THERMAL CONDUCTIVITY OF MIXTURES WITH INTERPENETRATING COMPONENTS

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The basic principles of investigation of transport processes used in generalized conduction theory are formulated. Studies in which a structure with interpenetrating components has been used for determining electrical and thermal conductivity are analyzed. It is shown that using models of such structures it is possible to calculate the thermal conductivity of gas mixtures, liquid solutions, solid disperse systems, certain alloys, and granular and fibrous materials.

1. Basic Definitions and Formulation of the Problem

In what follows we shall be concerned with heterogeneous and homogeneous mixtures consisting of two or more components. The entire range of heterogeneous structures can be divided into three groups: structures with isolated components, structures with interpenetrating components, and their combinations (Fig. 1). The principal qualitative feature of structures with interpenetrating components is the continuity of the material of each component. Many natural and synthetic materials have structures that relate them to the second or third groups. However, the question of the transport processes in such materials has received relatively little attention. At the same time, mixtures with closed inclusions have been the object of widespread research extending from the end of the last century to the present day [1-6].*

In generalized conduction theory the individual components of a system are treated as continua and on the basis of an analysis of the transport process a relation is established between the effective transport coefficient Λ and the structure of the system, the transport coefficients of the individual components Λ_1, Λ_2, ... and their concentrations m_1, m_2, ..., i.e.,

$$\Lambda = f(\Lambda_1, \Lambda_2, \ldots, \Lambda_i, \ldots, m_1, m_2, \ldots, m_i, \ldots). \tag{1}$$

We introduce the concept of mechanical and nonmechanical mixtures. For mechanical mixtures the generalized conductivity Λ_i of the starting components i is the same as that in the mixture Λ_i', i.e.,

$$\Lambda_i' = \Lambda_i \neq \varphi(\Lambda_1, \Lambda_2, \ldots, m_1, m_2, \ldots), \tag{2}$$

while for nonmechanical mixtures the conductivities Λ_i' in the mixture are not equal to the corresponding coefficients Λ_i of the starting components and depend on the transport coefficients Λ_1', Λ_2', ... and the concentrations m_1, m_2, ..., i.e.,

$$\Lambda_i \neq \Lambda_i' = \varphi(\Lambda_1', \Lambda_2', \ldots, m_1, m_2, \ldots). \tag{3}$$

As will be shown below, in studying the transport coefficients in homogeneous systems (gas mixtures, liquid solutions, etc.) it is desirable to represent them in the form of structures with interpenetrating components.

Below, we shall examine methods of theoretically determining the thermal conductivity λ of heterogeneous and homogeneous systems with interpenetrating components. However, the conclusions retain their force for other generalized conduction coefficients also.

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*References are given only to certain early studies in this area and to reviews published in recent years.

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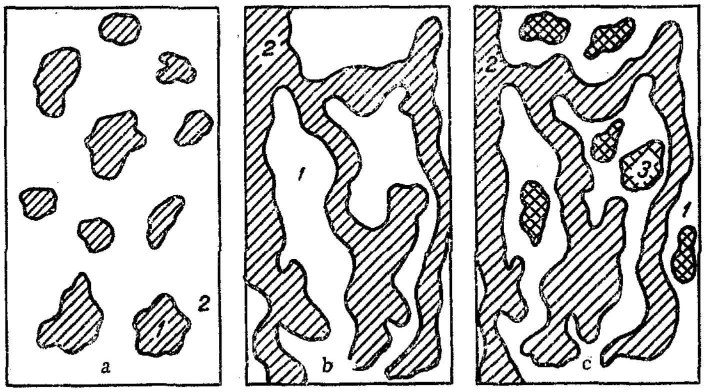

Fig. 1. Schematic two-dimensional representation of various structures: a) with closed inclusions; b) with interpenetrating components; c) combination of structures with closed and interpenetrating components; 1, 2, 3) numbers of the various components.

We will consider a structure with interpenetrating components which, in addition to continuity of the material of each component, possesses the following properties: isotropy, stability, and geometric equivalence of the components.

The property of isotropy is possessed by systems with components distributed either randomly (gas mixtures, liquid solutions, granular systems, etc.) or in an ordered arrangement.

We shall call a system stable if over a broad range of variation of component concentrations it does not lose mechanical equilibrium. The last property – geometric equivalence of the components – means that the effective value of the thermal conductivity is not affected by interchanging the positions of the components in the structure without disturbing their concentration. For example, for a binary system with component thermal conductivities λ_1 and λ_2 and concentrations m_1 and m_2 geometric equivalence implies

$$\lambda = f(\lambda_1, \lambda_2, m_1, m_2) = f(\lambda_2, \lambda_1, m_2, m_1). \tag{4}$$

This property is not possessed by a structure with closed inclusions (Fig. 1a); it is characteristic only of systems with interpenetrating components (Fig. 1b).

2. Method of Investigating Generalized Conductivities

In investigating transport processes in various structures the following basic assumption is made in explicit or implicit form:

a) The effective generalized conductivities of systems with ordered or random structures are equal if these structures are equivalent and the properties of the components and their volume concentrations are the same.

For systems with interpenetrating components equivalence of a random and an ordered structure means that they are characterized by isotropy, stability, and geometric equivalence of the components. A pair of random and ordered structures is shown two-dimensionally in Fig. 2a, b; the meaning of the individual circles in this figure is explained below.

The above assumption is of fundamental significance and determines the course of the subsequent investigation, since it permits any random system to be studied in terms of an ordered model, which considerably simplifies the mathematical description of the transport processes.

Assumption "a" is not, as generally supposed, based on experiment.

The effective thermal conductivity of a random structure is not affected if the specific "randomness" is replaced by some other equivalent random distribution. This follows from the very definition of a random or statistical system. The pattern shown in Fig. 2b is one possible structure of a random system. Although its probability is negligibly small, it is no less probable than any other random structure such as,

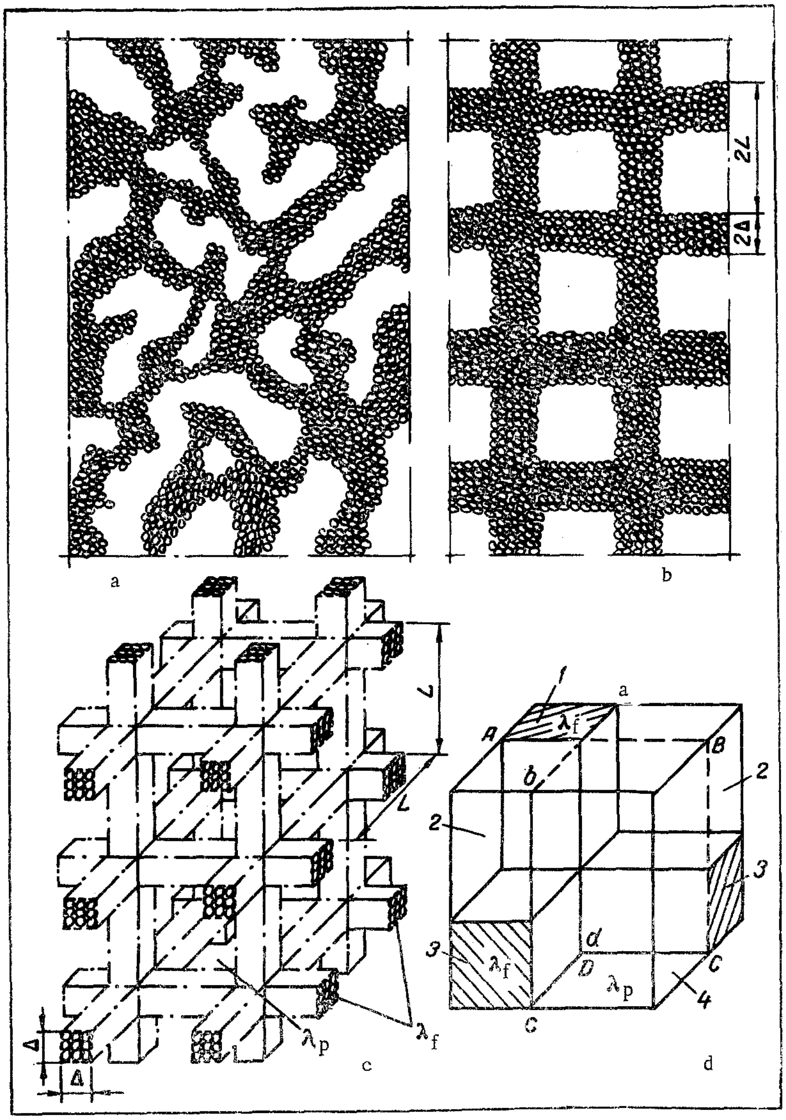

Fig. 2. Transition from a random structure with interpenetrating components (a) to two-dimensionally (b) and three-dimensionally (c) ordered structures and the unit cell (d); ABCD and abcd are adiabatic surfaces.

for example, the distribution shown in Fig. 2a. In other words, from the standpoint of the investigator an ordered structure is a particular case of a random structure and the effective transport properties will be the same if the conditions of equivalence are satisfied.* In this connection it is worth noting that for arbitrary structures there is a probability of a situation developing in which all the particles of one component are grouped in a certain region of space while the particles of the second component are grouped in another region of space. However, we shall not consider such cases, not owing to their improbability, but because such a structure is not equivalent to that represented in Fig. 2a (presence of anisotropy, geometric nonequivalence of the components).

If we conduct the subsequent investigation of the transport coefficients in terms of ordered models, then a second assumption becomes important:

b) The effective transport coefficient of a system with long-range order and that of its unit cell are the same.

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*This approach may seem peculiar owing to a certain psychological preconception, according to which randomness and order are always qualitatively different.

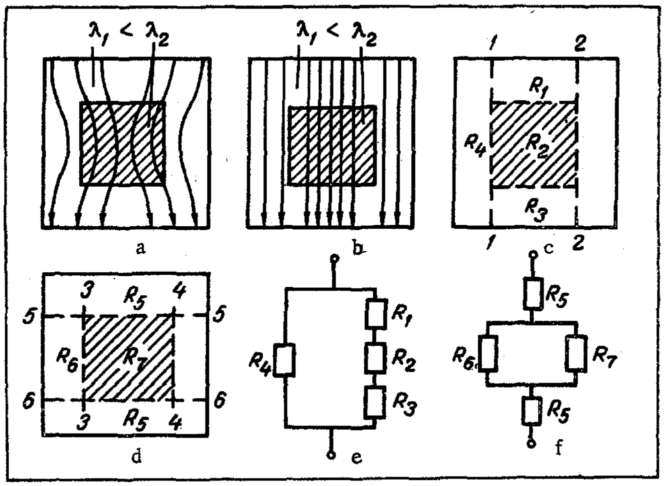

Fig. 3. Unit cell of structure with closed cubic inclusions: a) actual nature of the flow lines in the cell at $\lambda_2/\lambda_1 > 1$; b) approximate (linearized) representation of the flow lines; c, e) partition of the unit cell by adiabatic planes 1–1, 2–2, and thermal-resistance connection diagram; d, f) partition of unit cell by adiabatic 3–3, 4–4 and isothermal 5–5, 6–6 planes and thermal-resistance connection diagram.

We recall that the unit cell is the smallest volume element, by repeating which in a certain way it is possible to obtain the starting structure [7]. Consequently, the transport process can be studied in relation to the unit cell rather than over the entire volume, which considerably simplifies the subsequent investigation. Assumption "b" is amenable to rigorous proof.

In Figs. 2b and 2c an ordered structure with interpenetrating components is shown in two-dimensional and three-dimensional form; Fig. 2d is a representation of the unit cell.

A model of a structure with interpenetrating components was used as long ago as 1932 by Frey to investigate the electrical conductivity of binary eutectic alloys and porous systems filled with electrolyte [8]. In 1941, Franchuk [9] used a similar model to investigate the thermal conductivity of nonordered fibrous structures. In 1965, Dul'nev [10] used a model with interpenetrating components to determine the thermal conductivity of solids with communicating pores. We note that Frey, Franchuk, and Dul'nev arrived at their models from different starting points. Their unit cells, independently proposed, are different in form, but represent the same orthogonal three-dimensional cubic lattice. The mathematical description of the transport processes in the unit cell is usually approximate, which leads to different functional relations for the same cell. Sometimes the numerical results given by the different formulas differ markedly, which introduces some uncertainty. This is true, in particular, of the formulas proposed by Frey* and Dul'nev for the effective thermal conductivity of one and the same structure. Here we come to a very important point that requires closer consideration. We will explain the basic idea with reference to a simple system with closed inclusions. In early studies [1, 2, 11, 12] the curvature of the flow lines and isopotential surfaces (Fig. 3a) was taken into account. Typical in this respect is the work of Maxwell [1] and Rayleigh [2] at the end of the last century.

Subsequently, the flow lines were assumed to be approximately straight (Fig. 3b), which simplified the mathematical description of the investigated processes, but introduced a certain arbitrariness into the choice of the method of linearization of the flow lines or isopotential surfaces.

In order to linearize the flow in the unit cell it is partitioned by a system of auxiliary adiabatic or isothermal surfaces (or combinations of such surfaces) oriented in a certain way relative to the general flow direction. We will explain this with reference to a simple unit cell with closed cubic inclusions.

In Fig. 3c we show the unit cell partioned by auxiliary adiabatic surfaces 1–1, 2–2, which makes it possible to calculate the thermal resistances R_1, R_2, R_3, and R_4 of the individual parts of the cell from the

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*A similar relation was also obtained by Franchuk.

simple formulas for a plane wall. The way in which these resistances are connected is shown in Fig. 3e, from which the total resistance R of the entire cell can be calculated. This resistance can also be represented in the form $R = l/\lambda S$ and equated to the thermal resistance of the cell obtained above. After a series of transformations we obtain an analytic expression of the type (1) for the effective thermal conductivity of the structure. If the unit cell is partioned by adiabatic 3–3, 4–4 and isothermal 5–5, 6–6 surfaces (Fig. 3d), then the resistances themselves, the connection diagram (Fig. 3f), the form of the functional relation (1), and the calculated value of the effective thermal conductivity will be different. Partition by a system of adiabatic surfaces (Fig. 3c) leads to the minimum possible value $\lambda_{\min}$; partition by a combined system of isothermal and adiabatic surfaces (Fig. 3d) gives the maximum value of the effective thermal conductivity $\lambda_{\max}$ [13, 14].

It is necessary to establish the deviation of $\lambda_{\min}$ and $\lambda_{\max}$ from the true value and give preference to some particular method of linearization. Some investigators propose to take the average of $\lambda_{\min}$ and $\lambda_{\max}$ [14, 15], although any method of averaging introduces an element of arbitrariness.

In 1965, the author investigated the discrepancy between the results of calculations based on Odelevskii's formula* and data obtained by analog simulation. A comparison revealed that over a broad range of variation of the parameters λ_1, λ_2, and m the deviation of the calculations is not greater than 4%, which lies within the limits of instrumental error.

A more detailed investigation of this question was undertaken in 1966-1967 by Ivanov [13] using the USM-1 universal electric analog system. The principal conclusions of this study reduce to the following.

For adiabatic partition the value of λ for the unit cell differs from the true value by not more than 5% over a broad range of variation of the characteristic parameters; combined partition of the unit cell with a system of isothermal and adiabatic surfaces, as shown in Fig. 3d, gives a value of the effective thermal conductivity which in some cases differs from the true value by 150-200%.

An analysis of the results of [10, 13] shows that in all the cases considered adiabatic partition gives a good approximation of reality. We are not aware of any similar investigation of the unit cell of a structure with interpenetrating inclusions (Fig. 2c). However, the available experience in calculating the effective thermal conductivity of such structures for different methods of partioning the unit cell and comparison of the equations obtained with the experimental data clearly favor partioning the cell with adiabatic planes 1–1, 2–2 and ABCD, abcd, as shown in Figs. 2d and 3c. Accordingly, we can formulate the following proposition:

c) If for any reason it is not possible to describe accurately the curvature of the flow lines in the unit cell, then the latter should be partitioned by infinitely thin adiabatic surfaces parallel to the principal direction of heat flow in the cell.

In Fig. 2 we have reproduced the unit cell of a structure with interpenetrating components and show it partitioned by the adiabatic planes ABCD and abcd. The method described above was used in [10] to calculate the resistance of the individual regions of the cell and its total resistance and to find an analytic expression for the effective thermal conductivity λ of a binary system with interpenetrating components

$$\frac{\lambda}{\lambda_1} = c^2 \nu (1 - c)^2 + \frac{2\nu c + (1 - c)}{\nu c + 1 - c}, \quad \nu = \frac{\lambda_2}{\lambda_1}, \tag{5}$$

$$2c^3 - 3c^2 + 1 = m_2, \; m_1 = 1 - m_2. \tag{6}$$

Here, the subscripts 1 and 2 relate to the first and second components, while c is an auxiliary quantity uniquely determined by the volume concentration m_2. Of the three roots of Eq. (6) one is selected; a more detailed analysis of this equation is given in [10, 16, 17].

In investigating the transport process in a structure with interpenetrating components both Frey [8] and Franchuk [9] partitioned the unit cell by means of isothermal and adiabatic surfaces, which complicated the form of the expression for the effective thermal conductivity and led to considerably exaggerated theoretical values. Clearly, this explains why the model of a structure with interpenetrating components has been

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*V. I. Odelevskii has proposed a formula for calculating the generalized conductivity of a structure with closed cubic inclusions; in deriving his formula the author employed one of the methods of averaging $\lambda_{\min}$ and $\lambda_{\max}$ [14].

generally disregarded, although it was proposed almost forty years ago. All over the world investigators have continued to study different variants of structures with closed inclusions, although they correspond to a minority of natural and synthetic materials.

The above methods of calculating the effective thermal conductivity of binary systems can be extended to structures containing any number of both closed and interpenetrating components. For this purpose it is necessary to employ the method of successive reduction of the multicomponent mixture to a two-component mixture, whose thermophysical properties can be determined. For example, consider a structure consisting of three interpenetrating components.

Since in such a structure the components are geometrically equivalent, we may consider them in any order. First, having selected some pair of components (for example, 2–3), we determine their effective thermal conductivity from Eq. (5)

$$\lambda_{2-3} = f_1(\lambda_2,\ \lambda_3,\ m_2',\ m_3') \tag{7}$$

as the effective thermal conductivity of a mixture with interpenetrating inclusions and volume concentrations m_2' and m_3'. The latter are related with the starting concentrations by the expression [18]

$$m_2' = \frac{m_2}{m_2 + m_3},\quad m_3' = \frac{m_3}{m_2 + m_3}. \tag{8}$$

Returning to the starting structure, we assume that part of its volume corresponding to the concentration $m_{23} = m_2 + m_3$ is occupied by a continuous homogeneous isotropic material with thermal conductivity λ_{2-3}. The rest of the volume is occupied by material with thermal conductivity λ_1 and volume concentration m_1, i.e., the three-component system has been reduced to a two-component system and its thermal conductivity is then calculated from Eq. (5)

$$\lambda = f_2(\lambda_1,\ \lambda_{2-3},\ m_1,\ m_{23}). \tag{9}$$

A similar method is employed to analyze multicomponent mixtures with closed or combined inclusions [18]. Thus, we can now formulate the following proposition.

d) It is desirable to analyze the effective thermal conductivity of various structures with reference to binary systems, since a multicomponent system can usually be reduced to a two-component system.

3. Thermal Conductivity of Mixtures of Gases and Liquids

A gas mixture is a classical example of a homogeneous system with random structure. On the basis of assumption "a" above, the thermal conductivity of such a mixture can be investigated with reference to a model with ordered structure, if the latter is equivalent to the random pattern of distribution of the different gas molecules. These properties, as already mentioned, are possessed by a structure with interpenetrating components: the structure is isotropic, and the components are geometrically equivalent and uniformly distributed over the entire volume of the mixture. We note that relation (5), obtained for binary mixtures, can be applied only to mechanical mixtures, whereas the majority of gas mixtures are nonmechanical: the thermal conductivity of the components in the mixture may differ from that of the pure gas, which is attributable to a change in molecular mean free path when the gases are mixed. However, even in this case it is possible to employ Eq. (5) if we substitute for λ_1 and λ_2 the values of the thermal conductivities λ_1' and λ_2' of the components found for the mixture. For this purpose we can use the simple formulas [19]

$$\lambda_1' = \lambda_1 (m_1 + m_2 A_{12}')^{-1},\quad \lambda_2' = \lambda_2 (m_2 + m_1 A_{21}')^{-1}. \tag{10}$$

The values of the coefficients A_{12}' and A_{21}' are presented in [20]

$$A_{ij} = \frac{\gamma_{ij}}{\gamma_i}\left(\frac{\sigma}{\sigma_i}\right)^2\left(\frac{M_i + M_j}{2M_j}\right)^{1/2},\ i = 1,2,\ j = 1,2,$$

$$\gamma_i = 1 + \frac{S_i}{T},\ \gamma_j = 1 + \frac{S_j}{T},\ \gamma_{ij} = 1 + \frac{S_{ij}}{T}. \tag{11}$$

Here, S_i and S_j are Sutherland constants characterizing the intermolecular forces. The value of S_{ij} for a mixture of nonpolar gases is given by the expression [21] $S_{ij} = (S_iS_j)^{1/2}$, while for mixtures with polar components [20] $S_{ij} = 0.73\ (S_iS_j)^{1/2}$. The coefficients A_{ij}' can also be calculated from other more accurate expressions recently obtained. Let us consider the method of calculating the thermal conductivity of a binary gas mixture. From expressions (10) and (11) we determine the values of the thermal conductivity of the components in the mixture, i. e.,

$$\lambda_i' = f_3(\lambda_1, \lambda_2, m_1, m_2, \sigma_1, \sigma_2, S_1, S_2, M_1, M_2). \tag{12}$$

The values obtained for λ_1' and λ_2' are substituted in relation (5) for λ_1 and λ_2, respectively, and the effective thermal conductivity of the mixture is calculated:

$$\lambda = f_4(\lambda_1', \lambda_2', m_1, m_2).$$

The applicability of the proposed method has been tested by calculating λ for various mixtures of inert, polyatomic and polar gases over the entire range of variation of component concentration at temperatures from 273 to 1100°K.

An analysis of these results shows that the discrepancy between the calculated and experimental data does not exceed the error of experimental determination of the thermal conductivity of gas mixtures [19], i.e., on average 3-5%.

We will examine the possibility of using the model with interpenetrating components to calculate the thermal conductivity of another homogeneous system – a liquid solution. First of all, it is necessary to justify the representation of a liquid solution in the form of a mechanical mixture. To some extent this assumption can be based on an analysis of certain studies of the structure of solutions. Various hypotheses concerning liquid structure and, moreover, experimental studies of liquids and solutions suggest that unstable aggregations (complexes) of several thousands of molecules are formed in the liquid. Apparently, the thermal conductivities of these macrocomplexes remain constant and depend only slightly on the concentration of the components in the mixture. The existence of structural formations in solutions of associated liquids is even more probable [22-25].

If the liquid mixture is assumed to be mechanical, then it is expedient to calculate the thermal conductivity from Eq. (5) for binary solutions and from Eqs. (5)-(9) for multicomponent solutions. The applicability of the proposed model of liquid solutions has been established by comparing the theoretical and experimental values of the effective thermal conductivity of more than fifty different mixtures of normal and associated liquids; the mean deviation of the theoretical from the experimental data does not exceed 7% [16, 26].

4. Thermal Conductivity of Solid Porous Systems with Gaseous or Liquid Inclusions and Certain Alloys

The effective thermal conductivity of a solid with intercommunicating pores filled with a gas or liquid can also be determined with the aid of relation (5). If the solid skeleton itself is heterogeneous, i.e., has an inclusion in the form of communicating or closed components, then the thermal conductivity of the entire system can be calculated using the combination of equations (5)-(9). Certain difficulties arise in calculating the thermal conductivity λ_p of the gaseous inclusion, which consists of molecular λ_{pm} and radiative λ_{pr} components, i.e.,

$$\lambda_p = \lambda_{pm} + \lambda_{pr}. \tag{13}$$

The molecular conductivity can be calculated from the expression [27]

$$\lambda_{pm} = \frac{\lambda_0}{1 + B(H\delta)^{-1}}, \quad B = \frac{4k}{(1+k)\,\mathrm{Pr}_0} \cdot \frac{2-a}{a} H_0 \frac{\Lambda_\infty}{1 + \dfrac{S}{T}}. \tag{14}$$

Here, δ denotes the mean pore size.

If the skeleton material is nontransparent for radiation, and the porosity $m_p < 0.7$, then the radiative component λ_{pr} can be calculated from the expression [28]

$$\lambda_{pr} = 2\varepsilon^2 C_0 T^3 \delta, \ \mathrm{W/m \cdot deg}. \tag{15}$$

In systems with high porosity the gas represents most of the volume of the material and radiative heat transfer should be considered not only within the unit cell but throughout the thickness of the material. The justification for this approach is even greater if the solid skeleton is semitransparent for thermal radiation.

The heterogeneous system is represented in the form of a homogeneous isotropic medium with known characteristics – absorption and scattering coefficients; it is assumed that the external surfaces of the isotropic medium are parallel and isothermal. There have been numerous studies of radiative heat transfer through such a system [29-32]; we present certain results of these investigations.

In general, the radiation is attenuated by absorption and scattering on pore walls, particles, etc. The extinction coefficient is equal to the sum of the absorption and scattering coefficients

$$\beta = \alpha + \sigma_s. \tag{16}$$

For total absorption ($\sigma_s = 0$) $\beta = \alpha$. According to Poltz [32] the dependence of the radiative component on the absorption coefficient α, the temperature of the material T, the thickness l of the layer, and the emissivities $\varepsilon_1' = \varepsilon_2' = \varepsilon'$ of the surfaces bounding the layer is given by

$$\lambda_{pr} = \frac{16}{\lambda} \cdot \frac{C_0 T^3 Y}{\alpha}. \tag{17}$$

Here, $Y = Y(\varepsilon', \tau)$ denotes the functional relation presented and tabulated in [32].

In [29] an expression for the radiative component of the thermal conductivity is given for certain cases of attenuation caused by both absorption and scattering.

Thus, using Eqs. (13)-(17), we can calculate the thermal conductivity of the gaseous component in closed or communicating pores for various gas pressures over a broad range of temperatures. We will now consider the application of these relations to various heterogeneous systems.

In [33] values of the thermal conductivity calculated from Eqs. (5), (13)-(15) were compared with the experimental data for a group of structural and industrial materials: bricks of various kinds (pumice cement, slag, tripoli, silica, etc.) and concretes (foam concrete, slag concrete, aggregate concrete, etc.). Despite incomplete information on the properties of the components and the very complicated structure of the mechanical mixtures, the theoretical relations lead to results in satisfactory agreement with the experimental data of various authors.

In [4] the theoretical and experimental values of the thermal conductivity of chamotte refractories are compared on the temperature interval 80-1200°K. These ceramics form a multicomponent mixture: the skeleton consists of SiO_2 in the amorphous phase with inclusions of Al_2O_3 in the crystalline phase. The material is permeated by open pores, i.e., the solid and gaseous components form a system with interpenetrating components. In the experiments the pores were filled with helium, Freon-12, and air at a pressure of $(0.99-0.13) \cdot 10^5$ N/m^2. As shown in [4], the theoretical and experimental data are in satisfactory agreement.

Finally, the thermal conductivity of various liquid-filled porous solids has also been investigated: oil-bearing and water-bearing soils [5, 35], and systems composed of silica spheres and a liquid (benzene, ethanol, water, acetone) [36]. The results of calculating the effective thermal conductivity from Eq. (5) differed from the experimental data by on average 7%. In relation to the applicability of Eq. (5) to binary alloy mixtures, it was shown in [17] that the methods of investigation described above can be used to determine the thermal and electrical conductivity of alloys with components that are almost insoluble or have only limited solubility (eutectic alloys, alloy mixtures).

5. Thermal Conductivity of Dry Granular and Fibrous Materials

There have been numerous studies of heat transfer in granular systems and these are reviewed in [3, 4, 5, 35, 39, 40, 41]. Various authors have proposed different models of granular systems, which can be divided into two groups. The first group includes models that constitute a system of spheres, ellipsoids or cubes with a certain arrangement in space; the second group includes models based on a structure with interpenetrating components. An analysis of the models of the first group and the corresponding equations shows that they are not equivalent to actual granular systems, which have a random structure. As shown at the beginning of this article, a random structure possesses isotropy and stability, while the models of the first group lose stability at a porosity $m_p > 0.5$ (the spheres move apart and are, as it were, suspended in space). Moreover, none of the equations obtained on the basis of these models can express all the extreme cases (limiting values of the porosity and thermal conductivities) [37].

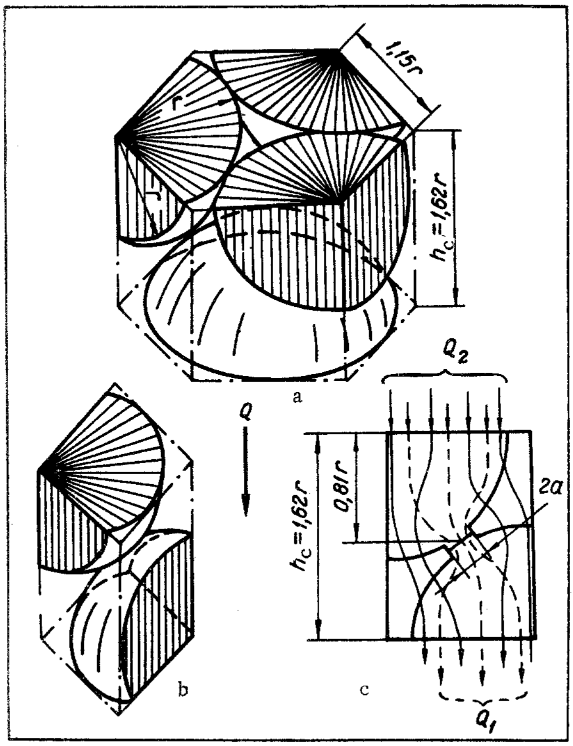

Fig. 4. Unit cell of the framework of a granular system. a) Unit cell in tetrahedral arrangement; b) third part of cell; c) flow lines through particle, contact spot, and gas gap.

The models of the second group possess isotropy and stability. The results of the first investigations of such models were published in [4, 42, 43].

As pointed out above, these models represent modifications of the structure with interpenetrating components: contractions are introduced into blocks of constant cross section. A model of this structure reflects an important property of granular systems – sharp contractions of the cross section of the solid component. The transport processes in such a model have been analyzed by the method described in section 2 and the following expression has been derived for the effective thermal conductivity [4, 43]

$$\frac{\lambda}{\lambda_s} = \left(\frac{1}{c^2} + A\right)^{-1} + \nu(1-c^2) + \frac{2\nu c(1-c)}{\nu c + 1 - c}, \quad \nu = \frac{\lambda_p}{\lambda_s}. \tag{18}$$

Here, λ_s and λ_p are the thermal conductivities of the grain and the gaseous component; the parameter A takes into account the thermal resistance of the gas between particles and, moreover, the curvature of the flow lines passing through the contraction and then spreading over the particle.

If we set A = 0, we go over to a block of constant cross section, and Eq. (18) takes the form (5). A shortcoming of these models [4, 43] is the rough schematization of the geometry of the gap between grains and the dependence of the grain shape on porosity. At high porosities ($m_p > 0.7$) the latter leads to distortion of the shape of the grains – they degenerate into thin crosses, which, of course, does not correspond to reality.

We will consider the first of these shortcomings in more detail. In [4] the gas gap in the contact zone is represented in the form of a gas wall with thickness equal to the height of the microroughness, i.e., approximately one thousandth of the grain diameter. It can be shown that the area-averaged thickness of the actual gap between spherical particles is approximately two orders greater. As our calculations have shown, underestimating the mean thickness of the gas gap should lead in certain cases to values of the effective thermal conductivity too high by a factor of two or more. Efforts to eliminate the principal disadvantages of the model described led, in 1969, to the development of a new stable model of granular systems [37]. The actual structure of a granular system is represented schematically in two dimensions in Fig. 2a. We note that the granular structure is determined by a "framework" consisting of a random, relatively dense arrangement of grains (first-order structure) and larger cavities that penetrate the framework and with it form a structure with interpenetrating components (second-order structure). This system possesses both isotropy and stability over the entire range of variation of porosity $0.26 \le m_p \le 1$.

On the basis of assumption "a" the thermal conductivity of the random system can be studied with reference to an ordered model (Fig. 2b); on the basis of assumption "b" it is expedient to analyze the transport process with reference to the unit cell (Fig. 2c); proposition "d" permits a structure of higher order to be reduced to first-order structure. Thus, using the methods described above, we can represent the effective thermal conductivity of a granular system with the aid of relation (5), which takes the form

$$\lambda = \lambda_f\left[c_2^2 + \nu_2(1-c_2)^2 + \frac{2\nu_2 c_2(1-c_2)}{\nu_2 c_2 + (1-c_2)}\right], \quad \nu_2 = \frac{\lambda_p}{\lambda_f},$$
$$m_{p_2} = 2c_2^3 - 3c_2^2 + 1, \quad m_{p_2} = (m_p - m_f)(1-m_f)^{-1}. \tag{19}$$

We note that relation (19) is capable of expressing all extreme cases. The calculation of the thermal conductivity λ_f of the framework is an independent problem. As already noted, the framework is composed of a relatively dense ($0.3 < m_f < 0.5$), random arrangement of particles of different size and arbitrary, but nonelongated, shape. The thermal conductivity of the framework has been analyzed by a method based on assumptions "a" and "b" (the framework is a system with long-range order composed of identical spherical particles in an isotropic tetrahedral arrangement). The unit cell is represented in the form of a right hexagonal prism described about a sphere of radius r with base area $S_c = 2\sqrt{3r^2}$ and height $h_c = 1.62r$ (Fig. 4a); owing to the axial symmetry the transport process can be investigated with reference to one third of the cell (Fig. 4b). In this cell it is necessary to take into account the curvature of the flow lines passing through the contact spot and the gas gap between particles (Fig. 4c). Special attention has been given to the method of determining the thermal resistance of the gas gap and the contact spot.

We shall omit the final expression for calculating λ_f, since it is given in [37]. We shall simply examine the method of calculating the thermal conductivity of the gas-filled pores. For this purpose it is possible to employ relation (13), in which the molecular component is found from Eq. (14). In this case different values of the pore dimensions δ are taken for the pores in the framework and those in the second-order structure.

The radiative component of the thermal conductivity in the first-order structure (framework) was determined from Eq. (15) and that in the second-order structure from (17). In this case we encounter an independent problem – the determination of the absorption coefficient α of the granular system. As shown in [44], in certain cases the latter can be determined analytically. The model of a structure with interpenetrating components gives a good description [44] of the heat-transfer process in dry fibrous systems (felt, fibrous insulating materials, etc.) over a broad range of variation of gas pressure at various material temperatures. The effective thermal conductivity of such systems can be calculated from Eqs. (5), (6). The molecular component λ_{pm} is calculated from Eq. (13). where the pore size δ is related with the fiber diameter D by the expression

$$\delta = 0.89\, D \left(\frac{1-c}{c^2} - 1\right). \tag{20}$$

The radiative component of the thermal conductivity of a fibrous system is determined from Eq. (17); if the radiation is completely absorbed by the fibers, the extinction coefficient α of the material can be estimated from the expression

$$\alpha = 2.26\, \frac{c^2(2-c)}{D},\ \mathrm{m}^{-1}. \tag{21}$$

In the presence of total or partial scattering of the radiation passing through the fibrous system the coefficient α can be estimated using the relations given in [44].

In conclusion we note that a comparison of the calculated and experimental values of λ for granular and fibrous systems over a broad range of variation of the characteristic parameters leads to satisfactory results.

Our analysis of the transport processes in heterogeneous and homogeneous systems leads us to the following conclusion: the model of a structure with interpenetrating components makes it possible to calculate the generalized conductivities of various solid, liquid, and gas mixtures by a unified method. Clearly, this does not exhaust the possibilities of the structure in question. It could possibly be used to find an analytic expression for the thermal conductivity of wetted systems and, moreover, certain nonmechanical mixtures (metal melts, solutions of salts and electrolytes, reacting gases, etc.). Naturally, this will require the further development of the model and a more detailed examination of the mechanism of the process.

NOTATION

Λ	is the generalized conductivity;
λ	is the effective thermal conductivity of the mixture;
λ_i and λ_i'	are the thermal conductivities of the initial i-th component and component i in the mixture;
λ_0	is the thermal conductivity of the gas under normal conditions;
λ_f, λ_p, and λ_s	are the thermal conductivities of the framework of a granular system, the pores, and the solid particles;
m_i	is the volume concentration of the i-th component;

m_p, m_{p2}, and m_f	are the total porosity of the granular system, and the volume concentrations of the gas component in the second-order structure and the framework;
σ_i and M_i	are the diameter and mass of the molecules of gas component i;
$k = c_p/c_v$	is the ratio of specific heats;
a	is the pore wall accomodation coefficient;
ε' and ε	are the emissivities of the external surfaces bounding the system and the particle surface;
Pr_0	is the Prandtl number under normal conditions;
H	is the filler-gas pressure;
Λ_∞	is the molecular mean free path at an infinitely high temperature;
S_i	is Sutherland's constant;
T	is the temperature of the material in °K;
$C_0 = 5.67 \cdot 10^8$ W/m · deg^4	is the Stefan–Boltzmann constant;
δ	is the mean pore size in the system;
β, α, and σ_s	are the radiation extinction coefficient and the absorption and scattering coefficients;
$\tau = \alpha l$	is the optical path length.

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