Zeitschrift: Helvetica Physica Acta
Band: 50 (1977)
Heft: 5

Artikel: Cluster approximations in the effective medium model of site random conductance networks

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DOI: https://doi.org/10.5169/seals-114885

Helvetica Physica Acta, Vol. 50 (1977), Birkhäuser Verlag, Basel

Cluster approximations in the effective medium model of site random conductance networks[1])

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(27. V. 1977)

Abstract. A Green function method is used to develop an effective medium theory for determining the electrical conductivity of site percolation networks. Commencing with a new definition of a site, the resistance of an effective network is derived directly in terms of site probabilities from the self-consistent condition that the configurational average shift in resistance due to clusters of random sites be equal to zero. The results are in agreement with perturbation theory and Monte Carlo calculations in the dilute limit of missing sites. Limitations of the effective medium approach to this problem for higher concentrations of missing sites are evidenced.

I. Introduction

The physical properties of a large class of random systems, e.g., alloys, are determined by the local characteristics of a medium around sites lying on a well defined lattice and by the interactions between these sites. The theory and properties of such systems is discussed in a recent review article by R. J. Elliott, J. A. Krumhansl and P. L. Leath [1]. It is apparent that one of the major theoretical problems is the calculation of the configurational average properties of systems in which the randomness of the interactions between sites cannot be neglected. Substitutional alloys in which the constituent atoms have quite different wave functions, random magnets, heavily doped semiconductors, and random conductance networks are examples of such systems. Since the behavior of the random electrical conductance network is, in some cases, analogous to the behavior of more complex quantum systems [2,3] and because it is the simplest system, analysis of the random conductance network can give insight into the treatment of problems in the quantum systems.

The bond percolation model, in which some fraction of the bonds between nodes of a network is assigned a conductance $\sigma = 0$, has been analysed quite successfully using an effective medium theory in the single random bond approximation [3,4,5]. By conductance averaging and introducing an effective network depending on a mean free scattering length, Erdös and Haley [5] obtained good agreement with experiments even for bond concentrations near the percolation point. Application of a similar approximation in the effective medium theory of the site percolation model in which some fraction of the nodes of the network is missing, i.e., assigning the value $\sigma = 0$ to the conductance of all bonds connected to a missing node, has not

[1]) Work supported by the Swiss National Science Foundation Grant No 2.403–0.75.

had such unqualified success. Although an effective medium approach has been developed [6,7], which gives the correct conductance in the dilute limit of missing nodes, it does not deal directly with node probabilities, does not adhere strictly to the node-bond probability relationships valid for the model used, and appears to have no possibility for extension to include internode correlations. A basic problem lies with the definition of a single site.

In this paper I introduce a new definition of a site which leaves no ambiguity in assigning bonds to nodes, gives the correct dilute limit directly in terms of missing node probabilities (which correspond to missing site probabilities here), and shows the effects of correlations between nodes. Before proceeding with the new site definition, it is elucidating to consider two approaches used to date.

Elliot et al. [1] discuss two effective medium approaches for site percolation on square networks. Both approaches are based on considerations of the configurational average additional voltage $\langle \Delta V_c \rangle$ induced axially across a homogeneous but random 'cross', i.e., a node with all attached bonds of equal conductance, imbedded in an effective medium. In the first approach, one assumes that $\langle \Delta V_c \rangle = \Delta V_c x + \Delta V_c' y$, where x is the probability that the central node of the cross is present and $y = 1 - x$ is the probability that this node is missing, with ΔV_c and $\Delta V_c'$ being the respective values of the additional voltage induced axially across the cross. This assumption does not give the correct dilute limit of missing nodes. The second approach, used by Watson and Leath [6] for square networks and by Bernasconi and Wiesmann [7] for simple cubic networks, is to calculate the average additional voltage $\langle \Delta V_b \rangle$ across a single bond in the homogeneous single cross. It is assumed that the bond considered lies parallel to a uniform externally applied electric field, in which case the voltage induced across the bond is related to the voltage induced across the cross by $\Delta V_b = 0.5 \Delta V_c$. The average voltage shift due to the bond is interpreted as being $\langle \Delta V_b \rangle = \Delta V_b p + \Delta V_b' (1-p)$, where p is the probability that a bond is present. Using the exact relationship $p = x^2$ (since the central node and a neighbor node must be present to have the connecting bond present [3]), both sets of authors determine the effective medium conductance from the condition that $\langle \Delta V_b \rangle = 0.5 \langle \Delta V_c \rangle = 0$. The authors' [6, 7] interpretation of $\langle \Delta V_c \rangle$ and $\langle \Delta V_b \rangle$ is incorrect. Implicit in the use of the relationship $p = x^2 = 1 - 2y + y^2$ is the notion that the neighboring nodes are random. Since they assumed from the start that the cross had all bonds of equal conductance, the voltage shifts $\langle \Delta V_b \rangle$ and $\langle \Delta V_c \rangle$ should be a function of p^s or x^{s+1}, where s is the number of nearest neighbor nodes. Only in the extreme dilute limit of non-neighboring missing nodes can it be correctly argued that a 'cross' model in which random full bond crosses centered on only even or odd lattice nodes can approximately represent the true lattice with randomly missing nodes. In this limit the probability that a cross is absent is $1 - p \approx 2y \ll 1$. For larger values of y, the retention of the y^2 term by the authors appears to have no justifiable basis.

In this paper, a site is defined as a node surrounded by a homogeneous cluster of s half-bonds of equal conductivity, where s is the number of nodes connected to a given node. With this definition the site probabilities are identical to node probabilities and there is no ambiguity concerning which bonds are associated with a given site, i.e., there is no so called overlap between sites [6]. Using this definition, one can exactly model a lattice of random nodes for all concentrations of missing nodes.

II. General development

Although it is not compulsory, we choose to utilize the general Green function technique previously developed for random conductance networks [5]. The general development will be briefly repeated here, roughly following the notation of Reference [5].

For networks that obey Ohm's law the external node currents I_l and the node potentials V_l in a network of $l = 0, 1, \ldots, N-1$ nodes (sites) are related by

$$I = \mathscr{H} V, \tag{2.1}$$

where I and V are column vectors whose components are I_l and V_l, and $\mathscr{H}$ is an $(N-1) \times (N-1)$ non-singular, symmetric conductance matrix of elements $\mathscr{H}_{lm}$ given by

$$\mathscr{H}_{lm} = \sum_{\Delta} (\delta_{l,m} - \delta_{l+\Delta,m}) \sigma_{l,l+\Delta}, \qquad \text{for } l,m = 0, 1, \ldots, N-2. \tag{2.2}$$

The sum is over the nearest neighbors Δ of the node l, and $\sigma_{l,l+\Delta}$ is the conductance of the bond connecting nodes l and $l + \Delta$.

We define a quantity $\Delta\sigma_{l,l+\Delta}$ as

$$\Delta\sigma_{l,l+\Delta} = \sigma_{l,l+\Delta} - \sigma_x, \tag{2.3}$$

where σ_x is the bond conductance of a homogeneous effective network to be determined. Hence $\Delta\sigma_{l,l+\Delta}$ is the shift in the conductance of bond $(l, l+\Delta)$ from σ_x due to the randomness of $\sigma_{l,l+\Delta}$. Using equation (2.3) we write the conductance matrix as $\mathscr{H} = H(\sigma_x) - U(\Delta\sigma)$. The conductance matrix of the effective network is H and U is the random part of $\mathscr{H}$ whose elements are

$$U_{lm} = -\sum_{\Delta} (\delta_{l,m} - \delta_{l+\Delta,m}) \Delta\sigma_{l,l+\Delta}. \tag{2.4}$$

Introducing resistance matrices $\mathscr{G}$ and G defined by $\mathscr{G}\mathscr{H} = 1$, and $GH = 1$, and a T-matrix defined by

$$T = (1 - UG)^{-1} U, \tag{2.5}$$

equation (2.1) is solved for the node potentials. This yields

$$V = V^x(\sigma_x) + \Delta V(\sigma, \sigma_x), \tag{2.6}$$

where V^x is the node potential vector of the homogeneous effective network, and ΔV is the random shift in V. These are

$$V^x = GI \quad \text{and} \quad \Delta V = GTGI. \tag{2.7}$$

The point contact resistance Z_{lm} between nodes l and m is defined by $V_l - V_m = Z_{lm} I_l$. Using equation (2.6), one obtains the expression

$$Z_{lm} = Z^x_{lm}(1 + R_{lm}). \tag{2.8}$$

The term Z^x_{lm} is the resistance in the effective network, which from (2.7) is

$$Z^x = 2\sigma_x^{-1} a_{0,l-m}, \tag{2.9}$$

with

$$a_{lm} = g_l - g_{l-m}. \tag{2.10}$$

The g's are $g_{lm} \equiv g_{l-m} = \sigma_x G_{lm}$, the lattice Green functions given in the Appendix. The additional random term $R_{lm} = \Delta Z_{lm}/Z^x_{lm}$, where $\Delta Z_{l,m}$ is the resistance shift depending on the distribution of $\Delta\sigma$'s, is given by

$$R_{lm} = (2\sigma_x a_{0,l-m})^{-1} \sum_{n,n'} (g_{l-n}T_{nn'}g_{n'-l} + g_{m-n}T_{nn'}g_{n'-m} - 2g_{l-n}T_{nn'}g_{n'-m}). \tag{2.11}$$

As shown in the Appendix, the Green function g_l for the simple cubic lattice is finite for all l and has the form $g_l = (4\pi l)^{-1}$ for $l > 1$. The Green function g_l for the square lattice is shown to be infinite for all l. Since Z_{lm} is finite for square lattice, unless $|l - m|$ is infinite, it is necessary to recast R_{lm} into another form involving only differences between Green functions. This is achieved in general by using the sum rule [5], $\sum_n T_{ln} = \sum_n T_{nl} = 0$, in Eq. (2.11) which yields

$$R_{lm} = (2\sigma_x a_{0,l-m})^{-1} \sum_{n,n'} (a_{ln} - a_{mn})(a_{ln'} - a_{mn'})T_{nn'}. \tag{2.12}$$

Noting that $a_{l0} = 0$, it is seen that the column T_{n0} and row T_{0n}, of the T-matrix have been eliminated from R_{lm}. It is demonstrated in Appendix A that R_{lm} is always finite.

The point contact conductance $\mathscr{S}_{lm}$ is defined by

$$\mathscr{S}_{lm} = Z^{-1}_{lm} = (Z^x_{lm})^{-1}(1 + R_{lm})^{-1}. \tag{2.13}$$

The determination of the conductance σ_x of the effective network is by no means a well defined procedure. One must rely on physical intuition in choosing a prescription for calculating σ_x. As discussed in Reference [5], two viable approaches are resistance averaging and conductance averaging. Since one of the main purposes of this paper is to obtain the dilute limit results in the site percolation model through correct probability arguments, resistance averaging is chosen. This approach is simpler and it is known to give excellent results for the bond percolation models [5].

The conductance $\sigma_z = \sigma_x$ is defined by the condition that the configuration ensemble average resistance $\langle Z_{lm}\rangle$ of the random network be equal to the resistance Z^z_{lm} of the effective network. From equation (2.8), it is evident that this condition is satisfied if

$$\langle R_{lm}(\sigma,\sigma_z)\rangle = 0. \tag{2.14}$$

Since in resistance averaging the total current I_l entering the network is kept constant, equation (2.14) is equivalent to the condition $\langle \Delta V\rangle = 0$.

For lattices in which the shift R_{lm} is in general non-zero, resistance averaging and conductance averaging yield different values of σ_x, as discussed in reference [5]. This is the case of the simple cubic lattice for which Z^x_{lm} is finite for all $|l - m|$. However, for lattices such as the square lattice for which Z^x_{lm} becomes infinite and R_{lm} approaches zero as $|l - m|$ goes to infinity, it is seen from an expansion of $\mathscr{S}_{lm}$ in equation (2.13) in powers of R_{lm} that conductance averaging gives essentially the same condition for determining σ^x as resistance averaging. Using condition (2.14) the leading remainder term in $\langle \mathscr{S}_{lm}\rangle$ is $\langle R^2_{lm}\rangle \ll 1$. This explains why the method of conductance averaging applied to the square lattice would not change the results of resistance averaging for the bond percolation model. The latter are exact for all values of the concentration of missing bonds [5].

Since equation (2.14) cannot be solved in general, we seek a reasonable approximation. We begin by formulating an effective medium theory directly in terms of the concentration of random sites by considering the resistance shift due to a single random site imbedded in the effective medium.

III. Single site approximation

Consider a single random site defined as a node centrally connected to a homogeneous cluster of s half-bonds of random conductance 2σ imbedded in an effective network of sites of fixed but unknown half-bond conductances $2\sigma_x$, as shown in Figure 1. Assuming the random site to be located at node $n = 0$, the conductance of a

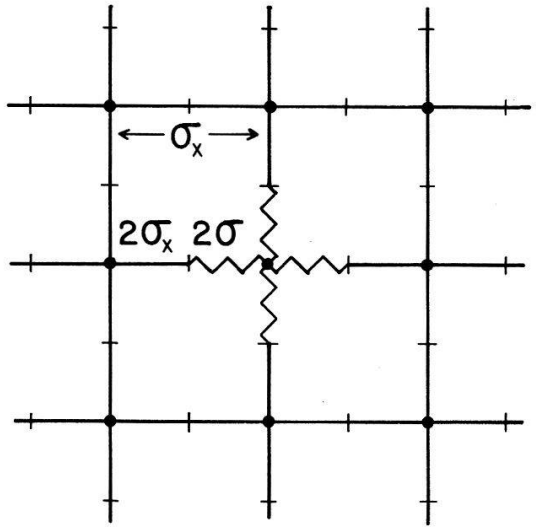

Figure 1
A single random site consisting of a node and $s = 4$ half-bond conductances 2σ is embedded in an effective square lattice network whose sites have half-bond conductance $2\sigma_x$.

full bond connected between node $n = 0$ and any neighbor node Δ is given by the conductance in series formula. It is

$$\sigma_{0,\Delta} = 2\sigma\sigma_x(\sigma + \sigma_x)^{-1}. \tag{3.1}$$

Taking the value of all other full bonds in the effective network to be σ_x, the conductance shift at the random site is

$$\Delta\sigma_{0,\Delta} = \sigma_x(\sigma - \sigma_x)(\sigma + \sigma_x)^{-1}. \tag{3.2}$$

For a large network we may assume that the contact m is far from both the contact l and the random site $n = 0$. Since the elements $T_{n,n'}$ of the T-matrix vanish for $n, n' \neq 0, \Delta$, only terms in equation (2.12) for which $|m - n|$ and $|m - n'|$ are large will be present. But $a_{m,n}$ goes to zero when $|m - n|$ become large, for both lattices under consideration; thus we may simplify equation (2.12) to read

$$R_{lm} = (2\sigma_x a_{0,l-m})^{-1} \sum_{n,n'} a_{ln} a_{ln'} T_{nn'}, \quad \text{for } ^m \gg 1. \tag{3.3}$$

Because this result is independent of the direction in which the contact m is taken to infinity, it is independent of the nature of the local electric field around the random site, and without loss of generality we may place the contact l along an axis passing through the site. Making use of the full lattice symmetries of the T-matrix for a homogeneous cluster, the resistance shift R_{lm} for the contact l on the x-axis of the cluster is

given by

$$R_{lm} = (2\sigma_x a_{0,l-m})^{-1}\{[a_{l,x}^2 + a_{l,-x}^2 + (s-2)a_{l,y}^2]T_{xx} + [2a_{l,x}a_{l,-x} + (s-2)a_{l,y}^2]T_{x,-x} + 2(s-2)[a_{l,x} + a_{l,-x} + \tfrac{1}{2}(s-4)a_{l,y}]a_{l,y}T_{x,y}, \quad (3.4)$$

where $s = 6$ for a simple cubic, and $s = 4$ for a square, and $a_{l,x}$ and T_{xy} are abreviated notations for $a_{(l,0,0,),(1,0,0)}$ etc.

In the limit of small concentrations of random sites, one may assume that the contact distance from the random site is large [5]. Using $l \gg 1$ form of $a_{l,\pm x}$ and $a_{l,y}$ from the Appendix yields

$$R_{lm} = (2\sigma_x a_{0,l-m})^{-1}\{2[(s-2)\pi]^{-2}(T_{xx} - T_{x,-x})l^{-(s-2)} + 0(l^{-s})\}. \quad (3.5)$$

To order $l^{-(s-2)}$ for both lattices, equation (3.5) substituted into equation (2.14) defines σ_z by the condition

$$\langle T_{xx}(\sigma,\sigma_z) - T_{x,-x}(\sigma,\sigma_z)\rangle = 0. \quad (3.6)$$

For a homogeneous cluster of $s = 4$, or 6 random bonds, or for a linear chain of $s = 2$ random but equivalent bonds, as shown in Figures 3(a) and 3(b), equation (2.5) yields

$$T_{xx} - T_{x,-x} = -\Delta\sigma_{0,\Delta}\sigma_x(\sigma_x + \gamma\Delta\sigma_{0,\Delta})^{-1}, \quad \text{with } \gamma = g_0 - g_2. \quad (3.7)$$

Using the site definining equation (3.2) for $\Delta\sigma$, we obtain from equations (3.6) and (3.7) the resistance averaging condition

$$\langle(1 - \sigma_z/\sigma)[\alpha - (1 - \sigma_z/\sigma)]^{-1}\rangle = 0, \quad (3.8)$$

with

$$\alpha = 2(1-\gamma)^{-1}. \quad (3.9)$$

Expression (3.8), which defines the effective network conductance σ_z, is valid in the limit of small concentrations of random sites for any probability distribution of random conductances σ. In the site percolation model in which σ is non-zero with probability $1 - y$ and zero with probability y, equation (3.8) defines σ_z by

$$\sigma_z/\sigma = 1 - \alpha y. \quad (3.10)$$

This expression for the resistance averaged effective conductance is identical to that obtained by perturbation theory for the dilute limit [8]. The values of α are π for $s = 4$, and 2.53 for $s = 6$. The linear dashed lines in Figure 4 represent equation (3.10) for both simple cubic and square lattices. It is evident that the effect of missing sites is overestimated for $y > 0.1$ by the single sight approximation. Carrying out resistance or conductance averaging of the complete expression (3.4) for R_{lm} does not give any significant improvement over equation (3.10). In an attempt to improve the values of $\sigma_z(y)$ for $y > 0.1$, we turn to effective medium calculations based on clusters of several random sites.

IV. **Cluster approximations**

An effective network is formulated by considering the resistance shift in an originally homogeneous network in which there has been substituted a cluster of

random sites consisting of a central site and its s nearest neighbors. The resistance shift R_{lm} of such a cluster averaged over all configurations of the sites in the cluster is defined by

$$\langle R_{lm} \rangle = \sum_{\alpha} P_{\alpha} R_{lm}^{\alpha}. \tag{4.1}$$

In the site percolation model, the probability of measuring a shift R_{lm}^{α} for a given cluster configuration α is

$$P_{\alpha} = x^{n_{\alpha}} y^{s+1-n_{\alpha}}, \tag{4.2}$$

where x is the concentration of sites present, i.e., the probability of finding a particular site present and $y = 1 - x$. The number $n_{\alpha} = 1, \ldots, s + 1$ is the number of sites present for a cluster in configuration α. The sum in (4.1) is taken over the 2^{s+1} configurations of the $s + 1$ sites of the cluster. When the central site is present, there are $2(s - 1)$ clusters having topologically non-equivalent bond configurations around this site. These clusters are shown in Figure 2 for $s = 4$ and $s = 6$. Different orientations of a given cluster will in general yield different values of R_{lm}^{α}. For the clusters shown in Figure 2, there are 9 orientations for $s = 4$, and 18 orientations for $s = 6$ generating different values of R_{lm}^{α}. These are indicated in the brackets below the figures, along with the degeneracy of orientations yielding the same values of R_{lm}^{α}. Thus Figure 2 represents 2^s configurations for which the central site is present. When it is absent, there are 2^s additional configurations similar to those illustrated. The probabilities P_{α} satisfy the normalization equations

$$\sum_{\alpha=1}^{2^s} P_{\alpha} = x \quad \text{and} \quad \sum_{\alpha=2^s+1} P_{\alpha} = y. \tag{4.3}$$

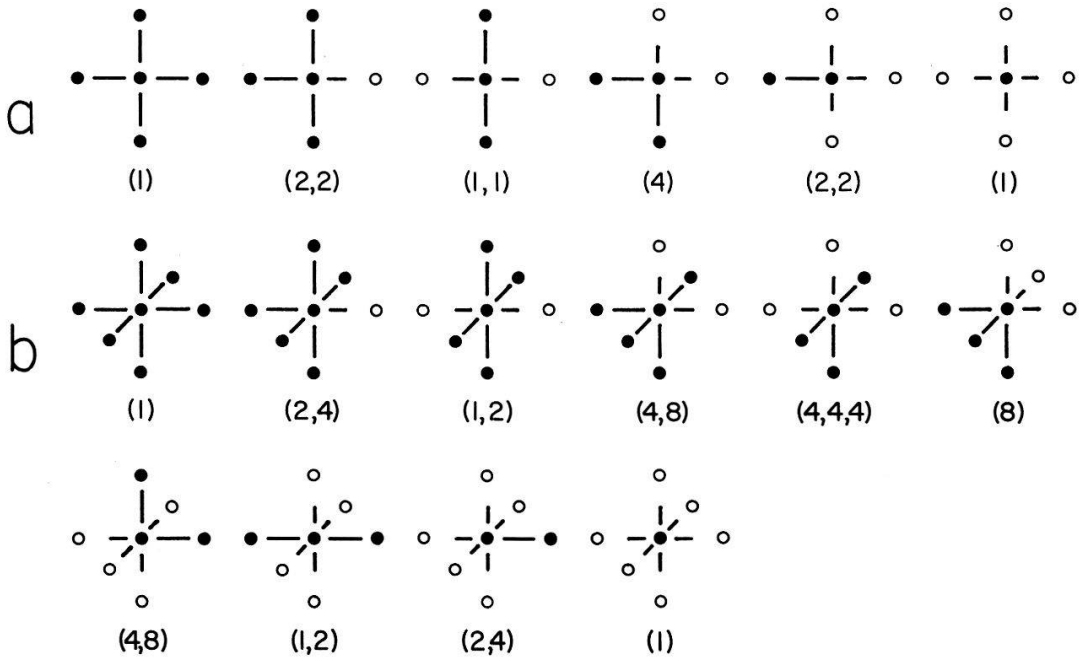

Figure 2
Random site cluster configurations in the site percolation model for the square lattice (a), and the simple cubic lattice (b). Black dots denote present sites and circles denote missing sites. The number of terms in the brackets indicates the number of cluster orientations generating different values of the resistance shift $R_{l,m}^{\alpha}$, and the numbers themselves give the degeneracy, yielding the same value.

To determine the effective network conductance $\sigma_x = \sigma_z$ from resistance averaging, one calculates the shifts R^{α}_{lm} defined by equation (2.11) and applies the condition $\langle R_{lm} \rangle = 0$. However, for a cluster of $s + 1 = 5$ or 7 sites with s^2 bonds, analytical calculation of the T-matrix elements is practically impossible.

We assume that the resistance shifts R^{α}_{lm} due to the $s + 1$ site clusters can all be approximated by shifts due to different linear combinations of bond chains. In the case of symmetry along the contact line, there are no transverse currents in the cluster and it is clear that a cluster such as number 1 in (a) of Figure 2 gives the same R^{α}_{lm} as the bond chain superposition consisting of two chains of type a plus one of type c illustrated in Figure 3.

All chains which occur in equation (4.1) are shown in Figure 3. It can be shown that for $l \gg 1$ the single random site can be replaced by two bond chains of types a or b in Figure 3, which leads to equations (3.5) and (3.7). When axial symmetry is absent there are transverse currents but their effect is assumed to be small compared to the effect of axial currents, and we use the same decomposition into $s - 2$ two bond chains of type a or b, plus a four bond chain chosen from types $c - h$ in Figure 3.

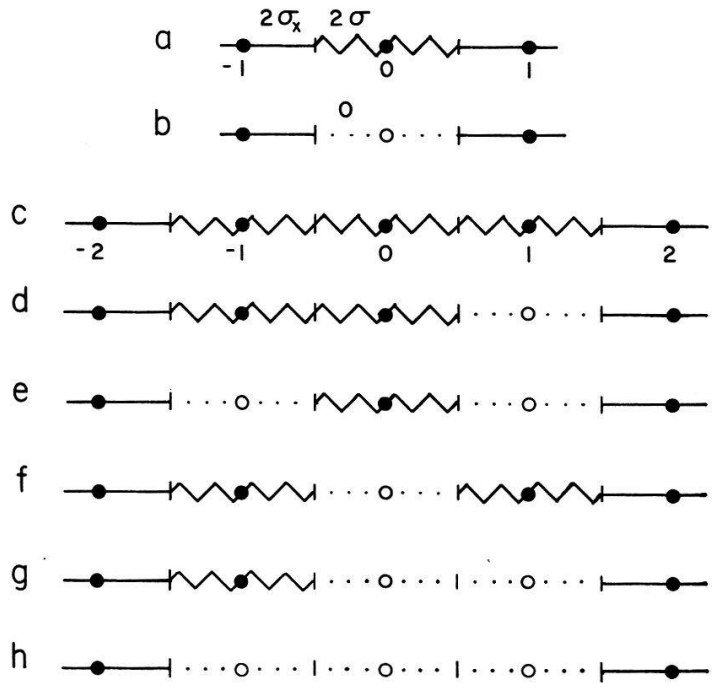

Figure 3
Random bond chains composed of half-bond conductance 2σ or 0, imbedded in an effective medium of half-bond conductance $2\sigma_x$.

Using equation (3.3) and the $l \gg 1$ expressions for a_{lm} from the appendix, one obtains for four bond chains placed on nodes $n = -2, -1, 0, 1, 2$ a shift

$$R^{\alpha}_{lm} = (2\sigma_x a_{0,l-m})^{-1}\{[(s-2)\pi]^{-2}\,\tau_{\alpha}(\{\sigma_n\},\sigma_x)l^{-(s-2)} + 0(l^{-s})\}, \tag{4.4}$$

where

$$\tau_{\alpha} = T^{\alpha}_{11} + T^{\alpha}_{-1,-1} - 2T^{\alpha}_{-1,1} + 4(T^{\alpha}_{22} + T^{\alpha}_{-2,-2} - 2T^{\alpha}_{-2,2} + T^{\alpha}_{12} + T^{\alpha}_{-1,-2} - T^{\alpha}_{-1,2} - T^{\alpha}_{-2,1}). \tag{4.5}$$

The T^{α}_{nn}, are matrix elements of $\mathbf{T}^{\alpha}$ linking nodes, $n, n' = -2, -1, 1, 2$ of the chain The set $\{\sigma_n\}$ for $n = -2, -1, 1, 2$ is the set of bond conductances appearing in the chain, and the subscript $\alpha = a, \ldots, h$ refers to the chains in Figure 3. One notes that for a chain with sites -2 and 2 in the effective network, $\tau_{\alpha} = 2(T^{\alpha}_{11} - T^{\alpha}_{-1,1})$ for $\alpha = a, b$, in which case equation (4.4) reduces to the single site shift equation (3.5).

Choosing the τ_{α}'s from the set $\{\tau_a, \ldots, \tau_h\}$, corresponding to the chains in Figure 3 to generate all the R^{α}_{lm} indicated by Figure 2, and using equations (4.1) – (4.3) together with the condition (2.14) yields the following equations which define σ_z:

$$\begin{aligned} &2(\tau_a x + \tau_b y) + \tau_c x^5 + (2\tau_c + 2\tau_d + \tau_f)x^4 y + (\tau_c + 4\tau_d + \tau_e + 2\tau_f + 2\tau_g)x^3 y^2 \\ &\quad + (2\tau_d + 3\tau_e + \tau_f + 4\tau_g)x^2 y^3 + (3\tau_e + 2\tau_g)xy^4 \\ &\quad + \tau_e y^5 = 0, \quad \text{for } s = 4, \end{aligned} \tag{4.6}$$

and

$$\begin{aligned} &4(\tau_a x + \tau_b y) + \tau_c x^7 + (4\tau_c + 2\tau_d + \tau_f)x^6 y \\ &\quad + (6\tau_c + 8\tau_d + \tau_e + 4\tau_f + 2\tau_g)x^5 y^2 \\ &\quad + (4\tau_c + 12\tau_d + 5\tau_e + 6\tau_f + 8\tau_g)x^4 y^3 \\ &\quad + (\tau_c + 8\tau_d + 10\tau_e + 4\tau_f + 12\tau_g)x^3 y^4 \\ &\quad + (2\tau_d + 10\tau_e + \tau_f + 8\tau_g)x^2 y^5 + (5\tau_e + 2\tau_g)xy^6 \\ &\quad + \tau_e y^7 = 0, \quad \text{for } s = 6. \end{aligned} \tag{4.7}$$

Calculation of the matrix elements T^{α}_{nn}, $(\{\sigma_n\})$ necessary to determine the τ_{α}'s for all the chains in Figure 3 requires a straight forward, although laborious, inversion in equation (2.5) of 5×5 matrices associated with the five nodes of the chains. This procedure was carried out analytically, and then equations (4.6) and (4.7) were solved numerically for $\sigma_n(y)$. The results are plotted in Figure 4. It is seen that for $s = 4$ the improvement over the single sight approximation is considerable. As the concentration y of missing sites increases, the slope of $\sigma_z(y)$ decreases in magnitude indicating less effect from missing sites. For six-fold coordination the improvement over the single site result is less remarkable.

In the preceding $s + 1$ site cluster approach the sites lying off the contact axis were treated as uncoupled single sites and the on-axis sites were treated exactly. It is evident that the curvature of $\sigma_z(y)$ generated by the coupled on-axis sites is weighted by the linear effect due to the $s - 2$ off-axis sites. To see this effect explicitly, the effective network conductivity was calculated from the resistance shift averaged over all configurations of a four bond chain composed of three random sites imbedded in the effective network. The calculation is analogous to the $s + 1$ site calculation, and it leads to the following equation which determines $\sigma_z(y)$:

$$\tau_c x^3 + (2\tau_d + \tau_f)x^2 y + (\tau_e + 2\tau_g)xy^2 + \tau_e y^3 = 0. \tag{4.8}$$

The conductance $\sigma_z(y)$ calculated from equation (4.8) is plotted in Figure 4. One sees that the effect of correlations among the sites along the contact line produces more curvature in $\sigma_z(y)$. The fit to the experimental data for $s = 4$ is good for all y, although

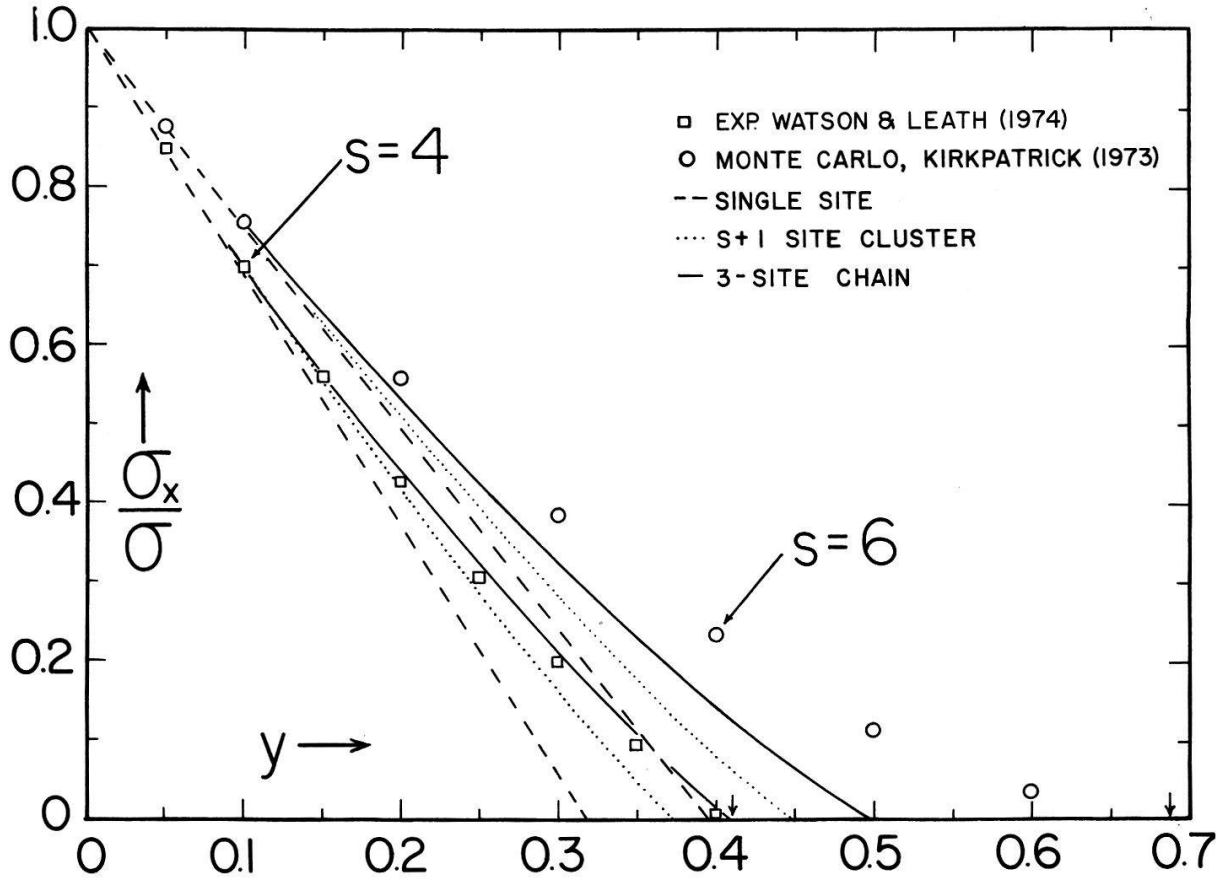

Figure 4
The normalized effective network conductance σ_x/σ calculated from various random cluster approximations is compared with experimental data for the site persolation model, for square $s = 4$ and simple cubic $s = 6$ lattices.

the effect of missing sites is slightly underestimated. For $s = 6$ the effect of missing sites is still overemphasized.

For analytical comparison of the various cluster approaches, equations (4.6) – (4.8) were expanded in powers of y. The expressions for $\sigma_z(y)/\sigma$ for coordinations $s = 4$ and $s = 6$ to order y^2, together with the single site expression (3.9) are

$s = 4$	$s = 6$	Approach	
$1 - \pi y$	$1 - 2.53y$	single site	
$1 - \pi y + 1.065y^2$	$1 - 2.53y + 0.347y^2$	$s + 1$ site cluster	(4.9)
$1 - \pi y + 1.776y^2$	$1 - 2.53y + 0.810y^2$	3 site chain	

It is of interest to compare these expansions with an equation of order y^2 which fits the experimental data quite well, except near the percolation point y_c at which $\sigma_z = 0$. This equation is

$$\sigma_z(y)/\sigma = 1 - \alpha y + \tfrac{1}{4}[(s - 2)\alpha - 2(s - 4)]y^2, \tag{4.10}$$

where α is given by equation (3.9). For $s = 4$ the coefficient of y^2 in equation (4.10) is $\alpha/2 = \pi/2$. This value was obtained in References [6] and [7] from the cross model, without apparent theoretical justification, as discussed in the introduction. In the case $s = 6$, equation (4.10) gives the coefficient of y^2 as $\alpha - 1 = 1.53$. Kirkpatrick [3] has

obtained this value from an A.C. technique in which he showed that the conductivity can be written as the product $P(y)\ D(y)/D(0)$, where $P(y)$ is the percolation probability and $D(y)$ is identical to the effective spin wave stiffness coefficient of the random Heisenberg ferromagnet. For $y < 0.55$ Monte Carlo calculations give $P(y) = 1 - y$. Perturbation theory [8] gives $D(y)/D(0) = 1 - (\alpha - 1)y + \ldots$. Kirkpatrick used these expressions for P and D to obtain equation (4.10) for $s = 6$. However, the quadratic term has not been calculated for D. Kirkpatrick's retention of the quadratic term in the product $P(y)\ D(y)/D(0)$ can only be justified *ad hoc*, based on his Monte Carlo calculations which show that D is essentially linear in y for $y < 0.6$.

V. Conclusions

Using a Green function formalism, a general expression for point contact resistance and conductance in random networks was developed, and an effective medium theory was introduced to calculate the conductance in site percolation network of coordination $s = 4$ and $s = 6$. For $s = 4$ the effective network conductance was shown to be the same for both the resistance and conductance averaging procedures. This result is independent of the distribution of condustances in the random network. Starting with the definition of a site as a node and a homogeneous set of s connecting half-bonds, effective network conductances were determined from various impurity conductance clusters. In the single site approximation, the method gives correctly the conductance in the extreme dilute limit of missing sites, i.e., $y < 0.1$; however it yields no quadratic term in the concentration of missing sites, which appears to be necessary to fit experimental data. Successive approximations using small clusters of random sites yield better values of conductance for $y > 0.1$. For $s = 4$ the results are quite good, but for $s = 6$ the effect of missing sites is overemphasized for all clusters used.

It is evident from these laborious cluster calculations that a consistent effective medium approach is not very practical in obtaining good results for the site percolation problem. The single site approximation is poor away from the extreme dilute limit, and the multi-site cluster approximations are too complicated for exact analytic calculation.

Roth [9] has shown that an *ad hoc* start using the virtual crystal spin system in random simple cubic ferromagnet gives good single site approximation results. There appears to be no equivalent procedure for resistance networks. Davidson and Thinkham [10] have recently developed phenomenological equations for the electrical conductivity of microscopically inhomogeneous materials. They combined a single site effective medium theory for continuous media with percolation theory. Their equation describing the conductivity σ was essentially guessed from the behavior of σ near the percolation point and in the extreme dilute limit. The utility of the effective medium approach as a reliable fundamental theoretical tool is rather weakened if one must combine it with guesswork.

Acknowledgement

I am grateful to Prof. P. Erdös for a number of useful discussions during the progress of this work and for reading the manuscript.

Appendix: Lattice green functions

The matrix elements of the Green operator g for the lattice of the effective networks are given by [5]

$$g_{lm} = N^{-1} \sum_k f_k^{-1} e^{ik \cdot (l-m)}, \quad \text{with } f_k = s - \sum_\Delta e^{ik \cdot \Delta}. \tag{A.1}$$

These matrix elements are related by the equation,

$$sg_{lm} - \sum_\Delta g_{l, m+\Delta} = \delta_{l,m}. \tag{A.2}$$

Since the $g_{l,m}$ depend only on $|l - m|$, it is convenient to set $m = 0$ and to define $g_{\mathbf{l}} = g_{\mathbf{l},0}$ in the sequel. To avoid confusion the vector notation $\mathbf{l} = (l_1, l_2, \ldots)$ is reintroduced when necessary.

Square lattice: $s = 2$

The integral form of $g_{\mathbf{l}}$ with $\mathbf{l} = (l_1, l_2)$ in the square lattice is

$$g_{\mathbf{l}} = (2\pi^2)^{-1} \int_0^\pi dx \int_0^\pi dy \cos(l_1 x) \cos(l_2 y)(2 - \cos x - \cos y)^{-1}. \tag{A.3}$$

Integrating over x and setting $t = 1 - y$ gives [11]

$$g_{\mathbf{l}} = (2\pi)^{-1} \int_0^2 dt V_{l_2}(t) t^{-1} (4 - t^2)^{-1/2} e^{-|l_1| U(t)}, \tag{A.4}$$

with

$$V_l(t) = \cos[l \cos^{-1}(1 - t)] \quad \text{and} \quad U(t) = \cosh^{-1}(1 + t).$$

The factor t^{-1} in (A.4) causes $g_{\mathbf{l}}$ to be infinite, independent of $\mathbf{l}$. The resistance, however, as seen in equations (2.9) and (2.12), depends only on the difference functions $a_{\mathbf{l},\mathbf{n}}$ defined by

$$a_{\mathbf{l},\mathbf{n}} = g_{\mathbf{l}} - g_{\mathbf{l}-\mathbf{n}} = (2\pi)^{-1} \int_0^2 dt t^{-1} (4 - t^2)^{-1/2} [V_{l_2}(t) e^{-|l_1| U(t)} - V_{l_2 - n_2}(t) e^{-|l_1 - n_1| U(t)}]. \tag{A.5}$$

The functions $a_{\mathbf{l},\mathbf{n}}$ are finite except for the case $\lim_{n \to \infty} a_{\mathbf{l},\mathbf{n}} = \infty$, with l, finite.

In view of equation (2.9), this means that $\lim_{m \to \infty} Z^x_{l,m} = \infty$ for the square lattice.

Two forms of $a_{\mathbf{l},\mathbf{n}}$ are of interest for the cluster calculations. They are

$$a_{(l,0),(0,n)} = g_l - g_{\sqrt{l^2 + n^2}} = (2\pi)^{-1} \int_0^2 dt t^{-1} (4 - t^2)^{-1/2} \times [1 - V_n(t) e^{-lU(t)}], \tag{A.6}$$

and

$$a_{(l,0),(n,0)} = g_l - g_{l-n} = (2\pi)^{-1} \int_0^2 dt t^{-1} (4 - t^2)^{-1/2} \times [1 - e^{nU(t)}] e^{-lU(t)}. \tag{A.7}$$

Using equations (A.6), (A.7) and (A.2), we have (see also Reference [12])

$$\begin{array}{lll} g_0 - g_1 = 1/4 & g_0 - g_{\sqrt{2}} = 1/\pi & g_0 - g_{\sqrt{13}} = 2/(3\pi) + 1/4 \\ g_0 - g_2 = 1 - 2/\pi & g_0 - g_{\sqrt{5}} = 2/\pi - 1/4 & \\ g_0 - g_3 = 17/4 - 12/\pi & g_0 - g_{\sqrt{8}} = 4/(3\pi) & g_0 - g_{\sqrt{18}} = 23/(15\pi) \\ g_0 - g_4 = 20 - 184/(3\pi) & g_0 - g_{\sqrt{10}} = 23/(3\pi) - 2. & \end{array} \tag{A.8}$$

For $l \gg 1$ in (A.6) and $l \gg n$ in (A.7) the only significant contribution in both integrals occurs when $t \ll 1$. Using the expansion $U(t) \approx \sqrt{2t}$ for $t \ll 1$ gives the asymptotic expressions

$$g_l - g_{\sqrt{l^2+1}} = (4\pi l^2)^{-1}, \quad \text{for } l \gg 1, \tag{A.9}$$

and

$$g_l - g_{l-n} = -n(2\pi l)^{-1}[1 + n(2l)^{-1}], \quad \text{for } l \gg n. \tag{A.10}$$

Simple cubic lattice: $s = 6$

Analytic evaluation of g_l for the simple cubic lattice has not been accomplished; however, an extremely accurate asymptotic expression for g_l when $l \gg 1$ is achieved by assuming that g_l is isotropic and integrating over the surface of a sphere of radius l [5, 13]. This expression is

$$g_l = (4\pi l)^{-1}, \quad \text{for } l \geqslant 1. \tag{A.11}$$

Using equation (A.11), we obtain

$$\begin{aligned} g_l - g_{\sqrt{l^2+1}} &= (8\pi)^{-1} l^{-3}(1 - \tfrac{1}{2}l^{-2} + \cdots), \\ g_l - g_{l-n} &= -n(4\pi)^{-1} l^{-2}(1 + nl^{-1} + \cdots). \end{aligned} \tag{A.12}$$

Koster and Slater [13] give the numerically integrated values

$$\begin{array}{lll} g_0 = 0.2495, & g_1 = 0.0829, & g_2 = 0.0389, \\ g_3 = 0.02505, & g_4 = 0.02055 & \end{array} \tag{A.13}$$

In contrast to the square lattice Green functions, the Green functions of the simple cubic lattice are always finite.

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