

THE PREDICTION OF THE THERMAL CONDUCTIVITY OF TWO AND THREE PHASE SOLID HETEROGENEOUS MIXTURES

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(Received 19 January 1968 and in revised form 12 June 1968)

Abstract—A theoretical technique to predict the thermal conductivity of heterogeneous solid mixtures has been developed. Tsao's model for predicting the thermal conductivity of two phase solid mixtures has been modified and extended. The technique of this paper does not require experimental data on the mean and standard deviations of the one dimensional porosity function describing the distribution of the discontinuous phase as is the case with Tsao's model. A parabolic distribution of the discontinuous phase is assumed and the constants of the parabolic distribution are determined by analysis and presented as a function of the discontinuous phase volume fraction. Thus, the need for values of the mean and standard deviations is circumvented. The equivalent thermal conductivity of a unit cube of the mixture is derived in terms of the distribution function, and the thermal conductivity of the constituents. The technique is shown to predict thermal conductivity values within 8 per cent of available experimental data.

NOMENCLATURE

- B , constant in equation (5);
 b , distance between the vertex and the edge of the square in Fig. 3 [ft or cm];
 C , constant in equation (5);
 C' , negative value of C ;
 $C_{1,}$ constant in equation (3);
 $C_{2,}$ constant in equation (3);
 d , diameter of pore [cm];
 e , emissivity;
 k , thermal conductivity [Btu/h ft °F or cal/s cm °C];
 n , $3/\psi$;
 P , phase volume fractions;
 $P_{1,}$ one dimensional porosity [ft⁻¹];
 $P_{2,}$ two dimensional porosity;
 $P_{3,}$ bulk porosity;
 $P_{cs,}$ cross-sectional pore fraction;
 $P_{j,}$ longitudinal pore fraction;
 R , thermal resistance [h °F/Btu];
 T , absolute temperature [°R or °K].

Greek symbols

- γ , geometrical pore factor;
 δ , a value used in Fig. 3 [ft];
 μ , mean of P_1 [ft⁻¹];
 σ , standard deviation of P_1 [ft⁻¹];
 σ' , radiation constant [erg/cm² s °C⁴];
 ψ , sphericity.

Subscripts

- c , continuous phase;
 d , discontinuous phase;
 e , equivalent;
 i , number of phase;
 m , mean;
 s , solid.

INTRODUCTION

A NUMBER of studies [1-10] have been conducted to develop techniques for predicting the thermal conductivity of heterogeneous systems. So far, no general equation exists to predict the thermal conductivity of two-phase mixtures. Tsao [11] has developed a relationship as seen in the Appendix for predicting the thermal conduc-

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tivity of two-phase materials; however, experimental data are necessary before values of conductivity can be calculated. These experimentally determined data are the conductivity of the constituents and μ and σ , the mean and standard deviation of a "one dimensional porosity" P_1 , which relate P_1 to a "two dimensional porosity", P_2 . However, it should be emphasized that μ and σ are difficult to obtain. The product of P_1 and P_2 equals P_3 , the bulk porosity. P_1 and P_2 were developed to overcome the inadequacy of characterizing the material by the bulk porosity, P_3 . Tsao demonstrated this inadequacy by showing that using the bulk porosity in the two simplest heterogeneous models—series or parallel arrangements of the constituents—for effective thermal conductivity produced different values of thermal conductivity for a given case. Tsao developed a relation for P_2 in terms of P_1 using probabilistic theory and then using the additivity of conductances in parallel developed a relation for the effective thermal conductivity of the mixture in terms of P_1 , μ , σ and the thermal conductivity of the constituents.

This study which extends Tsao's model circumvents the necessity of experimentally determining μ and σ since these data are not required. The proposed technique is based on assuming a parabolic distribution of the discontinuous phase in the continuous phase. The parabolic distribution is expressed in terms of constants dependent on the proportions of the constituents. Analysis yields values of these constants as a function of the constituent proportions. A unit cube of the mixture is divided into differential elements perpendicular to the assumed unidirectional heat flow. Each element contains some of the continuous and the discontinuous phases. An expression for equivalent thermal resistance is derived for the cube on the basis of the analogy between heat and electrical flow. This expression is in terms of the constants of the parabola and thermal conductivity of the constituents. Thus the only requirements for predicting the equivalent

conductivity of the mixture using the model are the conductivities and proportions of the constituents. The proposed model is extended further to predict the thermal conductivity of three and multiphase mixtures for certain cases. The prediction technique is supported by experimental data. Figure 1 classifies heterogeneous systems and indicates the area of concentration of this study.

RELATED STUDIES

Maxwell [12] pioneered in the study of the thermal conductivity of two-phase mixtures. He derived an equation to predict conductivity on the basis of potential theory. Rayleigh [13] in 1892 derived a series solution for heat conduction through a square array of uniform sized spheres. Fricke [14] extended Maxwell's analysis and derived an equation for ellipsoids suspended in a continuous phase. Niescl [15] developed an equation to predict the thermal conductivity of solid mixtures containing randomly-oriented, long, thin cylindrical dispersed particles. Bruggeman [16] also developed a relation for thermal conductivity of platelets in continuous phase. Powers [17] utilized Ohm's law for parallel and series orientations of the continuous and discontinuous phases. Hamilton [18, 19] classified mixtures into four groups.

$$\text{Class I. } k_c \gg k_d \text{ or } \frac{k_c}{k_d} > 100;$$

$$\text{Class II. } k_c \ll k_d \text{ or } \frac{k_d}{k_c} > 100;$$

$$\text{Class III. } 1 < \frac{k_c}{k_d} < 100;$$

$$\text{Class IV. } 1 < \frac{k_d}{k_c} < 100.$$

He was mainly concerned with Class II mixtures since Class I, III and IV mixtures are amenable to Maxwell's equation. Hamilton accounted for the shape of the dispersed phase in his technique for predicting thermal conductivity.

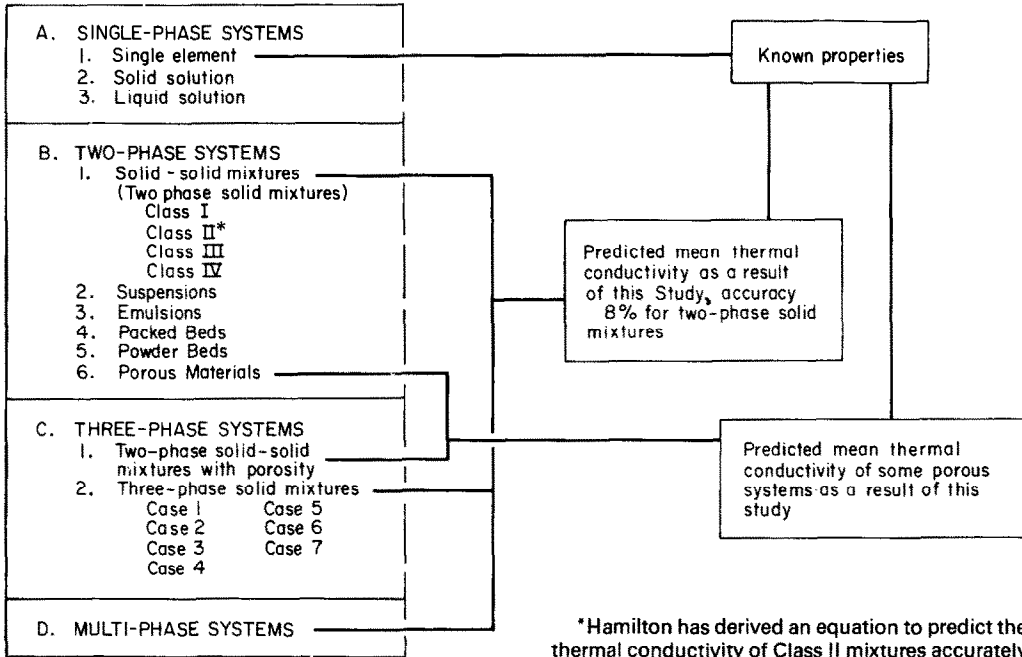


FIG. 1. Classification of heterogeneous systems and systems investigated in this study.

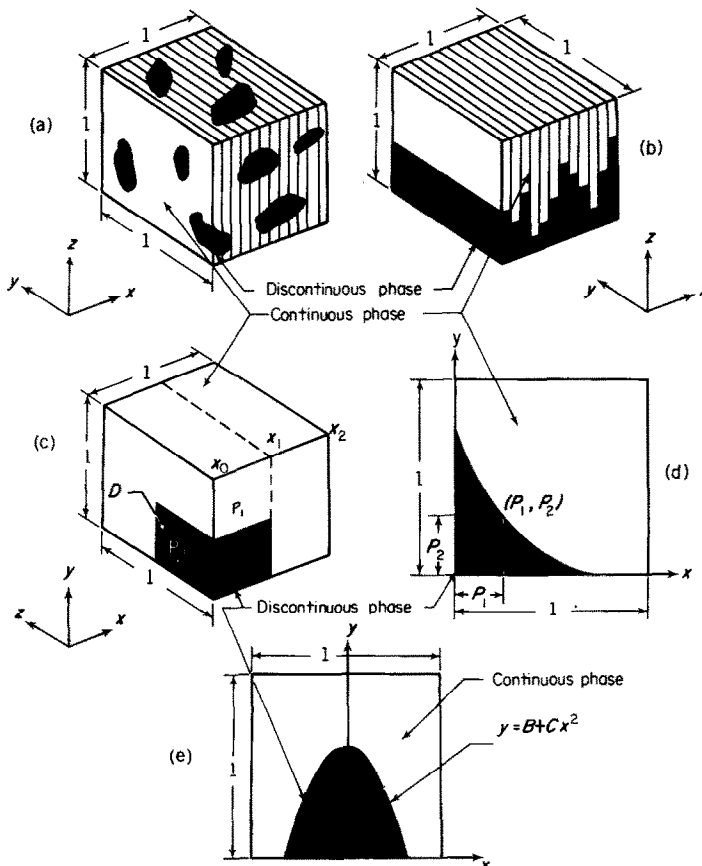


FIG. 2. Model for the study of the thermal conductivity of two-phase mixtures [11]

Hamilton also developed an equation for a mixture of n phases for known shapes of the discontinuous phase. Francl and Kingery [20] present an acceptable correlation for the prediction of the thermal conductivity of porous materials which can be extended to three phase materials for low temperatures—low enough to neglect radiation. Loeb [21] has attempted to compensate for radiation effects. Tsao's study, which has been cited, appeared to offer the greatest possibility for a general approach to predicting thermal conductivity of two phase mixtures and Tsao's study serves as the basis for this paper.

The Appendix gives some of the various equations presented in the literature to predict thermal conductivity of mixtures. References [1, 11, 12, 17–21] compare the equations and discuss their applicability. The literature reveals no general technique to predict the thermal conductivity of two-phase mixtures.

ANALYSIS

Two-phase mixtures

The analysis is based on the following assumptions for a unit cube of the mixture as seen in Fig. 2(a). These assumptions are:

1. The heat flux is unidirectional in the x direction;
2. Thermal convection and radiation are negligible;
3. Contact resistance between the continuous and discontinuous phase is negligible;
4. No porosity exists in the mixture;
5. The discontinuous phase is uniformly dispersed in the continuous phase;
6. Thermally, the mixture is isotropic;
7. In the mechanical mixing process, no chemical reaction occurs.

The approach of Tsao is used. A unit cube of the mixture as shown in Fig. 2(a) is sliced into many layers of width dx parallel to the yz -plane. Phase _{d} of each layer is arranged as shown in Fig. 2(b) since conductances in parallel are additive and the effective thermal

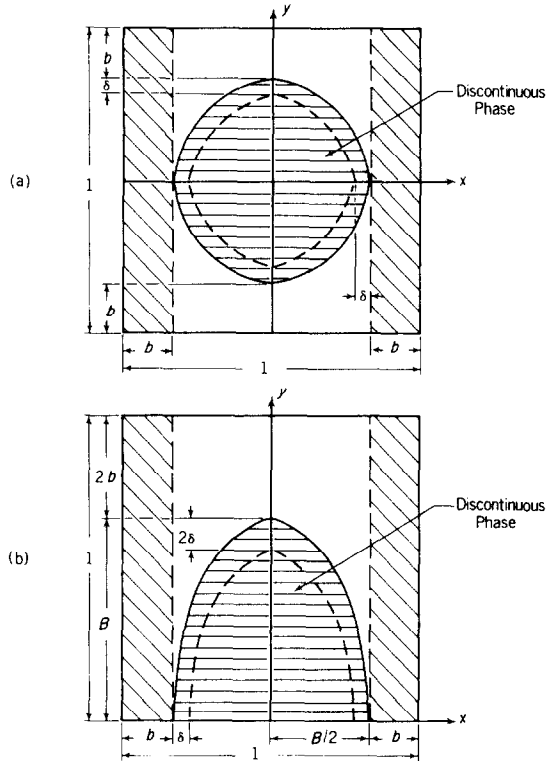


FIG. 3. Phase distribution for a two-phase mixture as represented by: (a) the x -axis bisecting the square (b) the x -axis coinciding with the lower border of the square. This figure is used in conjunction with equation (6).

conductivity is unaltered. Figure 2(c) is shown to fully explain P_1 and P_2 . The discontinuous phase is pictured as concentrated in one quadrant of the cube. Then

$$P_1 = \frac{x_0 - x_1}{\text{unit length}}$$

and

$$P_2 = \frac{\text{area of } D}{\text{unit area}}$$

Thus $P_3 = P_1 P_2$. Now instead of arranging the thin layers in the sequence as indicated in Fig. 2(d) as Tsao did, one can arrange these layers as shown in Fig. 2(e). Thus one can now attempt to develop an expression for the thermal conductivity in terms of $y(x)$ which is $P_2(P_1)$ and then determine $y(x)$ for various proportions of the constituents. It can be

shown that the equivalent thermal resistance of the configuration shown in Fig. 2(e) is

$$R_e = 2 \int_0^{\frac{1}{2}} \frac{dx}{k_c + (k_d - k_c)y} + \frac{1 - 2x}{k_c}, \quad (1)$$

which can be used to obtain the thermal conductivity since

$$k_m = \frac{1}{R_e}. \quad (2)$$

k_d and k_c are considered known, but $y(x)$ is unknown. If y is known, k_m can be calculated. It is first assumed that $P_2(P_1)$ or $y(x)$, the dispersion of the discontinuous phase which represents the discontinuous volume fraction is a normal distribution curve due to the assumed randomness of dispersion of the discontinuous phase in the continuous phase. Thus

$$y = C_1 \exp(-C_2 x^2). \quad (3)$$

Now C_1 and C_2 are almost impossible to determine unless the expression is expanded in a series such as

$$y = C_1 \left(1 - C_2 x^2 + \frac{C_2^2 x^4}{2!} - \dots \right). \quad (4)$$

The range of x can be seen to vary from $-\frac{1}{2}$ to $\frac{1}{2}$ for the coordinate system of Fig. 2(e). The above series converges rapidly for all x between $-\frac{1}{2}$ and $\frac{1}{2}$; consequently, one may eliminate all terms except the first two and

$$y = B + Cx^2. \quad (5)$$

Thus, the normal distribution has been reduced to a parabolic function. It can be seen that there will be a set of constants B and C for each discontinuous volume fraction, P_d , and consequently a given function $y(x)$ or $P_2(P_1)$ for equation (1). Thus, one can simplify the calculations involved in equation (1) by evaluating B and C values as a function of P_d since the discontinuous volume fraction would be a

known value for a given two-phase mixture. Now

$$P_d = 2 \int_0^{\frac{1}{2}} y \, dx.$$

The problem now resolves to evaluating the constants B and C for the limiting and intervening conditions and the corresponding P_d values. First assume boundary conditions as

$$y = 1 \quad \text{at} \quad x = 0$$

and

$$y = 0 \quad \text{at} \quad x = \frac{1}{2}$$

which represent the maximum discontinuous volume fraction. Equation (5) is an even function of x ; hence only positive values of x , i.e. $0 \leq x \leq \frac{1}{2}$ need be considered. Using the above stated boundary conditions one obtains

$$B = 1$$

and

$$C = -4$$

Now P_d , the discontinuous phase, is calculated to be 0.667 which is the maximum discontinuous phase volume fraction which equation (5) can represent.

The boundary conditions will change as P_d decreases from the maximum value. Thus for P_d less than 0.667, the general conditions are

$$y = B + Cx^2 \quad |x| \leq a < \frac{1}{2}$$

$$y = 0 \quad \text{at} \quad a \leq |x| \leq \frac{1}{2}$$

and

$$y < 1 \quad \text{at} \quad x = 0.$$

Other boundary conditions can be visualized by considering the distribution of the discontinuous in the continuous phase as shown in Figs. 3(a) and 3(b). Figure 3(a) pictures the discontinuous phase to be centred in the square. The boundary of the discontinuous phase is symmetrical with respect to the x and y axes. For simplicity, the assumption is made that

the distances, b , between the vertices of the boundary of the discontinuous phase and the edges of the squares are equal. The x axis is shifted to coincide with the lower edge of the square in Fig. 3(b). Thus Fig. 2(e) and Fig. 3(b) are the same. It is assumed further in Fig. 3 that as P_d decreases from its maximum value (0.667), the absolute value of y at $x = 0$ shrinks

and

$$C = -4\sqrt{\frac{2}{3}P_d}. \tag{6b}$$

B and C are plotted in Fig. 4 as functions of P_d .

The two-phase mixture is reduced to the limiting case of one-phase when $y = 0$ at $x = 0$ and $P_d = 0$. Now attention can be focused on equation (1). Substituting equation

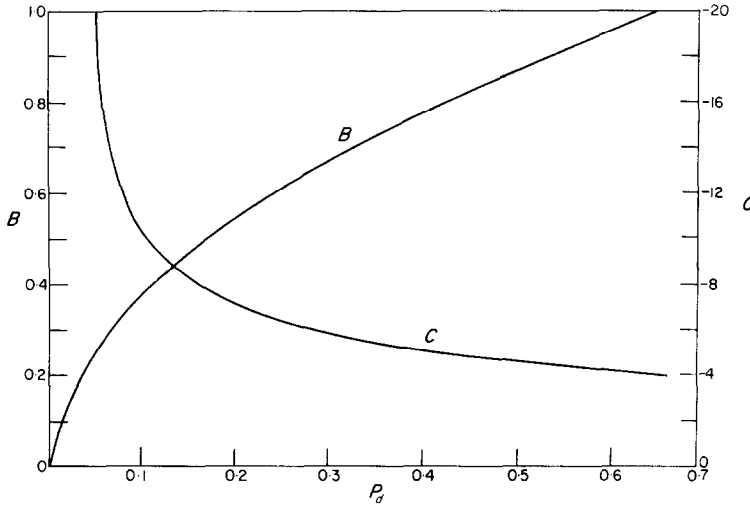


FIG. 4. B and C , constants in equation (5), vs. P_d , discontinuous phase volume fraction.

2δ and the absolute value of x shrinks 2δ at $y = 0$, too. From this assumption and equation (5), it is easy to show that

$$B = -4/C.$$

Constants B and C can be calculated in terms of P_d as follows. From Fig. 3(b),

$$\begin{aligned} P_d &= 2 \int_0^{B/2} y \, dx \\ &= 2 \int_0^{B/2} (B + Cx^2) \, dx \\ &= 2B^2/3 \end{aligned}$$

or

$$B = \sqrt{(3P_d/2)} \tag{6a}$$

(5) into equation (1), letting $C = C'$ since $C < 0$ yields

$$R_e = 2 \int_0^{B/2} \frac{dx}{[k_c + B(k_d - k_c)] - C'(k_d - k_c)x^2} + \frac{1 - B}{k_c}. \tag{7}$$

Rearranging the first term in the denominator of equation (7) gives

$$k_c + B(k_d - k_c) = BK_d + k_c(1 - B), \tag{8}$$

which is always greater than zero since B varies from 0 to 1. Equation (7) can be integrated resulting in

$$(A) \quad k_c > k_d.$$

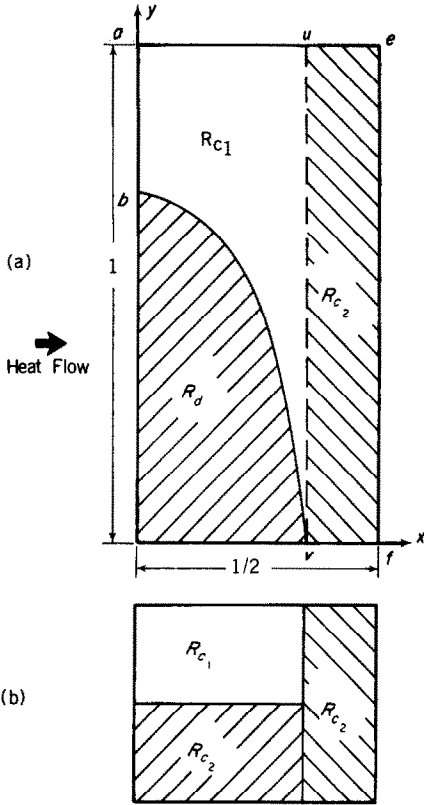


FIG. 5. (a) Phase distribution for class II mixtures (b) schematic representation of equivalent phase distribution for class II mixtures.

$$R_e = \frac{2}{\sqrt{\{-C'(k_d - k_c)[k_c + B(k_d - k_c)]\}}} \times \tan^{-1} \frac{B}{2} \sqrt{\frac{-C'(k_d - k_c)}{k_c + B(k_d - k_c)}} + \frac{1 - B}{k_c} \quad (9)$$

(B) $k_d > k_c$

$$R_e = \frac{1}{\sqrt{\{C'(k_d - k_c)[k_c + B(k_d - k_c)]\}}} \ln \frac{\sqrt{\{k_c + B(k_d - k_c)\}}}{\sqrt{\{k_c + B(k_d - k_c)\}}} + \frac{\frac{B}{2} \sqrt{\{C'(k_d - k_c)\}}}{-\frac{B}{2} \sqrt{\{C'(k_d - k_c)\}}} + \frac{1 - B}{k_c} \quad (10)$$

Thus equation (9) and equation (10) can be used in conjunction with B and C values obtained from equations (6) or Fig. 4 for a given P_d and the conductivities k_d and k_c to predict conductivity values of two-phase mixtures. Some caution must be used with equation (10) as will be seen.

Analysis of the denominator of the log term in equation (10) for Class II mixtures, $k_d \gg k_c$, indicates the equation must be used cautiously. It is possible to obtain $\log \infty$ when evaluating the log term if the denominator of the log term is not evaluated accurately. This can be seen as follows. Consider the denominator of the integrand of equation (7)

$$k_c + B(k_d - k_c) - C'(k_d - k_c)x^2$$

and it can be seen that there is a functional relationship between the above expression and the denominator of the log term in equation (10). Since $k_d \gg k_c$, one can write

$$k_c + B(k_d - k_c) - C'(k_d - k_c)x^2 \doteq k_d(B - C'x^2)$$

and the right-hand side of the above expression equals zero at $x = B/2$. Thus

$$k_c + B(k_d - k_c) - C'(k_d - k_c)x^2 \Big|_{x=B/2} = 0$$

or

$$\left[\sqrt{\{k_c + B(k_d - k_c)\}} - \frac{B}{2} \sqrt{\{C'(k_d - k_c)\}} \right] \left[\sqrt{\{k_c + B(k_d - k_c)\}} + \frac{B}{2} \sqrt{\{C'(k_d - k_c)\}} \right] \doteq 0.$$

since

$$\sqrt{\{k_c + B(k_d - k_c)\}} + \frac{B}{2} \sqrt{\{C'(k_d - k_c)\}} > 0,$$

then

$$\sqrt{\{k_c + B(k_d - k_c)\}} - \frac{B}{2} \sqrt{\{C'(k_d - k_c)\}} \doteq 0 \quad (11)$$

and equation (11) is identical to the denominator of the log term in equation (10). Thus for Class II mixtures, this term must be evaluated carefully

or $\log \infty$ which is ∞ results. This analysis is limited to Class II mixtures since $k_d \gg k_c$ for this class only.

Further analysis of equation (10) for Class II mixtures shows the equation can be simplified. Figure 3(b) is shown in Fig. 5(a). Since Fig. 3(b) is symmetrical with respect to the axis only

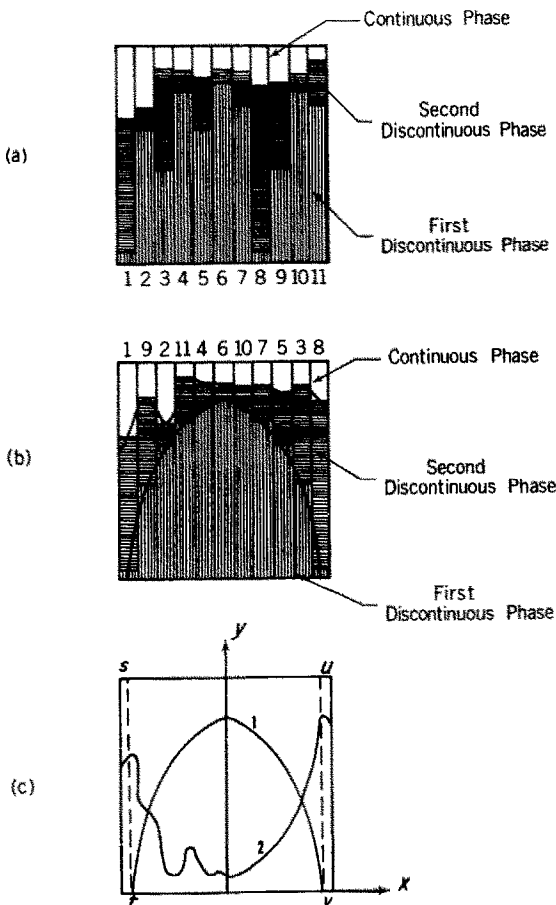


FIG. 6. Model for the study of the thermal conductivity of three-phase mixtures.

positive values of the figure are shown. Figure 5(b) represents the equivalent resistance orientation of the phases. Using Fig 5(b), one can write

$$R_e = \frac{R_{c1} R_d}{R_{c1} + R_d} + R_{c2}. \quad (12)$$

R_{c2} and R_{c1} represent the resistance of the continuous phase in rectangle $uwfe$ and the remainder of the continuous phase respectively. Since $k_d \gg k_c$, $R_c \gg R_d$, equation (12) can be written as

$$R_e \doteq \frac{R_{c1} R_d}{R_{c1}} + R_{c2} = R_d + R_{c2} \doteq R_{c2}. \quad (13)$$

Equation (13) indicates the majority of the resistance is dependent on the resistance of the rectangle $uwfe$ for Class II mixtures. Thus

$$k_m = \frac{1}{R_e} \doteq \frac{1}{R_{c2}}$$

and it can be shown that R_{c2} is the second term of equation (10). Hence

$$k_m \doteq \frac{k_c}{1 - B}, \quad (14)$$

which is valid as long as $P_d < 66.7$ per cent. If $P_d = 66.7$ per cent, k_m is calculated using equation (10) with $B = 1$.

Three-phase mixtures

The development of an equation to predict the thermal conductivity of three-phase mixtures and some multiphase mixtures is based on the independence of k_m on k_d when $R_d \ll R_c$ or $k_d \gg k_c$. The three-phase mixtures are reduced to equivalent one or more than one two-phase mixtures as will be seen. One can construct Figs. 6(a, b, c) for a mixture of two discontinuous phases in a continuous phase using the same assumptions as were used in the previous section for two-phase mixtures. Figure 6(c) is merely another representation of 6(b). This figure shows the relative phase distributions of the first discontinuous phase, curve 1, along with the distribution of the second discontinuous phase, curve 2. Curve 1 is in general a continuous curve which can be determined as was done for the two-phase case. In general, curve 2 is an arbitrary continuous, piece-wise continuous or discontinuous curve. No simple analytical technique exists to determine curve 2. Curve 2 can be

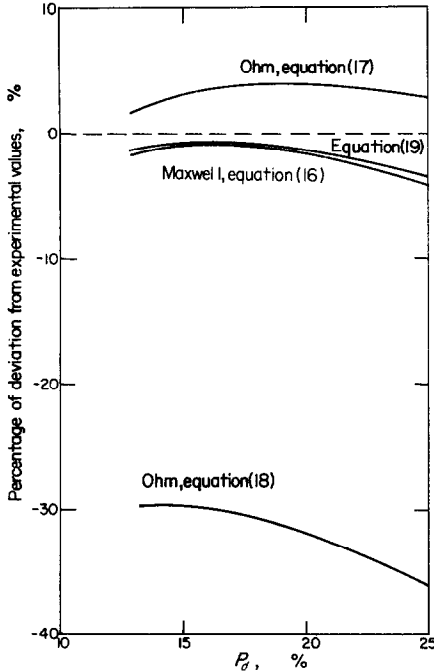


FIG. 7. Per cent deviation of predicted thermal conductivity values for class III mixtures from corresponding experimental values of thermal conductivity vs. P_d .

determined experimentally and then R_e and hence k_m can be determined from

$$R_e = \int \frac{dx}{k_c + (k_{d1} - k_c)y_1 + (k_{d2} - k_c)y_2} \quad (15)$$

However, it is not always possible to determine curve 2. Special cases of three-phase mixtures are developed as follows by reducing the three phase mixtures to equivalent two-phase mixtures.

Considering the infinite number of ratios and combinations of k_{d1}/k_c and k_{d2}/k_c , seven general cases are classified as follows:

Case 1. $\frac{k_{d1}}{k_c} > 100, \frac{k_{d2}}{k_c} > 100;$

Case 2. $\frac{k_{d1}}{k_c} > 100, 10 < \frac{k_{d2}}{k_c} < 100;$

Case 3. $10 < \frac{k_{d1}}{k_c} < 100, 10 < \frac{k_{d2}}{k_c} < 100;$

Case 4. $\frac{k_{d1}}{k_c} \sim 10, \frac{k_{d2}}{k_c} \sim 10;$

Case 5. $\frac{k_{d1}}{k_c} \sim 10, \frac{k_{d2}}{k_c} \sim 1;$

Case 6. $\frac{k_{d1}}{k_c} \sim \frac{k_{d2}}{k_c} \sim 1;$

Case 7. $\frac{k_{d1}}{k_c} < 1$ and/or $\frac{k_{d2}}{k_c} < 1.$

These cases are considered as follows:

Case 1. $\frac{k_{d1}}{k_c} > 100, \frac{k_{d2}}{k_c} > 100.$

The discontinuous phase can be considered to be composed of the first and second discontinuous phases. Thus $P_d = P_{d1} + P_{d2}$ and the mixture is reduced from a three-phase mixture to a two-phase mixture of Class II. Since k_{d1} and $k_{d2} \gg k_c$, the value of the conductivity of the combined discontinuous phases into one discontinuous phase is of no concern. Hence one can resort to the analysis for the Class II mixture and using equation (14) and write

$$k_m \doteq \frac{k_c}{1 - B}$$

B is obtained from equations (6) or Fig. 4 when P_d is known.

Case 2. $\frac{k_{d1}}{k_c} > 100, 10 < \frac{k_{d2}}{k_c} < 100.$

Consider Figs. 6(a, b, c), and concentrate on the first discontinuous phase which is contained under curve 1 in Fig. 6(b). It can be seen that since $k_{d1} \gg k_c$ and k_{d2} , one can consider the three-phase mixture to be reduced to a two-phase mixture in which the continuous phase is composed of the original continuous phase of the three-phase mixture and the second discontinuous phase. The discontinuous phase of this two-phase mixture is the first discontinuous phase of the three-phase mixture. The

resulting two phase mixture is of Class II and hence

$$k_m \doteq \frac{k_{ce}}{1 - B},$$

where k_{ce} represents the conductivity of the original continuous phase mixed with the second discontinuous phase of the three phase mixture. k_{ce} must be evaluated before k_m can be determined. This can be accomplished by considering the continuous phase of the resulting two-phase mixture. This two-phase mixture is composed of the original continuous phase of the three-phase mixture and the second discontinuous phase. Now the technique used to calculate k_{ce} will depend on the relation between k_{d2} and k_c . Since the ratio of k_{d2} to k_c determines if the mixture is of Class I, II, III or IV. Hence k_{ce} is calculated using an appropriate form of equation (9) and equation (10) and then k_m for the three-phase mixture is evaluated.

$$\text{Case 3. } 10 < \frac{k_{d1}}{k_c} < 100, 10 < \frac{k_{d2}}{k_c} < 100.$$

This case is similar to Case 2. Again, consider Figs. 6(a, b, c) and concentrate on the first discontinuous phase which is contained under curve 1 in Fig. 6(b). One can consider the three-phase mixture to be reduced to a two-phase mixture in which the continuous phase is composed of the original continuous phase of the three phase mixture and the second discontinuous phase. The discontinuous phase of this two-phase mixture is the first discontinuous phase of the three-phase mixture. Since k_{d1} is no longer far greater than k_c and k_{d2} , the mean thermal conductivity of the resulting two-phase mixture will be obtained by equation (10) where

$$P_{ce} = P_{d2} + P_c$$

$$P_d = P_{d1}$$

and

$$k_d = k_{d1}$$

and k_{ce} is obtained in the same way as shown in Case 2.

$$\text{Case 4. } \frac{k_{d1}}{k_c} \sim 10, \frac{k_{d2}}{k_c} \sim 10.$$

$$\text{Case 5. } \frac{k_{d1}}{k_c} \sim 10, \frac{k_{d2}}{k_c} \sim 1.$$

$$\text{Case 6. } \frac{k_{d1}}{k_c} \sim \frac{k_{d2}}{k_c} \sim 1.$$

Cases 4, 5 and 6 can be treated in exactly the same way as Case 3.

$$\text{Case 7. } \frac{k_{d1}}{k_c} < 1 \text{ and/or } \frac{k_{d2}}{k_c} < 1.$$

The mixtures belonging to this case can be treated in a manner similar to that for the preceding 6 cases. The three-phase mixtures are reduced to two-phase mixtures and equations (9) and (22) in the Appendix are employed.

For example,

$$\frac{k_{d1}}{k_c} \sim 10 \text{ and } \frac{k_{d2}}{k_c} < \frac{1}{100}.$$

This problem is solved by the same approach as in Case 3. The three-phase mixture is reduced to a two-phase mixture, thus allowing one to obtain

$$P_{ce} = P_{d2} + P_c$$

$$P_d = P_{d1}$$

and

$$k_d = k_{d1}.$$

However, since $k_c \gg k_{d2}$, now k_{ce} can be obtained from equation (22)

$$k_{ce} = k_{d2}(1 - P_c),$$

then equation (9) can be used to predict the mean thermal conductivity.

Thus the technique presented herein provides another means of predicting the conductivity of multiphase mixtures if this mixture can be reduced in successive steps to one or more

than one two-phase mixtures. Heretofore, Hamilton's equation (20) has represented the only means for predicting conductivity of multiphase mixtures. Hamilton's equation is somewhat limited in that the shape of the discontinuous phase must be known. Whereas in the proposed technique, the shape of the discontinuous phases are arbitrary.

Comparison of analytical results with experimental data

Comparison of predicted thermal conductivity values as a result of the previous analyses for two- and three-phase mixtures with experimental data are given in Tables 1-5. It is noted that the data are compared with results predicted using techniques of other studies.

Two-phase mixtures—Tables 1-4. Data for Class I materials were not found; however, Franci and Kingery [20] present data for Al_2O_3

Table 1. Thermal conductivity of alumina, Al_2O_3 , with isometric pores at 200°C.

Source of k_m	k_m (cal/s cm °C)	Percentage of deviation from experimental data
Maxwell, equation (16)	0.037	-7.5
equation (22)	0.041	2.5
equation (9)	0.037	-7.5
Experiment	0.040	

$k_c = 0.051$; $P_d = 20\%$; $t = 200^\circ C$; Experimental data Franci and Kingery [20].

with isometric pores. These data show the approach of this paper to be within 7.5 per cent which is acceptable considering the discontinuous phase is not a solid. Comparison of the data with the results for Class II, III and IV data indicate acceptable agreement with the data. Since the shape of the particles dispersed in the continuous phase of the Class II materials was not considered, agreement with the data is not

Table 2. Comparison of the predicted thermal conductivities with experimental data of class II mixtures

A. Aluminum spheres in silicone rubber

Source of k_m	k_m (Btu/h ft °F)	Percentage of deviation of experimental data
Maxwell, equation (16)	0.1968	3.58
Ohm, equation (17)	19	9900
Ohm, equation (18)	0.149	-21.6
Equation (10)	0.244	28.4
Experiment	0.19	

$k_c = 0.125$; $k_d = 118.0$; $P_d = 16\%$; Experimental data Hamilton [18, 19].

B. Aluminum cylinders in silicone rubber

Source of k_m	k_m (Btu/hr ft °F)	Percentage of deviation of experimental data
Hamilton, equation (19)	0.252	-3.08
Ohm, equation (17)	19	7200
Ohm, equation (18)	0.149	-42.7
Equation (10)	0.244	-6.15
Experiment	0.26	

$k_c = 0.125$; $k_d = 118.0$; $P_d = 16\%$; Experimental data Hamilton [18, 19].

as good with this analysis as is the case of Hamilton's technique. It is noticed that equation (10) predicts the same value of thermal conductivity for the mixture containing spherical particles as it does for the mixture containing cylindrical particles. Table 2, A and B, indicates a value of 0.19 for the mixture with the spheres, and a value of 0.26 for the cylindrical particles. The average of the experimentally measured thermal conductivities for the spherical and cylindrical particle mixtures is 0.225. Equation (10) predicts a value of 0.244 which is within 8 per cent of this average. This indicates that the technique is

Table 3. Comparison of the predicted thermal conductivities with experimental data of class III mixtures

A. Balsa discs in silicone rubber ($P_d = 25$ per cent)

Source of k_m	k_m (Btu/h ft °F)	Percentage of deviation from experimental data
Maxwell, equation (16)	0.093	-4.13
Ohm, equation (17)	0.0998	2.9
Ohm, equation (18)	0.0612	-36.1
Equation (9)	0.0934	-3.71
Experiment	0.097	

B. Balsa discs in silicone rubber ($P_d = 14$ per cent)

Source of k_m	k_m (Btu/h ft °F)	Percentage of deviation from experimental data
Maxwell, equation (16)	0.107	-0.925
Ohm, equation (17)	0.11089	2.68
Ohm, equation (18)	0.0788	-27
Equation (9)	0.107	-0.925
Experiment	0.108	

$k_c = 0.125$; $k_d = 0.0242$; $P_d = 14\%$; Experimental data Hamilton [18, 19].

C. Forsterite in magnesia (Mg_2SiO_4 -MgO)

Source of k_m	k_m (cal/s cm °C)	Percentage of deviation from experimental data
Maxwell, equation (16)	0.0577	-2.2
Ohm, equation (17)	0.06005	1.78
Ohm, equation (18)	0.04025	-31.8
Equation (9)	0.05825	-1.27
Experiment	0.059	

$k_c = 0.0675$; $k_d = 0.011$; $P_d = 13.2\%$; $t = 200^\circ\text{C}$; Experimental data Kingery [3].

Table 4. Comparison of the predicted thermal conductivities with experimental data of class IV mixtures

A. Synthetic silica in dimethyl (silicone rubbers)

Source of k_m	k_m (cal/s cm °C)	Percentage of deviation from experimental data
Maxwell, equation (16)	5.21×10^{-4}	-5.27
Ohm, equation (17)	7.78×10^{-4}	41.5
Ohm, equation (18)	4.62×10^{-4}	-16
Equation (10)	5.58×10^{-4}	1.45
Experiment	5.5×10^{-4}	

$k_c = 4.2 \times 10^{-4}$; $k_d = 40 \times 10^{-4}$; $P_d = 10\%$; $t = 25^\circ\text{C}$; Experimental data Ratcliffe [22].

B. Synthetic silica in methyl vinyl (silicone rubbers)

Source of k_m	k_m (cal/s cm °C)	Percentage of deviation from experimental data
Maxwell, equation (16)	6.53×10^{-4}	8.84
Ohm, equation (17)	9.53×10^{-4}	58.8
Ohm, equation (18)	4.8×10^{-4}	-20
Equation (10)	6.11×10^{-4}	1.83
Experiment	6.0×10^{-4}	

$k_c = 4.15 \times 10^{-4}$; $k_d = 40 \times 10^{-4}$; $P_d = 15\%$; $t = 25^\circ\text{C}$; Experimental data Ratcliffe [22].

good for particles of random shapes and gives acceptable values for a given particle shape.

Figures 7 and 8 indicate the per cent deviation of the predicted values of thermal conductivity as determined using the analysis and equation from the literature from available experimental data vs. P_d .

Three-phase mixtures—Table 5. Limited data are available for three-phase mixtures. Data are shown and compared with the analyses for Case 2 in Table 5. As can be seen, the analysis predicts a value within 3 per cent of the data.

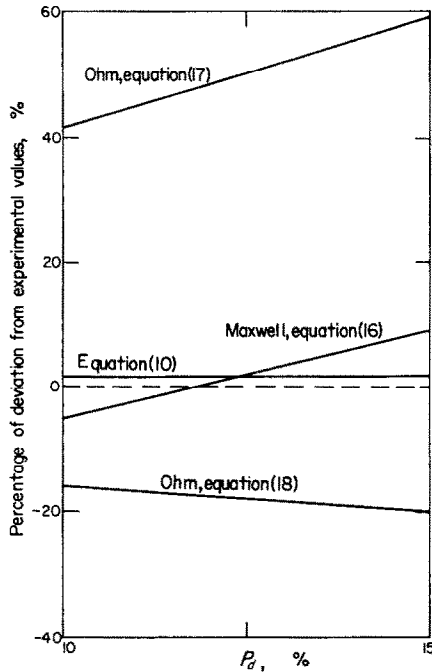


FIG. 8. Per cent deviation of predicted thermal conductivity values for class IV mixtures from corresponding experimental values of thermal conductivity vs. P_d .

SUMMARY

The extension of Tsao's model has resulted in equations (9) and (10) for predicting the thermal conductivity of two-phase heterogeneous mixtures. Equation (10) is applicable to Class II mixtures when the discontinuous phase particle shape is known or unknown. Hamilton's equation (19) yields the best result for Class II mixtures if the particles are spherical, cylindrical or any other geometrically simple shape. The reduction of certain cases of three-phase mixtures to equivalent two-phase mixtures allows application of the analysis to these cases of three-phase mixtures. Multiphase mixtures may be amenable to solution using the technique if they can be reduced to equivalent two or three-phase mixtures. The technique of this paper presents a general equation for the prediction of thermal conductivity of two-phase mixtures. This equation reduces the uncertainty in searching for the most appropriate conductivity equation for a

Table 5. Comparison of the predicted thermal conductivity with experimental data of case 2 of three-phase mixtures Titania and zinc-oxide in dimethyl at $t = 25^\circ\text{C}$

Source of k_m	k_m (cal/s cm $^\circ\text{C}$)	Percentage of deviation from experimental data
Analysis of Case 2	0.00136 ($k_{ce} = 0.00079$)	-3
Equation (20)	0.00155 (assuming discontinuous phases being spherical)	+10.7
Experiment	0.0014	

Dimethyl $k_c = 0.00042$; Zinc oxide $k_{d1} = 0.055$; Titania $k_{d2} = 0.019$, $P_{d1} = 12\%$, $P_{d2} = 18\%$; Experimental data Ratcliffe [22].

Table 6. Summary of the study of thermal conductivity of two-phase mixtures

	Recommended equations for predicting the thermal conductivity	
	For a specific shape of discontinuous phase	For random shape of discontinuous phase
Class I mixtures	Equations (22) and (9)	
Class II mixtures	Hamilton's equation (19)	Equation (10)
Class III mixtures	Equation (9)	
Class IV mixtures	Equation (10)	

particular class of material. The equation should be applicable to packed beds, emulsions and suspensions and other types of two-phase mixtures when convection and radiant heat transfer are negligible.

All the results have been summarized in Tables 6 and 7 for the study of thermal conductivity of two-phase and three-phase mixtures.

The technique will require further comparison with experimental data to prove its effectiveness.

Table 7. Summary of the study of thermal conductivity of three-phase mixtures

Relative values of k_{d1} , k_{d2} and k_c	Recommended equations for predicting thermal conductivity
Case 1: $\frac{k_{d1}}{k_c} > 100$; $\frac{k_{d2}}{k_c} > 100$	Equations (14) and (20)
Case 2: $\frac{k_{d1}}{k_c} > 100$; $10 < \frac{k_{d2}}{k_c} < 100$	Equations (14), (10) and (20)
Case 3: $10 < \frac{k_{d1}}{k_c} < 100$; $10 < \frac{k_{d2}}{k_c} < 100$	Equations (10) and (20)
Case 4: $\frac{k_{d1}}{k_c} \sim 10$; $\frac{k_{d2}}{k_c} \sim 10$	Equations (10) and (20)
Case 5: $\frac{k_{d1}}{k_c} \sim 10$; $\frac{k_{d2}}{k_c} \sim 1$	Equations (10) and (20)
Case 6: $\frac{k_{d1}}{k_c} \sim \frac{k_{d2}}{k_c} \sim 1$	Equations (9), (10) and (20)
Case 7: $\frac{k_{d1}}{k_c} < 1$ and/or $\frac{k_{d2}}{k_c} < 1$	Equations (9), (10), (14), (22) and (22)

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APPENDIX

Equations for Predicting Conductivity of Mixtures

A. Maxwell [12]—two-phase mixtures:

$$k_m = \frac{k_c[k_d + 2k_c - 2P_d(k_c - k_d)]}{k_d + 2k_c + P_d(k_c - k_d)} \quad (16)$$

B. Powers [17]—two-phase mixtures:

1. Laminae—parallel to heat flow

$$k_m = k_c P_c + k_d P_d \quad (17)$$

2. Multi-phase mixtures

$$k_m = k_1 \left[\frac{1 - \sum_{i=2}^m \frac{P_i(n_i - 1)(k_1 - k_i)}{k_i + (n_i - 1)k_1}}{1 + \sum_{i=2}^m \frac{P_i(k_1 - k_i)}{k_i + (n_i - 1)k_1}} \right] \quad (20)$$

$n_j = 3$ for spherical particles

D. Tsao [11]—two-phase mixtures:

$$k_m = \frac{1}{\int_{P_1} \frac{dP_1}{k_c + (k_d - k_c) \int_{P_1}^1 \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{1}{2} \left(\frac{P_1 - \mu}{\sigma} \right)^2} dP_1}} \quad (21)$$

2. Laminae—perpendicular to heat flow

$$k_m = \frac{k_c k_d}{P_d k_c + P_c k_d} \quad (18)$$

C. Hamilton [18, 19]—two-phase and multi-phase mixtures:

1. Class II mixtures with known particle shapes

$$k_m = \frac{k_c[k_d + (n - 1)k_c - (n - 1)P_d(k_c - k_d)]}{k_d + (n - 1)k_c + P_d(k_c - k_d)} \quad (19)$$

E. Francl and Kingery [20]—porous solids:

$$k_m = k_s(1 - P_d) \quad (22)$$

F. Loeb [21]—porous solids considering radiation:

$$k_m = k_s \left[(1 - P_{cs}) + \frac{P_{cs}}{P_j k_s / 4' \sigma \epsilon \gamma d T_m^3 + (1 - P_j)} \right] \quad (23)$$

Résumé—On a exposé une technique théorique pour prédire la conductivité thermique de mélanges solides hétérogènes. Le modèle de Tsao, qui prédit la conductivité thermique de mélanges de deux phases solides, a été modifié et étendu. La technique de cet article ne nécessite pas de données expérimentales sur les déviations moyenne et standard de la fonction de porosité unidimensionnelle qui décrit la distribution de la phase discontinue comme dans le cas du modèle de Tsao. On suppose une distribution parabolique de la phase discontinue et les constantes de la distribution parabolique sont déterminées par l'analyse et présentées en fonction de la fraction volumique de la phase discontinue. Ainsi, on évite d'avoir besoin des valeurs des

déviations moyenne et standard. La conductivité thermique équivalente d'un cube unité de mélange est obtenue à l'aide de la fonction de distribution et des conductivités thermiques des constituants. On montre que la technique employée prédit des valeurs de conductivité thermique à 8% près des résultats expérimentaux disponibles.

Zusammenfassung—Es wurde eine Theorie für die Berechnung der Wärmeleitfähigkeit heterogener fester Mischungen entwickelt. Tsao's Modell zur Bestimmung der Wärmeleitfähigkeit von zweiphasigen festen Gemischen wurde modifiziert und erweitert. Diese Theorie erfordert im Gegensatz zu Tsao's Modell keine experimentellen Daten über die mittleren und die Standardabweichungen der eindimensionalen Porositätsfunktion, welche die Verteilung der diskontinuierlichen Phase beschreibt. Es wird eine parabolische Verteilung der diskontinuierlichen Phase angenommen; die Konstanten dieser Verteilung werden durch Berechnung bestimmt und als Funktion des Volumenanteils der diskontinuierlichen Phase dargestellt. Damit sind die Werte der mittleren und der Standardabweichungen nicht erforderlich.

Die äquivalente Wärmeleitfähigkeit eines Einheitswürfels der Mischung wird in Form der Verteilungsfunktion und der Wärmeleitfähigkeit der Komponenten dargestellt. Es wird gezeigt, dass die mit Hilfe der Theorie vorhergesagten Werte der Wärmeleitfähigkeit innerhalb von 8% der verfügbaren Versuchsergebnisse liegen.

Аннотация—Разработаны теоретические методы расчета теплопроводности неоднородных смесей твердых веществ. Модифицирована модель Цао для расчета теплопроводности двухфазных смесей твердых веществ. По предложенной методике не требуется экспериментальных данных по среднему и стандартному отклонениям одномерной функции объемного содержания включения, описывающей распределение наполнителя. Это имеет место в модели Цао. Предполагается параболическое распределение включений, причем постоянные распределения определяются из анализа и представлены в виде функции объемного содержания включений. Таким образом, отпадает необходимость в среднем и стандартном отклонениях. Эквивалентная теплопроводность единицы объема смеси выведена в зависимости от функции распределения и теплопроводности составляющих. Приводится методика расчета теплопроводности, отличающаяся от известных экспериментальных данных не более чем на 8%.