

Relation Between Microscopic and Macroscopic Mechanical Properties in Random Mixtures of Elastic Media

Stefano Giordano

Department of Biophysical and Electronic
Engineering (DIBE),
University of Genoa,
Via Opera Pia 11a, 16145 Genoa, Italy¹
e-mail: stefgiord14@libero.it

A material composed of a mixture of distinct homogeneous media can be considered as a homogeneous one at a sufficiently large observation scale. In this work, the problem of the elastic mixture characterization is solved in the case of linear random mixtures, that is, materials for which the various components are isotropic, linear, and mixed together as an ensemble of particles having completely random shapes and positions. The proposed solution of this problem has been obtained in terms of the elastic properties of each constituent and of the stoichiometric coefficients. In other words, we have explicitly given the features of the micro-macro transition for a random mixture of elastic material. This result, in a large number of limiting cases, reduces to various analytical expressions that appear in earlier literature. Moreover, some comparisons with the similar problem concerning the electric characterization of random mixtures have been drawn. The specific analysis of porous random materials has been performed and largely discussed. Such an analysis leads to the evaluation of the percolation threshold, to the determination of the convergence properties of Poisson's ratio, and to good agreements with experimental data. [DOI: 10.1115/1.2400282]

Keywords: heterogeneous media, random mixtures, elastic moduli homogenization

Introduction

A widely dealt-with topic concerning the physical behavior of heterogeneous materials (mixtures) is that of calculating their elastic moduli starting from the knowledge of the moduli of each medium composing the mixture as well as of the structural properties of the mixture itself (percentage of each medium, shapes and relative positions of the single parts of the various media) [1,2]. Clearly, it concerns isotropic linear media, which combine to form linear mixtures. We find in the literature a large number of exact and approximate analytical expressions for the effective moduli of composed media as a function of the moduli of their homogeneous constituents and some stoichiometric parameters. At present, it is well known the details of the micro-geometry play a crucial role in determining the overall properties, particularly when the crystalline grains have highly anisotropic behavior or when there is a large difference in the properties of the constituent materials. Therefore, the elastic (thermal, electrical, and so on) properties of composite materials are strongly microstructure dependent. So, each approximate analytical expression, which appears in the literature, yields accurate predictions only for a particular kind of microstructure of the heterogeneous material. The most frequently analyzed elastic mixture theory regards a composite material formed by spherical inclusions embedded in a solid matrix. The related results have been reported by several authors (see, for example, Refs. [1,3]). Furthermore, the differential approach has been used to adapt this theory to higher volume fraction of the embedded inclusions [4–6]. Recent developments in the vast field of the homogenization in composite materials can be found in Ref. [7]. This work is devoted to an investigation on the

linear random mixtures (perfectly random microstructure). Roughly speaking, a random (or statistical) mixture is a material composed of little particles, having completely haphazard sizes, positions, and shapes; each particle is entirely composed of one of some given homogeneous isotropic materials. This definition has a clear intuitive meaning, though it does not withstand an accurate criticism. In a recent paper [8] the same problem has been addressed for the linear electrical conductivity and a generalization to nonlinear electrical mixtures has been made. In such a work, in the linear case, the authors dealt with random mixtures composed of N homogeneous media, having volume fractions c_1, c_2, \dots, c_N ($\sum c_i = 1$) and conductivities $\sigma_1, \sigma_2, \dots, \sigma_N$, respectively. They found an expression of the effective mixture conductivity σ in terms of the above quantities. This result depends on the dimensionality of the mixture. In the three-dimensional case, the equation for the effective conductivity is the following:

$$\frac{1}{3\sigma} = \sum_{k=1}^N \frac{c_k}{\sigma_k + 2\sigma} \quad (1)$$

Similarly, for two-dimensional mixture the result is given by:

$$\frac{1}{2\sigma} = \sum_{k=1}^N \frac{c_k}{\sigma_k + \sigma} \quad (2)$$

In this paper we study similar relationships, which describe a random mixture from the elastic point of view. In other words, we obtain some results, similar to Eq. (1) or (2), that allow us to estimate the elastic moduli (or more generally, the stiffness tensor) concerning the overall elastic behavior of a linear elastic random mixture.

From Diluted Dispersions to Random Mixtures

A composite material can be thought of as a heterogeneous solid continuum that bonds together different homogeneous continua: each part of the media has a well-defined sharp boundary.

¹New address to be used for all the correspondences: Department of Physics, University of Cagliari, Cittadella Universitaria, I-09042 Monserrato (Cagliari), Italy. E-mail: stefano.giordano@dsf.unica.it and stefgiord14@libero.it

Contributed by the Materials Division of ASME for publication in the JOURNAL OF ENGINEERING MATERIALS AND TECHNOLOGY. Manuscript received June 28, 2006; final manuscript received September 25, 2006. Review conducted by Thomas Sigmund.

The bonding at the interfaces remains intact in our models when the whole mixture is placed in an equilibrated state of infinitesimal elastic strain by external loads or constraints. So, the boundary conditions require that both the vector displacement and the stress tensor be continuous across any interfaces. Each separate homogeneous region has its characteristic stiffness tensor, which describes the stress-strain relation. If the materials are linear, isotropic, and homogeneous this relation is given by:

$$T_{ij} = L_{ijkl}^s E_{kl} \quad s = 1, 2, \dots, N \quad (3)$$

where T is the stress tensor, E is the strain tensor, and L is the constant stiffness tensor, which depends on the medium considered ($s=1, 2, \dots, N$ with N different phases). For isotropic media the latter is written, for example in terms of bulk modulus and shear modulus, as follows:

$$L_{ijkl}^s = k_s \delta_{ij} \delta_{kl} + 2\mu_s \left(\delta_{ik} \delta_{jl} - \frac{1}{3} \delta_{ij} \delta_{kl} \right) \quad s = 1, 2, \dots, N \quad (4)$$

where k_s and μ_s are the bulk and shear moduli of the s th medium and δ_{nm} is the Kronecke delta. For preliminary analysis of tensors and generic elastic behavior one can see Refs. [2,9].

To solve a mixture problem consists in finding the equivalent macroscopic stiffness tensor for the whole composite material and, then, for overall isotropic behavior, this means that we have to evaluate the equivalent k and μ constants.

The most famous and studied elastic mixture theory regards a composite material formed by spherical inclusions of medium 2 embedded in a solid matrix of medium 1. In this case the theory can be outlined as follows: first, one has to study the behavior of a single spherical inclusion inserted in a homogeneous matrix. This problem has been completely solved by Eshelby [10], who obtained the following fundamental result: if the strain tensor is constant in the matrix (whole three-dimensional space) before inserting any inclusion, when we embed a sphere of different material we obtain a constant strain inside the sphere itself. This result may be generalized to ellipsoidal inclusions and to the computation of the strain field outside the inclusions [10,11]. The relation between the constant strain inside the embedded inclusion and the constant bulk strain (in the matrix before the sphere embedding), obtained by Eshelby, allows the characterization of the dilute mixture of spheres in terms of equivalent bulk and shear moduli k and μ :

$$k = k_1 + \frac{4\mu_1 + 3k_1}{4\mu_1 + 3k_2} (k_2 - k_1)c + O(c^2)$$

$$\mu = \mu_1 + \frac{5\mu_1(4\mu_1 + 3k_1)(\mu_2 - \mu_1)}{\mu_1(9k_1 + 8\mu_1) + 6\mu_2(k_1 + 2\mu_1)} c + O(c^2) \quad (5)$$

This is the exact result for a material composed of a very dilute concentration of spherical inclusions (medium 2 with moduli k_2 and μ_2 and volume fraction c dispersed in a solid matrix (medium 1 with moduli k_1 , μ_1 and volume fraction $1-c$). The result is attributed to numerous authors [1]. A similar result holds on for the two-dimensional case (circles in the plane) [12]:

$$k = k_1 + \frac{\mu_1 + k_1}{\mu_1 + k_2} (k_2 - k_1)c + O(c^2)$$

$$\mu = \mu_1 + \frac{2\mu_1(\mu_1 + k_1)(\mu_2 - \mu_1)}{\mu_1(k_1 + \mu_2) + \mu_2(k_1 + \mu_1)} c + O(c^2) \quad (6)$$

It should be noted that the bulk modulus k , in Eq. (6), is not the same as the customarily used three-dimensional bulk modulus; however, for the problem of generalized plane stress where a thin plate of uniform thickness is deformed in its own plane, they are related by the formula: $k_{2D} = 9\mu_{3D}k_{3D}/(4\mu_{3D} + 3k_{3D})$. Moreover, we remember that the shear modulus has the same definition in two or three dimensions: $\mu_{2D} = \mu_{3D}$. Throughout this paper we

omit the indication $2D$ or $3D$, adopting the convention that k represents k_{2D} in all two-dimensional relationships. For more explanations one can see, for example, Ref. [9].

The higher orders terms, in the c expansions given in Eqs. (5) and (6), describe the interaction between particles, and so are negligible in the dilute limit and not necessary for our purposes.

In the sequel, these results will be used to derive some exact properties of two-phase random mixtures, that is, materials for which the components are isotropic, linear, and mixed together as an ensemble of particles having random shapes and positions. We consider the case of a random mixture (either two-dimensional or three-dimensional) composed by two media with concentrations $c_1 = 1 - c$ and $c_2 = c$, respectively. We assume by hypothesis that the only structural information on the mixture is the volume fraction of the second medium, since either medium is composed of particles completely randomized in size, position, and shape. In this problem we may not distinguish between the matrix and the inclusions. For example, in a polycrystalline media, each crystal may be treated as an inclusion embedded in the remaining crystals and, hence, all crystals have the same significance. So, there is complete symmetry in treating each crystal as an inclusion. Therefore, the concept of a matrix with embedded inclusions is no longer relevant. Nevertheless, it is possible to use Eqs. (5) and (6), in order to find some properties of a random mixture. For such a mixture we may use relations of this kind for the average moduli: $k = F(k_1, k_2, \mu_1, \mu_2, c)$ and $\mu = G(k_1, k_2, \mu_1, \mu_2, c)$. Functions F and G completely define the overall behavior of the random two-phase mixture and they are, for the moment, unknown in structure. This statement is actually a definition of random mixture: a mixture composed by parts so randomized, as stated above, that the only significant structural information is merely the volume fraction c of the second medium $1-c$ for the first medium). This definition is heuristically useful to calculate average parameters, as it is shown in the sequel. We search for some mathematical properties of functions F and G , which may be used in the following derivations to find out their complete analytical structure. Let us examine the situation for very low values of c ; we may think that a low value of c is reached when the structure contains only a single very small element of the second medium embedded in the matrix of the first medium. In this limiting case, Eqs. (5) and (6), obtained for diluted suspensions of spheres, hold on even for random mixture: i.e., the very small concentration behavior of functions F and G must be the same of that exhibited by Eqs. (5) and (6). More precisely, we think of a single embedded sphere with infinitesimal volume (or radius): this very small sphere represents a single point defect in the solid matrix and then it describes a random mixture with a single very small element of the second medium. Therefore, we may write down the derivatives of the functions F and G with respect to the volume fraction c , calculated for $c=0$. In the three-dimensional case we have:

$$\left. \frac{\partial F}{\partial c} \right|_{c=0} = \frac{4\mu_1 + 3k_1}{4\mu_1 + 3k_2} (k_2 - k_1)$$

$$\left. \frac{\partial G}{\partial c} \right|_{c=0} = \frac{5\mu_1(4\mu_1 + 3k_1)(\mu_2 - \mu_1)}{\mu_1(9k_1 + 8\mu_1) + 6\mu_2(k_1 + 2\mu_1)} \quad (7)$$

Similarly, for the two-dimensional case:

$$\left. \frac{\partial F}{\partial c} \right|_{c=0} = \frac{\mu_1 + k_1}{\mu_1 + k_2} (k_2 - k_1)$$

$$\left. \frac{\partial G}{\partial c} \right|_{c=0} = \frac{2\mu_1(\mu_1 + k_1)(\mu_2 - \mu_1)}{\mu_1(k_1 + \mu_2) + \mu_2(k_1 + \mu_1)} \quad (8)$$

Equations (7) and (8), holding true for two-phase random mixtures, play an essential role in the further development of the theory. By using these expressions, we may solve the complete problem of a random mixture composed by N different homogeneous components randomly mixed together to yield an overall

isotropic medium. In the sequel, to apply Eqs. (7) and (8), the significance given to the matrix (medium 1) must be removed.

Elastic Multiphase Random Mixtures

This section deals with random mixtures composed of N homogeneous media, having volume fractions c_1, c_2, \dots, c_N ($\sum_{i=1}^N c_i = 1, i = 1, \dots, N$) and moduli $(k_1, \mu_1), (k_2, \mu_2), \dots, (k_N, \mu_N)$, respectively. Our aim is to find the expressions of the mixture moduli in terms of the above quantities. We consider these assumptions on the statistical composition of the random heterogeneous material: we subdivide the whole medium in many smaller pieces having completely random shape and position; each of these parts is homogeneous and has moduli (k_j, μ_j) with probability c_j . The values of the moduli in a given little piece are statistically independent of the values assigned in the other pieces. This means, by using the law of large numbers, that the stoichiometric coefficient of the j th components is c_j . In other words, the density probability of the values of the elastic moduli in a given piece of material has the form $W(k, \mu) = \sum_{j=1}^N c_j \delta(k - k_j) \delta(\mu - \mu_j)$, where the k_j 's, the μ_j 's, and the c_j 's are the above defined quantities and $\delta(x)$ is the Dirac delta function: this means that the probability for (k, μ) to assume values in the set $(k, k + dk) \cup (\mu, \mu + d\mu)$ is exactly $W(k, \mu) dk d\mu$. These values are statistically independent for different parts of the whole material. This is the definition of the N -phase elastic random medium used to obtain the following results. Note that all the constituents have the same significance to define the whole heterogeneous material. It is only the volume fractions that are of concern.

Now, we are ready to consider a generic mixture with N different media. Each medium, in the generic mixture, has moduli k_i and μ_i and volume concentration c_i ($i = 1, \dots, N$); k and μ are the equivalent moduli of the mixture. If we add to the mixture a little volume dc with moduli k_j and μ_j , we create a new heterogeneous material formed by the original mixture (moduli k and μ) and a volume with moduli k_j and μ_j ; this new mixture can be analyzed considering it as a two-component one; therefore, its moduli, referred to as k'_j and μ'_j , are given by:

$$\begin{aligned} k'_j &= F\left(k, k_j, \mu, \mu_j, \frac{dc}{1+dc}\right) \cong F(k, k_j, \mu, \mu_j, dc) \\ \mu'_j &= G\left(k, k_j, \mu, \mu_j, \frac{dc}{1+dc}\right) \cong G(k, k_j, \mu, \mu_j, dc) \end{aligned} \quad (9)$$

This procedure is not new in principle, since it has been used, e.g., by Bruggemann [13] for little volumes of the medium added to the original mixture. Anyway, let us suppose that the procedure of adding a volume dc is made for each medium ($j = 1, 2, \dots, N$), giving a probability c_j to the case of moduli (k_j, μ_j) . The average moduli are clearly the very same k and μ of the original mixture, hence one may state that:

$$\begin{aligned} k &= \sum_{j=1}^N k'_j c_j = \sum_{j=1}^N F(k, k_j, \mu, \mu_j, dc) c_j \\ &= \sum_{j=1}^N \left[F(k, k_j, \mu, \mu_j, 0) + \frac{\partial F(k, k_j, \mu, \mu_j, c)}{\partial c} \Big|_{c=0} dc \right] c_j \\ \mu &= \sum_{j=1}^N \mu'_j c_j = \sum_{j=1}^N G(k, k_j, \mu, \mu_j, dc) c_j \\ &= \sum_{j=1}^N \left[G(k, k_j, \mu, \mu_j, 0) + \frac{\partial G(k, k_j, \mu, \mu_j, c)}{\partial c} \Big|_{c=0} dc \right] c_j \end{aligned} \quad (10)$$

By using the relations $F(k, k_j, \mu, \mu_j, 0) = k$, $G(k, k_j, \mu, \mu_j, 0) = \mu$, and $\sum_{j=1}^N c_j = 1$, we obtain, after some straightforward calculations:

$$\begin{aligned} \sum_{j=1}^N \frac{\partial F(k, k_j, \mu, \mu_j, c)}{\partial c} \Big|_{c=0} c_j &= 0 \\ \sum_{j=1}^N \frac{\partial G(k, k_j, \mu, \mu_j, c)}{\partial c} \Big|_{c=0} c_j &= 0 \end{aligned} \quad (11)$$

For three-dimensional random mixture we use Eq. (7) and we obtain:

$$\begin{aligned} \sum_{j=1}^N \frac{4\mu + 3k}{4\mu + 3k_j} (k_j - k) c_j &= 0 \\ \sum_{j=1}^N \frac{5\mu(4\mu + 3k)(\mu_j - \mu)}{\mu(9k + 8\mu) + 6\mu_j(k + 2\mu)} c_j &= 0 \end{aligned} \quad (12)$$

Similarly, for two-dimensional random mixtures, by using Eq. (8) we have:

$$\begin{aligned} \sum_{j=1}^N \frac{\mu + k}{\mu + k_j} (k_j - k) c_j &= 0 \\ \sum_{j=1}^N \frac{2\mu(\mu + k)(\mu_j - \mu)}{\mu(k + \mu_j) + \mu_j(k + \mu)} c_j &= 0 \end{aligned} \quad (13)$$

These results may be rearranged as follows for the three-dimensional case:

$$\begin{aligned} \frac{1}{3k + 4\mu} &= \sum_{j=1}^N \frac{c_j}{3k_j + 4\mu} \\ \frac{1}{5\mu(3k + 4\mu)} &= \sum_{j=1}^N \frac{c_j}{3k(2\mu_j + 3\mu) + 4\mu(2\mu + 3\mu_j)} \end{aligned} \quad (14)$$

For the two-dimensional case, we obtain:

$$\begin{aligned} \frac{1}{k + \mu} &= \sum_{j=1}^N \frac{c_j}{k_j + \mu} \\ \frac{1}{2\mu(k + \mu)} &= \sum_{j=1}^N \frac{c_j}{k(\mu_j + \mu) + 2\mu_j\mu} \end{aligned} \quad (15)$$

Equations (14) and (15) completely describe the elastic behavior of a random mixture and allow us a fast determination of the overall bulk and shear moduli of the overall structure. So, such expressions represent the explicit relation among the microscopic properties of the material and the macroscopic ones, which can be measured on a large region of medium. These are the main results of this work and, as we show in the following, they collect and unify many elastic relations that can be found in literature. Moreover, we may observe that each component intervenes in the same way, to define the whole structure of the formulas, exhibiting the complete symmetry among the constituents of the random medium. Finally, we may observe that Eqs. (14) and (15) are the elastic counterpart of the electrical relationships given by Eqs. (1) and (2). A particular case is given by the two-phase random medium: in such case we write down explicit expressions for three- and two-dimensional structures. By using Eq. (14), after some manipulations, we obtain, for three-dimensional two-phase mixtures, the equivalent shear modulus by means of the following fourth degree algebraic equation:

$$32\mu^4 + \alpha\mu^3 + \beta\mu^2 + \gamma\mu + \delta = 0$$

$$\alpha = 12ck_2 + 48\mu_2 + 36k_1 - 32\mu_1 - 12ck_1 - 80c\mu_2 + 80c\mu_1 + 24k_2$$

$$\begin{aligned} \beta &= 27k_1k_2 - 48\mu_1\mu_2 - 48c\mu_2k_1 + 72c\mu_1k_1 + 48\mu_1ck_2 - 72\mu_2ck_2 \\ &\quad - 36\mu_1k_1 + 24\mu_2k_1 + 36\mu_2k_2 - 24\mu_1k_2 \\ \gamma &= 18\mu_2k_1k_2 - 27\mu_1k_1k_2 - 24\mu_1\mu_2k_1 - 36\mu_1\mu_2k_2 - 12\mu_1\mu_2ck_1 \\ &\quad + 12\mu_1\mu_2ck_2 - 45c\mu_2k_1k_2 + 45c\mu_1k_1k_2 \\ \delta &= -18\mu_1\mu_2k_1k_2 \end{aligned} \quad (16)$$

Once the value of μ is computed, this relation directly gives the value of the equivalent bulk modulus k :

$$k = \frac{4\mu[(1-c)k_1 + ck_2] + 3k_1k_2}{3(1-c)k_2 + 3ck_1 + 4\mu} \quad (17)$$

In two-dimensional two-phase structures, Eq. (15) yields the following third degree algebraic equation for the equivalent shear modulus μ :

$$\begin{aligned} \alpha\mu^3 + \beta\mu^2 + \gamma\mu + \delta &= 0 \\ \alpha &= 2c\mu_2 - 2c\mu_1 - ck_2 - k_1 + ck_1 - 2\mu_2 \\ \beta &= -\mu_2k_1 - 2\mu_2k_2 + 3\mu_2ck_2 + \mu_1k_1 + c\mu_2k_1 - 3c\mu_1k_1 - k_1k_2 \\ &\quad + 2\mu_1\mu_2 - \mu_1ck_2 \\ \gamma &= -\mu_2k_1k_2 + \mu_1k_1k_2 + \mu_1\mu_2k_1 + 2c\mu_2k_1k_2 - 2c\mu_1k_1k_2 + 2\mu_1\mu_2k_2 \\ &\quad - \mu_1\mu_2ck_2 + \mu_1\mu_2ck_1 \\ \delta &= \mu_1\mu_2k_1k_2 \end{aligned} \quad (18)$$

Once again, the bulk modulus k is directly given by the following relationship:

$$k = \frac{\mu[(1-c)k_1 + ck_2] + k_1k_2}{\mu + (1-c)k_2 + ck_1} \quad (19)$$

In following sections we describe some comparison and agreement with various expressions, which appear in literature.

4 Equal Shear Modulus

When all constituents of an elastic composite have the same shear modulus μ , Hill [14,15] has shown that the effective modulus k , in three-dimensional structures, is given by the exact formula:

$$\frac{1}{3k + 4\mu} = \left\langle \frac{1}{3k(\mathbf{x}) + 4\mu} \right\rangle \quad (20)$$

where $\langle f(\mathbf{x}) \rangle$ represents the average value of the function $f(\mathbf{x})$ over the entire mixture volume. This result is true for any microstructure and may be also formulated for two-dimensional mixtures:

$$\frac{1}{k + \mu} = \left\langle \frac{1}{k(\mathbf{x}) + \mu} \right\rangle \quad (21)$$

This two-dimensional version of the theorem may be verified by means of the invariant properties of the stress in plane elasticity, which have been described by Cherkhaev-Lurie-Milton [16] and Milton [17].

Both these exact results, being independent on the microstructure, in particular, should be correct in the case of random mixtures. In effect, they are in complete agreement with the first expression in Eqs. (14) (three-dimensional problem) or Eq. (15) (two-dimensional problem). When we deal with two-phase mixtures the above relations became identical to Eqs. (17) and (19), where μ assumes the meaning of the common shear modulus.

5 Results Based on Duality for Planar Elasticity

The duality theory for incompressible planar elastic media discussed here is due to Berdichevski [18]. We consider an isotropic planar random elastic medium. It is incompressible at each point

(infinite bulk modulus) and it is formed by a mixture between two media with shear moduli μ_1 and μ_2 and infinite bulk modulus. The duality theorem can be stated as follows. We may write the effective shear modulus μ as a function $h(\mu_1, \mu_2)$ of the shear moduli of the phases and it exactly satisfies the phase interchange relation:

$$h(\mu_1, \mu_2)h(\mu_2, \mu_1) = \mu_1\mu_2 \quad (22)$$

In particular, if the composite is phase interchange invariant, i.e., $h(\mu_1, \mu_2) = h(\mu_2, \mu_1)$, like a two-dimensional checkerboard or like a two-phase two-dimensional equal fraction random mixture, then Eq. (22) implies the following formula of Lurie and Cherkhaev [19]:

$$\mu = \sqrt{\mu_1\mu_2} \quad (23)$$

By using the translation method [16,17] they generalized this result to two-dimensional structures composed of compressible media having the same bulk modulus and they found that the effective shear modulus μ of the mixture is given by:

$$\mu = \frac{k}{-1 + \sqrt{(k + \mu_1)(k + \mu_2)}/\mu_1\mu_2} \quad (24)$$

where k , μ_1 , and μ_2 are the common planar bulk and two shear moduli of the components. One can observe that Eq. (24), in the limiting case of $k \rightarrow \infty$, reduces to Eq. (23) as expected.

Now, we can simply show that our Eq. (15) yields the same results. To describe a phase interchange invariant structure we consider a two-phase two-dimensional random mixture with $c_1 = c_2 = 1/2$ and we suppose $k_1 = k_2 = k$. In these conditions the second relationship in Eq. (15) gives:

$$\frac{1}{2\mu(k + \mu)} = \frac{1/2}{k(\mu_1 + \mu) + 2\mu_1\mu} + \frac{1/2}{k(\mu_2 + \mu) + 2\mu_2\mu} \quad (25)$$

The positive solution of Eq. (25) is exactly given by Eq. (24). If we let $k \rightarrow \infty$, we simply obtain, after some straightforward calculations, Eq. (23). Therefore, we have shown that, also in this case, our theory yields results in agreement with those available in literature.

6 Porous Random Materials

The proposed approach may be applied to the elastic characterization of porous materials when the voids (zero stiffness inclusions) are randomly distributed and have random shape. From a general point of view we expect the equivalent Young's modulus E and the Poisson's ratio ν to depend on properties of the solid matrix E_1 and ν_1 . Therefore, the final mixing rules should appear as $E = E_1 f(c, \nu_1)$ and $\nu = g(c, \nu_1)$. Here c is the voids volume fraction (porosity) and the mathematical structure of the dimensionless functions f and g depend on the microstructure of the pores. For example, in Ref. [5] one can find the explicit solutions for randomly oriented ellipsoidal voids embedded in an isotropic matrix. Many theorems concerning this topic are well known and largely discussed in the literature. It is important to recall that, in two dimensions, the functions f and g satisfy two remarkable properties [20]. First, the Young's modulus is independent of ν_1 (Poisson's ratio of the solid matrix), i.e., $f(c, \nu_1) = f(c)$. Second, if the porosity c increases up to the percolation threshold c_0 , the effective Poisson's ratio converges to a fixed point independently on the solid Poisson's ratio, or $g(c, \nu_1) \rightarrow \nu_0$ as $c \rightarrow c_0$. Both results have been proved analytically in Refs. [16,21]. In the sequel we show that these two properties are exactly satisfied by the proposed approach for two-dimensional random porous materials.

In three-dimensional porous materials this behavior is not thought to hold rigorously. However, these results approximately hold also in three dimensions. In Refs. [5,22] it has been shown that although E cannot be independent on ν_1 in three dimensions, it is nearly so for materials with spheroidal voids over the range

$0 < \nu_1 < 1/2$. Moreover, in Ref. [5] it has been verified that the differential effective medium theory leads to a convergent behavior of the Poisson's ratio for a high volume fraction of randomly oriented generally shaped ellipsoidal voids, being the limiting value of the Poisson's ratio dependent only on the eccentricities of the embedded ellipsoidal voids. In the following we show the behavior of E and ν for a random three-dimensional porous material and we draw a comparison with experimental results.

We begin the analysis with two-dimensional random porous structures; so, Eqs. (18) and (19) are applied with a zero stiffness phase ($k_2=0$ and $\mu_2=0$). Equation (18) has two possible solutions, one equal to zero and another different from zero: since it is reasonable to assume that the shear modulus be a non-negative, continuous function of c , the true solution is given by the following relationship:

$$\mu = \begin{cases} \frac{\mu_1 k_1 (1-3c)}{k_1(1-c) + 2c\mu_1} & \text{if } c \leq \frac{1}{3} \\ 0 & \text{if } c > \frac{1}{3} \end{cases} \quad (26)$$

Therefore, for two-dimensional structure, we observe a percolation threshold given by $c_0=1/3$. Similarly, Eq. (19) allows us to find out the expression for the two-dimensional bulk modulus as follows:

$$k = \begin{cases} \frac{\mu_1 k_1 (1-3c)}{\mu_1(1-2c) + ck_1} & \text{if } c \leq \frac{1}{3} \\ 0 & \text{if } c > \frac{1}{3} \end{cases} \quad (27)$$

In order to obtain the behavior of the porous planar random medium in terms of the Young's modulus and the Poisson's ratio we recall the relationships among the two-dimensional elastic constants:

$$E = \frac{4k\mu}{\mu+k}; \quad \nu = \frac{k-\mu}{k+\mu} \Leftrightarrow \mu = \frac{E}{2(1+\nu)}; \quad k = \frac{E}{2(1-\nu)} \quad (28)$$

(we remember that the two-dimensional bulk modulus k is not the same as the customarily used three-dimensional bulk modulus and the relation between them is given in a previous section; this is coherent with Eq. (28)). So, applying Eq. (28) to Eqs. (26) and (27), we may write the following very simple formulas describing the equivalent elastic behavior of a planar random structure in terms of the elastic properties of the solid matrix and the volume fraction of the voids c (porosity):

$$E = \begin{cases} E_1(1-3c) & \text{if } c \leq \frac{1}{3} \\ 0 & \text{if } c > \frac{1}{3} \end{cases} \quad (29)$$

$$\nu = \begin{cases} c + \nu_1(1-3c) & \text{if } c \leq \frac{1}{3} \\ \frac{1}{3} & \text{if } c > \frac{1}{3} \end{cases} \quad (30)$$

These relations exactly exhibit the two general properties reported above for the functions f and g : the Young's modulus is independent on the solid Poisson's ratio and the equivalent Poisson's ratio

converges to the fixed point $\nu_0=1/3$ when $c \rightarrow c_0=1/3$. The value $c_0=1/3$ corresponds to the two-dimensional percolation threshold.

Now, we may analyze the three-dimensional case: we have to solve Eqs. (16) and (17) considering $k_2=0$ and $\mu_2=0$. The fourth degree algebraic equation for the equivalent shear modulus (Eq. (16)) has a double solution equal to zero and two different solutions of opposite sign. As before, assuming that the shear modulus is a non-negative, continuous function of the porosity, the correct solution is given by the following relationship:

$$\mu = \begin{cases} \frac{1}{4}\mu_1(2-5c) - \frac{3}{16}k_1(3-c) + \frac{1}{16}R & \text{if } c \leq \frac{1}{2} \\ 0 & \text{if } c > \frac{1}{2} \end{cases} \quad (31)$$

Here we have defined the quantity R as follows:

$$R = \sqrt{16\mu_1^2(2-5c)^2 + 24k_1\mu_1(2+c)(3-5c) + 9k_1^2(3-c)^2} \quad (32)$$

The bulk modulus, defined by Eq. (17), may be developed obtaining the final expression:

$$k = \begin{cases} k_1(1-c) \frac{4\mu_1(2-5c) - 3k_1(3-c) + R}{4\mu_1(2-5c) - 3k_1(3-5c) + R} & \text{if } c \leq \frac{1}{2} \\ 0 & \text{if } c > \frac{1}{2} \end{cases} \quad (33)$$

Finally, we are interested in the elastic behavior, described in terms of the Young's modulus and the Poisson's ratio; to this aim we take into account the relationships among the three-dimensional elastic constants:

$$E = \frac{9k\mu}{\mu+3k}; \quad \nu = \frac{3k-2\mu}{2(\mu+3k)} \Leftrightarrow \mu = \frac{E}{2(1+\nu)}; \quad k = \frac{E}{3(1-2\nu)} \quad (34)$$

By using Eq. (34), we may transform Eqs. (31) and (33) in the following ones:

$$E = \begin{cases} \frac{3E_1(1-c)1-9c+(21c-11)\nu_1+Q}{1-2\nu_117-21c+(5+9c)\nu_1+Q} & \text{if } c \leq \frac{1}{2} \\ 0 & \text{if } c > \frac{1}{2} \end{cases} \quad (35)$$

$$\nu = \begin{cases} \frac{7-3c+(19-33c)\nu_1-Q}{17-21c+(5+9c)\nu_1+Q} & \text{if } c \leq \frac{1}{2} \\ \frac{1}{5} & \text{if } c > \frac{1}{2} \end{cases} \quad (36)$$

where we have defined the quantity Q :

$$Q = \sqrt{\nu_1^2(441c^2 - 270c + 25) - 14\nu_1(9c - 5)(3c - 1) + (81c^2 - 114c + 49)} \quad (37)$$

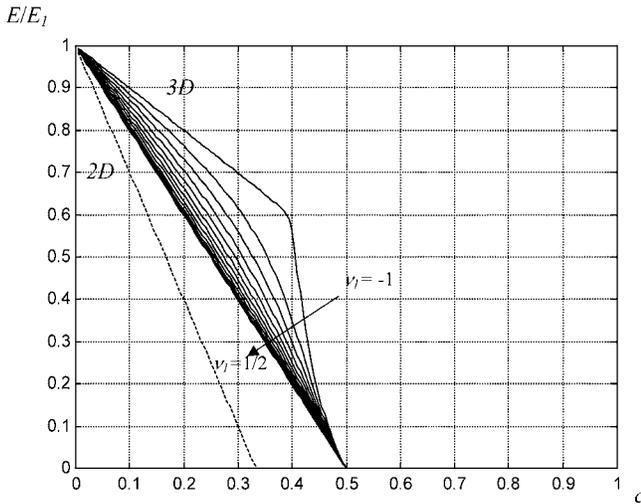


Fig. 1 Young's modulus for a random porous material versus the elastic moduli of the pure matrix and the porosity. Dashed line corresponds to the two-dimensional case, Eq. (29), continuous lines correspond to the three-dimensional case, Eq. (35). The two-dimensional result is independent on the matrix Poisson's ratio while the three-dimensional result is parameterized by the matrix Poisson's ratio (15 different values uniformly spaced ranging from -1 to $1/2$) but is practically independent on it in the range from 0 to $1/2$.

The Young's modulus exhibits a behavior analytically depending on the solid matrix Poisson's ratio; however, in the range $0 < \nu_1 < 1/2$ the values of the equivalent Young's modulus are quite independent of ν_1 . Moreover, this approach shows a convergent behavior of the equivalent Poisson's ratio to the value $\nu = 1/5$ when the porosity assumes the value $c_0 = 1/2$, which represents the three-dimensional percolation threshold. For instance, we observe that a similar convergence of the equivalent Poisson's ratio (to the value $1/5$) has been obtained by means of differential techniques for high concentration of spherical pores [5].

In Figs. 1 and 2 one can find the behavior of the Young's modulus and the Poisson's ratio for a random porous material, both in two- and three-dimensional cases.

Finally, we may draw a comparison with experimental data obtained on sintered glass beads [23]. The bulk and shear moduli of pure glass were $k_1 = 46.06$ GPa and $\mu_1 = 29.24$ GPa. These values correspond to the Young's modulus $E_1 = 72,39$ GPa and to the Poisson's ratio $\nu_1 = 0.23$. Bulk modulus was measured for porosity ranging from 0 to 0.43 [22]. In Fig. 3 a comparison between experimental data and values obtained by means of Eq. (33) (three-dimensional case) is shown. We note that for sintered glass-bead samples the model based on the completely random porous microstructure predicts well the elastic behavior. In Refs. [5,22] it is shown that for porous glass foam the better model is the differential one. Probably, this happens because of the different microstructure that characterizes sintered glass and glass foam: the former contains a completely random structure of the pores due to the sintering process; the latter is a sort of dispersion of spheroidal voids, eventually overlapping. So, this is a good example of different microstructures captured by different theoretical approaches for evaluating the corresponding elastic properties.

The ceramic materials give some other examples of porous materials that are well described by the present theory. In this field one of the most common procedures is sintering. During sintering a ceramic material is heated in a furnace or ovenlike device, where it is exposed to high temperatures. The sintering process has been used to produce ceramics with different porosity and the corresponding elasticity modulus has been measured in many different cases [24–26]. We draw a comparison between four types

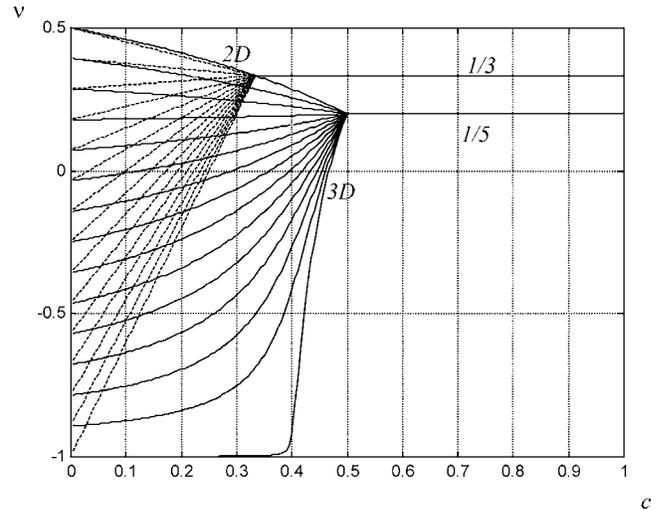


Fig. 2 Poisson's ratio for a random porous material versus matrix Poisson's ratio and porosity. Dashed lines correspond to the two-dimensional case, Eq. (30), continuous lines correspond to the three-dimensional case, Eq. (36). In both cases 15 different values of the matrix Poisson's ratio are considered ranging from -1 to $1/2$. The intercepts of the lines at zero porosity ($c=0$) correspond to the solid matrix Poisson's ratio. Note the convergence of the equivalent Poisson's ratio for $c = 1/3$ to the value $\nu = 1/3$ (2D) and for $c = 1/2$ to the value $\nu = 1/5$ (3D).

of ceramic oxides and the theory here outlined. In Fig. 4(a) the properties of holmium oxide, Ho_2O_3 (holmia, [24], diamonds in figure), and that of ytterbium oxide, Yb_2O_3 (ytterbia, [25], plus in figure), are represented. Moreover, in Fig. 4(b) the properties of yttrium oxide, Y_2O_3 (yttria, [24], triangles in figure), and that of samarium oxide, Sm_2O_3 (samaria, [26], circles in figure), are reported. The plots correspond to the values of the Young's modulus measured and calculated by means of the theory. A good agreement is quite evident.

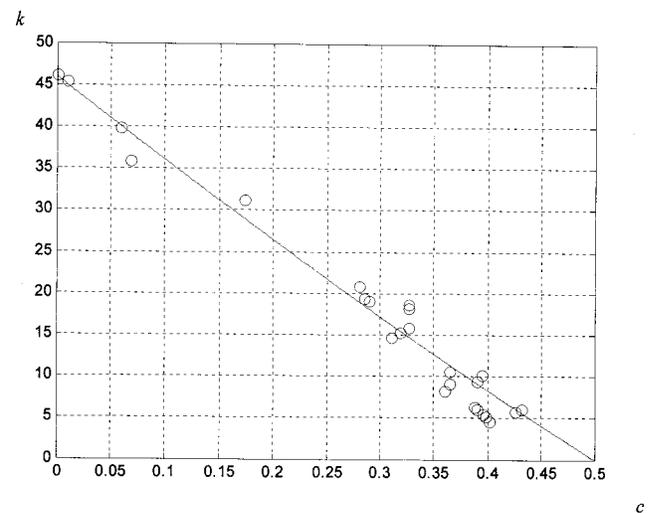


Fig. 3 Bulk modulus k in GPa of sintered glass (circles), measured (see Ref. [22]) for different values of the porosity c , compared with data obtained by Eq. (33) (solid line). Bulk and shear moduli of the pure glass were measured to be $k_1 = 46.06$ GPa and $\mu_1 = 29.24$ GPa.

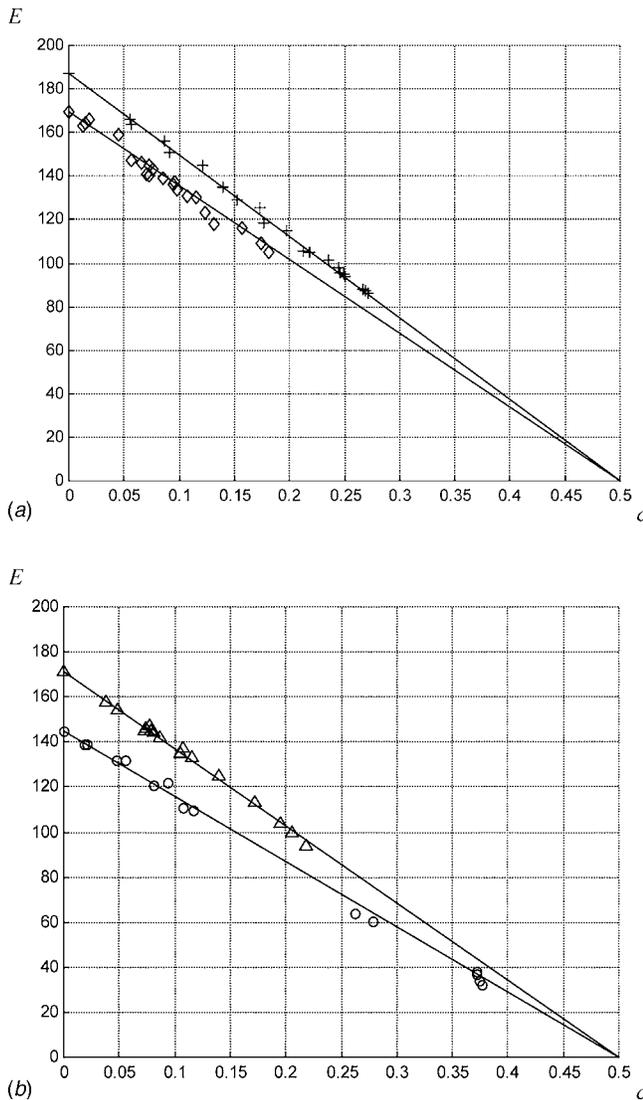


Fig. 4 Young's modulus of different ceramic oxides. In (a) the properties of holmium oxide, Ho_2O_3 (holmia, [23], diamonds), and those of ytterbium oxide, Yb_2O_3 (ytterbia, [24], plus), are represented. Moreover, in (b) the properties of yttrium oxide, Y_2O_3 (yttria, [23], triangles), and those of samarium oxide, Sm_2O_3 (samaria, [25], circles), are reported.

Small Contrast of Properties

When the difference between the properties of a two-phase material is small, some approximate relations may be useful to capture the effective behavior of heterogeneous materials. For example, a power series expansion in terms of this difference can be adopted to quantify the effective properties of a given composite materials. One of the first attempts to analyze heterogeneous materials from this point of view has been made by Brown [27]. He has verified a property for the electric conductivity of composite materials, which is true for general two-phase isotropic microstructures. We define the dimensionless quantities:

$$\eta = \frac{\sigma_2 - \sigma_1}{\sigma_1}, \quad x = \frac{\sigma}{\sigma_1} \quad (38)$$

Here σ_1 and σ_2 are the conductivities of the two phases and σ is the effective conductivity of the whole material. The result of Brown is given by the following expansion for the three-dimensional case:

$$x = 1 + c\eta - \frac{c(1-c)}{3}\eta^2 + O(\eta^3) \quad (39)$$

and by the following one for the two-dimensional case:

$$x = 1 + c\eta - \frac{c(1-c)}{2}\eta^2 + O(\eta^3) \quad (40)$$

It has been verified [27] that the coefficients for the $O(\eta^3)$ and higher order terms involve details of the microstructure and are given in terms of various correlation functions over the phase geometry. We make a comparison between these results and ours. The effective conductivity in two-phase random three-dimensional mixtures, as reported in Eq. (1), may be written in terms of the dimensionless variables defined in Eq. (38):

$$\frac{1}{3x} = \frac{1-c}{1+2x} + \frac{c}{1+\eta+2x} \quad (41)$$

The solution may be developed in series of the variable η , obtaining:

$$x = 1 + c\eta - \frac{c(1-c)}{3}\eta^2 + \frac{c(1-c^2)}{9}\eta^3 - \frac{c(1-c)(1+4c-c^2)}{27}\eta^4 + \frac{c(1-c^2)(1+8c-5c^2)}{81}\eta^5 + \dots \quad (42)$$

Similarly, in two-phase random two-dimensional mixtures, as reported in Eq. (2), we have:

$$\frac{1}{2x} = \frac{1-c}{1+x} + \frac{c}{1+\eta+x} \quad (43)$$

The series solution is the following:

$$x = 1 + c\eta - \frac{c(1-c)}{2}\eta^2 + \frac{c(1-c)}{4}\eta^3 - \frac{c(1-c)(1+c-c^2)}{8}\eta^4 + \frac{c(1-c)(1+3c-3c^2)}{16}\eta^5 + \dots \quad (44)$$

The expansions given in Eqs. (42) and (44) have the first and second order terms in perfect agreement with the results of Brown given in Eqs. (39) and (40). These terms are independent of the micro-geometry of the mixture. The higher order terms depend on the microstructure of the composite material, i.e., on the correlation functions over the phase geometry. It is interesting to observe that the ones appearing in Eqs. (42) and (44) are typical for random electric microstructure and thus they contain all the characteristic features of this kind of heterogeneous medium (percolative behavior, percolation threshold, and so on).

The same procedure can be carried out for the elastic moduli. A simple way to derive the elastic counterpart of the Brown expansion, at least up to second order in the modulus contrasts, is to take Hashin's bounds [1], which bound the effective properties between an upper and lower limit, and expand them to second order in the modulus differences. These bounds are known to be exact to second order in the modulus differences, and in fact the upper and lower bounds agree exactly to this order. We may define the difference of the elastic moduli as $\Delta k = k_2 - k_1$ and $\Delta\mu = \mu_2 - \mu_1$. This procedure leads to the following results in three-dimensional elasticity:

$$k = k_1 + c\Delta k - \frac{3c(1-c)}{3k_1 + 4\mu_1}\Delta k^2 + O(\Delta k^3)$$

$$\mu = \mu_1 + c\Delta\mu - \frac{6c(1-c)(k_1 + 2\mu_1)}{5\mu_1(3k_1 + 4\mu_1)}\Delta\mu^2 + O(\Delta\mu^3) \quad (45)$$

and to the following ones in two-dimensional elasticity:

$$k = k_1 + c\Delta k - \frac{c(1-c)}{k_1 + \mu_1}\Delta k^2 + O(\Delta k^3)$$

$$\mu = \mu_1 + c\Delta\mu - \frac{c(1-c)(k_1 + 2\mu_1)}{2\mu_1(k_1 + \mu_1)}\Delta\mu^2 + O(\Delta\mu^3) \quad (46)$$

As before, the third order coefficients and higher order terms involve details of the microstructure. Now, we may draw a comparison between Eqs. (45) and (46) and the random model described in this paper. Therefore, from Eq. (14) we may write the following equations for the two-phase three-dimensional case:

$$\begin{aligned} \frac{1}{3k + 4\mu} &= \frac{1-c}{3k_1 + 4\mu_1} + \frac{c}{3k_1 + 3\Delta k + 4\mu} \\ \frac{1}{5\mu(3k + 4\mu)} &= \frac{1-c}{3k(2\mu_1 + 3\mu) + 4\mu(2\mu + 3\mu_1)} \\ &+ \frac{c}{3k(2\mu_1 + 2\Delta\mu + 3\mu) + 4\mu(2\mu + 3\mu_1 + 3\Delta\mu)} \end{aligned} \quad (47)$$

After a very long but straightforward calculation, the series solutions in the differences Δk and $\Delta\mu$ have been computed as follows:

$$\begin{aligned} k &= k_1 + c\Delta k - \frac{3c(1-c)}{3k_1 + 4\mu_1}\Delta k^2 + \frac{12c^2(1-c)}{(3k_1 + 4\mu_1)^2}\Delta k^2\Delta\mu \\ &- \frac{24c^2(1-c)[3k_1(1-c) + 2\mu_1(2c + 3)]}{5\mu_1(3k_1 + 4\mu_1)^3}\Delta k^2\Delta\mu^2 + \dots \\ \mu &= \mu_1 + c\Delta\mu - \frac{6c(1-c)(k_1 + 2\mu_1)}{5\mu_1(3k_1 + 4\mu_1)}\Delta\mu^2 + \frac{12c^2(1-c)}{5(3k_1 + 4\mu_1)^2}\Delta k\Delta\mu^2 \\ &- \frac{36c^2(1-c)}{5(3k_1 + 4\mu_1)^3}\Delta k^2\Delta\mu^2 + \dots \end{aligned} \quad (48)$$

In two-dimensional mixture, the main equations are derived from Eq. (15):

$$\begin{aligned} \frac{1}{k + \mu} &= \frac{1-c}{k_1 + \mu_1} + \frac{c}{k_1 + \Delta k + \mu} \\ \frac{1}{2\mu(k + \mu)} &= \frac{1-c}{k(\mu_1 + \mu) + 2\mu_1\mu} + \frac{c}{k(\mu_1 + \Delta\mu + \mu) + 2(\mu_1 + \Delta\mu)\mu} \end{aligned} \quad (49)$$

As before the expansions are given by:

$$\begin{aligned} k &= k_1 + c\Delta k - \frac{c(1-c)}{k_1 + \mu_1}\Delta k^2 + \frac{c^2(1-c)}{(k_1 + \mu_1)^2}\Delta k^2\Delta\mu \\ &- \frac{c^2(1-c)[k_1(1-c) + 2\mu_1]}{2\mu_1(k_1 + \mu_1)^3}\Delta k^2\Delta\mu^2 + \dots \\ \mu &= \mu_1 + c\Delta\mu - \frac{c(1-c)(k_1 + 2\mu_1)}{2\mu_1(k_1 + \mu_1)}\Delta\mu^2 + \frac{c^2(1-c)}{2(k_1 + \mu_1)^2}\Delta k\Delta\mu^2 \\ &- \frac{c^2(1-c)}{2(k_1 + \mu_1)^3}\Delta k^2\Delta\mu^2 + \dots \end{aligned} \quad (50)$$

In Eqs. (48) and (50) the first and second order terms are the same that one can obtain from the Hashin's bounds (see Eq. (45) and (46)). They are independent of the geometry of the mixture. Just as in the electric case, the coefficients of higher order terms involve details of the microstructure and are given in terms of various correlation functions over the phase geometry [28]. The present study has been conducted to obtain the explicit expressions of the high terms, which are representative for the given microstructure. The high order terms appearing in Eqs. (48) and (50) are typical for a completely random elastic microstructure and therefore they contain all the peculiar characteristics of this composite material.

Conclusions

The present work describes the derivation of a theory, which characterizes linear random mixtures from the elastic point of view. The term "random mixture" represents a particular class of microstructures, which often appears in heterogeneous materials. It means that the whole medium is subdivided in many very small pieces, and each of this part is homogeneous and has given elastic moduli with a given probability (stoichiometric coefficient). The values of the moduli in a given little piece are statistically independent of the values assigned in the other pieces and each part of the material has random shape and position inside the whole structure. The results are concerned with the relation between the microscopic properties of the mixture (elastic response of the components and microstructure) and the macroscopic mechanical behavior of the overall composite material. The proposed solutions for the effective elastic moduli of the overall heterogeneous medium are in complete agreement with various properties well established in scientific literature. When all the phases composing the mixture have the same shear modulus the exact solution obtained by Hill leads to the same results obtained with our approach. In planar elasticity the duality theorem and the translation theorem lead to conclusions in perfect agreement with our mixing laws. The analysis of random porous materials reveals a good agreement with experimental data based on sintered glass and ceramics. Finally, the well-known expansions used when we are dealing with a small contrast of the properties are in perfect agreement with those obtained in the present work.

References

- [1] Hashin, Z., 1983, "Analysis of Composite Materials—A Survey," *ASME J. Appl. Mech.*, **50**, pp. 481–505.
- [2] Walpole, L. J., 1981, "Elastic Behaviour of Composite Materials: Theoretical Foundations," *Adv. Appl. Mech.*, **11**, pp. 169–242.
- [3] Douglas, J. F., and Garboczi, E. J., 1995, "Intrinsic Viscosity and Polarizability of Particles Having a Wide Range of Shapes," *Adv. Chem. Phys.*, **91**, pp. 85–153.
- [4] McLaughlin, R., 1977, "A Study of the Differential Scheme for Composite Materials," *Int. J. Eng. Sci.*, **15**, pp. 237–244.
- [5] Giordano, S., 2003, "Differential Schemes for the Elastic Characterisation of Dispersions of Randomly Oriented Ellipsoids," *Eur. J. Mech. A/Solids*, **22**, pp. 885–902.
- [6] Giordano, S., 2003, "Effective Medium Theory for Dispersions of Dielectric Ellipsoids," *J. Electrostat.*, **58**(1–2), pp. 59–76.
- [7] Kachanov, M., and Sevostianov, I., 2005, "On Quantitative Characterization of Microstructures and Effective Properties," *Int. J. Solids Struct.*, **42**, pp. 309–336.
- [8] Bianco, B., and Giordano, S., 2003, "Electrical Characterisation of Linear and Non-linear Random Networks and Mixtures," *Int. J. Circuit Theory Appl.*, **31**(2), pp. 199–218.
- [9] Atkin, R. J., and Fox, N., 1990, *An Introduction to the Theory of Elasticity*, Longman, London.
- [10] Eshelby, J. D., 1957, "The Determination of the Elastic Field of an Ellipsoidal Inclusion and Related Problems," *Proc. R. Soc. London, Ser. A*, **241**, pp. 376–396.
- [11] Eshelby, J. D., 1959, "The Elastic Field Outside an Ellipsoidal Inclusion," *Proc. R. Soc. London, Ser. A*, **252**, pp. 561–569.
- [12] Snyder, K. A., Garboczi, E. J., and Day, A. R., 1992, "The Elastic Moduli of Simple Two-Dimensional Isotropic Composites: Computer Simulation and Effective Medium Theory," *J. Appl. Phys.*, **72**, pp. 5948–5955.
- [13] Bruggeman, D. A. G., 1935, "Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen," *Ann. Phys.*, **24**, pp. 636–664.
- [14] Hill, R., 1963, "Elastic Properties of Reinforced Solids: Some Theoretical Principles," *J. Mech. Phys. Solids*, **11**, pp. 357–372.
- [15] Hill, R., 1964, "Theory of Mechanical Properties of Fibre-Strengthened Materials: I Elastic Behaviour," *J. Mech. Phys. Solids*, **12**, pp. 199–212.
- [16] Cherkav, A. V., Lurie, K. A., and Milton, G. W., 1992, "Invariant Properties of the Stress in Plane Elasticity and Equivalence Classes of Composites," *Proc. R. Soc. London, Ser. A*, **438**, pp. 519–529.
- [17] Milton, G. W., 1990, "On Characterising the Set of Possible Effective Tensors of Composites: The Variational Method- and the Translation Method," *Commun. Pure Appl. Math.*, **43**, pp. 63–125.
- [18] Berdichevski, V. L., 1983, *Variational Principles in Mechanics of Continuum Media*, Nauka, Moscow.
- [19] Lurie, K. A., and Cherkav, A. V., 1984, "G-closure of Some Particular Sets of Admissible Material Characteristics for the Problem of Bending of the Thin Elastic Plates," *J. Optim. Theory Appl.*, **42**(2), pp. 305–316.
- [20] Day, A. R., Snyder, K. A., Garboczi, E. J., and Thorpe, M. F., 1992, "The Elastic Moduli of Sheet Containing Spherical Holes," *J. Mech. Phys. Solids*,

- 40**, pp. 1031–1051.
- [21] Thorpe, M. F., and Jasiuk, I., 1992, “New Results in the Theory of Elasticity for Two-Dimensional Composites,” *Proc. R. Soc. London, Ser. A*, **438**, pp. 531–544.
- [22] Christensen, R. M., 1993, “Effective Properties of Composite Materials Containing Voids,” *Proc. R. Soc. London, Ser. A*, **440**, pp. 461–473.
- [23] Berge, P. A., Bonner, B. P., and Berryman, J. G., 1995, “Ultrasonic Velocity-Porosity Relationships for Sandstone Analogs Made From Fused Glass Beads,” *Geophysics*, **60**, pp. 108–119.
- [24] Manning, W. R., Hunter, O., Jr., and Powell, B. R., Jr., 1969, “Elastic Properties of Polycrystalline Yttrium Oxide, Dysprosium Oxide, Holmium Oxide, and Erbium Oxide: Room Temperature Measurements,” *J. Am. Ceram. Soc.*, **52**(8), pp. 436–442.
- [25] Powell, B. R., Jr., Hunter, O., Jr., and Manning, W. R., 1971, “Elastic Properties of Polycrystalline Ytterbium Oxide,” *J. Am. Ceram. Soc.*, **54**(10), pp. 488–490.
- [26] Hunter, O., Korklan, H. J., and Suchomel, R. R., 1974, “Elastic Properties of Polycrystalline Monoclinic Sm_2O_3 ,” *J. Am. Ceram. Soc.*, **57**(6), pp. 267–268.
- [27] Brown, W. F., 1955, “Solid Mixture Permittivities,” *J. Chem. Phys.*, **23**, pp. 1514–1517.
- [28] Torquato, S., 1997, “Effective Stiffness Tensor of Composite Media—I. Exact Series Expansions,” *J. Mech. Phys. Solids*, **45**, pp. 1421–1448.