CONDUCTIVITY OF COMPOSITES WITH CHAOTIC STRUCTURE

V.V. NOVIKOV, K.O. NEZHEVENKO

Odesa National Politechnical University
(1, Shevchenko Prosp., Odesa 65044, Ukraine; e-mails: novikov@te.net.ua, nejevenko@ukr.net)

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We have proposed a fractal model of a two-component composite with chaotic structure and calculated its fractal dimension and critical indices. The calculation of the conductivity of a composite with chaotic structure is reduced to that of both the conductivity of a composite with ordered structure and the probability function of the existence of a connecting set (CS) with conducting bonds.

1. Introduction

The prediction of the effective conductivity σ for composites with chaotic structure remains to be the actual problem till now. The survey of the literature [1–3] shows that the classical formulas for the conductivity of composites with chaotic structure do not agree with experimental data in the whole range of the concentration of the conducting component and for all values of the conductivities of components σ_1 and σ_2. The classical theories (for example, the Maxwell model, the method of effective medium, and the variational method) agree well with experimental data on σ if the conductivities of components (σ_2 and σ_1) of a composite differ by at most two orders ($10^{-2} < \sigma_2/\sigma_1 < 1$) or for small concentrations of one of the components (e.g., $p \ll 1$). If the ratio $\sigma_2/\sigma_1 < 10^{-2}$, then the results of calculations of the effective conductivity by formulas of the classical theories differ strongly from experimental data [1, 4].

In order to predict the effective conductivity of a composite, we can use the results of the theory of percolation [5, 6] if the ratio of the conductivities of components tends to zero ($\sigma_2/\sigma_1 \to 0$):

$$\begin{cases} \sigma \approx (p - p_c)^t, \ (p - p_c) > 0, \\ \sigma \approx (p_c - p)^{-s}, \ (p - p_c) < 0. \end{cases} \quad (1)$$

Here, t and s – the critical indices of conductivity ($t = s \approx 1.1$ for two-dimensional systems ($d = 2$), and $t \approx 1.6 \div 2$, $s \approx 0.6$ for three-dimensional systems ($d = 3$); and p_c – the percolation threshold).

If the ratio of the conductivities of components of a system belongs to the range $0 < \sigma_2/\sigma_1 < 10^{-2}$, no strict theory which would allow one to predict the effective conductivity of composites with chaotic structure is available. We propose a fractal model and the method of calculation of the conductivity of composites with chaotic structure, which allows us to solve this problem.

2. Model of Structure

As a model of the structure of a composite, we study a volumetric lattice composed from sites and bonds connecting them. Each of the bonds belongs with probability p to the component with conductivity $\sigma_1 = 1$ (Fig. 1). To construct a fractal set (a lattice), we will perform the iteration procedure, in which each bond is replaced on the next stage by the lattice obtained on the previous stage [7, 8]. Thus, we get a fractal set with the infinite number of bonds which depends on the initial type of a lattice.

We distinguish two configurations: in the first one, the conducting bonds form a CS by connecting the opposite sides of the lattice along the direction of percolation, whereas no connecting cluster exists in a nonconnecting set (NCS). On the transition of the NCS in a CS, an infinite cluster-fractal is formed.

In order to determine the parameters of a model, the critical point is the knowledge of the probability function $R(p)$ which is defined as the probability of a CS among all possible configurations. On its basis,

one can determine the critical concentration p_c, i.e. the concentration at which there appears a conducting chain, critical indices, and fractal dimensions.

In [9], the function $R(p)$ was calculated for lattices with the dimension 1×2×1, and, on its basis, the fractal dimension of lattices and the critical indices were determined. The experimental studies indicate that there exist the materials with a structure which possesses the percolation threshold, fractal dimension, and other structural parameters distinct from those described in [9]. In this connection, there appears the problem of the determination of other probability functions $R(p)$ describing materials with other structural parameters. We determined analytically the probability function $R(p)$ for lattices with the dimension 1×2×2 (the number of bonds was 19 on the initial iteration stage), 1×3×1 (the number of bonds was 20 on the initial iteration stage), and, for lattices with greater dimensions (the number of bonds is more than 25 on the initial iteration stage), the probability function $R(p)$ was found with the help of the Monte-Carlo method.

3. The Probability Function of the Formation of a CS

We determined the probability functions of the percolation $R(p)$ for the lattices $l_x \times l_y \times l_z$ (l_y is the direction of percolation) which is the sum of the probabilities of all possible variants of conducting configurations:

$$R(p) = \sum_{i=0}^{k} A_i p^i (1-p)^{k-i}, \qquad (2)$$

where k – the number of all bonds, i – the number of conducting bonds; and A_i – the number of possible configurations of a CS at the given p.

We determined the probability functions $R(p)$ for two-dimensional lattices with dimensions 2×1, 2×2, 2×3, 2×4, 2×5, 2×6, 2×7, 3×1, 3×2, 3×3, 3×4, 4×1, 4×2, and 4×3, as well as $R(p)$ for 3D lattices with dimensions 1×2×1, 1×3×1, and 1×2×2(2×2×1), for which the total number of bonds is less than 25. Below, we present several such functions:
Lattice 1×2×2(2×2×1):

$$R(p) = 6p^2(1-p)^{17} + 116p^3(1-p)^{16} + 1017p^4\times$$

$$\times(1-p)^{15} + 5301p^5(1-p)^{14} + 18077p^6(1-p)^{13}+$$

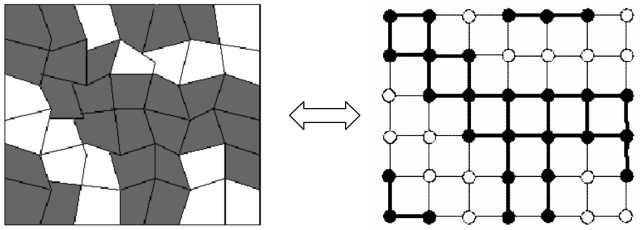

Fig. 1. Simulation of the structure of a composite

$$+42257p^7(1-p)^{12} + 70612p^8(1-p)^{11} + 90186p^9\times$$

$$\times(1-p)^{10} + 91664p^{10}(1-p)^9 + 75414p^{11}(1-p)^8+$$

$$+50362p^{12}(1-p)^7 + 27130p^{13}(1-p)^6 + 11628p^{14}\times$$

$$\times(1-p)^5 + 3876p^{15}(1-p)^4 + 969p^{16}(1-p)^3+$$

$$+171p^{17}(1-p)^2 + 19p^{18}(1-p) + p^{19}.$$

Lattice 1×3×1:

$$R(p) = 4p^3(1-p)^{17} + 84p^4(1-p)^{16} + 816p^5(1-p)^{15}+$$

$$+4818p^6(1-p)^{14} + 19100p^7(1-p)^{13} + 52822p^8\times$$

$$\times(1-p)^{12} + 102940p^9(1-p)^{11} + 142578p^{10}(1-p)^{10}+$$

$$+147528p^{11}(1-p)^9 + 118541p^{12}(1-p)^8 + 75520p^{13}\times$$

$$\times(1-p)^7 + 38376p^{14}(1-p)^6 + 15456p^{15}(1-p)^5+$$

$$+4842p^{16}(1-p)^4 + 1140p^{17}(1-p)^3 + 190p^{18}(1-p)^2+$$

$$+20p^{19}(1-p) + p^{20}.$$

It is clear that the sorting of all configurations of conducting and nonconducting bonds is a rather difficult problem in the general case. Therefore, in order to calculate the percolation function for volumetric lattices with the total number of bonds which is more than 25, we used the Monte-Carlo numerical method allowing the simulation of random distributions of bonds. The procedure is repeated N times so that each following distribution is independent of the previous one. After the averaging of the results of calculations, we obtain the probability function $R(p)$ and the conductivity of lattices.

T a b l e 1. Values of the percolation threshold p_c, derivative at the point of the percolation threshold λ_p, fractal dimensions d_f^0 and d_f, and critical indices β, α, and ν obtained by the sorting of all combinations of conducting and nonconducting bonds

$l_x \times L_y \times l_z$	p_c	d_f^0	d_f	$\lambda_p = \frac{dR}{dp}_{p=p_c}$	$\nu = \frac{\ln l_0}{\ln \lambda_p}$	$\alpha = \frac{\beta}{\nu}$	β
$1 \times 2 \times 1$	0.208	3.585	1.323	1.958	1.031	2.262	2.333
$1 \times 3 \times 1$	0.374	2.727	1.832	2.534	1.182	0.895	1.058
$1 \times 2 \times 2$	0.138	4.248	1.395	2.042	0.971	2.853	2.770

T a b l e 2. Values of the percolation threshold p_c, derivative at the point of the percolation threshold λ_p, fractal dimensions d_f^0 and d_f, and critical indices β, α, and ν obtained with the help of the Monte-Carlo method

$l_x \times L_y \times l_z$	p_c	d_f^0	d_f	$\lambda_p = \frac{dR}{dp}_{p=p_c}$	$\nu = \frac{\ln l_0}{\ln \lambda_p}$	$\alpha = \frac{\beta}{\nu}$	β
2×2×2	0.093	4.907	1.477	2.065	0.956	3.430	3.279
2×2×3	0.072	5.358	1.563	2.048	0.967	3.794	3.669
2×2×4	0.059	5.700	1.615	2.088	0.942	4.086	3.847
2×3×2	0.225	3.579	2.221	3.073	0.979	1.358	1.329
2×4×2	0.293	3.085	1.502	3.781	1.042	0.885	1.650
3×2×1	0.105	4.700	1.447	2.066	0.956	3.253	3.108
3×2×3	0.054	5.807	1.606	2.056	0.962	4.201	4.041
3×2×4	0.044	6.150	1.634	2.056	0.962	4.516	4.344
3×3×2	0.195	3.867	2.379	3.217	0.940	1.488	1.399
3×3×3	0.170	4.155	2.541	3.288	0.923	1.613	1.489
4×2×4	0.037	6.492	1.733	2.090	0.940	4.759	4.474
4×4×2	0.240	3.489	2.459	4.209	0.965	1.030	0.994
3×3×4	0.153	4.373	2.666	3.332	0.913	1.706	1.558
4×4×4	0.201	3.891	2.734	4.578	0.911	1.157	1.054

T a b l e 3. Values of the percolation threshold p_c, fractal dimension d_f, critical indices β and ν for the classical percolation cluster

p_c	d_f	$\nu = \frac{\ln l_0}{\ln \lambda_p}$	β
0.24 [10]	2.484 [11]	0.82 ± 0.05 [13]	0.39 ± 0.07 [13]
	2.529 [12]	0.905 ± 0.023 [14]	0.454 ± 0.008 [15]

4. Critical Indices

On the basis of the analytic probability function $R(p)$, we can determine the nonanalytic functions which characterize the fractal structure in a neighborhood of the percolation threshold p_c. We have determined: the percolation threshold p_c; the derivative of the probability function at the point of the percolation threshold λ_p; the fractal dimension of the set d_f^0 in the case where all bonds are conducting, i.e. p=1; the fractal dimension of the set at the percolation threshold d_f; the critical index of the correlation length ν; the critical index of the density of connecting sets β; and the critical index α equal to β/ν. The results of calculations are given in Tables 1 and 2. The constructed fractal sets in a neighborhood of the percolation threshold differ from the classical percolation cluster in a neighborhood of the percolation threshold in the three-dimensional case which has characteristics presented in Table 3. It follows from the comparison that the fractal sets obtained here differ essentially from the classical percolation cluster and can be used in the simulation of inhomogeneous media such as, for example, polymers or polymeric composites.

5. Conductivity

To determine the effective conductivity σ of a composite with chaotic structure, we developed a computer program calculating the conductivity of lattices as a function of the concentration of conducting bonds. The task of the determination of the effective conductivity σ of a composite with chaotic structure is quite complicated. Therefore, while solving this problem, we admit some simplifications (assumptions), the main assumption being the neglect of the correlation between different bonds on a lattice under study [16].

The calculations were carried out for a two-component composite. The conductivity of the first component $\sigma_1 = 1$, and the conductivity of the second one $\sigma_2 = 10^{-x}$, where $1 < x < 10$. For lattices with the total number of bonds less than 25, we performed the sorting of all possible variants of the positions of conducting and nonconducting bonds. For lattices with the number of bonds greater than 25, we realized chaotic distributions of bonds with the help of the Monte-Carlo method. The results of calculations of the effective

conductivity were compared with experimental data [4], which showed the adequacy of both the proposed model and the developed computer program to real systems.

In a separate way, we calculated the effective conductivity of a lattice σ in the case where it contains a CS with conducting bonds. This calculation was carried out in the following manner: first, the initial number of conducting bonds was taken to be equal to l_y, because a CS is not formed for less values. Taking the number of bonds to be equal to l_y, we performed the sorting of all possible distributions of bonds. For each distribution of bonds, we analyzed the lattice for the presence of a CS. If it was present, we calculated its conductivity. Then the obtained values of the effective conductivity were averaged over all the configurations of bonds. Thereafter, the number of conducting bonds was increased by 1, and the sorting of all possible configurations was realized. During the sorting, the lattices were analyzed for the presence a CS, and the calculation of the average value of the conductivity was carried out. Then again the number of conducting bonds was increased by 1, etc., until it becomes equal to k, and the effective conductivity of lattices becomes equal to $\sigma_1 = 1$. The results of calculations are given in Table 4 and Fig. 2.

The use of direct computer-based methods for the prediction of the effective conductivity of composites with chaotic structure requires quite great expenditures. To obtain the high-precision results, we need powerful computers and much computer time, which yields the necessity to develop a simple scheme of prediction of the effective conductivity of composites with chaotic structure, but with at least the same accuracy of calculations. We propose a rather simple scheme of calculations which is illustrated by the example of the lattice 1×2×1. For this lattice, we made comparison of the results of calculations of the effective conductivity in the presence of a CS with those obtained by the formula for a "cube in cube" cell [1] and multiplied by the probability function $R(p)$ (see Fig. 2).

T a b l e 4. Averaged values of the effective conductivity for three-dimensional lattices which contain a CS, $\sigma_1 = 1$, $\sigma_2 = 10^{-4}$

Quantity of conducting bonds	$1 \times 2 \times 1$, $k = 12$	$1 \times 2 \times 2$ $(2 \times 2 \times 1)$, $k = 19$	$1 \times 3 \times 1$, $k = 20$
1	–	–	–
2	0.015	0.006	–
3	0.052	0.019	0.0009
4	0.113	0.041	0.004
5	0.200	0.074	0.012
6	0.303	0.116	0.028
7	0.413	0.167	0.054
8	0.529	0.225	0.094
9	0.646	0.288	0.147
10	0.764	0.354	0.211
11	0.882	0.423	0.282
12	1.000	0.494	0.357
13		0.565	0.435
14		0.638	0.515
15		0.710	0.596
16		0.783	0.677
17		0.855	0.758
18		0.928	0.839
19		1.000	0.917
20			1.000

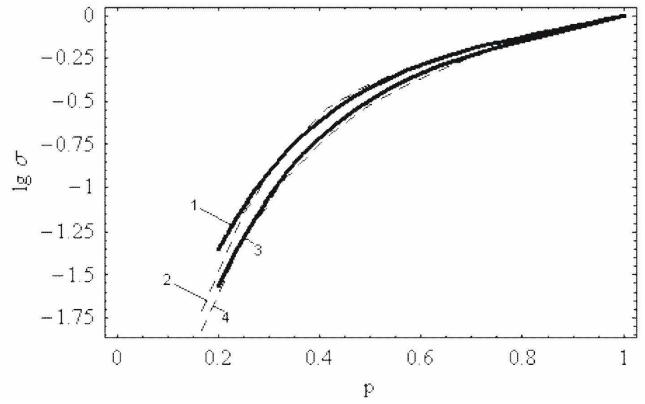

Fig. 2. Comparison of the effective conductivity in the presence of the CS (solid curve) and the effective conductivity for a "cube in cube" cell multiplied by the probability function $R(p)$ (dashed line), *1, 2* – $\sigma_2 = 10^{-1}$ and $\sigma_1 = 1$; *3,4* – $\sigma_2 = 10^{-6}$ and $\sigma_1 = 1$

From Fig. 2, we see that the curves practically coincide. This fact allows us to simplify the calculations of the effective conductivity of a composite with chaotic structure.

On the basis of the performed calculations, we consider the problem of the reduction of the calculation of the conductivity of a composite with chaotic structure to that of the conductivity of a composite with ordered structure. The obtained results allow us to substantiate the following scheme of calculations of the effective conductivity of composites with chaotic structure: the conductivity of a composite containing a CS with a random distribution of bonds equals the conductivity of a composite containing a CS with an ordered distribution of bonds (of the "cube in cube" type) multiplied by the probability function $R(p)$ (Fig. 2).

The calculation of the effective conductivity of an ordered structure was performed in the following way: we use the formula for the conductivity of a cell, in which a cube with conductivity σ_2 is positioned in a cube with

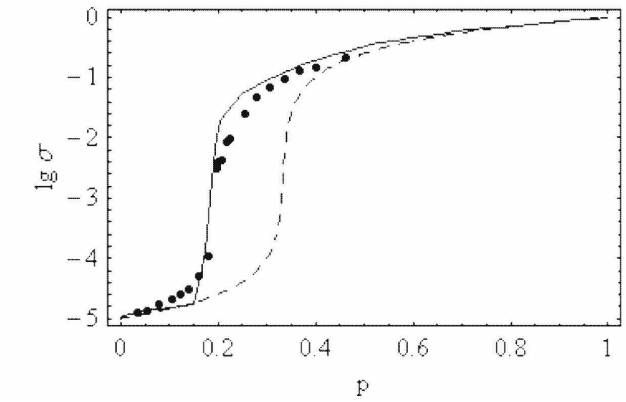

Fig. 3. Effective conductivity versus the concentration of conducting bonds at $\sigma_2 = 10^{-5}$ and $\sigma_1 = 1$. Dots – experimental data, solid curve – the results of calculations for a "cube in cube" cell multiplied by the probability function $R(p)$, and the dashed curve is obtained by the method of effective medium

conductivity σ_1 [1] (the cell is a CS):

$$\sigma = \frac{\sigma_1}{2}\left(\psi_1 + \psi_2\right), \tag{3}$$

where

$$\psi_1 = \frac{\sigma_1 + (\sigma_2 - \sigma_1)\,(1-p)^{2/3}}{\sigma_1 + (\sigma_2 - \sigma_1)\,(1-p)^{2/3}\left[1-(1-p)^{1/3}\right]},$$

$$\psi_2 = \frac{\sigma_2 + (\sigma_1 - \sigma_2)\,(1-p)^{1/3}\left[1-(1-p)^{2/3}\right]}{\sigma_2 + (\sigma_1 - \sigma_2)\,(1-p)^{1/3}}.$$

Here, p – the volumetric concentration of the phase with conductivity σ_1. In order to calculate the conductivity of a cell, in which a cube with conductivity σ_1 is positioned in a cube with conductivity σ_2 (the cell is an NCS), it is necessary to change the indices $1 \leftrightarrow 2$ and to replace $(1-p) \leftrightarrow p$.

To illustrate the calculation of the effective conductivity of a composite with chaotic structure, we use a probability function of the lattice 1×2×1 of the form

$$R(p) = 4p^2(1-p)^{10} + 48p^3(1-p)^9 + 238p^4(1-p)^8 +$$

$$+616p^5(1-p)^7 + 856p^6(1-p)^6 + 776p^7(1-p)^5 +$$

$$+493p^8(1-p)^4 + 220p^9(1-p)^3 + 66p^{10}(1-p)^2 +$$

$$+12p^{11}(1-p) + p^{12}.$$

On the basis of the function $R(p)$, we determined the value of the percolation threshold $p(p_c = 0.2086...)$ characterizing the transition of the NCS to a CS. Respectively, the percolation threshold determines the formulas for the calculation of the effective conductivity. Prior to the percolation threshold, the effective conductivity is calculated by the formula for a cell, in which a cube with conductivity σ_1 is positioned in a cube with conductivity σ_2 (the probability of that the given volume element of a composite belongs to the NCS is equal to 1). After the percolation threshold, the effective conductivity is calculated by the formula for a cell, in which a cube with conductivity σ_2 is positioned in a cube with conductivity σ_1 (the probability of that the given volume element of a composite belongs to the CS is equal to a value of the probability function $R(p)$, and the probability of that it does not belong to the CS is $(1 - R(p))$).

Therefore, the effective conductivity can be calculated by the formula

$$\sigma = \begin{cases} \sigma_{\rm NCS}, & p < p_c \\ \sigma_{\rm CS} R(p), & p > p_c. \end{cases} \tag{4}$$

The effective conductivity has a jump near the percolation threshold. In this connection, in a neighborhood of the percolation threshold (at a change of the concentration from 0.15 to 0.25), the calculation of the conductivity was carried out by the following scheme. We determined the arithmetic mean of the conductivities at $p = 0.15$ and at $p = 0.25$, i.e. we got the value of conductivity at the concentration $p = 0.2$. Then the procedure was repeated for the points p=0.15 and $p = 0.2$, the points $p = 0.2$ and $p = 0.25$, etc.

Thus, the calculation of the effective conductivity of composites with fractal structure is performed by formula (4) in the concentration ranges $0 \leq p \leq 0.15$ and $0.25 \leq p \leq 1$. In a neighborhood of the percolation threshold $0.15 < p < 0.25$, the calculation was performed by the above-described scheme.

The comparison of the results of calculations of the effective conductivity of a composite possessing a chaotic structure by the presented scheme and experimental data [9] is shown in Fig. 3. There, we present also the results of calculations within the method of effective medium (self-consistent field) [3] by the formulas

$$\sigma = \sigma_1\left[(3p_1 - 1) + (3p_2 - 1)\,\frac{\sigma_2}{\sigma_1}\right]\Big/ 4 +$$

$$+\sigma_1\sqrt{\left[(3p_1-1)+(3p_2-1)\,\frac{\sigma_2}{\sigma_1}\right]^2\Big/16+\frac{\sigma_2}{2\sigma_1}} \qquad (5)$$

According to calculations (Fig. 3), the result for a "cube in cube" cell multiplied by the probability function $R(p)$ coincides rather well with experimental data, whereas the method of effective medium at the concentration of conducting bonds $0 < p < 0.4$ leads to significant discrepancies [4].

The calculations showed that if the discrepancy between the conductivities of components at $\sigma_2/\sigma_1 > 10^{-4}$ decreases, and the results of calculations by the model of effective medium and by the scheme proposed by us practically coincide.

6. Conclusions

We have proposed a model of the chaotic fractal structure of a composite in the three-dimensional case and determined the probability function $R(p)$ (when the total number of bonds of a lattice is less than 25, $R(p)$ was determined exactly; when the number of bonds was greater than 25, we used the Monte-Carlo method). On the basis of the function $R(p)$, we calculated both the percolation threshold of a lattice p_c which characterizes the transition from the "weakly" conducting state to a "well" conducting one, and the derivative at the point of the percolation threshold $\lambda_p = \frac{dR}{dp}\Big|_{p=p_c}$. We also calculated the fractal dimensions and critical indices of the model.

By using the developed computer program, we determined the conductivity of lattices with chaotic distribution of bonds in the presence of the connecting set formed by conducting bonds. We also determined the conductivity of lattices with an ordered distribution of bonds of the "cube in cube" type by the above-presented formulas. The obtained results allow us to reduce the calculation of the conductivity of a composite with chaotic structure to that of the conductivity of a composite with ordered structure by using the probability function $R(p)$.

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ПРОВІДНІСТЬ КОМПОЗИТІВ З ХАОТИЧНОЮ СТРУКТУРОЮ

В.В. Новіков, К.О. Нежевенко

Р е з ю м е

Запропоновано фрактальну модель двокомпонентного композита з хаотичною структурою, розраховано її фрактальну розмірність та критичні показники. Розрахунок провідності композита з хаотичною структурою зведено до розрахунку провідності композита з упорядкованою структурою та функції ймовірності існування з'єднуючої множини з провідних зв'язків.