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A cross-property relation between the tensile modulus and the thermal conductivity of porous materials

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Abstract

Elastic moduli and thermal conductivity are key properties determining a material's response to mechanical deformations and temperature gradients. Although in the case of heterogeneous materials the effective properties are uniquely determined by the material's microstructure, in the case of porous materials, due to the large difference in the phase properties, it is usually not possible to predict the porosity dependence of any of these properties based on volume fraction information alone. Thus, for real-world materials experimental measurement is often considered to be the only feasible way to obtain a reliable porosity dependence for the property in question. Here we show, however, that for isotropic materials either the relative tensile modulus E_r or the relative thermal conductivity k_r can be calculated from the other via the cross-property relation $3 \ln E_r = 4 \ln k_r$, as soon as one of them has been measured.

Keywords: B. Porosity; B. Microstructure-final; C. Thermal conductivity; C. Mechanical properties

In many practically important situations material behavior can be modeled via linear constitutive equations [1–3], e.g. Hooke's law describing the stress response of an isotropic material subject to small strains (deformations)

$$\boldsymbol{T} = \frac{E}{1+\nu}\left[\boldsymbol{E} + \frac{\nu}{1-2\nu}(\mathrm{tr}\mathbf{E})\mathbf{1}\right] \tag{1}$$

or Fourier's law describing the heat flux response of an isotropic material subject to a temperature gradient

$$\boldsymbol{q} = -k \,\mathrm{grad}\, T. \tag{2}$$

In these equations $\mathbf{T}$ denotes the Cauchy stress tensor, $\mathbf{E}$ the small strain tensor, tr$\mathbf{E}$ its trace, $\mathbf{1}$ the second order unit tensor, $\mathbf{q}$ the heat flux vector, $\mathbf{T}$ temperature and grad T its gradient. The coefficients E, ν and k are the material properties tensile modulus, Poisson ratio and thermal conductivity, respectively [1–3]. Note that two elastic constants are required to fully describe the elastic behavior of isotropic materials.

Within the framework of classical continuum theory there is no generally applicable method to predict the values of these material properties for mixtures, i.e. usually they have to be determined experimentally. There is, however, a notable exception: multiphase mixtures, where the constituents form individual phases. In this case (hetergeneous materials), the effective properties are uniquely determined by the phase properties and the microstructure of the material. Of course, an exact prediction would require all details of microstructure as input data, cf. [4–6]. Although the correlation function approach [4,5] is a promising step in this direction, at the moment the practical problems connected with determining higher-order microstructural information (i.e. multi-point correlation functions) are still immense. In practice, the researcher or engineer will often be lucky to dispose of a reliable volume fraction information of the constituent phases, i.e. the lowest-order microstructural information (one-point correlation function). It is clear that in such a case, using only volume fractions as input data, the prediction cannot be arbitrarily sharp. It can, however, be sharp enough to be useful for practical purposes. In particular, for isotropic microstructures the effective properties lie within the well-known Hashin–Shtrikman bounds [4–6]. When the phase properties are in the ratio 2:1, say, the difference between the upper and lower Hashin–Shtrikman bound will usually be smaller than typical errors of measurement, cf. e.g. the tensile modulus of dense (i.e. fully sintered and pore-free) alumina-zirconia composites,

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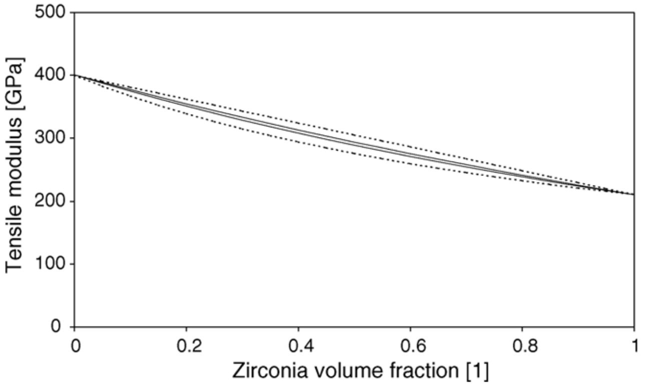

Fig. 1. Voigt–Reuss bounds (upper and lower dotted curve, respectively) and Hashin–Shtrikman bounds (upper and lower solid curve, respectively) as predicted for the effective tensile modulus of dense (i.e. fully sintered and pore-free) alumina-zirconia composite ceramics.

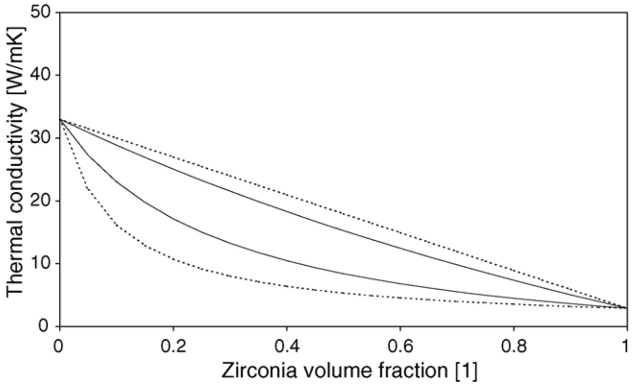

Fig. 2. Voigt–Reuss bounds (upper and lower dotted curve, respectively) and Hashin–Shtrikman bounds (upper and lower solid curve, respectively) as predicted for the effective thermal conductivity of dense (i.e. fully sintered and pore-free) alumina-zirconia composite ceramics.

where the phase moduli are E_0 (Al_2O_3) = 400 GPa and E_0 (ZrO_2) = 210 GPa, respectively [7], cf. Fig. 1, where the Hashin–Shtrikman bounds are shown together with the arithmetic mean (Voigt bound) and the harmonic mean (Reuss bound), cf. [6]. With increasing difference in the phase properties, however, the Hashin–Shtrikman bounds become wider. When the phase properties are in the ratio 10:1, say, they are almost useless for prediction purposes, cf. Fig. 2, which shows the Hashin–Shtrikman bounds for the effective thermal conductivity of dense alumina-zirconia composites at room temperature, assuming k_0 (Al_2O_3) = 33 W/mK and k_0 (ZrO_2) = 2.9 W/mK [8–11].

Porous materials can be considered as a special case of two-phase composites, with the void inclusions exhibiting essentially "zero properties". In this case, the Reuss bounds and the Hashin–Shtrikman lower bounds degenerate to zero, whereas the Voigt bounds are $E_r = k_r = 1 - \phi$ and the Hashin–Shtrikman upper bounds can be written in the remarkably simple form

$$E_r = \frac{1-\phi}{1+\phi} \tag{3}$$

for the tensile modulus (approximately) [12] and

$$k_r = \frac{1-\phi}{1+(\phi/2)} \tag{4}$$

for the thermal conductivity (exactly) [13–15]. In these equations $E_r = E/E_0$ is the relative tensile modulus (with E denoting the effective tensile modulus of the porous material and E_0 the tensile modulus of the dense solid, i.e. the skeleton or matrix phase), $k_r = k/k_0$ the relative thermal conductivity (with k denoting the effective thermal conductivity of the porous material and k_0 the thermal conductivity of the dense solid) and ϕ the porosity (volume fraction of the void inclusions).

Apart from these rigorous upper bounds there are linear approximations for the case of small porosities, based on the exact solution of the problem of a single spherical void embedded in an infinite solid matrix [16–18]. These are

$$E_r = 1 - 2\phi \tag{5}$$

for the tensile modulus (approximately) [12,19–21] and

$$k_r = 1 - \frac{3}{2}\phi \tag{6}$$

for the thermal conductivity (exactly) [10,11,13–15]. Note that the coefficient in Eq. (5) is a function of the matrix Poisson ratio ν_0 (a subtle consequence of the aforementioned fact that always two elastic constants are needed to describe the elastic behavior of an isotropic material) and is exactly 2 only when the matrix Poisson ratio is $\nu_0 = 0.2$ or $\nu_0 = 1/3$. It has been shown, however, that this value is a fairly good approximation for all commonly encountered matrix Poisson ratios in the range between $0.1 < \nu_0 < 0.4$ [6,12].

A third group of equations are power-law relations. These are

$$E_r = (1-\phi)^2 \tag{7}$$

for the tensile modulus [6,12,21,22] and

$$k_r = (1-\phi)^{3/2} \tag{8}$$

for the thermal conductivity [5,13]. In contrast to the latter two relations, which are rather well known, theoretically sound exponential relations have been proposed only recently. These are

$$E_r = \exp\left(\frac{-2\phi}{1-\phi}\right) \tag{9}$$

for the tensile modulus [23] and

$$k_r = \exp\left(\frac{(-3/2)\phi}{1-\phi}\right) \tag{10}$$

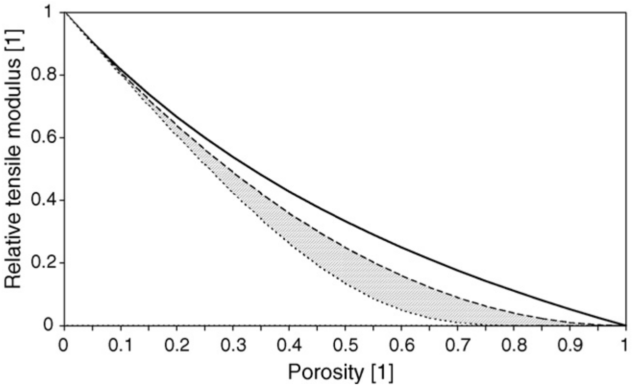

Fig. 3. Hashin–Shtrikman upper bound (Eq. (3), solid curve), power-law relation (Eq. (7), dashed curve) and modified exponential relation (Eq. (9), dotted curve) as predicted for the relative tensile modulus of porous materials.

for the thermal conductivity [11]. We emphasize that all these nonlinear relations, Eq. (7) through (10), provide a prediction of the porosity dependence of E_r and k_r over the whole range of porosities $0 < \phi < 1$. Furthermore, all of them provide physically correct statements for the extreme cases $\phi = 0$ and $\phi = 1$ and neither of them violates the upper Hashin–Shtrikman bounds (3) and (4). Note in particular that Eq. (9) is a significant improvement over the simple exponential relation proposed by Spriggs [24], which necessarily violates the upper bounds, in contrast to physical reality. With the numerical coefficients chosen as above (i.e. 2 and 3/2 for E_r and k_r, respectively) both the power-law relations (7) and (8) and the exponential relations (9) and (10) reduce to the corresponding linear approximations, Eqs. (5) and (6), in the case of small porosities ($\phi \to 0$), as required. Note, however, that for intermediate and high porosities the predictions they provide are widely different, cf. Figs. 3 and 4. The power-law relations (7), (8) are closer to the corresponding Hashin–Shtrikman upper bounds (which can be realized via the so-called Hashin-assemblage [5,25], consisting of polydisperse hollow spheres with an infinitely wide size distribution that enables space filling and features a fractal, closed cell microstructure) and are remarkably successful also in the description of open-cell foams or aerogels [26,27]. The exponential relations (9), (10), on the other hand, result in a porosity-dependence curve with a steeper decrease and have been shown to deliver a satisfactory prediction e.g. for certain matrix-inclusion-based microstructures [11,12]. It has been shown recently that both power-law relations and exponential relations can be derived using the so-called functional equation approach and that the fundamentally different form of these relations has its origin in one decisive step in this derivation [11,21,23].

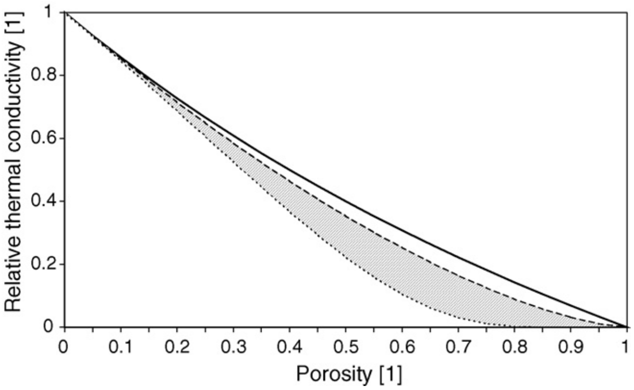

Fig. 4. Hashin–Shtrikman upper bound (Eq. (4), solid curve), power-law relation (Eq. (8), dashed curve) and modified exponential relation (Eq. (10), dotted curve) as predicted for the relative thermal conductivity of porous materials.

Although a priori it may not be clear whether power-law relations or exponential relations provide a better prediction for a certain real-world material, it must be expected that when Eq. (7) provides an adequate prediction for E_r, then Eq. (8) will provide the adequate prediction for k_r. A completely analogous conclusion holds for Eq. (9) in relation to Eq. (10). These statements imply the following cross-property relation

$$3 \ln E_r = 4 \ln k_r \tag{11}$$

It seems that this simple and useful relation has never been stated in the literature before. It enables one to calculate E_r for an arbitrary porosity level, without measuring it, from the (measured) value of k_r (and vice versa). Thus, when the value E_0 (or k_0) for the pore-free skeleton or matrix material is available, the effective tensile modulus (or effective thermal conductivity) can readily be calculated for the porosity in question.

Of course, in the limit of small porosities ($\phi \to 0$, i.e. $E_r \to 1$ and $k_r \to 1$) Eq. (11) reduces to the approximate cross-property relation

$$3E_r = 4k_r - 1, \tag{12}$$

which can also be obtained directly by combining Eqs. (5) and (6).

Although the cross-property relation (11) cannot be valid for arbitrary microstructures (e.g. in the case of parallel arrangement of the phases $E_r = k_r$, since both E_r and k_r are given by the Voigt bound) and a thorough investigation of its range of validity must remain a desideratum of future research, there is no doubt that it will be valid for a large set of materials with isotropic microstructures, at least for those with porosity-dependences between the power-law curves (upper curves, dashed) and the exponential curves (lower curves, dotted), cf. the shaded areas in Figs. 3 and 4. It should be of practical usefulness especially in cases where either E_r or k_r is difficult to measure.

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