Influence of interfaces on effective properties of nanomaterials with stochastically distributed spherical inclusions

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The method of conditional moments is generalized to include evaluation of the effective elastic properties of particulate nanomaterials and to investigate the size effect in those materials. Determining the effective constants necessitates finding a stochastically averaged solution to the fundamental equations of linear elasticity coupled with surface/interface conditions (Gurtin–Murdoch model). To obtain such a solution the system of governing stochastic differential equations is first transformed to an equivalent system of stochastic integral equations. Using statistical averaging, the boundary-value problem is then converted to an infinite system of linear algebraic equations. A two-point approximation is considered and the stress fluctuations within the inclusions are neglected in order to obtain a finite system of algebraic equations in terms of component-average strains. Closed-form expressions are derived for the effective moduli of a composite consisting of a matrix and randomly distributed spherical inhomogeneities. As a numerical example a nanoporous material is investigated assuming a model in which the interface effects influence only the bulk modulus of the material. In that model the resulting shear modulus is the same as for the material without surface effects. Dependence of the bulk moduli on the radius of nanopores and on the pore volume fraction is analyzed. The results are compared to, and discussed in the context of other theoretical predictions.

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1. Introduction

Surface residual stresses at the interface between matrix and inclusions have a significant effect on the effective properties of particulate nanomaterials, wherein the size of the nanoparticles (nanoinhomogeneities) is at the atomic scale. Various approaches can be adopted to quantify that effect. Studies of the size dependent behavior of particulate nanomaterials can be conducted by direct atomistic computer simulation (see, e.g., Garg and Sinnott, 1998; Garg et al., 1998; Robertson et al., 1992). Miller and Shenoy (2000) developed a continuum model which accounts for surface elasticity to describe the size dependence of the elastic rigidities of nanosized structural elements. Further, they presented the bulk and surface elastic properties of aluminum and silica, calculated from empirical atomistic potentials.

The model of elastic surfaces developed by Gurtin and Murdoch (1975, 1978) and Gurtin et al. (1998) is employed in many recent publications on nanocomposites (see, e.g., Gurtin and Voorhees, 1993; Kienzler and Herrmann, 2000; Maugin, 1993, 1995; Steinmann, 2002, 2008). The Gurtin–Murdoch model introduces the size-dependence of the overall properties of nanocomposite materials through the inclusion of residual surface stresses and the additional elastic properties at the interface between the matrix and the inhomogeneities. The influence of the resulting interface stress jump is extremely small if the inhomogeneities are sufficiently large (and, therefore, are neglected in classical mechanical analyses of composites). However, it becomes significant if the curvature radii of the inhomogeneities are in the range of nanometers (below 50 nm). By using Gurtin and Murdoch’s theory, several authors modified the known deterministic micromechanical models and introduced the surface elasticity and/or surface tension into relationships for homogenized effective properties of nanocomposites (McBride et al., 2011, 2012; Mitrushchenkov et al., 2010, among others).

Although the Gurtin–Murdoch surface model has been proposed almost 40 years ago, the 3D theory addressing the problem of the effective properties of the particulate nanocomposites with Gurtin–Murdoch interfaces is still not sufficiently well developed and analyzed. The approximate approaches used for evaluating effective elastic moduli of particulate nanocomposites with Gurtin–Murdoch interface include the “dilute”, or non-interacting, model (Yang, 2004) and various self-consistent schemes (see Chen...
et al., 2007; Duan et al., 2005c, 2007, among others). The variational bounds on the bulk modulus of a nanocomposite with spherical inhomogeneities and interface effects have been obtained by Brisard et al. (2010). Most of those publications use a “single inhomogeneity in an unbounded solid” model (see Cahn and Larché, 1982; Duan et al., 2005a-b; He and Li, 2006; Lim et al., 2006; Sharma and Ganti, 2004). Consequently, these results are only justified for composites with a low content of dispersed phase particles. In addition, all of these papers surface tension is neglected.

Recently, Kushch et al. (2011) have developed an approach based on multipole expansion and obtained a solution of the elasticity problem for an infinite space containing multiple interacting spherical inhomogeneities with the complete Gurtin and Murdoch interface model. This approach can be regarded as the micromechanical, finite cluster model of nanocomposites. The analogous finite cluster model was developed and used by Mogilevskaya et al. (2008, 2010a,b) to study the effects of surface elasticity and surface tension on the overall transverse elastic behavior of unidirectional fiber-reinforced nanocomposites. The representative unit cell model of nanocomposites is developed further by Kushch et al. (2013). To obtain a complete solution of the problem, the theory of periodic multipoles has been modified and adapted. In the approach the displacement vector within the matrix domain is written as a superposition of vector periodic solutions of the Lamé equation. Some of the particulate nanocomposites considered in those publications had a random (or quasi-random) structure. Independent of that structure, however, if the effective properties are of interest in those contributions, the elastic fields in the entire domain (matrix and inhomogeneities) are found first. Subsequently, either averaging of the obtained strain and stress fields or the equivalent inhomogeneity approach (in which the local elastic fields were also used) was employed to find the overall properties of the material.

In all of the above publications analysis of nanocomposites with randomly distributed particles (or fibers) was essentially based on deterministic calculations of just one, or more, realizations of particle distribution. Such approaches are valid, in particular if the results obtained from analyses of many specific realizations of particle distribution were evaluated statistically. However, a computational approach to the problem does not really permit to easily discern how various parameters of the problem affect the overall mechanical properties of the nanomaterial at hand. That requires a significant post processing effort and parametric studies leading to multiple diagrams and charts, but even with those diagrams the functional dependence of the effective properties on the data of the problem is elusive.

In the current work random particulate nanocomposites are considered. The statistical approach employed is different than the existing techniques presented in the literature on that subject. To this end, the method of conditional moments will be generalized to cover the case of particulate nanomaterials. The method of conditional moments proposed by Khoroshun (1978) and further developed by Khoroshun and Nazarenko (1992), Khoroshun et al. (1993) and Nazarenko et al. (2008), is a statistical method dealing with constructing the statistically averaged solution and determining the effective properties of composites with a stochastic structure. If the structure is stochastic, one can use the ergodicity property and determine the overall properties of the material without having to find any local fields in the composite. Instead of finding the effective properties through macro-volume averaging of the local elastic fields, the solution process begins by statistical averaging of the governing equations themselves at one micro-point. By eliminating the need to find the local elastic fields the present approach considerably simplifies the formulation and the solution of the problem. Still, the approach captures a very significant amount of information about the nanocomposite, including information about the shape and orientation of nanoparticles (anisotropy) and interaction between them. In some cases (including the example considered in this work), the approach presented here gives a possibility to obtain closed-form expressions for the effective properties of a material with Gurtin–Murdoch interface conditions.

In this work the problem of an infinite solid subjected to a uniform loading (at infinity) and containing stochastically distributed interacting spherical nanoinhomogeneities with interface residual stress and elasticity is solved by method of conditional moments. This approach is applied to the boundary value problem and, in general, leads to an infinite system of linear algebraic equations. As in most mathematical formulations of problems leading to infinite system of equations, if one solves such a system, the result constitutes the exact solution of the problem. In practice such infinite systems have to be truncated, which introduces a certain amount of approximation dependent on the degree of that truncation. In the current contribution, the finite system of equations is obtained by employing a two-point approximation and by neglecting the stress fluctuations within inclusions. The unknowns in that system are the statistical component-average strains. As a numerical example a nanoporous material is investigated assuming that influence of the interface effects on the effective bulk modulus of the composite is of only interest. Within the framework of such a model the resulting shear modulus is the same as for the material without surface effects. The dependence of the bulk moduli on the radius of nanopores (for certain fixed pore volume fractions) and on the pore volume fraction (for certain fixed radius of nanopores) are analyzed.

2. The classical problem of effective constants

2.1. Basic classical relations for a micro-point

We consider a representative macro-volume \( V \) consisting of a matrix with randomly distributed inclusions. For linear-elastic materials the problem is described by the following set of equations:

- equations of equilibrium:
  \[ \text{div}\sigma(\mathbf{x}) = 0. \]  \( (2.1) \)

- Hooke’s law:
  \[ \sigma(\mathbf{x}) = C(\mathbf{x}) : \varepsilon(\mathbf{x}), \]  \( (2.2) \)

- linear kinematic relation:
  \[ \varepsilon(\mathbf{x}) = \text{sym}(\nabla \mathbf{u}(\mathbf{x})). \]  \( (2.3) \)

where the fourth-order tensor of elastic constants \( C(\mathbf{x}) \) is a random, statistically homogeneous function of coordinates with a finite scale of correlation and linked to the inclusion and to the matrix properties as follows:

\[ C(\mathbf{x}) = C_1 H(z(\mathbf{x})) + C_2 H(-z(\mathbf{x})). \]  \( (2.4) \)

Here, \( H \) is the Heaviside function and \( C_1 \) and \( C_2 \) denote the values of the tensors of elastic moduli in the inclusions and in the matrix, respectively. The function \( z(\mathbf{x}) \) is defined as follows:

\[ z(\mathbf{x}) > 0, \quad \text{if} \quad \mathbf{x} \in V_1, \]  \( (2.5) \)

\[ z(\mathbf{x}) < 0, \quad \text{if} \quad \mathbf{x} \in V_2, \]  \( (2.6) \)

where \( V_1 \) and \( V_2 \) are the domains of the inclusions and the matrix, respectively.

Insertion of Eqs. (2.2) and (2.3) into Eq. (2.1) yields

\[ \text{div}(C(\mathbf{x}) : \text{sym}(\nabla \mathbf{u}(\mathbf{x})) = 0. \]  \( (2.6) \)
It is customary to decompose the random fields $\mathbf{C}(\mathbf{x})$ and $\mathbf{u}(\mathbf{x})$ into fluctuations, marked by the superscript "0", and averages:

$$\mathbf{C}(\mathbf{x}) = \mathbf{C}^0(\mathbf{x}) + \mathbf{C}_i, \quad \mathbf{u}(\mathbf{x}) = \mathbf{u}^0(\mathbf{x}) + \mathbf{z} \cdot \mathbf{x}. \quad (2.7)$$

The tensor $\mathbf{C}_i$ can be represented by constant components as follows:

$$\mathbf{C}_i = \begin{cases} \mathbf{C} & \text{if } C_i \leq C_2 \\ \mathbf{C} & \text{if } C_i \geq C_1 \end{cases} \quad (2.8)$$

with $\mathbf{C} = c_1 \mathbf{C}_1 + c_2 \mathbf{C}_2$ and $\mathbf{C}_i = (c_1 \mathbf{C}_1)^{-1} + c_2 (\mathbf{C}_2)^{-1}$, where $c_1$ and $c_2 = 1 - c_1$ denote the volume fractions of the inclusions and of the matrix, respectively, i.e., $c_1 = V_1/(V_1 + V_2)$. Although $\mathbf{C}_i$ can be chosen in a number of different ways (and each choice may lead to a different result), it has been shown in the existing literature (see Khoroshun 1978; Khoroshun et al., 1993, where the present and other choices for $\mathbf{C}_i$ have been discussed) that the definition of $\mathbf{C}_i$ specified in Eq. (2.8) is, in a sense, beneficial. Upon inserting the Eq. (2.7) into (2.6), Eq. (2.6) can be rewritten in the following equivalent form:

$$\text{div} (\mathbf{C}_i : \text{sym} (\nabla \mathbf{u}^0(\mathbf{x}))) + \text{div} (\mathbf{C}^0(\mathbf{x}) : \mathbf{e}(\mathbf{x})) = 0. \quad (2.9)$$

In the equation above, the first term only contains one random function (it is linear from the point of view of stochastic analysis), whereas the second contains a product of two random functions (stochastically nonlinear). This split is of importance in the subsequent conversion of the stochastic differential Eq. (2.9) into a stochastic integral equation.

The boundary conditions on the surface of the macro-volume are

$$\mathbf{u}^0(\mathbf{x})|_S = 0. \quad (2.10)$$

The characteristic dimensions of the macro-volumes and macro-surfaces must be significantly larger than those of the inclusions. Therefore, in the subsequent development we will consider them as infinite and the boundary conditions will take the form:

$$\mathbf{u}^0(\mathbf{x})|_{\infty} = 0. \quad (2.11)$$

It is noted that as the macro-volumes increase, the concentrations are kept constant as are the average distances between the inclusions. Thus, with the increase of those volumes the number of the inhomogeneities also increases and the structure of the material remains unchanged.

By using Gauss’s function, the solution of the system of differential equations (2.9) can be rewritten in terms of an integral over the infinite region $V$ (see Khoroshun 1978; Willis 1977):

$$\mathbf{u}^0(\mathbf{x}) = \int_{V} \mathbf{G}(\mathbf{x} - \mathbf{y}) \cdot \text{div} (\mathbf{C}^0(\mathbf{y}) : \mathbf{e}(\mathbf{y})) dV_y$$

$$= \int_V \mathbf{C}(\mathbf{x} - \mathbf{y}) \cdot \text{div} (\mathbf{C}^0(\mathbf{y}) : \mathbf{e}(\mathbf{y}) - \beta \mathbf{y}) dV_y, \quad (2.12)$$

where $\beta$ is an arbitrary constant, and the Green’s function $\mathbf{G}(\mathbf{x})$ satisfies the following equation:

$$\text{div} (\mathbf{C}_i : \nabla \mathbf{G}(\mathbf{x})) + \mathbf{e}(\mathbf{x}) \cdot \mathbf{I} = 0, \quad \mathbf{G}(\mathbf{x})|_{\infty} = 0. \quad (2.13)$$

Here, $\delta(\mathbf{x})$ denotes the Dirac delta function and $\mathbf{I}$ is the identity tensor of second rank in the three-dimensional space. Taking into account the linear kinematic relations (2.3) as well as Eq. (2.12) and applying Gauss’ theorem leads to the following non-linear stochastic integral equations (i.e., integral equations that contain a product of stochastic functions of coordinates) for the random strain field:

$$\mathbf{e}(\mathbf{x}) = \mathbf{z} + \mathbf{K}(\mathbf{x} - \mathbf{y}) \ast (\mathbf{C}^0(\mathbf{y}) : \mathbf{e}(\mathbf{y})). \quad (2.14)$$

Formally, this is a Fredholm equation of the second kind, also referred to as Lippmann–Schwinger equation (see Kröner, 1977). In the equation above, the integral operator $\mathbf{K}(\mathbf{x} - \mathbf{y})$ is the integral operator, involving Green’s function defined by Eq. (2.13) and associated with an elastic body with a constant elastic-moduli tensor $\mathbf{C}_i$ (Khoroshun 1978; Khoroshun et al. 1993).

Some comments about the preceding development and about the specific form of the operator $\mathbf{K}(\mathbf{x} - \mathbf{y})$ of Eq. (2.14) used in this work are now in order. For a finite volume $V$ the operator $\mathbf{K}(\mathbf{x} - \mathbf{y})$ would act according to the rule:

$$\mathbf{K}(\mathbf{x} - \mathbf{y}) \ast \mathbf{e}(\mathbf{y}) = \int_{V} \text{sym} (\nabla_v (\nabla_v \mathbf{G}(\mathbf{x} - \mathbf{y}))) : (\mathbf{e}(\mathbf{y}) - \beta \mathbf{y}) dV_y$$

$$+ \int_{S} \text{sym} (\nabla_v \mathbf{G}(\mathbf{x} - \mathbf{y})) : (\mathbf{e}(\mathbf{y}) - \beta \mathbf{y}) \cdot \mathbf{n}(\mathbf{y}) dS_y. \quad (2.15)$$

where the first integral is taken over the entire region $V$, the second over the surface of that region, $\mathbf{n}$ represents the unit vector orthogonal to the surface $S$ (bounding the volume $V$) and pointing away from $V$. The influence of the boundary integral can be neglected (Willis (1977), Khoroshun (1968, 1978) among others) if $\beta$ is assumed to be the mean (or expected) value of $\mathbf{e}(\mathbf{y})$, that is when $\beta = \overline{\mathbf{e}}$, and if the volume $V$ is large. Then $\mathbf{e}(\mathbf{y})$ is oscillatory around $\overline{\mathbf{e}}$ and the mean value of $\mathbf{e}(\mathbf{y}) - \overline{\mathbf{e}}$ equals zero. Involving the Saint–Venant’s principle, its oscillatory boundary values influence the result of the operation of Eq. (2.15) only in a narrow region adjacent to the boundary. Consequently, for large $V$, the averaging process performed later to obtain the effective properties of the material is accurate without the surface integral in Eq. (2.15). Clearly, neglecting the surface integral is particularly justifiable when volume $V$ is taken to be infinite, which is done in this work. This reasoning is reflected in the transition from the boundary condition given in Eq. (2.10) to that of Eq. (2.11), and, subsequently, in the boundary condition for the Green’s function given in Eq. (2.13). As a result the following form of Eq. (2.15) used in this work is arrived at:

$$\mathbf{K}(\mathbf{x} - \mathbf{y}) \ast \mathbf{e}(\mathbf{y}) = \int_{V} \text{sym} (\nabla_v (\nabla_v \mathbf{G}(\mathbf{x} - \mathbf{y}))) : (\mathbf{e}(\mathbf{y}) - \overline{\mathbf{e}}) dV_y, \quad (2.15a)$$

where, again, $\overline{\mathbf{e}}$ is taken as a mean value (expectation) of $\mathbf{e}(\mathbf{y})$ and the Green’s function $\mathbf{G}$ corresponds to the infinite domain $V$.

An important issue in the preceding development is integrability of the function appearing under the integral sign in Eq. (2.15). In this regard a rapid decay of the second derivatives of the Green’s function $\mathbf{G}$ is one very important characteristic of that function. However, for the integration of Eq. (2.15) to be meaningful the argument $\mathbf{e}(\mathbf{y})$ of the operator $\mathbf{K}$ in Eq. (2.15) is required to have certain additional properties. At this stage of development the function $\mathbf{e}(\mathbf{y})$ is not known, and one can only assume (and subsequently verify) that it does possess those required properties. However, in the subsequent developments it will be shown that, in addition to allowing elimination of the surface integral in Eq. (2.15), in the method of conditional moments adopted herein, the term $\overline{\mathbf{e}}$ present in Eq. (2.15a) leads to integrands which are integrable over $\mathbb{R}^3$.

2.2. The Method of conditional moments

The integral equation (2.14) can be rewritten in the following form:

$$\mathbf{e}^{(i)} = \mathbf{z} + \mathbf{K}(\mathbf{x}^{(i)} - \mathbf{x}^{(2)}) \ast \left( \mathbf{C}^{(2)} : \mathbf{e}^{(2)} \right), \quad (2.16)$$

where:

$$\mathbf{e}^{(1)} = \mathbf{e}(\mathbf{x}^{(1)}), \quad \mathbf{e}^{(2)} = \mathbf{e}(\mathbf{x}^{(2)}) \quad \text{and} \quad \mathbf{C}^{(2)} = \mathbf{C}^{(\mathbf{x}^{(2)})}. \quad (2.17)$$
Employing conditional statistical averaging (Khoroshun 1978; Khoroshun et al., 1993) to Eq. (2.16) with respect to the two-point conditional density \( f(e^{(1)}, e^{(2)}, C^{(2)}_k) \) \( |y \rangle \) and i.e., the density of strain distributions at the points \( x^{(1)}, x^{(2)} \) and the elasticity moduli at point \( x^{(3)} \) provided that point \( x^{(1)} \) belongs to the \( v \)th component, \( v \in \{1, 2\} \), we obtain the following system of algebraic equations:

\[
\left\langle e^{(1)} \right|_{v}^{(1)} = \tau + K(x^{(1)} - x^{(2)}) + \sum_{k=1}^{2} f\left( (2) \right|_{k}^{(1)} \left[ C^{(0)}_{k} : \left\langle e^{(2)} \right|_{k}^{(2)} \right] \right|_{v}, \quad v \in \{1, 2\},
\] (2.18)

where \( C \) is the elastic modulus tensor in the \( k \)th component of the nanocomposite and \( C^{(0)}_{k} \) is defined as

\[
C^{(0)}_{k} = C_{k} - C_{c}.
\] (2.19)

The function \( f\left( (2) \right|_{k}^{(1)} \) denotes the probability that the point \( x^{(2)} \) belongs to the \( k \)th component, provided that point \( x^{(1)} \) belongs to the \( v \)th component, and \( \left\langle e^{(2)} \right|_{k}^{(2)} \) is the expectation value of the strain tensor at point \( x^{(2)} \), provided that points \( x^{(2)} \) and \( x^{(1)} \) belong to the \( k \)th component and to the \( v \)th component, respectively.

In order to solve this system, the two-point conditional moment \( \left\langle e^{(2)} \right|_{k}^{(2)} \) must be determined. For this purpose, Eq. (2.16) is averaged over the three-point conditional density \( f(e^{(1)}, e^{(2)}, C^{(3)}_k) \) \( |y \rangle \) to obtain the following system of algebraic equations:

\[
\left\langle e^{(1)} \right|_{v}^{(1)} \left| k \right\rangle = \tau + K(x^{(1)} - x^{(2)}) + \sum_{k=1}^{2} f\left( (2) \right|_{v}^{(1)} \left| k \right\rangle \left[ C^{(0)}_{k} : \left\langle e^{(2)} \right|_{v}^{(2)} \right|_{k}^{(2)} \right], \quad k, v \in \{1, 2\}.
\] (2.20)

By continuing this process, one obtains an infinite system of equations defining the conditional moments:

\[
\left\langle e^{(1)} \right|_{v_{1}}^{(1)}, \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{2} \right\rangle, \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{2} \right\rangle ..., \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{2} \right\rangle, \left. \right|_{v_{1}, v_{2}, ..., \in \{1, 2\}}.
\] (2.21)

To solve the obtained system, it is necessary to specify the conditional multipoint probability functions

\[
\tilde{f}\left( (2) \right|_{v_{1}}^{(1)} \left| v_{1} \right\rangle, \tilde{f}\left( (2) \right|_{v_{1}}^{(1)} \left| v_{2} \right\rangle ..., \tilde{f}\left( (2) \right|_{v_{1}}^{(1)} \left| v_{2} \right\rangle \right),
\] (2.22)

In the description above, the concept of a component is interpreted more generally by including a set of structural elements not only with identical physical properties but also with identical parameters such as shape, orientation, dimensions, etc. (i.e., unidirectional, uniformly distributed,...). It is noted that conditional multipoint probability functions may serve to characterize all such features of inclusions.

If the infinite system just described could be solved, the resulting conditional moments of Eq. (2.21) would completely and exactly characterize the analyzed nanocomposite. In reality, the process of constructing successive equations of the problem has to be terminated at some point. However, this requires additional conditions to close the truncated system of equations. To this end, one can take, for instance, one of the following conditions:

\[
\left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{1} \right\rangle, \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{2} \right\rangle ..., \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{1} \right\rangle = \tau,
\] (2.23)

In this work, to obtain a finite system of algebraic equations, a two-point approximation is used and the closure of the system is achieved by imposing the condition:

\[
\left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{1} \right\rangle, \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{2} \right\rangle ..., \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{1} \right\rangle = \tau.
\] (2.24)

For a two-point approximation it is necessary to specify the two-point conditional probabilities (two-point conditional distribution functions) \( \tilde{f}\left( (2) \right|_{v_{1}}^{(1)} \right) \). With that specification it is sufficient to only consider Eq. (2.18) and the additional condition \( \left\langle e^{(1)} \right|_{v_{1}}^{(1)} \left| v_{1} \right\rangle = \tau \), which implies that the strain fluctuations within each component are neglected. In this case, the following system of algebraic equations in terms of component-average strains will result:

\[
\tau_{v} = \tau + K(x^{(1)} - x^{(2)}) + \sum_{k=1}^{2} p_{k} (x^{(1)} - x^{(2)}) \left[ C^{(0)}_{k} : \left\langle e^{(2)} \right|_{k}^{(2)} \right|_{v}^{(2)} \right],
\] (2.25)

where

\[
\tau_{v} = \left\langle e^{(1)} \right|_{v}^{(1)}, p_{k} (x^{(1)} - x^{(2)}) = \tilde{f}\left( (2) \right|_{v_{1}}^{(1)} \right).
\] (2.26)

In order to evaluate Eq. (2.25) we specify the two-point conditional probabilities \( p_{k} (x^{(1)} - x^{(2)}) \), which characterize the shape and arrangement of the inclusions, and construct the tensor of elastic moduli \( C_{k} \) of a reference body. This tensor is present in the equations of two-point approximations due to neglecting moments of higher order. The choice of the tensor \( C_{k} \) determines in many respects the closeness of the calculated values of the effective constants to the true values. It is known that when one chooses \( C_{k} = 0 \) or \( C_{k} = \infty \) the Reuss and the Voigt bounds will result, respectively (Khoroshun 1978). By assuming that \( C_{k} \) is equal to the tensor of elastic constants of the components with the maximum and minimum rigidities, we arrive at the upper and lower Hashin–Shtrikman bounds (Hashin and Shtrikman 1963).

3. The problem of effective constants accounting for Gurtin–Murdoch conditions

3.1. Gurtin–Murdoch equations for the matrix-inhomogeneity interface

In order to investigate the interface effect on the overall elastic properties of a composite with nanoparticles, further governing equations in addition to those of classical elasticity, are needed. Those include the Gurtin–Murdoch equations (see Gurtin and Murdoch, 1975, 1978) describing the kinematic and equilibrium compatibility conditions between the matrix and the noninohomogeneities at the interface \( S_{i} \), which can be written as:

\[
\{u(x)\}_{S_{i}} = 0, \quad \{\sigma(x)\}_{S_{i}} = n(x) \cdot \nabla_{S_{i}} \sigma_{S_{i}}(x) = 0.
\] (3.1)

The unit vector \( n \) is normal to the interface. This vector can point in any of the two possible directions as long as all of the
subsequent developments are consistent with a particular choice. In the current contribution, it is assumed that at each interface the normal \( \mathbf{n} \) points away from the inclusion. The square brackets indicate the jump of the field quantities across the interface, defined as their value on the side towards which the normal \( \mathbf{n} \) is pointing minus their value on the side from which it is pointing. Thus, the first of the two equations in (3.1) represents continuity of the displacement vector across the interface (coherent interface) and the second describes equilibrium conditions of the interface itself. The additional equations also include the following definition of the interface/surface stress tensor \( \sigma_s \), present in the term \( \text{div}_S \sigma_s \) denoting the surface divergence of the surface tensor \( \sigma_s \) (Gurtin and Murdoch, 1978):

\[
\sigma_s(x) = \tau_0 \mathbf{I} + [\lambda_3 + \tau_0 \text{tr}(\zeta_0(x))] \mathbf{I} + 2[\mu_3 - \tau_0 \zeta_0(x)]
+ \tau_0 \nabla_x \mathbf{u}(x), \quad \tau_0 \equiv \lambda_2/(\lambda_1 + \lambda_2) + 1/(2\mu), \quad \lambda \equiv \lambda_1 + \lambda_2 + 2\mu.
\] (3.2)

In the equation above, \( \zeta \) is the interface/surface strain tensor, \( \mathbf{I} \) represents the identity tensor in the plane tangent to the surface, \( \tau_0 \) is the magnitude of the deformation-independent surface/interfacial tension (assumed “hydrostatic” and constant in Gurtin–Murdoch model), and \( \lambda, \mu \) are surface Lamé constants.

It is convenient to introduce the projection tensor \( \mathbf{P} \) employed by Gurtin and Murdoch (1975):

\[
\mathbf{P} = \mathbf{I} - \mathbf{n} \otimes \mathbf{n},
\] (3.3)

where \( \mathbf{I} \) is the bulk identity tensor of second rank. \( \mathbf{P} \) maps a tensor field from the bulk to the plane normal \( \mathbf{n} \). Thus, for an arbitrary vector field \( \mathbf{v} \), the surface gradient and surface divergence read (see Gurtin et al., 1998):

\[
\nabla_S \mathbf{v} = (\nabla \mathbf{v}) \cdot \mathbf{P}, \quad \text{div}_S (\mathbf{v}) = \text{tr} (\nabla_S \mathbf{v}).
\] (3.4)

### 3.2. Bulk-surface relations for a micro-point

Inserting Eq. (2.2) into (2.1), taking the divergence and accounting for the stress jump across the particle/matrix interface of Eq. (3.1) we obtain:

\[
\text{div}(\mathbf{C}(x) : \varepsilon(x)) + (\sigma(x) \cdot \mathbf{n}) \delta(\mathbf{z}(x)) = 0, \quad \mathbf{z}(x) = \{x(x)\}. \quad \varepsilon(x) = 0, \quad \text{at } x(x) = x_0(x_0). \quad (3.5)
\]

Here \( \delta(\mathbf{z}) \) is the Dirac delta function, while \( \mathbf{z}(x) \) defines the interface. In classical composite material with large inhomogeneities, the last term in Eq. (3.5) is absent since the jump in the normal traction is negligibly small. In the present case of nanoinhomogeneities whose curvature radius is small, this term is not negligible and can be interpreted as a body force applied along the interface.

Inserting Eq. (2.3) into Eq. (3.5) and taking into account the second condition in (3.1), we rewrite Eq. (3.5) as:

\[
\text{div}(\mathbf{C}(x) : \text{sym}(\nabla \mathbf{u}(x))) - \delta(\mathbf{z}(x)) \text{div}_S \sigma_s(x) = 0. \quad \varepsilon(x) = 0, \quad \text{at } x(x) = x_0(x_0). \quad (3.6)
\]

Upon inserting the Eq. (2.7) into Eq. (3.6), separating the linear part of the differential operator in (3.6) and using Green’s function, the following formula defining the fluctuations in the displacement field within the entire region \( V \) is obtained:

\[
\mathbf{u}^0(x) = \int_{S_I} \mathbf{G}(x-y) : \text{div}(\mathbf{C}(y) : \varepsilon(y) - \vec{\beta}) \text{d}V_y
- \int_{S_I} \mathbf{G}(x-y) : \text{div}_S \sigma_s(y) \text{d}S_y. \quad (3.7)
\]

This expression (with \( \vec{\beta} \) playing the same role as in Eq. (2.12)) relates the displacement field \( \mathbf{u}^0(x) \) to the unknown strain field \( \varepsilon(x) \) and the interface values of the displacements which enter the definition of \( \sigma_s(x) \), as seen in Eq. (3.2). The first integral in Eq. (3.7) is the classical part (see Eq. (2.12)), while the second integral represents the additional contribution of the surface forces, present because of the particular model of the interface adopted herein.

Inserting Eq. (3.7) into the linear kinematic relations (2.3), as well as accounting for Eq. (2.7) and employing Gauss’ theorem, leads to the following stochastic integral equation for the strain field:

\[
\varepsilon(x) = \varepsilon + \mathbf{K}(x-y) \cdot \mathbf{C}(y) \cdot \varepsilon(y)
- \text{sym}\{\nabla_x \int_{S_I} \mathbf{G}(x-y) : \text{div}_S \sigma_s(y) \text{d}S_y \}, \quad (3.8)
\]

where \( \mathbf{K}(x-y) \) acts according Eq. (2.15a).

Under the assumption that the surface gradient of displacements is negligible, and with the help of the surface projection tensor introduced earlier, the surface divergence of the surface stress tensor can be written in the following form

\[
\text{div}_S \sigma_s(x) = \text{div}_S \mathbf{C}_s : \mathbf{P}(x) : \varepsilon(x) \cdot \mathbf{P}(x) + \tau_0 \mathbf{I}(x), \quad (3.9)
\]

where tensor \( \mathbf{C}_s \) is the standard, two-dimensional tensor of surface isotropic elasticity resulting from Eq. (3.2), with the effective Lamé constants \( \lambda_0^{s} = \lambda_5 + \tau_0 \), \( \mu_0^{s} = \mu_5 - \tau_0 \). Replacing the surface divergence present in Eq. (3.8) by the right-hand side of the above formula gives the following equation

\[
\varepsilon(x) = \varepsilon + \mathbf{K}(x-y) \cdot \mathbf{C}(y) \cdot \varepsilon(y)
- \text{sym}\{\nabla_x \int_{S_I} \mathbf{G}(x-y) : \text{div}_S \mathbf{C}_s \cdot \mathbf{P}(y) : \varepsilon(y) \cdot \mathbf{P}(y) + \tau_0 \mathbf{I}(y) \text{d}S_y \} \quad (3.10)
\]

explicitly showing that Eq. (3.10) is a stochastic integral equation with the strain field as the unknown random function.

The influence of the surface displacement gradient present in Eq. (3.2) (and neglected in Eq. (3.9)) on the effective properties of nanocomposites definitely deserves further and more rigorous investigations. From the point of view of the approach presented in this work, however, its retention in Eq. (3.9) introduces the second unknown random function, displacement \( \mathbf{u}(x) \), which is related to strains and which requires a different approach to the problem. This will be undertaken in the future. Still, aside from this technical difficulty, there exists some evidence indicating that the inclusion of the surface displacement gradient in Eq. (3.9) may not affect the effective properties in any meaningful way. That evidence can be found in the analysis of Mogilevskaya et al. (2008, 2010a,b) which shows that the changes in the local elastic fields (stresses and strains) due to inclusion (or omission) of surface displacement gradient is essentially imperceptible. Some changes can be seen only in a very rare situation when two neighboring inhomogeneities, one significantly smaller than the other, are in a very close proximity to one another. Then, the smaller of the two constitutes some kind of stress concentrator on the surface of the larger inhomogeneity, and even then the changes in the values of strains and stresses are small and very localized. Thus, in a typical nanocomposite containing particles of comparable size, the local elastic fields – and, thus, their averages which are used to define the material effective properties – are not likely to be significantly affected by inclusion of surface displacement gradient. This observation provides a physical justification for neglecting the surface displacement gradient in Eq. (3.9).

Irrespective of the existing evidence justifying complete removal of the surface displacement gradient in Eq. (3.9) presented in the preceding paragraph, it is easy, and always possible, to include its symmetric part in the present development. This part, arguably, constitutes the dominant and the most important piece of the surface displacement gradient (with the remaining part being the local rotation of the surface). As shown in Mogilevskaya et al. (2008), the symmetric part of that gradient gives surface...
strains and its inclusion in Eq. (3.2) in place of the entire surface gradient would eliminate the last term but it would change the coefficient multiplying the strain tensor \(\varepsilon_5\) in that equation from \(2/\mu_s - \tau_0\) to \(2/\mu_s - \tau_0\). With such partial inclusion of the surface deformation gradient, the general form of Eq. (3.9) and the approach adopted herein would remain intact.

In this work, the surface displacement gradient has been neglected completely. The principal reason for that was that it is the first work including surface effects in the analysis of nanocomposites with random structure and based on the conditional moments. Thus, it was deemed to be important to compare the results obtained by the present method with those obtained by other similar techniques. Here, the results obtained by the proposed method of conditional moments will be compared with those of Duan et al. (2005c), which is similar in the sense that it also employs an averaging technique (although of a different kind) and does not include the last term of Eq. (3.2).

### 3.3. Spherical nanoinhomogeneities

We consider a matrix with randomly distributed spherical inclusions under a homogeneous load at infinity. Furthermore, we consider a model in which the emphasis is placed only on the contribution of the surface properties to the effective bulk modulus of the composite. With that in mind, one plausible assumption is that the state of strains in the inhomogeneities is nearly pure volumetric. Then, the surface strains represent "isotropic" stretch (or contraction); the longitudinal strains at the interface (and elsewhere in the nano-inhomogeneities) are identical in all directions. Under those conditions the expression for the surface stress tensor reduces to

\[ \sigma_3(x) = \delta k \sigma(x) \]

(3.11)

with

\[ s = \tau_0 + [\delta_s + \mu_s] \text{tr}[\Pi(x) \cdot \varepsilon_1 \cdot \Pi(x)], \]

(3.12)

being a constant specifying the magnitude of the total interface stress. It is noted that Sharma and Ganti (2004) arrive at a similar result using different arguments. Also, it needs to be emphasized that, even though the second term of Eq. (3.12) does not include the surface tension \(\tau_0\) under the assumption that strain field within the inhomogeneities is nearly purely volumetric, this equation represents all details of the Gurtin–Murdoch formula of Eq. (3.2). The residual stress \(\tau_0\) is present in those terms of Eq. (3.2) which contain the surface strains, cancels out as a result of this particular assumption. Finally, even though the method used in this work leads to a complete tensor of material constants, it is anticipated that the shear modulus resulting from the model introduced herein will be the same as for a composite without surface effects.

With parameter \(s\) of Eqs. (3.11) and (3.12) constant, evaluation of surface divergence of the surface stress tensor reduces to the surface divergence of the surface identity tensor (see Appendix A):

\[ \text{div}_s \sigma_3(x) = 2 \kappa \Pi(x), \]

(3.13)

where \(\kappa\) is the mean curvature of the inclusions (i.e., the curvature of the spheres in the present case with an appropriate sign, depending on the orientation of vector \(n\)). Consequently, in the case of a nanocomposite with spherical inclusions, Eq. (3.10) yields:

\[ \varepsilon(x) = \varepsilon + \kappa \Pi(x) - (\mathbf{C}^0(x) : \mathbf{e}(y)) - 2s \text{sym} \left\{ \nabla_x \int_{\Gamma} \mathbf{G}(x-y) \cdot \mathbf{n}(y) \, dS \right\}. \]

(3.14)

Applying Gauss’ theorem, the surface integral is converted into a volume integral

\[ \varepsilon(x) = \varepsilon + \mathbf{K}(x-y) + (\mathbf{C}^0(x) : \mathbf{e}(y)) + 2s \text{sym} \left\{ \nabla_x \int_{\Omega} \mathbf{G}(x-y) \cdot \mathbf{n}(y) \, dV \right\} : \mathbf{I}. \]

(3.15)

The second integral in the above equation can be transformed further to yield the following expression containing the classical Eshelby tensor (i.e., the term in the curly brackets) for the reference medium (see Mura, 1987):

\[ \varepsilon(x) = \varepsilon + \kappa \Pi(x) - (\mathbf{C}^0(x) : \mathbf{e}(y)) + 2s \text{sym} \left\{ \nabla_x \mathbf{C}_i : \int_v \nabla_x \mathbf{G}(x-y) \, dV \right\} : \mathbf{I}. \]

(3.16)

The tensors \(\mathbf{C}^0\) and \(\mathbf{C}_i\) in Eqs. (3.14)–(3.16) are determined by Eqs. (2.7), (2.8).

### 3.4. Application of the method of conditional moments

Employing conditional averaging (Khoroshun 1978) in Eq. (3.16), limiting the analysis to a two-point approximation, and performing some necessary transformations, the following system of linear algebraic equations is obtained from which the component-average strains can be computed:

\[ \varepsilon_v = \varepsilon + \sum_{k=1}^{2f} \mathbf{K}^k : \varepsilon_0^k + 2s \kappa \int_{\Omega} \varepsilon_1 \cdot \mathbf{C}_i \text{tr}[\Pi(x) \cdot \varepsilon_1 \cdot \Pi(x)] (\mathbf{C}_i) : \mathbf{S} : \mathbf{I}, \]

(3.17)

where \(\mathbf{K}^k\) is the classical Eshelby tensor (see Mura, 1987) and the tensor \(\mathbf{C}_i\) is defined by Eq. (2.19); the operator \(\mathbf{K}^k\) is defined as follows:

\[ \mathbf{K}^k = \mathbf{K}(x-y) + \rho_{pk}(x-y), \]

(3.18)

where \(\rho_{pk}(x-y)\) denotes the conditional probability that point \(y\) belongs to the \(k\)th component if point \(x\) belongs to the \(v\)th component or, in other words, the transition probability from the \(v\)th condition to the \(k\)th condition (Khoroshun 1978; Khoroshun et al., 1993) and integral operator \(\mathbf{K}(x-y)\) acts according to the rule (2.15a).

Some comments of general nature may be of interest before further specification of the operator \(\mathbf{K}^k\) defined in Eq. (3.18). To this end it is first noted that the transition probabilities satisfy the following conditions:

\[ \sum_{k=1}^{2f} \rho_{pk}(x) = 1, \quad c_k \rho_{pk}(x) = c_k \rho_{pk}(x), \]

(3.19)

\[ \rho_{pk}(0) = \delta_{vk}, \quad \rho_{pk}(\infty) = c_k, \quad v \in \{1, 2\}. \]

Eq. (3.19) states that each point belongs either to \(v\)th component or \(k\)th component of the system, whereas Eq. (3.19) is the result of a simple transformation based on the fact that \(\mathbf{J}(\mathbf{1}) = c_k, \sum_{k=1}^{2f} c_k = 1\) and on the theorem of total probability stating that \(\mathbf{J}(\mathbf{1}) = \sum_{v=1}^{2} \mathbf{J}^{(v)} \times \mathbf{J}(\mathbf{2}) / k \). In the preceding expression \(\mathbf{J}^{(1)}\) and \(\mathbf{J}^{(2)}\) denote the probabilities that the points \(x^{(1)}\), \(x^{(2)}\) belong to the \(v\)th component of the system and \(c_v\) denotes the volume fraction of that component. Eq. (3.19) represents the fact that a point \(x\) can belong only to one component, and finally, Eq. (3.19) follows from the condition that there is no long-range order in the composite.

From the properties expressed by Eq. (3.19) the following form of representation for the transition probabilities can be deduced (Khoroshun et al., 1993):

\[ \rho_{pk}(x) = c_k + [\delta_{vk} - c_k] \Phi_{vk}(x), \]

(3.20)
where the functions $\phi_{kl}(x)$ possess the following properties

$$\phi_{kl}(x) = \phi_{kl}(x), \quad \phi_{kl}(x) = \sum_{k=1}^{3} C_{kl} \phi_{kl}(x),$$

$$\phi_{kl}(0) = 1, \quad \phi_{kl}(\infty) = 0, \quad k, \ell \in \{1, 2\}. $$

For a two-component composite the above properties further imply that

$$\phi_{11}(x) = \phi_{12}(x) = \phi_{21}(x) = \phi_{22}(x) = \phi(x).$$

An example of a specific correlation function $\phi(x)$ (which only depends on the distance between points) for a composite with randomly distributed spherical inclusions of radius $R_0$ can be specified on the basis of probability theory (see in Khoroshun et al., 1993; Nazarenko et al., 2009). This correlation function has the following form:

$$\phi(x) = \exp \left( -\frac{8}{\pi^2 C_0 R_0} \sqrt{x_1^2 + x_2^2 + x_3^2} \right).$$  \hspace{1cm} (3.21)

It can be verified that in the process of statistical averaging the correlation term $\bar{\phi}(y) = (C(y) : e(y))$ of Eqs. (2.14) and (2.15a) becomes $p_{kl}(\infty)$. Thus, the operator $K^{ik}$ of Eq. (3.18) takes the following form:

$$K^{ik} = K(x) \cdot p_{ik}(x) =\int_V \text{sym}(\nabla_x (\nabla_x G(x))) (p_{ik}(x) - p_{ik}(\infty)) dV = (\delta_{ik} - c_i) \int_V \text{sym}(\nabla_x (\nabla_x G(x))) \phi(x) dV,$$  \hspace{1cm} (3.22)

since, in view of Eqs. (3.20) and (3.21), $p_{ik}(\infty) = c_k$ and $p_{ik}(x) - p_{ik}(\infty) = (\delta_{ik} - c_k) \phi(x)$. Considering that the second gradient of the Green function $G$ behaves as $r^{-3}$ with $r \rightarrow \infty$, while function $\phi$ of Eq. (3.21) is integrable when raised to any power $q \geq 1$, the convolution $K(x) \cdot p_{ik}(x)$ is defined by integration of a function integrable over $R^3$.

Taking into account Eq. (3.21) the operator $K^{ik}$ can be represented by

$$K^{ik} = (\delta_{ik} - c_i) L,$$  \hspace{1cm} (3.23)

where $L$ is an isotropic rank four tensor. It is determined in terms of two scalars $a$ and $b$.

$$L_{ijkl} = a \delta_{ij} \delta_{kl} + b (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}),$$  \hspace{1cm} (3.24)

with

$$a = \frac{\lambda_c + \mu_c}{15 \mu_c \left[ \lambda_c + 2 \mu_c \right]}, \quad b = -\frac{3 \lambda_c + 8 \mu_c}{30 \mu_c \left[ \lambda_c + 2 \mu_c \right]},$$  \hspace{1cm} (3.25)

and with $\lambda_c$, $\mu_c$ being the Lamé constants of the reference medium (Khoroshun et al., 1993).

The tensor $L$ is the classical Hill tensor (see Hill, 1975), which is a product of the inverse of the elasticity tensor and the Eshelby's tensors as given, for instance, by Mura (1987). As mentioned earlier, in the present work the elastic constants defining that tensor are related to the properties of the reference medium.

Having outlined some general issues related to the evaluation of the operator $K^{ik}$ of Eq. (3.18), certain details of this evaluation will be presented next.

Correlation function $\phi(x)$ of Eq. (3.21) and, as a consequence, the two-point transition probabilities $p_{ik}(x)$ of Eq. (3.20) depend only on the norm of vector $x$ (not on its direction). Under those conditions the operator $K(x - y)$ of Eq. (3.22) can be decomposed as follows

$$K(x - y) = p_{ik}(x - y) = 0 \star K(x - y) + K(x - y) \star p_{ik}(x - y) = 0 .$$  \hspace{1cm} (3.26)

The integral operation $K(x - y)$ in the above equation extends over the entire domain, excluding the points $\theta = x$ and $\eta = y$, $s$ being the surface of the macrovolume). Furthermore, if the correlation function only depends on the distances $|x - y|$ between two points, then the integral operator $K(x - y)$ of Eq. (3.26) yields $K(x - y) \star \phi(x - y) = 0$ (see Eshelby 1957; Willis 1977; Khoroshun 1978; Buryachenko 2001; among others). Then, the relationship for the operator $K^{ik}$ can be represented by Eq. (3.23), (3.24), (3.25) independently of the specific form of $\phi(x - y)$.

In summary, for the case of a composite with isotropic components and randomly distributed spherical inclusions the explicit representation of the correlation functions is not needed and the method of conditional moments is equivalent to the method of moments by Khoroshun (1967, 1968). Further, it is identical with the statistical assumptions later introduced by Willis (1977).

Taking into account Eq. (3.23), the system of linear algebraic equations (3.17) can be rewritten in the following form:

$$\bar{x}_i = c_i L \cdot (C_i^1 \cdot \bar{x}_1 - C_i^2 \cdot \bar{x}_2) + 2 \kappa [\tau_0 + (\delta_{ij} + \mu_c) \text{tr} (P : \bar{x}_i, P)] (C_i - 1) : \bar{I}.$$  \hspace{1cm} (3.27)

This last equation (3.27) can be simplified using the fact that $\kappa = -1/R_0$ for spheres, where $R_0$ is their radius (the minus sign is due to the assumption that the normal to the interface vector $n$ is pointing away from the inhomogeneity). Furthermore, it is noted that an isotropic rank four tensor $C_i$ can be written in terms of Lamé constants

$$C_{ij} = \lambda_c \delta_{ij} + \mu_c (\delta_{i3} \delta_{j3} + \delta_{i2} \delta_{j2} + \delta_{i1} \delta_{j1}).$$  \hspace{1cm} (3.28)

As shown by Sharma and Ganti (2004) and as follows from Eq. (B.7f) and the definition of tensors $C_i \cdot I, H, D$ in Appendix B, the following relation holds

$$(C_i)^{-1} = \frac{1}{(1/3K_i)^2} \bar{I}.$$  \hspace{1cm} (3.29)

in which $K_i$ is the bulk modulus of the reference medium. By inserting Eqs. (3.28) and (3.29) into Eq. (3.27), taking into account that $\tau = c_i \bar{x}_i + c_3 \bar{x}_i$, and noting that for isotropic spherical inclusions (see Mura, 1987):

$$S : \bar{I} = \frac{1 + v_c}{3(1 - v_c)} \bar{I},$$

we can eliminate $\bar{x}_3$ from Eq. (3.27) to obtain

$$\bar{x}_1 = \left[ \bar{I} - L : C_i \right] : \bar{x} + L : C_i : \bar{x},$$

$$= \frac{4(\delta_{ij} + \mu_c)}{27 R_0 K_i} \left[ \frac{1 + v_c}{1 - v_c} \text{tr} (\bar{x}_1) - \frac{2}{9 R_0 K_i} \frac{1 + v_c}{1 - v_c} \tau_0 \bar{I} \right].$$  \hspace{1cm} (3.30)

where $v_c$ is the Poisson's coefficient of the reference medium and $C_i = C_i - C_i$, $C_i = c_i C_i + c_3 C_i$.  \hspace{1cm} (3.31)

In view of Eq. (2.8) the new tensor $C_i$ defined in the above equation is isotropic and can be characterized by two constants $K'$ and $\mu'$ (cf. Appendix B) which are dependent on the constants defining $C_i$ and $C_i$ and on the concentration of the constituents.

Noting that $\text{tr} (\bar{x}_1) = \left[ (1 + 2) : \bar{x}_1 \right.$, the relationship between the mean strain in the inclusions $\bar{x}_1$ and the mean strain in the macroscopic volume $\bar{x}$ reads as follows:

$$\bar{x}_1 = \left( \bar{I} - L : C_i + \frac{4(\delta_{ij} + \mu_c)}{27 R_0 K_i} \left[ \frac{1 + v_c}{1 - v_c} \bar{I} \right] \tau_0 \right)^{-1} : \left[ \bar{I} - L : C_i \right] : \bar{x}$$

$$= \left( 2 \frac{1 + v_c}{9 R_0 K_i} \tau_0 \left[ \frac{1 + v_c}{1 - v_c} \bar{I} \right] \right)^{-1} : \left( \bar{I} - L : C_i + \frac{4(\delta_{ij} + \mu_c)}{27 R_0 K_i} \left[ \frac{1 + v_c}{1 - v_c} \bar{I} \right] \right) : \bar{x}.$$  \hspace{1cm} (3.32)
Using the relationships for macro stresses \( \sigma = c_1 C_1 : \mathbf{E} + c_2 C_2 : \mathbf{E} \) and Eq. (3.32) for the averaged strain in the inclusions and the averaged strain in the macroscopic volume, we can write the constitutive equation for the macro-volume in the following form:

\[
\sigma = C' \cdot \mathbf{e} - c_1 \frac{2}{9k_0 K^c} \left[ \frac{1 + \nu_c}{1 - \nu_c} \right] \mathbf{I} C_1
\]

\[
: \left[ \mathbf{I} - C : \mathbf{C} + \frac{4 [2a + \mu_c]}{27 k_0 K^c} \left[ \frac{1 + \nu_c}{1 - \nu_c} \right] \mathbf{I} \otimes \mathbf{I} \right]^{-1} \mathbf{I}
\]\n
(3.33)

The relationship for determination of the effective stiffness tensor (which depends on the radius of nanoparticles) can be deduced to be:

\[
C' = \mathbf{C} + c_1 C_1 : \left[ \mathbf{I} - C : \mathbf{C} + \frac{4 [2a + \mu_c]}{27 k_0 K^c} \left[ \frac{1 + \nu_c}{1 - \nu_c} \right] \mathbf{I} \otimes \mathbf{I} \right]^{-1}
\]

\[
: \left[ c_2 L : \mathbf{C} - \frac{4 [2a + \mu_c]}{27 k_0 K^c} \left[ \frac{1 + \nu_c}{1 - \nu_c} \right] \mathbf{I} \otimes \mathbf{I} \right],
\]\n
(3.34)

where \( C_1 \) is

\[
C_1 = C_1 - C_2.
\]

The relationship (3.33) between the macro stresses and the macro strains depends on the radius of the nanoparticles. The radius is also included in the expression for the effective stiffness tensor (3.34). It is interesting to note that the second term in the right hand side of Eq. (3.33) is the only term containing the strain-independent surface tension on the matrix/nanoparticle interface. Surface tension is not considered in the investigations of Duan et al. (2005c), Chen et al. (2007) and Brisard et al. (2010) with whose results the results obtained herein are compared. So, the second part of Eq. (3.33) cannot be recovered by those Authors, but here it only vanishes in the absence of surface tension because none of the two terms of the right hand side of Eq. (3.12) contains both surface tension and surface elasticity at the same time. In other words, in Eq. (3.12) the effects of surface tension and surface elasticity are separated. As explained following Eq. (3.12), this separation is present in Eq. (3.12) in spite of the fact that the Gurtin–Murdoch material surface model is used here without any simplifications – it occurs only because of the special model of the problem introduced in this work. It is also interesting to note that, in the present approach, the split between the two terms in Eq. (3.33) emerges naturally and the identification of the effective properties is unambiguous. Finally, it is noted that if the radius of a spherical particles \( R_0 \) is large, then \([2a + \mu_c]/R_0 \to 0\) and Eqs. (3.33), (3.34) reduce to the classical ones without the interface effect (Nazarenko et al., 2009):

\[
\sigma = C' \cdot \mathbf{e},
\]

\[
C' = \mathbf{C} + c_1 c_2 C_2 \left( \mathbf{I} - L : \mathbf{C} \right)^{-1} \mathbf{L} : C_2.
\]

(3.35)

The constitutive equation for the macro-volume (3.33) and the relationship for determination of the effective stiffness tensor (3.34) obtained by the method of conditional moments functions take into account a random distribution of nanoparticles in the matrix and interactions between nanoparticles in the framework of two-point approximation. This formulation, combined with the particular model used in this work, accounts also for volumetric contribution of the surface stresses due to the nanosize of the particles in the composite.

As shown in Appendix B, the following closed-form scalar expression for the effective bulk modulus can be extracted from a more general tensorial formula of Eq. (3.34)

\[
K' = K + \frac{9 c_1 K(K - K_2)[c_2(K - K_2) + K]}{1 - 9K(c_2 K + c_2 K_1 - K_2) + K}. \quad (3.36)
\]

In this expression, \( c_1, K_1 \) and \( c_2, K_2 \) are the volume fractions and bulk moduli of the inclusions and of the matrix, respectively; \( K \) is the bulk modulus of the selected reference medium; \( K \) depends on \( a \) and \( b \) of Eq. (3.25) (as seen in Eq. (B.7a)) and, therefore, on the properties of the reference medium as well; \( K_3 = \frac{4(\lambda + \mu)}{3\mu} \) can be interpreted as an apparent increase in the bulk modulus of the inhomogeneities associated with presence of the material surface surrounding them. Formula (3.36) appears different that the one presented in the paper by Duan et al. (2005c).

When \( K_3 = 0 \) (no surface effects) the following expression is obtained from Eq. (3.36)

\[
K' = R + \frac{9 c_1 c_2 K(K - K_2)^2}{1 - 9K(c_2 K_2 + c_2 K_1 - K_2)}
\]

\[
= R + \frac{9 c_1 c_2 K(K - K_2)^2}{1 - 9K(c_2 K_2 + c_2 K_1 - K_2)}, \quad (3.37)
\]

which, noting that \( K = 1/(\lambda + 2\mu) \), is further transformed to yield

\[
K' = R + \frac{9 c_1 c_2 K(K - K_2)^2}{c_1 c_2 K_2 + c_2 K_1 + 4/3 \mu}, \quad (3.38)
\]

Expression (3.38) is identical to the relationship obtained by the method of moments (see in Khoroshun et al., 1993) for the bulk modulus of the material with the same stochastic structure as the one considered here. This constitutes a confirmation that Eq. (3.34) obtained by the method of conditional moments is correct.

The additional variable \( K_3 \) in the expression for the effective bulk moduli given in Eq. (3.36), occurs due to introduction of the Gurtin Murdoch surface model, and is identical to the correction term obtained by Duan et al. (2005c), Chen et al. (2007) and Brisard et al. (2010), who in their solutions used the same surface elasticity model (albeit without surface tension). However, the relations for determination of the effective bulk moduli are different here than in those papers, which can only be attributed to differences in the approaches used in the respective analyses.

We would like to note that, when matrix is selected as the reference medium, Eq. (3.38) coincides with the upper Hashin–Shtrikman bound presented in Hashin and Shtrikman (1963). Brisard et al. (2010) extended the Hashin–Shtrikman bound formula to include surface elasticity. In their work the same parameter \( K_3 \) that appears in Eq. (3.36) is introduced as a correction to the bulk modulus of the inclusions. This leads to Hashin–Shtrikman bounds accounting for surface elasticity which are formally identical with those without surface effects but with the real bulk modulus of the inclusions replaced with their modified bulk modulus. In the present manuscript parameter \( K_3 \) appears as a result of averaging of the stochastic integral equation (3.16). Comparison of Eq. (3.36) with Eq. (3.37) reveals that the former cannot be obtained by replacing \( K_3 \) with \( K_3 + K \) in Eq. (3.37), as is possible in the case of Hashin–Shtrikman bounds by Brisard et al. (2010). This is another yet indication of the (somewhat expected) fact that the stochastic averaging introduced here by the method of conditional moments accounts for interactions between the inclusions, or between various constituents of the composite, in a different, more complicated way than other methods.

Finally, it is noted that in Appendix B a scalar formula for the effective shear modulus is also derived. As expected, the specific modeling assumptions introduced in this work lead to the expression for the effective shear modulus which is unaffected by the interface properties and coincides with that obtained earlier by Khoroshun (1978), Khoroshun et al. (1993).
4. Numerical results

The relationship for the effective properties of a composite material containing randomly distributed spherical nanoparticles derived in the preceding sections is used to analyze a material containing spherical pores \((\mu_1 = K_1 = 0)\), as illustrated in Fig. 1.

The numerical results are presented for an aluminum matrix with the following properties: \(K_2 = 75.2\) GPa and \(V_2 = 0.3\). The free surface properties used in the present work are the same as those in Duan et al. (2005c). In their work two sets of surface properties are used, corresponding to the surfaces oriented along two different crystallographic directions: A: \(\lambda_S = 3.48912\) N/m and \(\mu_S = -6.2178\) N/m for surface \([100]\) and B: \(\lambda_S = 6.842\) N/m and \(\mu_S = -0.3755\) N/m for surface \([111]\).

In Fig. 2 the normalized bulk modulus \(K^*/K_{cl}\) for different surface properties is presented as a function of the cavity radius \(R_0\) (nm), for the pore volume fraction \(c_1 = 0.5\). The subscript “cl” is used to represent the results for the classical solution, i.e., the solution without interface stress. The normalized bulk modulus \(K^*/K_{cl}\) calculated for different void volume fractions for two different void radii is shown in Fig. 3. The surface effect on the effective bulk modulus becomes negligible if the radius of the cavity is larger than about 20 nm. As expected, this numerical illustration indicates that the surface effect is particularly significant for smaller sizes of pores. Depending on the type of the material surface, the effective properties of the above porous material can be stiffer or less stiff. For a close-packed aluminum surface Al \([111]\) the material becomes stiffer for smaller pores, while for the less dense surface Al \([100]\) the bulk modulus decreases with the pore size.

The variation of the normalized bulk modulus \(K^*/K_{cl}\) with the void volume fractions calculated by the method of conditional moments (solid line – surface A, and dot-dashed line – surface B) for the material containing spherical cavities of radius \(R_0 = 5\) nm is shown in Fig. 4. For comparison, the normalized bulk modulus for the same material, obtained on the basis of self-consistent scheme by Duan et al. (2005c) is also shown in Fig. 4. Both approaches use a Gurtin–Murdoch surface model and the same values of the model parameters. Even though Duan et al. (2005c) use the Gurtin–Murdoch model without surface tension \(\tau_0\) and in the present approach \(\tau_0\) is included, the bulk modulus formula developed here does not contain surface tension either, which is a result of the approach adopted. Thus, although different in their approaches, those two formulations are comparable. Fig. 4 shows that the normalized bulk moduli obtained by different approaches are very similar for small volume fraction of pores, smaller than \(c_1 = 0.3\), which provides an evidence that the Gurtin–Murdoch surface model has been successfully introduced to the method of conditional moments. For higher value of volume fraction the values of those moduli differ by a larger amount.

The relationship for the effective stiffness tensor of Eq. (3.34) is obtained by the method of conditional moments within the framework of the two-point approximation. As mentioned earlier, for the case of composite with isotropic components and randomly distributed spherical inclusions the method of conditional moments is equivalent to the method of moments by Khoroshun (1967, 1968). It is also identical with the statistical assumptions introduced by Willis (1977) and with Mori–Tanaka approach used by Duan et al. (2005c). The difference between the results calculated by the method of conditional moments and by Duan et al. (2005c) can be explained by the fact that Duan’s results are obtained on the basis of the Eshelby solution for a single inclusion.
in an infinite medium with subsequent application of self-consistent technique. In the method of conditional moments the statistical averaging is performed on the exact governing integral equations for composite with randomly distributed spherical inclusions (which account for all possible interactions); the solution for macroparameters emerges naturally from such averaging process.

Nanoparticles can have various shapes and can be anisotropic (like nanotube fibers, for example). Application of the method of conditional moments to analyze materials containing inhomogeneities with those, more complex geometric and mechanical characteristics is likely to be more interesting and more important. It is also likely to be more effective than other methods, given its past success in analysis of composites with anisotropic components and spherical or ellipsoidal inclusions without surface effects.

Comparison of the results derived by the method of conditional moments with the calculations done via other methods and experiments was presented in Nazarenko et al. (2009) and it shows that the method of conditional moments can successfully be used for composites in the case of high contrast in the properties of the constituents, anisotropy of components and high volume fraction of inclusions.

5. Conclusions

A mathematical model for investigation of the effective properties of a material with randomly distributed nanoparticles, which requires a special treatment of the surface between matrix and nanoparticles, has been proposed. The surface effect is introduced via Gurtin–Murdoch equations (Gurtin and Murdoch, 1975, 1978) describing properties of the matrix/nanoparticles interface, which are added to the system of stochastic differential equations formulated within the framework of linear elasticity.

In the current work, the problem of finding the effective constants is ultimately reduced to finding a stochastically averaged solution of a system of stochastic differential equations based on the fundamental equations of linear elasticity which are coupled with surface/interface elasticity fully accounting for the presence of surface tension. In the process of deriving that solution, use is made of Green’s function to first transform this system to a system of statistically non-linear integral equations. Instead of seeking the solution for the local elastic fields and averaging them in order to find the effective properties of the material, in this approach the first (or preliminary) step of the analysis is the statistical averaging performed on the governing integral equations themselves. Theoretically, this leads to an infinite system of linear algebraic equations in terms of multipoint conditional moments. Such a system can be truncated at any level of approximation. In this work, a finite system of algebraic equations for component-average strains is obtained by neglecting the stress fluctuations within the inclusions and restricting the derivation to a two-point approximation. Two-point conditional probabilities which are included in this system characterize the shape of nanoparticles and their arrangement, albeit only in an approximate manner. As explained in the paper, at that level of approximation, and for the particular application considered here, the method of conditional moments used here coincides with the method of moments introduced by Khoroshun (1967, 1968).

For the sake of numerical illustration of the approach, a nonporous material consisting of an isotropic matrix and spherical nanocavities has been chosen. The bulk modulus of such a material has been analyzed for varying volume content and varying radius of the nanocavities within the specific model which focuses on the influence of the interfaces on the effective bulk modulus of the composite.

The size effect introduced due to addition of the residual stresses and elasticity on the matrix/nanoparticles interface (surface of nanocavities in the chosen numerical example) is accounted for in the expressions for effective bulk moduli of the composite. The numerical example shows that the proposed statistical approach is capable to reveal that even in random nanocomposites the surface effect is significant for smaller sizes of pores. It is also able to capture the qualitative influence that a particular type of the material surface between matrix and nanoparticles has on the effective properties of porous aluminum with random distribution of pores. Comparison with results obtained on the basis of the self-consistent scheme shows that the method of conditional moments is comparable in accuracy and can be successfully used for investigation of particulate nanomaterials. A higher discrepancy for larger volume fractions is probably associated with inadequacies of both methods as each of them introduces some, although different, approximations to make the solution possible. Those approximations are very likely to play a more significant role for higher levels of pore concentration.

Even though random composites can be analyzed using other techniques, including various increasingly popular numerical techniques (such as finite element method and methods based on the boundary integral formulations), the method of conditional moments has its distinct merits. One of them is its elegant treatment of truly random composite structures. The other is its ability to provide closed-form expressions for the effective properties of nanocomposites from which the influence of different problem parameters can be inferred, at least qualitatively. These features alone have an important intellectual value.

Appendix A. Surface divergence of the surface identity tensor field

A.1. Background

Let’s assume that the surface of interest is locally parameterized by \( \zeta^A \), \( A \in \{1, 2, 3\} \), that is the position vector of a point on that surface is expressed as \( \mathbf{r}(\zeta^A) \). Then, one can define a couple of vectors \( \mathbf{G}_A \),

\[
\mathbf{G}_A = \frac{\partial \mathbf{r}}{\partial \zeta^A} = \mathbf{r}_A, \quad (A1)
\]

which forms the vector basis in the linear space tangent to the surface \( S \), called the natural basis. Another basis in the same tangent space, denoted by \( \mathbf{G}^A \) and called dual or reciprocal, is defined via the following orthogonality condition

\[
\mathbf{G}_A \cdot \mathbf{G}^\Lambda = \delta^\Lambda_A \quad (A2)
\]

where the symbol “*” represents the “dot” (or “inner”) product of vectors and \( \delta^\Lambda_A \) is the Kronecker “delta”.

The bases \( \mathbf{G}_A \) and \( \mathbf{G}^A \) are functions of \( \zeta^A \) and their derivatives can be expressed by the well-known Gauss–Weingarten formulas (see Itskov (2007), for example). For the natural basis these formulas are (cf. Eq. (A1) for notations)

\[
\mathbf{G}_{A, \Sigma} = \Gamma_{\alpha \Sigma}^A \mathbf{G}^\alpha + B_{A, \Sigma} \mathbf{n} \equiv \Gamma_{\alpha \Sigma}^A \mathbf{G}^\alpha + \Gamma_{\alpha \Sigma}^A \mathbf{G}^1 + \Gamma_{\alpha \Sigma}^A \mathbf{G}^2 + B_{A, \Sigma} \mathbf{n}, \quad (A3)
\]

with a unit vector \( \mathbf{n} \) normal to the surface. Here, an index repeated in the subscript and superscript position implies summation, \( \Gamma_{\alpha \Sigma}^A \) are the so-called Christoffel symbols of the second kind and \( B_{A, \Sigma} = \mathbf{G}_{A, \Sigma} \cdot \mathbf{n} \) are the components of the local curvature tensor. Eq. (A3) together with Eq. (A1) implies that \( B_{A, \Sigma} = \mathbf{G}_{A, \Sigma} \cdot \mathbf{n} \) whereas the definition of the Christoffel symbols and Eq. (A1) imply the following symmetry property \( \Gamma_{\alpha \Sigma}^A = \Gamma_{\Sigma \alpha}^A \). The analogous formulas for the derivatives of vectors of the dual basis are

\[
\mathbf{G}^\Lambda_{, \Sigma} = -\Gamma_{\Lambda \Sigma}^A \mathbf{G}^\Lambda + B^\Lambda_{, \Sigma} \mathbf{n} \equiv -\Gamma_{\Lambda \Sigma}^A \mathbf{G}^1 - \Gamma_{\Lambda \Sigma}^A \mathbf{G}^2 - B^\Lambda_{, \Sigma} \mathbf{n}, \quad (A4)
\]
where \( B^1_k \) are the so-called mixed components of the local curvature tensor.

As in other situations, tensors in the tangent space represent linear transformations of the vectors in that tangent space into vectors in the same space. They can be represented as linear combinations of dyadic products of some vectors in that space. If a tensor is represented by a single dyadic of two vectors, e.g., \( T = a \otimes b \), it operates on a vector \( v \) as follows

\[
T \cdot v = (a \otimes b) \cdot v = (b \cdot v)a.
\]  

(A5)

Any tensor in the tangent space can be represented by a linear combination of dyadic composed of vectors of the basis \( G_i \) alone, \( G_i \) alone, or a combination of those two sets of vectors. For example, the curvature tensor \( B \) (components of which appear in Eqs. (A3) and (A4)) can be represented in several ways shown below (as well as many other ways)

\[
B = B_{i\alpha}G^\alpha \otimes G^\alpha = B_{i\alpha}G^\alpha \otimes G^\alpha = B_{i\alpha}^\alpha G^\alpha \otimes G^\alpha.
\]  

(A6)

In the above equation double summation is implied and the (indexed) coefficients multiplying the dyadic are various components of the tensor \( B \). They all can be different, but they are related to each other by transformation formulas involving the so-called Gram matrices related to the natural or dual bases. Those matrices are defined as follows

\[
G_{\alpha\beta} = G_{\alpha} \cdot G_{\beta}, \quad G^{\alpha\beta} = G^\alpha \cdot G^\beta.
\]  

(A7)

As an example of the relationship between various components of the curvature tensor \( B \) one can present the following

\[
B^{\alpha\beta \gamma\delta} = B_{i\alpha}^{\beta \gamma\delta}G_i.
\]  

(A8)

Components of tensor \( B \) appearing in the above equation are present in Eqs. (A3) and (A4).

A.2. Surface identity tensor field and its surface divergence

With the above background information it is easy to see that the surface unit tensor at each point of the surface can be (for example) defined as follows

\[
I_S = G_a \otimes G^a.
\]  

(A9)

It is so because, for any vector \( v \), which can always be represented as \( v = v^a G_a \),

\[
I_S \cdot v = \left(G_a \otimes G^a\right) \cdot (v^b G_b) = v^b \left(G_a \cdot G^a\right) G_b = v^b \delta^b_a G_a = v^a.
\]  

(A10)

Surface divergence of a tensor field \( T \) of any rank, defined on surface \( S \), is described by the following general formula (see an analogical formula for volumetric divergence in Itskov (2007))

\[
\text{div}_S T = T : G^\alpha \cdot G^\alpha.
\]  

(A11)

Applying this formula to the field of the surface unit tensors of Eq. (A9) yields

\[
\text{div}_S I_S = \text{div}_S (G_a \otimes G^a) = (G_a \otimes G^a)_\alpha \cdot G^\alpha
\]

\[
= \left(G_{\alpha\beta}G_{\alpha} \otimes G_{\alpha} + G_{\alpha\beta}G^\alpha \otimes G^\alpha\right) \cdot G^\alpha.
\]  

(A12)

With the use of Eqs. (A3) and (A4), the above formula is transformed further

\[
\text{div}_S I_S = \left((\Gamma_{\alpha\beta\gamma}^\delta G_{\alpha} \otimes G^\delta + B_{i\alpha}G_{\alpha} \otimes (-\Gamma_{\alpha\beta\gamma}^\delta G^\delta - B_{i\alpha}G^\delta)) \cdot G^\alpha\right)
\]

\[
= \left(\Gamma_{\alpha\beta\gamma}^\delta G_{\alpha} \otimes G^\delta + B_{i\alpha}G_{\alpha} \otimes G^\delta - \Gamma_{\alpha\beta\gamma}^\delta G_{\alpha} \otimes G^\delta - B_{i\alpha}G_{\alpha} \otimes G^\delta\right) \cdot G^\alpha
\]

\[
= (\Gamma_{\alpha\beta\gamma}^\delta G_{\alpha} \otimes G_{\alpha} + B_{i\alpha}G_{\alpha} \otimes G_{\alpha} - \Gamma_{\alpha\beta\gamma}^\delta G_{\alpha} \otimes G^\delta - B_{i\alpha}G_{\alpha} \otimes G^\delta) \cdot G^\alpha
\]

\[
= B_{i\alpha}G^\alpha \cdot n = B^\alpha \cdot n.
\]  

(A13)

where, in the last couple of transformations, a change of (dummy) indices was introduced, the relationships of Eqs. (A7) and (A8) were utilized, and orthogonality of \( n \) and \( G^\alpha \) was taken into account.

Considering that the mean curvature of a surface is defined as \( k = 0.5 \text{tr}(B) = 0.5(B_{11} + B_{22}) = 0.5B^\alpha \), it follows that

\[
\text{div}_S I_S = 2kn,
\]  

(A14)

which is the formula used in the main body of this paper.

Appendix B. Scalar formulas for the effective material properties

B.1. Some basic operations on rank four isotropic tensors

The operations presented here are standard, but they are reiterated here for a more detailed explanation of some transformations used in the main body of this paper.

Considering that both the matrix and the nanoinhomogeneities are assumed isotropic and linearly elastic, all tensors involved in the tensorial form of the formula for the effective elastic properties, Eq. (3.34), are isotropic fourth order tensors. Thus, for example,

\[
C_1 = \lambda_1^2 I_0 + \mu_1 [4I + (12)I],
\]

(B.1)

\[
C_2 = \lambda_2^2 I_0 + \mu_2 [4I + (12)I],
\]

where \( \lambda_1, \mu_1, \lambda_2, \mu_2 \) are Lamé constants characterizing the bulk material of the nanoinhomogeneities and the material of the matrix, respectively, \( I_0 \) and \( I \) are the rank two and rank four identity tensors, and the operation \((12)\) represents the “swap” (or transposition) on the first and the second position of the following tensor. To be more specific, if \( G_i, G^j, i = 1, 2, 3, \) denote a vector basis and its reciprocal (or dual) vector basis (cf. Appendix A)

\[
\overrightarrow{I} = G_i \otimes G^i = G^i \otimes G_i, \quad \overrightarrow{I} = G_i \otimes G^i \otimes G^i \otimes G_i = G^i \otimes G^i \otimes G^i \otimes G_i,
\]

\[
(12)I = G_j \otimes G^j \otimes G^j \otimes G_j = G^j \otimes G^j \otimes G^j \otimes G_j.
\]  

(B.2)

It is noted that the tensor \( L \) of Eq. (3.24), which is not a constitutive tensor, also has the form of Eq. (B.1), and that all linear combinations of tensors having that form (such as those present in Eqs. (2.5), (3.31)) are tensors possessing the same form, with the same linear combination of the parameters \( \lambda \) and \( \mu \).

It is clear that, if the tensors like those presented in Eq. (B.1) operate on second rank non-symmetric tensors, their part containing the swap \((12)\) is needed to yield the symmetric second order tensor as the outcome of this operation. Given that, in this particular application, the second order tensors on which all fourth rank tensors entering Eq. (3.34) operate are symmetric, the swaps included in Eq. (B.1) are not needed. Thus, in the present case, Eqs. (B.1) may be cast in the following equivalent forms, a common practice in describing problems of linear elasticity,

\[
C_1 = \lambda_1^2 I_0 + 2\mu_1 [4I + (12)I],
\]

(B.3)

\[
= 3K_1 H + 2\mu_1 D,
\]

\[
C_2 = \lambda_2^2 I_0 + 2\mu_2 [4I + (12)I],
\]

where \( K_1 = (3\lambda_1 + 2\mu_1)/3, \) \( K_2 = (3\lambda_2 + 2\mu_2)/3, \) are the bulk moduli of the corresponding materials and the fourth rank tensors \( H \) and \( D, \) interpreted as operators, are projectors of the second order tensors on their volumetric (or hydrostatic) subspace and deviatoric.
subspace, correspondingly (cf. Brisard et al. (2010) or Duan et al. (2005c)). It can be verified, either directly by employing Eqs. (B.2) or simply by interpretation of the operations of the projection, that

$$H : \mathbf{H} = \mathbf{H} : D = D : H = 0, \quad D : D = D.$$  

(B.4)

All rank four tensors present in Eq. (3.34), have the form expressed in the rightmost part of Eq. (B.3). For tensors possessing such representation extremely convenient formulas for the superposition of the operations those tensors represent (i.e., their multiplication, or double contraction) and for their inversion are deduced when the properties of Eq. (B.4) are taken into account. For the superposition one has

$$C_1 \cdot C_2 = C_1 + 9 K_c H + 4 \mu_1 \mu_2 D,$$  

(B.5)

and for the inversion (illustrated here only for tensor $C_1$)

$$C_1^{-1} = \frac{1}{3 K_1} H + \frac{1}{2 \mu_1} D.$$  

So, in the case of multiplication the corresponding constants have to be multiplied whereas in the case of inversion they need to be inverted; otherwise the form of the resulting tensor remains unchanged. These formulas greatly facilitate further evaluation of Eq. (3.34).

**B.2. Development of the scalar formulas for the effective material properties**

It is first noted that tensors involved in Eq. (3.34), and defined in the main body of the paper, can be presented in the following forms ($\mathbf{C}$ of Eq. (2.8) with the help of Eq. (B.6))

$$L = a \mathbf{i} \otimes \mathbf{i} + b \left[ \mathbf{i} + (12) \mathbf{i} \right] = \frac{3}{2} \mathbf{a} \mathbf{i} \otimes \mathbf{i} + 2 b \mathbf{i}^2$$  

$$= \frac{3}{2} \left[ \mathbf{a} \mathbf{i} \otimes \mathbf{i} \right] + 2 b \left[ \frac{1}{3} \mathbf{i} \otimes \mathbf{i} \right] = 3 K_1 H + 2 b D.$$  

(B.7a)

$$C_3 = 3 K_1 H + 2 (\mu_1 - \mu_2) D = 3 K_3 H + 2 \mu D.$$  

(B.7b)

$$C_4 = C_1 = 2 c_1 K_1 + c_2 K_2 + 2 (c_1 \mu_1 + c_2 \mu_2) D = 3 K_1 H + 2 \mu D.$$  

(B.7c)

$$C = \frac{3}{2} \left[ \frac{K_1 - K_2}{c_1 \mu_1 + c_2 \mu_2} \right] H + 2 \left( \frac{H_1 - H_2}{c_1 \mu_1 + c_2 \mu_2} \right) D = 3 K_1 H + 2 \mu D.$$  

(B.7d)

$$C_e = 3 K_1 H + 2 \mu D, \quad C_c = \mathbf{C}, \quad C_1 \leq C_2 \quad \text{and} \quad C_1 \leq C, \quad C_2 \leq C.$$  

(B.7f)

$$C' = 3 c_2 K_1 + c_1 K_2 - K_1 H + 2 (c_1 \mu_1 + c_2 \mu_2 - \mu) D = 3 K_1 H + 2 \mu D.$$  

(B.7g)

The meaning of the new symbols introduced at the rightmost part of the above equations is easily inferred from those equations, except that for the symbols in Eq. (B.7g) two possibilities exist, depending on which of the two conditions specified in Eq. (B.7f) characterizes the material under consideration. In either case, all of those variables are related to $K_1, \mu_1, K_2, \mu_2, c_1$ and $c_2 = 1 - c_1$.

Furthermore, as can be seen in Eq. (B.3), $H : D = 4$, so the rank four tensor object, present in Eq. (3.34), can also be represented in the same form as all of the other tensors in that equations, specified earlier in this section. With that observation, evaluation of Eq. (3.34) is easy if use is made of Eqs. (B.5), (B.6) and (B.7). It leads to the following formula for the tensor of effective elastic constants

$$C' = 3 K_1 H + 2 \mu D.$$  

(B.8)

where $K'$ depends only on the $K$'s defined in Eqs. (B.3) and (B.7), and $\mu'$ depends only on $\mu$'s in those equations (although $K$ and $b' = b(0)$ of Eq. (B.7a) are further dependent on $K_c$ and $\mu_c$ in view of Eq. (3.25)).

In what follows both the scalar formulas for the effective bulk modulus $K'$ and for the effective shear modulus $\mu'$ will be developed. However, due to the assumptions made in this work, which were designed only to estimate the influence of the surface effects on the bulk modulus, no influence of the surface properties on the effective shear modulus $\mu'$ is expected. In the subsequent development the following (easily verifiable) identity will be used

$$\frac{4 [\mu + \mu_c]}{2 R K_c} \left[ \frac{1 + \nu_c}{1 - \nu_c} \right] \frac{1}{9} \otimes \mathbf{I} = - \mathbf{L} : \left[ 3 K_l H + 2 \mu D \right],$$  

(B.9)

in which $K_l$ and $\mu_c$ evaluated taking into account definition of tensor $L$ given in Eqs. (3.23), (3.24), and (3.25), are

$$K_l = \frac{4}{3 R} [\mu + \mu_c], \quad \mu_c = 0.$$  

(B.10)

Then, the expression in the rightmost bracket of Eq. (3.34) can be transformed to the following form

$$c_2 L : C_3 - \frac{4 [\mu + \mu_c]}{9 R K_c} \left[ \frac{1 + \nu_c}{1 - \nu_c} \right] \frac{1}{9} \otimes \mathbf{I} = \mathbf{L} : [c_2 C_3 + 3 K_l H] = 9 K [c_2 K_l - K_3] + K_3 H + 4 b_c [\mu_c - \mu_2] D.$$  

(B.11)

After a similar evaluation of the expression in Eq. (3.34) is inverted, after its inversion (in accord with Eq. (B.6)), its combination with $I = H + D$ and, finally, after its contraction with the tensor of Eq. (B.11), the formula presented in Eq. (B.8) is arrived at, with the following scalar expression for the effective bulk modulus

$$K' = R + \frac{9 c_1 K_l (K_l - K_3) c_2 (K_l - K_3) + K_3}{1 - 9 K [c_2 K_1 + c_2 K_1 - K_1 + K_3]}.$$  

(B.12)

We recall that in the above expression $K$ depends on $a$ and $b$ of Eq. (3.25) (as seen in Eq. (B.7a)) and, therefore, on the properties of the reference medium; $K_3$ is defined in Eq. (B.10); and $K_c$ is equal to either $K$ or $K_l$, depending on which of the conditions specified in Eq. (B.7f) is satisfied.

The scalar formula for the shear modulus that is obtained within the framework of the model constructed in this work is found to be

$$\mu' = \pi' + \frac{4 c_1 c_2 b (\mu_1 - \mu_2)^2}{1 - 4 b c_2 H_1 + c_2 H_1 - H_1}.$$  

(B.13)

As expected, this formula does not include the interface effects and coincides with the one developed by Khoroshun (1978) and Khoroshun et al. (1993).


