

II. VARIATION OF THE BASIC MODEL OF AN INHOMOGENEOUS MEDIUM

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On the basis of a basic model of an inhomogeneous medium, different variations are proposed. Analytical dependences are obtained for the conduction of the inhomogeneous medium and the results of calculation and experiment are compared.

In [1], a model of a binary inhomogeneous medium with randomly distributed components was proposed; the mathematical realization of the model involves a combination of flow theory and the method of reduction to an elementary cell. The pattern of the change in structure of such a medium is based on the following concepts: with change in volume concentration  $m_1$  of the first component in the second, isolated inclusions or clusters (IC) of the first component are formed; at some critical concentration  $m_1 = m_c$  (flow threshold), the isolated clusters coalesce to an infinite cluster (InC). The relative dimensions of the IC are modeled here in the form of a cube of side

$$l_2 = l_2/L = \sqrt[3]{m_1}, \quad 0 \leq m_1 \leq m_c, \tag{1}$$

$$\bar{l}_2 = \sqrt[3]{m_c}, \quad m_c \leq m_1 \leq 0.5.$$

The dashed curve in Fig. 1 shows the change in relative dimension of the central core of the cluster in the range  $0 \leq m_1 \leq 0.5$ . On reaching the flow threshold  $m_1 = m_c$ , bridges appear between the IC; these are modeled in the form of rods of square cross section ( $l_2^2$ ) of length  $L - l_2$ . It is assumed in the model that when  $m_1 > m_c$  the dimension  $l_2$  of the central core remains unchanged, while the cross-section area  $l_2^2$  of the rod varies according to the law [1]

$$\bar{S}_1 = \bar{l}_1^2 = (l_1/L)^2 = \left( \frac{m_1 - m_c}{1 - m_c} \right)^{1.6}. \tag{2}$$

In Eq. (2), account is taken of the entire complexity of the variation in structure of the infinite cluster and the probabilistic character of its formation. When  $m_1 = 0.5$ , the structure is converted into a system with interpenetrating components, when  $l_1 = l_2$ . After the formation of a structure with interpenetrating components, increase in  $m_1$  leads in the model to uniform increase in rod dimensions of the first component and decrease in the second, until  $m_1 = 1$ , i.e., the binary system is converted to a homogeneous system.

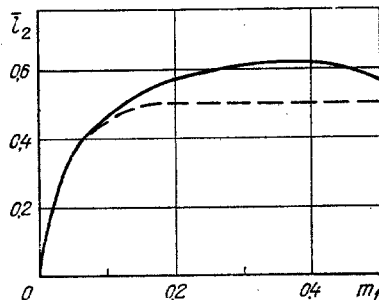


Fig. 1 Dependence of the relative dimension  $l_2$  of the central core of the cluster on the volume concentration of the conducting component  $m_2$  plotted according to Eq. (1) (dashed curve) and Eqs. (4) and (5) (continuous curve).

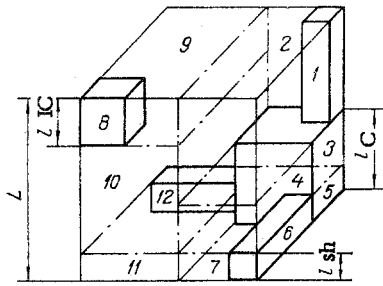


Fig. 2

Fig. 2. Elementary cell of the third variation of the basic model: 1-12) individual sections of the elementary cell.

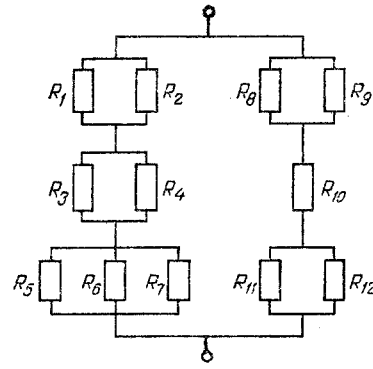


Fig. 3

Fig. 3. Circuit diagram of the thermal resistances of the individual sections.

first component and decrease in the second, until  $m_1 = 1$ , i.e., the binary system is converted to a homogeneous system.

The following formula was proposed in [1] for calculating the conductivity of an inhomogeneous medium

$$\frac{\Lambda}{\Lambda_1} = \bar{S}_1 + \nu \left[ \frac{\Delta \bar{S}}{1 - (1 - \nu) \bar{l}_2} + 2 \frac{\bar{S}_3}{1 - (1 - \nu) \bar{l}_1} + \bar{S}_4 \right], \quad (3)$$

where the parameters  $\bar{l}_1$  and  $\bar{l}_2$  are determined from Eqs. (1) and (2) and

$$\bar{S}_2 = \bar{l}_2^2, \quad \Delta \bar{S} = \bar{S}_2 - \bar{S}_1, \quad \bar{S}_3 = (1 - \bar{l}_2) \bar{l}_1, \quad \bar{S}_4 = 1 - \bar{S}_2 - 2\bar{S}_3,$$

$\Delta \bar{S} = 0$  when  $0 < m_1 < m_c$  and  $\Delta \bar{S} = 0, \bar{l}_2 = \bar{l}_1$  when  $0.5 < m_1 < 1$ . The assumption of constancy of  $\bar{l}_2$  in the range  $m_c < m_1 < 0.5$  adopted in the model in Eq. (1) leads to violation of the condition of equality of the volume concentration of components in the model and in the real system.

As shown by comparison with numerical modeling, Eqs. (1)-(3) allow results with an accuracy sufficient for practical purposes to be obtained [2]. In what follows, the noted deficiencies in the construction of the model and its mathematical realization are removed by introducing the correction function  $H = H(m_1, \nu)$ . In addition, it is taken into account that in real structures, the nonconducting component at first forms an infinite cluster in the conducting component when  $m_1 \geq 0.5$ , and then forms an isolated cluster when  $m_1 < 1 - m_c$ . Therefore, Eq. (3) takes a more general form and the model proposed in [2] is described as the basic model.

On the basis of the fundamental ideas of constructing the basic model, different variations may be proposed, distinguished by introduction of certain additional elements in the basic model or by different methods of calculating the individual parameters. Thus, the model considered in [1] is called the first variation of the basic model; its principal differences from the basic model are noted above and in [2]. Other possible variations of the basic model will now be considered.

In the second variation of the basic model, the requirement of constancy of the dimension  $\bar{l}_2$  in the concentration range  $m_c < m_1 < 0.5$  is lifted, so as to maintain equality of the volume concentrations in the model and in the real system. Remember that this requirement was imposed in the first variation of the basic model [1] and that the resulting errors were compensated by the correction function  $H$  in the basic model [2]. In the present case, the relative dimension of the central core of the infinite cluster is determined from two equations: the first relates the volume concentration to the geometric parameters of the model

$$m_1 = 3\bar{l}_1^2(1 - \bar{l}_2) + \bar{l}_2^3, \quad (4)$$

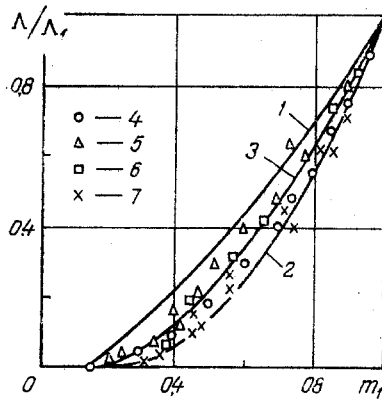


Fig. 4

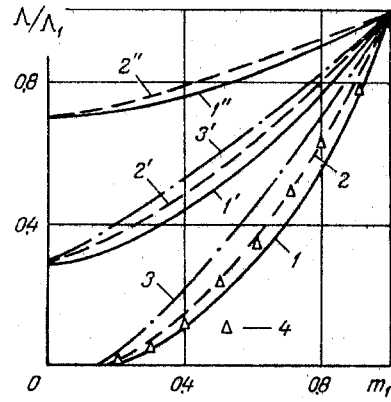


Fig. 5

Fig. 4. Comparison of the conductivity of extremely inhomogeneous media ( $\nu = 0$ ) as a function of the concentration of the conducting component: 1-3) according to Eq. (10) with  $m_c = 0.12$ ,  $k = 1.3$  (1), 0.18 and 2.0 (2), 0.15 and 1.6 (3); 4) results of computer modeling [1]; 5-7) experimental data: 5)  $\text{NH}_3\text{-Li}$  [1]; 6) copper powder with alumina additions [6]; 7) tungsten bronze [4-5].

Fig. 5. Comparison of the results of calculations of the conductivity of binary inhomogeneous media: 1, 1', 1'') numerical calculation [2]; 2, 2', 2'') second variation; 3, 3') third variation; 4) basic model and first variation; 1-3)  $\nu = 0$ ; 1'-3') 0.3; 1''-2'') 0.7.

and the second relates the cross section of the infinite cluster to the volume concentration of the first component. For this purpose, Eq. (2) is modified so that, when  $m_1 = 0.5$  and  $\bar{L}_1 = \bar{L}_2 = 0.5$  (interpenetrating system), this equation would lead to the obvious result

$$\bar{S}_1^* = \bar{L}_1^2 = 0.25 \left( \frac{m_1 - m_c}{0.5 - m_c} \right)^{1.6} \quad (5)$$

The continuous curve in Fig. 1 shows the dependence of the relative dimension  $\bar{L}_2 = f(m_1)$  of the central core of the cluster. The conductivity for the second variation of the model is determined from Eq. (3), while the parameters  $\bar{L}_1$  and  $\bar{L}_2$  are determined from Eqs. (4) and (5).

In determining the conductivity for  $m_1 > 0.5$ , the subscripts of  $\Lambda_1$  and  $m_1$  are exchanged, i.e., the parameter  $\nu = \Lambda_2/\Lambda_1$  is replaced by  $\nu' = \Lambda_1/\Lambda_2$  and  $m_1$  by  $(1 - m_1)$ . This allows the structure of the nonconducting component with  $m_1 > 0.5$  to be made the same as the structure of the conducting component with a concentration  $(1 - m_1)$ , i.e., both the structure and Eq. (3) take on the property of symmetry with respect to  $m_1 = m_2 = 0.5$ .

In the third variation of the basic model, the possibility of simultaneous existence of isolated and infinite clusters at  $m_c < m_1 < 0.5$  is taken into account. Suppose that in the concentration range  $0 < m_1 < m_c$  there exist two types of isolated clusters of different size. Assume that the smaller component occupies a fraction  $V_{IC} = \bar{L}_3^3$  of the volume and remains in the form of an isolated cluster even at concentrations of the conducting component above the flow threshold  $m_1 > m_c$ . The larger IC occupy a fraction  $V_C = \bar{L}_2^3$  of the volume, which follows a linear law of change with increase in concentration of the conducting component

$$m_c = V_C/V = \alpha m_1 \quad (6)$$

The proportionality factor  $\alpha$  is chosen so that the relative dimension of the side of the core is 0.5 when the volume concentration of the conducting component is equal to the flow threshold ( $m_1 = m_c$ )

$$\alpha = 0.125/m_c \quad (7)$$

and then remains unchanged, forming the core of an infinite cluster. The chosen method of specifying the core dimensions of an infinite cluster ensures that, in the limiting case  $m_1 = 0.5$ , this model is identical with the well-known models of a structure with interpenetrating components [3]. If the concentration of the conducting component increases above the threshold value  $m_c < m_1 \leq 0.5$ , the core of the infinite cluster, at a distance  $\bar{L} = (L - \bar{L}_2)$ , grows connecting bridges, the cross section of which  $S_1 = \bar{L}_1^2$  is determined from Eq. (5). Thus, account is taken of the presence of some proportion of the volume with isolated

clusters when infinite clusters appear beyond the flow threshold. The volume concentration of the infinite cluster is found from Eqs. (4) and (5) and that of the isolated cluster from the formula

$$m_{IC} = m_1 - m_{InC}, \quad (8)$$

while  $\bar{S}_1 = 0$  in the volume-concentration range from zero to the flow threshold and  $\bar{S}_1$  is calculated from Eq. (5) in the range  $m_c < m_1 < 0.5$ .

To determine the effective conductivity of the model, the combined division of the elementary cell by means of isothermal and adiabatic planes is employed (Fig. 2); this allows the character of the streamlines to be taken more precisely into account in the model [3]. An equivalent diagram of the connections between the resistances of the individual sections is shown in Fig. 3. Then the effective conductivity  $\sigma$  of the elementary cell is

$$\sigma = [(R_1^{-1} + R_2^{-1})^{-1} + (R_3^{-1} + R_4^{-1})^{-1} + (R_5^{-1} + R_6^{-1} + R_7^{-1})^{-1}]^{-1} + [(R_8^{-1} + R_9^{-1})^{-1} + R_{10} + (R_{11}^{-1} + R_{12}^{-1})^{-1}]^{-1}, \quad \sigma = R^{-1}.$$

Calculating the resistance of each section as the resistance of a plane wall and bearing in mind the dimension of the sections noted in Fig. 3, the following equation may be written

$$\frac{\Lambda}{\Lambda_1} = \left\{ \frac{1 - \bar{l}_2}{\bar{l}_1^2 + \nu(\bar{l}_2 - \bar{l}_1^2)} + \frac{\bar{l}_3 - \bar{l}_1}{\bar{l}_2^2 + \nu\bar{l}_2(1 - \bar{l}_2)} + \frac{\bar{l}_1}{\bar{l}_2^2 + \bar{l}_1(1 - \bar{l}_2) + \nu(1 - \bar{l}_2)(\bar{l}_2 - \bar{l}_1)} \right\}^{-1} + \left\{ \frac{\bar{l}_3}{\bar{l}_3 + \nu(1 - \bar{l}_2 - \bar{l}_3^2)} + \frac{1 - \bar{l}_3 - \bar{l}_1}{\nu(1 - \bar{l}_2)} + \frac{\bar{l}_1}{\nu(1 - \bar{l}_2)(1 - \bar{l}_1) + \bar{l}_1(1 - \bar{l}_2)} \right\}^{-1}. \quad (9)$$

If  $0 < m_1 < m_c$ , then  $\bar{l}_1 = 0$ ,  $\bar{l}_2 = (\bar{l}_{2max} m_1 / m_c)^{1/3}$ ,  $\bar{l}_3 = (m_1 - m_{InC})^{1/3}$ ,  $m_{InC} = \bar{l}_3^3$ . If  $m_c < m_1 < 0.5$ , then  $\bar{l}_1 = 0.5[(m_1 - m_c) / (0.5 - m_c)]^{0.8}$ ,  $\bar{l}_2 = 0.5$ ;  $\bar{l}_3 = (m_1 - m_{InC})^{1/3}$ ,  $m_{InC} = \bar{l}_3^3 + 3\bar{l}_1^2(1 - \bar{l}_{2max})$ ,  $\bar{l}_{2max} = 0.5$ .

If the concentration of the conducting component exceeds 0.5, then  $m_1$  and  $\Lambda_1$  are replaced by  $m_2$  and  $\Lambda_2$  and the effective conductivity is then calculated from the same relations. The results of calculation by all the models are now compared with the experimental data and, above all, the extreme case  $\nu = 0$  is considered.

Experimental curves taken from [1, 4-7] for various inhomogeneous media of the basic dielectric-metal are shown in Fig. 4. The results of model experiments obtained by numerical methods for three-dimensional grids are taken from [1].

As shown in [1], the conductivity of the binary heterogeneous systems with  $\nu \leq 10^{-2}$  is described by a dependence obtained by the method of machine modeling on a computer

$$\frac{\Lambda}{\Lambda_1} = \left( \frac{m_1 - m_c}{1 - m_c} \right)^k, \quad m_c = 0.15 \pm 0.03; \quad k = 1.6 \pm 0.4. \quad (10)$$

Curves calculated for the limiting parameter values  $m_c = 0.12$  and  $0.18$  and  $k = 1.2$  and  $2.0$  and also for the mean values  $m_c = 0.15$  and  $k = 1.6$  are shown in Fig. 4. The limiting curves cover the whole range of experimental data, while the mean values of the parameters  $m_c$  and  $k$  allow the most probable trend of the curve in Eq. (10) to be determined.

The results of numerical modeling [7] of the conductivity of binary inhomogeneous media are compared with calculations for the basic model and its variations in Fig. 5.

As follows from Eqs. (4) and (5), the most reliable results come from the basic model [2] and its first variation - Eq. (3). The second variation of the basic model, calculated from Eqs. (3)-(5), leads to a nonmonotonic trend in the dependence of the conductivity on the concentration. The third variation of the basic model is calculated from Eq. (9) and leads to conductivity values that coincide only with the upper limit of the range of experimental data. This limit for  $\nu = 0$  differs from the most reliable results by 90% when  $m_1 = 0.3$ , by 20% when  $m_1 = 0.5$ , and by 12% when  $m_1 = 0.85$ . Comparison of the various formulas allows the following conclusions to be drawn. The conductivity of inhomogeneous media should be calculated from the formula of [2] for the basic model or from Eq. (3) for the first variation, although Eq. (3) is based on assumptions that are insufficiently correct.

If it is necessary to distinguish isolated clusters in explicit form, as well as infinite clusters, Eq. (9) for the third variation of the basic model may be used, bearing in mind that the results of the calculation will be overestimated.

#### NOTATION

$m_1$ , volume concentration of the first component;  $m_c$ , threshold concentration (flow threshold);  $\bar{L}_1, \bar{L}_2, L, L'$ , linear dimensions of the cluster model;  $S_1, S_2, S_3, S_4, \Delta S$ , cross-sectional areas of cluster;  $V_{IC}, V_C$ , total volume and core volume of isolated cluster;  $\Lambda$ , conductivity of inhomogeneous medium;  $\Lambda_1, \Lambda_2, \nu$ , conductivity of first and second components and their ratio;  $H$ , correction function;  $\alpha$ , proportionality factor;  $\sigma$ , conductivity of elementary cell;  $R_i$ , thermal resistance of  $i$ -th section of elementary cell.

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#### EFFECT OF ELECTROLYTES ON THERMAL MOISTURE TRANSPORT IN CAPILLARY-POROUS MEDIA

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Experimental data on the effect of electrolytes upon thermal moisture mobility in quartz sand and cellulose are presented. The results are interpreted from the viewpoint of change in properties of moisture boundary layers.

As is well known [1], as the moisture content of a material  $U$  varies, the thermogradient coefficient  $\delta = dU/dT$  passes through a maximum, corresponding to the greatest mobility of moisture acted upon by a temperature gradient. As  $U \rightarrow 0$  the moisture mobility decreases due to an increase in the binding energy of surface forces, while as  $U \rightarrow U_0$  the possibility of change in mass content  $dU$  under the action of  $dT$  decreases. Thus, for example, at  $U = U_0$  only thermal circulation of the mass is possible, with no redistribution over the body volume ( $dU = 0$ ), which corresponds to  $\delta = 0$ . Moreover, with increase in  $U$  there is a decrease in the liquid-gas interface surface, which determines thermal moisture transport under the influence of a surface tension gradient  $\partial\sigma/\partial T$ . The latter induces a flow of capillary moisture caused by a capillary tension gradient, as well as a film thermocapillary flow.

Thus, the largest values of  $\delta$  correspond to a liquid state in a porous body in which the pores are not completely filled by moisture and there is a sufficiently developed liquid-gas

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