The sigmoidal average – a powerful tool for predicting the thermal conductivity of composite ceramics

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Abstract. The sigmoidal average between the upper and lower Hashin-Shtrikman bounds is shown to be the appropriate average relation for isotropic two-phase composites consisting of geometrically equivalent grains. This average ensures that the prediction is close to the upper bound for low volume fractions of the low-conductivity phase (corresponding to low-conductivity inclusions in a high-conductivity matrix) and vice versa. In the intermediate concentration range the sigmoidal average reflects the fact that the microstructure is bicontinuous and can undergo a percolation-type transition. It is shown that the sigmoidal average of the Hashin-Shtrikman bounds lies automatically within the three-point bounds (Miller bounds) for a practically important class of microstructures (symmetric-cell materials with spherical cells) and that in the infinite-phase-contrast case (porous media) it is close to the exponential relation, which has been very successful in describing the porosity dependence of properties. Theoretical predictions are compared with experimentally measured values for alumina-zirconia composites in the whole range of volume fractions, from pure alumina to pure zirconia. Even after appropriate correction for porosity, essentially all experimental data are below the sigmoidal average. The fact that some values are even below the lower Hashin-Shtrikman bound is indicative of microcracking and/or grain size (interface) effects.

1. Introduction
The micromechanical approach [1] is widely acknowledged for estimating the effective thermal conductivity of composite ceramics. In particular, when heat transfer by other mechanisms (radiation, convection) can be neglected, rigorous bounds can be given, providing very reliable estimates, of course with the accuracy depending on the type of microstructural information available. When only the phase volume fractions are known, one-point (Wiener) bounds can be calculated, which are often too wide to be of practical usefulness. More restrictive two-point (Hashin-Shtrikman) bounds can be calculated when isotropy can be assumed. Indeed, experimental data published for composite ceramics obey these bounds in the vast majority of cases, when the influence of porosity is appropriately taken into account, e.g. by applying an exponential relation [2]. Violation of these bounds is usually indicative of highly anisometric (e.g. oblate, i.e. crack-like) pores or of grain size effects (interface effects due to interfacial thermal resistance), which can be modeled either via the Hasselman-Johnson relation [3] or by the phase mixture approach [4,5]. On the other hand, when higher-order microstructural information is available, typically in the form of three-point parameters obtained from image analysis, even more restrictive bounds can be calculated: the three-point (Beran) bounds. In practice, the extraction of these parameters for real materials is very cumbersome (often more difficult...
than direct property measurement), but in the special (but practically important) case of symmetric-cell microstructures, representing dense granular mixtures (polycrystalline composites) of two geometrically similar phases (grain types), values of these parameters are known from numerical simulations [1]. Since the key papers of Kingery and coworkers [6-8] it is well known that composites of this type typically exhibit a sigmoidal dependence of thermal (and electrical) conductivity on the volume fraction. In this contribution we show that a simple empirical average (sigmoidal average) provides a realistic estimate of the effective conductivity of two-phase composites. In particular, it is shown that – without requiring explicit knowledge of the three-point parameters – the sigmoidal average of the two-point (Hashin-Shtrikman) bounds is automatically close to the arithmetic average of the three-point bounds for symmetric-cell materials with spherical cells, which is the best choice when more specific microstructural information is lacking. The application of the sigmoidal average as a predictive tool is shown and confronted with other micromechanical predictions, including model-based ones, as well as recent experimental data on alumina-zirconia composites [9-11]. Throughout the text we confine ourselves to two-phase composites and assume that the volume fraction of one of the phases is the only quantitative microstructural information available.

2. Rigorous micromechanical bounds
The effective thermal conductivity of two-phase composites is principally restricted from above and below by the upper and lower Wiener bounds (one-point bounds) [12], which correspond to the volume-weighted arithmetic and harmonic mean, respectively, i.e.

\[ k^+_w = \langle k \rangle = \phi_1 k_1 + \phi_2 k_2, \]  

\[ k^-w = \langle k^{-1} \rangle = \frac{k_1 k_2}{\phi_1 k_2 + \phi_2 k_1}, \]  

where the superscript + and − indicate the type of bound (upper or lower), \( \phi_1, \phi_2 \) are the phase volume fractions and \( k_1, k_2 \) the phase conductivities. These bounds are valid for arbitrary microstructures, including anisotropic ones, like sandwich composites (laminates) and aligned-fiber composites. However, many composite ceramics are isotropic, especially those which are built up from isometric (equiaxed) grains or crystallites. In this case, where isotropy can be assumed, the effective thermal conductivity is bounded by the more restrictive Hashin-Shtrikman (HS) bounds (two-point bounds) [13]:

\[ k^+_{HS} = \langle k \rangle - \phi_1 \phi_2 \frac{(k_2 - k_1)^2}{\langle k \rangle + 2 k_1} = \phi_1 k_1 + \phi_2 k_2 - \frac{\phi_1 \phi_2 (k_1 - k_2)^2}{3 k_1 - \phi_1 (k_1 - k_2)}, \]  

\[ k^-_{HS} = \langle k \rangle - \phi_1 \phi_2 \frac{(k_2 - k_1)^2}{\langle k \rangle + 2 k_2} = \phi_1 k_1 + \phi_2 k_2 - \frac{\phi_1 \phi_2 (k_1 - k_2)^2}{3 k_2 + \phi_2 (k_1 - k_2)}, \]

(here written for the case \( k_1 > k_2 \), otherwise all indices have to be mutually changed) where

\[ \langle k \rangle = \phi_1 k_2 + \phi_2 k_1. \]  

This is all that can be rigorously stated, given only volume fractions. However, higher-order bounds (such as three-point bounds) can be calculated when higher-order microstructural information is
available, e.g. in the form of three-point correlation functions. In this case it is possible to calculate three-point microstructural parameters $\xi_1$, $\xi_2$ which have properties similar to volume fractions (e.g. they lie in the interval $0 \leq \xi_i \leq 1$ and they sum up to unity, i.e. for a two-phase composite $\xi_1 + \xi_2 = 1$) and allow an explicit calculation of the Beran bounds (three-point bounds) [14]:

$$k_B^+ = \langle k \rangle - \frac{\phi_1 \phi_2 (k_2 - k_1)^2}{\langle k \rangle + 2 \langle k \rangle_\xi}, \quad k_B^- = \langle k \rangle - \frac{\phi_1 \phi_2 (k_2 - k_1)^2}{\langle k \rangle + 2 \langle k \rangle_\xi^{-1}},$$

where

$$\langle k \rangle_\xi = \xi_1 k_1 + \xi_2 k_2.$$  \hspace{1cm} (7)

An important special case of the three-point bounds is that of symmetric-cell materials with spherical cells (also called Miller bounds [15]). In this case the three-point parameters are identical to the volume fractions, i.e. $\xi_i = \phi_i$, and the three-points bounds restrict an S-shaped region, approaching the upper Hashin-Shrikman bound when the high-conductivity phase is dominating and vice versa. Thus these bounds are appropriate to describe the typical behaviour of granular mixtures (polycrystalline composites with two geometrically equivalent grain types). In these mixtures, with increasing volume fraction (of phase 2, say), the topology changes from matrix-inclusion (phase 1 matrix, phase 2 inclusion) through bicontinuous (both phases connected or percolating) back to matrix-inclusion (of course now with phase 2 being the matrix and phase 1 the dispersed inclusions).

### 3. Empirical averages and the sigmoidal average

In order to predict the effective thermal conductivity of two-phase composites it is common practice to calculate an average (mean) value between the upper and lower bounds. As long as the phase contrast is low, i.e. ratio of phase conductivities is of order unity (in practice a factor of 2 or slightly higher), it is not important whether the arithmetic mean, the harmonic mean or, intermediate between these two, the geometric mean is used. However, when the phase contrast is about one order of magnitude or higher, the choice of an appropriate average is a tricky question, because in the limit of infinite phase contrast the lower bounds (one-, two- and three-point) approach zero identically. The simplest type of average that avoids this pitfall is the sigmoidal average [16]

$$k = \phi^* k^+ + (1 - \phi^*) k^-,$$  \hspace{1cm} (8)

where $k$ is the effective thermal conductivity, $k^+$ and $k^-$ are the upper and lower bounds, respectively, and $\phi^*$ is the volume-fraction of the high-conductivity phase. In principle, this type of average can be applied in connection with any type of bound (one-, two- and three-point). In practice, however, the three-point bounds are often not available, and it is therefore more convenient to model the sigmoidal behaviour ("S-shaped" dependence of the thermal conductivity on the second-phase volume fraction) simply by taking the sigmoidal average of the Hashin-Shtrikman bounds. It can be shown that the sigmoidal average of the Hashin-Shtrikman bounds lies automatically within the (practically important) aforementioned three-point bounds for symmetric-cell materials with spherical cells (Miller bounds). That means, the sigmoidal average is expected to be reasonable approximation in all cases where matrix and inclusions can change their roles in dependence of the volume fraction. It is in fact the expected exact result when two grain types with different properties (here conductivities) have statistically the same geometry (size and shape).
4. Comparison to model-based relations
Early work on conductivity and similar properties (e.g. dielectric permittivity and magnetic permeability) used the so-called Lichtenecker relation \[17\], i.e. the volume-weighted geometric mean

\[ k = k_1^{\phi_1} k_2^{\phi_2} \]  \hspace{1cm} (9)

as an estimate for the effective conductivity of composites. Its use can be justified by simplicity and by fact that it automatically lies between the upper and lower Wiener bounds. However, as can be seen from figure 1, it violates the Miller bounds and cannot predict sigmoidal dependences. The Maxwell model (in this context also called Maxwell-Eucken relation), although model-based, can be shown to be identical to one of the Hashin-Shtrikman bounds, although the latter are, of course, model-independent \[1\]. One of the most popular model-based relations (effective medium approximations) is the Bruggeman-Landauer relation (self-consistent model) \[18,19\], which can be written as

\[ k = \frac{\lambda + \sqrt{\lambda^2 + 8 k_1 k_2}}{4}, \] \hspace{1cm} (10)

with

\[ \lambda = k_1 (3 \phi_1 - 1) + k_2 (3 \phi_2 - 1). \] \hspace{1cm} (11)

Interestingly, this model is relatively close to the sigmoidal average and has similar features for two-phase composites, as long as the phase contrast is not too high: it lies in between the Miller bounds and indicates an S-shaped behaviour, see figure 1. However, the differences between the self-consistent prediction and the sigmoidal average become clear as soon as the phase contrast becomes higher or, in the extreme, approaches infinity, see next section.

![Figure 1. Rigorous bounds and model predictions for the thermal conductivity of alumina-zirconia composite ceramics at room temperature; Wiener bounds (thin dotted curves), Hashin-Shtrikman bounds (thin full curves), Miller bounds (thin dashed curves) and (thick full curves from top to bottom) Bruggeman-Landauer self-consistent model (curve with symbols x), sigmoidal average of the Hashin-Shtrikman bounds (symbols –) and Lichtenecker relation (without symbols).]
5. Infinite phase contrast: an efficient testing ground for predictive relations

Porous media can be considered as two-phase composites in which one of the phases has negligible conductivity \( k_1 >> k_2 \), i.e. the phase contrast between the (conductivity of the) solid phase and the pore phase (gas-filled or vacuous void space) approaches infinity. In this case the above relations simplify and reveal their essential mathematical structure and physical meaning. In order to simplify notation it is useful in this case to denote the second-phase volume fraction (porosity) simply \( \phi \) and to introduce a dimensionless relative conductivity as \( k_r = k/k_0 \), with \( k_0 \) being the conductivity of the solid phase. Using this notation we have the following relations

- Upper Wiener bound: \( k_r = 1 - \phi \), \( (12) \)

- Upper Hashin-Shtrikman bound (Maxwell model): \( k_r = \frac{1 - \phi}{1 + \phi/2} \), \( (13) \)

- Upper Miller bound: \( k_r = \frac{(1 - \phi)^2}{1 + \phi/2} \), \( (14) \)

- Sigmoidal average of the Hashin-Shtrikman bounds: \( k_r = \frac{(1 - \phi)^2}{1 + \phi/2} \), \( (15) \)

- Self-consistent model (Bruggeman-Landauer relation): \( k_r = 1 - \frac{3}{2} \phi \). \( (16) \)

Note that the lower bounds and the Lichtenecker relation are identically zero when \( k_2 = 0 \). It is evident that in the infinite-contrast case the self-consistent model reduces to the linear approximation (exact non-interaction solution for dilute systems of spherical pores in an infinite matrix) and predicts a spurious (because apparently universal) percolation threshold of \( 2/3 \approx 67 \% \) [1].

Apart from these relations there are several nonlinear model relations that can be recommended for predicting the effective conductivity of porous materials, among them Coble-Kingery-type relation [20], the power-law relation [21]

\[ k_r = (1 - \phi)^{3/2}, \quad (17) \]

which is the infinite-phase-contrast limit of a more general differential model for composites that is given by an implicit relation [1,21] (therefore not mentioned above), and the exponential relation [2,22]

\[ k_r = \exp \left( -\frac{1}{3} \phi \right), \quad (20) \]

From figure 2 it is evident that the sigmoidal average is relatively close to the latter relation. Both relations have been successfully used for describing the porosity dependence of thermal conductivity [23] and elastic moduli [24]. Therefore, the sigmoidal average can be used to extrapolate data measured for materials with residual porosity to zero porosity (this has been done in the present work).
Porosity or insulating phase volume fraction \[1\]

Relative conductivity \[1\]

**Figure 2.** Rigorous upper bounds and model predictions for the relative conductivity of porous ceramics; Wiener upper bound (thin dotted curve), HS upper bound (thin full curve), Miller upper bound (thin dashed curve) and (thick full curves from top to bottom) power-law prediction (curve with symbols +), Bruggeman-Landauer self-consistent model (symbols x), sigmoidal average of the Hashin-Shtrikman bounds and (symbols −) exponential prediction (thick; data for porous alumina (triangles [23]), zirconia (squares [22]) and alumina-zirconia composites (diamonds [22])).

6. Effective thermal conductivity of alumina–zirconia composites

Alumina-zirconia composites are probably the best investigated composite ceramics. For these materials the effective thermal conductivity has been recently measured in whole range of volume fractions, from pure alumina to pure ( yttria-doped) zirconia [9-11]. Moreover, values for singular compositions are scattered throughout the literature. Figures 3 and 4 compare experimental values of the thermal conductivity measured via the laser-flash and xenon-flash methods (using the specific heat values published in [25]) in the temperature range 200–1000 °C with theoretical predictions via the Hashin-Shtrikman bounds and their sigmoidal averages. For this purpose the values measured for the end members have been averaged from [9-11]. Alternatively, to obtain predictions completely independent of these measurements, the predictions could be based on the well-known temperature dependence of the thermal conductivity of alumina and (yttria-doped) zirconia as published in [25].

**Figure 3.** Dependence of the thermal conductivity of alumina–zirconia composite ceramics at 200 °C on the composition (zirconia volume fraction) compared to the Hashin-Shtrikman bounds (thin outer curves) and their sigmoidal average (thick inner curve); data from [9] – empty circles (10Y-ZrO₂), [10] – empty squares (8Y-ZrO₂) and [11] – full triangles (3Y-ZrO₂).
Figure 4. Dependence of the thermal conductivity of alumina-zirconia composites at 400 (top left), 600 (top right), 800 (bottom left) and 1000 °C (bottom right) on the composition, see figure 3.

All measured values have been corrected for porosity using the exponential relation, equation (18). It is evident that all data tend to lie in the lower part of the region restricted via the Hashin-Shtrikman bounds, i.e. below the sigmoidal average and the lower Hashin-Shtrikman bound. With increasing temperature the phase contrast is reduced and consequently the predictions become more restrictive (obviously too precise to reflect experimental data scatter). The fact that in some cases the data measured for composites are even below the lower bounds has been traditionally attributed to microcracks, i.e. extremely anisometric (oblate) pores. In spite of their low volume fraction (usually undetectable by traditional porosity measurement techniques e.g. the Archimedes method) they are – due to their extreme shape – highly efficient in reducing the thermal conductivity and other properties. In alumina-zirconia composites the occurrence of microcracks can be explained by the difference in thermal expansion coefficients [25]. Note that anisotropy of the microstructure can in principle be responsible for values below the lower Hashin-Shtrikman bounds. However, a very high degree of anisotropy is needed to achieve this (hardly ever achieved in practice, except for sandwich composites or laminate structures). Of course, another reason for thermal conductivities being lower than the lower Hashin-Shtrikman bounds can be grain size effects. For alumina-zirconia composite ceramics these grain size effects have been discussed from the viewpoint of phase mixture models in [4].

7. Summary and conclusion

It has been shown that the sigmoidal average between two rigorous bounds, e.g. the Hashin-Shtrikman bounds in the case of isotropic two-phase composites, is the appropriate average relation to be used when a composite is composed of different phases with geometrically equivalent grains. The sigmoidal average ensures that the prediction is close the upper bound for low volume fractions of the low-conductivity phase (corresponding to low-conductivity inclusions in a high-conductivity matrix) and vice versa. In the intermediate concentration range the sigmoidal average is intermediate between the bounds (reducing to the arithmetic mean for a volume fraction of 0.5), reflecting the fact that the microstructure is bicontinuous in this range and can undergo a percolation-type transition. It has been shown that the sigmoidal average of the Hashin-Shtrikman bounds lies automatically within the three-
point bounds (Miller bounds) for a practically important class of microstructures (symmetric-cell materials with spherical cells). Moreover, it has been shown, that in the infinite-phase-contrast case (porous media) the sigmoidal average is close to the exponential relation, which has been very successful in describing the porosity dependence of properties. Theoretical predictions have been compared with experimentally measured values for alumina-zirconia composites, for which the effective thermal conductivity is known in the whole range of volume fractions, from pure alumina to pure (yttria-doped) zirconia. Even after appropriate correction for porosity, essentially all data experimentally measured independently by three groups of authors are below the sigmoidal average (and thus far below the upper Hashin-Shtrikman bound). The fact that some values are even below the lower Hashin-Shtrikman bound is indicative of microcracking and/or grain size (interface) effects.

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