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Effective properties of suspensions, composites and porous materials

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Abstract

Three effective properties of heterogeneous systems are discussed from the viewpoint of rational mechanics and micromechanics: viscosity of suspensions and the tensile modulus and thermal conductivity of solid composites, including porous materials. Rigorous bounds (Voigt–Reuss and Hashin–Shtrikman bounds) are given as well as model relations for prediction and fitting purposes (dilute approximations, power-law relations, exponential relations, Coble–Kingery relations and new relations recently proposed by the authors). The semi-empirical nonlinear relations for the volume fraction (or porosity) dependence, including exponential and power-law relations with and without percolation threshold, are presented in a new systematic way which emphasizes the formal analogies between these relations and might become a useful tool in the future education of materials scientists and engineers.

Keywords: Mechanical properties; Composites; Porosity; Thermal properties; Suspension viscosity

1. Introduction

Suspension viscosity is a key property for traditional ceramic shaping technologies (e.g. slip-casting, tape-casting and extrusion), while the elastic properties (e.g. the tensile modulus) determine the mechanical behavior of ceramic materials and thermal properties (e.g. thermal conductivity) are responsible for their conductive or insulating behavior, high-temperature performance and thermal shock resistance.

A view into the current literature reveals that, although widely studied experimentally, these properties are not thoroughly understood from a theoretical point of view. At least most experimenters seem not to be aware of the progress which has been made in their understanding from the viewpoint of rational mechanics[1,2] and micromechanics.[3,4]

For this reason, in many fields the analysis of experimental data often still applies oldfashioned relations, although far better relations are available today, for prediction as well as for fitting purposes. Furthermore, many of the relations commonly used should clearly be avoided (e.g. the Spriggs exponential relation for the analysis of the porosity dependence of the elastic moduli) because they are definitely known to violate universally acknowledged principles (viz. the upper bounds of micromechanics).

Of course the underlying cause of this situation has to be sought in the standard textbooks available and the present state of education. Most current teaching schedules present an overflow of detail knowledge but lack the logical clarity that makes things simple and relatively correct. It is the purpose of this paper to contribute to such an understanding and to present suspension viscosity as well as the tensile modulus and the thermal conductivity of composites and porous materials in a unified framework that should be useful for experimental practice as well as inspiring from the didactic viewpoint.

2. The rational view on elastic moduli, viscosities and thermal conductivity

The constitutive equation of a linearly elastic anisotropic solid is

$$\boldsymbol{T} = \mathbf{CE}, \tag{1}$$

where **T** is the Cauchy stress tensor (a symmetric second-order tensor), **C** the stiffness tensor (a fully symmetric fourth-order tensor, also called elasticity tensor) and **E** is the so-called small strain tensor (a symmetric second-order tensor).[1,2,5] Similarly, the constitutive equation of a *linearly viscous anisotropic fluid* is

$$\boldsymbol{T} + p\mathbf{1} = \boldsymbol{V}\,\boldsymbol{D}, \tag{2}$$

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where p is the pressure, $\mathbf{1}$ the second-order unit tensor, $\mathbf{V}$ the viscosity tensor[1] (again a fully symmetric fourth-order tensor) and $\mathbf{D}$ is the stretching tensor or rate-of-deformation tensor (the symmetric part of the velocity gradient, i.e. a symmetric second-order tensor).[2,6] The constitutive equation of a *linearly elastic isotropic solid* is

$$\boldsymbol{T} = \lambda \cdot (tr\, \boldsymbol{E}) \cdot \mathbf{1} + 2\mu \boldsymbol{E} \quad \text{(Cauchy–Hooke solids)}, \tag{3}$$

where λ and μ are elastic constants (the so-called Lamé moduli, in (Pa)), and the constitutive equation of a *linearly viscous isotropic fluid* is

$$\boldsymbol{T} + p\mathbf{1} = \zeta \cdot (tr\, \boldsymbol{D}) \cdot \mathbf{1} + 2\eta \boldsymbol{D} \quad \text{(Navier–Stokes–Newton fluids)}, \tag{4}$$

where ζ and η are viscosity coefficients (or simply "viscosities", in (Pa)). In these two equations tr denotes the trace of a tensor.[1,2,5,6]

In contrast to viscosity and elasticity, which require a tensorial constitutive equation for the stress (a second-order tensor), *heat conduction* is determined by a vectorial constitutive equation for the heat flux vector. For *anisotropic materials* it is

$$\boldsymbol{q} = -\boldsymbol{K}\, \text{grad}\, T, \tag{5}$$

where $\mathbf{q}$ is the heat flux, grad T the temperature gradient and $\mathbf{K}$ is the thermal conductivity tensor (a second-order tensor), and for *isotropic materials* we have:

$$\boldsymbol{q} = -k\, \text{grad}\, T \quad \text{(Fourier's law)}, \tag{6}$$

where k is a scalar, the thermal conductivity. Note that in the case of isotropic solids and fluids, respectively, both elastic and viscous behavior is generally determined by two scalar quantities, while the conductive behavior is determined by only one scalar. In elasticity and viscosity context it is common practice to introduce other quantities besides λ, μ, ζ and η. In particular, $K = \lambda + (2/3)\mu$ and $\zeta = \zeta + (2/3)\eta$ are the bulk modulus and bulk viscosity, while μ and η are the shear modulus and the shear viscosity (in the following simply called "viscosity"), respectively.[2] However, for plausible reasons, in fluids there is no viscosity analogue to the tensile modulus and the Poisson ratio, which are $E = \mu(3\lambda + 2\mu)/(\lambda + \mu)$ and $\nu = \lambda/2(\lambda + \mu)$, respectively.[5] Although the analogy between the shear modulus μ and the shear viscosity η is closer, in what follows we compare the micromechancal relations for the thermal conductivity k with those for the tensile modulus E and the shear viscosity η, simply because of the greater practical significance of the latter two.

3. Effective properties from the viewpoint of micromechanics

The properties of multiphase media are called effective properties.[3,4] For reasons of convenience we omit the subscript "effective" in what follows, but it is understood that all properties without subscript are effective properties. Furthermore, we confine our treatment to isotropic two-phase materials and in order to simplify notation we use the symbol ϕ for the volume fraction of one phase, with the understanding that for suspensions ϕ denotes the solids volume fraction while for porous materials ϕ is the volume fraction of voids, i.e. the porosity. Micromechanical analogies arise as a consequence of identical microstructural models adopted to model real materials.[3,4]

Since the solid particles in a suspension can be considered as infinitely stiff (i.e. rigid) compared to the surrounding liquid medium there is no upper bound to the effective viscosity of a suspension (in contrast to an emulsion) and the lower bound is simply the viscosity of the liquid medium. What is more, the effective suspension viscosity goes to infinity at a critical solid volume fraction ϕ_C smaller that unity.[6]

In the case of solid composites the effective tensile modulus is bounded from below by the Reuss bound (harmonic mean) and from above by the Paul upper bound, which in the special case of void inclusions reduces to the Voigt bound (arithmetic mean).[7,8] The effective thermal conductivity of composites, including porous materials, is bounded from below by the harmonic mean and from above by the arithmetic mean (in this context called Wiener bounds). For materials with void inclusions the lower bounds degenerate to zero and the upper bound is for both the tensile modulus and the thermal conductivity:

$$E_r = k_r = 1 - \phi. \tag{7}$$

In the case of isotropic microstructures the effective tensile modulus and the effective thermal conductivity are bounded by the Hashin–Shtrikman bounds.[3,4] Again, for materials with void inclusions the lower bounds degenerate to zero and the Hashin–Shtrikman upper bounds reduce in the special case of void inclusions to[7–10]

$$E_r = \frac{1-\phi}{1+\phi} \tag{8a}$$

and

$$k_r = \frac{1-\phi}{1+\phi/2} \tag{8b}$$

for the tensile modulus (approximately)[7,8] and for the thermal conductivity,[9,10] respectively. In these equations $E_r = E/E_0$ is the relative tensile modulus (with E denoting the effective tensile modulus of the porous material and E_0 the tensile modulus of the dense solid, i.e. the skeleton or matrix phase) and similar for $k_r = k/k_0$. ϕ is the porosity (volume fraction of the void inclusions).

Depending on the microstructural information available, the bounds can be further refined,[3,4] but we restrict ourselves to those cases in which the rigorous bounds fail altogether, i.e. to cases of infinite phase property contrast: suspensions with rigid particles and porous materials with void inclusions.

4. Predictive and fit models for effective properties

The simplest predictive models are based on the exact solution of the problem of a spherical inclusion in an infinite medium.[3,4] With regard to the fairly restricted applications of these solutions they are called "dilute approximations". These are

$$\eta_r = 1 + 2.5\phi, \tag{9a}$$

$$E_r = 1 - 2\phi, \tag{9b}$$

$$k_r = 1 - 1.5\phi \tag{9c}$$

for the viscosity (with the relative viscosity η_r), the tensile modulus (approximately) and the thermal conductivity, respectively.[3,4,6–12] A group of model relations for higher volume fractions can be derived via the so-called differential approach or via the functional equation approach.[6,9,13,14] This leads to the power law relations:

$$\eta_r = (1-\phi)^{-2.5}, \tag{10a}$$

$$E_r = (1-\phi)^2, \tag{10b}$$

$$k_r = (1-\phi)^{1.5} \tag{10c}$$

for the viscosity, the tensile modulus and the thermal conductivity, respectively. Alternatively, the following exponential models can be obtained via the functional equation approach[6,9,13,14]:

$$\eta_r = \exp\left(\frac{2.5\,\phi}{1-\phi}\right), \tag{11a}$$

$$E_r = \exp\left(\frac{-2\,\phi}{1-\phi}\right), \tag{11b}$$

$$k_r = \exp\left(\frac{-1.5\,\phi}{1-\phi}\right) \tag{11c}$$

for the viscosity, the tensile modulus and the thermal conductivity, respectively. We emphasize that all these models are theoretically sound, i.e. they do not violate the rigorous bounds and exhibit reasonable limit behavior for $\phi \to 0$ and $\phi \to 1$. The same is true for the Coble–Kingery relations:

$$E_r = 1 - 2.0\,\phi + 1.0\,\phi^2, \tag{12a}$$

$$k_r = 1 - 1.5\,\phi + 0.5\,\phi^2 \tag{12b}$$

for the tensile modulus and the thermal conductivity, respectively.[11,12] Note that Eq. (12a) is identical to the power law Eq. (10b) and that no Coble–Kingery relation can be constructed for the viscosity.

In practice, the viscosity of suspensions approaches infinite values at volume fractions much smaller than 100%. This "blocking" phenomenon can be accounted for by introducting a critical volume fraction of solids ϕ_C.[6] Analogously, a critical volume fraction of second phase (or critical porosity) ϕ_C can be introduced for composites (or porous materials).[7,8] In the absence of a more specific information it is wise to assume ϕ_C for suspensions to be close to the maximum packing fraction of monodisperse rigid spheres,[6] i.e. $\phi_C \approx 0.64$, but usually a reliable estimate of ϕ_C (percolation threshold) is not available *a priori*. It is common practice, therefore, to treat ϕ_C as a fit parameter for an *a posteriori* description of measured data. Complete consistency of Eqs. (10) and (11) with the dilute approximations Eq. (9) is achieved when the term $(1-\phi)$ is replaced by $(1-\phi/\phi_C)$ and the exponents in Eq. (10) are multiplied by ϕ_C. It is common practice, however, to use Eqs. (10) and (11) as two-parameter fit equations, replacing the numerical coefficients 2.5, 2 and 1.5 by variable fit parameters. Alternative fit relations have been proposed recently for the tensile modulus[15] and the thermal conductivity,[10] respectively, viz.:

$$E_r = (1-\phi)\left(1 - \frac{\phi}{\phi_C}\right) \tag{13a}$$

and

$$k_r = \left(1 - \frac{\phi}{2}\right)\left(1 - \frac{\phi}{\phi_C}\right). \tag{13b}$$

These relations reduce to the respective Coble–Kingery relations, Eq. (12), when $\phi_C = 1$ and further to the dilute approximations, Eq. (9), for $\phi \to 0$. The application of these relations to real systems has been demonstrated in related papers.[7,9,16,17]

5. Conclusion

It has been recalled that viscosity and elasticity are governed by completely analogous tensorial constitutive equations (while thermal conductivity is defined via a vectorial constitutive equation) and that the effective tensile modulus and thermal conductivity of isotropic multiphase materials (composites and porous media) are bounded (at least from above) by the Hashin–Shtrikman bounds, in contrast to the suspension viscosity, for which no upper bound is available. Further it has been shown that the majority of predictive and fit models for the effective properties of suspensions and porous materials are power-law or exponential relations of the type:

$$P_r = \left(1 - \frac{\phi}{\phi_C}\right)^{[P]\phi_C}$$

and

$$P_r = \exp\left(\frac{-[P]\,\phi}{1-\phi/\phi_C}\right),$$

where P_r is the relative property (ratio of effective property and property of the matrix or skeleton phase), ϕ the volume fraction, ϕ_C the critical volume fraction (percolation threshold) and $[P]$ is the first-order coefficient in the dilute approximation (intrinsic property). Based on the well-known exact solution of a spherical inclusion problem the intrinsic properties can be assumed to be $[P] = -2.5$ for the viscosity of suspensions, $[P] = 2$ for the tensile modulus and $[P] = 1.5$ for the thermal conductivity of porous media. All these relations are theoretically sound, i.e. they do not violate the rigorous bounds, exhibit reasonable limit behavior for $\phi \to \phi_C$ and reduce to the dilute approximation $P_r = 1 - [P]\,\phi$ in the case $\phi \to 0$. Inserting the above values for $[P]$ and setting $\phi_C = 1$ yields useful predictive relations for the tensile modulus and the thermal conductivity. Finally, one-parameter fit relations have been given for the tensile modulus and the thermal conductivity which reduce to the respective Coble–Kingery relations when $\phi_C = 1$ and further to the dilute approximations for $\phi \to 0$.

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