METHODS FOR THE ANALYTIC DETERMINATION OF THE EFFECTIVE CONDUCTIVITIES OF HETEROGENEOUS SYSTEMS

G. N. Dul'nev and V. V. Novikov

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1. Closure of Transfer Equations in Heterogeneous Systems

Heterogeneous systems with a disordered structure (composite and granular materials, eutectic alloys and their melts, composites, metal ceramics, solutions, etc.) constitute macroscopic uniform systems made up of small nonuniform regions (components) and delimited interfaces. The dimension of the nonuniformity, d, is much smaller than the characteristic dimension L of the specimen, but much larger than the length of the free path Λ_0 of the carriers of heat flux, electricity, etc., i.e., $\Lambda_0 \ll d \ll L$.

Heterogeneous systems are usually regarded as a quasihomogeneous medium possessing effective properties which depend on the properties, concentrations, and nature of interaction of the components and the structure. The effective conductivity Λ is determined from the equation

$$\langle \vec{j} \rangle = -\Lambda \langle \vec{\nabla\varphi} \rangle, \tag{1}$$

where $\langle \vec{j} \rangle$ is the flux of the substance (heat, mass, electricity), averaged over the volume V (of the heterogeneous system); $\langle \vec{\nabla}\varphi \rangle$ is the potential gradient averaged over the volume;

$$\langle \vec{j} \rangle = \frac{1}{V} \int_V \vec{j}_i(\vec{r})\, dV,$$

$$\langle \vec{\nabla\varphi} \rangle = \frac{1}{V} \int_V \vec{\nabla\varphi}_i(\vec{r})\, dV. \tag{2}$$

For local regions i the following equations hold:

$$\vec{j}_i(\vec{r}) = -\Lambda_i(\vec{r})\, \vec{\nabla\varphi}_i(\vec{r}),$$

$$\operatorname{div} \vec{j}_i(\vec{r}) = 0, \tag{3}$$

$$\operatorname{rot} \vec{\nabla\varphi}(\vec{r}) = 0.$$

An analysis of transfer processes (in heterogeneous systems) can be carried out, without loss of generality, for two-component systems. In this case (2) can be written in the form

$$\langle \vec{j} \rangle = -\Lambda_1 m_1 \langle \vec{\nabla\varphi}_1 \rangle - \Lambda_2 m_2 \langle \vec{\nabla\varphi}_2 \rangle,$$

$$\langle \vec{\nabla\varphi} \rangle = m_1 \langle \vec{\nabla\varphi} \rangle + m_2 \langle \vec{\nabla\varphi}_2 \rangle, \tag{4}$$

$$\langle \vec{\nabla\varphi}_i \rangle = \frac{1}{V_i} \int_{V_i} \vec{\nabla\varphi}_i(r_i)\, dV_i.$$

Equations (4), taking account of (1), can be written in dimensionless form:

$$N = m_1\Psi_1 + \nu m_2\Psi_2, \quad N = \frac{\Lambda}{\Lambda_1}, \quad \nu = \frac{\Lambda_2}{\Lambda_1},$$

$$m_1\Psi_1 + m_2\Psi_2 = 1, \quad \langle \vec{\nabla\varphi}_i \rangle = \Psi_1 \langle \vec{\nabla\varphi} \rangle. \tag{5}$$

From system (5) it can be seen that in order to determine N, Ψ_1, Ψ_2, we must have additional information, since there are two equations and three unknowns: N, Ψ_1, Ψ_2; e.g., we need information on the structure of

the heterogeneous system. Thus, for a stratified system, when the layers are parallel to the flux $\langle \vec{j} \rangle$,

$$\Psi_1 = \Psi_2 = 1. \tag{6}$$

Solving (5) and (6) for N, we obtain the well-known equation

$$N_{\parallel} = m_1 + \nu m_2. \tag{7}$$

If the layers are perpendicular to the average flux $\langle \vec{j} \rangle$ of the substance, then

$$\Lambda_1 \langle \vec{\nabla\varphi_1} \rangle = \Lambda_2 \langle \vec{\nabla\varphi} \rangle \quad \text{or} \quad \Psi_1 = \nu\Psi_2.$$

Solving this equation, together with (5), for N, we obtain the effective conductivity for perpendicular layers

$$N_{\perp} = \nu\,(\nu m_1 + m_2)^{-1}. \tag{8}$$

The method used for the closure of the system of transfer equations will determine the further course of the investigation and lead to the appearance of a large number of methods and formulas for N. The known methods for the closure of the equations (5) may be classified as follows: the use of experimental data; geometric simulation of the structure of heterogeneous systems; formal construction of a function for N; and so-called asymptotic methods.

This classification will serve as a plan for a survey of the various methods of determining the effective conductivity of heterogeneous systems. An analysis of [1-4], which considered systems with a low concentration of nonuniformities, in which each of them is in a uniform field $\langle \vec{\nabla\varphi} \rangle$, not introducing any perturbations, will not be carried out here, since this is discussed in [5-8].

In analyzing the models and formulas, we shall start with the general requirements which they must satisfy [8]: compatibility of the model and the real system; possibility of obtaining physically correct results in limiting cases; absence of internal contradictions in the theoretical scheme; satisfactory correspondence between the results of the calculations and the experimental data over a wide range of variation of the determining parameters.

2. Modeling of the Structure of Heterogeneous Systems

The methods of this group directly or indirectly specify a model of the structure, on the basis of which we determine the expression for Ψ_i, and this enables us to close the equations (5) and determine the effective conductivity.

2.1. "Effective Medium" Method. Any model of a heterogeneous system, and in particular a model of an effective medium, is so constructed as to enable us to determine Ψ_1 or Ψ_2, which, together with (5), enables us to determine N. Therefore the main attention will be devoted to the question of how we can determine the function Ψ_i (explicitly or implicitly) and what kind of model the method is based upon. If possible, we shall digress from the mathematical representations used by various authors [9-15].

In the effective-medium method a heterogeneous system is simulated by an arbitrarily chosen particle which is surrounded by a medium with the effective (desired) properties. In this case the function Ψ_1 can be determined from the relations for a particle having dielectric permeability ε_1 which is immersed in a medium with effective dielectric permeability ε [16]:

$$\vec{E}_1 = \frac{3\varepsilon}{\varepsilon_1 + 2\varepsilon}\,\vec{E}, \tag{9}$$

where $\vec{E}_1$, $\vec{E}$ represent the electric field intensity in the particle and in the medium, respectively.

On the basis of an analogy between electrostatics and thermal and electrical conductivity, we can replace $\vec{E}_1$ and $\vec{E}$ with the potential density $\langle \vec{\nabla\varphi} \rangle$ and $\langle \nabla\varphi_1 \rangle$ and replace ε_1 and ε with the conductivities Λ_1 and Λ, i.e.,

$$\langle \vec{\nabla\varphi_1} \rangle = \frac{3\Lambda}{\Lambda_1 + 2\Lambda} \quad \text{or} \quad \Psi_1 = \frac{3N}{2N + 1}. \tag{10}$$

Solving (5) and (10) for N, we obtain

$$N = [(3m_1 - 1) + (3m_2 - 1)\,\nu]/4 + \sqrt{[(3m_1 - 1) + (3m_2 - 1)\,\nu]^2/16 + \frac{\nu}{2}}. \tag{11}$$

The expression (11) for N was first obtained in 1935 [9] and introduced repeatedly thereafter [10-15] and is known in the Soviet literature as the Kondorskii−Odelevskii equation [5, 7, 8, 17].

It should be noted that the authors of [9-15], in making their determinations, used various approaches and mathematical methods but always based their studies on the same effective-medium model, so that they obtained identical expressions for N. This confirms the importance of the problem of closure of the transfer equations. If in the closure of Eq. (5) we use the same information on the structure of the system (identical models), then the expressions for N will also be identical. The main defects of the effective-medium model are the following: for $\nu = 0$ and $m_1 < 0.3$, $N < 0$; for $\nu < 10^{-2}$ we observe a deviation from the experimental data [18, 19]; the method does not take account of surface and contact phenomena on the interface between the components, which in a number of cases determine the transfer processes in heterogeneous systems.

If we assume that the dielectric permeability of a particle is ε_2 and that of the surrounding medium is ε_1, then (9) can be written as follows:

$$\vec{E}_1 = \frac{3\varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \quad \text{or} \quad \Psi_1 = \frac{3\Lambda_2}{\Lambda_1 + 2\Lambda_2} \ . \tag{12}$$

Solving (6) and (12) for N, we obtain an expression for the effective conductivity which is valid for low concentrations of the discrete component, i.e., for $m_1 \ll 1$ [16]

$$N = 1 + m_2 \frac{3(\nu - 1)}{\nu + 2} \ , \quad \nu = \frac{\Lambda_2}{\Lambda_1} \ . \tag{13}$$

2.2. Integral Method. This method was first proposed by Bruggemann [9] and later mentioned again in [20]; it was used by Skorokhod in [21, 22].

In the integral method we consider the increment added to the conductivity of the mixture when we add to it a small quantity of dispersed particles with volume dn per unit volume and we set up a differential equation for $d\Lambda$. This problem is solved in the same way as the electrostatic problem [9].

The variation in the effective generalized conductivity for a small admixture of a second (discrete) component, according to (13), can be written in the form:

$$\Delta\Lambda = \Lambda - \Lambda_1 = \frac{3(\Lambda_2 - \Lambda_1)\Lambda_1}{\Lambda_2 + 2\Lambda_1} \ \Delta n, \quad \Delta n = \frac{\Delta V_2}{V} \ . \tag{14}$$

Suppose that V_2 is the volume occupied by the second component; the addition of a volume ΔV_2 to it leads to a change of m_2^* in the initial volumetric concentration m_2:

$$m_2^* = \frac{V_2 + \Delta V_2}{V_1 + V_2 + \Delta V_2} \ . \tag{15}$$

Then from (15) we obtain

$$m_2^* = \frac{m_2 + \Delta n}{1 + \Delta n} \ ,$$

and hence the increment in the volumetric concentration is equal to

$$\Delta m_2 = m_2^* - m_2 = (1 - m_2)\,\Delta n$$

or, in differential form,

$$dm_2 = (1 - m_2)\,dn. \tag{16}$$

Substituting (16) into (14), we obtain

$$d\Lambda = \frac{3(\Lambda_2 - \Lambda_1)\Lambda_1}{\Lambda_2 + 2\Lambda_1} \cdot \frac{dm_2}{1 - m_2} \ . \tag{17}$$

After this, as in the effective-medium method, we assume that each particle is surrounded by a medium with the effective properties, i.e., in (17) we replace Λ_1 with Λ:

$$d\Lambda = \frac{3(\Lambda_2 - \Lambda)\Lambda}{\Lambda_2 + 2\Lambda} \cdot \frac{dm_2}{1 - m_2} \ . \tag{18}$$

Integrating (18), taking account of the condition $\Lambda\,|\,m_{2=0} = \Lambda_1$, we obtain

$$\frac{\Lambda - \Lambda_2}{\Lambda_1 - \Lambda_2}\left(\frac{\Lambda_1}{\Lambda}\right)^{\frac{1}{3}} = (1 - m_2). \tag{19}$$

There is an inherent internal inconsistency in this method. If we replace Λ_1 with Λ, we are actually specifying the form of the function Ψ_1 to be the form given in (10), i.e., specifying the model of the structure. Then there is no need to set up and solve Eq. (18); we must substitute Ψ_1 into Eq. (5) and determine N. This brings in a second inconsistency: specifying identical input information (identical models), we have arrived at different results for the solution of (5) and (18); all of this indicates that the integral method is incorrect.

From (19) it follows that when $\Lambda_1 = 0$, the effective coefficient $\Lambda = 0$ for all values of m_2, which is not true for mixtures with a disordered distribution of the components. The above defects limit the use of the integral method in predicting the properties of heterogeneous systems.

2.3. Methods Taking Account of the Disordered Distribution of the Components and the Shape of the Interfaces between Them. In this group of methods we specify some probabilistic law of distribution of the components and construct a geometric model of the structure of the real heterogeneous system. This model is used to determine the function Ψ_i and close the Eqs. (5) [23-26]. An analysis of these studies [27] showed that taking account of the disordered distribution of the components and the shape of the granules provides no advantage over previously known studies in calculating the effective conductivity but leads, instead, to more cumbersome expressions for N.

Zarichnyak [28] proposed the following formula for calculating the effective conductivity of heterogeneous systems with a disordered distribution of the components:

$$\Lambda_{2d} = \lambda_1 m_1^2 + 4\,\frac{\lambda_1\lambda_2}{\lambda_1 + \lambda_2}\,m_1 m_2 + \lambda_2 m_2^2. \tag{20}$$

To determine this quantity, he considered a mixture of two kinds of cubes randomly distributed in space, where a plane passing through a face of any cube does not intersect the other cubes. The determination of the effective conductivity of the heterogeneous system reduces to the determination of the conductivity of a layer of thickness 2d (where d is the dimension of an edge of the cube). The layer was subdivided by adiabatic planes parallel to the average flux $<\vec{j}>$ (which were perpendicular to the planes bounding the layer), i.e., the three-dimensional problem of determining Λ reduced to a one-dimensional problem, and this was followed by a determination of the probability of a combination of similar and dissimilar cubes along the height of the layer.

Expression (20) for Λ_{2d} coincides with the expression for the effective conductivity obtained for fibrous systems on the basis of an ordered structure [8]. The model of a layer of height 2d and the ordered model of a fibrous system do not possess three-dimensional symmetry. The correspondence of these structures led to the finding of identical formulas for Λ.

It must be noted that the method proposed in [28] for determining Λ has the following defects. The larger the value h chosen for the thickness of the layer, the closer the values of Λ_{nd} must be to the true effective conductivity Λ of the entire system, i.e.,

$$\lim_{n\to\infty} \Lambda_{nd} = \Lambda,$$

where n is the number of cubes along the height of the layer. Consequently, Λ_{3d} must describe the effective conductivity better than Λ_{2d}, etc. However, a comparison of the values of Λ_{3d}, Λ_{2d}, and the experimental data contradicts this conclusion, which indicates that there are internal contradictions in this method for the determination of Λ (as $n\to\infty$, the value of $\Lambda_{nd}\to 0$ for any concentration of the components $m_i < 1$). This is partially solved in [29].

A comparison of the calculation of Λ by formula (20) with the experimental data on the effective conductivity of heterogeneous systems showed good agreement between them only for $\nu > 10^{-2}$, where ν is the ratio of the conductivities of the components. For $\nu < 10^{-2}$ the calculated values are much higher than the experimental values. Furthermore, formula (20) fails to describe the jump in the effective conductivity near the flow threshold for $\nu = 0$, which was found in [30-34].

2.4. Method of Transition to an Elementary Cell. This method is based on the following assumption [8]: the effective conductivity values for ordered and disordered structure are equal to each other if they are adequate

and the properties and the volumetric concentrations of the components are identical (the concept of adequacy must be defined more precisely for each class of structures).

The ordered system has long-range order, and in any such system we can distinguish an elementary cell — an element of volume which we can repeat in a specified way to obtain the volume of the initial structure.

Thus, the determination of the effective properties of heterogeneous systems reduces to the determination of the properties of an elementary cell.

In determining the effective conductivity of an elementary cell, it is customary to use the method of cross sections. This method consists in determining the effective conductivity of bodies composed of a number of pieces by subdividing them by means of auxiliary isopotential planes through which no streamlines can pass. This method enables us to pass from differential equations and partial derivatives to algebraic equations, which greatly simplifies the solution of the problem. The method of cross sections is an approximate method, and the exact value of the effective conductivity lies between the values Λ_{iso}, obtained by using the intersections of the composite body with the isopotential planes perpendicular to the flux $<\vec{j}>$, and the values Λ_A, obtained by using the intersections with planes through which no streamlines can pass and which are parallel to the flux

$$\Lambda_{iso} \geqslant \Lambda \geqslant \Lambda_A.$$

In [35] we proposed using a combined method of cross sections of composite bodies, which enables us to obtain an expression for the effective conductivity whose maximum possible error is less than 7% of the numerical solution of the problem.

The transition to an elementary cell in the determination of the effective conductivity was used in [6, 8, 13, 36-38]. For structures with isolated inclusions the Éikin–Odelevskii model is widely used; this model yields for N the expression [13]

$$N = 1 - m_2 [(1 - v)^{-1} - (1 - m_2)/3]^{-1}. \tag{21}$$

For structures with interpenetrating components the Frey–Dul'nev model is used. The expression for N obtained by means of an "adiabatic" subdivision of an elementary cell of this model has the form [38]

$$N = C^2 + v(1 - C)^2 + 2vC(1 - C)[Cv + (1 - C)]^{-1}, \tag{22}$$

where C is a geometric parameter of the model which is related in a unique manner to the volumetric concentration of the components [8].

The monograph [8] analyzes the elementary-cell method in detail and notes (establishes) the good agreement between the calculated and experimental results for various heterogeneous systems which are in various states of aggregation. However, it was not possible by this method to describe satisfactorily the phenomenon of transfer of extremely nonuniform heterogeneous systems (of the type of metallic inclusions in a dielectric or a pressed mixture of metal and alumina particles) when $\Lambda_2/\Lambda_1 \to 0$. In this case the calculated and experimental data differed substantially, and furthermore, it was not possible to explain the "discontinuous conductivity" found in [30-34] for certain concentrations of the components.

2.5. Method of Averaging Geometric Parameters. This method is a natural development of the studies using a transition from a disordered to an ordered structure with the distinguishing of an elementary cell. Here we find an element with averaged geometric parameters (the averaged element), whose conductivity is equal to the conductivity of the system as a whole. Methods for averaging the geometric parameters of a model were tested in investigations designed to determine the conductivity of granular and related systems with disordered structure, described in detail in [8], and they supplement the elementary-cell method. This method of investigation has the same defects as the method analyzed in 2.4.

3. Semiempirical Methods

In a number of studies [6, 39-43] attempts were made to extract information for the closure of Eq. (5) from experimental data. In this case one or two experimental parameters, k_0 and n, were introduced into the expression for Λ in order to describe the effective thermal conductivity for at least one class of materials [39-43]. The reason for this is that N depends on many parameters (porosity, dimensions of the pores, temperature, pressure of the filler gas, contact conductivity between granules, etc.), which makes it more difficult to take account in detail of their effect on the conductivity of the system without information concerning its structure. It is impossible to analytically establish the limits of applicability of the expression for N in the determination of Ψ_i from the experiment. Another method for determining N in the heterogeneous structures

was proposed by Misnar [6]. For a two-component system with component conductivities Λ_1 and Λ_2, the value of Λ was calculated twice by formula (21): Λ' for the case when the inclusion and the base have conductivities Λ_2 and Λ_1, and Λ'' for the case in which the conductivities of the inclusions and the base were Λ_1 and Λ_2. Then Misnar selected the function $\Lambda = a\Lambda' + b\Lambda''$, where a and b are empirically determined coefficients equal in the particular case to $a = b = 0.5$. It is interesting that the thermal conductivity of many mixtures of solids, liquids, and gases can be satisfactorily described by this formula.

In calculating the thermal conductivity of moist solid porous structural materials, Krischer used a combination of the method of the elementary cell and the method of empirical coefficients [42]. Despite the crude schematization of the structure of the materials, the author took account of the essential properties of the object under study, the presence of dry and moist segments in the solid particles and pores, which may be arranged either in parallel or in series with the head flux. It is not known in the Krischer model what fraction of the segments are oriented perpendicular (a) and parallel $(1 - a)$ to the general direction of the heat flux. Another unknown quantity is the fraction of these segments in the surface of the solid body wetted by the moisture. Using the known relations (7) and (8) for the effective thermal conductivity of layers connected in parallel and in series with each other and also determining from the experiment the parameters a and b, Krischer proposed a method for calculating the effective thermal conductivity. This method was developed in [43], where the basic unit considered was an elementary cell of the system with interpenetrating components, which made it possible to calculate the parameter a; however, one empirical parameter b still remained in the formulas.

The analysis of the various semiempirical methods for investigating transfer processes could be continued still further. However, the above-mentioned studies are sufficient to draw some conclusions concerning this group of methods. If we completely ignore the structural properties of the material, as was done in [6, 39-41], then this line of investigation, in our opinion, is not very promising, for the reasons indicated above. Much more informative and better justified are those semiempirical methods in which in determining Λ we take account of the topology of the heterogeneous system and empirical coefficients are used only to make some individual features of the process more precise [42, 43].

4. Methods Using Construction of the Functions N

In the studies of this group the form of the function N is usually determined not from the solution of the physical problem but by a formal continuation of functions satisfying the limiting conditions and a number of qualitative requirements such as invariance with respect to components and invertibility of the expressions.

The method of constructing the function N was developed by Lichtenecker et al. [44-46] more than 25 years ago. An analysis of these studies was carried out in detail in [8] and the survey article [27], in which it was shown that the formulas obtained for N yield incorrect results even in the passage to the limit.

A more correct application of the method of constructing the functions N enables us to avoid this defect and propose for N a formula which remains valid in the passage to the limit and satisfactorily describes a number of experimental data. For example, from the upper and lower bounds for Λ

$$\Lambda_1 m_1 + \Lambda_2 m_2 \geqslant \Lambda \geqslant \Lambda_1^{-1} m_1 + \Lambda_2^{-1} m_2 \tag{23}$$

we obtain an expression for Λ in the form [47]

$$\Lambda^n = \Lambda_1^n m_1 + \Lambda_2^n m_2. \tag{24}$$

The exponent n was selected as follows:

$$n = (1 + \langle l \rangle d^{-1})^{-1}, \tag{25}$$

where $\langle l \rangle$ is the average distance between the centers of the particles with best conductivity

$$\langle l \rangle = d m_1^{-\frac{1}{3}}, \tag{26}$$

and d is the average diameter of the particles. Then the expression (25) for n, taking account of (26), can be rewritten in the form

$$n = m_1^{\frac{1}{3}} (1 + m_1^{\frac{1}{3}})^{-1}. \tag{27}$$

A comparison of the calculation of Λ according to (24) and (27) with the experimental data showed good agreement when $\nu \geq 10^{-4}$. However, the functions constructed by this method do not reflect the real structure of the material, and therefore, they are not sensitive to such essential properties of the transfer process (the

structure) as contraction cracks in the surface, anisotropy, transition from a structure with connected inclusions to one with isolated inclusions, etc.

Despite the correctness of the results, we believe that, on the whole, the method of construction of functions is not very promising.

5. Asymptotic Methods

This group of methods is called asymptotic because it uses a process of successive approximation, in which the chosen mathematical model is investigated and refined until we obtain the best possible agreement between the values calculated by the theoretical method and the experimental data.

5.1. Expansion in a Small Parameter. In a number of studies [16, 48, 49], in the determination of Λ the authors did not use a model of the structure of the heterogeneous system but based their investigation on a small-parameter series expansion of the fluxes $\vec{j}(r)$, the gradients $\vec{\nabla\varphi}(r)$, and the conductivities $\Lambda(\vec{r})$. In this group of methods a necessary condition for determining Λ is the presence of a small parameter which can be distinguished if the following conditions are satisfied:

a) $\delta\Lambda \rightarrow 0$ for all values $\delta(\vec{\nabla\varphi}) < \infty$, i.e., when the difference between the conductivities of the components of the mixture, $\Delta\Lambda = \Lambda_1 - \Lambda_2$, is small in comparison with the values of Λ_1 and Λ_2;

b) $\delta(\vec{\nabla}\varphi) \rightarrow 0$ for all values $\delta\Lambda < \infty$. This will be satisfied if the local values of the gradient $\vec{\nabla}\varphi(\vec{r})$ do not differ greatly from the average value $< \vec{\nabla}\varphi >$.

If these conditions are satisfied, the effective conductivity can be determined in the form [49]

$$\Lambda = \langle \Lambda \rangle \left[1 - \frac{1}{3} \frac{\langle (\Lambda - \langle \Lambda \rangle)^2 \rangle}{\langle \Lambda \rangle^2} + \left(\frac{1}{3} \right)^2 \frac{\langle (\Lambda - \langle \Lambda \rangle)^3 \rangle}{\langle \Lambda \rangle^3} - \dots \right]. \tag{28}$$

An important defect of this method is that it does not take account of the structure of the mixture, and, e.g., for spherical, fibrous, or ellipsoidal particles the expression for Λ has the same form, while experiment shows that for such systems Λ varies differently as a function of concentration.

5.2. Variational Upper and Lower Bounds for Λ. In a number of studies [50-60] upper and lower bounds were found for Λ. Thus, in [59], on the basis of the principle of minimum production of entropy, it was established that

$$\Lambda_{\|} \geqslant \Lambda \geqslant \Lambda_{\perp},$$

where $\Lambda_{\|}$ and $\Lambda_{\perp}$ can be obtained from formulas (7), (8).

Such an estimate (23) has too wide a range, and therefore in a number of studies attempts were made to narrow it. The most interesting results, in our opinion, were obtained in [53, 54]. Thus, [53] proposed the formula

$$\Lambda_1 + \frac{m_1}{(\Lambda_2 - \Lambda_1)^{-1} + m_1/3\Lambda_1} \leqslant \Lambda \leqslant \Lambda_2 + \frac{m_2}{(\Lambda_2 - \Lambda_1)^{-1} + m_2/3\Lambda_2}. \tag{29}$$

The formula obtained in [54] was

$$\Lambda_{\|} - \frac{m_1 m_2 (\Lambda_1 - \Lambda_2)^2}{m_1\Lambda_2 + m_2\Lambda_1 + \Lambda_1} \leqslant \Lambda \leqslant \Lambda_{\|} = \frac{m_1 m_2 (\Lambda_1 - \Lambda_2)^2}{m_1\Lambda_2 + m_2\Lambda_1 + \Lambda_2} - . \tag{30}$$

With respect to all the estimates for Λ made within the framework of the variational method, it must be noted that as $\nu \rightarrow 0$, the difference between the upper and lower bounds increases and takes on the same order of magnitude as the quantities being estimated. It is possible to have cases in which the values of Λ go beyond the limits of the upper and lower bounds given in (29) and (30) [58].

6. Percolation Theory

The theory of percolation processes [30-34] has been used recently in determining the properties of heterogeneous systems for $\nu = 0$. In this theory it was shown that when $\Lambda_1 \neq 0$ and $\Lambda_2 = 0$, there is a jump, depending on the effective conductivity Λ, for the effective concentration of the component $m_1 = m_c$ (if $m_1 < m_c$, then $\Lambda = 0$; if $m_1 > m_c$, then $\Lambda \neq 0$). The quantity m_c is called the percolation threshold and indicates the volumetric concentration m_1 at which in a nonuniform system there arises an infinite chain of the conduc-

tive component – an infinite cluster (IC). In percolation theory the following expression is proposed for the case $\Lambda_2 = 0$ and $m_c \leq m_1 \leq 0.5$ [33-34]:

$$N = A(m_1 - m_c)^k . \tag{31}$$

It should be noted that the occurrence of discontinuous conductivity when the percolation threshold $m_1 = m_c$ is reached is a new result, which was not reflected in any of the previously considered structural models or formal methods for determining N. The simulation of heterogeneous structures and their analysis by the Monte Carlo method, using electronic computers as well as natural experiments, have made it possible to establish for three-dimensional systems the values $k = 1.8 \pm 0.2$, $m_c = 0.15 \pm 0.03$.

The recommendations with respect to the quantity A are less clearly defined. Thus, in [18, 19], on the basis of model experiments, it was found that for $m_c < m_1 \leq 0.5$,

$$N = 1,6(m_1 - m_c)^{1,6} .$$

In [31] it was found with the aid of computer simulation that $A = 1$ for $m_c \leq m_1 \leq 0.5$. In [18, 19] attempts were made to generalize the results of percolation theory to the case in which $\Lambda_2 \ll \Lambda_1$ but $\Lambda_2 \neq 0$ and m_1 varies in the range $0 \leq m_1 \leq 1$. For this purpose, the entire range of concentrations of the components was subdivided into three segments, and a separate function for N was recommended for each segment. Thus, if $\nu \leq 5 \cdot 10^{-4}$, then N is equal to:

$$N = \nu(1 - 5m_1)^{-1}, \quad \text{if} \quad m_1 < m_c,$$

$$N = 1,6(m_1 - m_c)^{1,6}, \quad \text{if} \quad m_c \leqslant m_1 \leqslant 0,5.$$

For $m_1 > 0.5$, N was determined by (11), obtained on the basis of the effective-medium model. This formula is recommended over the entire range of concentrations if $\nu \geq 3 \cdot 10^{-2}$. For $5 \cdot 10^{-4} \leq \nu \leq 10^{-2}$ the authors of [18, 19] introduced into formula (11) an experimental parameter which enabled them to reconcile the calculation with the experimental data.

In our opinion, the use of the effective-medium model as the basis for generalizing the results of percolation theory and the experimental data for structures with a disordered distribution of components and with $\nu < 10^{-2}$ is formal in nature. The effective-medium model does not reflect the topology of the IC and does not take account of its variation (branching) as the concentration varies. Another shortcoming of the generalizations made in [18, 19] is the multiplicity of the formulas: for each range of concentrations and conductivity ratios ν there exists a separate formula which is unrelated to the structure of the nonuniform system, i.e., the proposed formulas are not connected with the topology of the IC.

In conclusion, it may be noted that the problem of the closure of the system of equations which was formulated in Sec. 1 explains many of the methods and procedures followed in the investigation of the conductivity of heterogeneous systems. If we take account of the diversity of structures, inclusion shapes, differences in state of aggregation, physical properties of the materials, etc., we can get an idea of the tremendous number of combinations of methods for calculating Λ, each of which differs in some respect from the others. Over the many years of development of this problem, there have been accumulated such a great number of methods and formulas that upon first acquaintance with it one might get the impression that it is extraordinarily complicated and completely hopeless.

In spite of this, however, it is possible to deduce some definite recommendations even from the present survey. First of all, the most promising methods are those which do not ignore the real topology of the system under study: the elementary-cell, averaged-element, and percolation methods. We noted above the specific limitations of each of these methods. It seems natural to formulate the following problem: to construct a model of a heterogeneous system which will have the geometric visualizability found in the models used in the elementary-cell and averaged-element methods; which will take account of the static nature of the distribution of the components, the tortuous paths of the heat flux, and the presence of dead-end paths; which will have a probability of the formation of conductive bridges and the appearance of discontinuous conductivity at the threshold value of concentration, as found in the percolation method; and which, in limiting cases, will pass to well-known and highly desirable models (the principle of correspondence).

It appears that such a model will be constructed on the basis of a combination of the elementary-cell, averaged-element, and percolation methods, since each of these methods meets some of the requirements formulated above. At the same time, it should be noted that many heterogeneous systems even today can satisfactorily be studied on the basis of the methods considered here. What is needed is simply to have a good understanding of the possibilities of each method, and that is what we have attempted to give in this survey.

LITERATURE CITED

1. J. C. Maxwell, Treatise on Electricity and Magnetism, Vol. 1, Oxford Univ. Press, London (1892).
2. L. Lorenz, "Über die Refractionsconstant," Wiedemann Ann., 11, 70-103 (1880).
3. H. A. Lorentz, "Über die Beziehung zwischen der Fortpflanzung des Lichtes und der Körperdichte," Wiedemann Ann., 9, 641-664 (1880).
4. Lord Rayleigh, "On the influence of obstacles arranged in rectangular order upon the properties of a medium," Phil. Mag. J. Sci., 34, 481-495 (1892).
5. A. F. Chudnovskii, Thermophysical Characteristics of Dispersed Materials [in Russian], Fizmatgiz, Moscow (1962).
6. A. Misner, Thermal Conductivity of Solids, Liquids, and Gases and Their Combinations [in Russian], Mir, Moscow (1968).
7. L. L. Vasil'ev and S. A. Tanaeva, Thermophysical Properties of Porous Materials [in Russian], Nauka i Tekhnika, Minsk (1971).
8. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composite Materials [in Russian], Énergiya, Leningrad (1974).
9. D. A. G. Bruggemann, "Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen," Ann. Phys. (Leipzig), 24, F. 5, No. 7, 636-650 (1935).
10. E. K. Kondorskii, "On the theory of coercive force and magnetic receptivity of ferromagnetic powders," Dokl. Akad. Nauk SSSR, 80, No. 2, 197-200 (1951).
11. R. F. Landauer, "The electrical resistance of binary metallic mixtures," Appl. Phys., 23, No. 7, 779-784 (1952).
12. D. A. Dreizin and A. M. Dykhne, "Anomalous conductivity of nonuniform media in a strong magnetic field," Zh. Eksp. Tekh. Fiz., 63, No. 1, 24-26 (1972).
13. V. I. Odelevskii, "Calculation of the generalized conductivity of heterogeneous systems," Zh. Tekh. Fiz., 21, No. 6, 667-685 (1951).
14. Yu. A. Buevich, "Effective thermal conductivity of granular materials," Zh. Prikl. Mekh. Tekh. Fiz., No. 4, 57-66 (1973).
15. Yu. A. Buevich and Yu. A. Korneev, "Heat and mass transfer in a dispersed medium," Zh. Prikl. Mekh. Tekh. Fiz., No. 4, 79-87 (1974).
16. L. D. Landau and E. M. Lifshits, Electrodynamics of Continuous Media [in Russian], GITTL, Moscow (1957).
17. K. N. Polivanov, Ferromagnetic Materials [in Russian], Gosenérgoizdat, Moscow (1957).
18. I. Webman, J. Jartner, and M. N. Cohen, "Electronic transport in alkali−tungsten bronzes," Phys. Rev. B., Vol. 13, No. 2, 713-724 (1976).
19. I. Webman, J. Jartner, and M. N. Cohen, "Numerical simulation of electrical conductivity in microscopically inhomogeneous materials," Phys. Rev. B., Vol. 11, No. 8, 2885-2892 (1975).
20. A. K. Veinberg, "Magnetic permeability, electrical conductivity, dielectric permeability, and thermal conductivity of a medium containing spherical and ellipsoidal inclusions," Dokl. Akad. Nauk SSSR, 169, No. 3, 543-547 (1966).
21. V. V. Skorokhod, "Some physical properties of highly porous solids," Poroshk. Metall., No. 6, 33-38 (1967).
22. V. V. Skorokhod and S. M. Solonin, "Kinetics of the growth of interparticle contacts in the sintering of unpressed powders," Poroshk. Metall., No. 2, 74-79 (1972).
23. L. T. M. Tsao, "Thermal conductivity of two-phase materials," Ind. Eng. Chem., 53, No. 5, 395-397.
24. S. C. Cheng and R. I. Vachon, "The prediction of the thermal conductivity of two- and three-phase solid homogeneous mixtures," Int. J. Heat Mass Transfer, 12, No. 3, 249-264 (1970).
25. S. C. Cheng and R. I. Vachon, "A technique for predicting the thermal conductivity of suspensions, emulsions, and porous materials," Int. J. Heat Mass Transfer, 13, 537-546 (1970).
26. V. N. Demidchenko, "Investigation of thermal and electrical conductivity of metal-ceramic heterogeneous systems," Author's Abstract of Candidate's Dissertation, KPI, Krasnodar (1972).
27. G. N. Dul'nev, Yu. P. Zarichnyak, and V. V. Novikov, "Generalized conductivities of heterogeneous systems with disordered structure," Inzh.-Fiz. Zh., 31, No. 1, 150-168 (1976).
28. Yu. P. Zarichnyak and T. A. Lisnenko, "Investigations of the thermophysical properties of two-component solid solutions of titanium, zirconium, and hafnium," Izv. Vyssh. Uchebn. Zaved., Priborostr., 19, No. 5, 117-123 (1976).
29. Yu. P. Zarichnyak and V. V. Novikov, "Effective conductivity of heterogeneous systems with disordered structure," Inzh.-Fiz. Zh., 34, No. 4, 648-655 (1978).

30. B. I. Shklovskii, "Critical behavior of the Hall coefficient near the flow threshold," Zh. Tekh. Fiz., $\underline{72}$, No. 1, 288-295 (1972).

31. A. S. Skal and B. I. Shklovskii, "Topology of an infinite cluster in the theory of flow and the theory of jump conductivity," Fiz. Tekh. Poluprovodn., $\underline{8}$, 1586-1591 (1974).

32. D. Adler, L. A. Flora, and S. P. Santuria, "Electrical conductivity in disordered systems," Solid State Commun., $\underline{12}$, 9-11 (1973).

33. S. Kirkpatrick, "Percolation and conductivity," in: Theory and Properties of Disordered Materials [Russian translation], Mir, Moscow (1977), pp. 249-292.

34. B. M. Shklovskii and A. L. Éfros, "Theory of flow and conductivity of strongly nonuniform media," Usp. Fiz. Nauk, $\underline{117}$, No. 3, 401-433 (1975).

35. G. N. Dul'nev and V. V. Novikov, "Effective conductivity of systems with interpenetrating components," Inzh.-Fiz. Zh., $\underline{33}$, No. 2, 271-274 (1977).

36. S. Frey, "Über die elektrische Leitfähigkeit binarer Aggregate," Z. Elektrochem., $\underline{38}$, No. 5, 260-274 (1932).

37. G. N. Dul'nev, "Heat transfer through solid dispersed systems," Inzh.-Fiz. Zh., $\underline{9}$, No. 3, 339-404 (1965).

38. V. A. Osipova and Kh. A. Kayar, "Thermophysical properties of Al_2O_3-Mo metal-ceramic composite systems," At. Energ., $\underline{32}$, No. 2, 31-40 (1972).

39. A. V. Andreev, V. P. Mal'ter, and N. B. Gutman, "Generalization of calculated functions for heat-transfer coefficients in heterogeneous media," in: Elektrotekh. Prom. Elektroterm., No. 11, 6-8 (1973).

40. A. V. Andreev and V. P. Mal'ter, "Generalization of experimental data on the thermal conductivity of gas mixtures from the viewpoint of a structural approach," Inzh.-Fiz. Zh., $\underline{34}$, No. 4, 161-167 (1975).

41. H. W. Godbee and W. T. Singler, "Thermal conductivity of MgO, Al_2O_3, and ZrO_2 powders to 850°C," Appl. Phys., $\underline{37}$, No. 1, 40-65 (1966).

42. O. Krischer, Scientific Foundations of Drying [Russian translation], IL, Moscow (1961).

43. G. N. Dul'nev, Yu. P. Zarichnyak, and B. L. Muratova, "Thermal conductivity of moist solid porous materials," Inzh.-Fiz. Zh., $\underline{31}$, No. 2, 278-283 (1976).

44. K. Lichtenecker, "Der elektrische Leitungswiderstand künstlicher und natürlicher Aggregate," Phys. Z., $\underline{10}$, 1005-1008 (1909).

45. K. Lichtenecker, "Zur Widerstandberechnung mischkristallfreier Legierungen," Phys. Z., $\underline{25}$, Nos. 8-9, 193-204 (1924).

46. K. Lichtenecker and K. Rother, "Die Herleitung des logarithmischen Mischungsgesetzes aus allgemeinen Prinzipien der stationaren Strömung," Phys. Z., $\underline{32}$, No. 6, 3255-3267 (1931).

47. V. V. Novikov, "Thermal and electrical conductivity of heterogeneous systems," Author's Abstract of Candidate's Dissertation, LITMO (1978).

48. C. Herring, "Inhomogeneities in electrical and galvanomagnetic measurements," J. Appl. Phys., $\underline{31}$, 1939-1953 (1960).

49. V. A. Kundinov and B. Ya. Moizhes, "Effective conductivity of a nonuniform isotropic medium," Zh. Tekh. Fiz., $\underline{42}$, No. 3, 591-599 (1972).

50. S. Prager, "Viscous flow through porous media," Phys. Fluids, $\underline{4}$, 1477-1489 (1961).

51. S. Prager, "Diffusion and viscous flow in concentrated suspension," Physics, $\underline{29}$, 129-136 (1963).

52. A. G. Fokin and T. D. Shermergor, "Dielectric permeability of nonuniform materials," Zh. Tekh. Fiz., $\underline{39}$, No. 7, 1308-1344 (1969).

53. T. D. Shermergor and A. G. Fokin, "Effective permeability of nonuniform film structures," in: Collection of Studies on Problems of Microelectronics, Physical and Mathematical Series [in Russian], MIÉT, No. 5 (1970), pp. 12-16.

54. Z. Hashin and S. Shtrikman, "A variational approach to the theory of the effective magnetic permeability of multiphase materials," J. Appl. Phys., $\underline{33}$, 3125-3131 (1962).

55. G. A. Ermakov, A. G. Fokin, and T. D. Shermergor, "Calculation of boundaries for effective dielectric permeabilities of nonuniform dielectrics," Zh. Tekh. Fiz., $\underline{44}$, No. 2, 249-254 (1974).

56. B. W. Rosen and Z. Hashin, "Effective thermal expansion coefficients and specific heat of composite materials," Int. J. Eng. Sci., $\underline{8}$, No. 2, 157-161 (1970).

57. S. V. Stepanov, "Thermal conductivity of two-phase systems," Inzh.-Fiz. Zh., $\underline{18}$, No. 2, 247-252 (1970).

58. K. Shulgasser, "Relationship between single-crystal and polycrystal electrical conductivity," J. Appl. Phys., $\underline{47}$, No. 5, 1880-1886 (1976).

59. A. M. Dykhne, "Calculation of the kinetic coefficients of media with random nonuniformities," Zh. Eksp. Teor. Fiz., $\underline{52}$, No. 1, 264-267 (1967).

60. V. P. Kazantsev, "Variational estimates of the effective conductivity of a medium with macroscopic inclusions," Izv. Vyssh. Uchebn. Zaved., Fiz., No. 5, 53-59 (1979).