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Short communication

A new percolation-threshold relation for the porosity dependence of thermal conductivity

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Abstract

A simple second-order relation for the porosity dependence of thermal conductivity is proposed which allows for the occurrence of a critical porosity (percolation threshold). This new relation is simpler than McLachlan's power-law relation and thus more advantageous for fitting purposes. It is based on a Coble–Kingery-type relation for the effective thermal conductivity and formally analogous to a relation for the effective tensile modulus recently proposed by the authors. In the case of model systems where the percolation threshold is known a priori it can provide a prediction of the porosity dependence of thermal conductivity.
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It is known that there are many analogies in the micromechanical relations describing different effective properties (i.e. coefficients of linear constitutive equations) of porous media [1,2] and even between effective properties of porous media and suspensions [3–5]. This concerns e.g. rigorous bounds (Voigt–Reuss bounds, Hashin–Shtrikman bounds) as well as dilute approximations (linear) and the nonlinear approximations resulting from the self-consistent, differential and Coble–Kingery approach. The reason for these formal mathematical analogies is that – however different the underlying physics of different phenomena for real materials may be – guided by the attempt to achieve greatest possible simplicity in the calculations, analogous model microstructures (with largely identical geometric and topological features, e.g. matrix-inclusion type microstructures with isolated spherical inclusions) are taken to describe idealized model materials.

The current interest in modeling the effective thermal conductivity of porous materials is partly triggered by the application of certain ceramic materials as thermal barrier coatings [6]. Recently, the Coble–Kingery approach [7–9] has been adopted to derive a simple second-order expression for the porosity dependence of the thermal conductivity [10]. This second-order expression is

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

where $k_{\mathrm{r}} = k/k_0$ is the relative (or "reduced") thermal conductivity (with k being the effective thermal conductivity of the porous material as a whole and k_0 being the thermal conductivity of the matrix or skeleton phase) and ϕ the porosity (volume fraction of pores). The value 3/2 for the first-order coefficient in this relation is well known and can be obtained for the special case $k_1 = 0$ (i.e. when the thermal conductivity k_1 of the gas phase possibly filling the pores or voids is negligible) from the value of the "intrinsic thermal conductivity" $[k]$, which is in the case of spherical inclusions

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

cf. [10]. The value 1/2 obtained via the Coble–Kingery approach for the second-order coefficient seems to be rather realistic since it lies right in between the values for the

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second-order approximation of the cluster expansion performed by Jeffrey [11] for impenetrable insulating spheres,

$$k_{\mathrm{r}} = 1 - \frac{3}{2}\phi + 0.588\phi^2, \tag{3}$$

and that performed by Torquato [12] for fully penetrable insulating spheres,

$$k_{\mathrm{r}} = 1 - \frac{3}{2}\phi + 0.345\phi^2. \tag{4}$$

Moreover, the value 1/2 for the second-order coefficient ensures that the curve described by Eq. (1) does not violate the Hashin–Shtrikman upper bound (i.e. is always lower than the Maxwell approximation) for porous materials,

$$k_{\mathrm{r}} = \frac{1-\phi}{1+\phi/2}, \tag{5}$$

as required [10]. Note, however, that the particular value 3/2 for the first-order coefficient has been derived for a model microstructure with spherical pores, while in general the intrinsic thermal conductivity must be assumed to vary with pore shape. In the case of non-spherical pores, Eq. (1) can be written in the generalized form:

$$k_{\mathrm{r}} = 1 - [k]\phi + ([k]-1)\phi^2. \tag{6}$$

Nevertheless, in practice the spherical pore shape model can be expected to be a satisfactory approximation for all pore types exhibiting approximately isometric shape, whether closed (isolated) or open (overlapping). Similar to the situation in elasticity context [13], it seems that extremely anisometric pore shapes are needed to cause uniquely assignable deviations from the value $[k] = 3/2$. In contrast to the linear approximation

$$k_{\mathrm{r}} = 1 - [k]\phi \tag{7}$$

which predicts e.g. for spherical pores ($[k] = 3/2$) a percolation threshold at $\phi = \phi_C = 2/3 \approx 0.67$, Eq. (1) (and also the general Eq. (6) as long as $[k] < 2$) predict finite thermal conductivities up to porosities approaching 100%. Although from a principal point of view this possibility must not be excluded (it should be taken into account, e.g. for solid foams or aerogels), many materials will in practice exhibit almost zero conductivity for porosities ϕ significantly lower than 100%, with the critical porosity value ϕ_C representing a percolation threshold (characteristic of a conductor–insulator transition) depending on the type of microstructure.

The most famous non-linear relation including a percolation threshold or critical porosity ϕ_C is the power-law relation proposed by McLachlan [14]

$$k_{\mathrm{r}} = \left(1 - \frac{\phi}{\phi_C}\right)^N, \tag{8}$$

for which accordance with Eq. (7) can be achieved for small porosities $\phi \to 0$ when the exponent N is chosen to be $N = [k]\phi_C$. This power-law relation is completely analogous to the Phani–Niyogi relation used in elasticity context [15] and the Krieger relation used in suspension rheology [16]. In practice this relation is often used for fitting purposes [6], usually with two adjustable parameters, ϕ_C and N. With respect to the frequently encountered practical problems with non-linear regression using multi-parameter power-law fits, however, the question can be raised whether it is possible to construct a simpler nonlinear relation with percolation threshold. This can indeed be done in complete analogy to a relation recently proposed in elasticity context [17]. The corresponding relation for the relative thermal conductivity reads

$$k_{\mathrm{r}} = (1 - [k]\phi + ([k]-1)\phi^2)\frac{(1-\phi/\phi_C)}{(1-\phi)}. \tag{9}$$

Since in the case of spherical pores the intrinsic thermal conductivity $[k]$ attains the value 3/2 (and in the case of other isometric pores a value at least very close to 3/2), cf. Eqs. (1)–(4) above, the new relation simplifies (at least approximately) to

$$k_{\mathrm{r}} = \left(1 - \frac{\phi}{2}\right)\left(1 - \frac{\phi}{\phi_C}\right) \tag{10}$$

Similar to McLachlan's power-law relation (8) the new simplified relation (10) is nonlinear and predicts $k_{\mathrm{r}} = 0$ at the percolation threshold (i.e. when a critical porosity ϕ_C is exceeded). Being formally simpler and computationally more robust, Eq. (10) represents a viable alternative to Eq. (8) for fitting purposes. In particular, since the number of adjustable fit parameters is reduced by one (compared to McLachlan's power law relation (8)), the numerical value of ϕ_C can be extrapolated with greater reliability. When the percolation phenomenon is absent (i.e. for $\phi_C = 1$) Eq. (10) reduces to the Coble–Kingery type relation (1), which further reduces to the linear approximation (7) for very small porosities ($\phi \to 0$), as required. Eq. (10) will be generally useful for fitting purposes. Of course, in the exceptional cases where the percolation threshold can be estimated a priori for well-defined model microstructures, cf. e.g. [18], Eq. (10) can provide a prediction (estimate) of the effective thermal conductivity corresponding to a certain porosity level.

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