Simple second-order expression: For the porosity dependence of thermal conductivity

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In a series of recent publications it has been shown that there is an almost complete formal analogy in the micromechanical relations describing the effective shear viscosity of suspensions and the effective tensile modulus of porous media [1–5]. In particular, the Coble-Kingery approach [6] to describe the nonlinear porosity dependence of the effective elastic moduli has been recalled [1, 3] and, based on the corrected version of the Coble-Kingery relation for the effective tensile modulus [1], a new relation, the simplest with percolation threshold (critical porosity), has been proposed for the porosity dependence of the effective tensile modulus [5]. We emphasize again, that the aforementioned analogy originates from the possibly analogous microstructures or microstructural models of suspensions and porous media, i.e., it concerns micromechanical relations and is therefore of an entirely different character than the well-known continuum mechanical analogy between linear elasticity and linear viscosity [7].

In this paper we use the Coble-Kingery approach [6] to derive a handy formula for the porosity dependence of the effective thermal conductivity k. Probably the earliest formula applicable to this property in composites of the matrix-inclusion type is the Maxwell approximation of 1873 [7–9], which describes a model material with spherical inclusions. For a two-phase material it can be written in the form

$$k_r = \frac{1 - \frac{2}{3}[k]\,\phi}{1 + \frac{1}{3}[k]\,\phi}, \tag{1}$$

where

$$[k] = \frac{3 \cdot (k_0 - k_1)}{2k_0 + k_1} \tag{2}$$

can be called "intrinsic thermal conductivity" (see below), with k_0 being the thermal conductivity of the matrix phase, k_1 that of the inclusion phase, $k_r = k/k_0$ the relative (or "reduced") thermal conductivity and $\phi = \phi_1$ the volume fraction of the inclusions. Note that for a two-phase material the volume fractions of the constituent phases must sum up to unity, i.e., the volume fraction of the matrix phase is complementary to ϕ, i.e., $\phi_0 = 1 - \phi$. Definition (2) has been chosen with regard to the fact that in the dilute limit ($\phi \to 0$) Equation 1 can be approximated by the linear expression (neglecting terms of higher order in ϕ)

$$k_r = 1 - [k]\,\phi, \tag{3}$$

which is the conductivity counterpart of the Jeffery–Einstein relation [10, 11] in suspension rheology

$$\eta_r = 1 + [\eta]\,\phi_S, \tag{4}$$

(with shear viscosity η and solids volume fraction ϕ_S) and can be viewed as being in complete analogy to the Dewey-Mackenzie-Christensen relations [12–14] in elasticity context

$$M_r = 1 - [M]\,\phi, \tag{5}$$

(with M being the shear, bulk, or tensile modulus, respectively and $[M]$ being a function of the Poisson ratio of the matrix phase). In all these linear dilute approximations, Equations 3 through 5, the quantities in square brackets denote "intrinsic" properties, generalizing to the widely used term "intrinsic viscosity" in the context of suspension rheology [15]. Note that here the definitions of the intrinsic properties $[k]$, $[\eta]$, and $[M]$ have been chosen in such a way to make their values positive, i.e.,

$$[\eta] \equiv \lim_{\phi \to 0} \frac{\eta_r - 1}{\phi} \tag{6a}$$

for the intrinsic viscosity, but

$$[M] \equiv -\lim_{\phi \to 0} \frac{M_r - 1}{\phi}. \tag{6b}$$

and

$$[k] \equiv -\lim_{\phi \to 0} \frac{k_r - 1}{\phi} \tag{6c}$$

for the intrinsic conductivity and intrinsic elastic moduli, respectively, in contrast to [1–5]. These new definitions are more convenient (since otherwise all $[k]$ and $[M]$ values would be negative) and emphasize the intuitive notion of a decreasing property value with increasing porosity.

The intrinsic properties are generally (albeit possibly non-unique) functions of inclusion shape, e.g., the aspect ratio of spheroidal particles in suspension rheology. For spherical inclusions exhibiting certain extreme properties (rigid particles in the case of suspensions, voids with zero property value in the case of porous materials) they adopt the values $[\eta] = 2.5$ (Einstein value [10]), $[M] = 2$ (only in the peculiar case of a matrix

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Poisson ratio value of 0.2, cf. [9, 16, 17]) and $[k] = 1.5$ (see below).

It is well known that, accidentally, the Maxwell approximation, Equation 1, is equivalent to one of the Hashin-Shtrikman bounds [7, 9], which have been derived on the basis of variational principles [18] for a coated-spheres model [19] (also called composite spheres model [20], polydisperse model [21], or "Hashin assemblage" model [9]) and can be written as follows:

$$k_{\mathrm{HS}}^{-} \leq k_{\mathrm{r}} \leq k_{\mathrm{HS}}^{+}. \tag{7}$$

In this expression

$$k_{\mathrm{HS}}^{-} = \frac{\bar{k}}{k_0} - \frac{\phi\,(1-\phi)\,(k_0-k_1)^2}{k_0\,(3k_1+\phi\,(k_0-k_1))} \tag{8a}$$

and

$$k_{\mathrm{HS}}^{+} = \frac{\bar{k}}{k_0} - \frac{\phi\,(1-\phi)\,(k_0-k_1)^2}{k_0\,(3k_0-(1-\phi)\,(k_0-k_1))}, \tag{8b}$$

with indices 0 and 1 referring to the matrix and the inclusion phase, respectively. It can easily be shown that in the case of porous materials ($k_0 \gg k_1$), Equation 1 is equivalent to the upper Hashin-Shtrikman bound given by Equation 8b, i.e., $k_{\mathrm{r}} = k_{\mathrm{HS}}^{+}$.

Another equivalent formulation of the Maxwell approximation, Equation 1, is due to Christensen [20], who derived it via his three phase model:

$$k_{\mathrm{r}} = 1 + \left(\frac{1-\phi}{3} + \frac{k_0}{k_1-k_0}\right)^{-1} \cdot \phi. \tag{9}$$

We note that this relation, in either of the alternative formulations (1), (8b), or (9), has been rederived by Kerner in 1956 in the context of electrical conductivity [20–22]. However, in thermal conductivity context it has been derived by Eucken as early as 1932 [23, 24]. Indeed, it can be used for all scalar coefficients in linear constitutive equations of the same type (Torquato's "class A" steady-state effective media problems [7]), i.e., apart from thermal conductivity [23, 24] e.g., for electrical conductivity (in this context also called "Maxwell-Garnett approximation" [8, 22, 25]), magnetic permeability [18], dielectric constant (in this context called "Clausius-Mossotti formula" [26]), and refractive index (in this context called "Lorenz-Lorentz formula" [26]), cf. [7, 9, 20].

While the Maxwell approximation is based on an effective field concept (single inclusion embedded in a matrix phase, presence of the remaining inclusions accounted for by imposing an external mean field different from the one applied macroscopically), the so-called self-consistent approximation rests on an effective medium concept and treats the inclusions as embedded in a homogeneous medium of unknown effective properties [7, 9]. According to the self-consistent approximation [25, 27, 28], the relative thermal conductivity of a two-phase material is given by the expression (7)

$$k_{\mathrm{r}} = \frac{C + \sqrt{C^2 + 8k_0k_1}}{4k_0}, \tag{10}$$

where the parameter C is defined as

$$C \equiv (2-3\phi)\,k_0 + (3\phi-1)\,k_1. \tag{11}$$

As mentioned before, in the case of empty (vacuous) or air-filled voids (phase 1) the thermal conductivity of the inclusion phase k_1 (pores) can be neglected in comparison with that of the matrix phase (phase 0), i.e., $k_1 \ll k_0$. In this case the intrinsic conductivity calculated according to Equation 2 is $[k] = 3/2$ and thus the relative conductivity calculated according to the linear approximation, Equation 3, valid in the dilute limit ($\phi \to 0$), is

$$k_{\mathrm{r}} = 1 - \frac{3}{2}\,\phi, \tag{12}$$

which corresponds to the prediction of the self-consistent approximation, Equation 10, for this case. Note that both the linear approximation (3) and the self-consistent approximation (12) predict for this case a percolation threshold (i.e., a critical porosity at which the conductivity becomes zero) at approx. 67 vol%, in contrast to the Maxwell approximation, which is nonlinear and admits the possibility of finite thermal conducitivities up to porosities close to 100%, cf. Fig. 1. Without doubt, the latter possibility must be taken into account for closed-pore cellular solids (foams) or open-pore network structures [29].

Now we adopt the Coble-Kingery approach [6] to derive a simple formula which can account for nonlinear porosity dependences of the effective thermal conductivity and allows the occurrence of finite conductivities up to very high porosities. Therefore we set

$$k_{\mathrm{r}} = 1 - \frac{3}{2}\,\phi + A\,\phi^2 \tag{13}$$

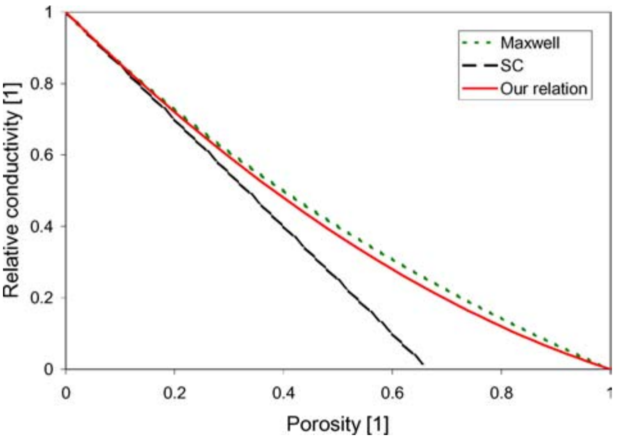

Figure 1 Prediction of the relative conductivity of porous materials according to the Maxwell model or Hashin-Shtrikman upper bound (dotted), the self-consistent (SC) approximation (dashed), and our relation (full line); the conductivity of the void phase is assumed to be negligibly small.

and determine the value of the second-order coefficient A from the plausible condition that $k_r = 0$ when $\phi = 1$. Obviously $A = 0.5$ and thus the new relation can be written in the form

$$k_r = 1 - \frac{3}{2}\,\phi + \frac{1}{2}\,\phi^2. \tag{14}$$

This handy expression is probably the simplest nonlinear relation which might serve for rough estimates and prediction purposes. The k_r values it predicts are all slightly lower than those predicted via the Maxwell approximation, Equations 1 or 9, which in the present case of pores ($k_1 \ll k_0$) attains the form

$$k_r = 1 - \frac{3\,\phi}{2+\phi} = 1 - \left(\frac{3}{2} - \frac{3}{4}\,\phi + \frac{3}{8}\,\phi^2 + \cdots + (-1)^{n+1}\cdot\frac{3}{2^n}\cdot\phi^{n-1}\right)\cdot\phi, \tag{15}$$

which always yields higher values than Equation 14, cf. Fig. 1. Evidently, this is reasonable from the theoretical point of view, because the Maxwell approximation embodies the upper Hashin-Shtrikman bound, Equation 8b. Interestingly, the maximum deviation (approx. 10% lower value) of the prediction via Equation 14 compared to the prediction via Equation 15 occurs at a porosity of 64 vol%. We also note that our second-order expression (14) comes to lie between the second-order approximation of the cluster expansion performed by Jeffrey [30] for impenetrable insulating spheres,

$$k_r = 1 - \frac{3}{2}\,\phi + 0.588\,\phi^2 \tag{16}$$

and the second-order approximation of the cluster expansion performed by Torquato [31] for fully penetrable insulating spheres,

$$k_r = 1 - \frac{3}{2}\,\phi + 0.345\,\phi^2. \tag{17}$$

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