to the classic picture of a dilute ferromagnet (Morgan and Rushbrooke, 1961, 1963; Rushbrooke, 1970; Rushbrooke *et al.*, 1972), a regular array of spins with nearest-neighbor interactions from which some fraction of the spins, on randomly chosen sites, are missing. Model A, the bond percolation model, corresponds to a more unusual dilute magnetic system, in which some of the J_{ij}'s chosen without regard to whether their neighboring bonds are also absent, are missing. Such a situation might occur, for example, in insulating magnetic systems in which indirect exchange is dominant and sensitive to the identity of the anion. We can state the relation between the spin stiffness in these systems and the conductance of the corresponding resistor networks in a simple normalized form:

$$G(x)=P^{(s)}(x)D(x)/D(1). \tag{6.20}$$

Several useful consequences follow from Eq. (6.20). First, a knowledge of any two of the quantities, G, $P^{(s)}$, or D, is sufficient to predict the third. For example, a calculation of D for the dilute ferromagnet which is exact in the limit of a few missing sites (Izyumov, 1966) gives

$$D(x)/D(1)=1-1.52(1-x)+\mathcal{O}[(1-x)^2]. \tag{6.21}$$

The corresponding approximation to $G(x)$ is [using $P^{(s)}(x)\sim x$]

$$G(x)=x-1.52x(1-x)+\mathcal{O}[(1-x)^2], \tag{6.22}$$

which gives the solid line labelled "THEORY" in Fig. 4. Alternately, one can use Monte Carlo values for $P^{(s)}$ and G to calculate D numerically over the whole range of concentrations from x_c to 1. Values of $D(x)/D(1)$ obtained in this way for the site percolation model are

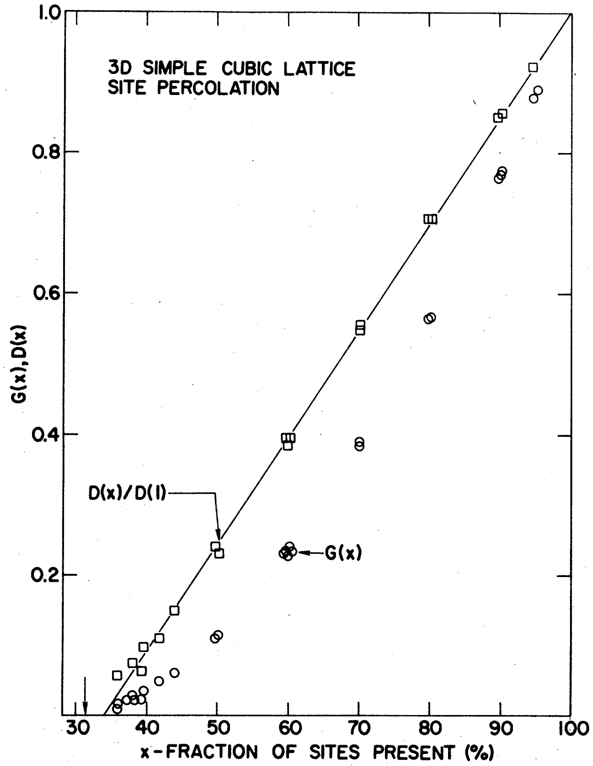

Fig. 9. Monte Carlo calculations of conductance $G(x)$ and the normalized spin-stiffness coefficient, $D(x)/D(1)$, for site percolation on simple cubic networks. G was obtained directly, and D calculated from Eq. (6.20), using interpolated values of $P^{(s)}$ from Fig. 1. The straight line indicates the prediction of Izyumov (1966) for D, derived from concentrations near $x=1$. The arrow indicates the percolation threshold.

plotted in Fig. 9. The deviation of the numerical results for $D(x)/D(1)$ from the low-density theory is small for all $x\gtrsim 0.6$. These calculated points provide the only direct test of theories of the disordered magnetic system (Harris and Leath, 1973) which attempt to go beyond the low-density approximation.

Equation (6.20) can also be used to put an end to the speculation (see Kirkpatrick, 1973a for a brief history) that $D(x)$ for the dilute ferromagnet might vanish at some concentration x^* significantly greater than x_c. $P^{(s)}(x)$ and $G(x)$ for model B appear to have a common threshold at $x_c=0.312$, and quite different critical behavior near x_c, which implies that $x^*=x_c$. The data appear sufficiently reliable to rule out any discrepancy between x^* and x_c larger than 0.01. Finally, $D>0$ implies a density of spin excitations

$$n(E)\propto E^{1/2}, \tag{6.23}$$

at low energies. These facts can be used to check some hypotheses about the topology of the infinite cluster.

Oguchi (1969), for example, has speculated that the effects of disorder on various properties of dilute magnetic systems, of which the most intriguing is the concentration-dependence of certain thermodynamic critical exponents, can be accounted for by the statement that the infinite cluster has an "effective dimensionality" which decreases monotonically from 3 to 1 as x decreases from 1 to x_c.

A simpler, but more concrete hypothesis is the visualization of the infinite cluster at concentrations near threshold as consisting of "percolation channels" which are locally one dimensional (Eggarter and Cohen, 1970, 1971; Cohen, 1971; Zallen and Scher, 1971; Eggarter, 1972). It has been argued (Fritzsche, 1973) that such channels may dominate conduction in a wide class of glassy semiconductors with activated conductivities, and also that hopping conduction in amorphous Si and Ge occurs mainly along the "channels" of least resistance (Pollak, 1972). If the channels are regarded as literally one-dimensional, quantitative predictions for transport are obtained by, e.g., estimating the average length and cross section of a channel [Cohen, quoted in Eggarter (1972)], or performing averages along a typical chain (Pollak, 1972) of connected sites.

From Eq. (6.23) and an argument due to Kumar and Harris (1973), one can show that neither of the hypotheses involving reduced dimensionality is correct. Kumar and Harris have argued that an infinite cluster consisting only of nonintersecting one- or two-dimensional pieces has a vanishingly small probability of occurrence. More generally, excitations for which $E\propto k^2$ in a space of dimensionality d give rise to a density of states in which

$$n(E)\propto E^{(d-2)/2}. \tag{6.24}$$

A density of states characteristic of lowered dimensionality would also result if $D=0$, and $E\propto k^3$ or k^4. But in deriving (6.23) we found that, except perhaps at x_c, this does not occur. This rules out Oguchi's (1969) hypothesis.

In fact, further reflection suggests that the channels are too densely cross-linked to be regarded as even locally one dimensional. In the lattice percolation models one can study cross-linking by estimating the density of short cycles—closed connected paths along allowed bonds in which no bond is repeated—in the infinite cluster. Since the infinite cluster is formed by agglomeration of smaller clusters, scarcity of short cycles in the infinite cluster requires that the isolated clusters also lack cycles. But this can be checked by explicit enumeration, and is not so: for $3D$ site percolation, for example, among isolated clusters of 4 or 5 allowed sites those containing cycles constitute several percent of the total at concentrations near x_c, and this fraction does not appear to decrease as the cluster size increases. A density of cycles this great or larger in the infinite cluster implies that even at threshold cross links occur every two or three sites.

However, Eq. (6.23) and the arguments of Kumar and Harris (1973) and the above remain insufficient to determine the topology of the infinite cluster, an intriguing question.

VII. CONCLUSIONS

Several of the results of this work should be of use in calculating transport properties of real inhomogeneous systems. These include the general character of the threshold in G:

$$G(x) \propto (x-x_c)^{1.5-1.6}, \tag{7.1}$$

the rather sharp distinction between the critical region and the domain of simple theories, and the success of the effective medium theory in describing transport outside the critical region. In addition, the numerical technique of modelling the effects of disorder via appropriately constructed Monte Carlo resistor networks can be applied to a wide range of situations. It has recently been used to predict the special problems that can arise when very fine inhomogeneous wires are used as interconnections in silicon chip microcircuitry (Kirkpatrick and Mayadas, 1973).

Other transport properties besides the conductivity are affected by inhomogeneities (Herring, 1960), and each may have its own characteristic behavior at the percolation threshold. In a previous paper (Kirkpatrick, 1973a) we drew upon some calculations and experiments by Juretschke *et al.* (1957) and Goldin and Juretschke (1958) to show that excluded volume effects can enhance the Hall coefficient, R, by as much as an order of magnitude, and argued that, near threshold,

$$R^{-1} \propto P(x). \tag{7.2}$$

In deriving Eq. (7.2) it was assumed that the percolation channels were quasi-one dimensional, so that according to the results of Sec. VI the detailed dependence of R upon concentration in Eq. (7.2) may be incorrect. However, the conclusion that R should diverge at the threshold remains probable in $3D$.

Precisely this behavior is observed in several systems exhibiting metal–semiconductor transitions. The conductivity decreases gradually and R increases sharply as functions of the external parameters affecting the volume over which the system is metallic. Plots (Kirkpatrick, 1972a) of R^{-1} and σ against, e.g., the molar concentration of metal in metal–NH_3 solutions, or the density of a supercritical metal vapor look like Figs. 2, 5, and 6. Quantitative agreement is achieved for the high-density impurity conductor Na_xWO_3 (Lightsey, 1972), for which the conductivity is observed to obey an $(x-x_c)^{1.8}$ power law.

It also seems likely that the energy dependence of the low-temperature mobility $\mu(E)$ of the electrons moving in the band tail associated with a random potential can be related to $G(x)$ (Kirkpatrick, 1971; Adler *et al.*, 1973; Fritzsche, 1973). The discussion which led to Eq. (2.5) also implies the relationship

$$\mu(E) \propto G[v(E)], \tag{7.3}$$

giving rise to a "soft mobility edge." Adler *et al.* (1973) have demonstrated that the use of Eq. (7.3) in the usual semiconductor transport formulas gives a conductivity which can be mistaken for the hopping form $\ln \sigma \propto T^{-1/4}$ if the band tail is sufficiently wide.

We should note two effects which may modify or invalidate Eq. (7.3). First, if the band tail is not much wider than kT, thermally assisted processes may mask the temperature-independent part of $\mu(E)$. This appears to be the case in two highly disordered crystalline systems, Ce_2S_3 (Cutler and Mott, 1969) and EuS (Thompson *et al.*, 1972), for which transport has been analyzed in terms of a band tail. The band tails in these materials extend over about 0.02 eV. Second, in relating transport in an inhomogeneous medium to the resistor network problem we tacitly assumed that all conduction electrons see the same medium. Thus, strictly speaking, Eq. (7.3) applies to a metallic material with its Fermi energy at E. It may be modified when some of the electrons contributing to screening and to the local fields around obstacles are more or less confined than those with energy E.

Finally, the numerical results presented showed that the effective medium theory can be extremely accurate, and that the critical region in which it fails covers only a modest range of concentrations. This conclusion has been underscored by Stinchcombe's recent exact solution of bond percolation resistor network models defined on branching networks (Stinchcombe, 1973). He finds a critical region narrower than ours, outside of which $G(p)$ is quite linear.

The effective medium theory is easily generalized to treat situations in which the conductivity is a tensor quantity everywhere, as must occur in the presence of a magnetic field, or for compacts of noncubic materials. Cohen and Jortner (1973) have recently derived expressions for the Hall coefficient of a two-phase system by this procedure, and have applied them to several liquid semiconducting systems. Their analysis can be extended to predict the consequences of inhomogeneities on other transport coefficients, e.g., thermopower, or magnetoresistance. Thus it appears to be possible to use measurements of such related transport properties to separate out inhomogeneity effects from the results of disorder-induced phase incoherence in electronic wave functions which Mott and Davis (1971) have stressed. Various derivatives of transport properties have recently been used by LeLieur (1973) to make such a separation in metal–NH_3 solutions. He observes that the decrease in σ under pressure is incompatible with a uniform picture of the electronic states, yet can be explained by the fact that the metallic regions in these materials are more compressible than the insulating regions.

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