# Predictive model for the thermal conductivity of porous materials with matrix-inclusion type microstructure

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The thermal conductivity of porous materials is a topic of general interest. It has been part of scientific research on refractory materials from its very beginning [1–8]. The increased interest today is partly triggered by the need to design optimized thermal barrier coatings [9–14] and substrates for electronic circuit packages [15, 16]. With no doubt, the best method to obtain reliable values of the effective thermal conductivity of porous materials is direct measurement (e.g., using the laser-flash technique [17]). This is particularly true in those cases where the microstructure is insufficiently specified. On the other hand, from the viewpoint of time and cost savings it might be desirable to have at one's disposal a handy estimate of the porosity dependence of thermal conductivity, e.g., for the purpose of materials selection and design.

In this contribution we present a modified exponential relation which may serve as a useful tool for the approximate prediction of the effective thermal conductivity $k$ of porous materials. For reasons of convenience we assume the voids (usually gas-filled pores) to be non-conducting. With regard to the expected accuracy of available or measured data this will often be justified also from a practical point of view. Furthermore, we assume a matrix-inclusion type microstructure, i.e. closed pores in a matrix with known thermal conductivity $k_0$. The proposed relation allows a realistic estimation of the relative (or "reduced") thermal conductivity $k_r = k/k_0$.

Apart from the rule of mixtures

$$k_r = 1 - \phi \qquad (1)$$

(with $\phi$ being the porosity), which is known to be inadequate for isotropic materials, one of the most popular relations for the relative thermal conductivity is the Maxwell–Eucken relation [1, 2, 18–20], which reduces to the very simple form

$$k_r = \frac{1 - \phi}{1 + \frac{\phi}{2}}, \qquad (2)$$

when the conductivity of the pore phase is negligible [21]. Note that Equation 2 is identical to the Hashin–Shtrikman upper bound for macroscopically isotropic porous materials [20, 21]. In a recent paper [22], the Coble–Kingery approach [23–25] has been used to derive another simple predictive relation:

$$k_r = 1 - \frac{3}{2}\phi + \frac{1}{2}\phi^2. \qquad (3)$$

For small porosities ($\phi \rightarrow 0$) this relation reduces to the well-known dilute-limit or self-consistent approximation [20, 21]

$$k_r = 1 - \frac{3}{2}\phi \qquad (4)$$

Of course, the linear porosity dependence predicted by Equation 4 can be expected only for small ranges of porosity. On the other hand, from Fig. 1 it is evident, that the nonlinear Coble–Kingery type relation (3) is too close to the Maxwell–Eucken prediction (2) to be a significant improvement over the latter, whereas measured data usually exhibit a significantly steeper porosity dependence.

Now, in close analogy to Mooney's classical work in suspension rheology [26] we invoke the functional equation approach (cf. [27–29] for its application in viscosity and elasticity context) to derive a modified exponential relation which has never been used in thermal conductivity context before. Recall that the total porosity $\phi$ can be subdivided into two fractions, $\phi_1$ and $\phi_2$ (neither of them necessarily small),

$$\phi = \frac{V_1 + V_2}{V_0 + V_1 + V_2} = \frac{V_1}{V_0 + V_1 + V_2} + \frac{V_2}{V_0 + V_1 + V_2}$$
$$= \phi_1 + \phi_2, \qquad (5)$$

where $V_0$ is the volume occupied by the matrix phase and $V_1 + V_2$ the total volume occupied by the pores (i.e., by the two virtual pore fractions). Trivially, the relative thermal conductivity corresponding to this virtual

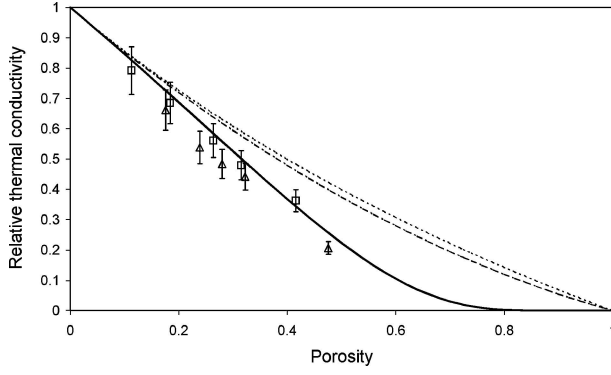* Author to whom all correspondence should be addressed.

*Figure 1* Porosity dependence of relative thermal conductivity; two sets of measured data (triangles: alumina, squares: zirconia) and three model predictions (dotted: Maxwell–Eucken/Hashin–Shtrikman upper bound, dashed: Coble–Kingery, solid: modified exponential)

decomposition can be written as

$$k_r(\phi) = k_r(\phi_1 + \phi_2). \qquad (6)$$

In order to obtain a partial porosity $\phi_1$ after "mixing" with the second fraction, the first fraction of pores to be added to the dense material (i.e., before the second fraction is present) must be larger than $\phi_1$, by a factor of $(1 - \phi_2)^{-1}$. Thus, obviously, after adding this first partial volume fraction of pores,

$$\phi_{12} = \frac{V_1}{V_0 + V_1} = \frac{\phi_1}{1 - \phi_2}, \qquad (7)$$

the corresponding relative thermal conductivity is $k_r(\phi_{12})$. In principle, following Mooney's suggestion [26], the same reasoning applies to the second fraction with

$$\phi_{21} = \frac{V_2}{V_0 + V_2} = \frac{\phi_2}{1 - \phi_1}, \qquad (8)$$

and the corresponding relative thermal conductivity $k_r(\phi_{21})$. Note that this is the key step to arrive at an exponential relation (and not a power law relation) via the functional equation approach, cf. [27–29]. The relative thermal conductivity is then given by a multiplicative decomposition of the form

$$k_r(\phi) = k_r(\phi_{12}) \cdot k_r(\phi_{21}), \qquad (9)$$

(cf. [29–31 ] for a more detailed explanation of this decomposition). Equating (6) and (9) we obtain a functional equation of the form

$$k_r(\phi_1 + \phi_2) = k_r(\phi_{12}) \cdot k_r(\phi_{21}), \qquad (10)$$

which has a solution of the form

$$k_r = \exp\left(\frac{-B\phi}{1 - \phi}\right), \qquad (11)$$

where $B$ is an adjustable parameter at this point.

Up to this point we have not made any assumptions on pore shape or connectivity. However, since in the case of small porosities ($\phi \to 0$), Equation 11 has a series expansion of the form

$$\exp\left(\frac{-B\phi}{1 - \phi}\right) \approx 1 - B\phi + \cdots, \qquad (12)$$

it is reasonable to relate $B$ with the so-called intrinsic thermal conductivity $[k]$ defined in [22] as

$$[k] \equiv - \lim_{\phi \to 0} \frac{k_r - 1}{\phi}. \qquad (13)$$

In the case of spherical pores one may then set $B = [k] = 3/2$. Although precisely valid only for spherical pores, this value can be expected to be a reasonable approximation also for other isometric shapes, cf. analogous findings in the elasticity context [30]. Thus, when the thermal conductivity of the matrix phase $k_0$ is reliably known, the modified exponential relation (11) should provide a parameter-free model prediction of the effective thermal conductivity $k$ for isotropic porous materials of a rather general class, at least for those with matrix-inclusion type microstructure.

In order to underpin this statement with at least one paradigmatic example, we have tested our model prediction against recently measured data for two types of oxide ceramics (alumina and zirconia), cf. Fig. 1. Both types were prepared by starch-consolidation casting (a new shaping technique for ceramic suspensions where starch acts as a body-forming agent and a pore-forming agent) at the ICT Prague [31] and measured by the laser-flash technique [32] at the ENSCI Limoges. Principles and details of processing and measurement can be found elsewhere [33–37]. Potato starch (with a median size of approx. 50 $\mu$m) was used and resulted in an isotropic microstructure with isometric, nearly spherical, essentially closed pores [38]. The oxide powders, used in this work, were submicron (Sumitomo AA04/Japan and Tosoh TZ-3YE/Japan) and the grain size after sintering still remained 1–2 orders of magnitude smaller than the pore size.

The thermal conductivities $k_0$ of the matrix materials were taken to be 33 and 2.9 W/mK for alumina and zirconia (with 3 mol.% yttria), respectively. Although these values are based on a recent literature research [31], and believed to be the most reliable, it is clear that the uncertainty of these values is still relatively high, say at least 10% (this value is indicated by the error bars in Fig. 1). Additionally, it must be kept in mind, that the value for zirconia is strongly dependent on the yttria content and the corresponding oxygen vacancy concentration [39, 40] and can be lower by 30%, say, for higher yttria content. On the other hand, much lower values, which also exist in the literature, are almost always caused by porosity effects.

From Fig. 1, it is evident that the modified exponential relation (11) provides a satisfactory prediction for porous alumina and porous zirconia ceramics prepared by starch consolidation casting. The prediction is relatively close to the self-consistent approximation

(dilute approximation), cf. Equation 4, but in contrast to the latter it is nonlinear and does not predict a percolation threshold. It can expected that the handy relation (11) will be a useful tool for roughly estimating the effective thermal conductivity of a rather wide class of isotropic porous materials. Although it seems that experimentally measured data for alumina or zirconia with porosities higher than 50% (whether prepared using a pore-forming agent or otherwise) are not available so far in the literature there is no principal limit of validity for our model, since no approximations have been invoked for its derivation. We note, however, that the model presented in this letter is intended to serve as a guide to overall behavior. With respect to this, the simplification we made by assuming voids with zero conductivity appears to be a valid approximation for most real materials (recall that, e.g., at room temperature the thermal conductivity of air at atmospheric pressure is approx. 0.025 W/mK, i.e. two orders of magnitude lower than that of zirconia, one of the thermally most insulating oxide ceramics). Moreover, the effect of grain boundaries (grain size effect) has not been taken into account. For refinements of this kind the reader may refer to [35–37]. Although it seems that, at least in the case of zirconia, where this topic has been satisfactorily investigated, grain sizes much smaller than 100 nm are required to give a sensible effect [10, 40, 41], it is clear that principally small grain size can lead to a decrease in the thermal conductivity, similar to porosity. In a theoretically sound treatment, however, the grain size effect should be clearly separated from the porosity effect. In terms of our letter, grain size can have an influence both on $k_0$ and $k$, but not on $k_r$.

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