REVIEWS

COEFFICIENTS OF GENERALIZED CONDUCTIVITY OF HETEROGENEOUS SYSTEMS WITH CHAOTIC STRUCTURE

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I. Statement of the Problem

In view of the widespread use of heterogeneous systems with a chaotic structure, it is important to analyze methods of investigating the coefficients of generalized conductivity* of these systems. Examples of these systems include metal ceramics produced by the compression molding of a mixture of two powders with plastic grains in the form of unextended isometric particles, granular systems or mixtures formed by a powder distributed in a binder component (compounds), emulsions, solutions of nonreactive fluids, etc. This review is restricted to an examination of the case of a mixture of components that are not changed when their original properties merge both within the different components and at their interfaces.

The problem is that of analytically determining the form of the function relating the effective coefficients of generalized conductivity Λ to the coefficients of conductivity of the components $\lambda_1, \lambda_2, \ldots, \lambda_n$ and to their volumetric concentrations $m_1, m_2, \ldots, m_n$, i.e.,

$$\Lambda = \Phi(\lambda_1, \lambda_2, \ldots, \lambda_n, m_1, m_2, \ldots, m_n). \tag{1}$$

The form of function (1) is dependent on the choice of model for the geometrical structure of the heterogeneous system and on the means used to mathematically describe the transfer process being studied (heat flow, charge, electrical and magnetic induction, etc.).

Two basic approaches to solving the problem analytically can be distinguished. In the first the chaotic structure is replaced immediately by a spatially ordered model with a long- and short-range order and a unit cell is then isolated. The transfer process being studied is mathematically described in the volume of the unit cell and the effective properties of the system — the coefficients of generalized conductivity [1-4] — are determined.

The essence of the second approach is an attempt to account for the chaotic nature of the structure of the heterogeneous system directly by field [5-12,14,16] and statistical methods [23-30, 35, 37].

As shown by an analysis of papers adhering to this school of thought, authors assume either expressly or tacitly that these methods of analysis are characterized by certain merits, namely:

a wide field of application and the absence of the internal contradictions created by simulating the structure;

the facility to account for the random shape of the particles and the chaotic nature of their distribution in space.

It is then to be expected that an improved analytical apparatus can be devised and that the properties of the heterogeneous systems being studied can be forecast better if these special characteristics are taken into account.

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* Coefficients of thermal conductivity, electrical conductivity, electrical and magnetic induction, dielectric permittivity, viscosity, and diffusion.

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The term "statistical methods," which is widely used in the titles and texts of articles and is often identified with the study of chaotic (disordered) structures, calls for a more precise definition. In fact, normally when the potential fields in heterogeneous systems are described and when the properties of these systems are determined, two qualitatively different mathematical apparatuses are used: the field theory apparatus and the probability theory apparatus.

In many cases the concept of "statistical analysis procedures" implies averaging physical fields over the volume occupied by the heterogeneous system, which is not related directly to principles of probability. It is thus expedient by analogy with the problems of statistical physics to refer to the different procedures for using the probability theory apparatus as "statistical methods."

Many published works are examined in accordance with this classification of approach and they are evaluated in terms of whether and to what extent they possess the merits outlined above.

II. Potential Field Averaging Methods

The field method is based on the following assumption: the physical field is averaged over volumes that are major in comparison with the scale of the heterogeneities. In terms of such a field the mixture is a homogeneous and isotropic medium. These restrictions should then be satisfied:

a) the particles are isotropic and isometric;

b) the difference in generalized conductivity* ($\Delta\lambda = \lambda_1 - \lambda_2$) between the components is small compared with the magnitude of the conductivities λ_1 and λ_2 or for a random difference $\Delta\lambda$ there should be a low concentration of one of the phases, i.e., $m_1/m_2 \ll 1$ or $m_2/m_1 \ll 1$;

c) there are no significant surface or contact phenomena at the interface of the components.

It is shown below that if these restrictions are disregarded when the effective coefficient of conductivity of the mixture Λ is determined, absurd results may ensue.

Field methods are used to determine Λ in [5-12,14,16]. The mathematical procedures for field determination that are used are examined in order to clarify the origins of the restrictions enumerated above and in order to analyze the results obtained in these papers.

The concept of the volume-mean flow of substance (heat, charge, induction, etc.) is introduced:

$$\langle \vec{j} \rangle = \frac{1}{V}\int\limits_V \vec{j}dV = \frac{1}{V}\int\limits_V \lambda\vec{E}dV = \langle \lambda\vec{E} \rangle, \tag{2}$$

where $\vec{j}$ is the local flow of substance, λ is the local value of the conductivity of the mixture, $\vec{E}$ is the local value of the field strength generating the substance flow, V is the volume of mixture over which the averaging is carried out, and the angled brackets here and hereafter denote averaging over a volume.

The mean value of the field strength $\vec{E}$ is

$$\langle \vec{E} \rangle = \frac{1}{V}\int\limits_V \vec{E}dV, \tag{3}$$

and the mean value of the conductivity is

$$\langle \lambda \rangle = \frac{1}{V}\int\limits_V \lambda dV. \tag{4}$$

The averaged magnitude of the flow $<\vec{j}>$ is related to the mean value of $<\vec{E}>$ by the relation

$$\langle \vec{j} \rangle = \Lambda \langle \vec{E} \rangle. \tag{5}$$

The local values of λ and $\vec{E}$ can be presented in the form

$$\lambda = \langle \lambda \rangle + \delta\lambda, \tag{6}$$

$$\vec{E} = \langle \vec{E} \rangle + \delta\vec{E}, \tag{7}$$

where $\delta\lambda$, $\delta\vec{E}$ are, respectively, the deviation of the local values of λ and $\vec{E}$ from the mean values.

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*For the sake of brevity, the term "conductivity" will be used hereinafter.

By substituting (6) and (7) into (2), we obtain

$$\langle \vec{j} \rangle = \langle \lambda \rangle \ \langle \vec{E} \rangle + \langle \delta\lambda\delta\vec{E} \rangle. \tag{8}$$

The following obvious relations are used in deriving (8):

$$\langle \delta\lambda \rangle = \frac{1}{V} \int\limits_V \delta\lambda dV = 0; \quad \langle \delta\vec{E} \rangle = \frac{1}{V} \int\limits_V \delta\vec{E} dV = 0.$$

By substituting (8) into (5) we obtain

$$\Lambda = \langle \lambda \rangle + \frac{\langle \delta\lambda\delta\vec{E} \rangle}{\langle \vec{E} \rangle}. \tag{9}$$

The problem of determining the effective coefficient of conductivity by field methods can be solved only in the presence of a small parameter in expression (9) [6,8]. The small parameter in (9) can be isolated when $\langle \vec{E} \rangle > 0$, if:

1) $\delta\lambda \to 0$ for any values of $\delta\vec{E} < \infty$, i.e., when the difference between the conductivities of the components of the mixture $\Delta\lambda$ is small compared with the values of λ_1 and λ_2;

2) $\delta\vec{E} \to 0$ for any values of $\delta\lambda < \infty$. The local value of the field strength $\vec{E}$ does not differ greatly from the mean value $\langle \vec{E} \rangle$, if the concentration of inhomogeneities is low, i.e., for a random difference $\Delta\lambda$ there should be a low concentration of one of the components;

3) $\delta\vec{E} \to 0$ and $\delta\lambda \to 0$. In this case, which is of little interest, $\Lambda \simeq \langle \lambda \rangle$.

If there is no small parameter in (9), Λ can be evaluated from the conditions required for minimum entropy generation only from above and from below [8]:

$$\frac{1}{\langle \lambda \rangle} < \Lambda < \langle \lambda \rangle. \tag{10}$$

The field methods can be used only when the restrictions stated above are satisfied, and if they are not satisfied, the results obtained by the field methods may give rise to false conclusions.

Thus, in [5] when the effective conductivity of a mixture with a chaotic structure (statistical mixtures) is determined within the framework of the field method, the following formula is obtained:

$$\sum_{i=1}^{n} \frac{\lambda_i - \Lambda}{\lambda_i + 2\Lambda} = 0, \tag{11}$$

where n is the number of components in the mixture and λ_i is the conductivity of the i-th component.

For a two-component mixture expression (11) takes the form

$$\Lambda = \frac{(3m_1 - 1)\lambda_1 + (3m_2 - 1)\lambda_2}{4} + \left[\frac{[(3m_1 - 1)\lambda_1 + (3m_2 - 1)\lambda_2]^2}{16} + \frac{\lambda_1\lambda_2}{2} \right]^{\frac{1}{2}}. \tag{12}$$

It follows from (12) that when $\lambda_2/\lambda_1 \to 0$

$$\Lambda = \frac{1}{2}(3m_1 - 1)\lambda_1 \tag{13}$$

and when $m_1 < 1/3$ we obtain $\Lambda < 0$, i.e., a physically absurd result has been achieved, as indicated in [13]. It becomes clear that when the difference in conductivities λ_1 and λ_2 is great the relationship of (11) and (12) can be justified only for low concentrations of the second component $m_2 \ll 1$.

In [6] a relationship for Λ is obtained for a random number of components, the conductivities of which do not differ too much from each other, in the form

$$\Lambda^{\frac{1}{3}} = \sum_{i=1}^{n} m_i \lambda_i^{\frac{1}{3}}. \tag{14}$$

For a binary mixture with a low concentration of one of the components ($m_2 \ll m_1$) but random values for the conductivities, the following formula is obtained for Λ [6]:

$$\Lambda = \lambda_1 + m_2 \frac{3(\lambda_2 - \lambda_1)\lambda_1}{\lambda_2 + 2\lambda_1}. \tag{15}$$

In the derivation of (15) it is assumed that the particles with a low concentration m_2 are spherical in form.

When $\lambda_1/\lambda_2 \to 0$ the relationship takes the form

$$\Lambda = \left(1 - \frac{3}{2} m_2\right)\lambda_1. \tag{16}$$

If restriction b) is not observed, a result may be obtained to the effect that $\Lambda < 0$, which is physically nonsensical, i.e., expression (15) can be applied only when restrictions a), b), and c) are satisfied.

A mixture with $\lambda_2/\lambda_1 = 0$ is examined in [7] within the framework of this approach and a relationship for Λ is sought for high concentrations of m_2, i.e., the author in using the field methods indicated to determine Λ does not take into account the restrictions on which the use of the method is based.

Skorokhod [7] examines, as do Landau and Lifshits [6], the following integral in order to expose the linking of the physical properties of the mixture:

$$\frac{1}{V}\int_V (\vec{j} - \lambda_1 \vec{E})\, dV = \langle \vec{j} \rangle - \lambda_1 \langle \vec{E} \rangle, \tag{17}$$

where λ_1 is the conductivity of the first component ($\lambda_1 = \text{const}$).

Expression (17) evaluates the deviation of the current in the mixture $\langle \vec{j} \rangle$ from the current in the mixture if $\Lambda = \lambda_1$, i.e., the magnitude of the perturbation on the background is

$$\langle \vec{j}_1 \rangle = \lambda_1 \langle \vec{E} \rangle.$$

The subintegral expression in (17) differs from zero only within the second component. In fact, if (17) is represented in the form

$$\frac{1}{V}\int_V (\vec{j} - \lambda_1 \vec{E})\, dV = \frac{1}{V}\left[\sum_{i=1}^{n} \int_{V_{1i}} (\vec{j}_{1i} - \lambda_1 \vec{E}_{1i})\, dV_{1i} + \sum_{k=1}^{m} \int_{V_{2k}} (\vec{j}_{2k} - \lambda_1 \vec{E}_{2k})\, dV_{2k}\right] = \vec{I}_1 + \vec{I}_2, \tag{18}$$

where $i = 1, 2, \ldots, n$ is the number of elements in the first component and $k = 1, 2, \ldots, m$ is the number of elements in the second component. The first integral $\vec{I}_1$ in (18) is equal to zero (since $\vec{j}_{1i} = \lambda_1 \vec{E}_{1i}$). The second integral $\vec{I}_2$ can be rewritten as

$$\vec{I}_2 = \frac{1}{V}\sum_{k=1}^{m} \int_{V_{2k}} (\lambda_2 \vec{E}_{2k} - \lambda_1 \vec{E}_{2k})\, dV_{2k} = \sum_{k=1}^{m} m_{2k} (\lambda_2 - \lambda_1) \langle \vec{E}_{2k} \rangle. \tag{19}$$

Here $m_{2k} = V_{2k}/V$ is the concentration of the k-th element in the second component;

$$\langle \vec{E}_{2k} \rangle = \frac{1}{V_{2k}} \int_{V_{2k}} \vec{E}_{2k}\, dV_{2k}; \tag{20}$$

$\langle \vec{E}_{2k} \rangle$ is the mean value of the field strength within the element in the second component (sphere, cylinder, etc.).

If the elements of the components are isometric, then (19) takes the form

$$\vec{I}_2 = m_2 (\lambda_2 - \lambda_1) \langle \vec{E}_{20} \rangle, \tag{21}$$

since in this case

$$m_{21} = m_{22} = \ldots = m_{2k} = \frac{V_{20}}{V}, \tag{22}$$

$$m_2 = \frac{m V_{20}}{V} = \frac{V_2}{V}, \tag{23}$$

$$\langle \vec{E}_{20} \rangle = \frac{1}{V_{20}} \int\limits_{V_{20}} \vec{E}_{20} dV_{20}, \tag{24}$$

where V_{20} is the volume of the isometric element of the second component.

By substituting (21) into the right-hand side of (18), taking into account that $\vec{I}_1 = 0$, we find

$$\langle \vec{j} \rangle - \lambda_1 \langle \vec{E} \rangle = m_2 (\lambda_2 - \lambda_1) \langle \vec{E}_{20} \rangle . \tag{25}$$

By replacing $\langle \vec{j} \rangle$ with expression (5) or (25), we obtain

$$\Lambda = \lambda_1 + m_2 (\lambda_2 - \lambda_1) \frac{\langle \vec{E}_{20} \rangle}{\langle \vec{E} \rangle} . \tag{26}$$

In other words, the isometricity of the elements of the components of the mixture is a necessary condition for the transition from (19) to (21) and then to (26).

It is, therefore, assumed in [6] that the elements of the components are a spherical form. For such particles [6]

$$\frac{\langle \vec{E}_{20} \rangle}{\langle \vec{E} \rangle} = \frac{3\lambda_1}{\lambda_2 + 2\lambda_1} \tag{27}$$

and after substitution of (27) into (26) we obtain (15).

Skorokhod [7] assumes that each component is a mixture of spherical, ellipsoidal, and cylindrical formations and records ($\lambda_2 = 0$) the expression for Λ in the form

$$\Lambda = \lambda_1 (1 - m_2) \frac{\langle \vec{E}_2 \rangle}{\langle \vec{E} \rangle} . \tag{28}$$

The $\langle \vec{E}_2 \rangle$ value found in (28) is equal to

$$\langle \vec{E}_2 \rangle = \sum_{k=1}^{m} m_{2k} \langle \vec{E}_{2k} \rangle , \tag{29}$$

whereas it would have been expected [see (19) and (17)] that

$$\Lambda = \lambda_1 \left(1 - \sum_{k=1}^{m} \frac{\langle \vec{E}_{2k} \rangle}{\langle \vec{E} \rangle} m_{2k} \right) . \tag{30}$$

The error made by Skorokhod [7] in recording (28) makes it possible to avoid restriction b), i.e., to find the relationship for Λ over the whole range of variations in concentration when $\lambda_2/\lambda_1 = 0$. In this case restriction b) is expressed formally in the fact that the following should be satisfied in (29):

$$\sum_{k=1}^{m} m_{2k} \frac{\langle \vec{E}_{2k} \rangle}{\langle \vec{E} \rangle} < 1, \tag{31}$$

and this imposes a restriction on m_2, thus,

$$\frac{\langle \vec{E}_{2k} \rangle}{\langle \vec{E} \rangle} > 1 \text{ when } \frac{\lambda_2}{\lambda_1} = 0. \tag{32}$$

According to the recording of (28) used in [7], for any m_2, the following is satisfied:

$$\Lambda > 0.$$

Thus, although the final expression for Λ coincides, according to Skorokhod, with experimental data, it cannot be considered accurate.

A further shortcoming of this method of calculating Λ [7] is that the relationship for Λ is obtained only for a special case when $\lambda_2/\lambda_1 = 0$.

In some of the latest papers field methods are used to determine the effective thermal conductivity of a composite material comprising a continuous medium (the binder) and solid particles of filler distributed at random in it [9-12].

When Λ is determined in these papers it is assumed that

$$\langle \vec{j} \rangle = (1 - m_2) \langle \vec{j}_1 \rangle + m_2 \langle \vec{j}_2 \rangle, \tag{33}$$

$$\langle \nabla \vec{T} \rangle = (1 - m_2) \langle \nabla \vec{T}_1 \rangle + m_2 \langle \nabla \vec{T}_2 \rangle, \tag{34}$$

where

$$\langle \vec{j} \rangle = -\Lambda \langle \nabla \vec{T} \rangle; \ \langle \vec{j}_1 \rangle = -\lambda_1 \langle \nabla \vec{T}_1 \rangle; \ \langle \vec{j}_2 \rangle = -\lambda_2 \langle \nabla \vec{T}_2 \rangle. \tag{35}$$

Here the indices 1 and 2 refer to the binder and filler, respectively.

It is clear from Eqs. (33) and (34) that the authors accept that the volumetric concentration of inclusions is equal to the surface concentration of inclusions in any given cross section perpendicular to the heat flow and equal to the linear concentration. Such a model of mixture structure represents a mixture with a uniform concentration of inclusions in any given volume, i.e., the mixture is treated as structurally homogeneous. To determine Λ with such a mixture, as can be seen from Eqs. (33)-(35), it is enough to find the connection between $\langle \nabla \vec{T} \rangle$, $\langle \nabla \vec{T}_1 \rangle$, and $\langle \nabla \vec{T}_2 \rangle$. To this end the authors replace the original problem of determining Λ with the problem of determining the temperature field of an isolated particle located in the binder medium and the point thermal dipoles, imitating other filler particles, which are distributed in it. The relation between $\langle \nabla \vec{T} \rangle$ and $\langle \nabla \vec{T}_2 \rangle$ is then found using the well-known polarization correlation [6]. Thus, if the interspersions are spherical in form, then

$$\frac{\langle \nabla \vec{T}_2 \rangle}{\langle \nabla \vec{T} \rangle} = \frac{3\Lambda}{\lambda_2 + 2\Lambda}, \tag{36}$$

where Λ is the effective thermal conductivity of the mixture [see formula (27)].

According to condition (33) in [12] the magnitude $\langle \vec{j} \rangle$ is expressed by the relation

$$\langle \vec{j} \rangle = -\frac{1}{V}\left(\lambda_1 \int_{V_1} \nabla \vec{T} dV_1 + \lambda_2 \int_{V_2} \nabla \vec{T} dV_2 \right) = -\frac{1}{V}\left[\lambda_1 \int_{V} \nabla \vec{T} dV + (\lambda_2 - \lambda_1) \int_{V_2} \nabla \vec{T} dV_2 \right] = -\lambda_1 \langle \nabla \vec{T} \rangle - m_2 (\lambda_2 - \lambda_1) \langle \nabla \vec{T}_2 \rangle,$$

i.e.,

$$\langle \vec{j} \rangle = -\lambda_1 \langle \nabla \vec{T} \rangle - m_2 (\lambda_2 - \lambda_1) \langle \nabla \vec{T}_2 \rangle, \tag{37}$$

and by taking into account (36) we obtain

$$\Lambda = \lambda_1 + \frac{3\Lambda(\lambda_2 - \lambda_1)}{\lambda_2 + 2\Lambda} m_2. \tag{38}$$

The formula obtained, (38), is analogous to (15) and when $\lambda_2 = 0$ it too leads to an absurd result when $m_2 > 2/3$. For high concentrations, therefore, the authors use the condition that the test particle (isolated) be separated from a fictional environment with a thermal conductivity Λ by a layer with a binder thermal conductivity λ_1 and we obtain the expression

$$\Lambda = \lambda_1 + m_2 \frac{36\Lambda(\lambda_2 - \lambda_1)\lambda_1}{\Lambda(7\lambda_2 - 17\lambda_1) + \lambda_1(5\lambda_2 + 7\lambda_1)}. \tag{39}$$

The competence of this model for studying densely packed interspersions is open to doubt. From (39) it is clear that

$$\Lambda = \Phi(\lambda_1, \lambda_2, m_2) \neq \Phi(\lambda_2, \lambda_1, m_2), \tag{40}$$

which is true for a mixture with isolated interspersions [4]. Expression (39) does not therefore undergo a limit transition when $m_2 = 1$:

$$\Lambda \neq \lambda_2.$$

Expression (39) is true only when $m_2 < 0.6$.

All these shortcomings mean that the expressions for Λ obtained in [9-12] can be applied to a restricted group of mixtures and they coincide, in fact, with the calculated relationships of Odelevskii and Landau [5, 6].

It should be noted that it is possible, by virtue of the concept of multipole interactions, to formulate a strict statement of the problem of determining the coefficient of generalized conductivity for mixtures with a chaotic structure if there are no surface and contact phenomena [14]. The essence of this strict formulation is that the field of any given system of charges can be represented in the form of an infinite series of multipoles. The field at any given point of a heterogeneous system is expressed as a superimposition of the field generated by each of the particles, i.e., as equal to a double sum, in terms of the particles and in terms of the multipoles localized in the particle centers. The local surroundings of the particles are then different and the number of different alternatives for the spatial distribution of the particles is huge, indicating that the problem must be formulated as many-particle problems and, in particular, as fluid theory problems.

The function of the coordinates must be introduced in order to take into account local inhomogeneities:

$$g_i(\vec{r}) = \begin{cases} 0, & \text{if} \quad \vec{r} \in V_i, \\ 1, & \text{if} \quad \vec{r} \in V_i, \end{cases} \tag{41}$$

where V_i is the volume occupied by the i-th component.

In fluid theory $g_i(\vec{r})$ bears the name of the correlative distribution function [15] and determines the probability of finding particles $n = 1, 2, \ldots, m$ near points $r_1, r_2, \ldots, r_m$. The mean value of the magnitude $M(\vec{r})$ in this case takes the form

$$\langle M \rangle = \frac{1}{V} \int\limits_V M(\vec{r})\, g(\vec{r})\, dV. \tag{42}$$

Due, however, to mathematical complications arising when the strictly formulated problem is solved and when the form of the $g_i(\vec{r})$ function is determined, only an approximate solution can be obtained for Λ when $m_2 \geq 0.6$ [14,16].

Thus, effective conductivity with a chaotic structure can be calculated if requirements a), b), and c) are satisfied when the field methods are used. When the general premises on which the investigation method is based are not observed, errors and contradictions result. For mixtures in which the structure and correlation of component conductivities are such that conditions a), b), and c) are not observed, therefore, standard representations are brought into play, using which the special characteristics of the process of transfer at the junction of the different components can be taken into account and the relationship for Λ can be found over a wide range of variations in the determining parameters of the mixture.

III. Methods of Determining the Geometrical Parameters of the Unit Cell

In this group of methods the effective conductivity of the heterogeneous system is sought not by averaging over a volume the local flows and gradients of the potential field structure, but by averaging in geometrical parameters of a heterogeneous system model in which the process being studied, which is concluded by determining the effective conductivity of the system, is then described mathematically.

The procedures for averaging the geometrical parameters of the model are developed more clearly in investigations into the determination of the conductivity of grained heterogeneous systems with a chaotic structure [17-20].

Let us examine papers classified within this group.

The dimensions of the region around the contact (Fig. 1) are determined by the number of grains in contact with any given particle among those under consideration. In ordered models with spherical grains of the same size the number of contacts is known to be identical for all the particles and to be determined by the coordination number N of the packing (hexagonal close-packed and face-centered cubic $N = 12$, orthorhombic $N = 8$, cubic loose-packed $N = 6$, and diamond $N = 4$) which is related unambiguously to the volumetric concentration of spheres. In ordered spherical grain packing the porosity dependence of the coordination number $N = f(m_2)$ is discrete in nature, which reflects the fact that it is possible to synthesize only certain types of ordered structures in systems made up of spheres of the same diameter.

Actual grained materials have a chaotic structure by virtue of a difference in the shape and dimensions of the particles and in their positioning relative to each other. Assuming that in actual burdens with a chaotic structure the volume-mean number of contacts $\langle N \rangle$ will be monotonically dependent on the concentration of components, Kunii and Smith [17] propose a semiempirical correlation for evaluating the dimensions of the region around the contact (r, H, Fig. 1), derived from a generalization of the $N = f(m_2)$ relationship for ordered

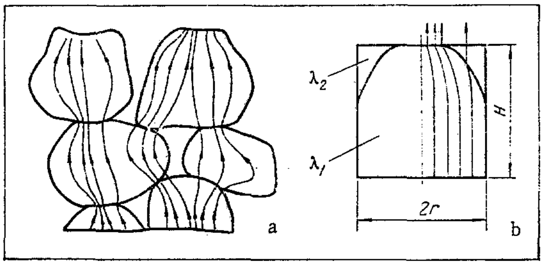

Fig.1. Determining the averaged geometrical parameters of a constant spot: a) line of flux in mixture with chaotic structure; b) element of chaotic structure with averaged parameters.

packing of spheres of the same size. The semiempirical relationship assumed is restricted to a fairly narrow range of variations in the volumetric concentration of the m_2 component in the space between grains.

Correlating the results obtained by Kiselev [21] by measuring the coordination number of grained systems, Kaganev [18] proposes an empirical correlation for evaluating $\langle N \rangle$ which is suitable for calculations over a wide range of variations in the concentration of the component between grains $0.26 < m_2 < 1$ in the form

$$\langle N \rangle = 11.6(1 - m_2), \tag{43}$$

which is used for calculating the effective thermal conductivity of grained systems.

An analytical determination of the dependence of the mean value of the coordination number on the component concentration is proposed by Eremeev [22]:

$$\langle N \rangle = \frac{m_2 + 3 + (m_2^2 - 10m_2 + 9)^{\frac{1}{2}}}{2m_2} \tag{44}$$

and it is then used to evaluate the averaged values of the geometrical parameters of the region around the contact when calculating the effective thermal conductivity of grained and bonded (sintered and compacted) materials in [19-20]. The averaged values of the geometrical parameters of the heterogeneous system models can be calculated from the papers in this group and the magnitude of the conductivity of the system as a whole can then be forecast.

It should be noted that the fundamental problems (and possible sources of error) in the methods in this group are transposed from the region of the analytical (formal) description of potential and flow fields in the system to the simulation of the geometry of a system with a chaotic structure. The clarity of representation of the spatial models makes it easier to represent separate aspects of the process under investigation but generates as many problems as it solves in the form of requirements which are hard to satisfy imposed on the development of geometrical models adequate for the chaotic structure under investigation.

IV. Methods of Constructing the Form of the Function $\Lambda = \Phi(\lambda_1, \lambda_2 \ldots \lambda_n, m_1 \ldots m_n)$ Using Probability Principles

In this group of methods of investigating the conductivity of heterogeneous systems with a chaotic structure, volumetric averaging procedures are not used for potential fields or the parameters of the geometrical model and the procedures employed are somewhat formal in character.

The following assumptions can be characterized as the initial premises of the works in this group:

the conductivity of the chaotic mixture of noninteracting components is an unambiguous monotonic function of the conductivity of the components;

an adequate mathematical apparatus, such as the probability theory, is required to account for the chaotic nature of the distribution of the components in the volume of the heterogeneous system.

In the papers in this group the form of the function is, as a rule, determined not from solving the physical problem, but by the formal selection (construction) of a function satisfying the boundary conditions and a number of qualitative requirements such as invariance in terms of the components and reversibility (being possible to calculate both the conductivities and the resistivities).

The method of constructing the form of function (1) is used in the works of Lichtenekker [25-27] published between 1924 and 1930.

Working from general qualitative considerations, Lichtenekker assumes that in heterogeneous systems with disordered structures, the effective resistivity of the system R can be expressed unambiguosly in terms of the resistance of the components ρ_i and their volumetric concentrations m_i. For a two-component system

$$R = \Phi(\rho_1, \rho_2, m_2). \tag{45}$$

The author further requires that the effective conductivity be expressible in terms of the conductivity of the components λ_1 and λ_2 using the same functional relationship, i.e.,

$$\Lambda = \Phi(\lambda_1, \lambda_2, m_2) \quad \text{or} \quad \frac{1}{R} = \Phi\left(\frac{1}{\rho_1}, \frac{1}{\rho_2}, m_2\right). \tag{46}$$

It follows from (43) and (44) that

$$\Phi\left(\frac{1}{\rho_1}, \frac{1}{\rho_2}, m_2\right) = \frac{1}{\Phi(\rho_1, \rho_2, m_2)}. \tag{47}$$

In the limiting cases for a concentration of any of the components of 0 or 1, function (45) should give the magnitude of the resistivity of the corresponding component, i.e.,

$$\Phi(\rho_1, \rho_2, 0) = \rho_1; \quad \Phi(\rho_1, \rho_2, 1) = \rho_2. \tag{48}$$

Conditions (47) and (48) as formulated are satisfied by the function

$$R = \rho_1^{(1-m_2)} \rho_2^{m_2} \quad \text{or} \quad \Lambda = \lambda_1^{(1-m_2)} \lambda_2^{m_2}. \tag{49}$$

As Lichtenekker records, relationship (49) gives a satisfactory agreement with experiment.

By taking the log of (49) we obtain

$$\log \Lambda = (1 - m_2) \log \lambda_1 + m_2 \log \lambda_2. \tag{50}$$

The last expression gives Lichtenekker grounds for proposing the following rule "... with binary systems with a disordered distribution of components it is not the conductivities but the logs of the conductivities which merge."

It is interesting to note that Lichtenekker treats the logarithmic relationship (50) obtained for the properties of the heterogeneous system as a new result of his own, whereas the same form of relationship is proposed previously by Arrhenius [24] for binary solutions.

The procedures for constructing functions are developed in the works of Deimek [26], Lichtenekker, and Roter [25,27]. The two possible extreme types of structure are examined — with plates lying in parallel or in series relative to the flow. The thermal conductivity of a system with such plates is expressed as follows:

$$\lambda_{\parallel} = (1 - m_2)\lambda_1 + m_2\lambda_2; \quad \lambda_{\perp} = \left(\frac{1 - m_2}{\lambda_1} + \frac{m_2}{\lambda_2}\right)^{-1}, \tag{51}$$

where $\lambda_{\parallel}$ and $\lambda_{\perp}$ are the values of the coefficients of thermal conductivity with parallel and perpendicular orientation of the plates with reference to the flow.

Each of the $\lambda_{\parallel}$ and $\lambda_{\perp}$ magnitudes is treated as a measure of the elementary probability of the processes determining the effective magnitude of the property being studied. For example, the closer the general disposition of particles approximates to the limiting case of series connection, the closer is Λ to $\lambda_{\perp}$. Designating the relative frequency (probability of occurrence) of this case as u and the relative frequency of the opposite case as (1—u), Lichtenekker constructs a function taking the following form:

$$\Lambda = \frac{[(1 - m_2)\lambda_2 + m_2\lambda_2]^u}{\left(\frac{1 - m_2}{\lambda_1} + \frac{m_2}{\lambda_2}\right)^{1-u}}, \tag{52}$$

such that when u = 1 and u = 0 it is converted into formula (51).

If it is accepted that the probabilities of different plate orientation are equal, i.e., u = 0.5, then

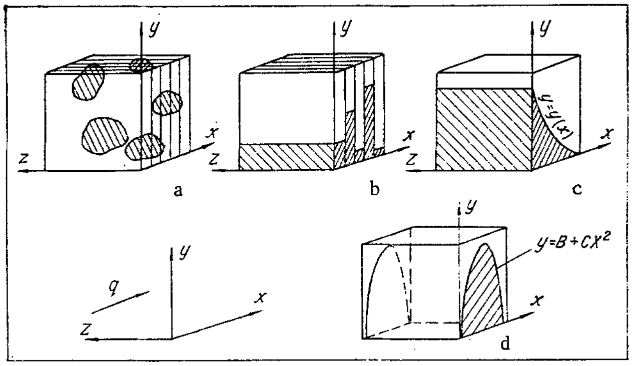

Fig. 2. Model for calculating the effective thermal conductivity of mixtures with a chaotic structure: a, b, and c) Tsao model [28]; d) Cheng and Vachon model [29]; q) direction of heat flow.

$$\Lambda = \left[\lambda_1\lambda_2 \frac{(1-m_2)\lambda_1 + m_2\lambda_2}{(1-m_2)\lambda_2 + m_2\lambda_1}\right]^{\frac{1}{2}}. \tag{53}$$

With a concentration $m_2 = 0.5$ the formulas in (51) are transformed into

$$\Lambda = (\lambda_1\lambda_2)^{\frac{1}{2}}.$$

This relationship coincides with (47) if m_2 is taken to be 0.5 in it.

Lichtenekker recommends the use of function (52) for mixtures with geometrically equal components and the use of the logarithmic merging law (49) for mixtures with nonequal components.

Certain special characteristics of formulas of the type of (49) and (52) obtained on the basis of the function "construction" method should be noted. First and foremost, these formulas do not undergo a significant limiting transition when the conductivity of one of the components takes values of zero or infinity.

A structure with closed inclusions is examined and a value of $\lambda_1 \neq 0$, $\lambda_2 = 0$, or $\lambda_2 = \infty$ is assumed. In this case the thermal conductivity of the whole system should have finite values and formula (49) gives a result of $\Lambda = 0$ or $\Lambda = \infty$.

If in a structure with interpenetrating components a value is assumed for the conductivity of one of the components, for example, $\lambda_2 = 0$, then the whole mixture should exhibit a thermal conductivity value of $\Lambda > 0$ but a different result is obtained from formula (49), namely, $\Lambda = 0$. Further, relationships like (49) or (52) do not reflect the actual structure of the material, so they are insensitive to such special characteristics of the structure as the existence of constrictions in the transverse cross section of the conducting component, the existence of a cracked state or of anisotropy, etc., which are of significance to the transfer process. In certain cases the calculation of the thermal conductivity of one of the components becomes problematical without some knowledge of the structure. For example, in a porous solid material the geometrical and physical parameters of the pores must be taken into account in order to determine the thermal conductivity of the component in the pores. In other words, despite the apparent attractions of the merging laws obtained by Lichtenekker and despite the accuracy of individual results, this method is considered by the present authors to be, on the whole, not very promising.

V. Methods of Accounting for the Chaotic Disposition and the Form of the Interfaces of the Components

Among the earliest published works in this group are the papers by Tsao [28] and his followers Cheng and Vachon [29,30]. First of all, a unit volume of a two-phase heterogeneous system (Fig. 2a) is examined which is divided up into infinitely thin layers by planes perpendicular to the heat flow (parallel with the yz plane). The component concentration in each of the layers is considered to vary randomly. By displacing one of the components in each unit layer toward the xz plane (Fig. 2b) and by shifting the actual layers here and there, a stepped component interface which is later replaced by a smooth interface (Fig. 2c) can be obtained.

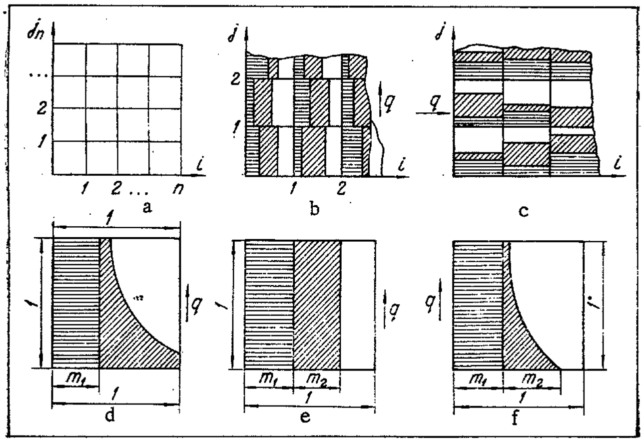

Fig. 3. Transformation of Demidchenko model [37].

If the geometry of this interface, i.e., the form of the relationship y = y(x), is known, then the effective thermal conductivity Λ of the heterogeneous system can be found as the inverse of the sum of the thermal resistance of all the layers of the unit volume. Tsao proposes the following calculation formula:

$$\Lambda = \int_0^1 \frac{dl_1}{\lambda_2 + (\lambda_1 - \lambda_2) \int_{l_1}^{1} \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{l_1 - m_1}{\sigma}\right)\right] dl_1}, \tag{54}$$

where λ_1 and λ_2 are the thermal conductivities of the components; l_1 is the "linear" concentration of the component with thermal conductivity λ_1; m_1 is the mean value of l_1; and σ is the standard deviation of the "linear" concentration l_1 from m_1.

The fundamental difficulty, according to Tsao, lies in the calculation of the integral in the denominator for which the law governing the probability distribution of the components in the unit layers must be known as well as the values of the "linear" concentration of components which is, according to Tsao's definition, equal to the ratio of volumetric and surface concentrations of these components. In expression (54) a normal law of component distribution is assumed. This expression can therefore be calculated only by numerical methods.

The Cheng and Vachon model [29] (Fig. 2d) differs from the Tsao model only in that the law governing the distribution of the concentrations in the layers $l = l(x)$ is given in the form of a parabola $l = B + Cx^2$ with the B and C coefficients related to the component concentration in such a way that the ratio of the area bounded by the parabola $l = B + Cx^2$ to the unit area (1 × 1) of the volume under consideration (1 × 1 × 1) is equal to the concentration of a component represented by noncontacting inclusions. The Cheng and Vachon calculation formula when $\lambda_1 < \lambda_2$ appears as follows:

$$\Lambda = \frac{\{C(\lambda_1 - \lambda_2)[\lambda_2 + B(\lambda_1 - \lambda_2)]\}^{\frac{1}{2}}}{\ln \dfrac{[\lambda_1 + B(\lambda_1 - \lambda_2)]^{1/2} + \frac{B}{2}[C(\lambda_1 - \lambda_2)]^{\frac{1}{2}}}{[\lambda_2 + B(\lambda_1 - \lambda_2)^{1/2} - \frac{B}{2}[C(\lambda_1 - \lambda_2)]^{\frac{1}{2}}} + \dfrac{\{C(\lambda_1 - \lambda_2)[\lambda_2 + B(\lambda_1 - \lambda_2)I(1 - B)\}^{\frac{1}{2}}}{\lambda_2}}, \tag{55}$$

where m_1 is the concentration of the component with thermal conductivity λ_1, $B = [3m_1/2]^{1/2}$, and $C = -B/4$.

The special characteristics held in common by the models under examination are formulated below.

1. The difference between these models and other previously known models (cubic, spherical, ellipsoidal, etc., inclusions) lies only in the shape of the inclusions. In the Cheng and Vachon model the inclusions and the description of the shape of the component interface are equivalent to the representation of the unit cell in the form of a parallelepiped with interspersions in the form of a cylindrical paraboloid (Fig. 2d).

2. The procedure used to break down the volume into infinitely fine isometric planes perpendicular to the heat flow with the subsequent transformation of cell geometry is incorrect. For a heterogeneous system, the dimensions of which are much greater than the particle dimensions, there should be an identical correlation

between component concentrations in each unit cell, the model being therefore one of parallel-connected plates each of which reflects the heat transfer in the corresponding component. Such a model is known [31] to cause a considerable exaggeration in the calculated magnitude of thermal conductivity. It is possible that Tsao, Cheng, and Vachon [28,29] resort to this incorrect procedure in order to avoid the inevitable transition to the parallel plate model.

3. The method of calculating the effective thermal conductivity is applicable, if only to a limited extent, to heterogeneous systems in which one of the components is made up of noncontacting inclusions.

To sum up the foregoing, one may conclude that consideration of the statistical patterns established in the procedures developed in [28,29] not only fail to offer any advantages, but, quite the reverse, restrict the range of applicability of the models produced (item 3) and (item 1). No advantages to be gained from taking into account the chaotic nature of the structure of heterogeneous systems in calculations of their effective thermal conductivity are revealed by the comparison given in [30] of calculations and experiment and data calculated by the Maxwell [32], Ohm [33], and Hamilton [34] formulas in a narrow range of correlations between thermal conductivity and component concentrations.

Ivanov also attempts in [35] to use statistical patterns to make calculations for grained and fibrous systems. Without going into detail on the arbitrariness of the assumption made in [35] when carrying out awkward mathematical calculations, it should be noted that for grained two-component systems made up of particles with the same diameter Ivanov establishes a linear relationship between the effective thermal conductivity of the system Λ and the porosity m_n and that the structural model is a parallel connection of plates. This is known [36] to be the least successful model for the structure of grained systems, the discrepancy between the calculated values obtained for Λ on this model being, as a rule, more than 100%, since the real (experimental) relationships $\Lambda = \Lambda(m_n)$ for grained systems are clearly nonlinear in nature.

Ivanov attributes this discrepancy to the presence of a spectrum of particle diameter values in actual grained systems and introduces a correction (determined in such a way as to cast doubt on its own correctness) in the dependence on the experimentally studied laws governing particle distribution by diameter. It is, however, well known that for grained systems made up of identical particles (small spheres with the same diameter) the effective conductivity values Λ fall in the region of the experimental values for chaotic grained systems made up of particles with differing diameters and that when $\lambda_1 \gg \lambda_2$ they differ considerably from the values determined by the linear relationship $\Lambda = km_n$. It seems likely that the difficulties involved in taking the statistical patterns in disperse bodies into account directly lead Ivanov in the first stage of his investigation to use the incorrect parallel plate model which does not reflect the special structural characteristics of grained systems and which causes a substantial exaggeration (100% or more) in Λ and in the second stage to introduce a correction to eliminate this exaggeration, which can be determined only given a knowledge of the law of particle distribution by dimensions.

The method for calculating the effective thermal conductivity of composites and sintered metallic powders (metal ceramics) described by Demidchenko [37] is based on taking into account the probability patterns governing the distribution of components in the volume of the system. The author calls this method the "differential-statistical" method. A plane square cross section is isolated in the volume of a statistical mixture with component concentrations of m_1 and m_2 and with a porosity m_3 (the third component); the component concentrations and effective thermal conductivity of the cross section under examination and of the system as a whole are assumed to be equal. The cross section is broken down into n^2 squares (n along the vertical and n along the horizontal as depicted in Fig. 3a). The component concentration values in each square (cell) of the cross section (matrix) are set at random by a random number generator with the following restrictions:

in each horizontal row (rank) (Fig. 3b) the component concentrations are equal to the corresponding concentrations in the system and the component concentrations in the cells of a row can then take on any random values;

in each vertical row (file) an equality of concentrations in it and in the whole system is satisfied only for any one component.

The effective thermal conductivity of the matrix is calculated in two stages.

First stage: the heat flow is aligned vertically (along the $\vec{j}$ axis). The components of the system in each cell are represented as plates, as shown in Fig. 3b; the rank interfaces are isothermal planes. The thermal conductivity of n ranks, i.e., of the λ_I matrix, is recorded as follows:

$$\lambda_{j_{\text{rank}}} = \lambda_I = \lambda_1 m_1 + \lambda_2 m_2 + \lambda_3 m_3. \qquad (56)$$

Second stage: the heat flow is aligned horizontally (along the i axis). The components are also represented as plates (Fig. 3c); the file interfaces are isothermal. The thermal conductivity of the files (of the whole matrix) is

$$\lambda_{i\,\text{file}} = \lambda_{\text{II}} = \lambda_1 m_1 + \lambda_2 m_2^* + \lambda_3 m_3^*, \tag{57}$$

with m_2^* and m_3^* varying arbitrarily but satisfying the condition stated above.

It is proposed to find the "true" value of the effective thermal conductivity as the arithmetic mean from λ_{I} and λ_{II}, i.e.,

$$\Lambda = \frac{\lambda_{\text{I}} + \lambda_{\text{II}}}{2}. \tag{58}$$

The calculation method is later improved as applied to metal ceramic composites: special coefficients which make due allowance for the heat resistance of the contact between the particles for different types of two-particle contacts are determined as are correlations of the number of these types. Finally, calculated relationships are derived for determining the thermal conductivity of each of the types of two-particle contacts and their concentration in the system is determined. When the effective thermal conductivity of the system is calculated by formulas (56)-(58), λ_1, λ_2, and λ_3 are substituted by the corresponding values $k_1\lambda_1$, $k_2\lambda_2$, and $k_3\lambda_3$.

The first and second stages from which formulas (56)-(58) are obtained are analyzed below.

It can be shown that in the first stage the model represents a set of parallel plates (Fig. 3e); such a model is known; calculations based on this kind of model give considerably exaggerated values for the conductivity of the system when the conductivities of the components differ significantly.

In the second stage the model should be reduced to the form shown in Fig. 3d by use of the following arguments: since the file interfaces are the crux of the isothermal plane, the files can change places without altering the thermal conductivity of the system and the components (plates) in each file can change places in the same way as in the papers examined above [28,29]. With the files changing places in such a way as to produce a smooth component interface, the end result for a two-component system is a combination of the Tsao model [28] and a plate imitating a component with a high thermal conductivity (Fig. 3d) and for a three-component system it is a plate in conjunction with the model examined by Cheng and Vachon [29].

Since the true value of the effective thermal conductivity is found in this paper as the arithmetical mean from the thermal conductivities of the models of the first and second stages of the calculation, the final averaging is equivalent to a parallel connection of these models (Fig. 3d and e). Like components can be combined in this connection and it can be represented as the model shown in Fig. 3f.

The model thus established has the shortcomings inherent in the Tsao and Cheng–Vachon models and, in addition, a number of other shortcomings, namely:

1) the replacement of one of the components of the model by a plate must give rise to an exaggerated calculated value for the effective thermal conductivity if the conductivity of this component is greater than the thermal conductivity of the remaining components;

2) the model does not reflect the components geometrically if the latter exist in the form of closed inclusions (interspersions);

3) the calculation of the effective thermal conductivity becomes unjustifiably awkward.

The comparison between calculation and experiment made in [37] cannot, in the opinion of the present authors, fully serve as justification for the applicability of the model, since, first, it is made for low-porosity metal ceramic materials with components differing only slightly in thermal conductivity, and, secondly, the divergence of the values calculated for the effective thermal conductivity in comparison with the results of calculations by other well-known procedures is comparable with the vagueness of our knowledge of the coefficient of conductivity of the components.

Thus, from this analysis of [5-37] a conclusion may be drawn to the effect that the models and procedures for the analytical determination of Λ produced when the statistical patterns in the structure of heterogeneous systems are taken into account are at present less complete than the models produced by reducing actual chaotic heterogeneous systems to ordered systems and then to their unit cells.

A synthesis of the two schools of thought (field and probability methods) observed in the investigation of the generalized conductivity of heterogeneous systems appears to be promising. Such a step would combine the simplicity and clarity of representation of the ordered models, while at the same time taking into account the random nature of the distribution of components in the volume of the mixture.

NOTATION

Λ, effective coefficient of generalized conductivity; λ_i, ρ_i, m_i, coefficients of conductivity, resistance, and volumetric concentration of the i-th component; l_i, linear concentration of the i-th component; σ, standard deviation of linear concentration l_i from the mean value m_i; $\langle \vec{j} \rangle$, $\langle \vec{E} \rangle$, mean flow of substance and field strength; $\vec{j}$, $\vec{E}$, local values of substance flow and field strength; $\langle \lambda \rangle$, mean value of coefficient of conductivity of heterogeneous system; $\delta\vec{E}$, $\delta\lambda$, local deviation of field strength and coefficient of conductivity from their mean values.

LITERATURE CITED

1. A. F. Chudnovskii, Thermal and Physical Characteristics of Disperse Materials [in Russian], Moscow (1962).
2. A. Misnar, Thermal Conductivity of Solids, Fluids, Gases, and Their Composites [Russian translation], Mir, Moscow (1968).
3. L. L. Vasil'ev and S. A. Tanaeva, Thermal and Physical Properties of Porous Materials [in Russian], Nauka i Tekhnika, Moscow (1971).
4. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composite Materials [in Russian], Énergiya, Leningrad (1974).
5. V. I. Odelevskii, Zh. Tekh. Fiz., 21, No.6 (1951).
6. L. D. Landau and E. M. Lifshits, Electrodynamics of Continuous Media, Addison-Wesley (1960).
7. V. V. Skorokhod, Inzh.-Fiz. Zh., No.8 (1958).
8. A. M. Dykhne, Zh. Éksp. Teor. Fiz., 52, No.1 (1967).
9. Yu. A. Buevich, Zh. Prikl. Mekh. Tekh. Fiz., No.4 (1973).
10. Yu. A. Buevich (Buyevich), Chem. Eng. Sci., 29, No. 01 (1974).
11. I. N. Shchelchkova, Zh. Prikl. Mekh. Tekh. Fiz., No.1 (1974).
12. Yu. A. Buevich and Yu. A. Korneev, Zh. Prikl. Mekh. Tekh. Fiz., No.4 (1974).
13. G. N. Dul'nev, Inzh.-Fiz. Zh., 19, No.3 (1970).
14. W. F. Brown, J. Chem. Phys., 23, 1514 (1955).
15. N. N. Bogolyubov, Dynamic Theory Problems in Statistical Physics [in Russian], Gostekhizdat (1946).
16. R. Gunter and D. Heinrich, Z. Phys., 185, 345-374 (1965).
17. D. Kunii and S. M. Smith, AIChE J., 6, No.1 (1960).
18. M. G. Kaganer, Thermal Insulation in Low Temperature Technology [in Russian], Mashinostroenie, Moscow (1966).
19. G. N. Dul'nev, M. A. Eremeev, and Yu. P. Zarichnyak, Inzh.-Fiz. Zh., 26, No.5 (1974).
20. G. N. Dul'nev, M. A. Eremeev, and Yu. P. Zarichnyak, Inzh.-Fiz. Zh., 27, No.1 (1974).
21. A. V. Kiselev, in: Methods of Investigating Highly Disperse and Porous Bodies [in Russian], Izd. Akad. Nauk SSSR (1958), pp.47-59.
22. M. A. Eremeev, in: Energy and Material Transfer Processes at Low Temperatures in a Vacuum [in Russian], Énergiya (1973).
23. K. Lichtenekker, Phys. Z., 10, No.25, 1005-1009 (1909).
24. S. Arrhenius, Z. Phys. Chem., 1, 285 (1887).
25. K. Lichtenekker and K. Roter, Phys. Z., 32, No.6 (1931).
26. U. Deimek, Phys. Z., 28, No.11 (1927).
27. K. Lichtenekker, Phys. Z., 25, Nos.8-9 (1924).
28. G. T. N. Tsao, Ind. Eng. Chem., 53, 395-397 (1961).
29. S. C. Cheng and R. I. Vachon, Intern. J. Heat Mass Transfer, 12, 249-264 (1969).
30. S. C. Cheng and R. I. Vachon, Intern. J. Heat Mass Transfer, 13, 537-546 (1970).
31. Yu. P. Zarichnyak, Author's Abstract of Candidate's Dissertation, Leningrad Institute of Precision Mechanics and Optics (1970).
32. J. C. Maxwell, Treatise on Electricity and Magnetism, Vols. 1 and 2, Dover, New York (1954), Chap. 9, Art. 314.
33. A. E. Powers, A. S. C. Research and Development Report (1961), p. 2145.
34. R. R. Hamilton, Ind. Eng. Chem., 1, No.3 (1960).
35. N. S. Ivanov, in: Frozen Areas of the Earth's Crust [in Russian], No. 8, Izd. Akad. Nauk SSSR (1962).
36. H. W. Godbee and W. T. Ziegler, J. Appl. Phys., 37, No.1 (1966).
37. V. I. Demidchenko, Author's Abstract of Candidate's Dissertation, Krasnodar Polytechnic Institute (1972).