

# Elasticity of porous ceramics—A critical study of modulus–porosity relations

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## Abstract

Based on the concept of intrinsic elastic moduli an overview of modulus–porosity relations is given, which includes exponential and power-law expressions as well as the Hasselman relation and a relation recently proposed by Pabst and Gregorová. The formal structure of these relations is compared and the physical meaning of the parameters discussed. It is recalled that certain popular relations violate the Hashin–Shtrikman upper bounds and are, therefore, useless (Spriggs relation, Ishai–Cohen relation). Coble–Kingery relations are recalled in their correct form and an improved version of the Gibson–Ashby relation for the shear modulus is proposed. Selected relations are applied to describe the porosity dependence of the relative tensile moduli of alumina, zirconia, silicon nitride and silicon carbide prepared with corn-starch as a pore-forming agent. Porous ceramics with this type of (matrix-inclusion-based) microstructure are shown to follow approximately a modified exponential relation and can be fitted by a master curve with critical porosity 68.4%.

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## 1. Introduction

Elastic properties play a key role in determining the mechanical behavior of ceramic materials, including glasses, and, not surprisingly, an immense literature is available on the porosity dependence of elastic moduli. It is not the purpose of this contribution to review the many important theoretical and experimental papers that have been published in this field. On the contrary, here it is our aim to provide a fresh view on this old theme, as far as possible unbiased by tradition. We investigate the formal mathematical structure of commonly used, less commonly used and recently introduced modulus–porosity relations and present a hopefully rational classification and a more or less exhaustive overview of these, at least for approximately isometric pores.

We will discuss commonly encountered problems and misunderstandings with respect to modulus–porosity relations in general and will demonstrate—with recently pub-

lished data on porous alumina, zirconia, silicon carbide and silicon nitride—the usefulness of some of these relations for the description (fitting) of experimentally measured data as well as for the prediction (estimate) of elastic moduli of porous ceramics based on an elementary information on the type of microstructure.

Although the present text is to a large degree self-contained, we assume the reader to be familiar with the exact theory of linear elasticity<sup>1,2</sup> and with the fundamentals of micromechanics.<sup>3–6</sup>

## 2. Elastic moduli from the viewpoint of rational mechanics

The elastic behavior of brittle materials can be described within the framework of linear elasticity theory. In the case of small deformations (i.e. invoking geometrical linearization) Hooke's law for anisotropic elastic solids (i.e. the physically linearized constitutive equation) can be written in direct ten-

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tensor notation as

$$\mathbf{T} = \mathbf{C}\mathbf{E}, \quad (1)$$

where  $\mathbf{T}$  is the Cauchy stress tensor (a symmetric second-order tensor),  $\mathbf{C}$  the stiffness tensor (a fully symmetric fourth-order tensor, also called elasticity tensor or tensor of elastic constants) and  $\mathbf{E}$  the so-called small strain tensor (a symmetric second-order tensor).<sup>1,2,7,8</sup>

In the case of isotropic materials Hooke's law, Eq. (1) adopts the form

$$\mathbf{T} = \lambda(\text{tr}\mathbf{E})\mathbf{1} + 2\mu\mathbf{E}, \quad (2)$$

(Cauchy–Hooke law), where the elastic constants (elastic moduli)  $\lambda$  and  $\mu$  are called Lamé constants (or Lamé moduli, units [GPa]),  $\text{tr}$  denotes the trace of a tensor and  $\mathbf{1}$  is the second-order unit tensor.

In terms of the tensile modulus  $E$  and the Poisson ratio  $\nu$  the Cauchy–Hooke law for isotropic materials can be written as

$$\mathbf{T} = \frac{E}{(1+\nu)} \left[ \mathbf{E} + \frac{\nu}{(1-2\nu)} (\text{tr}\mathbf{E})\mathbf{1} \right] \quad (3)$$

From Eq. (3) it is evident that for the Poisson ratio  $\nu$  the values 0.5 and  $-1$  are not allowed. Actually, as a consequence of the second law of thermodynamics the following inequality must hold for isotropic materials:<sup>1,6</sup>

$$-1 < \nu < 0.5. \quad (4)$$

Although in some of the older literature the opinion has prevailed that (according to some alleged “experience with real materials”) the Poisson ratio should always be positive for isotropic materials (i.e.  $0 < \nu < 0.5$ ), it is well known today that isotropic materials with negative Poisson ratio, so-called “auxetic materials”, do exist and can be designed and produced, cf. Refs. 4, 6, 9 and the literature cited therein. These materials show the contra-intuitive behavior, that when extended in one direction, they extend in all perpendicular directions. Of course, most ceramic materials, including glasses, exhibit Poisson ratios in the range 0.1–0.4 and for many purposes the approximate value of 0.2 or 0.3 will be a reasonable estimate in the absence of more precise information. Nevertheless, newer research in ceramic science (e.g. Ref. 10) takes the possibility of negative Poisson ratios into account.

### 3. Effective elastic moduli from the viewpoint of micromechanics

Porous materials can be considered as a special case of multiphase mixtures, composites or, more generally, materials with microstructure (the subject of micromechanics or composite theory). In micromechanics or composite theory<sup>3–6</sup> an effective stiffness tensor  $\mathbf{C}_e$  can be defined via the linear constitutive equation

$$\langle \mathbf{T} \rangle = \mathbf{C}_e \langle \mathbf{E} \rangle \quad (5)$$

(i.e. an averaged Hooke's law for heterogeneous materials), where the angular brackets denote volume averages of the Cauchy stress tensor and the small strain tensor, respectively.<sup>6</sup> In principle, the effective stiffness tensor can be predicted exactly when the properties of the constituent phases (i.e. for porous materials essentially those of the matrix or skeleton phase, since the void phase usually exhibits more or less “zero properties”) and all details of the microstructure are known. In practice this is of course not the case.

Micromechanics provides theoretical concepts for quantifying microstructural information to an arbitrary degree of precision and including it into the description of a material in the form of so-called correlation functions.<sup>3,4,6</sup> The lowest-order microstructural information (one-point correlation function) concerns only the volume fractions of the phases. Higher-order microstructural information (two-point, three-point, in general multi-point correlation functions) can account for size, shape and orientation features, including the corresponding distributions.<sup>3,6</sup> However, for real materials higher-order microstructural information is accessible only via tomographic techniques (direct 3D information) or, although to a limited degree only, by image analysis of planar sections (partial 3D information indirectly inferred from 2D information). Computer simulations, of course, are a powerful tool to analyze model microstructures, cf., e.g. Ref. 10 and the extensive work of Torquato and his coworkers cited in Ref. 6.

For the remaining part of this paper we confine ourselves to isotropic materials with effective elastic moduli  $M$  (where  $M$  stands for the effective tensile modulus  $E$ , shear modulus  $G$  or bulk modulus  $K$ , respectively, and the subscript “e”, denoting “effective”, has been omitted for convenience) which are in general temperature-dependent, c.f. Refs. 11, 12. We suppose them to be functions of the phase moduli  $M_i$  and microstructural information of lowest-order only, i.e. phase volume fractions  $\phi_i$  (that means, we restrict ourselves to compositional information only). In this sense we introduce the following basic assumption<sup>13</sup>

$$M = f(M_i, \phi_i), \quad (6)$$

where  $M_i$  ( $i=0, 1, 2, \dots, n$ ) are the phase moduli of all  $n$  constituent phases and  $\phi_i$  the volume fractions of the  $n$  phases. The most general average value is the general power mean (weighted by volume fractions)<sup>13</sup>

$$\bar{M}_X = \left( \sum \phi_i M_i^N \right)^{1/N}, \quad (7)$$

with the summation extending over all  $n$  constituent phases. The arithmetic mean ( $N=1$ ) corresponds to the Voigt bound (upper bound) of the shear and bulk moduli,  $G_V$  and  $K_V$ , respectively, and the harmonic mean ( $N=-1$ ) corresponds to the Reuss bound (lower bound) of the elastic moduli  $M_R$ . Of course, in the case of two-phase materials one of the two volume fractions is redundant, and one can adopt the notation  $\phi_1 \equiv 1 - \phi$  and  $\phi_2 \equiv \phi$ . When, additionally, the second phase is the void phase (with zero elastic moduli  $M_2 = 0$ ), and

the elastic moduli of the solid matrix or skeleton phase are denoted as  $M_1 \equiv M_0$  as usual, the Voigt bounds reduce to

$$M_V = (1 - \phi)M_0 \quad (8)$$

and the Reuss bounds degenerate to zero identically.

The best possible bounds for the effective elastic moduli of macroscopically isotropic two-phase composites, given just volume-fraction information, are the Hashin–Shtrikman bounds (HS bounds),<sup>14</sup> cf. also Refs. 3–6, 12, 13. In the special case of porous materials, where voids are one of the phases (with zero elastic moduli  $G_2 = 0$ ,  $K_2 = 0$ ),  $\phi_2 \equiv \phi$  is the porosity and the elastic moduli of the solid matrix or skeleton phase are denoted as  $G_1 \equiv G_0$ ,  $K_1 \equiv K_0$  as usual, the HS upper bounds reduce to

$$\frac{G_{HS}^+}{G_0} = 1 - \left[ \frac{15K_0 + 20G_0}{9K_0 + 8G_0 + (6K_0 + 12G_0)\phi} \right] \phi, \quad (9)$$

$$\frac{K_{HS}^+}{K_0} = 1 - \left[ \frac{3K_0 + 4G_0}{3K_0\phi + 4G_0} \right] \phi. \quad (10)$$

and the HS lower bounds degenerate to zero. HS bounds have been theoretically derived for the shear modulus  $G$  and the bulk modulus  $K$ . An estimate for the corresponding HS bound for the tensile modulus  $E$  can be obtained via the standard relation<sup>12,13</sup>

$$E_{HS} = \frac{9K_{HS}G_{HS}}{3K_{HS} + G_{HS}}. \quad (11)$$

In the very special case of porous materials with a matrix or skeleton Poisson ratio of 0.2 ( $\nu_0 = 0.2$ , corresponding to  $3K_0 = 4G_0$ ) it can be shown that the HS upper bounds reduce to

$$\frac{E_{HS}^+}{E_0} = \frac{G_{HS}^+}{G_0} = \frac{K_{HS}^+}{K_0} = \frac{1 - \phi}{1 + \phi}. \quad (12)$$

Note that for this case the HS upper bounds are identical to the Mori–Tanaka predictions for random materials of matrix-inclusion type with spherical pores<sup>15</sup> and to the Kuster–Toksöz relation,<sup>16</sup> cf. Refs. 17, 18. It has been shown recently<sup>12</sup> that in the alumina–zirconia system the Mori–Tanaka prediction or Kuster–Toksöz relation is an excellent approximation to the HS upper bound for the tensile modulus (error < 0.1%) and for the shear modulus (error < 2.6%), but not for the bulk modulus (error up to 14.3%). For the purpose of later reference we note that Eq. (12) can be approximated by the following second-order polynomial:

$$\frac{E_{HS}^+}{E_0} = \frac{G_{HS}^+}{G_0} = \frac{K_{HS}^+}{K_0} \approx 1 - 1.71\phi + 0.71\phi^2. \quad (13)$$

Generally the microstructure corresponding to the HS bounds is the so-called Hashin assemblage,<sup>19</sup> consisting of polydisperse composite spheres containing concentric spherical inclusions. In the case of macroscopically isotropic porous materials the Hashin assemblage would be approximated by a material consisting of hollow spheres with an infinitely wide

size distribution that enables space filling, featuring a fractal microstructure.

Note that in general the effective Poisson ratio does not obey the Voigt and Reuss bounds and need not even lie between that of the constituent phases.<sup>3,17,20</sup> While in the case of dense composites, in the absence of a better alternative, it is often recommended to calculate the effective Poisson ratio of composites via the mixture rule (i.e. as an arithmetic mean weighted by volume fractions), this simple remedy evidently fails in the case of porous materials. According to the self-consistent and differential approaches (see below) the asymptotic value, towards which the matrix or skeleton Poisson ratio tends for high porosities, is invariably  $\nu^* = 0.2$ , while according to the Mori–Tanaka approach<sup>15</sup> the predicted asymptotic value lies somewhere between the matrix or skeleton Poisson ratio  $\nu_0$  and the value 0.2, and is for porous materials (with spherical pores) given by the formula

$$\nu^* = \frac{1 - 5\nu_0}{9 + 5\nu_0}. \quad (14)$$

#### 4. Effective elastic moduli of porous materials: linear approximations

In the case of porous materials it is convenient to define a relative elastic modulus as

$$M_r \equiv \frac{M}{M_0}, \quad (15)$$

where  $M$  is the effective elastic modulus (as before) and  $M_0$  the elastic modulus of the matrix phase (in the case of porous materials of the matrix-inclusion type, i.e. porous materials with closed pores) or else the elastic modulus of the solid skeleton phase (in the case of bicontinuous porous materials, e.g. open-pore cellular solids or foams). Using this notation the Voigt bounds of the relative elastic moduli  $M_{rV}$  of porous materials decrease linearly with increasing porosity, exhibiting a slope of  $-1$ ,

$$M_{rV} = \frac{M_V}{M_0} = 1 - \phi, \quad (16)$$

while the HS upper bounds are non-linearly decreasing, e.g. with an initial tangent slope of  $-1.71$  for a material with  $\nu_0 = 0.2$ , cf. Eq. (13). For very low porosities ( $\phi \rightarrow 0$ ), where mutual interactions between the pores can be neglected (so-called dilute approximation) it is justified to assume a linear dependence of the relative elastic moduli on the porosity,

$$M_r = 1 - [M]\phi, \quad (17)$$

where  $[M]$  is the intrinsic elastic modulus defined as

$$[M] \equiv - \lim_{\phi \rightarrow 0} \frac{M_r - 1}{\phi}. \quad (18)$$

Note the new sign convention in this definition, which is in contrast to our previous papers<sup>21–23</sup> and to common practice

in suspension rheology<sup>24</sup> but contributes much to clarity and simplification, cf. also Ref. 12 and our recent paper concerning thermal conductivity.<sup>25</sup>

Based on the exact classical solution of the spherical-cavity problem (single spherical void embedded in an infinite elastic medium)<sup>26</sup> explicit limit approximations to the problem of non-interacting spherical cavities (i.e. a dilute system of pores) in an elastic matrix have been obtained by Dewey<sup>27</sup> and Mackenzie.<sup>28</sup> For the relative shear modulus  $G_r$ , the relative bulk modulus  $K_r$ , the relative tensile modulus  $E_r$  and the relative Poisson ratio  $\nu_r$  these so-called dilute approximations (or Dewey–Mackenzie relations) are<sup>5,6,29</sup>

$$G_r = 1 - \frac{15(1 - \nu_0)}{7 - 5\nu_0}\phi, \quad (19)$$

$$K_r = 1 - \frac{3(1 - \nu_0)}{2(1 - 2\nu_0)}\phi, \quad (20)$$

$$E_r = 1 - \frac{3(1 - \nu_0)(9 + 5\nu_0)}{2(7 - 5\nu_0)}\phi, \quad (21)$$

$$\nu_r = 1 + \frac{3(1 - \nu_0^2)(1 - 5\nu_0)}{2\nu_0(7 - 5\nu_0)}\phi. \quad (22)$$

Nemat-Nasser and Hori<sup>5</sup> have shown that these relations have been derived under the assumption of prescribed macrostrain. When macrostress is prescribed the results are of the form<sup>5,18</sup>

$$M_r = \frac{1}{1 + [M]\phi}, \quad (23)$$

which can be developed into a series expansion in  $\phi$  and truncated after the first-order term (in  $\phi$ ) to give again the dilute-limit expressions corresponding to Eqs. (19)–(22), cf. Eq. (17). It is evident that the first-order coefficients (intrinsic elastic moduli) are all functions of the matrix Poisson ratio  $\nu_0$ . Note that, according to the dilute approximation, in the special case  $\nu_0 = 0.2$  the relative Poisson ratio of a porous material with spherical pores is equal to unity, i.e. the effective Poisson ratio remains unchanged with increasing porosity. Note also that the so-called self-consistent approach, which in a certain sense takes interactions into account, results in very similar relations, except for the fact that the intrinsic elastic moduli are functions of the effective Poisson ratio  $\nu$  instead of the matrix or skeleton Poisson ratio  $\nu_0$ , cf. Refs. 5, 6. Of course, in the special case of porous materials with spherical pores and  $\nu_0 = 0.2$  both the dilute approximation (in the dilute limit  $\phi \rightarrow 0$ ) and the self-consistent approach (principally intended for finite  $\phi$ ) lead to the identical result

$$M_r = 1 - 2\phi, \quad (24)$$

i.e. the intrinsic elastic modulus is exactly equal to two (i.e.  $[M] = 2$ ) for the case of spherical pores in a  $\nu_0 = 0.2$  material. Note that deviations from this value might be attributed to deviations of the pore shape from sphericity (including a topological transition from isolated to connected) but can as well be caused by deviations of the matrix or skeleton Poisson ratio from the value  $\nu_0 = 0.2$ .

Table 1

Intrinsic elastic moduli $[G]$ , $[K]$ , $[E]$ for different matrix Poisson ratios $\nu_0$			
$\nu_0$	$[G]$	$[K]$	$[E]$
−1.0	2.5	1	1
−0.5	2.368	1.125	1.539
−0.2	2.250	1.286	1.800
−0.1	2.200	1.375	1.870
0	2.143	1.5	1.929
0.1	2.077	1.688	1.973
0.17	2.024	1.886	1.994
0.2	2	2	2
0.23	1.974	2.139	2.004
0.25	1.957	2.25	2.005
0.26	1.947	2.313	2.006
0.268667	1.939	2.371	2.006
0.27	1.938	2.380	2.006
0.3	1.909	2.625	2.005
0.31	1.899	2.724	2.004
0.333333	1.875	3	2
0.4	1.800	4.5	1.980
0.5	1.667	$\infty$	1.917

Values of the intrinsic elastic moduli are listed in Table 1 in dependence of the matrix or skeleton Poisson ratio  $\nu_0$ . Note that for the “normal” Poisson ratios  $\nu_0$  between 0 and 0.5 the intrinsic tensile modulus remains very close to the benchmark value of two (i.e.  $[E] \approx 2$ ), increasing from  $[E] = 1.929$  (for  $\nu_0 = 0$ ) to a maximum value of  $[E] = 2.006$  (for  $\nu_0 = 0.268667$ ), followed by a decrease to  $[E] = 1.917$  (for  $\nu_0 = 0.5$ ). Due to this “anomalous” behavior of  $[E]$  the value  $[E] = 2$  is attained for two different values of  $\nu_0$  (viz.  $\nu_0 = 0.2$  and  $\nu_0 = 1/3$ ). The limiting values of the bulk modulus and the tensile modulus for materials with a negative matrix Poisson ratio (approaching  $\nu_0 = -1$  in the extreme case) are  $[K] = [E] = 1$ , corresponding to the Voigt bounds (values  $[M] < 1$  cannot occur). Curiously, the limiting value of the intrinsic shear modulus for  $\nu_0 = -1$  materials is  $[G] = 2.5$ , obviously the counterpart of the Einstein value<sup>30</sup> for the intrinsic shear viscosity occurring in suspension rheology, cf. Ref. 31. Note also that for the “typical”  $\nu_0$  values in the range  $0.17 < \nu_0 < 0.33$  the values of the intrinsic shear modulus are always relatively close to the benchmark value of two  $[G] \approx 2$  (range  $1.875 < [G] < 2.024$ ), while for the bulk modulus this is not the case. For  $\nu_0 = 0.5$  (corresponding to a completely incompressible matrix) the intrinsic bulk modulus “collapses”, i.e. a very small amount of pores would be extremely efficient (detrimental) in such a case. In other words, there would be a singularity in the  $K$ – $\phi$  diagram at  $\phi = 0$ , where the effective bulk modulus steeply falls down from the value of the matrix bulk modulus  $K_0$  to zero. In this connection we note that, due to the condition  $[M] \geq 1$ , all linear relations (19)–(22), cf. Eq. (17), whether based on the dilute approximation or the self-consistent approach, predict a critical porosity  $\phi_C = [M]^{-1} \leq 1$ , for which the effective elastic moduli become zero, i.e. the material loses integrity. In the context of percolation theory  $\phi_C$  can be interpreted in terms of a percolation threshold.<sup>3,32</sup>

## 5. Effective elastic moduli of porous materials: non-linear relations

Experience shows that usually the porosity dependence of the effective elastic moduli is not linear. The simplest way to allow for a non-linear dependence is the Coble–Kingery approach,<sup>33</sup> which is as follows:<sup>13,34</sup> take the linear relation, Eq. (17), for the matrix Poisson ratio in question and add a quadratic term in  $\phi$ , so that

$$M_r = 1 - [M]\phi + \alpha\phi^2. \quad (25)$$

Then determine the value of the coefficient  $\alpha$  from the condition that  $M_r = 0$  at least for  $\phi = 1$  (which is necessary in order not to violate the Voigt bound). Thus, in general one obtains the second-order polynomial<sup>13,23</sup>

$$M_r = 1 - [M]\phi + ([M] - 1)\phi^2. \quad (26)$$

In the special case of porous materials with spherical pores and  $\nu_0 = 0.2$  this reduces to<sup>13,34</sup>

$$M_r = (1 - \phi)^2. \quad (27)$$

This relation can be theoretically derived as a special case of a more general power-law relation (the Archie relation mentioned below) and via the functional equation approach.<sup>21</sup> At the same time it is identical with the prediction of the so-called differential approach for porous materials with spherical pores and  $\nu_0 = 0.2$ .<sup>17,18</sup> Interestingly, the same result was found for the tensile modulus by fitting a large amount of experimental data on real materials with the semi-empirical Gibson–Ashby model<sup>35</sup> for low-density open-pore cellular solids (foams), cf. Fig. 1. We emphasize that the general form of the Gibson–Ashby relations has been derived via dimensional arguments (using standard beam theory) for a cellular model solid consisting of a network of open cubes, i.e. without any recourse to the assumptions of spherical pore shape or isolated-pore topology. This indicates that in many cases not sphericity itself but only approximate isometry is the decisive

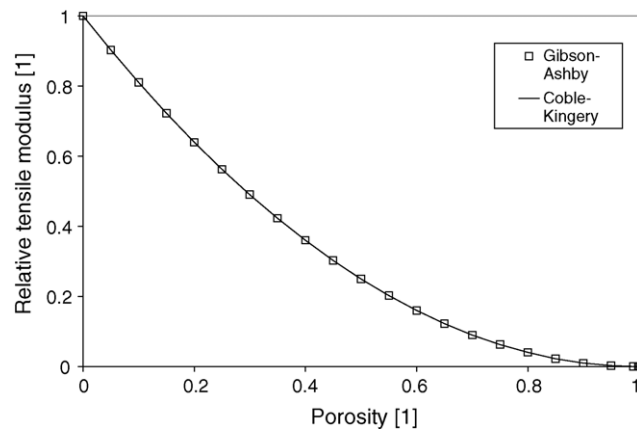


Fig. 1. Relative tensile modulus of porous ceramics; the predictions of the Coble–Kingery relation (for closed isolated pores of spherical shape) coincide with those of the Gibson–Ashby approach (for open connected pores of non-spherical shape).

criterion controlling the applicability of modulus–porosity relations and that connectedness of pores does not automatically exclude the use of any relation.

Also for the shear modulus the Gibson–Ashby relation is of the general form

$$G_r = \gamma(1 - \phi)^2, \quad (28)$$

but according to Gibson and Ashby<sup>9</sup> the prefactor  $\gamma$  (an adjustable parameter) is  $\gamma = 3(1 + \nu_0)/4$  (as determined by their fitting collected data), which has the unpleasant consequence that it is not unity for porous materials with  $\nu_0 = 0.2$  (but curiously for materials with  $\nu_0 = 1/3$ , which is strange at best). Therefore, we conjecture that the prefactor  $\gamma = 3(1 + \nu_0)/4$  proposed by Gibson and Ashby<sup>9</sup> is slightly too low and propose to replace it by  $\gamma = 5(1 + \nu_0)/6$  for Eq. (28) to be in complete accordance with the benchmark form, Eq. (27), at least in the case of porous materials with  $\nu_0 = 0.2$ . The principal problem, however, remains that for all matrix or skeleton Poisson ratios other than  $\nu_0 = 0.2$ , the Gibson–Ashby relation for the shear modulus leads to the unphysical result that  $G_r \neq 1$  at  $\phi = 0$  (which defies the definition of relative moduli). This, of course, is more than only an aesthetic deficiency, since, strictly speaking, it renders the Gibson–Ashby relation for the shear modulus, Eq. (28), useless in the range of small porosities, cf. Fig. 2.

Irrespective of the matrix or skeleton Poisson ratio the Coble–Kingery relation (27) may be expected to be a relatively reasonable prediction for the tensile modulus  $E$  (and also for the shear modulus  $G$  when  $\nu_0 \approx 0.2$ ), but certainly not for the bulk modulus  $K$ . This is connected with a principal problem of Coble–Kingery relations: if  $[M] > 2$  the second-order polynomials exhibit a minimum with negative  $M_r$  values at porosities  $< 100\%$ , which is a natural consequence of the parabolic form of these relations but is clearly nonsense from the physical point of view. Obviously, this problem is harder in the case of the bulk modulus than with the other two

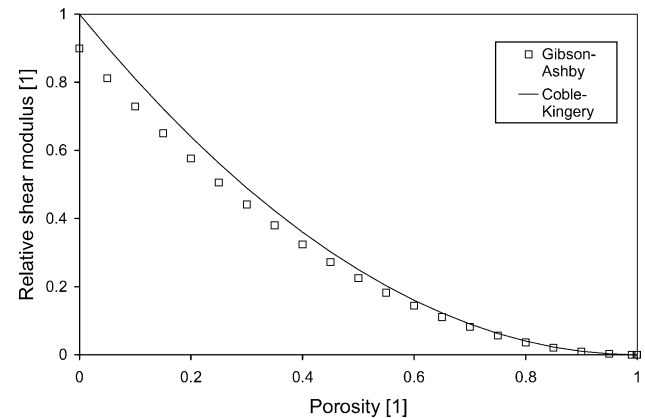


Fig. 2. Relative shear modulus of porous ceramics with  $\nu_0 = 0.2$ ; the predictions of the Coble–Kingery relation (curve) do not coincide with those of the Gibson–Ashby approach (squares) when the prefactor is taken to be  $3(1 + \nu_0)/4$  (corresponding to 0.9 in the case  $\nu_0 = 0.2$ ), cf. Ref. 9, they do coincide, however, when the prefactor is chosen to be  $5(1 + \nu_0)/6$ , which reduces to 1 in the case  $\nu_0 = 0.2$ .

moduli, cf. Table 1. An entirely different relation has been proposed by Christensen<sup>36</sup> and Warren and Kraynik<sup>37</sup> for the bulk modulus of low-density cellular solids (i.e. for very high porosities):

$$K_r = \frac{1 - 2\nu_0}{3}(1 - \phi). \quad (29)$$

Evidently the linear form of this relation prohibits its use in the range of low porosities. For example, in the case of porous materials with  $\nu_0 = 0.2$  it predicts  $K_r = 0.2(1 - \phi)$ , which is wrong of course (since it defies the definition of relative moduli, see above). A possibility, though awkward, to overcome this problem is to combine the Warren–Kraynik–Christensen (WKC) relation (which can be a realistic prediction in the high-porosity region) with the Coble–Kingery relation (which can be realistic in the low-porosity region). To ensure in any case positivity of the  $K_r$  values the porosity  $\phi_X$  at the crossover of the two curves (calculated by simply equating the Coble–Kingery relation (26) for the bulk modulus and the WKC relation (29) for the  $\nu_0$  value in question) should be used as the point of continuation, cf. Fig. 3. Note again that for materials with  $\nu_0 > 0.2$  the Coble–Kingery relation is useless for high porosities (due to the negative bulk moduli predicted for porosities  $< 1$ , which is nonsense from the physical point of view) while the WKC relation is generally useless for low porosities (due to the prediction of a relative bulk modulus  $< 1$  for zero porosity, which is in contradiction with the definition of relative bulk moduli). For example, for materials with a matrix Poisson ratio of  $\nu_0 = 0.3$ , both curves meet at a porosity of  $\phi_X = 0.534$ , cf. Fig. 3. For materials with higher matrix Poisson ratios the curves meet at lower porosities and vice versa. Only in the (unrealistic) limiting cases of incompressible materials with  $\nu_0 = 0.5$  and maximally auxetic materials with  $\nu_0 = -1$  the Coble–Kingery prediction and the WKC prediction coincide.

In the remaining part of this section let us restrict ourselves to the tensile modulus. For evident reasons (discussed

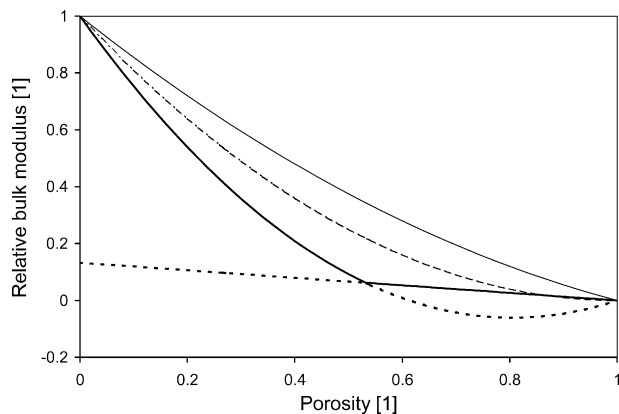


Fig. 3. Relative bulk modulus according to the Coble–Kingery relation for  $\nu_0 = 0$  (thin solid curve),  $\nu_0 = 0.2$  (thin dashed curve) and  $\nu_0 = 0.3$  (thick parabolic curve) and the Warren–Kraynik–Christensen (WKC) relation for  $\nu_0 = 0.3$  (thick straight line).

above) it is in practice unnecessary to emphasize the condition  $\nu_0 = 0.2$  in this case, because for pores of spherical (or only isometric) shape the intrinsic tensile modulus is always very close to the benchmark value of two (i.e.  $[E] \approx 2$ , range  $1.97 < [E] < 2.01$ ), even if the matrix or skeleton Poisson ratio varies in the extremely wide range between  $\nu_0 = 0.1$  and  $\nu_0 = 0.4$  (which covers practically the whole range of interest for ceramic materials), cf. Table 1. Notwithstanding the problems with the bulk modulus, in the case of the tensile modulus the Coble–Kingery relations can yield a prediction of the porosity dependence that satisfies all basic criteria of physical plausibility: it ensures that  $M_r = 0$  for  $\phi = 1$  and it does not violate the Hashin–Shtrikman upper bound. For example, in the case of porous materials with  $\nu_0 = 0.2$  the initial tangent slope is  $-2$  and the curvature is  $1$ , whereas the HS upper bound is characterized by an initial tangent slope of approximately  $-1.71$  and a curvature of  $0.71$  in this case, cf. Eq. (13).

Following the key paper by Coble and Kingery<sup>33</sup> many other relations have been proposed to describe the porosity dependence of the relative tensile modulus. In the sequel we give a brief, but in a certain sense exhaustive, overview of these. In order to clearly emphasize the similarities and differences between them we adopt a unified notation, using the critical porosity  $\phi_C$  and the concept of intrinsic elastic moduli  $[M]$  introduced above wherever feasible.

It is understood, that in practice these parameters will usually be treated as fit parameters to be determined from experimentally measured data a posteriori. This is particularly true for the critical porosity  $\phi_C$ , for which reliable and sufficiently precise a priori estimates will hardly be available for real materials.<sup>32</sup> Note that for porous materials there exists no reliable benchmark value for  $\phi_C$  comparable to the value of approximately  $0.64$  (i.e. 64%) for the packing density of monodisperse rigid spheres in random close packed (rcp) arrangement.<sup>38,39</sup> Nevertheless, in exceptional cases (i.e. for precisely defined model microstructures) there exist estimates of  $\phi_C$  which seem to be realistic, obtained via computer simulations.<sup>10</sup> When these model materials are considered to reflect the microstructure of any real material to a sufficient degree, then of course any of the following relations may be used for prediction purposes as well. In a similar spirit (only replacing the virtual computer simulation by a real-world experiment), when a sufficient number of data has been measured for materials which have certain typical microstructural features in common (e.g. closed spherical pores), a master curve can be fitted to the measured data, which can then be used to roughly predict the behavior of similar materials.

Spriggs<sup>40</sup> has suggested the use of a simple exponential relation of the form

$$E_r = \exp(-[E]\phi), \quad (30)$$

where the intrinsic tensile modulus  $[E]$  is principally a parameter to be determined by fitting experimentally measured

data. Obviously, for small porosities ( $\phi \rightarrow 0$ ) Eq. (30) reduces to Eq. (17).

A derivation of the Spriggs relation via the so-called functional equation approach has been given recently.<sup>21</sup> It seems that Zimmerman<sup>41</sup> was the first to use a differential scheme approach to derive a special case of the Spriggs relation, which leads to the simple prediction

$$E_r = \exp(-2\phi). \quad (31)$$

Of course, both the Spriggs relation (30) and its special case, Eq. (31), suffer from a serious principal drawback:  $E_r$  is not zero for  $\phi = 1$ . That means, the Spriggs relation necessarily violates the HS upper bound (and even the Voigt bound). For this reason Hasselman,<sup>42</sup> based on previous work by Hashin,<sup>19</sup> suggested a relation which can be written as

$$E_r = \frac{1 - \phi}{1 + C_H \phi}, \quad (32)$$

where  $C_H$  has to be determined principally by fitting experimentally measured data. This relation is clearly non-linear and monotonically decreasing, and  $E = 0$  is guaranteed for  $\phi = 1$ . Unfortunately, however, the inverse of  $-C_H$  cannot be interpreted as a critical porosity since in the limit  $\phi \rightarrow -1/C_H$  Eq. (32) diverges ( $|E| \rightarrow \infty$ ), i.e.  $-1/C_H$  must always lie outside of the interval  $0 < \phi < 1$ . Thus, the interpretation of  $-1/C_H$  in terms of a critical porosity is principally inadmissible and there is no physical meaning left in the Hasselman relation (32).<sup>13,23</sup> This finding corresponds to the fact that fitting of experimentally measured values invariably leads to positive values of  $C_H$ .<sup>43,44</sup> Nevertheless, a very special case of the Hasselman relation (32) can still be useful for predictive purposes, viz. the case  $C_H = 1$ . In this case the Hasselman relation reduces to the Mori–Tanaka/Kuster–Toksöz relation,

$$E_r = \frac{1 - \phi}{1 + \phi}, \quad (33)$$

cf. Eq. (12), which is identical to the HS upper bound for porous materials with spherical pores and  $\nu_0 = 0.2$ , as discussed above.

Only recently it has been recognized that also the modified exponential relation<sup>22</sup>

$$E_r = \exp\left(\frac{-[E]\phi}{1 - \phi}\right) \quad (34)$$

circumvents the aforementioned compatibility problem at  $\phi = 1$ . In Ref. 22 a derivation of this relation has been given via the functional equation approach. Trivially, in the case of porous materials with spherical pores the modified exponential leads to the prediction

$$E_r = \exp\left(\frac{-2\phi}{1 - \phi}\right). \quad (35)$$

Note that, strictly speaking, this modified exponential model results in a zero relative tensile modulus only in the limiting case of 100% porosity. In order to allow for the possibility

of  $E_r = 0$  at porosities lower than 100 % (i.e.  $\phi < 1$ ), one can include an additional parameter in the modulus–porosity relation, the critical porosity  $\phi_C$ , which is able to take the possible occurrence of a percolation threshold into account. This results in Mooney-type exponential relations,<sup>13,22,45</sup> which are of the form

$$E_r = \exp\left(\frac{-[E]\phi}{1 - \phi/\phi_C}\right). \quad (36)$$

As before, under the assumption of spherical pores we can set  $[E] = 2$ , which reduces the number of adjustable fit parameters by one.

Power-law relations represent another class of models, principally different from the exponential relations just presented. The simplest relation of this kind is the Archie-type relation<sup>3</sup>

$$E_r = (1 - \phi)^{[E]}, \quad (37)$$

a derivation of which via the functional equation approach has been given recently.<sup>21</sup> Of course, in the case of the tensile modulus the Archie relation can be considered as a generalization of the Coble–Kingery relation

$$E_r = (1 - \phi)^2. \quad (38)$$

Neither of these relations exhibits a compatibility problem at  $\phi = 1$  and, again, in the dilute limit ( $\phi \rightarrow 0$ ) they reduce to Eq. (17). Moreover, as before with the exponential relations, in order to allow the possible occurrence of a percolation threshold, i.e.  $E_r = 0$  for porosities  $\phi < 1$ , the critical porosity  $\phi_C$  can be introduced as an additional parameter. This results in a Krieger-type power-law relation,<sup>24,31</sup> in elasticity context often called Phani–Niyogi relation<sup>46</sup>

$$E_r = \left(1 - \frac{\phi}{\phi_C}\right)^{[E]\phi_C}. \quad (39)$$

As before, under the assumption of spherical pores we can set  $[E] = 2$ , which again reduces the number of adjustable fit parameters by one. We would like to emphasize again that, although sometimes considered to be purely empirical, all the exponential and power-law relations mentioned above can be derived via a functional equation approach.<sup>21,22,31</sup> What makes them semi-empirical fit models in practice is only the fact that, due to variations in pore shape (strong anisotropy), the first-order coefficient (intrinsic tensile modulus) may not be reliably known and that, due to the difficulty to assess and quantify pore size distribution and connectivity, a priori estimates of the critical porosity are usually not available. Note, however, that Eqs. (31), (33), (35) and (38) are parameter-free predictive models, not fit equations.

Recently, a new relation has been proposed by Pabst and Gregorová<sup>23</sup>

$$E_r = (1 - [E]\phi + ([E] - 1)\phi^2) \frac{(1 - \phi/\phi_C)}{(1 - \phi)}. \quad (40)$$

This relation has been found heuristically and reduces to Eq. (17) in the dilute limit ( $\phi \rightarrow 0$ , implying  $\phi \ll \phi_C$ ). Furthermore it ensures that  $E_r = 0$  when  $\phi = \phi_C$ , as required. Setting  $[E] = 2$  this relation adopts the extremely simple form

$$E_r = (1 - \phi) \left( 1 - \frac{\phi}{\phi_C} \right), \quad (41)$$

which seems to be the simplest thinkable relation allowing for a percolation threshold (via the critical porosity  $\phi_C$ ). In the absence of a percolation threshold (i.e.  $\phi_C = 1$ ) it reduces to the Coble–Kingery relation (38), as required. We recall that  $[E] = 2$  is always a reasonable approximation for porous materials with isometric pores, independently of the precise value of the matrix or skeleton Poisson ratio  $\nu_0$ , cf. Table 1 and the discussion above. Of course, unless the critical porosity  $\phi_C$  is known a priori (a rather exceptional case) and an application of Eq. (41) for predictive purposes is intended, this discussion is of more or less philosophical character anyway. As long as Eq. (41) is used as a fit model, its application to cases where the assumption  $[E] = 2$  is (approximately) justified may be called semi-empirical (because its form is a special case of Eq. (40)), while its application to cases where the assumption  $[E] = 2$  is not justified must be considered as purely empirical. In any case, contrary to the situation with the parameter  $-1/C_H$  occurring in the Hasselman relation (32), cf. the discussion above, there are no principal objections against the interpretation of  $\phi_C$  in terms of a critical porosity. In other words, even if taken as a purely empirical fit equation, our relation remains principally meaningful from the physical point of view.

We emphasize that, except for the Spriggs relation (30) and its special case, Eq. (31), none of the relations cited above necessarily violates the HS upper bound. This is the case, however, e.g. for the model derived for cubic pores by Ishai and Cohen<sup>47</sup>

$$E_r = 1 - \phi^{2/3}. \quad (42)$$

Needless to say, the use of such a model should be avoided. Boccaccini et al.<sup>48</sup> have modified this relation in a way that the HS upper bound need not be violated any more. The practical significance of their relation, however, concerns strongly anisometric pores, which are beyond the scope of this paper.

In principle, it can be attempted to interpret deviations of the intrinsic tensile modulus determined by fitting with any of the relations above from the benchmark value  $[E] = 2$  in terms of an influence of pore shape. This is possible because usually the deviations in  $[E]$  caused by a variation of the matrix or skeleton Poisson ratio are in practice negligible. Apart from the obvious advice that such an interpretation should be based on a reliable determination of  $[E]$  (e.g. by comparing the coincidence of fitting results using several of the relations above) it should be kept in mind, that significant deviations in  $[E]$  require a considerable degree of pore anisometry (elongation or flattening). Non-spherical pores which are more or less isometric (e.g. of polyhedral shape or pores with con-

cave faces) cannot be expected to be responsible for measurable deviations in the intrinsic elastic moduli. Their intrinsic tensile modulus will still be close to the benchmark value ( $[E] \approx 2$ ).

In concluding this section we would like to emphasize that of course all relations presented here for the relative tensile modulus can be used for fitting experimentally measured data for any kind of elastic modulus (and many other properties as well). Also in these cases it may under certain circumstances be legitimate to interpret the values obtained for the intrinsic moduli by fitting in terms of a pore shape influence. It has to be kept in mind, however, that the intrinsic value of 2 in the case of porous materials with spherical or isometric pores is specific only to the tensile modulus (where  $[E] = 2$  exactly for  $\nu_0 = 0.2$  and  $\nu_0 = 1/3$  and  $[E] \approx 2$  for all matrix Poisson ratios  $0 < \nu_0 < 0.5$ ). It can be a good approximation for the shear modulus as well (for the matrix or skeleton Poisson ratios commonly encountered in practice), but certainly not for the bulk modulus or other properties. That means, only for the tensile modulus (and approximately for the shear modulus) the parameter-free special relations (31), (35) and (38) given above (specialized by setting  $[E] = 2$ ), including the Mori–Tanaka/Kuster–Toksöz relation (33), can be expected to provide useful predictions. Eq. (31), of course, is principally disqualified for a completely different reason (viz. because it violates the HS upper bound and even the Voigt bound, cf. the discussion above), while the Kuster–Toksöz relation (33) represents no improvement over the HS upper bound (because it is identical to it). Similarly, we recall that the Pabst–Gregorová relation (40) adopts its elegant and simple form (41) only in the case  $[E] = 2$ . This relation, however, is not per se meant to be a predictive model (since the critical porosity  $\phi_C$  can usually not be expected to be known a priori), but a fit equation. As such, of course, it can be used quite universally.

We believe that the classification given in this section is rational and exhaustive, at least for approximately isometric pores, in the sense that all relations not mentioned in this section have to be considered with great scepticism. This must be said, e.g. of the sophisticated relation derived by Nielsen,<sup>49</sup> a special case of which is the relation of Ramakrishnan and Arunachalam<sup>50</sup> (which is similar to the Hasselman relation and suffers from the same drawbacks) and of the remarkable relation proposed by Boccaccini and Fan.<sup>51</sup> Fortunately, at least, all of these relations contain the Coble–Kingery relation (38) as a special case.

## 6. Case study: effective tensile moduli of porous alumina, zirconia, silicon carbide and silicon nitride

As a practical example of the application of some of the above relations we consider alumina ( $\text{Al}_2\text{O}_3$ ), zirconia ( $\text{ZrO}_2$ ), silicon carbide ( $\text{SiC}$ ) and silicon nitride ( $\text{Si}_3\text{N}_4$ ), all prepared with corn-starch (median size approximately  $14 \mu\text{m}$  in all cases) as a pore-forming agent and all with a compa-



Table 2

Elastic properties of almost pore-free (densely sintered), macroscopically isotropic polycrystalline alumina, zirconia, silicon carbide and silicon nitride

Elastic property	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	SiC	Si <sub>3</sub> N <sub>4</sub>
$E_0$	400	210	420	320
$G_0$	163	80	179	126
$K_0$	247	184	212	232
$\nu_0$	0.23	0.31	0.17	0.27

table microstructure (matrix-inclusion-based microstructure with the possibility of pore contact or overlap). The (experimentally measured) data for alumina and zirconia are taken from Refs. 43, 44 the data for silicon carbide from Ref. 52 and for silicon nitride from Ref. 53 to which the reader should refer for a specification of the chemical and phase composition as well as processing details. The elastic properties of the pore-free, densely sintered polycrystalline ceramics (matrix material), which are necessary input data for the calculation of relative moduli, have been extracted from literature values determined at room temperature ( $25 \pm 3$  °C) for samples with a total porosity <3% and are listed in Table 2. For alumina and zirconia these input data are taken from the critical comparison in Ref. 54, for silicon carbide and silicon nitride they are the result of an extensive literature research, partly, but not exclusively, based on the electronic NIST data bases.<sup>55</sup>

Introducing artificial porosity via pore-forming agents (e.g. starch) is a common way to produce ceramics with controlled porosity, characterized by a pore size significantly larger (typically 1–2 orders of magnitude) than the grain size. Essentially this processing technique results in porous materials with large void inclusions, i.e. large closed pores, but the possibility of pore contact or even a certain degree of overlap cannot be absolutely excluded. Large pores (typically tens of  $\mu\text{m}$ ) embedded in a fine-grained (typically around 1  $\mu\text{m}$ ) matrix of host material, will not exhibit significant shrinkage during firing (even at temperatures and in time schedules where the matrix becomes densely sintered, i.e. attains almost theoretical density) and will remain as void inclusions in the final ceramic. These will then determine the effective elastic properties. For such materials it is possible to consider the matrix (dense host material) as a homogenized medium and to invoke the Voigt bounds and the upper Hashin–Shtrikman bounds in their simple form for two-phase materials.

Figs. 4 and 5 show the HS upper bounds of the relative shear and bulk moduli, respectively, of SiC and ZrO<sub>2</sub>. These two ceramics exhibit the most extreme matrix Poisson ratios  $\nu_0$  of the four ceramics investigated, viz.  $\nu_0 = 0.17$  (SiC) and  $\nu_0 = 0.31$  (ZrO<sub>2</sub>), i.e. Al<sub>2</sub>O<sub>3</sub> and Si<sub>3</sub>N<sub>4</sub> are always intermediate between these two extremes. Note that for the shear modulus (Fig. 4) the HS upper bound is always slightly lower for the material with smaller  $\nu_0$ , whereas for the bulk modulus (Fig. 5) it is much higher for the material with smaller  $\nu_0$ . The influence of  $\nu_0$  is practically negligible for the tensile modulus and, therefore, the HS upper bound can be drawn as one single line for all ceramics, corresponding to Eq. (33).

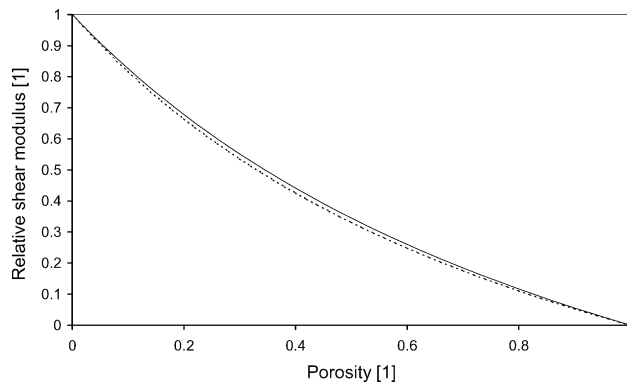


Fig. 4. HS upper bounds for the relative shear modulus of porous ceramics with spherical or isometric pores (upper solid curve: ZrO<sub>2</sub>; lower dashed curve: SiC, Al<sub>2</sub>O<sub>3</sub> and Si<sub>3</sub>N<sub>4</sub> are in between).

Fig. 6 shows the porosity dependence of tensile moduli data reported for alumina,<sup>43,44</sup> zirconia,<sup>43,44</sup> silicon carbide<sup>52</sup> and silicon nitride.<sup>53</sup> In spite of the relatively large scatter of the values a common trend exhibited by all these ceramics can be recognized. This is indicative of the same or at least a very similar type of microstructure. Although, due to its organic character, the pore-forming agent (starch) is burnt out and vanishes completely during heating up to the sintering temperature of the ceramics, the pores will remain isometric and the microstructure will be essentially matrix-inclusion-based, permitting only a small degree of pore overlap. All values shown in Fig. 6 obey the HS upper bound (33), as required for macroscopically isotropic ceramics. Evidently, the special case of the Spriggs relation, Eq. (31), is useless for prediction, because it violates the HS upper bound.

The Coble–Kingery relation has evidently a better score: at least it does not violate the HS upper bound and it is clearly an improvement over the latter when a rough estimate is needed. However, when all data are fitted with one master curve using the Archie-type relation (37) the resulting intrinsic tensile modulus obtained from fitting is  $[E] = 2.61$ , cf. Table 3. Similarly, when the Phani–Niyogi relation (39) is used for fitting the intrinsic tensile modulus is  $[E] = 2.41$  (the expo-

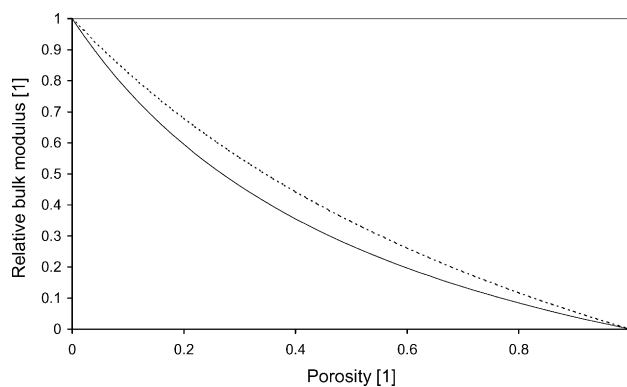


Fig. 5. HS upper bounds for the relative bulk modulus of porous ceramics with spherical or isometric pores (upper dashed curve: SiC; lower solid curve: ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Si<sub>3</sub>N<sub>4</sub> are in between).

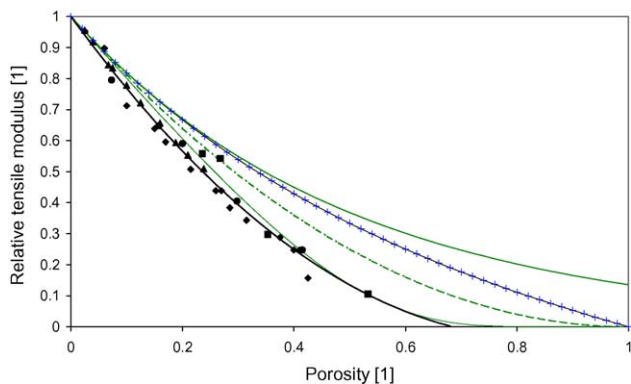


Fig. 6. Relative tensile modulus of porous ceramics prepared with corn-starch as a pore-forming agent (measured values and predictions); HS upper bound (thin solid line with crosses), experimentally measured values (squares:  $\text{Al}_2\text{O}_3$ , diamonds:  $\text{SiC}$ , cf. Ref. 52, triangles:  $\text{Si}_3\text{N}_4$ , cf. Ref. 53, circles:  $\text{ZrO}_2$ ), predictions for spherical pores (thin dotted curve: Spriggs relation (31); thin dashed curve: Coble–Kingery relation (38), thin solid curve: modified exponential relation (35)) and fitted master curve (thick solid curve obtained by fitting with our new relation, Eq. (41),  $\phi_C = 0.684$ ).

ment  $[E]\phi_C$  being 1.45 and the critical porosity,  $\phi_C = 0.725$ , cf. Table 3). This indicates, that when the exponent 2 in the Coble–Kingery relation (38) is allowed to vary freely (as an adjustable fit parameter), the fitted curve corresponds to a value significantly larger than 2. This is clear quantitative evidence (apart from the obvious qualitative findings of visual inspection of Fig. 6) of the fact that the Coble–Kingery prediction is not completely satisfactory in this case.

By far the best prediction is achieved with the modified exponential relation (35). We emphasize that the latter is, similar to the HS upper bound and the Coble–Kingery prediction, an unbiased a priori prediction, without the need for fitting. It is solely based on the assumption that the pores are spherical. In this case, if the intrinsic tensile modulus is allowed to vary, i.e. if we consider  $[E]$  as an adjustable parameter to be determined by fitting according to Eq. (34), cf. Table 3, the result is  $[E] = 2.20$ , which is a value fairly close to  $[E] = 2$ . Similarly, when a critical volume fraction is introduced as a fit parameter, i.e. the Mooney-type relation (36) is used with  $[E] = 2$ , this critical volume fraction turns out to be  $\phi_C = 1.146$ , i.e.  $\phi_C \approx 1$ . Both findings confirm in a

Table 3

Fit parameters determined for the master curve of the porosity dependence of the tensile modulus of four types of ceramics (alumina, zirconia, silicon carbide, silicon nitride) with matrix-inclusion type microstructure prepared with corn-starch as a pore-forming agent

	Fit model	$[E]$	$\phi_C$
Modified exponential	$E_r = \exp\left(\frac{-[E]\phi}{1-\phi}\right)$	2.20	–
Mooney-type with $[E] = 2$	$E_r = \exp\left(\frac{-2\phi}{1-\phi/\phi_C}\right)$	–	1.146
Archie-type	$E_r = (1 - \phi)^{[E]}$	2.61	–
Phani–Niyogi	$E_r = (1 - \phi/\phi_C)^{[E]\phi_C}$	2.41	0.725
Pabst–Gregorová	$E_r = (1 - \phi)(1 - \phi/\phi_C)$	–	0.684

quantitative way the good quality of the prediction via the modified exponential relation (35).

In order to obtain a master curve characterizing as precisely as possible the general trend of the porosity-dependence of the elastic moduli, which is common to all materials of a given type of microstructure (irrespective of the chemical or phase composition of the matrix or skeleton phase), it is generally advisable to use the new relation (41) for fitting. In the present case we obtain

$$E_r = (1 - \phi) \left(1 - \frac{\phi}{0.684}\right).$$

This finding is physically reasonable and visual inspection shows that it provides an excellent description of the measured data, cf. Fig. 6. Moreover, the value determined here for the critical porosity falls well within the approximate range  $\phi_C = 0.74 \pm 0.09$ , representing the arithmetic average (and standard deviation) of critical porosity values determined for materials with similar microstructure in previous work.<sup>43,44</sup> We emphasize that these critical porosities have been obtained by extrapolation of real-world experiments on real materials. Percolation theory has to clarify the question whether these results can in any way be reconciled with simulations (virtual experiments) performed with model materials of known and well characterized microstructures.<sup>32</sup>

## 7. Discussion and conclusions

The theoretical framework of elastic properties has been recalled from the viewpoint of rational mechanics (continuum theory) and micromechanics (composite theory). Based on the concept of intrinsic elastic moduli a rational classification and a relatively exhaustive overview of modulus–porosity relations has been given, which includes exponential and power-law expressions as well as several other relations, among them the Hasselman relation and a relation with percolation threshold (critical porosity) recently proposed by Pabst and Gregorová.<sup>23</sup>

It has been shown that no physical meaning can be ascribed to the adjustable fit parameter occurring in the Hasselman relation (32). Only a very special case of the Hasselman relation (viz. the one for which the fit parameter degenerates to unity) is useful for the porosity dependence of the tensile modulus, viz. Eq. (33). In this case the Hasselman relation corresponds to the HS upper bound.

It has been shown that, contrary to the Hasselman relation (32), the parameter  $\phi_C$  occurring in Eq. (41) can always be interpreted as a critical porosity. It corresponds to the percolation threshold, at which a porous material loses integrity and/or attains zero elastic moduli. Eq. (41) is simpler than the Phani–Niyogi relation (39) (which also allows for a critical porosity or percolation threshold), but also contains the Coble–Kingery relation (38) as a special case, in contrast to the Hasselman relation (32).

The simple and elegant second-order modulus–property relations of the Coble–Kingery type, Eq. (26), including (38), which have been unduly ignored, or incorrectly cited, in most relevant papers and textbooks, have been recalled and their use is advocated for the porosity dependence of the tensile and shear moduli. In spite of their simplistic derivation and the unphysical artifacts they produce when the intrinsic elastic moduli are (significantly) larger than two, i.e.  $[M] > 2$ , it seems that the Coble–Kingery relations are relatively sound from the viewpoint of micromechanics (because they do not violate the Hashin–Shtrikman upper bounds), in contrast, e.g. to the frequently used Spriggs relation (30), including its special case, Eq. (31), and the Ishai–Cohen relation (42). Needless to say, the use of the latter two should be generally avoided.

Moreover, although the (non-linear) Coble–Kingery relations are based on the (linear) Dewey–Mackenzie relations (19)–(22), which have been rigorously derived only for a dilute (i.e. non-interacting) system ( $\phi \rightarrow 0$ ) of isolated (i.e. closed and non-overlapping) pores of spherical shape, it has been shown that the principally different, semi-empirical Gibson–Ashby approach, which is based solely on dimensional arguments for an idealized structure consisting of a space-filling arrangement of cubic skeletons (modeling an open-cell cellular solid or foam) supplemented by a numerical value obtained from a master fit of a large amount of data measured for low-density ( $\phi \rightarrow 1$ ) cellular solids, leads to exactly same result for the porosity dependence of the effective tensile modulus. This fact, together with the well-known finding that exactly the same result is also obtained in micromechanics using the differential or functional equation approach, greatly enhances the confidence in Eq. (38) as a practical benchmark relation for the whole range of porosities, from  $\phi = 0$  to  $\phi = 1$ , without necessary recourse to the special assumption of spherical pore shape (as long as they are not anisometric), irrespective of pore topology (isolation or connectedness of pores) and (approximately) independent of the matrix or skeleton Poisson ratio (at least in the range  $0.1 < \nu_0 < 0.4$ ). Being the only available power-law type benchmark relation of this kind, all other reasonable non-exponential relations, e.g. those proposed for (strongly) anisometric pores, should be required to reduce to Eq. (38) in the special case of isometric pores. Note, however, that Eq. (38) cannot be considered as a rigorous upper bound, since, e.g. the aforementioned Hashin assemblage<sup>19</sup> can principally exceed it (even if only slightly).

We emphasize that in the special case of materials with a matrix or skeleton Poisson ratio of  $\nu_0 = 0.2$  the same type of relation, Eq. (27), can be considered as a benchmark relation for all three elastic moduli ( $E$ ,  $G$  and  $K$ ). For this reason we have proposed to correct the prefactor  $\gamma$  in the Gibson–Ashby relation for the shear modulus from  $\gamma = 3(1 + \nu_0)/4$  (originally proposed by Gibson and Ashby) to  $\gamma = 5(1 + \nu_0)/6$ , which is the appropriate expression to ensure exact agreement with Eq. (27) in the case of materials with a matrix or skeleton Poisson ratio of  $\nu_0 = 0.2$ , as required. This small correction,

which renders the Gibson–Ashby relation more acceptable from the theoretical point of view as an approximation for the shear modulus, corresponds to a change in the prefactor by 10%. Such a small change may well be within the uncertainty of Gibson and Ashby’s master curve fit or within the natural scatter caused by the relative arbitrariness of sampling (data selection). To make things clear, we think that Gibson and Ashby’s value for this prefactor, although obtained on the basis of fitting a large amount of measured and published data, was presumably also guided by the attempt to achieve agreement with Eq. (27) for  $\nu_0 = 1/3$ . As shown in the present paper, however, the latter is unjustified on theoretical grounds, because the intrinsic shear modulus for  $\nu_0 = 1/3$  is not  $[G] = 2$  but  $[G] = 1.875$ , which prohibits to write the Coble–Kingery relation for this case in the binomial form of Eq. (27).

As a paradigmatic example, selected relations have been applied to describe the porosity dependence of the relative tensile modulus for alumina, zirconia, silicon nitride and silicon carbide prepared with corn-starch as a pore-forming agent. It has become apparent that, irrespective of the processing details, porous ceramics with this type of microstructure (essentially matrix-inclusion-based) follow a common trend, which is dominant in spite of experimental scatter. Fitting the master curve with the new relation (41) yields a critical porosity of  $\phi_C = 0.684$ . In practice this value is roughly indicative of the maximum porosity that can be achieved by the processing method applied (here, e.g. using starch as a pore-forming agent). Of course it may vary for different processing techniques, but it should be independent of the material in question.

It has been pointed out that for materials with the type of microstructure investigated here, the modified exponential relation (35), derived via a functional equation approach,<sup>22</sup> provides a satisfactory prediction of the actually measured porosity dependence. Thus, for the microstructures resulting from starch burnout the prediction via this new relation is far better than the Coble–Kingery prediction, Eq. (38), and rather close to the master curve obtained by fitting with Eq. (41). This remarkable fact, never stated in the literature before, seems to be rooted in the different model assumptions that led to the derivation of Eqs. (35) and (38), respectively, using the functional equation approach.<sup>21,22,31</sup>

Note that, although visual inspection confirms the quality of the prediction (35) and the proximity to the master curve fitted via Eq. (41), the modified exponential relation (35) does not predict a critical porosity. As a consequence of its form it remains principally finite even for very high porosities ( $\phi \rightarrow 1$ ). This does not mean, however, that Eq. (35) would be suitable for predicting the porosity dependence of the tensile moduli of low-density cellular materials with a bicontinuous microstructure (i.e. solid networks or open-cell foams). When measured data are lacking in such a case, the Coble–Kingery relation (38) is clearly the better choice for approximate modulus prediction.

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