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METHOD AND CERTAIN RESULTS OF A SEMIEMPIRICAL DESCRIPTION

OF THE HEAT CONDUCTIVITY OF COMPOSITE MATERIALS

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A semiempirical method of describing the heat conductivity of composite materials is described. Examples are presented of its application to determine the heat conductivity of gas mixtures, solid-porous quartz materials, and aluminosilicate refractories.

The expression of the effective transport coefficients of heterogeneous systems in terms of the transport coefficients of the components is the main content of research by a large number of authors to whom references can be found in [1, 2].

Some new results which have successfully been obtained in a consideration of the heat transport in a heterogeneous material from the aspect of one of the known approaches

TABLE 1. Comparison of Results of Computing the Heat Conductivity of Binary Mixtures of Monatomic Gases by the Hirschfelder et al. Method [9] ($\lambda_{[9]}$, W/m·deg) and Formula (4) with the Constant $K_{1.2}$ (λ, W/m·deg)

| Mixture composition	Parameter	Volume light gas concentration				
		0,1	0,3	0,5	0,7	0,9
He — Ne	$\lambda_{[9]}$	0,05348	0,06553	0,08181	0,10390	0,13443
	λ	0,05381	0,06600	0,08181	0,10317	0,13357
	$\dfrac{\lambda_{[9]}-\lambda}{\lambda_{[9]}}\cdot 100\%$	0,620	0,710	0,00	—0,710	—0,640
He — Ar	»	0,02273	0,03533	0,05291	0,07899	0,12137
		0,02277	0,03539	0,05291	0,07883	0,12113
		0,160	0,170	0,00	—0,190	—0,200
He — Kr	»	0,01415	0,02616	0,04330	0,06970	0,11562
		0,01416	0,02617	0,04330	0,06967	0,11558
		0,033	0,033	0	—0,032	—0,032
He — Xe	»	0,00998	0,02061	0,03626	0,06159	0,10953
		0,00998	0,02061	0,03626	0,06155	0,10952
		0,013	0,004	0	—0,009	—0,012
Ne — Ar	»	0,01956	0,02384	0,02904	0,03549	0,04370
		0,01956	0,02384	0,02904	0,03549	0,04370
		0,0057	0,0072	0,00	—0,0075	—0,0071
Ne — Kr	»	0,01115	0,01539	0,02104	0,02891	0,04054
		0,01116	0,01541	0,02104	0,02888	0,04050
		0,094	0,108	0	—0,104	—0,106
Ne — Xe	»	0,00736	0,01116	0,01651	0,02458	0,03801
		0,00737	0,01117	0,01651	0,02453	0,03794
		0,140	0,150	0	—0,170	—0,180
Ar — Kr	»	0,00994	0,01118	0,01265	0,01439	0,01649
		0,00995	0,01119	0,01265	0,01438	0,01647
		0,110	0,130	0	—0,130	—0,110
Ar — Xe	»	0,00642	0,00782	0,00967	0,01213	0,01551
		0,00644	0,00785	0,00967	0,01208	0,01545
		0,330	0,410	0	—0,420	—0,370
Kr — Xe	»	0,00607	0,00660	0,00723	0,00799	0,00889
		0,00608	0,00661	0,00723	0,00798	0,00888
		0,100	0,120	0	—0,120	—0,110
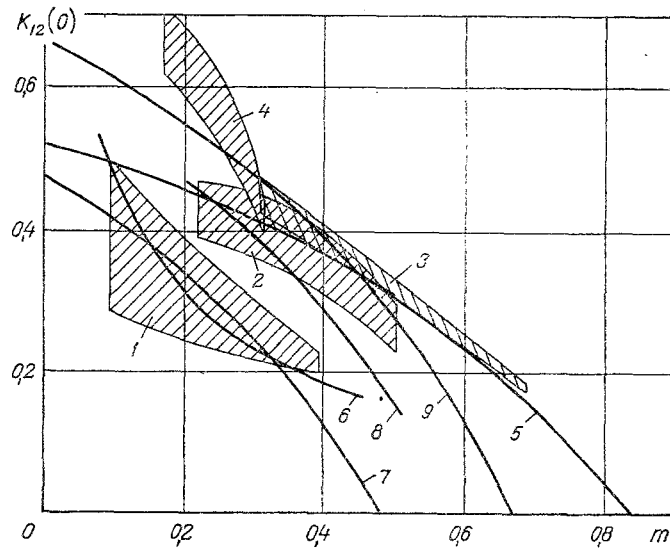
Fig. 1. Dependence of the coupling coefficient on porosity for metals and alloys: 1, 6) steel, bronze [11]; 2) iron [12]; 3) nickel [13]; 4) tungsten (the authors' results); 5) by the Dul'nev—Novikov formula [5]; 7) Misnar [7]; 8) L'vov [6]; 9) Odelevskii [1] (the field of data scatter is shaded, and the curves are the computation).

beginning with [3] are elucidated below. According to the Wiener definition, the effective heat conductivity of an isotropic composite material is related to the mean heat flux and mean temperature gradient by the relationship

$$\lambda_{ef} = -\frac{\dfrac{1}{V}\displaystyle\int_V q\,dV}{\dfrac{1}{V}\displaystyle\int_V \nabla T\,dV} = -\frac{\langle q \rangle}{\langle \nabla T \rangle}. \tag{1}$$

The components of the effective heat conductivity tensor in the direction of the principal axes of the anisotropic material are found analogously. Let us note that (1) is combined organically with the macroscopic equation of heat conductivity by giving it the transitional form of writing the average temperature [4], and as in the transport equation itself, is also meaningful only if under the conditions of the problem under consideration, an elementary macrovolume V whose dimensions greatly exceed the microinhomogeneity dimensions, while the location of the microinhomogeneities and the temperature distribution therein are statistically homogeneous in nature, can always be isolated around an arbitrary point.

Using the obvious relationship from [2] for the field function ψ:

$$\frac{1}{V}\int_V \psi\,dV = \frac{V_1}{V}\left(\frac{1}{V_1}\int_{V_1}\psi\,dV\right) + \frac{V_2}{V}\left(\frac{1}{V_2}\int_{V_2}\psi\,dV\right), \tag{2}$$

where V_1 and V_2 are parts of the averaging volume V with the components 1 and 2, $V = V_1 + V_2$, and introducing the volume concentrations of the components $c_i = V_i/V$ and the notation $\langle\psi\rangle_i = \dfrac{1}{V_i}\displaystyle\int_{V_i}\psi\,dV$, for the function components averaged with respect to the volume, we reduce (1)

to a form convenient for subsequent analysis

$$\lambda_{ef} = -\frac{c_1\langle q\rangle_1 + c_2\langle q\rangle_2}{c_1\langle \nabla T\rangle_1 + c_2\langle \nabla T\rangle_2}. \tag{3}$$
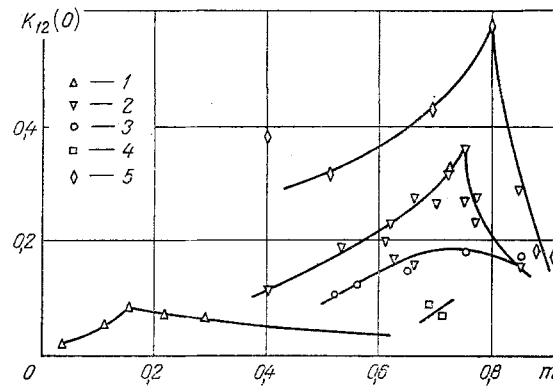
Fig. 2. Dependence of the coupling
coefficient on the porosity for ceram-
ic materials: 1) sandstone; 2)
chamotte; 3) high-argillaceous light-
weights; 4) corundum (by the method
of burning up additives); 5) corundum
foam; the curves are smoothed values.

For the case when the heat flux at each point of the composite material is related to
the temperature gradient by the Fourier law $q_i = -\lambda_i \nabla T$ (λ_i equals λ_1 or λ_2, respectively,
in the components 1 and 2), the expression (3) becomes

$$\lambda_{ef} = \frac{c_1\lambda_1 \langle \nabla T \rangle_1 + c_2\lambda_2 \langle \nabla T \rangle_2}{c_1 \langle \nabla T \rangle_1 + c_2 \langle \nabla T \rangle_2} = \frac{c_1\lambda_1 K_{12} + c_2\lambda_2}{c_1 K_{12} + c_2},$$ (4)

where $K_{12} = \langle \nabla T \rangle_1 / \langle \nabla T \rangle_2$ ($K_{21} = 1/K_{12}$ could also be introduced, or, $K_1 = \langle \nabla T \rangle_1 / \langle \nabla T \rangle$ or $K_2 = \langle \nabla T \rangle_2 / \langle \nabla T \rangle$ as in [2], however, the introduction of K_{12} (K_{21}) affords definite advantages, as
will be seen later).

As is noted in [5], additional information is necessary to determine λ_{ef} by means of
(4), where information about the structure (topology) of the heterogeneous system is used in
known extensions, which permit closure of the system under consideration. However, a descrip-
tion of the effective heat conductivity is obtained successfully by such a method for only
a limited quantity of model structures [1, 2].

A number of authors use a purely empirical approach to describe the effective heat con-
ductivity of composite materials, which permits obtaining satisfactory approximate depen-
dences for certain investigated groups of materials [6, 7].

The method proposed provides for seeking the dependences of the function K_{12} (or K_{21})
by using test data and a number of its proven properties with a subsequent computation of
the effective heat conductivity by means of (4). Being semiempirical, the method permits
obtaining the desired description of the effective heat conductivity of composite materials
of arbitrary structure with reliance on a minimum of test data.

The function K_{12} expressed from (4) hence enters as a similarity number to be deter-
mined since it contains the desired quantity λ_{ef}:

$$K_{12} = \frac{\lambda_{ef} - \lambda_2}{\lambda_1 - \lambda_{ef}} \cdot \frac{c_2}{c_1}.$$ (5)

It is known that the limit values of the heat conductivity of a composite material are
the maximum and minimum heat conductivities for a structure of alternating interlayers. The
corresponding boundaries for K_{12} are given by the relationships

$$K_{12\,max} = 1, \quad K_{12\,min} = \lambda_2/\lambda_1$$ (6)

and are independent of the component concentrations. Therefore, the domains of possible
values of the heat conductivity of composite materials are combined in the coordinates
$[K_{12}, \nu = \lambda_2/\lambda_1]$ independently of the component concentrations.
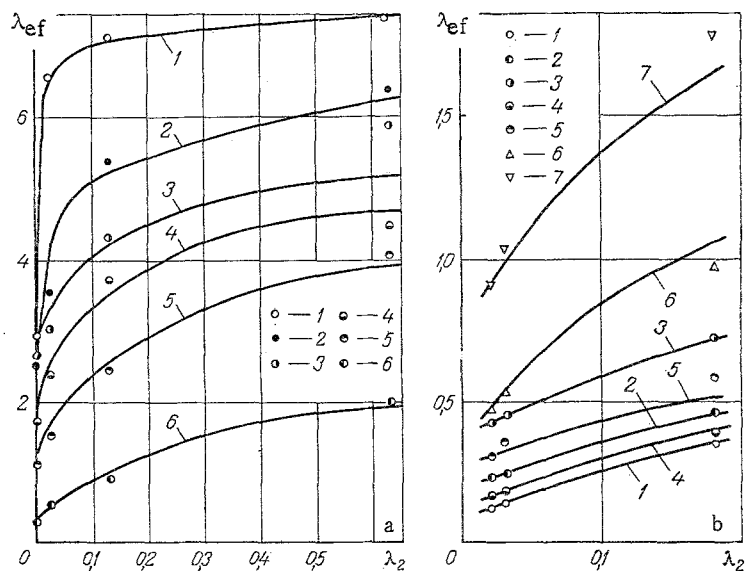
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Fig. 3. Comparison of experimental data on heat conductivity: a) sandstones [14] [1) $m = 0.03$; 2) 0.11; 3) 0.155; 4) 0.22; 5) 0.29; 6) 0.59]; b) refractories [18] (1 — ShLB-0.4; 2 — ShTL-0.6; 3 — ShLB-1; 4 — VGLDS-0.5; 5 — VGLDS-0.7; 6 — VGL-1.3; 7 — KORL-1.3) with (4) and (11) taken into account; the points are experiment and the curves a computation; λ, W/m·deg.

Let us note that the above-mentioned functions K_1 and K_2 turn out to be dependent on the component concentrations for the limit structures, hence their analysis yields nothing new versus the direct consideration of λ_{ef}.

Presented below are examples of applying the approach proposed to the description of the heat conductivity of binary systems, from which it follows that certain aspects can, in a number of cases, turn out to be a convenient supplement to existing methods, e.g., in the selection of appropriate models or formulas for a specific material.

1. Although the theory presented above has a rigorous foundation only for inhomogeneous materials with quite definite boundaries between the components, the first practical application of the method proposed is for a description of the heat conductivity of binary gas mixtures [8]. Without going into a polemic on the applicability of the structural approach to gas mixtures, let us note one curious fact: it turns out that the quantity K_{12} is practically independent of the component concentrations for mixtures of monatomic gases. Results of a computation of the heat conductivity of binary monatomic gas mixtures by means of (4) are presented in the table for a constant value of K_{12} calculated for the concentrations $c_1 = c_2 = 0.5$, and also for computations by the method of Hirschfelder et al. [9]. As follows from their comparison, the discrepancy does not exceed 1% in the worst case, and therefore, is within the limits of accuracy of the method of Hirschfelder et al. The result obtained above indicates the generalizing nature of the number K_{12} even in this case, in addition to the practical convenience of converting from the known heat conductivity of a mixture of one composition to an arbitrary concentration. As follows from [10], for a mixture of given composition the quantity K_{12} is practically independent of the mixture temperature.

2. Values of the functions K_{12} and K_{21} for zero conductivity of the second and first components, respectively, are determined just by the structure of the composite material and are an interesting characteristic that has the meaning of a dimensionless degree of coupling of the conducting components. An analysis of the data for a large number of isotropic materials permitted the clarification of the correlation coupling for them:

$$K_{12}(\lambda_2 = 0) + K_{21}(\lambda_1 = 0) = 0.4 - 0.67, \tag{7}$$

which has the obvious physical meaning: an increase in the degree of coupling of one component involves diminution in the degree of coupling of the other. The introduction of

the component coupling coefficients permits analysis of the structure of real materials. Test values of the coupling coefficients for porous metals as well as curves for the variation of the coupling coefficients of a skeleton which was computed by means of [6, 7, 11–13] are presented in Fig. 1.

The physically founded tendency in porous metals to an increase in the skeleton coupling coefficient with the diminution in porosity should be noted. The significant width of the domain of their coupling coefficients is explained by the difference in structure because of technological features in obtaining specimens by the conditions of pressure, temperature, and time of sintering. Hence, despite the fact that each of the computational formulas satisfactorily describes a definite group of investigated materials, none is suitable for the extension of the heat conductivity of all the presented porous materials.

At the same time, it follows from Fig. 1 that knowledge of the coupling coefficient of a specific material will, in principle, permit the selection of that formula from the set of those known that would assure the best description for the heat conductivity of this material under any combinations of the heat conductivity of the components. Presented in Fig. 2 are experimental results on the coupling coefficients for groups of sandstones [14] and aluminosilicate refractories [15–18]. Attention is turned to the test-data behavior for ceramic materials, which differs from the case of porous metals, viz., the nonmonotonic nature of the dependence of $K_{12}(0)$ on m. This can be explained by the developing fracturing of the skeleton during diminution of the material porosity (the diminution of $K_{12}(0)$ for $m < 0.75$ for refractories). The presence of high fracturing in the skeleton of materials with a large crystalline phase content can also explains the stratification for refractories of different chemical composition, obtained by the method of burning up additives (the diminution in $k_{12}(0)$ as the Al_2O_3 content increases). At the same time, the essential dependence of the coupling coefficient on the fabrication technology is seen in the example of the corundum refractory materials obtained by different methods. The large spread in $K_{12}(0)$ for the chamotte refractories is also evidently associated with the individual specimen fabrication technology features.

Therefore, processing the test data in the form of coupling coefficients permits clarification of the specific structural features of different materials and taking account of them in the description of the effective heat conductivity.

3. The dependence $K_{12}(\nu)$ is a monotonically increasing function of the argument ν, and the following properties which govern its behavior for $\nu = 1$ can be proved rigorously:

$$K_{12}(1) = 1; \quad \frac{\partial K_{12,x}}{\partial \nu}(1) + \frac{\partial K_{12,y}}{\partial \nu}(1) + \frac{\partial K_{12,z}}{\partial \nu}(1) = 1, \tag{8}$$

where $K_{12,x}$, $K_{12,y}$, $K_{12,z}$ are components of the tensor K_{12} in the directions of the principal anisotropy axes. In particular, from (8) there follows for an isotropic material

$$\frac{\partial K_{12}}{\partial \nu}(1) = \frac{1}{3}. \tag{9}$$

Furthermore, if two parameters governing the value of $K_{12}(\nu)$ on the boundaries of the domain of variation of ν, $K_0 = K_{12}(0)$ and $K_\infty = K_{12}(\infty)$, are introduced, then by taking account of the properties (8) and (9) we can try to select a four-parameter approximate formula for the dependence $K(\nu) = K_{12}(\nu)$. In particular, by taking into account that $K(\nu)$ can be represented in the form of the quotient of two infinite power series

$$K(\nu) = \frac{a_0 + a_1\nu + a_2\nu^2 + \cdots}{b_0 + b_1\nu + b_2\nu^2 + \cdots}, \tag{10}$$

we obtain the following approximate formula:

$$K(\nu) = K_0 \left[\frac{1 + \dfrac{1 - K_0^{1/n}}{K_\infty^{1/n} - 1} \left(\dfrac{K_\infty}{K_0} \right)^{1/n} \nu}{1 + \dfrac{1 - K_0^{1/n}}{K_\infty^{1/n} - 1} \nu} \right]^n, \tag{11}$$

by imposing an additional condition on the coefficients a_p, b_p, e.g., by taking them as binomial coefficients, where the exponent n is determined from the equation

$$n = \frac{\partial K_{12,i}}{\partial v} \quad (1) \quad \frac{K_\infty^{1/n} - K_0^{1/n}}{(1 - K_0^{1/n})(K_\infty^{1/n} - 1)}. \tag{12}$$

The experimental data on the effective heat conductivity on sandstones [14] and aluminosilicate refractories [18] are compared in different media in Figs. 3a and b with a computation by means of (4) using the approximation (11). In connection with the lack of experimental values of K_∞ it was assumed $K_\infty = 2.5$ in the computation with (7) taken into account.

The quantity K_0 for sandstones was computed from experimental values of λ_{ef} in a vacuum, and for the aluminosilicates from experimental data for filling the pores with argon. The rms deviation of the computed and experimental data for 45 points was 6.2%.

Therefore, as follows from the examples presented, the semiempirical method proposed to describe the effective heat conductivity of composite materials can turn out to be useful in solving applied problems.

NOTATION

V, averaging volume; T, temperature; q, heat flux; λ_{ef}, λ_1, λ_2, effective, and first and second component heat conductivities; c, volume component concentration; $v = \lambda_2/\lambda_1$, relative heat conductivity of the component; K_{12}, similarity number to be determined; $K_{12}(0)$, $K_{21}(0)$, coupling coefficients of the conducting components; K_0, K_∞, values of K_{12} for $v = 0$ and $v = \infty$.

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SELECTION OF THE OPTIMAL QUANTITY OF INITIAL DATA

AND THE NUMBER OF COEFFICIENTS IN COMPILING EQUATIONS

TO COMPUTE THE THERMOPHYSICAL PROPERTIES OF SUBSTANCES

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The question of limiting the quantity of data used in compiling the equations to
compute the thermophysical properties of substances is investigated, and a method
to optimize the number of coefficients therein is developed.

The use of an electronic computer permits compilation of multiconstant equations of
state and equations of the transport properties by numerous experimental data. However, an
increase in the volume of the data being used and in the number of coefficients does not
always by far contribute to a rise in the accuracy of the equations. This is explained by
calculational instabilities which occur in the solution of the appropriate system of high-
order normal equations. The use of duplicate data in the formation of such a system can
degrade its specificity. It is hence expedient to consider the question of a logical con-
straint on the volume of test data and the number of coefficients of the empirical equations.

Finding the optimal number of test points needed for a reliable description of a sur-
face, and the density of their distribution on this surface requires the solution, in prin-
ciple, of a very complex problem of the calculus of variations. Sufficiently general results
can also be obtained by performing computations on reliable data for a well-studied substance,
by using an electronic computer.

Initially, the possibility of limiting the number of p, v, T data in the compilation of
the equation of state of a fluid whose thermodynamic surface is sufficiently simple was
investigated [1]. To do this, a number of equations of state of water were compiled on the
basis of a different number of tabulated data [2]. The array of initial data was separated
into a number of groups, each of which included practically the whole surface being described.
The number of groups being used was successively reduced in compiling the different equations
of state, but a comparison was performed for the total array. A reduction in the number of
points taking part in compilation of the equation from 882 to 55 contributed to a twofold
reduction in the rms error of the description of the whole array.

The results in [1] were confirmed in a compilation of a single equation of state for
water and steam for the 273–1073°K temperature range and pressures to 100 MPa. To approxi-
mate actual conditions in the machine experiment, random errors, normally distributed within
±0.10% limits, were inserted in the tabulated values of the specific volume at this stage
of the investigation.

Besides the comparison with thermal data, the influence of curtailing the number of
p, v, T data being used on the accuracy of describing the derivatives $(\partial p/\partial v)_T$, $(\partial p/\partial T)_v$
and the specific heat C_v was estimated by comparing the appropriate computed values and the
data in [3, 4]. As in computations with the tabulated data, cutting down the number of
"test" points used contributes to a rise in the accuracy of describing the initial data
array (Fig. 1). The optimal accuracy is achieved in compiling equations on the basis of 816