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A STOCHASTIC MODEL OF DISPERSE SYSTEMS

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We suggest a model of the structure of a disperse system that reflects the random character of the topology. We evaluate the effect of the stochastic nature of the topology on the effective conductivity. An asymptotic decrease in the conductivity with increase in the scale of the heat and mass transfer is established and explained.

Introduction. At the present time disperse systems are finding ever wider use in various areas of science and technology. But the problem of predicting their properties remains far from being solved. This relates in full measure to a parameter of disperse systems such as their conductivity. A large number of works (see [1, 2] and the literature cited there) are devoted to the problem of determining the conductivity of inhomogeneous systems. The models and experiments considered in those works are aimed at studying the effect of the porosity of disperse systems on their conductivity. The basic assumption here is an ergodic hypothesis according to which averaging over an ensemble of specimens is replaced by averaging over a volume. For this purpose, the disordered structure of real systems is replaced by an ordered one by singling out a certain element with averaged parameters whose conductivity is equal to the conductivity of the system as a whole. In this approach, the fact that the size of the particles and their relative position are random quantities drops out of consideration. The random character of the position of the particles is reflected by the model of [3], in which ballistic precipitation of particles is considered. In this model, particles in the form of squares or rectangles precipitate successively, and each becomes attached by one of its sides to some already precipitated particle located on the surface of a disperse structure. The site where attachment will occur is determined randomly. The conductivity of structures formed in this way was not investigated in [3]. Furthermore, it should be noted that the problem of the effect exerted by the heat- and mass-transfer scale on the conductivity of disperse systems has been studied inadequately at the present time.

Using averaging over an ensemble of specimens and the method of mathematical simulation, we carried out an analysis of the effect exerted by the random character of the topology of a disperse system on its conductivity. The numerical simulation is supplemented with results obtained by means of a deterministic model, which made it possible to explain the asymptotic decrease in the conductivity with increase in the heat- and mass-transfer scale.

A Stochastic Model of the Structure of a Disperse System. In the present work we model systems whose particles are formed by the technology of gas-phase condensation [4], which allows one to obtain a homogeneous fractional composition of particles. Proceeding from this, in the model of the system the particles are simulated by squares of the same size. The model of the structure is created by means of an algorithm that consists in multiple use of the following procedure on a two-dimensional computational grid with the number of nodes $(N_x \times N_y)$ and equal steps along the X and Y axes.

Step 1. An integer uniformly distributed on the interval $[1, N_x]$ is sampled by means of a generator of pseudorandom numbers. It is the coordinate on the X axis along which the center of the next square (hereafter, simply a particle) descends from the upper boundary of the grid (the coordinate of the upper boundary is $y = N_y$).

Step 2. The particle descends. Here, two variants are possible.

1. The lower side of the particle reaches the lower boundary of the grid ($y = 1$). In this case, the particle is considered to be finally laid. Here and at subsequent steps, if a particle becomes finally laid, the nodes of the computational grid that lie within the region belonging to the particle are labeled as occupied. Then step 4 follows.

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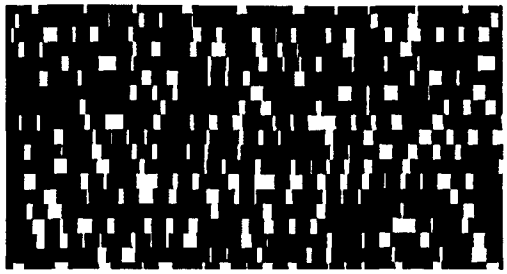


Fig. 1. A random realization of the structure of a disperse system.

2. The particle reaches a particle that was laid earlier. In this case the particle is considered to be preliminarily laid, and passage to step 3 follows.

Step 3. At this step a rather obvious fact is simulated, namely, the preliminarily laid particle may "slide" to the nearest cavity (down). For this purpose, we analyze the particle onto which the preliminarily laid particle descended and determine the distance from its left and right side to the middle of the preliminarily laid particle. The nearer direction is selected. If the nearest cavity has enough space for the preliminarily laid particle to be placed, the particle is laid in this cavity and goes over into the state of finally laid. If there is insufficient space in the nearest cavity, the preliminarily laid particle remains where it is, and it is transferred to the state of finally laid. Then passage to step 4 follows. Computational experiments showed that it is quite sufficient to perform a single sliding of a preliminarily laid particle.

Step 4. Checking whether the upper side of the finally laid particle goes beyond the upper boundary of the computational domain is done. If it does not, passage to step 1 is made. If it does, formation of the disperse system is completed, and then passage to step 5 follows.

Step 5. To eliminate effects caused by the boundaries, nodes of the computational grid that are adjacent to the boundaries are discarded. Bands with a width of 2 particles are discarded along the vertical sides, a band with a height of 5 particles is discarded along the lower side, and a band with a height of at least 100 particles is discarded along the upper side. In other words, the middle of the packing is cut out.

Thus, when the operation of the algorithm ceases, we have a two-dimensional array (a computational grid) in which each element is set in correspondence with a number that signifies the phase of the disperse system to which the $(\Delta/2)$-vicinity of this element refers. The porosity of a specimen is defined as the ratio between the nodes that belong to pores and the total number of nodes.

Repeating the above-described algorithm with different sequencies of random numbers, we obtain different realizations of the random system. One possible realization of the structure obtained by the algorithm described above is shown in Fig. 1.

The foregoing algorithm in which particles "fall from above" simulates the production of densely packed disperse systems by the technology of sputtering and deposition. The proposed algorithm of formation of two-dimensional models of disperse systems is distinguished from that given in [3] by the following: a) the surface formed only by the upper sides of the particles already laid is the surface where a descending particle can be fixed; b) there is the possibility for a particle to "slide" from a preliminarily laid state; c) the area of contact of the particles is a multiple of the step of the computational grid and can be smaller than the area of the side of the particle.

A Model of Generalized Conductivity. The generalized conductivity is numerically equal to the coefficient that relates the vector of the flow to the vector of the gradient of the potential [2]:

$$\mathbf{i} = -\sigma \nabla \varphi , \tag{1}$$

where $\mathbf{i}$ is the vector of the flow; $\nabla\varphi$ is the vector of the gradient of the potential.

It is necessary that equality of the flows hold on the interface:

$$\sigma_i \frac{\partial \varphi_i}{\partial n} = \sigma_{i-1} \frac{\partial \varphi_{i-1}}{\partial n} , \tag{2}$$

Here i and $(i-1)$ are indices relating to different phases; n is the normal to the interface.

For the entire specimen the following condition must hold:

$$\operatorname{div}(\mathbf{i}) = 0, \tag{3}$$

where the vector $\mathbf{i}$ is determined by Eq. (1).

Equation (3) was solved in a two-dimensional formulation in a rectangular region occupied by a two-phase stochastic medium by a time-dependent technique [5] in which the solution of the stationary problem was considered as the limiting solution (for $\tau \to \infty$) of a nonstationary equation of parabolic type:

$$\frac{\partial \varphi}{\partial \tau} = \frac{\partial}{\partial x}\sigma\frac{\partial \varphi}{\partial x} + \frac{\partial}{\partial y}\sigma\frac{\partial \varphi}{\partial y}, \tag{4}$$

$$\sigma = \sigma(x, y) = \begin{cases} \sigma_1, & \text{if the node } (x, y) \text{ belongs to phase 1;} \\ \sigma_2, & \text{if the node } (x, y) \text{ belongs to phase 2;} \end{cases}$$

$$0 \le x \le H_x, \quad 0 \le y \le H_y, \quad \tau \ge 0.$$

The initial and boundary conditions have the following form:

$$\varphi(\tau, x, 0) = \varphi_1, \quad \varphi(\tau, x, H_y) = \varphi_0, \quad 0 \le x \le H_x, \quad \tau \ge 0;$$

$$\frac{\partial \varphi(\tau, 0, y)}{\partial x} = 0, \quad \frac{\partial \varphi(\tau, H_x, y)}{\partial x} = 0, \quad 0 \le y \le H_y, \quad \tau \ge 0;$$

$$\varphi(0, x, y) = \varphi_0, \quad 0 \le x \le H_x, \quad 0 \le y \le H_y.$$

The procedure for determining the generalized conductivity consisted in the following. From the stationary solution of Eq. (4) we obtained the values of the potential φ for each node of the computational grid, and, using formula (1), we determined the flux i in the direction of the Y axis for each node of the computational grid. After this, we determined the average flux over the entire specimen:

$$i_{av} = \frac{1}{H_x}\frac{1}{H_y}\int_0^{H_x}\int_0^{H_y} i\,dx\,dy. \tag{5}$$

The effective conductivity was determined in the following way:

$$\sigma_{eff} = \frac{i_{av}}{(\varphi_1 - \varphi_0)/H_y}. \tag{6}$$

In a real specimen the flux flows from the side with a higher potential to the side with a lower potential. On the average, transfer along these sides is equal to zero, and therefore use of the two-dimensional model (1)-(4) as a first approximation is quite admissible. In all the calculations the conductivity of the interparticle (pore) space was assumed to be equal to zero.

To solve Eq. (4) we employed the numerical method of finite differences using a conservative difference scheme of variable directions [6]. Stationarity was assumed to be attained if the change in the solution after ten steps in time became smaller than the preassigned residual. Using computational experiments, we determined that with a residual of 0.1% a further decrease in it leads to a change in the conductivity of less than 1%. At this level of the residual the value of φ_1 was varied in a wide range, and it was found that an increase in it by more than 200 dimensionless units (at $\varphi_0 = 100$) leads to a change in the conductivity of less than 1%. Therefore in the

calculations a residual of 0.1% was assigned, and the accuracy of determination of the conductivity by means of numerical solution of system (4)-(6) was assumed to be equal to 1%.

In the work we investigated the conductivity along the Y axis, and therefore it was necessary to settle the question of the size of the computational domain along the X axis. For this purpose, disperse systems with particles with dimensions of 10 × 10 nodes of the computational grid were generated. The height of all these systems was equal to ten particles, and the width took on values of 20, 50, 100, 150, and 200 particles. For each width 25 structures were generated; for all of them the conductivity was calculated, and the average and the standard deviation (SD) of these 25 values were determined. The calculations showed that when the width of the structure was increased above 50 particles, the change in the mean value of the conductivity was ~0.5%. For a the width of the structure above 100 particles the change in the mean value of the conductivity was ~0.1%. This value is an order of magnitude smaller than the computational error, and therefore in what follows, all the calculations were carried out on structures with a width of 100 particles.

Effect of the Random Character of the Topology on the Conductivity. In order to elucidate the question of the effect of the random character of the topology of a disperse system and the scale of transfer on its conductivity the following procedure was used. A specimen of a disperse system with a size of 100 × 100 particles was generated. The size of a particle was equal to 10 × 10 nodes of the computational grid. The porosity of the specimen was stored. Then, a lower part with a width of 100 particles and a height of one particle was "cut out" of this specimen. The conductivity of this "cut out" region was determined and stored. Then, lower regions with a height of 2, 5, 10, 20, 35, 50, 70, and 100 particles were successively "cut out" of this specimen. For each of these regions the conductivity was determined and stored. The sequential increase in the height of the computational domain corresponded to the increase in the region of transfer. Then, the characteristic scale of transfer was defined as the ratio of the size of the specimen to the size of a particle. In all, an ensemble of 45 specimens with a size of 100 × 100 particles was generated, and for each specimen the dependence of the conductivity on the scale of transfer was determined.

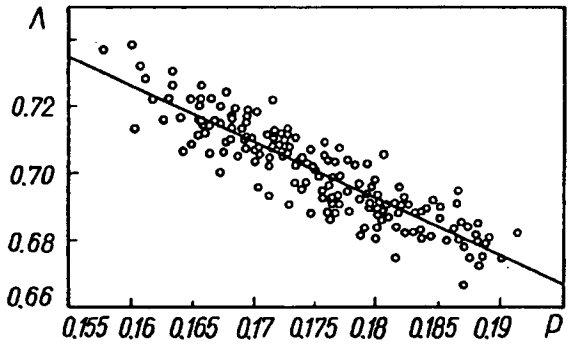
On the assumption that the porosity and the conductivity have a normal law of distribution, it is possible to get some idea of the accuracy of the evaluation of the mathematical expectation and the variance by means of the statistical simulation over 45 realizations used in the present work [7]. The standard deviation is 15% for the mean value and 21% for the variance, which can be regarded as satisfactory.

To evaluate the accuracy with which the conductivity of the disperse system is determined by means of the proposed statistical model, we compared the mean values of the conductivity with values obtained on the basis of the notion of an averaged element [1, 2] and used the mean value of the conductivity of regions having a height of 100 particles. As a result of the statistical simulation described above, we obtained that the mean value and the SD are $\overline{P} = 0.176$ and $S_p = 0.28 \cdot 10^{-2}$ for the porosity and $\overline{\Lambda} = 0.681$, $S_\Lambda = 0.86 \cdot 10^{-2}$ for the conductivity. In accordance with [2], we determined the conductivity of an elementary cell with a cubic nonconducting inclusion with porosity $P = 0.176$. For adiabatic and isothermal division of the cell this conductivity is equal to 0.686 and 0.795, respectively. The discrepancy between the conductivity of the cell with adiabatic division and the mean value of the conductivity obtained by the proposed statistical model is less than 1%, which can be regarded as satisfactory agreement.

We will demonstrate the effect of the random character of the topology of a disperse system on its conductivity using specimens with a height of 10 particles as an example. The statistical dependence between the porosity and the conductivity for 200 realizations is given in Fig. 2. A straight line is drawn through the obtained points by the least-squares method, and the mean coefficient of variation of the deviation of the conductivity from this line is calculated by the formulas [8]

$$S = \left[\frac{1}{N}\sum_{i=1}^{N}(aP_i + b - \sigma_i)^2\right]^{1/2}, \quad F = \frac{S}{\overline{\sigma}},$$

where N is the number of computational points; $\overline{\sigma}$ is the mean value of the conductivity; P_i, σ_i are the porosity and the conductivity of a specific realization of the porous system. Calculation by these formulas yields F =



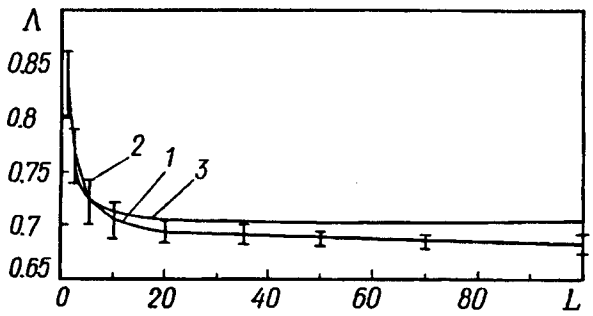


Fig. 2. Dependence of the conductivity on the porosity for specimens with a height of 10 particles.

Fig. 3. Dependence of the mean value and the SD of the conductivity on the scale of transfer: 1) statistical simulation, 2) the range ±SD, 3) analytical model (10).

$0.86 \cdot 10^{-2}$. Thus, in measurements of the conductivity of different specimens there is scattering in the values of the conductivity, along with random errors of measurement, due to the random character of the topology of the heterogeneous system.

Effect of the Scale of Transfer on the Conductivity of Disperse Systems. Figure 3 shows the dependences of the mean value and the SD of the conductivity on the scale of transfer calculated by means of statistical simulation (lines 1 and 2). It is seen from the figure that with increase in the scale of transfer from 1 to 20 particles, the mean value of the conductivity decreases by about 20%. If we calculate the coefficient of variation on this interval, it will decrease from 3.6 to 1.6%.

To interpret the dependence of the conductivity on the scale of transfer, let us return to Fig. 1, from which it is seen that the considered model of a disperse system is a set of porous layers with a height of one particle. The relative conductivity of each individual layer is equal to

$$\lambda = 1 - P. \tag{7}$$

Let us consider a system of two layers of identical porosity, with the pores and particles in each layer being distributed randomly and uniformly. For this system the mean area of intersection of pores on the boundary between the layers is equal to P^2, and the area of contact of a pore of one layer with a particle of the other layer is equal to $P - P^2$. Taking this into account, the relative area of contact of particles on the boundary of contact of the layers is

$$\Omega_{\text{rel}} = 1 - (P - P^2) = 1 - P(1 - P). \tag{8}$$

Using the relation given in [2] for the conductivity of a system of two porous plates (the layers are perpendicular to the flow), we will obtain a recurrence formula for the conductivity of a structure consisting of an arbitrary number of layers:

$$\Lambda_i = \frac{i}{(i-1)/\Lambda_{i-1} + 1/(\lambda\,\Omega_{\text{rel}})}, \quad i = 2, 3, \ldots, \tag{9}$$

where i is the number of the layer.

Taking into account Eqs. (7) and (8), for a system of layers of fixed porosity we finally obtain

$$\Lambda_i = \frac{i}{(i-1)/\Lambda_{i-1} + 1/((1-P)(1-P(1-P))}, \quad \Lambda_1 = 1 - P. \tag{10}$$

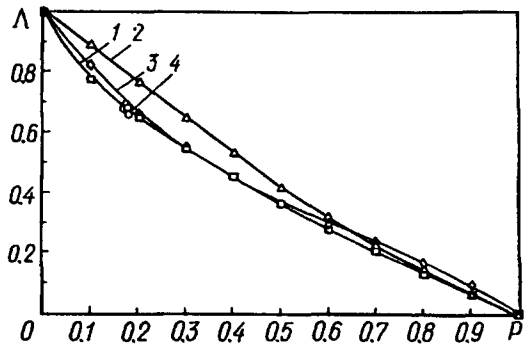


Fig. 4. Dependence of the conductivity on the porosity: 1) a cell with adiabatic fragmentation, 2) a cell with isothermal fragmentation, 3) calculation by model (10), 4) statistical simulation.

The dependence of the conductivity on the number of layers obtained by model (10) for $P = 0.176$ is presented in Fig. 3.

In Fig. 4 results obtained by model (10) for $i \to \infty$ are compared with data of [2] for the relative conductivity of an elementary cell with cubic nonconducting inclusions in the case of adiabatic and isothermal fragmentation of the cell. This figure also contains calculated values of the conductivity found by statistical simulation for specimens with a thickness of 100 particles.

The satisfactory agreement of (10) with the classical models of [2] in the entire range of variation of the porosity and with statistical simulation makes it possible to use model (10) to explain the decrease in the mean value of the conductivity of disperse systems with increase in the scale of transfer. From model (10) it follows that the decrease in the conductivity of the system with increase in the number of layers is due to the decrease in the ratio of the sum of the areas of contact between the layers and the number of layers.

Conclusion. Employment of the proposed stochastic model and (or) analytical recurrence model of disperse systems allows one to raise the level of detail in simulation of processes of transfer in disperse systems. The results obtained must be taken into account in studying processes of heat and mass transfer occurring in thin layers of disperse materials such as ignition and burning of pyrotechnic compositions and explosives, electrical conductivity in thin-layer electrochemical systems, and others.

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NOTATION

N_x, N_y, maximum size of the computational domain along the X and Y axes, respectively; Δ, step of the computational grid; i, vector of the flow; σ, conductivity; φ, potential; τ, time; $\Lambda = \sigma_{\text{eff}}/\sigma_1$, relative generalized conductivity; σ_1, conductivity of the material of the particles; P, porosity; $\overline{P}$, mean value (mathematical expectation) of the porosity; S, standard deviation (SD); $\overline{\Lambda}$, mean value (mathematical expectation) of the relative generalized conductivity; S_p, standard deviation of the porosity; S_Λ, standard deviation of the conductivity; a, b, parameters of the linear approximation; F, coefficient of variation; L, characteristic scale (ratio of the linear size of the specimen to the size of the particles); λ, conductivity of a layer with a height of one particle; Ω_{rel}, relative area of contact of the particles on the boundary of contact of the layers.

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