BOUNDS FOR THE EFFECTIVE THERMAL PROPERTIES OF COMPOSITES

M. BEN-AMOZ

General Electric Company, 1000 Western Avenue (240G7), Lynn, MA 01910, U.S.A.

Abstract—The paper deals with the effective linear thermal properties of composites. Using a dynamic method, bounds are derived for the effective conductivity and specific-heat of matrix/inclusion composites containing compact inclusions. It is shown that such bounds remain finite, which establishes the principle of an upper (lower) limit on the attainable overall conductivity (resistivity) irrespective of how large (small) the inclusion conductivity may be compared with the matrix conductivity. Bounds are also derived for a variety of classes of disordered composites, including the particular class discussed recently by Kröner[2], the so-called materials of grade (∞, ∞, n). Altogether, bounds are derived for 16 different classes of materials and the statistical information pertaining to each class is given.

1. INTRODUCTION

In a recent paper[1], a dynamic method has been developed which led to estimates of the effective moduli by a method that employs simplifying assumptions akin to those of Voigt and Reuss in the elastostatic theory. In this paper, this method is employed to determine the effective linear thermal properties of multiphase composites in terms of volume concentrations and phase conductivities. Each phase is assumed to be isotropic and homogeneous and the mixture as a whole is also macroscopically homogeneous and isotropic. Two types of composites are considered: (a) matrix/inclusion composites and (b) heterogeneous mixtures where none of the phases is a continuous matrix. We show that for class (a) composites. assuming inclusions of compact form, both bounds remain finite in the limit of thermally rigid inclusions (or cavities), thereby establishing the principle of an upper (lower) limit on the attainable overall conductivity (resistivity), irrespective of how large (small) the inclusion conductivities may be in comparison with those of the matrix. This is considered in Section 3. In Section 4, we derive bounds for disordered composites by a method similar to that given in [1]. We show that if the diffusivity's dependence on wave-number is first established, one obtains optimum bounds on the local effective thermal properties Kröner's[2] recent classification of composites by degree of disorder is generalized to include disordered composites of mixed grade (with respect to disorder). This broader framework is found to contain bounds for a large class of composite materials hitherto not considered. Among such composites, we find a class of composites consisting entirely of cells, with each cell containing foreign impurities in the form of inclusions. The method leads to a total of 16 sets of bounds for various composite classes. The classes of materials associated with these bounds are discussed in Section 5, where appropriate statistical information is adjoined to each set of bounds.

2. METHOD OF ANALYSIS

Consider a mixture of N phases, each phase being homogeneous, isotropic, and of arbitrary geometry. The fractional volume of a phase is given by $a_r = V_r/V$. The mixture as a whole is both isotropic and homogeneous. The phase conductivities are denoted by K_r, the specific heats by C_r and the diffusivities by $\chi_r = K_r/C_r$. Let Q_i^r and $T_{,i}^r$ denote, respectively, the heat-flux and temperature gradient in the rth phase and let H_i^r represent a heat-flow vector in the rth phase. The heat-flow vector H_i is to be defined below. One can then define an effective conductivity K^* and an effective specific-heat C^* through the two relations

$$\langle Q_i \rangle \equiv \langle \partial H_i/\partial t \rangle = - K^* \langle T_{,i} \rangle = - \sum_{r=1}^{N} K_r a_r \bar{T}_{,i}^r$$

$$\langle \dot{H}_{,i} \rangle \equiv C^* \langle \partial T/\partial t \rangle = \sum_{r=1}^{N} C_r a_r \bar{\dot{T}}^r$$

(2.1)

where a dot denotes a partial time derivative and the brackets $\langle\rangle$ designate mixture averages taken over a representative volume *and* over a time-interval much longer than some characteristic cell time. The overbars in (2.1) refer to phase averages. Suppose that the phase averages are proportional to a prescribed temperature-gradient $T^0_{,i}$ and a prescribed rate $\dot{T}^0$, both applied to the surface of a representative volume element. Let

$$[\bar{T}_{,i}^r, \ \bar{\dot{T}}^r] = [A_r T^0_{,i}, \ B_r \dot{T}^0] \tag{2.2}$$

where A_r, B_r are factors of proportionality that are subject to the constraints

$$\sum_r [A_r, B_r] a_r = 1. \tag{2.3}$$

The effect of the assumed linear proportionality is that the following analysis is necessarily restricted to linear properties inasmuch as, inherent in this assumption, is the independence of the effective properties from the applied surface temperature-gradients or temperature-rates. With this understanding, we obtain upon substitution of (2.2) into (2.1)

$$K^* \langle T_{,i} \rangle = \sum_r K_r A_r a_r T^0_{,i}$$

$$C^* \langle \dot{T} \rangle = \sum_r C_r B_r a_r \dot{T}^0. \tag{2.4}$$

Since the mixture averages are equal to the applied thermal gradients and thermal rates, by virtue of relations (2.3), we obtain immediately from (2.4) the effective properties

$$K^* = \sum_r K_r A_r a_r$$

$$C^* = \sum_r C_r B_r a_r, \tag{2.5}$$

so that if the proportionality factors are known, the effective properties can be determined from (2.5). By following the same procedure one can formulate the inverse relations

$$\langle T_{,i} \rangle = -R^* \langle \dot{H}_i \rangle = -\sum_r R_r a_r \bar{\dot{H}}_i^r$$

$$\langle T \rangle = m^* \langle H_{i,i} \rangle = \sum_r m_r a_r \bar{H}^r_{i,i} \tag{2.6}$$

where $m_r = 1/C_r$ and R_r is the thermal-resistivity. Again, introducing proportionality factors A'_r, B'_r and requiring that $\langle \dot{H}_i \rangle = \dot{H}_i^0$ and $\langle H_{i,i} \rangle = H^0_{i,i}$, we obtain

$$R^* = \sum_r R_r A'_r a_r$$

$$m^* = \sum_r m_r B'_r a_r \tag{2.7}$$

the A'_r, B'_r being subject to the constraints

$$\sum_r [A'_r, B'_r] a_r = 1 \tag{2.8}$$

which are similar to (2.3). However, in the foregoing relations the temperature-gradient and temperature-rate (or $\dot{H}_i$ and $H_{i,i}$) are not entirely independent of each other. Rather, they are

related by a kinematical condition to be derived next. Consider the isothermal surface

$$T[x_k(\xi(t)), t] = C, \tag{2.9}$$

C being a parameter and $\xi(t)$ the position-vector of a point on the isothermal surface. The equation following the motion of the isothermal surface is

$$\frac{DT}{Dt} = 0 = \frac{\partial T}{\partial x_k}\frac{\mathrm{d}x_k}{\mathrm{d}t} + \frac{\partial T}{\partial t} \tag{2.10}$$

where $\mathrm{d}x_k/\mathrm{d}t$ is the speed of displacement of the isothermal surface in the direction of the normal to the surface. Since (2.10) is also valid in each phase of the composite medium, the relevant kinematical relation in the rth phase assumes the form

$$\partial T^r / \partial x_j + v_j^r(x_k) T^r (\tau_r / \chi_r)^{1/2} = 0 \tag{2.11}$$

where v_j^r is the normal to the moving isothermal surface in the rth phase, $(\chi_r/\tau_r)^{1/2}$ is the corresponding speed of displacement, and τ_r is a characteristic time associated with the rth phase. From (2.11), the squared speed-of-displacement is given by

$$\chi_r / \tau_r = |\dot{T}^r|^2 / |T,_j^r|^2, \tag{2.12}$$

so that, given χ_r, eqn (2.12) defines the characteristic time τ_r. Taking now averages of (2.11) over each phase and using the decompositions

$$\begin{aligned} v_j'^r &= v_j^r - \bar{v}_j^r \\ \dot{T}'^r &= \dot{T}^r - \bar{\dot{T}}^r, \end{aligned} \tag{2.13}$$

multiplying by the fractional volumes a_r and summing over all phases gives

$$\sum_{r=1}^{N} a_r \bar{T}^r,_j + \sum_{r=1}^{N} \bar{v}_j^r \bar{\dot{T}}^r a_r (\tau_r / \chi_r)^{1/2} = -\sum_r a_r \overline{v_j'^r \dot{T}'^r} (\tau_r / \chi_r)^{1/2} = -(\tau_r / \chi_r)^{1/2} R_j''. \tag{2.14}$$

Introducing into (2.14) the proportionality factors A_r, B_r we obtain

$$\langle T,_j \rangle + \sum_r B_r a_r \bar{v}_j^r (\tau_r / \chi_r)^{1/2} \langle \dot{T} \rangle = -(\tau_r / \chi_r)^{1/2} \langle R_j' \rangle \tag{2.15}$$

where $\langle R_j' \rangle = \sum_r R_j'^r a_r$. It is immediately apparent from (2.15) that necessary and sufficient conditions for the existence of mean isothermal surfaces in the composite medium moving at the effective speed-of-displacement $(\chi_r/\tau_r)^{1/2}$ is that

$$\langle R_j' \rangle = 0 \quad \text{and} \quad \bar{v}_j^r = v_j^* (\tau/\tau_r)^{1/2} \tag{2.16}$$

where v_j^* is the normal to the *mean* isothermal surface (about which the actual isotherm fluctuates) and τ is a characteristic time of the mixture as a whole. In view of (2.16), eqn (2.15) takes the form

$$\langle T,_j \rangle + \left(\sum_r a_r B_r / \chi_r^{1/2} \right) \tau^{1/2} v_j^* \langle \dot{T} \rangle = 0 \tag{2.17}$$

which is the effective kinematical relation for the mixture as a whole. From (2.17), the squared speed-of-displacement is given by

$$\chi^*/\tau = \left(\sum_r B_r a_r / \chi_r^{1/2} \right)^{-2} / \tau = |\langle \dot{T} \rangle|^2 / |\langle T,_j \rangle|^2 \tag{2.18}$$

so that if the effective diffusivity is known, eqn (2.18) defines the mixture characteristic time τ. Note that the condition $\langle R_j' \rangle = 0$ in (2.16) will be satisfied subsequently by proper assumptions about the temperature field. By exactly the same procedure, and considering the motion of a surface of constant heat-flow, we obtain the complementary equation

$$\langle H_{i,i} \rangle + \left(\sum_r A_r a_r / \chi_r^{1/2} \right) \tau^{1/2} \nu_i^* \langle \dot{H}_i \rangle = 0. \tag{2.19}$$

Equations (2.3), (2.5) and (2.17) apply when surface temperatures are specified while (2.7), (2.8) and (2.19) apply when the heat-flux is prescribed. Both sets form the basis of the following analysis.

3 EFFECTIVE PROPERTIES OF MATRIX/INCLUSION COMPOSITES

We consider in this section composites in which inclusions of compact form are distributed in a matrix. The inclusions do not deviate appreciably from the spherical shape and do not touch each other. They may be harder or softer than the matrix and we distinguish accordingly between these two cases. Although the results apply to composites of any number of phases, it will be useful for clarity, to focus on a two-phase composite with conductivities K_1, $K_2(K_1 > K_2)$, specific heats $C_1, C_2(C_1 > C_2)$ and fractional volumes a_1, a_2. We shall seek to determine the effective properties in terms of the given information, namely, the phase properties and fractional volumes. In principle, these could be determined if all the proportionality factors in eqns (2.5) and (2.15), or in (2.7) and (2.19) were known. However, the constraint conditions (2.3) or (2.8) are not sufficient for this purpose, so that some simplifying assumptions as to temperature gradients and temperature rates must be introduced. Using this approach, bounds are derived on the effective conductivity and specific heat. In deriving such bounds, the basic idea is that given two different intervals, corresponding to applied surface temperatures or heatfluxes, the effective conductivity can lie only in the intersecting interval (common to both intervals) since then, and only then, would the effective conductivity be independent of the type of boundary condition, as it should. Hence, our aim will be to make the two intervals coalesce into a single interval and thus such an interval necessarily becomes a bounding interval for the effective conductivity.

3.1 High conductivity inclusions in a low conductivity matrix

The composite to be considered consists of high conductivity inclusions of compact form, not touching each other,† and embedded in a low conductivity matrix. Let us first consider relations (2.7), (2.8) and (2.19). The simplifying assumptions to be introduced must take into account that in the limiting case of perfectly conducting inclusions ($K_1 \to \infty$) the bounds must remain finite. A related consideration is that the temperature gradients in the inclusions must tend to zero as $K_1 \to \infty$, although the heat-fluxes remain finite. Taking also into consideration that at phase interfaces the flux must be continuous, a suitable assumption is that the flux is the same in both phases, which is equivalent to Reuss' approximation of constant stress in elastostatics. It follows from (2.7) that $A_1' = A_2' = 1$. Thus eqns (2.7) and (2.19) yield

$$R^* = \sum R_r a_r = 1/K_R \qquad K_R = (A_1/K_1 + a_2/K_2)^{-1}$$

$$m^* = \sum m_r B_r' a_r \tag{3.1}$$

$$\nu_i^* \langle \dot{H}_i \rangle (\tau/\chi_R)^{1/2} + \langle H_{i,i} \rangle = 0, \qquad (\sqrt{\chi})_R = (a_1/\sqrt{(\chi_1)} + a_2/\sqrt{(\chi_2)})^{-1}$$

and the factors B_r' are still to be determined. Consider now relations (2.5) and (2.17) which hold when surface temperatures are prescribed. Since the temperature gradients in the inclusions

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†This assumption, together with assumption of compact inclusions implies a finite temperature gradient in the matrix. Hence, the effective conductivity can never attain an infinite, or zero value, when the inclusions are thermally rigid or cavities.

must tend to zero as $K_1 \to \infty$, the assumption of uniform gradients in both phases is inadmissible. However, continuity of temperatures must be maintained at phase interfaces so that the assumption of equal temperature rates in both phases is suitable. It follows that $B_1 = B_2 = 1$, so that from (2.5) and (2.17)

$$K^* = \sum K_r A_r a_r$$

$$C^* = \sum C_r a_r = C_v \tag{3.2}$$

$$\langle T_{,i} \rangle + v_i^* \langle \dot{T} \rangle (\tau/\chi_R)^{1/2} = 0.$$

The problem now is to determine B_r' in $(3.1)_2$ and A_r in $(3.2)_1$. Although K^* in $(3.2)_1$ is the exact effective conductivity *if* the A_r are exact, we shall here invert the problem by requiring that K^* be merely the inverse of K_R^{-1} and determine the approximate A_r accordingly. To this end, multiply $(3.1)_1$ and $(3.2)_1$. Hence

$$K^* R^* = 1 = \sum K_r A_r a_r / K_R \tag{3.3}$$

whereas from (2.3)

$$A_1 a_1 + A_2 a_2 = 1. \tag{3.4}$$

Thus both A_1 and A_2 can be determined.† By applying a similar argument to eqns $(3.1)_2$ and $(3.2)_2$ we obtain

$$B_1' a_1 / C_1 + B_2' a_2 / C_2 = 1/C_v$$

$$B_1' a_1 + B_2' a_2 = 1. \tag{3.5}$$

These can be solved for B_1' and B_2'. It follows from (3.1) and (3.2) that $K^* = K_R$ on one hand, and $K^* C_v (\sqrt{(\chi)})_R^2$ on the other (using the definition $K^*/C^* = \chi^*$). The latter conductivity reduces in the steady-state limit $C_1 \to C_2 \to 0$ to $(\sqrt{(K)})_R^2$.‡ Hence, irrespective of the boundary conditions the effective conductivity is given either by K_R or by $(\sqrt{(K)})_R^2$. This duality implies that the actual effective conductivity cannot be uniquely determined. Rather, it must lie somewhere in the interval

$$K_R \leq K^* \leq (\sqrt{K})_R^2 \qquad (\sqrt{K})_R = (a_1/\sqrt{(K_1)} + a_2/\sqrt{(K_2)})^{-1}. \tag{3.6}$$

Since this interval is one and the same for either type of boundary condition, it is necessarily a bounding interval for the effective conductivity.§ The limiting case $K_1 \to \infty$ is of particular interest. Let $K_1 \to \infty$ *in* (3.6),

$$K_2/a_2 \leq K^* \leq K_2/a_2^2, \tag{3.7}$$

and thus both bounds remain finite, as anticipated. The factors A_r are also of interest. These are

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†In a multiphase composite it is necessary to assume that the gradients in all phases except phase "one" are equal to those of the matrix, phase "two". The bounds are then of the same form as the bounds for a two-phase composite.

‡The meaning of the assumption $C_1 \to C_2 \to 0$ is best understood in reference to the equation of heat-conduction $\text{Div}(K \, \text{Grad} \, T) = C \, \partial T/\partial t$. If the temperature is slowly varying it is permissible to ignore "thermal inertia" effects by letting $C \to 0$ which leads to the equation $\text{Div}(K \, \text{Grad} \, T) = 0$, governing the quasi-steady field.

§The reader who might consider the present proof insufficiently rigorous, may view the bounds (3.6) as mere estimates. However, subsequent results show, independently of the present proof, that $K_R \leq K^* \leq K_R(K_v^{1/2}/K_R^{1/2})$ are rigorous bounds (see eqn 4.21_1) for a mixture of lengthy and compact inclusions distributed in a matrix, whereas $(\sqrt{K})_R^2 \leq K^* \leq K_R(K_v^{1/2}/K_R^{1/2})$ are rigorous bounds (see eqn 4.21_2) for lengthy inclusions. It follows that $(\sqrt{K})_R^2$ is a dividing line between the intervals for lengthy and compact inclusions and thus $K_R \leq K^* \leq (\sqrt{K})_R^2$ are necessarily rigorous bounds for compact inclusions. This constitutes an independent proof of such bounds. Similar remarks apply to the bounds (3.15).

given by

$$A_1 = [1 + a_2(K_1/K_2 - 1)]^{-1}; \qquad A_2 = [1 - a_1(1 - K_2/K_1)]^{-1}. \tag{3.8}$$

In the limit $K_1 \to \infty$, we have $A_1 = 0$ and $A_2 = 1/a_2$. The corresponding average gradients are $\overline{\nabla T}_1 = 0$ and $\overline{\nabla T}_2 = \langle \nabla T \rangle / a_2$ as expected. Analogously, relations (3.1) and (3.2) lead to the effective specific heats $C^* = C_v$ and $C^* = K_R/(\sqrt{\chi})_R^2$. The latter reduces in the steady state limit $K_1 \to K_2 \to 0$ to $C^* = C_v$ and $C^* = (\sqrt{C})_v^2$. Hence the effective specific heat is bounded by

$$(\sqrt{C})_v^2 \leq C^* \leq C_v. \tag{3.9}$$

3.2 Low conductivity inclusions in a high conductivity matrix

This configuration is obtained from the previous one by reversing the roles of the phases while the fractional volumes are kept unchanged. In deriving bounds for this case, it must be taken into account that in the limit of cavities ($K_2 \to 0$), both bounds must remain finite. Hence the assumption of equal fluxes in both phases would be unsuitable since continuity at interfaces would imply zero flux everywhere. For the present purpose it will be useful to re-arrange (2.17) and (2.19) in the alternative forms

$$\left(\sum A_r a_r (\chi_r/\tau)^{1/2} \right) v^* \langle \nabla T \rangle + \langle \dot{T} \rangle = - \sum a_r (\tau/\chi_r)^{1/2} \overline{v'' \nabla T''}$$

$$\langle \dot{H}_i \rangle + \sum B'_r a_r (\chi_r/\tau)^{1/2} v_i^* \langle H_{j,i} \rangle = - \sum a_r (\chi_r/\tau)^{1/2} \overline{v_i'' H_{j,j}''}. \tag{3.10}$$

To eqn $(3.10)_1$ we adjoin relations (2.5), or

$$K^* = \sum K_r A_r a_r; \qquad C^* = \sum C_r B_r a_r \tag{3.11}$$

whereas to eqn $(3.10)_2$ we adjoin relations (2.7), or

$$R^* = \sum R_r A'_r a_r; \qquad m^* = \sum m_r B'_r a_r. \tag{3.12}$$

We assume next that the gradients are the same in both phases, so that $A_1 = A_2 = 1$. On the other hand, with respect to $(3.10)_2$ and (3.12) we assume that the divergence of H_i is equal in both phases so that $B'_1 = B'_2 = 1$. Relations (3.10)–(3.12) yield then

$$K^* = \sum K_r a_r = K_v; \qquad C^* = \sum C_r B_r a_r \qquad K_v = K_1 a_1 + K_2 a_2$$

$$(\sqrt{(\chi/\tau)})_v v^* \langle \nabla T \rangle + \langle \dot{T} \rangle = 0 \tag{3.13}$$

and

$$R^* = \sum R_r A'_r a_r; \qquad m^* = \sum m_r a_r = 1/C_R \qquad C_R = (a_1/C_1 + a_2/C_2)^{-1}$$

$$\langle \dot{H}_i \rangle + (\sqrt{(\chi/\tau)})_v v_i^* \langle H_{j,i} \rangle = 0. \tag{3.14}$$

It can be shown by the previous reasoning that the effective conductivity, either from (3.13) or (3.14), is given by $K^* = K_v$ and $K^* = (\sqrt{K})_v^2$. The actual effective conductivity is thus bounded by

$$(\sqrt{K})_v^2 \leq K^* \leq K_v. \tag{3.15}$$

Consider now the limiting case $K_2 \to 0$. It follows from (3.15) that

$$K_1 a_1^2 \leq K^* \leq K_1 a_1. \tag{3.16}$$

Thus both bounds remain finite as anticipated. The proportionality factors A'_r are given by

$$A'_1 = [1 - a_2(1 - K_2/K_1)]^{-1}$$

$$A'_2 = [1 + a_1(K_1/K_2 - 1)].^{-1} \tag{3.17}$$

Thus in the limit of cavities ($K_2 \to 0$), these reduce to $A'_1 = 1/a_1$ and $A'_2 = 0$ so that the average phase fluxes are $\bar{Q}_1 = \langle Q \rangle / a_1$ and $\bar{Q}_2 \equiv 0$, as it should. It can also be shown, on taking the limit $R_1 \to R_2 \to 0$ that the effective specific-heat is bounded by

$$C_R \leqslant C^* \leqslant (\sqrt{C})_R^2. \tag{3.18}$$

4. SYSTEMATIC DERIVATION OF BOUNDS FOR DISORDERED COMPOSITIES

The bounds (3.6) and (3.15) represent special cases of a more general set of bounds to be derived in this section for disordered composites of much more general topology. In this derivation, we follow Kröner's recent systematic theory[2]. According to Kröner's theory a material is said to be of grade (∞, ∞, n) if it is (statistically) perfectly isotropic and homogeneous and if the information with respect to statistical disorder has been verified only up to correlation functions of order n. In this classification, Hashin and Shtrikman's bounds correspond to grade ($\infty, \infty, 2$) and hence an intrinsic assumption is that the distribution of thermal conductivities and domain shape statistics are uncorrelated of grade 2. Our object, in this section, is to derive bounds by a systematic procedure that allows a classification of composite materials analogous but more general than Kröner's classification. Assuming perfect statistical homogeneity and isotropy we show that materials can be classified as of mixed grade $ij(n)$ with respect to statistical disorder. The advantage is that this classification contains general matrix/inclusion structures as well as structures with cell domains, in addition to the special class of materials considered by Kröner[2], whose underlying assumption is that moduli and topology are uncorrelated. Besides, we find according to this classification, a new class of hybrid composites consisting of M inclusion phases distributed in $N - M$ other phases whose topology may consist of cell domains or matrix/inclusion domains. In this manner, the present classification encompasses a total of 16 different classes of composite materials, for which distinct bounds are derived.

The present analysis is similar to that given in [1], whereby the diffusivity's dependence on wave-number is first established. Once such a relation is available, the resulting constitutive thermal relations are found to be nonlocal and furthermore, in the quasi-steady case, these lead to bounds on the effective conductivities. The point of departure are the constitutive relations (2.1) and the kinematical condition (2.17)

$$\langle \dot{H}_i \rangle = - \sum K_r A_r a_r \langle T, i \rangle$$

$$\langle \dot{H}_{i,t} \rangle = \sum C_r B_r a_r \langle \dot{T} \rangle \tag{4.1}$$

$$\langle T_{,i} \rangle + \sum B_r a_r \sqrt{(\tau/\chi_r)} \, v_i^* \langle \dot{T} \rangle = - \overline{v_i' T''} \, a_r \sqrt{(\tau/\chi_r)}.$$

For present purposes it proves convenient to write (4.1) in an alternative form by utilizing the kinematical conditions in each phase and the fact that the diffusion-speed ($\sqrt{\chi_r/\tau}$) can be expressed in the alternative forms

$$\sqrt{(\chi_r/\tau)} = [K_r/I_r, \ I_r/C_r, \ \sqrt{(K_r)}/\sqrt{(C_r)}, \ (\sqrt{\chi_r})^\beta (\sqrt{\chi_r})^{1-\beta}]/\sqrt{\tau} \tag{4.2}$$

where $I_r = (K_r C_r)^{1/2}$ is defined as a "thermal impedance", and the parameter β ranges continuously from zero to 1/2. Using (4.2), eqns (4.1) can be written in the alternative form

$$\langle \dot{H}_i \rangle - \sum I_r B_r a_r \nu_i^* \langle \dot{T} \rangle = \sum I_r a_r \overline{\nu_i'^r T''}$$

$$\langle \dot{H}_{i,i} \rangle + \sum I_r A_r a_r \nu_i^* \langle T_{,i} \rangle = - \sum I_r a_r \overline{\nu_i'^r T_{,i}'^r} \tag{4.3}$$

$$\sum A_r a_r [(\sqrt{\chi_r})^\beta, \ (\sqrt{\chi_r})^{1-\beta}, \ K_r, \ I_r^{-1}, \ I_r, \ C_r^{-1}, \ \sqrt{(K_r)}, \ \sqrt{(C_r)}] \langle T_{,i} \rangle$$

$$+ \sum B_r a_r [(\sqrt{\chi_r})^{\beta-1}, \ (\sqrt{\chi_r})^{-\beta}, \ I_r, \ K_r^{-1}, \ C_r, \ I_r^{-1}, \ \sqrt{(C_r)}, \ (\sqrt{K_r})^{-1}] \nu_i^* \langle \dot{T} \rangle = R_i'$$

where R_i' depends only on the deviations $\nu_i'^r T'$. It is not difficult to show that corresponding to (4.3) are the inverse relations

$$\langle T_{,i} \rangle - \left(\sum B_r' a_r / I_r \right) \nu_i^* \dot{H}_{i,j} = \sum a_r \overline{\nu_i'^r H_{j,j}'^r} / I_r$$

$$\langle \dot{T} \rangle + \left(\sum A_r' a_r / I_r \right) \nu_i^* \langle \dot{H}_i \rangle = - \sum a_r \overline{\nu_i'^r H_i'^r} / I_r \tag{4.4}$$

$$\sum A_r' a_r [(\sqrt{\chi_r})^{\beta-1}, \ (\sqrt{\chi_r})^{-\beta}, \ I_r, \ K_r^{-1}, \ C_r, \ I_r^{-1}, \ \sqrt{C_r}, \ (\sqrt{K_r})^{-1}] \langle \dot{H}_i \rangle$$

$$+ \sum B_r' a_r [(\sqrt{\chi_r})^\beta, \ \sqrt{\chi_r})^{1-\beta}, \ K_r, \ I_r^{-1}, \ I_r, \ C_r^{-1}, \ \sqrt{K_r}, \ \sqrt{C_r}^{-1}] \nu_i^* \langle \dot{H}_{i,j} \rangle = S_i'$$

where S_i' depends only on the deviations $\overline{\nu_i'' H_{j,j}'^r}$. To determine the proportionality factors in (4.3), we assume that the temperature gradients and rates are the same in all phases, which means that all concentration factors are unity. Thus

$$I^* = I_v, \qquad I_v = I_1 a_1 + I_2 a_2 \tag{4.5}$$

from the first two relations (4.3). From the third relation (4.3), we obtain the alternative effective diffusion-speeds:

$$\sqrt{(\chi^*/\tau)} = [K_v/I_v, \ I_v/C_v, \ (\sqrt{K})_v/(\sqrt{C})_v, \ (\sqrt{(\chi)^{1-\beta}})_v (\sqrt{(\chi)^\beta})_R, \ (\sqrt{(\chi)^{1-\beta}})_R (\sqrt{(\chi)^\beta})_v,$$

$$(\sqrt{(K)})_R/(\sqrt{C})_R, \ I_R/C_R, \ K_R/I_R]. \tag{4.6}$$

Similarly, assuming in (4.4) that the flux, the divergence of $\dot{H}_i$ are the same in all phases, all proportionality factors are unity and thus

$$I^* = I_R, \qquad I_R = (a_1/I_1 + a_2/I_2)^{-1} \tag{4.7}$$

whereas (4.4)$_3$ leads to the set (4.6) of effective diffusion-speeds. The problem now is to determine wave-numbers appropriate to each speed in the set (4.6). This is accomplished by considering the kinematical conditions belonging to each pair in (4.6). For instance, the equations associated with the outer pair are

$$\langle T_{,i} \rangle + \nu_i^* \langle \dot{T} \rangle / \sqrt{(\chi_{max}/\tau)} = 0$$

$$\langle T_{,i} \rangle + \nu_i^* \langle \dot{T} \rangle / \sqrt{(\chi_{min}/\tau)} = 0 \tag{4.8}$$

where $\sqrt{(\chi_{max})} = K_v/I_v$ and $\sqrt{(\chi_{min})} = K_R/I_R$. Let $T_{,i}$ be of order T_0/l and $\dot{T}$ of order T_0/τ, where T_0 is some representative temperature, l is a suitable length scale and τ a suitable time-scale. Define the "outer" and "inner" time scales

$$\tau_0 = \bar{d}^2 / \chi_{min}$$

$$\tau_i = \bar{d}^2 / \chi_{max} \tag{4.9}$$

where $\bar{d}$ is, for instance, a representative dimension of an average cell. Introducing $(4.9)_1$ into $(4.8)_1$ and $(4.9)_2$ in $(4.8)_2$ it is found that for the two terms $\dot{T}$ and $T_{,i}$ to be of equal order it is necessary that

$$\bar{d}/l_0 = \sqrt{(\chi_{\min}/\chi_{\max})}$$
$$\bar{d}/l_i = \sqrt{(\chi_{\max}/\chi_{\min})}. \tag{4.10}$$

This defines therefore two dimensionless wave-numbers that satisfy the reciprocity relation

$$(\bar{d}/l_0)(\bar{d}/l_i) = 1. \tag{4.11}$$

By applying the same procedure one can define wave-number pairs belonging to the inner pairs of diffusion-velocities in (4.6) so that the diffusion vs wave number relation can be constructed as shown in Fig. 1, by erecting the diffusivities given by (4.6) at the corresponding wave numbers as determined from relations similar to (4.10). Note that because β is continuous, the diffusivity curve is continuous within the central range shown by a solid line in Fig. 1. This fact is crucial to the subsequent derivation of an infinite set of bounds. We prove next that the thermal "impedances" I_v and I_R derived from the systems (4.3) and (4.4) are actually upper and lower bounds on the effective thermal impedance. Once this is proved it follows automatically that the effective thermal conductivity ($K^{\text{eff}} = I^{\text{eff}} (\sqrt{\chi^*/\tau})$) is bounded by

$$I_R \sqrt{(\chi^*/\tau)} \leq K^{\text{eff}} \leq I_v \sqrt{(\chi^*/\tau)}, \tag{4.12}$$

where $\sqrt{(\chi^*/\tau)}$ is given by the set (4.6). The proof starts from the simple Voigt and Reuss bounds

$$K_R \leq K^{\text{eff}} \leq K_v. \tag{4.13}$$

Dividing (4.13) through by $\sqrt{(\chi^*/\tau)}$ (given by 4.6), we obtain immediately the following sets of bounds on the effective thermal impedance

$$I^{\text{eff}} \leq [I_v, K_v C_v/I_v, K_v(\sqrt{C})_v/(\sqrt{K})_v, K_v/(\sqrt{(\chi)}^{1-\beta})_v(\sqrt{(\chi)}^{\beta})_R, K_v/(\sqrt{(\chi)}^{1-\beta})_R(\sqrt{(\chi)}^{\beta})_v,$$
$$K_v(\sqrt{C})_R/(\sqrt{K})_R, K_v C_R/I_R, K_v I_R/K_R]$$
$$\geq [I_R, K_R C_R/I_R, K_R(\sqrt{C})_R/(\sqrt{K})_R, K_R/(\sqrt{(\chi)}^{1-\beta})_R(\sqrt{(\chi)}^{\beta})_v, K_R/(\sqrt{(\chi)}^{1-\beta})_v(\sqrt{(\chi)}^{\beta})_R,$$
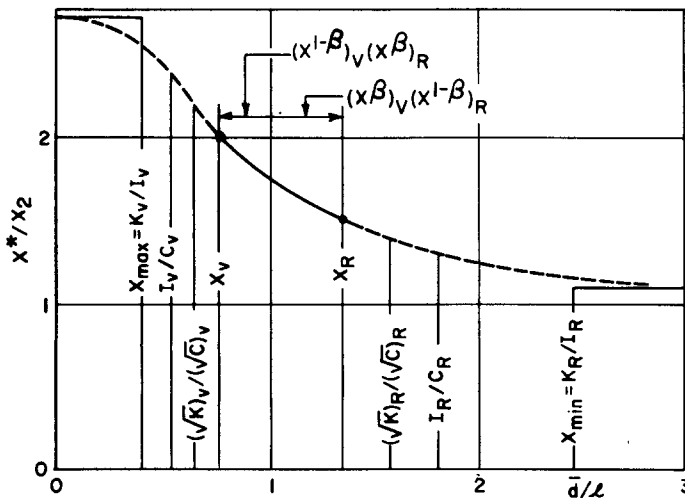$$K_R(\sqrt{C})_v/(\sqrt{K})_v, K_R C_v/I_v, K_R I_v/K_v] \tag{4.14}$$

Fig. 1. Diffusivity vs wave-number.

and thus

$$I_R \leqslant I^{\text{eff}} \leqslant I_v \tag{4.15}$$

represent the narrowest, and thus the optimum bounds of the entire set appearing in (4.14). It follows therefore that the bounds (4.12) also represent optimum bounds on the wave-number-dependent effective conductivity. Taking the limit $C_1 \to C_2 \to 0$ we obtain the following sets of bounds for the effective quasi-steady thermal conductivity

$$K^{\text{eff}} \leqslant [K_v, (\sqrt{K})_v (K^{(1-\beta)/2})_v (K^{\beta/2})_R, (\sqrt{K})_v (K^{\beta/2})_v (K^{(1-\beta)/2})_R, (\sqrt{K})_v K_R/(\sqrt{K})_R]$$

$$\geqslant [K_R, (\sqrt{K})_R (K^{(1-\beta)/2})_R (K^{\beta/2})_v, (\sqrt{K})_R (K^{\beta/2})_R (K^{(1-\beta)/2})_v, (\sqrt{K})_R K_v/(\sqrt{K})_v]. \tag{4.16}$$

Since each upper bound in (4.16) can be associated with any of the four lower bounds, we obtain in this manner sets of mixed bounds which are best arranged in a 4×4 matrix form

$$K_{ij}^{\text{eff}}(\beta) = \begin{vmatrix} K_{11}^* & K_{12}^* & K_{13}^* & K_{14}^* \\ K_{21}^* & K_{22}^* & K_{23}^* & K_{24}^* \\ K_{31}^* & K_{32}^* & K_{33}^* & K_{34}^* \\ K_{41}^* & K_{42}^* & K_{43}^* & K_{44}^* \end{vmatrix} \tag{4.17}$$

where

$$\left.\begin{aligned} K_R &\leqslant K_{11}^* \leqslant K_v \\ (\sqrt{K})_R (K^{\beta/2})_v (K^{(1-\beta)/2})_R &\leqslant K_{12}^* \leqslant K_v \\ (\sqrt{K})_R (K^{(1-\beta)/2})_v (K^{\beta/2})_R &\leqslant K_{13}^* \leqslant K_v \\ (\sqrt{K})_R K_v/(\sqrt{K})_v &\leqslant K_{14}^* \leqslant K_v \end{aligned}\right\} \tag{4.18}$$

$$\left.\begin{aligned} K_R &\leqslant K_{21}^* \leqslant (\sqrt{K})_v (K^{(1-\beta)/2})_v (K^{\beta/2})_R \\ (\sqrt{K})_R (K^{\beta/2})_v (K^{(1-\beta)/2})_R &\leqslant K_{22}^* \leqslant (\sqrt{K})_v (K^{(1-\beta)/2})_v (K^{\beta/2})_R \\ (\sqrt{K})_R (K^{(1-\beta)/2})_v (K^{\beta/2})_R &\leqslant K_{23}^* \leqslant (\sqrt{K})_v (K^{(1-\beta)/2})_v (K^{\beta/2})_R \\ (\sqrt{K})_R K_v/(\sqrt{K})_v &\leqslant K_{24}^* \leqslant (\sqrt{K})_v (K^{(1-\beta)/2})_v (K^{\beta/2})_R \end{aligned}\right\} \tag{4.19}$$

$$\left.\begin{aligned} K_R &\leqslant K_{31}^* \leqslant (\sqrt{K})_v (K^{\beta/2})_v (K^{(1-\beta)/2})_R \\ (\sqrt{K})_R (K^{\beta/2})_v (K^{(1-\beta)/2})_R &\leqslant K_{32}^* \leqslant (\sqrt{K})_v (K^{\beta/2})_v (K^{(1-\beta)/2})_R \\ (\sqrt{K})_R (K^{(1-\beta)/2})_v (K^{\beta/2})_R &\leqslant K_{33}^* \leqslant (\sqrt{K})_v (K^{\beta/2})_v (K^{(1-\beta)/2})_R \\ (\sqrt{K})_R K_v/(\sqrt{K})_v &\leqslant K_{34}^* \leqslant (\sqrt{K})_v (K^{\beta/2})_v (K^{(1-\beta)/2})_R \end{aligned}\right\} \tag{4.20}$$

$$\left.\begin{aligned} K_R &\leqslant K_{41}^* \leqslant (\sqrt{K})_v K_R/(\sqrt{K})_R \\ (\sqrt{K})_R (K^{\beta/2})_v (K^{(1-\beta)/2})_R &\leqslant K_{42}^* \leqslant (\sqrt{K})_v K_R/(\sqrt{K})_R \\ (\sqrt{K})_R (K^{(1-\beta)/2})_v (K^{\beta/2})_R &\leqslant K_{43}^* \leqslant (\sqrt{K})_v K_R/(\sqrt{K})_R \\ K_{44}^* &\leqslant (\sqrt{K})_v K_R/(\sqrt{K})_R \quad \text{or} \quad K_{44}^* \geqslant (\sqrt{K})_R K_v/(\sqrt{K})_v. \end{aligned}\right\} \tag{4.21}$$

The bounds K_{ii} in (4.17) as well as K_{i4} and K_{4j} are of particular interest. To establish a correspondence with Kröner's classification note that the K_{ij} are functions of the continuous parameter β, which ranges from zero to 1/2. There is therefore no loss in generality if β is related to the order n of the correlation functions in Kröner's theory. For example, these may be related in the alternative ways

$$\beta_n = 1/2 - 1/n \quad \text{or} \quad \gamma_n = 1/n \qquad n \geqslant 2 \tag{4.22}$$

where $n = 2$ corresponds to $\beta = 0$ (or $\gamma = 1/2$) and $n = \infty$ corresponds to $\beta = 1/2$ (or $\gamma = 0$). The first relation (4.22) is then used in the second terms of the set (4.16) while $(4.22)_2$ is used in the third terms. In this manner the bounds (4.17) become functions of n and thus the connection to Kröner's grade (∞, ∞, n) materials is established. Note, however, that in the present classification the single term $K_{22}^*(n)$ contains Kröner's bounds. In particular, $K_{22}^*(2)$ correspond to Hashin and Shtrikman's bounds. On the other hand, all other terms in the matrix (4.17) represent new bounds which will be termed bounds of *mixed* order. The classes of materials to which each set of bounds belongs are discussed in Section 5.

5. DISCUSSION OF BOUNDS

The bounds (4.17) belong to various classes of materials. Our aim, in this section, is to establish a correspondence between each bound K_{ij}^* and the class of materials to which it belongs. Let us start with the simplest bounds K_{11}^* which are the well-known Voigt and Reuss bounds. These are the worst bounds since the only information are the phase conductivities and volume concentrations. To discuss the other bounds it is convenient to define the following hybrid material: Suppose a composite of N phases $(N > 2)$, of which M phases $(M < N - 1)$ are inclusions distributed in the other $N - M$ phases. Suppose now that the further information is given that the M inclusion phases are distributed in $N - M$ phases of unspecified topology. If the inclusion conductivities are, on average, lower than the conductivities of the $N - M$ phases, the relevant bounds are K_{12}^* and if they are higher, on average, the relevant bounds are K_{21}^*. Suppose, now, that $M = 0$ and that distribution of conductivities and domain shape statistics are uncorrelated, then the relevant bounds are $K_{22}^*(n)$. The bounds' dependence on n defines in this case the class of materials designated by Kröner[2] as uncorrelated of grade (∞, ∞, n). Thus, the bounds $K_{22}^*(2)$ correspond to Hashin and Shtrikman's bounds,[†] while $K_{22}^*(3)$ corresponds to Kröner's grade $(\infty, \infty, 3)$ bounds. Note that in this class the narrowest bounds, from $(4.19)_2$, are

$$(\sqrt{K})_R (K^{1/4})_v (K^{1/4})_R \leqslant K_{22}^*(\infty) \leqslant (\sqrt{K})_v (K^{1/4})_v (K^{1/4})_R. \qquad (5.1)$$

These correspond to grade (∞, ∞, ∞) materials in Kröner's classification. The interesting point here is that the bounds (5.1) do not coincide even with perfect disorder, which should not be surprising since the topology in this case is not specified. That is to say, it is not known yet whether the composite domains are cells or have a matrix/inclusion structure. The bounds (5.1) are plotted in Fig. 2 for a ratio $K_1/K_2 = 100$ and it is seen that the bounds $K_{22}^*(\infty)$ are much narrower than $K_{22}^*(2)$. Suppose next that the M inclusion phases are distributed in $N - M$ phases which consist entirely of cells. Assuming further that inclusion conductivities are, on average, lower than those of the cell phases and that lengthy inclusions are, on average, of lower conductivity than compact inclusions, then the relevant bounds are K_{13}^*. If, on the other hand, inclusions are of higher conductivity than the cell phases and furthermore if lengthy inclusions are of higher conductivity than compact inclusions (on average), the relevant bounds are K_{31}^*. Suppose, now, that the information pertaining to K_{13}^* or K_{31}^* is restricted by the fact that all inclusions are lengthy. Then the relevant bounds are either K_{23}^* or K_{32}^*. Suppose, next, that $M = 0$ so that all composite domains consist of *cells*. Then the relevant bounds are $K_{33}^*(n)$, given by $(4.20)_3$. Note that the worst bounds belonging to this class as $K_{33}^*(2)$, which are precisely the best bounds in the class $K_{22}^*(n)$, viz. $K_{22}^*(\infty)$. The main point of interest in this class of bounds is that the $K_{33}^*(\infty)$ bounds coincide to give the exact effective modulus.[‡]

$$K_{33}^*(\infty) = (\sqrt{K})_v (\sqrt{K})_R. \qquad (5.2)$$

This result is entirely plausible since the topology in this case is well specified. The bounds $K_{33}^*(n)$ are plotted in Fig. 3 for a ratio $K_1/K_2 = 100$.

Consider, now, the case where the M inclusion phases are distributed in $N - M$ phases which have a matrix/inclusion structure. Note that the M inclusion phases may be embedded

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†The correspondence is only in the sense that the present bounds are numerically essentially the same as Hashin and Shtrikman's bounds for sufficiently small ratios of phase conductivities. However, the structure of the formulae is entirely different.
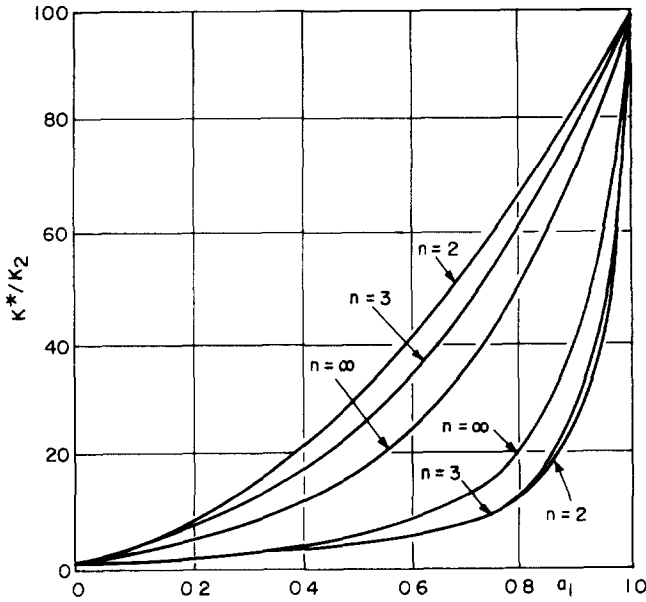‡This modulus corresponds to the modulus obtained by the self-consistent method.

Fig. 2. Bounds $K_{22}^*(n)$ for disordered composites (conductivities/topology uncorrelated).
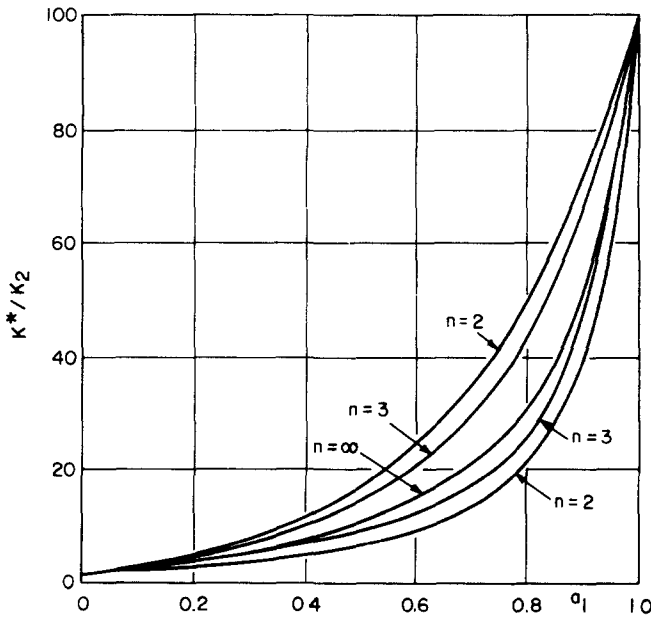

Fig. 3. Bounds $K_{33}^*(n)$ for disordered composites (cell domains).

either in other inclusions or in a matrix phase. In either case, the bounds belonging to this information are L_{44}^* given by (4.21)$_4$. These bounds state only that the effective conductivities must be *either* greater than $(\sqrt{K})_R K_v/(\sqrt{K})_v$ *or* less than $(\sqrt{K})_v K_R/(\sqrt{K})_R$. This dichotomy reflects the fact that the given information does not specify which of the phases is a matrix. Hence, by adding that the inclusions are, on average, of lower or higher conductivity than the matrix, the relevant bounds are K_{34}^* and K_{43}^*, respectively. Note that the upper bound in K_{34}^*, or lower bound in K_{43}^* are not valid since they violate the inequalities (4.16) by being lower (higher) than the lower (upper) bounds. So that $K_{34}^* \geqslant (\sqrt{K})_R K_v/(\sqrt{K})_v$ and $K_{43}^* \leqslant (\sqrt{K})_v K_R/(\sqrt{K})_R$, correspond to the above information. Finally, if we add the further information that lengthy inclusions are, on average, of lower conductivity than compact inclusions the relevant bounds are K_{14}^*, whereas if they are of higher conductivity, the relevant bounds are K_{41}^*. If we now restrict all inclusions to be lengthy then we obtain the narrower bounds K_{24}^* or K_{42}^*. Suppose, now, that instead of lengthy inclusions we restrict all inclusions to

be compact. Then we obtain the bounds (3.6) and (3.15) given in Section 3. Note also that the upper bound K_{24}^* is not valid if $(\sqrt{K})_v^2 < (\sqrt{K})_R K_v/(\sqrt{K}_v)$. This occurs when

$$a_1 < a_1^*, \quad \text{where} \quad a_1^* = [1 + (K_1/K_2)^{1/4}]^{-1}. \tag{5.3}$$

The effective conductivity in this case must nevertheless fall within the larger bounds K_{14}^* for matrix/inclusion composites, so that for $a_1 < a_1^*$ the bounds K_{24}^* must be replaced by K_{14}^*. The same applies to the lower bound (3.15) so that for $a_1 < a_1^*$ the bounds K_{14}^* apply to all matrix/inclusion composites irrespective of whether the inclusions are lengthy or compact, or both. It can be shown by an analogous argument that for $a_1 > 1 - a_1^*$ the lower bound K_{42}^* ceases to be valid and so does the upper bound in (3.6). Hence the bounds K_{41}^* apply to all
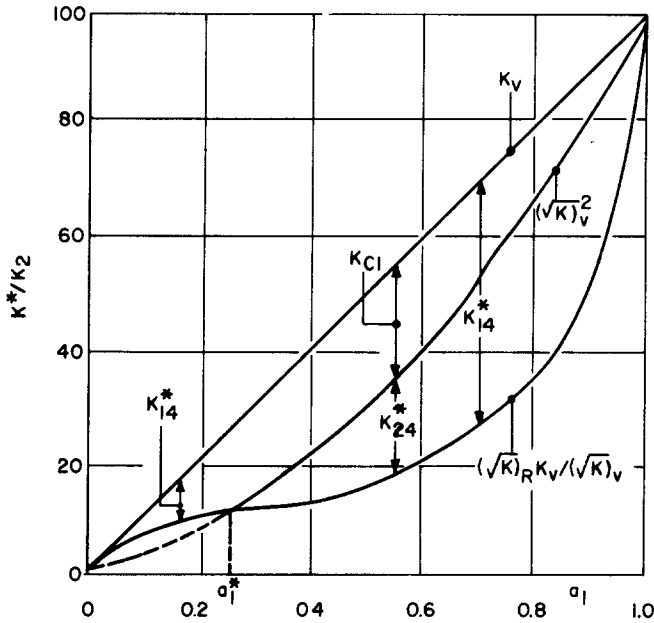

Fig. 4. Bounds for matrix/inclusion composites. (K_{14}^*—lengthy and compact inclusions; KCl compact inclusions; K_{24}^* lengthy inclusions.)
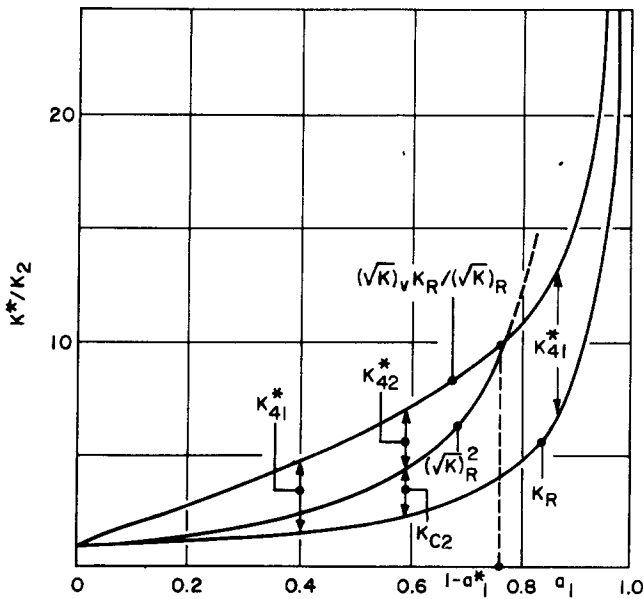

Fig. 5. Bounds for matrix/inclusion composites. (K_{41}^* lengthy and compact inclusion; K^*c2 compact inclusions; K_{42}^* lengthy inclusions.)

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matrix/inclusion composites regardless of inclusion shapes. The bounds for matrix/inclusion composites are plotted in Figs. 4–5 for a ratio $K_1/K_2 = 100$.

From the preceding discussion it seems clear that except for the bounds (3.6) and (3.15), the present systematic method yields bounds for practically all conceivable classes of composite materials.† That the bounds (3.6) and (3.15) are not contained in this general scheme was only to be expected since their derivation stems from a different set of simplifying assumptions. More basically, the bounds (3.6) and (3.15) involve the distinct physical principle of both bounds remaining finite in the limit of thermally rigid inclusions or cavities. This principle, incidentally, does not apply to any of the bounds (4.17). It is also interesting to note that all bounds for

Table 1. Summary of results

Effective conductivity	Upper bound	Lower bound	Relevant information
K_{11}^*	K_L	K_R	Conductivities; volume fractions.
K_{22}^*	$(\sqrt{K})_v (K^{(1-\beta_n)/2})_v (K^{\beta_n/2})_R$	$(\sqrt{K})_R (K^{\beta_n/2})_v (K^{(1-\beta_n)/2})_R$	Conductivities/topology uncorrelated.
K_{33}^*	$(\sqrt{K})_L (K^{\gamma_n/2})_v (K^{(1-\gamma_n)/2})_R$	$(\sqrt{K})_R (K^{(1-\gamma_n)/2})_v (K^{\gamma_n/2})_R$	Cell domains.
K_{44}^*	$\geq (\sqrt{K})_R K_v/(\sqrt{K})_v$ or	$\leq (\sqrt{K})_L K_R/(\sqrt{K})_R$	Matrix/inclusion composite.
K_{34}^*	—	$(\sqrt{K})_R K_v/(\sqrt{K})_v$	Matrix/inclusion composite; inclusions softer (on average) than matrix.
K_{43}^*	$(\sqrt{K})_v K_R/(\sqrt{K})_R$	—	Matrix/inclusion composite; inclusions harder (on average) than matrix.
K_{24}^*	$\dfrac{(\sqrt{K})_v^2 \qquad a_1 > a_1^*}{K_v \qquad a_1 < a_1^*}$	$(\sqrt{K})_R K_v/(\sqrt{K})_L$	Matrix/inclusion composite; lengthy inclusions: inclusions softer (on average) than matrix.
K_{42}^*	$(\sqrt{K})_v K_R/(\sqrt{K})_R$	$\dfrac{(\sqrt{K})_R^2 \qquad a_1 < 1 - a_1^*}{K_R \qquad a_1 > 1 - a_1^*}$	Matrix/inclusion composite; lengthy inclusions;inclusions harder (on average) than matrix.
K_{14}^*	K_v	$(\sqrt{K})_R K_v/(\sqrt{K})_v$	Matrix/inclusion composite; lengthy inclusions softer (on average) than compact inclusions and matrix.
K_{41}^*	$(\sqrt{K})_v K_R/(\sqrt{K})_R$	K_R	Matrix/inclusion composite; lengthy inclusions harder (on average) than compact inclusions and matrix.
Eqn (3.15)	K_v	$\dfrac{(\sqrt{K})_L^2 \qquad a_1 > a_1^*}{(\sqrt{K})_R K_v/(\sqrt{K})_v \qquad a_1 < a_1^*}$	Matrix/inclusion or cell/inclusion composite; compact inclusions; inclusions softer than matrix or cells.
Eqn (3.6)	$\dfrac{(\sqrt{K})_R^2 \qquad a_1 < 1 - a_1^*}{(\sqrt{K})_v K_R/(\sqrt{K})_R \qquad a_1 > 1 - a_1^*}$	K_R	Matrix/inclusion or cell/inclusion composite; compact inclusions; inclusions harder than matrix or cells.
K_{12}^*	K_V	$(\sqrt{K})_R (K^{\beta_n/2})_L (K^{(1-\beta_n)/2})_R$	$N - M$ Phases of unspecified topology containing M inclusion phases; inclusions softer (on average) than $N - M$ phases.
K_{21}^*	$(\sqrt{K})_v (K^{(1-\beta_n)/2})_v (K^{\beta_n/2})_R$	K_R	$N - M$ Phases of unspecified topology containing M inclusion phases; inclusions harder (on average) than $N - M$ phases.
K_{13}^*	K_v	$(\sqrt{K})_R (K^{(1-\gamma_n)/2})_v (K^{\gamma_n/2})_R$	Inclusion/cell composite; lengthy inclusions softer (on average) than compact inclusions and cells.
K_{31}^*	$(\sqrt{K})_v (K^{\gamma_n/2})_v (K^{(1-\gamma_n)/2})_R$	K_R	Inclusion/cell composite; lengthy inclusions harder (on average) than compact inclusions and cells.
K_{23}^*	$(\sqrt{K})_v (K^{(1-\beta_n)/2})_v (K^{\beta_n/2})_R$	$(\sqrt{K})_R (K^{(1-\gamma_n)/2})_v (K^{\gamma_n/2})_R$	Inclusion/cell composite; lengthy inclusions; inclusions softer (on average) than cells.
K_{32}^*	$(\sqrt{K})_v (K^{\gamma_n/2})_v (K^{(1-\gamma_n)/2})_R$	$(\sqrt{\kappa})_R (K^{\beta_n/2})_v (K^{(1-\beta_n)/2})_R$	Inclusion/cell composite; lengthy inclusions; inclusions harder (on average) than cells.

$$\beta_n = 1/2 - 1/n \qquad \gamma_n = 1/n$$

†As has been found in-between, there exists an additional matrix of bounds, analogous to (4.17), for compact domains in which the bounds (3.6) and (3.15) are two elements of the matrix. This will be discussed in a forthcoming paper on the effective elastic properties.

matrix/inclusion composites turn out to be independent of β or γ (and thus of the order n of the correlation functions). That this should be the case is obvious from the fact that a matrix/inclusion structure is not disordered in the same sense as the structures belonging to the bounds $K_{22}^*(n)$ or $K_{33}^*(n)$. This, however, does not imply any order in the distribution of inclusions throughout the matrix.

We remark finally, that the introduction of the hybrid composite described earlier not only helps to identify the various classes of materials to which the bounds (4.17) belong. Rather, we have thereby included a large number of composite materials not previously considered. As a concrete example, we have in mind a composite that may consist entirely of cells but each cell contains foreign impurities in the form of inclusions; as limiting cases these may be perfectly conducting inclusions or cavities. Note also that the bounds (3.6) and (3.15) apply equally to such composites if the inclusions are compact, since the derivation of these bounds does not depend on the inclusions being necessarily distributed in a matrix. As a further example of such hybrid composites, we mention the case of a matrix/inclusion structure in which each inclusion contains an aggregate of smaller inclusions.

Due to the large number of bounds it seemed worthwhile to summarize the results in a table as given below.

6. CONCLUSION

Although the main emphasis has been on bounding the quasi-steady state conductivities, it should be mentioned that if the assumption of quasi-steadiness is dropped, this leads to two enlarged (8×8) matrices of bounds for the conductivity and specific heat. The bounds correspond to 64 different classes of materials. It can be shown that the enlarged number of material classes is related to the fact that both conductivities and specific heats are now random variables. So that one has to define a generalized material of grade (n, m) where n means "conductivities and topology uncorrelated of grade n" and m refers to "conductivities and specific heats perfectly correlated of grade m". Note that if $m < n$, it cannot be inferred that both conductivities *and* specific heats are uncorrelated with domain shape statistics (to nth order correlation functions). It will be shown in a forthcoming paper that the enlarged matrices lead to bounds on both local and nonlocal effective properties. In particular, the bounds on nonlocal properties enable the construction of dispersion relations (diffusivity vs wave number) for each of the 64 material classes, from which nonlocal continuum equations can be derived for each class of materials.

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