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A new approach to modelling the effective thermal conductivity of heterogeneous materials

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Abstract

A unifying equation for five fundamental effective thermal conductivity structural models (Series, Parallel, two forms of Maxwell–Eucken, Effective Medium Theory) was derived. A procedure for modelling complex materials as composites of these five basic structural models using simple combinatory rules based on *structure volume fractions* was proposed. The combined models have advantages over other generic models such as the semi-empirical Krischer model, in that each has a distinct physical basis, and that they are not dependent on any empirical parameter. As a by-product, a physical description has been identified for Levy's model, which was previously used with reservation by some researchers because it was derived solely by mathematical reasoning without any explicit physical basis.

Keywords: Effective thermal conductivity; Models; Heterogeneous material; Anisotropic material

1. Introduction

Modelling the effective thermal conductivity of heterogeneous or composite materials is of interest in many heat transfer applications. Progelhof et al. [1] and Carson et al. [2] provide reviews of relevant modelling approaches. A substantial number of effective thermal conductivity models have been proposed, some of which have been intended for highly specific applications, while others have wider applicability. A heterogeneous material's effective thermal conductivity is strongly affected by its composition and structure, and, as yet, there does not appear to be any single model equation that is applicable to all types of structure. Instead, a common approach has been to develop a set of equations based on a conceptual 'parent' model, that is modified to varying extents to account for variations in composition and structure [3–6]. Alternatively, an empirical parameter may be inserted to account for differences in structure [2,7]. Another common way of estimating effective thermal conductivity for composite materials with known microstructures is to make rigorous numerical simulations using the finite difference or finite element methods [8–10]. However, analytical models are preferred over numerical models in many applications due to their physical basis, rapid and low cost of calculation, and reasonable accuracy even when microstructure is uncertain.

Many (if not most) effective thermal conductivity models found in the literature are based on one or more of five basic structural models; specifically, the Series, Parallel, Maxwell–Eucken (two forms) [11,12] and Effective Medium Theory (EMT) models [13,14]. The physical structures assumed in the derivations of the Series and Parallel models are of layers of the components aligned either perpendicular or parallel to the heat flow, as their names indicate. The Maxwell–Eucken model assumes a dispersion of small spheres within a continuous matrix of a different component, with the spheres being far enough apart such that the local distortions to the temperature distributions

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Nomenclature

A, B, C, D, F, G	intermediate variables defined within the text
d	shape factor
f	empirical weighting factor
k	thermal conductivity of a component ($W\,m^{-1}\,K^{-1}$)
K	effective thermal conductivity of a material ($W\,m^{-1}\,K^{-1}$)
m	number of components
n	number of structures
v	volume fraction of component

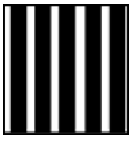
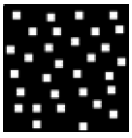
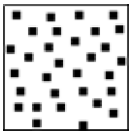
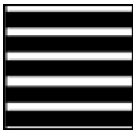
Greek symbols

ε	structure volume fraction
ϕ	structure composition factor
κ	effective thermal conductivity of a structure ($W\,m^{-1}\,K^{-1}$)

Subscripts

i	ith component
j	jth structure

Table 1
Five fundamental effective thermal conductivity structural models for two-component materials (assuming the heat flow is in the vertical direction)

Model	Structure schematic	Effective thermal conductivity equation	Reference	Eq. (1) parameter values
Parallel model		$K = v_1k_1 + v_2k_2$		$d_i \to \infty$ or $\tilde{k} = k_i$
Maxwell–Eucken 1 (ME1) (k_1 = continuous phase, k_2 = dispersed phase)		$K = \dfrac{k_1v_1 + k_2v_2\dfrac{3k_1}{2k_1+k_2}}{v_1 + v_2\dfrac{3k_1}{2k_1+k_2}}$	[8,9]	$d_i = 3$ and $\tilde{k} = k_1$
EMT model		$v_1\dfrac{k_1-K}{k_1+2K} + v_2\dfrac{k_2-K}{k_2+2K} = 0$	[10,11]	$d_i = 3$ and $\tilde{k} = K$
Maxwell–Eucken 2 (ME2) (k_1 = dispersed phase, k_2 = continuous phase)		$K = \dfrac{k_2v_2 + k_1v_1\dfrac{3k_2}{2k_2+k_1}}{v_2 + v_1\dfrac{3k_2}{2k_2+k_1}}$	[8,9]	$d_i = 3$ and $\tilde{k} = k_2$
Series model		$K = \dfrac{1}{v_1/k_1 + v_2/k_2}$		$d_i = 1$ or $\tilde{k} \to 0$

around each of the spheres do not interfere with their neighbours' temperature distributions. For a two-component material, two forms of the Maxwell–Eucken model arise depending on which of the components forms the continuous phase. The EMT model assumes a completely random distribution of all the components. Table 1 lists the two-component forms of the equations for each of these models along with a schematic of its assumed physical structure.

Several effective thermal conductivity studies have recognised the importance of these basic structural models in theoretical analyses and for developing more complex models, in particular with regards to defining thermal conductivity bounds for certain classes of physical structure [15–18]. In this paper we present a procedure for modelling complex physical structures as composites of these basic elementary structural models using simple combinatory rules.

2. Model development

2.1. A unifying equation for the basic structural models

Following on from work by Brailsford and Major [16] each of the model equations shown for two components

in Table 1 may be derived for a multi-component material from Eq. (1) by suitable choice of the parameters d_i and $\tilde{k}$:

$$K = \frac{\sum_{i=1}^{m} k_i v_i \frac{d_i \tilde{k}}{(d_i-1)\tilde{k}+k_i}}{\sum_{i=1}^{m} v_i \frac{d_i \tilde{k}}{(d_i-1)\tilde{k}+k_i}} \tag{1}$$

As indicated in Table 1, the Series model is obtained when $d_i = 1$, or $\tilde{k} \to 0$; the Parallel model is obtained when $d_i \to \infty$ or $\tilde{k} = k_i$; the Maxwell–Eucken equation is obtained when $d_i = 3$, $\tilde{k} = k_{\text{cont}}$; and the EMT equation is obtained when $d_i = 3$, $\tilde{k} = K$.

The d_i parameter can have a physical interpretation. Kirkpatrick [19] related a similar parameter to the number of Euclidean dimensions of the system involved, while Fricke [20] and Hamilton and Crosser [21] related it to the sphericity of the dispersed phase. However, it may be possible to define a parameter that combines both aspects of component shape and number of Euclidean dimensions. This is the topic of ongoing investigations by the authors, but falls outside the scope of this paper. The most common approach is to take $d_i = 3$ (spherical dispersed phase).

2.2. Empirically weighted mixtures of basic physical structures

A common approach has been to combine structural models using empirical weighting. The Series and Parallel models define the upper and lower bounds (sometimes referred to as the Wiener bounds [22]) for the effective thermal conductivity of any heterogeneous material for which the components' volume fractions and thermal conductivities are known accurately, provided conduction is the only mechanism of heat transfer involved. Krischer [7] reasoned that since the thermal conductivity of any two-component material must lie between the Wiener bounds, its structure could be modelled as a mixture of Series and Parallel structures. He proposed that the effective thermal conductivity of the combined structure should be the weighted harmonic mean of the Series and Parallel conductivities:

$$K = \frac{1}{f/k_{\text{series}} + (1-f)/k_{\text{parallel}}} \tag{2}$$

Chaudhary and Bhandari [23] and Renaud et al. [24] used similar approaches, based on weighted geometric and arithmetic means, respectively.

Clearly this reasoning may be extended using narrower bounds, such as those proposed by Hashin and Shtrikman [15] which were equivalent to the two forms of the Maxwell–Eucken model, or Carson et al. [18], which were based on the Maxwell–Eucken and EMT models. Making use of Krischer's approach and Eq. (1), a generic weighted model can be defined that would allow a combination of any of the equations listed in Table 1, and therefore would be suitable for structures that fit between any of these bounds:

$$K = f\left(\frac{\sum_{i=1}^{m} k_i v_i \frac{d_i \tilde{k}}{(d_i-1)\tilde{k}+k_i}}{\sum_{i=1}^{m} v_i \frac{d_i \tilde{k}}{(d_i-1)\tilde{k}+k_i}}\right)_{\text{structure-1}} + (1-f)\left(\frac{\sum_{i'=1}^{m'} k'_i v'_i \frac{d'_i \tilde{k}'}{(d'_i-1)\tilde{k}'+k'_i}}{\sum_{i'=1}^{m'} v'_i \frac{d'_i \tilde{k}'}{(d'_i-1)\tilde{k}'+k'_i}}\right)_{\text{structure-2}} \tag{3}$$

However, while such weighted mean combination models may be useful in some situations, the fact that the value of the weighting parameters cannot be determined mechanistically from information about the physical structure is a significant shortcoming. Therefore, we do not advocate such an approach unless a more analytical and mechanistic approach cannot be found.

2.3. Structure volume fractions and structure composition factors

Krischer's approach assumed that a complex structure could be approximated by a mixture of simpler structures, where the relative amounts of each of the simpler structures was determined empirically. In this work we define "structure volume fractions" (as distinct from *component* volume fractions) for the jth type of structure by Eq. (4):

$$\varepsilon_j = \sum_i v_i \phi_{ij} \tag{4}$$

where ε_j represents the volume fraction of a material that is made up of structure j. Since the ε_j are fractions of the total volume:

$$\sum_j \varepsilon_j = 1 \tag{5}$$

The "structure composition factors", ϕ_{ij}, are a measure of the fraction of component material i that is part of structure j, and therefore since the total amount of component i must be distributed between the structures:

$$\sum_j \phi_{ij} = 1 \tag{6}$$

For m components, the thermal conductivity of structure j is a function of the v'_is, ϕ'_{ij}s and k'_is:

$$\kappa_j = \kappa_j(v_1, v_2, \ldots, v_m, \phi_{1j}, \phi_{2j}, \ldots, \phi_{mj}, k_1, k_2, \ldots, k_m) \tag{7}$$

If the structure is modelled by one of the five fundamental models listed in Table 1, Eq. (7) may be written:

$$\kappa_j = \frac{\sum_{i=1}^{m} k_i v_i \phi_{ij} \frac{d_i \tilde{k}}{(d_i-1)\tilde{k}+k_i}}{\sum_{i=1}^{m} v_i \phi_{ij} \frac{d_i \tilde{k}}{(d_i-1)\tilde{k}+k_i}} \tag{8}$$

For n structures, the overall material effective thermal conductivity, K, is a function of the κ'_js:

$$K = K(\kappa_1, \kappa_2, \ldots, \kappa_n) \tag{9}$$

In order to solve Eq. (9), based only on k_i and v_i and not on any empirical parameters, it is necessary to determine expressions for ϕ_{ij} as functions of k_i and v_i. This may

be achieved by making assumptions about the relative amounts of each structure, ε_j, in the total volume and the relative contributions of the different κ_j to K. There are an infinite number of relationships between the ε'_js and κ_j that could be chosen. It may be possible to relate the ε'_js to structural characteristics. However, such detailed information is often unavailable. Therefore the simplest possible relationships were adopted. They are to assume that each structure comprises an equal fraction of the total volume:

$$\varepsilon_j = \frac{1}{n} \tag{10}$$

and that the thermal conductivity of each structure is equal to the effective thermal conductivity:

$$K = \kappa_1 = \kappa_2 = \cdots = \kappa_n \tag{11}$$

Other more complex approaches may be justified in some circumstances. For example, for a material made up of three structures the distribution of structure volumes does not have to be uniform and could arbitrarily be $\varepsilon_1 = 0.2$, $\varepsilon_2 = 0.5$, $\varepsilon_3 = 0.3$ or similar. However, the overall methodology is applicable irrespective of what relative values of ε'_js and κ'_js are chosen.

The model is now completely defined for two-component materials. The effective thermal conductivity, K, can be calculated by solving Eqs. (4), (8), (10) and (11) simultaneously subject to Eqs. (5) and (6) for a material with known components and specified structures. Worked examples of the detailed model derivation process are shown below for two-component materials. If alternative relationships are used instead of Eqs. (10) and (11), the mathematics of solving for K will become slightly more complex.

For materials with more than two components, extra assumptions must be made in order for the model to be completely and uniquely specified. Models for multi-component materials are not considered further in this paper; instead it is assumed that they may be dealt with by sequential application of the two-component models. For example, for a material with three components x, y and z, the overall effective thermal conductivity is calculated in two stages. First, the effective thermal conductivity K_{xy} for the mixture of two components, x and y, is predicted using a two-component structural models with the following adjusted volume fractions: $v_{xx} = v_x/(v_x + v_y)$ and $v_{yy} = v_y/(v_x + v_y)$. Second, the overall effective thermal conductivity, K, is predicted for the mixture of xy as one component and z as the other component. The volume fraction of component xy is $v_{xy} = v_x + v_y$, while the volume fraction of z is v_z, and the conductivities are K_{xy} and k_z, respectively. The two-component structural model used for this second stage may, or may not, be the same as that used in the first stage. Clearly, there are two other possible sequences for the calculations based on the choice of components to include in the first mixture (i.e. xz or yz instead of xy). The three alternative sequential calculations will usually not give identical results.

3. Selected binary-structure models

The schematics in Fig. 1a–d represent four of the 10 theoretical two-component models with an equal mixture of two of the five basic structures. Fig. 1a shows half of the volume has the Maxwell–Eucken structure with component 1 as the continuous phase (structure 1 = ME1), while the other half of the volume has the Maxwell–Eucken structure with component 2 as the continuous phase (structure 2 = ME2); similarly, in Fig. 1b structure 1 = Parallel and structure 2 = ME2; in Fig. 1c structure 1 = ME1 and structure 2 = EMT; and in Fig. 1d structure 1 = ME2 and structure 2 = EMT.

3.1. ME1 + ME2 model

Starting with Eq. (8), the appropriate values of d_i and $\tilde{k}$ are chosen such that structure 1 is the ME1 structure and structure 2 is the ME2 (Table 1). Hence from Eqs. (8) and (11):

$$K = \kappa_1 = \frac{k_1 v_1 \phi_{11} + k_2 v_2 \phi_{21} \frac{3k_1}{2k_1 + k_2}}{v_1 \phi_{11} + v_2 \phi_{21} \frac{3k_1}{2k_1 + k_2}} = \kappa_2 = \frac{k_2 v_2 \phi_{22} + k_1 v_1 \phi_{12} \frac{3k_2}{2k_2 + k_1}}{v_2 \phi_{22} + v_1 \phi_{12} \frac{3k_2}{2k_2 + k_1}} \tag{12}$$

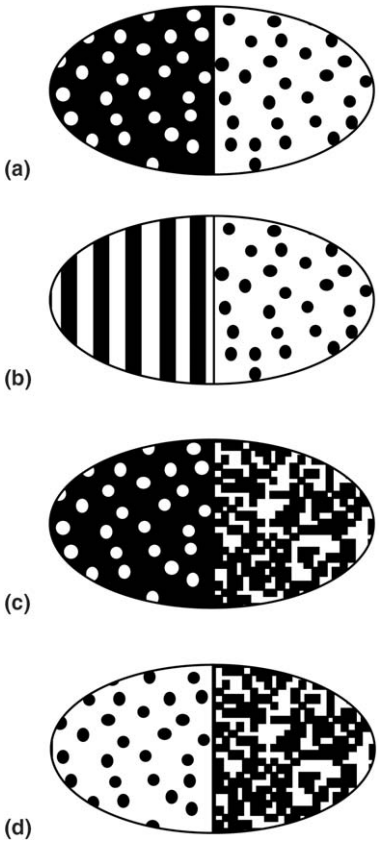


Fig. 1. Schematic representations of some two-component materials as uniform mixtures of two fundamental structural models: (a) ME1 + ME2, (b) Parallel + EMT, (c) ME1 + EMT and (d) ME2 + EMT.

Rearranging Eq. (12) and cancelling terms yields:

$$\phi_{11}\phi_{22}A + \phi_{12}\phi_{21}B = 0 \tag{13}$$

where

$$A = v_1 v_2 (k_1 - k_2) \tag{14}$$

and

$$B = -A\frac{3k_1}{(2k_1+k_2)}\frac{3k_2}{(2k_2+k_1)} = \frac{-9A}{5+2k_1/k_2+2k_2/k_1} \tag{15}$$

Based on Eqs. (4) and (10):

$$v_1\phi_{11} + v_2\phi_{21} = 1/2 \tag{16}$$

$$v_1\phi_{12} + v_2\phi_{22} = 1/2 \tag{17}$$

From Eq. (6):

$$\phi_{11} + \phi_{12} = 1 \tag{18}$$

$$\phi_{21} + \phi_{22} = 1 \tag{19}$$

Eqs. (12) or (13) plus (16)–(19) must be solved simultaneously to give values of ϕ_{11}, ϕ_{12}, ϕ_{21}, ϕ_{22} and K given that values of k_1, k_2, v_1 and v_2 are known. For this structure combination an analytical solution is possible. ϕ_{12}, ϕ_{21} and ϕ_{22} may all be written in terms of ϕ_{11}:

$$\phi_{12} = 1 - \phi_{11} \tag{20}$$

$$\phi_{21} = \left(\frac{1-2v_1\phi_{11}}{2v_2}\right) \tag{21}$$

$$\phi_{22} = \left(\frac{2v_2+2v_1\phi_{11}-1}{2v_2}\right) \tag{22}$$

Substituting for ϕ_{12}, ϕ_{21} and ϕ_{22} in Eq. (13):

$$\phi_{11}\left(\frac{2v_2+2v_1\phi_{11}-1}{2v_2}\right)A + \left(\frac{1-2v_1\phi_{11}}{2v_2}\right)(1-\phi_{11})B = 0 \tag{23}$$

Rearranging Eq. (23) to be explicit in terms of ϕ_{11}:

$$\phi_{11} = \frac{B(2v_1+1) - A(2v_2-1) \pm \sqrt{[A(2v_2-1) - B(2v_1+1)]^2 - 8Bv_1(A+B)}}{4v_1(A+B)} \tag{24}$$

(Note: if $k_1 > k_2$ then the positive square root in Eq. (24) should be used, and vice versa). K can be calculated from the left-hand side version of Eq. (12) by substituting ϕ_{21} using Eq. (21) and using the ϕ_{11} value calculated from Eq. (24):

$$K = \frac{k_1 v_1 \phi_{11} + k_2 v_2 \left(\frac{1-2v_1\phi_{11}}{2v_2}\right)\left(\frac{3k_1}{2k_1+k_2}\right)}{v_1\phi_{11} + v_2\left(\frac{1-2v_1\phi_{11}}{2v_2}\right)\left(\frac{3k_1}{2k_1+k_2}\right)} \tag{25}$$

A plot of K/k_1 vs. v_2 for the ME1 + ME2 model is shown in Fig. 2 for a material with $k_1/k_2 = 20$.

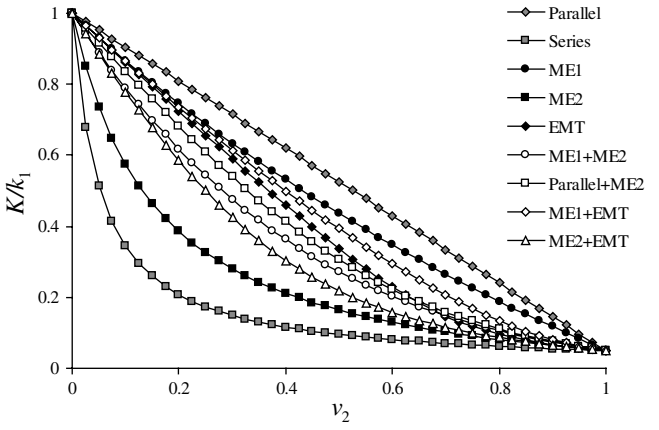


Fig. 2. Plots of the five fundamental effective thermal conductivity structural models listed in Table 1, along with plots of the binary-structure models shown schematically in Fig. 1a–d for a two component material with $k_1/k_2 = 20$.

3.2. Parallel + ME2 model

For the Parallel + ME2 model, Eqs. (8) and (11) give

$$K = \frac{k_1 v_1 \phi_{11} + k_2 v_2 \phi_{21}}{v_1\phi_{11} + v_2\phi_{21}} = \frac{k_2 v_2 \phi_{22} + k_1 v_1 \phi_{12}\frac{3k_2}{2k_2+k_1}}{v_2\phi_{22} + v_1\phi_{12}\frac{3k_2}{2k_2+k_1}} \tag{26}$$

Again, an analytical solution is possible. Eq. (26) is very similar to Eq. (12), which suggests that an expression for ϕ_{11} will be similar to Eq. (24). In fact, it can be shown that Eqs. (24) and (25) may be used to calculate K for the Parallel + ME2 model provided B is calculated from Eq. (27) rather than Eq. (15):

$$B = \frac{3k_2 A}{2k_2 + k_1} \tag{27}$$

A plot of K/k_1 vs. v_2 for the Parallel + ME2 model is shown in Fig. 2.

3.3. ME1 + EMT model

For the ME1 + EMT model, Eqs. (8) and (11) give

$$K = \frac{k_1 v_1 \phi_{11} + k_2 v_2 \phi_{21}\frac{3k_1}{2k_1+k_2}}{v_1\phi_{11} + v_2\phi_{21}\frac{3k_1}{2k_1+k_2}} = \frac{k_1 v_1 \phi_{12}\frac{3K}{2K+k_1} + k_2 v_2 \phi_{22}\frac{3K}{2K+k_2}}{v_1\phi_{12}\frac{3K}{2K+k_1} + v_2\phi_{22}\frac{3K}{2K+k_2}} \tag{28}$$

The right-hand side of Eq. (28) may be rearranged to be explicit in terms of K:

$$K = \frac{(2k_1-k_2)v_1\phi_{12} + (2k_2-k_1)v_2\phi_{22} + \sqrt{[(2k_1-k_2)v_1\phi_{12} + (2k_2-k_1)v_2\phi_{22}]^2 + 2k_1k_2}}{2} \tag{29}$$

Expressing ϕ_{11}, ϕ_{12} and ϕ_{22} in terms of ϕ_{21}, Eq. (28) becomes:

$$K = \frac{k_1 v_1 \left(\frac{1-2v_2\phi_{21}}{2v_1}\right) + k_2 v_2 \phi_{21} \frac{3k_1}{2k_1+k_2}}{v_1 \left(\frac{1-2v_2\phi_{21}}{2v_1}\right) + v_2 \phi_{21} \frac{3k_1}{2k_1+k_2}} = \frac{C + \sqrt{C^2 + 2k_1k_2}}{2} \tag{30}$$

where

$$C = (2k_1 - k_2)v_1 \left(\frac{2v_1 + 2v_2\phi_{21} - 1}{2v_1}\right) + (2k_2 - k_1)v_2(1 - \phi_{21}) \tag{31}$$

Due to the non-integral powers of ϕ_{21} on its right-hand side, Eq. (30) cannot be simply rearranged to be explicit in terms of ϕ_{21}. Therefore alternative solution procedures must be adopted. One possibility is to solve Eqs. (30), (31) and (16)–(19) by numerical iteration. Fig. 3a shows the plots of ϕ_{11}, ϕ_{12}, ϕ_{21} and ϕ_{22} calculated by numerical iteration using the *Solver* function in *Microsoft Excel*™ for a two-component material with $k_1/k_2 = 20.0$. The shape of the curve for ϕ_{21} suggests that it could be accurately fitted by a polynomial function, which would then allow ϕ_{21} to be expressed explicitly. Eq. (32) has been fitted to ϕ_{21} curves for k_1/k_2 values between 1 and 100:

$$\phi_{21} = \{0.1353\ln(k_1/k_2) - 0.1193\}v_1^3 + \{0.2551\ln(k_1/k_2) - 0.1711\}v_1^2 + \{0.1203\ln(k_1/k_2) - 0.0523\}v_1 + 0.5 \tag{32}$$

Fig. 4 shows that Eq. (32) provides good approximations of ϕ_{21} without the inconvenience of using an iterative numerical solution of the simultaneous equations. At k_1/k_2 values lower than 100, the agreement is closer than shown in Fig. 4. A plot of K/k_1 vs. v_2 for the ME1 + EMT model is shown in Fig. 2.

3.4. ME2 + EMT model

For the ME2 + EMT model, Eqs. (8) and (11) give

$$K = \frac{k_2 v_2 \phi_{21} + k_1 v_1 \phi_{11} \frac{3k_2}{2k_2+k_1}}{v_2 \phi_{21} + v_1 \phi_{11} \frac{3k_2}{2k_2+k_1}} = \frac{k_1 v_1 \phi_{12} \frac{3K}{2K+k_1} + k_2 v_2 \phi_{22} \frac{3K}{2K+k_2}}{v_1 \phi_{12} \frac{3K}{2K+k_1} + v_2 \phi_{22} \frac{3K}{2K+k_2}} \tag{33}$$

Following the same approach as for the ME1 + EMT model, Eq. (33) becomes

$$K = \frac{k_2 v_2 \left(\frac{1-2v_1\phi_{11}}{2v_2}\right) + k_1 v_1 \phi_{11} \frac{3k_2}{2k_2+k_1}}{v_2 \left(\frac{1-2v_1\phi_{11}}{2v_2}\right) + v_1 \phi_{11} \frac{3k_2}{2k_2+k_1}} = \frac{D + \sqrt{D^2 + 2k_1k_2}}{2} \tag{34}$$

where

$$D = (2k_1 - k_2)v_1(1 - \phi_{11}) + (2k_2 - k_1)v_2 \left(\frac{2v_2 + 2v_1\phi_{11} - 1}{2v_2}\right) \tag{35}$$

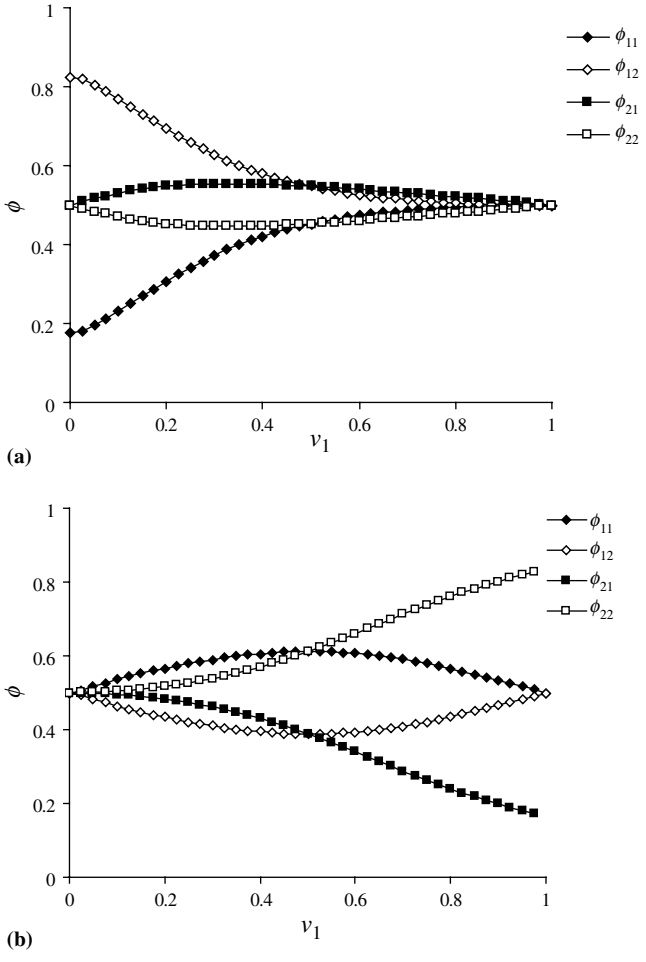


Fig. 3. Plots of structure volume factors ϕ_{11}, ϕ_{12}, ϕ_{21} and ϕ_{22} for a two-component material with $k_1/k_2 = 20$: (a) ME1 + EMT model and (b) ME2 + EMT model.

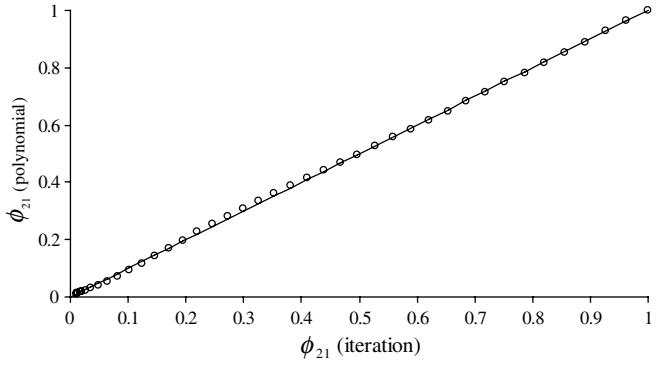


Fig. 4. Comparison of ϕ_{21} for the ME1 + EMT model calculated by numerical iteration with ϕ_{21} calculated using Eq. (32) for a two component material with $k_1/k_2 = 100$.

Again, a simple analytical solution is not possible. Fig. 3b shows the plots of ϕ_{11}, ϕ_{12}, ϕ_{21} and ϕ_{22} calculated by numerical iteration for the ME2 + EMT model for a two component material with $k_1/k_2 = 20$. As with the ME1 + EMT model, a polynomial expression for ϕ_{11} can be derived to avoid solution of Eq. (34) by numerical iteration. For k_1/k_2 between 1 and 100:

$$\begin{aligned}\phi_{11} = {} & \{-0.0526\ln(k_1/k_2)^2 + 0.2125\ln(k_1/k_2) - 0.1689\}v_1^3 \\ & + \{0.0886\ln(k_1/k_2)^2 - 0.5758\ln(k_1/k_2) + 0.4879\}v_1^2 \\ & + \{-0.0407\ln(k_1/k_2)^2 + 0.3881\ln(k_1/k_2) + 0.3478\}v_1 + 0.5\end{aligned} \tag{36}$$

A plot of K/k_1 vs. v_2 for the ME2 + EMT model is shown in Fig. 2.

4. Multi-structure models

Extension of the procedure to a ternary-structure model (EMT + ME2 + Series) gives:

$$K = \frac{v_1\phi_{11} + v_2\phi_{21}}{v_1\phi_{11}/k_1 + v_2\phi_{21}/k_2} = \frac{k_1v_1\phi_{12}\dfrac{3K}{2K+k_1} + k_2v_2\phi_{22}\dfrac{3K}{2K+k_2}}{v_1\phi_{12}\dfrac{3K}{2K+k_1} + v_2\phi_{22}\dfrac{3K}{2K+k_2}} \tag{37}$$

$$K = \frac{k_2v_2\phi_{23} + k_1v_1\phi_{13}\dfrac{3k_2}{2k_2+k_1}}{v_2\phi_{23} + v_1\phi_{13}\dfrac{3k_2}{2k_2+k_1}} = \frac{k_1v_1\phi_{12}\dfrac{3K}{2K+k_1} + k_2v_2\phi_{22}\dfrac{3K}{2K+k_2}}{v_1\phi_{12}\dfrac{3K}{2K+k_1} + v_2\phi_{22}\dfrac{3K}{2K+k_2}} \tag{38}$$

$$v_1\phi_{11} + v_2\phi_{21} = 1/3 \tag{39}$$

$$v_1\phi_{12} + v_2\phi_{22} = 1/3 \tag{40}$$

$$v_1\phi_{13} + v_2\phi_{23} = 1/3 \tag{41}$$

$$\phi_{11} + \phi_{12} + \phi_{13} = 1 \tag{42}$$

$$\phi_{21} + \phi_{22} + \phi_{23} = 1 \tag{43}$$

Due to the complexity of the algebra involved in solving Eqs. (37)–(43) simultaneously, solution by iteration with the aid of a tool such as *Excel*™ *Solver* becomes a more practical option than solving algebraically. Fig. 5 shows a plot of the EMT + ME2 + Series model calculated using *Excel*™, along with plots of the five basic structural models. Quaternary models (an example of which is plotted in Fig. 5) and the five-structure model (plotted in Fig. 5) may also be derived by further extension of this method.

By using every possible combination of the five basic structural models, 10 binary models, 10 ternary models, five quaternary models and one five-structure model may be derived, giving a total of 26 new effective thermal conductivity models, each with a distinct physical basis.

5. Practical application

Clearly these combined models may not be applicable for materials whose structures could be mathematically defined. In such cases, more specific models are often justified by greater prediction accuracy. But for naturally occurring materials which are characterised by high degrees of variability (such as soils and biological materials), simpler, more generic models, are more convenient.

The five basic structural models listed in Table 1 have been widely used, but without modification they cannot account for wide ranges of structure. Models such as Krischer's use an empirical approach to account for differences in structure; however, unless there are data in the literature for f, the value of this parameter must be determined by experimentation. This often defeats the purpose of thermal conductivity prediction because it is very difficult to perform an intuitive estimate of the value of f

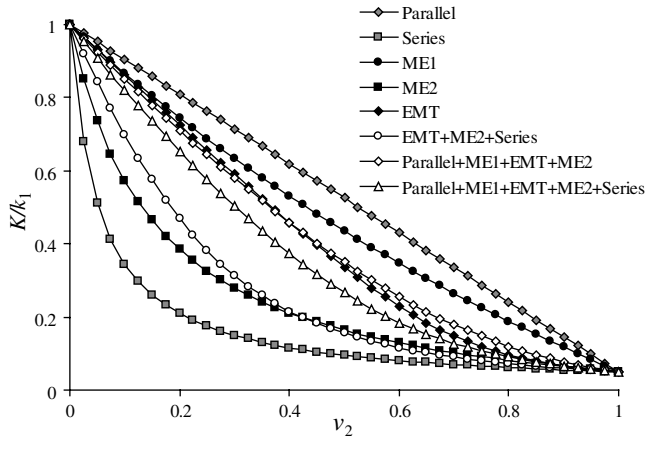


Fig. 5. Plots of five fundamental effective thermal conductivity structural models along with plots of selected ternary, quaternary and five-structure models for a two-component material with $k_1/k_2 = 20$.

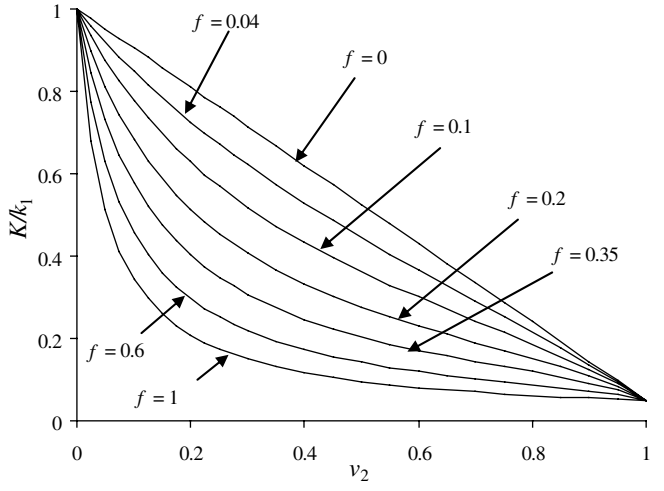


Fig. 6. Plots of Krischer's model (Eq. (2)) for different values of f for a two-component material with $k_1/k_2 = 20$.

due to the highly non-linear dependence of K on f for a given v_2 as shown in Fig. 6.

Models derived by the procedure outlined above have two major advantages over models such as Krischer's that use empirical, structure-related parameters. Firstly, regardless of the value of f, Krischer's model assumes a highly anisotropic physical structure. Carson [25] has shown that over a range of compositions, thermal conductivity models that assume anisotropic structures will not fit experimental data for isotropic structures as well as conductivity models that are based on isotropic physical models, and, it is reasonable to assume, vice versa. Models derived from Eq. (1) may have either isotropic or anisotropic structures.

Secondly, the models described in this work have distinct individual physical bases, which allow for an intuitive approach to the selection of the appropriate model. For example, Carson et al. [18] proposed thermal conductivity bounds for two classes of porous materials. "Internal porosity materials" were defined as materials in which the gaseous phase was dispersed in a continuous high conductivity phase – the upper bound of thermal conductivity of internal porosity materials was given by the Maxwell–Eucken model with the gaseous phase dispersed (ME1 in this paper), while the lower bound was defined by the EMT model. The ME1 + EMT model provides a logical intermediate structure between these two extremes that may be more accurate for an internal porosity material that has neither a true Maxwell structure nor a true EMT structure. With a model such as Krischer's, the choice of f (or the equivalent parameter) might be little more than a guess.

6. A physical basis for Levy's model

Levy [26] produced a model based on the Maxwell–Eucken model that avoided the perceived "problem" of deciding which of the two Maxwell–Eucken equations to use for a given material, since they produced different results (in actual fact this was not a problem, since the two forms were not supposed to produce the same result). The model was

$$K = k_1 \frac{2k_1 + k_2 - 2(k_1 - k_2)F}{2k_1 + k_2 + (k_1 - k_2)F} \tag{44}$$

where

$$F = \frac{2/G - 1 + 2v_2 - \sqrt{(2/G - 1 + 2v_2)^2 - 8v_2/G}}{2} \tag{45}$$

and

$$G = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2 + k_1 k_2/2} \tag{46}$$

However, since this model was derived solely by algebraic manipulation, with no stated physical basis, some subsequent researchers have been hesitant to recommend its use. For example, Pham and Willix [27], who were modelling the thermal conductivity of frozen meat and offal products, stated that: "The best predictions by far are obtained with Levy's model, which yields correct values...over the whole range of compositions...and temperatures...considered. The drawback of Levy's equation is a certain lack of physical justification, since it was based on mathematical rather than physical arguments."

A comparison of the effective thermal conductivities produced by Levy's model and the ME1 + ME2 model above shows that they are identical, and hence the two models are equivalent. Therefore the physical model of Levy's equation, which must be the same as the ME1 + ME2 model, is a homogeneous mixture (on the macroscopic scale) of equal volumes of the two Maxwell structures, in which the conductivities of both component structures are equal, as represented schematically in Fig. 1a.

7. Conclusions

A unifying equation has been developed for five fundamental effective thermal conductivity structural models (Series, Parallel, two forms of Maxwell–Eucken, Effective Medium theory), which form the basis of many of the more complex models available in the literature. *Structure volume fractions* and *structure composition factors* were defined and used in a new procedure for modelling complex materials as composites of these five basic structures, using simple combinatory rules (equal structure volumes and equal structure effective thermal conductivities). Worked examples for deriving models using the proposed procedure were presented. Each new model derived using this procedure is dependent only on the component materials' volume fractions and thermal conductivities, and not on any empirical parameter. In addition, each model has a distinct physical basis. The model combining the two forms of the Maxwell–Eucken model was shown to be equivalent to Levy's equation, thereby providing Levy's model with a physical basis.

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