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Three-Dimensional Site Percolation Problem and Effective-Medium Theory: A Computer Study

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A site percolation approach to classical transport in disordered two-phase materials is presented. A Monte Carlo computer experiment gives the bulk conductivity of a 30 × 30 × 30 site simple cubic resistor network consisting of two kinds of unit resistor with different conductance. A modified effective-medium theory predicts very accurately the bulk conductivity of the network. This theory is found to agree well with available data for the thermal conductivity of real two-phase materials: glass particle–silicon rubber; glass fiber–plastics; air-saturated porous sandstone; and air-saturated fire brick.

KEY WORDS: Site percolation; effective-medium theory; random resistor network; electrical conductivity; thermal conductivity; Monte Carlo experiment; disordered materials.

1. INTRODUCTION

The physical properties of a two-phase material are dependent on the phase geometry of the material as well as on the properties of each phase. It has been argued by several authors[1,2] that electronic conduction in disordered materials can be related to solutions of the classical percolation problem. Also, electrical conduction in resistor networks has been studied as a paradigm of classical transport in disordered materials.[3,4] Much significant work has been done in this area.[5,6] Among many other advances, Kirkpatrick has conducted many Monte Carlo experiments on the bulk conductivity of resistor networks and developed a detailed theory.[3,4] Recently, site percolation theory has been used for a theoretical model of fluid through porous media.[7]

There is, however, no site percolation approach to the thermal conduc-

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tivity of a disordered two-phase material in which one phase is much more conductive than the other. In this paper, we have evaluated numerically the bulk conductivity of a simple cubic resistor network which is derived from a site percolation model of two-phase materials. Our site percolation model has the advantage that the probability assigned to each phase is equivalent to the volume fraction of each phase in a real composite material. Moreover, we have developed a new theory to predict the bulk conductivity of the random resistor network, using the effective-medium theory.

This study originated from the problem of heat conduction in macroscopically homogeneous and isotropic two-phase soils (such as air-saturated or water-saturated soils). To understand the thermal properties of soils is one of the fundamental problems encountered in agricultural engineering projects, and can lead to the accurate prediction of the temperature gradient in farm soils.

In Section 2 we describe a site percolation model of two-phase materials. The model is converted into a simple cubic resistor network composed of two kinds of unit resistor with different conductance. Next, we present new Monte Carlo results on the bulk conductivity of the random resistor network with $30 \times 30 \times 30$ sites. The results clearly indicate that the bulk conductivity of the random resistor network is statistically a stable property. In Section 3, we propose a modified effective-medium theory, which gives a surprisingly accurate prediction of the Monte Carlo data for our site percolation network. This theory is derived from the fact that our site percolation system is a special case of a correlated bond system composed of three types of bond, and that the single-bond effective-medium theory[3,4] can be applied, by statistical reasoning, to this correlated bond system. In Section 4, we show that the theory can accurately predict the effective thermal conductivity of real two-phase materials. The theory is compared with recent experimental results on the following mixtures: glass particle–silicon rubber; glass fiber–plastic; air-saturated porous sandstone; and air-saturated fire brick. We feel that the present site percolation approach is very promising for the study of classical transport in disordered materials.

2. RANDOM MODEL AND SIMPLE CUBIC RESISTOR NETWORK

A random model of two-phase materials,[7] in which two kinds of unit cube of equal size are present at random, is shown in Fig. 1. The black cubes represent the first phase and the white cubes the second phase. If the two kinds of unit cube are piled at random into an $N \times N \times N$ cube and n is a total number of black cubes contained in it, the volume fraction p of the

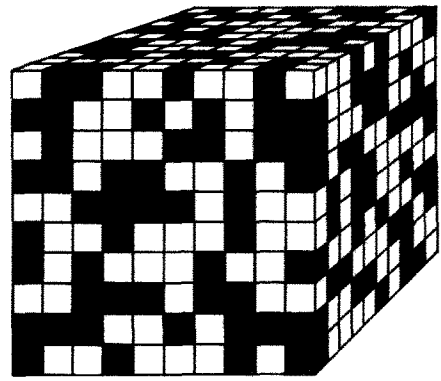

Fig. 1. Model of a two-phase material. Black (first phase) and white (second phase) unit cubes are piled at random into an $N \times N \times N$ cube.

first phase is defined by $p = n/N^3$, where $0 \leqslant p \leqslant 1$. Note that the volume fraction p is interpreted as the probability p that one will find a black cube at an arbitrary site in the model.[7]

Suppose that the black cubes in this model are replaced with special unit resistors having the conductance of the first phase and the white cubes are replaced with those having the conductance of the second phase; a three-dimensional random resistor network illustrated two-dimensionally in Fig. 2 is obtained. If K_1 is the conductance of the first phase and K_2 is that of the second phase, the bulk conductivity $K(p)$ of the network is statistically determined with K_1, K_2, and p.

We have evaluated numerically the bulk conductivity of the network. Consider that the network is sandwiched between two plane electrodes made of perfect conductors connected with a unit voltage source. Then the voltages at the nodes of each network, and from them the total current flow for the fixed external applied voltages, are obtained by a successive overrelaxation procedure based upon the Kirchhoff current law.[3,4,7] The positive initial values fitted to the applied voltage gradient are assigned to the nodes of the

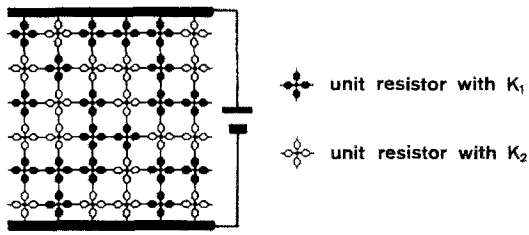

Fig. 2. Section of a three-dimensional site percolation network composed of special unit resistors.

network. If K_{ij} is the conductance of the link between adjacent nodes i and j, the voltage V_i of node i, after the $(k+1)$th iteration, is given by

$$V_i^{k+1} = V_i^k + \omega\left(\frac{\sum_j K_{ij} V_j^*}{\sum_j K_{ij}} - V_i^k\right) \tag{1}$$

where ω is the variable acceleration parameter of the overrelaxation procedure and $0 < \omega < 2$, and V_j^* is the voltage of node j after the $(k+1)$th iteration or kth iteration. The solution for a network of $30 \times 30 \times 30$ sites was obtained with a gradually varied value of ω starting from 1.6 and ending with 1.9. This operation with the parameter ω is genuinely an empirical procedure which has been found effective in this type of calculation.[8] It required from 28 to 55 iterations.

In Fig. 3, the values of the conductivity $K(p)$ of the $30 \times 30 \times 30$ site network are plotted against the volume fraction p of the first phase, where $K(p)$ is normalized so that $K(1) = 1$. For each set of points, $K_1 = 1$ and K_2, taken to be less than K_1, is indicated. In the extreme case of $K_2 = 0$, the values of $K(p)$ have already been reported (data points A in Fig. 3).[4,7] In the trivial case where $K_1 = K_2$, $K(p)$ is equal to unity (horizontal line B in Fig. 3). The solid lines are the predictions of the modified effective-medium theory in Section 3.

The numerical results for the conductivity $K(p)$ are presented in Table I. For each value of p, one or two Monte Carlo samples of the model are calculated. The value of K_1 is 1, and the value of K_2 described in the table is taken to be less than K_1. Each value of $K(p)$ is the average of interlayer currents calculated at the end of the iteration process. The errors given in the table are the maximum limits estimated from half of the difference between the minimum and the maximum of the interlayer currents. The exact value of $K(1)$ is 1 and that of $K(0)$ is K_2/K_1 (footnote b in Table I).

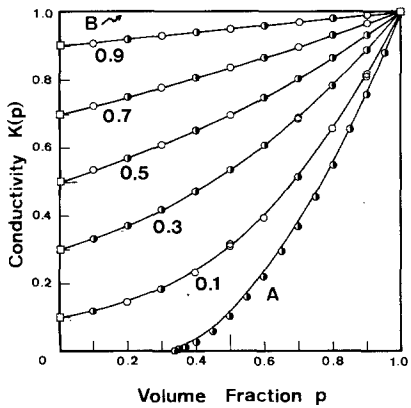

Fig. 3. Conductivity $K(p)$ of a simple cubic network with $30 \times 30 \times 30$ sites versus volume fraction p of the first phase. Calculations for the network (data points) and predictions of the modified effective-medium theory described in Section 3 (solid lines) are displayed for six values of K_2 as labeled. Data points A (critical region) indicate the results of the computer simulation of Onizuka[7] for simple cubic networks with $50 \times 50 \times 50$ sites. Squares: exact value; half-shaded circles: two overlapping points.

Table I. Calculation of the Bulk Conductivity $K(p)$ for a Network with 30 × 30 × 30 Sites[a]

	Bulk conductivity $K(p)$									
	$K_2 = 0.9$		$K_2 = 0.7$		$K_2 = 0.5$		$K_2 = 0.3$		$K_2 = 0.1$	
p	MC1	MC2	MC1	MC2	MC1	MC2	MC1	MC2	MC1	MC2
0.0	0.9[b]	—	0.7[b]	—	0.5[b]	—	0.3[b]	—	0.1[b]	—
0.1	0.909	—	0.724	—	0.533	—	0.332	0.332	0.118	0.117
0.2	0.919	0.919	0.750	0.749	0.569	0.569	0.371	0.372	0.145	—
0.3	0.928	—	0.778	—	0.608	—	0.419	0.419	0.182	0.180
0.4	0.938	0.938	0.806	0.804	0.652	0.652	0.472	0.472	0.233	—
0.5	0.948	—	0.835	—	0.697	—	0.536	0.535	0.305	0.315
0.6	0.958	0.958	0.866	0.864	0.749	0.750[c]	0.609	0.607	0.395	—
0.7	0.969	—	0.896	—	0.804	0.808[c]	0.693	0.689	0.515	0.512
0.8	0.979	0.979	0.930	0.929	0.865	0.868[c]	0.783	0.784	0.657	—
0.9	0.989	—	0.964	—	0.931	0.931[d]	0.888	0.887	0.811	0.818[c]
1.0	1.0[b]	—	1.0[b]	—	1.0[b]	—	1.0[b]	—	1.0[b]	—

[a] Values of the conductances are $K_1 = 1$ (with probability p) and $K_2 < 1$ (with probability $1 - p$). Numerical values of the network conductivity for each value of p are obtained from one or two Monte Carlo (MC) samples. Except where otherwise indicated, the error is ± 0.001.

[b] Exact value.

[c] Error is ± 0.002.

[d] Error is ± 0.003.

Note that each pair of points obtained from two different Monte Carlo samples for a given value of p almost overlap in Fig. 3. This implies that the bulk conductivity of the random resistor network is statistically a stable property.

3. MODIFIED EFFECTIVE-MEDIUM THEORY

The effective-medium theory based upon the self-consistent local field concept has been applied in predicting other physical constants, such as electrical and mechanical properties of disordered materials.[9–17] The essence of this method is to solve the field equation for a representative element of the material, which is taken to be embedded in an effective medium with the unknown physical constant. The effective constant is determined in turn by requiring that the effects of the deviation from the true constant shall, on the average, cancel out.[16] This theory has been studied to treat resistor networks, and found to be an accurate approximation to the bond percolation model, except in a critical region.[3,4] This theory, however, fails to provide a quantitative description of the present site percolation system.

Here, if we notice that our site percolation system is a special case of a correlated bond system composed of three types of bond, having conductance K_1, $K_3[= 2K_1K_2/(K_1 + K_2)]$, and K_2, and occurring with the probability p^2, $2p(1-p)$, and $(1-p)^2$, respectively, then we can modify the effective-medium theory in the following manner.

Consider the average conductance of a bond around site A in Fig. 4. An external electric field is applied along the right–left direction. If site A represents a K_1 site, a K_1 bond occurs with probability p and a K_3 bond with probability $1-p$ in connecting site A with a neighboring site. The average value K_{m1} of the bond is given by

$$K_{m1} = pK_1 + (1-p)K_3 \tag{2}$$

where K_3 is the average $2K_1K_2/(K_1 + K_2)$.

In a similar way, for a K_2 site, a K_2 bond occurs with probability $1-p$ and a K_3 bond occurs with probability p. The average value K_{m2} is given by

$$K_{m2} = (1-p)K_2 + pK_3 \tag{3}$$

In our resistor network, the average values K_{m1} and K_{m2} obtained above occur with probabilities p and $1-p$, respectively. The average effect of the values K_{m1} and K_{m2} can be expressed by giving all of them a single value K_{eff} and choosing K_{eff} such that the effects of changing any one conductance back to its true value will, on the average, cancel out.

If a bond with conductance K_0 is embedded in an infinite medium of conductivity K_{eff}, altering the value of a conductance aligned along the electric field from K_{eff} to K_0 causes an additional voltage V_0 to be induced across K_0,[3]

$$V_0 = V_{\text{eff}}(K_{\text{eff}} - K_0)/(K_0 + 2K_{\text{eff}}) \tag{4}$$

where V_{eff} is the voltage drop between adjacent rows far from K_0. Thus, if $p(K_m)$ is the probability distribution of the average bond conductance K_m,

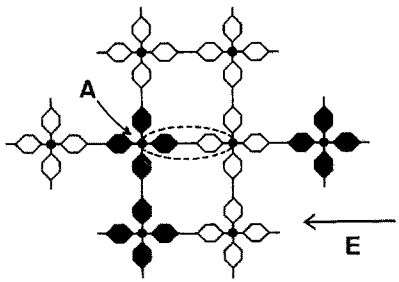

Fig. 4. The average conductance of a bond around site A. If site A is a K_1 site, $K_{m1} = pK_1 + (1-p)K_3$. If site A is a K_2 site, $K_{m2} = (1-p)K_2 + pK_3$, where $K_3 = 2K_1K_2/(K_1 + K_2)$. E denotes an externally applied field.

we have, for a cubic network,

$$0 = \int dK_m\, p(K_m)(K_{\text{eff}} - K_m)/(K_m + 2K_{\text{eff}}) \tag{5}$$

If $p(K_m)$ is a binary distribution, Eq. (5) becomes a quadratic equation for K_{eff}. Thus, according to the single-bond EMT,[3,4] the bulk conductivity $K_{\text{eff}}(p)$ of the resistor network is, with the root, given by

$$4K_{\text{eff}}(p) = (3p - 1)K_{m1} + [3(1 - p) - 1]K_{m2} + (\{(3p - 1)K_{m1} + [3(1 - p) - 1]K_{m2}\}^2 + 8K_{m1}K_{m2})^{1/2} \tag{6}$$

The effective conductivity $K_{\text{eff}}(p)$ is plotted as the solid lines in Fig. 3.

For the extreme case of $K_2 = 0$, the random model of two-phase material is a mixture of a conducting material with conductance K_1 and volume fraction p and an insulating material with volume fraction $1 - p$. Thus we obtain

$$K_{\text{eff}}(p) = \begin{cases} 0 & \text{for } p < \frac{1}{3} \\ \frac{1}{2}p(3p - 1) & \text{for } p > \frac{1}{3} \end{cases} \tag{7}$$

In other words, the concentration p_c at which the effective conductivity $K_{\text{eff}}(p)$ vanishes is 1/3. From numerical results of computer simulations, Kirkpatrick[4] and Onizuka[7] have suggested a power law for the network conductivity at $K_2 = 0$; namely, $K(p) \propto (p - p_c)^t$, where $p_c \approx 0.312$–0.318 and $t \approx 1.5$–1.73.

For cases in which K_1 and K_2 are comparable, agreement between the proposed theory (6) and the existing experiment results is very good. Also, for the critical region of $K_2 = 0$, Eq. (7) is in good agreement with the Monte Carlo data[7] (data points *A*). This shows that our theory based upon the effective-medium theory provides a surprisingly accurate approximation to the quantitative description of the bulk conductivity of a random resistor network for all concentrations.

4. COMPARISON WITH EXPERIMENT

When the thermal conductivities of the first and second phases and their respective volume fractions are known, we can expect to predict the effective thermal conductivity of random mixtures from them. Let p stand for the fraction of the total volume occupied by the first-phase material and let K_1 and K_2 be the thermal conductivities of first and second phases, respectively. The effective thermal conductivity K can be predicted according to Eq. (6) from K_1, K_2, and p.

Figures 5 and 6 give comparisons for glass particle–silicon rubber and glass fiber–plastic systems. Similar comparisons are made in Figs. 7 and 8

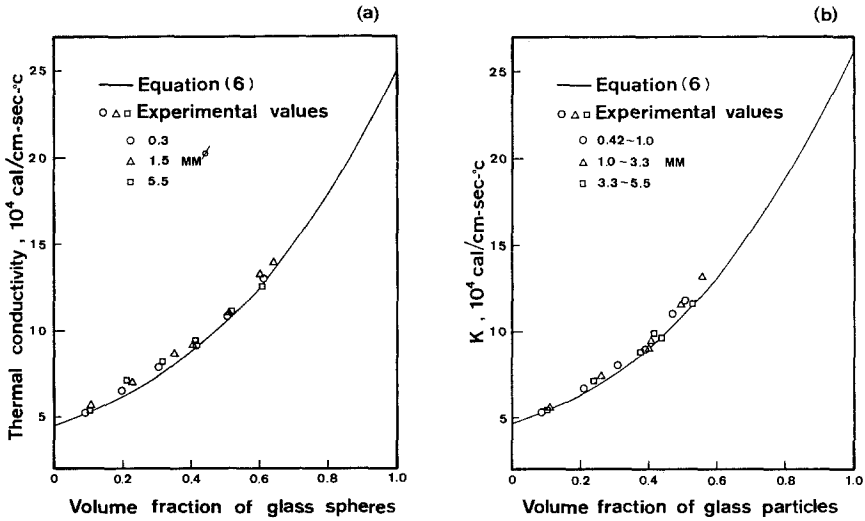

Fig. 5. Comparison of the experimental effective thermal conductivity with the theory in Section 3. The experimental values were measured by Hayashi *et al.*[18] at 25°C. (a) Effective thermal conductivity of mixtures composed of glass spheres and silicon rubber versus volume fraction of glass spheres. (b) Effective thermal conductivity of mixtures composed of irregular glass particles and silicon rubber versus volume fraction of glass particles.

for systems saturated with air: porous sandstone and fire brick. Three of the four cases give excellent agreement. Only the air-saturated fire brick system really fails to fit the theory. The poor agreement may come from the fact that the experimentally prepared mixtures do not represent a random system.

The results shown in Figs. 5–8 are sufficient to show the excellent agreement of the theory with experimental data. This shows that these materials

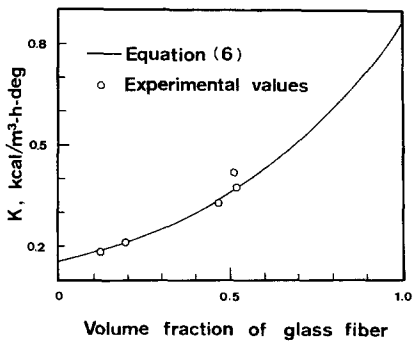

Fig. 6. Effective thermal conductivity of mixtures composed of glass fiber and plastic versus volume fraction of glass fiber. The experimental values are quoted from Holliday.[19]

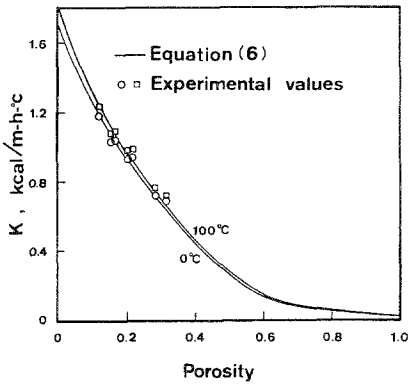

Fig. 7. Effective thermal conductivity of air-saturated porous sandstone versus porosity. The experimental values were measured by Sugawara and Yoshizawa[20] at 0 and 100°C.

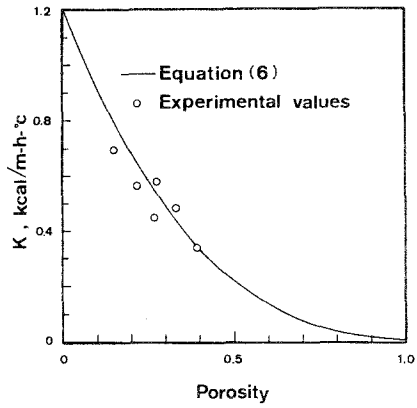

Fig. 8. Effective thermal conductivity of air-saturated fire brick versus porosity. The experimental points fail to fit the theory. This may come from the fact that the experimental measurements themselves show poor reproducibility. The experimental values were measured by Sugawara and Yoshizawa[21] at 50°C.

can be regarded as random systems. Thus, the phase geometry as well as the phase conductivities are of considerable importance in determining the physical properties of disordered two-phase materials. Finally, the theory based upon the site percolation system can be widely applied in predicting other physical properties, such as electrical and mechanical properties of disordered materials.

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