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ORIGINAL ARTICLE

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Closed-form formulas for the effective properties of random particulate nanocomposites with complete Gurtin–Murdoch model of material surfaces

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Abstract The objective of this work is to present an approach allowing for inclusion of the complete Gurtin–Murdoch material surface equations in methods leading to closed-form formulas defining effective properties of particle-reinforced nanocomposites. Considering that all previous developments of the closed-form formulas for effective properties employ only some parts of the Gurtin–Murdoch model, its complete inclusion constitutes the main focus of this work. To this end, the recently introduced new notion of the energy-equivalent inhomogeneity is generalized to precisely include all terms of the model. The crucial aspect of that generalization is the identification of the energy associated with the last term of the Gurtin–Murdoch equation, i.e., with the surface gradient of displacements. With the help of that definition, the real nanoparticle and its surface possessing its own distinct elastic properties and residual stresses are replaced by an energy-equivalent inhomogeneity with properties incorporating all surface effects. Such equivalent inhomogeneity can then be used in combination with any existing homogenization method. In this work, the method of conditional moments is used to analyze composites with randomly dispersed spherical nanoparticles. Closed-form expressions for effective moduli are derived for both bulk and shear moduli. As numerical examples, nanoporous aluminum is investigated. The normalized bulk and shear moduli of nanoporous aluminum as a function of residual stresses are analyzed and evaluated in the context of other theoretical predictions.

Keywords Nanoparticles · Nanocomposite · Composite of stochastic structure · Size-dependent effective properties · Gurtin–Murdoch interface conditions · Nanoporous metals

1 Introduction

It is well known that both local fields and average properties of materials containing heterogeneities on the nanoscale level, referred to as nanomaterials, are often appreciably influenced by effects taking place at the

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matrix–inhomogeneity interface. Those effects may include the presence of residual stresses and changed material properties or various topological changes, such as presence of cracks, for example. Depending on which of those effects are considered dominant, analysis of such materials should include appropriate models of interfaces, in combination with equations describing the bulk materials of the matrix and the inhomogeneities.

One of the models that have recently become very widely used is that proposed by Gurtin and Murdoch [13]. It assumes that interfaces are coherent (i.e., displacements are continuous), infinitesimally thin, and characterized by the presence of residual stresses and material properties different from those of the bulk material on either side of those interfaces. In the linear version of the model, the complete constitutive equation of the interface reads

$$\boldsymbol{\sigma}_S(\mathbf{x}) = \tau_0 \overset{2}{\mathbf{I}}_S + 2\,[\mu_S - \tau_0]\,\boldsymbol{\varepsilon}_S(\mathbf{x}) + [\lambda_S + \tau_0]\,\mathrm{tr}(\boldsymbol{\varepsilon}_S(\mathbf{x}))\,\overset{2}{\mathbf{I}}_S + \tau_0 \nabla_S \mathbf{u}(\mathbf{x}), \tag{1.1}$$

where $\boldsymbol{\sigma}_S$ is the surface stress tensor, $\boldsymbol{\varepsilon}_S$ is the interface/surface strain tensor, $\overset{2}{\mathbf{I}}_S$ represents the identity tensor in the plane tangent to the surface, τ_0 is the magnitude of the deformation-independent (residual) surface/interfacial tension (assumed "hydrostatic" and constant in Gurtin–Murdoch model), λ_S, μ_S are surface Lamé constants, while $\nabla_S \mathbf{u}(\mathbf{x})$ denotes the surface gradient of the interface displacement field. This model of interfaces is also adopted herein. From the point of view of mechanics, τ_0 appears in Eq. (1.1) as a result of small perturbations superposed on the existing equilibrium state associated with the stress τ_0 (as clearly seen in development of Gurtin and Murdoch [13]). The last three terms of that equation represent the corresponding perturbation in the stress field, and the very last of them reflects what (in structural engineering) is called "P–Δ effect". Because of this last term, the local stress perturbations may be present even when $\boldsymbol{\varepsilon}_S$ vanishes.

There are two issues that may be mentioned in the context of this model, however. The first one is that the three constants characterizing this model are available only for a small number of materials [e.g., [31]]. The second issue is that this model is a special case of a more general interphase model introduced in [15] which is arguably the most comprehensive model possible for an interphase. Its general case is characterized by as many as 78 parameters [45, Section 5], and its use in any practical analysis seems currently impossible.

For various (often unspecified) reasons, in many existing publications adopting Gurtin–Murdoch interface model Eq. (1.1) is not used in its complete form. In some of them, τ_0 is ignored altogether [1,2,4,7,8,11,41,44], whereas in others the last term is left out [4,36,37] or only the normal component of the last term is not included [20,30]. The complete Gurtin–Murdoch equation is used in [19,28], but only in the analysis of a single spherical cavity. To the authors' best knowledge, the first publication in which Eq. (1.1) was used in its entirety to analyze a material with multiple inclusions is that of Mogilevskaya et al. [32]. However, in that paper, to obtain the local (stress and strain) fields governing equations are solved numerically in terms of a series expansion. Within such approach, incorporation of the complete equation (1.1) appeared straightforward via properly modified interface conditions. Mogilevskaya et al. [32] paved the way for many subsequent developments in which local fields for problems involving many inclusions are found through some sort of analytical solution of the governing equations incorporating complete Eq. (1.1) [6,26,33]. In addition to the significance of the so-determined local fields in the evaluation of nanomaterials' strengths, through their averaging they have been used in determination of effective properties of nanomaterials [26,33]. Evaluation of the effective properties without knowledge of the local fields and partial inclusion of the last term of Eq. (1.1) has been presented by Huang and Sun in [21]. In their work, the Authors omit those parts of the surface displacement gradient which are related to rotation of the surface element about a vector tangent to the surface. Without them, the approach used in [21] does not differ from those in which the last term of Eq. (1.1) is neglected altogether, and only constitutive parameters need to be changed (cf. [8]). As a result, the conclusions of Huang and Sun [21] concerning the influence of the last term in Eq. (1.1) on the effective properties of composites may not be entirely valid. More specific justification of these comments will be provided in Sect. 3 of this work, after a rigorous formula for the surface gradient of displacements is developed.

While the use of complete Eq. (1.1) is relatively straightforward if local fields are to be found via the analytic or numerical solution of the governing equations, technical difficulties necessitated some simplifications of that equation in case of methods used for determination of effective properties of nanomaterials directly, i.e., without knowledge of local strain and stress fields. Although the need for simplifications of the Gurtin–Murdoch equation may be seen as a drawback of those methods, in some situations such simplifications are justifiable on physical ground, considering the relative magnitude of the constants involved in Eq. (1.1). In addition, the fact that direct approaches do not require solutions for local fields, and that they are often capable of providing closed-form formulas for the required effective properties, constitutes their enormous advantage. Closed-form expressions for effective properties should be more efficient and convenient to use in the design

of materials (cf. [40]), which—if necessary—can then be double-checked by methods based on the knowledge of local fields. It is those positive features that justify continuous development of methods aimed at direct determination of effective properties (in addition to the ones based on averaging of local fields). Yet, to the authors' best knowledge (exposed in the comments presented earlier) none of the existing closed-form results for effective material properties obtained via direct approaches (i.e., not based on evaluation of local fields) correctly include the complete Gurtin–Murdoch surface equation, and it is the objective of this work to present a remedy to this situation. In that context, the literature review presented in this manuscript focuses on the main original articles that attempt to incorporate the last term of Eq. (1.1) in evaluation of the effective properties of nanocomposites in some (even incomplete) way. There are a number of other publications on the subject that do not substantially differ from those quoted herein, or are unrelated to evaluation of the effective properties, and many of them are evaluated in these authors' previous publications [36,37] or in the articles cited in this work.

The only closed-form expression involving complete Gurtin–Murdoch model appears to be that for the effective bulk modulus of nanoporous material presented in [26]. However, it was not obtained using a methodology explicitly developed to obtain closed-form estimates of effective properties. Instead, solution of the governing differential equations was sought in form of series expansion, and restriction of the series to just the first term of that solution led to a closed-form formula for the effective bulk modulus. As remarked earlier, all approaches of that kind allow for a relatively straightforward inclusion of complete Eq. (1.1) into the equations they are based on. However, in general, they are quite complex and typically limited to simple shapes of inhomogeneities (spheres). In addition, only the formula for the effective bulk modulus has been developed that way. In contrast, the approach based on the equivalent inhomogeneity proposed here offers a rather transparent way of including complete Gurtin–Murdoch model in several existing approaches designed to obtained closed-form effective properties for standard composite materials, including numerical approaches (although equivalent inhomogeneity is not necessary in those cases). It is also applicable to more complex shapes of in homogeneities, such as cylinders or spheroids, for example.

We consider nanomaterials with inhomogeneities randomly dispersed in the matrix. Other characteristics that may undergo some random variations are shape and size of nanoinhomogeneities, their orientation or their material properties. Evaluation of the effective properties of such materials based on local fields requires the solution of the governing equations for many realizations, with subsequent statistical analysis of the results; it is thus tedious and time consuming. Under those circumstances, a robust method allowing for direct evaluation of effective properties would clearly be advantageous. An approach partially accomplishing that goal in context of materials with isotropic effective properties is Hashin's [16] composite sphere assembly. Self-consistent schemes [3,5] are also capable of rendering closed-form estimates for a class of random composites. Each of those approaches, while effective in many situations, is based on rather intuitive arguments and—like any other approach—possesses their own limitations, particularly if various interface effects need to be analyzed. For example, in the analysis of a composite with spring layer model of the interface presented in [17,18] the composite sphere approach could provide a closed-form expression only for the effective bulk modulus. To obtain the effective shear modulus, Hashin [18] employs the generalized self-consistent scheme, but only a numerical solution could be obtained in this case.

An effective method capable of rendering closed-form effective properties for a large class of random composite materials is the method of conditional moments (MCM) [23,24]. Its comparative evaluation in context of other methods is presented in [25,35,38]. It is a statistical method expressly designed to evaluate effective properties of materials with random characteristics, and it is based on rigorous mathematical foundations.

No contribution aiming at the direct development of closed-form formulas for effective properties of composites was able to correctly incorporate the complete Gurtin–Murdoch model of interface. This is not likely to be the result of its perceived small significance, as within the same time span it was included in several numerical analyses of composites, e.g., [6,26,33]. The last term in Eq. (1.1) had been ignored in [36], and even then only the effective bulk modulus of the considered nanomaterial could be determined. Subsequently, to determine bulk and shear moduli of nanomaterials using MCM, in [37] a different approach was proposed, but—for technical reasons—the last term of Eq. (1.1) still had to be neglected. The approach is based on the notion of the energy-equivalent inhomogeneity and is capable of providing closed-form expressions for both bulk and shear moduli.

The main goal of this work is to show that the new concept of energy-equivalent inhomogeneity, recently presented in [37,39], permits direct evaluation of effective properties of nanomaterials which includes complete Eq. (1.1). By showing this, we close a gap that existed in the literature on direct evaluation of effective properties for at least the past 10 years. In addition, we aim at evaluating the effectiveness of the proposed approach by

means of numerical examples and comparisons with results obtained using other techniques, also those based on the knowledge of local stress and strain fields.

With the new definition of the energy-equivalent inhomogeneity, any micromechanical method used to evaluate the overall properties of composites with perfect interfaces can be employed to evaluate properties of composites with Gurtin–Murdoch model of interphases (as well as with other models). The only issue that remains to be resolved pertains to the accuracy of such an approach. That its accuracy may be acceptable can be gleaned from the existing analysis of some specific cases. For example, Duan et al. [7] used the self-consistent approach to obtain the effective properties of the particulate composites with Gurtin–Murdoch interphase model. The obtained formulas revealed that the same effective properties could be obtained if the inhomogeneity and its interphase are replaced with a single inhomogeneity of suitable chosen properties (that is, equivalent inhomogeneity) that is perfectly bonded with the matrix. The effective bulk modulus reported by Duan et al. [7] is the same as those derived in the present manuscript (and in [37]), if the contribution of the last term of the Gurtin–Murdoch model is removed (as done by Duan et al. [7]). This implies that the energy-equivalent inhomogeneity discussed in this work is applicable in the context of the self-consistent approach. The same logic is applicable in relation to the spring layer model of interphases, and identical conclusion follows from comparison of the results for the bulk modulus presented by Hashin [17] and those reported in [39]. Thus Hashin's composite sphere assemblage approach can also successfully employ the notion of energy-equivalent inhomogeneity discussed herein. It is understood, however, that these cases constitute only a limited support for the approach proposed in this work and further investigations, particularly in the context of numerical approaches, are needed.

A different, energy-based formulation of equivalent inhomogeneity has been proposed in [8,11] (cf. also [21]). In both of these contributions, the stiffness tensor of the equivalent inhomogeneity was determined using the Eshelby's formula for the change of elastic energy caused by insertion of an inhomogeneity in an infinite matrix [9]. They assume that such change due to embedding the equivalent inhomogeneity is equal to the change caused by embedding the original inhomogeneity together with its interface. This approach yields shear modulus of the equivalent particles (or fibers) which are dependent on the properties of the matrix material. Dependence on properties of the matrix constitutes the fundamental difference between the definitions of the equivalent inhomogeneity presented in [8,11] and that introduced here. In addition, the equivalent inhomogeneity presented in this work does include complete Eq. (1.1), whereas the ones proposed in [8,11] (or [21]) do not.

For completeness of the presentation, it is noted that Gurtin–Murdoch model plays also a role in analysis of problems which are somewhat different from what is discussed in this work. For example, the surfaces affect behavior of nanosize structural elements, such as beams, plates and shells (e.g., [1,27,29]). In this context, the analysis of stability and vibrations of nanobeams described, e.g., by Liu et al. [29], leads to the conclusion that presence of surface tension changes the buckling load and the natural frequencies of nanobeams. This appears to be a subject of an ongoing debate as it seems to confirm the observations reported in [27] but contradicts the subsequent discussion in Gurtin et al. [14]. The present authors are in favor of the arguments presented by Gurtin et al. [14].

To illustrate that the presented notion of equivalent inhomogeneity can be used in combination with any method of evaluating the effective properties of composites, our choice is the MCM rather than the self-consistent approach that is used more commonly. MCM has several attributes, which have been described earlier in this introduction. Even though the choice of the method used to develop the effective properties of a composite is in this work a secondary issue, to make it self-contained in the next section the governing equations and a brief description of the MCM are provided. The discussion and the results of this section will outline the manner in which surface effects (including some aspects related to surface tension) are introduced in the context of MCM, accentuate the advantages associated with the notion of equivalent inhomogeneity adopted herein and will establish a framework for subsequent developments. Section 3 deals with the notion of energy-equivalent nanoinhomogeneities. In that section, contributions of various terms of Eq. (1.1) to the effective properties on energy-equivalent nanoinhomogeneities are presented in general terms, with the development quantifying those contributions relegated to "Appendix". The subsequent two sections present formulas for effective properties of considered nanomaterials obtained using the method advocated herein (Sect. 4) and discussion of numerical results (Sect. 5). Some reflections on the proposed approach and on the results obtained are described in Sect. 6.

2 Fundamentals of the proposed approach

2.1 Governing equations

Consider a representative macrovolume V consisting of a matrix with randomly distributed nanoinhomogeneities (see e.g., Fig. 1). Under usual separation of scales condition and under uniform loading the macroscopic stress $\bar{\boldsymbol{\sigma}}$ and strain $\bar{\boldsymbol{\varepsilon}}$ are connected by

$$\bar{\boldsymbol{\sigma}} = \mathbf{C}^*:\bar{\boldsymbol{\varepsilon}}, \tag{2.1}$$

where $\mathbf{C}^*$ is the effective stiffness tensor, and the over-bar denotes the operation of statistical averaging.

For linear elastic materials, the problem of finding the effective stiffness tensor requires solving the following set of equations

- equations of equilibrium:

$$\operatorname{div} \boldsymbol{\sigma}(\mathbf{x}) = \mathbf{0}, \tag{2.2}$$

- Hooke's law:

$$\boldsymbol{\sigma}(\mathbf{x}) = \mathbf{C}(\mathbf{x}):\boldsymbol{\varepsilon}(\mathbf{x}), \tag{2.3}$$

- linear kinematic relation:

$$\boldsymbol{\varepsilon}(\mathbf{x}) = \operatorname{sym}\left(\nabla \mathbf{u}(\mathbf{x})\right), \tag{2.4}$$

where $\mathbf{x}$ is the position vector within the considered continuum. If the surface (interface) effects are adequately described by the Gurtin–Murdoch model [12,13], these equations need to be supplemented by the following relations at the interface S between matrix and nanoinhomogeneities, oriented by the unit vector $\mathbf{n}$ normal to S,

$$[\mathbf{u}(\mathbf{x})]_S = \mathbf{0}, \quad [\boldsymbol{\sigma}(\mathbf{x})]_S \cdot \mathbf{n}(\mathbf{x}) + \operatorname{div}_S \boldsymbol{\sigma}_S(\mathbf{x}) = \mathbf{0}. \tag{2.5a}$$

The term $\operatorname{div}_S \boldsymbol{\sigma}_S$ denotes the surface divergence of the surface stress tensor $\boldsymbol{\sigma}_S$ [13] defined by Eq. (1.1). Before explaining the meaning of the remaining standard symbols present in Eqs. (2.2)–(2.5a), the first (deformation-independent) term of Eq. (1.1) is separated from the rest of that equation to facilitate the

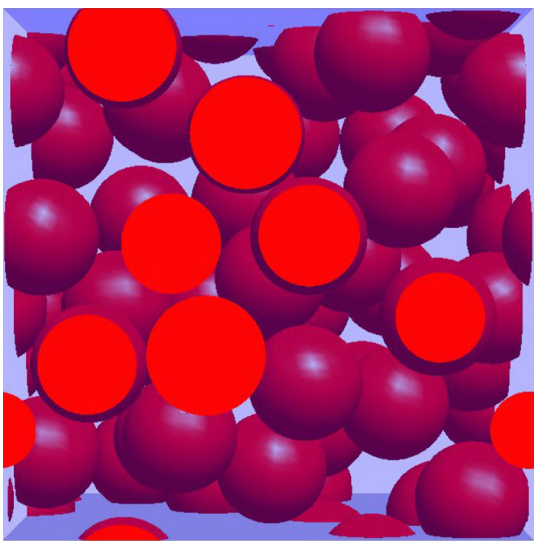

Fig. 1 Representative macrovolume V consisting of a matrix with randomly distributed nano-inhomogeneities

subsequent development. Given that τ_0 is assumed constant, divergence of this term is easily evaluated considering that $\mathrm{div}_S \mathbf{I}_S = 2\kappa \mathbf{n}$ (cf. [12]), where κ is the mean curvature of the interface. Consequently, the second of the above equations can be written in the following form

$$[\boldsymbol{\sigma}(\mathbf{x})]_S \cdot \mathbf{n}(\mathbf{x}) + \mathrm{div}_S \boldsymbol{\sigma}^u_S(\mathbf{x}) + 2\tau_0 \kappa \mathbf{n} = \mathbf{0}, \tag{2.5b}$$

where

$$\boldsymbol{\sigma}^u_S(\mathbf{x}) = 2\left[\mu_S - \tau_0\right] \boldsymbol{\varepsilon}_S(\mathbf{x}) + \left[\lambda_S + \tau_0\right] \mathrm{tr}\left(\boldsymbol{\varepsilon}_S(\mathbf{x})\right) \mathbf{I}_S + \tau_0 \nabla_S \mathbf{u}(\mathbf{x}) \tag{2.5c}$$

is the deformation-dependent part of the surface stress tensor.

In Eqs. (2.2)–(2.5) $\boldsymbol{\sigma}(\mathbf{x})$ and $\boldsymbol{\varepsilon}(\mathbf{x})$ are the stress and strain tensors in the bulk material (matrix or inhomogeneity), $\mathbf{u}(\mathbf{x})$ is the displacement vector. The fourth-order tensor of elastic constants $\mathbf{C}(\mathbf{x})$ is a random, statistically homogeneous function of coordinates with a finite scale of correlation and linked to inclusion and matrix properties via

$$\mathbf{C}(\mathbf{x}) = \mathbf{C}_1 H\left(z(\mathbf{x})\right) + \mathbf{C}_2 H\left(-z(\mathbf{x})\right), \tag{2.6}$$

where H is the Heaviside function and $\mathbf{C}_1$ and $\mathbf{C}_2$ denote values of the tensors of elastic moduli in the inclusions and matrix, respectively. The function $z(\mathbf{x})$ is any function satisfying

$$\begin{array}{ll} z(\mathbf{x}) > 0, & \text{if } \mathbf{x} \in V_1 \\ z(\mathbf{x}) = 0, & \text{if } \mathbf{x} \in S \\ z(\mathbf{x}) < 0, & \text{if } \mathbf{x} \in V_2 \end{array}, \tag{2.7}$$

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

It is assumed that at each interface the normal $\mathbf{n}$ points away from the inclusion. The square brackets in Eqs. (2.5a) and (2.5b) indicate the jump of field quantities across the interface, defined as their value on the side toward which the normal $\mathbf{n}$ is pointing minus their value on the side from which it is pointing.

The system of differential equations (2.2)–(2.5) is transformed to the system of integral equations with the help of Green's function $\mathbf{G}$, which is defined by the following boundary-value problem

$$\mathrm{div}\left(\mathbf{C}_c : \nabla \mathbf{G}(\mathbf{x})\right) + \delta(\mathbf{x}) \overset{2}{\mathbf{I}} = \mathbf{0}, \quad \mathbf{G}(\mathbf{x})\,|_\infty = \mathbf{0}, \tag{2.8}$$

where $\mathbf{C}_c$ is the constant tensor describing elasticity of the selected reference medium, $\delta(\mathbf{x})$ denotes the Dirac delta function and $\overset{2}{\mathbf{I}}$ is the identity tensor of rank two. Then, fluctuations in the displacement field within the entire region V are described by (see [35,36]):

$$\mathbf{u}^0(\mathbf{x}) = \int_V \mathbf{G}(\mathbf{x}-\mathbf{y}) \cdot \mathrm{div}\left(\mathbf{C}^0(\mathbf{y}) : \boldsymbol{\varepsilon}(\mathbf{y}) - \boldsymbol{\beta}\right) \mathrm{d}V_y - \oint_S \mathbf{G}(\mathbf{x}-\mathbf{y}) \cdot \left[\mathrm{div}_S \boldsymbol{\sigma}^u_S(\mathbf{y}) + 2\tau_0 \kappa \mathbf{n}(\mathbf{y})\right] \mathrm{d}S_y, \tag{2.9}$$

where $\boldsymbol{\beta}$ is an arbitrary constant.

We consider macrovolumes and macrosurfaces as infinite (they need to be considerably lager than the dimensions of inhomogeneities) and the boundary conditions have the form:

$$\mathbf{u}^0(\mathbf{x})\,|_\infty = \mathbf{0}. \tag{2.10}$$

The linear kinematic relations of Eq. (2.4) combined with Eq. (2.9) and with the Gauss' theorem lead to stochastically nonlinear integral equations for the random strain field (see [36] for more details)

$$\boldsymbol{\varepsilon}(\mathbf{x}) = \bar{\boldsymbol{\varepsilon}} + \mathbf{K}(\mathbf{x}-\mathbf{y}) * \left[\mathbf{C}^0(\mathbf{y}) : \boldsymbol{\varepsilon}(\mathbf{y})\right] - \mathrm{sym}\left\{\nabla_x \oint_{S_I} \mathbf{G}(\mathbf{x}-\mathbf{y}) \cdot \left[\mathrm{div}_S \boldsymbol{\sigma}^u_S(\mathbf{y}) + 2\tau_0 \kappa \mathbf{n}(\mathbf{y})\right] \mathrm{d}S_y\right\}. \tag{2.11}$$

The operator $\mathbf{K}(\mathbf{x}-\mathbf{y})$ acts according to

$$\mathbf{K}(\mathbf{x}-\mathbf{y}) * \boldsymbol{\psi}(\mathbf{y}) = \int_V \mathrm{sym}\left(\nabla_x \left(\nabla_x \mathbf{G}(\mathbf{x}-\mathbf{y})\right)\right) : \left[\boldsymbol{\psi}(\mathbf{y}) - \bar{\boldsymbol{\psi}}\right] \mathrm{d}V_y, \tag{2.12}$$

with $\bar{\boldsymbol{\varepsilon}}$ and $\bar{\boldsymbol{\psi}}$ being mean (expectation) values of $\boldsymbol{\varepsilon}(\mathbf{x})$ and $\boldsymbol{\psi}(\mathbf{y})$. $\mathbf{C}^0(\mathbf{y})$ in Eq. (2.11) is the fluctuations in elastic constants and defined as

$$\mathbf{C}^0(\mathbf{y}) = \mathbf{C}(\mathbf{y}) - \mathbf{C}_\mathrm{c}. \tag{2.13}$$

Issues related to selection of $\mathbf{C}_\mathrm{c}$ are discussed in [25,35–37] and also addressed in the next sections of this work.

The way to account for surface effects described by Eq. (2.11) is rigorous. However, evaluation of the surface integral containing $\boldsymbol{\sigma}_\mathrm{S}^\mathrm{u}$ on the right-hand side of Eq. (2.11) is a rather complex for arbitrary uniform loading. In [36], this was done under some approximating assumptions, valid only for overall volumetric deformations. To bypass that difficulty, an approach based on MCM in combination with a notion of energy-equivalent inhomogeneity was proposed in [37,39]. In that approach, the contribution of the surface integral in Eq. (2.11) related to $\boldsymbol{\sigma}_\mathrm{S}^\mathrm{u}$ is accounted for by a proper adjustment of bulk properties of the inclusions. The material is then analyzed as standard composite, i.e., involving no surfaces possessing their own mechanical characteristics. However, the external force of magnitude $2\tau_0\kappa\mathbf{n}$ representing the residual stress τ_0, present in Eq. (2.11), still needs to be integrated over the surface of the inclusions.

In accord with the above remarks, in the energy-equivalent inhomogeneity approach Eq. (2.11) is replaced by the equation for the energy-equivalent system (see [37])

$$\boldsymbol{\varepsilon}(\mathbf{x}) = \bar{\boldsymbol{\varepsilon}} + \mathbf{K}(\mathbf{x}-\mathbf{y}) * \left[\tilde{\mathbf{C}}^0(\mathbf{y}) : \boldsymbol{\varepsilon}(\mathbf{y})\right] - 2\tau_0\kappa\,\mathrm{sym}\left\{\nabla_x \oint_{\mathrm{S}_I} \mathbf{G}(\mathbf{x}-\mathbf{y})\cdot\mathbf{n}(\mathbf{y})\mathrm{d}S_y\right\}, \tag{2.14}$$

in which the surface integral of Eq. (2.11) containing $\boldsymbol{\sigma}_\mathrm{S}^\mathrm{u}$ is incorporated into $\tilde{\mathbf{C}}^0(\mathbf{x})$ as a result of changing properties of the inclusions from $\mathbf{C}_1$ to $\tilde{\mathbf{C}}_1$. Detailed developments leading to $\tilde{\mathbf{C}}_1$ are presented in Sect. 3. Tensor $\tilde{\mathbf{C}}^0(\mathbf{x})$ is defined as

$$\tilde{\mathbf{C}}^0(\mathbf{x}) = \tilde{\mathbf{C}}(\mathbf{x}) - \mathbf{C}_\mathrm{c} \quad \text{and} \quad \tilde{\mathbf{C}}(\mathbf{x}) = \tilde{\mathbf{C}}_1 H\left(z(\mathbf{x})\right) + \mathbf{C}_2 H\left(-z(\mathbf{x})\right). \tag{2.15}$$

Equation (2.14) is solved in an averaged sense by MCM to extract average strains. As described subsequently, this leads to the determination of average stresses and effective elastic constants.

2.2 Method of conditional moments

The integral equation (2.14) is rewritten as

$$\boldsymbol{\varepsilon}^{(1)} = \bar{\boldsymbol{\varepsilon}} + \mathbf{K}(\mathbf{x}^{(1)}-\mathbf{x}^{(2)}) * \left(\tilde{\mathbf{C}}^{0(2)} : \boldsymbol{\varepsilon}^{(2)}\right) - 2\tau_0\kappa\,\mathrm{sym}\left\{\nabla_{x^{(1)}} \oint_{\mathrm{S}_I} \mathbf{G}(\mathbf{x}^{(1)}-\mathbf{x}^{(2)})\cdot\mathbf{n}(\mathbf{x}^{(2)})\mathrm{d}S_{x^{(2)}}\right\}, \tag{2.16}$$

where the operator $\mathbf{K}(\mathbf{x}-\mathbf{y})$ is determined in Eq. (2.12) and the following abbreviated notation is introduced

$$\boldsymbol{\varepsilon}^{(1)} = \boldsymbol{\varepsilon}(\mathbf{x}^{(1)}), \quad \boldsymbol{\varepsilon}^{(2)} = \boldsymbol{\varepsilon}(\mathbf{x}^{(2)}), \quad \boldsymbol{\sigma}_\mathrm{S}^{(2)} = \boldsymbol{\sigma}_\mathrm{S}(\mathbf{x}^{(2)}), \quad \text{and} \quad \tilde{\mathbf{C}}^{0(2)} = \tilde{\mathbf{C}}^0(\mathbf{x}^{(2)}). \tag{2.17}$$

Employing statistical averaging [23,25] to Eq. (2.16) with respect to multi-point conditional densities and restricting the approach to two-point approximation (which implies the same strain distribution within each inclusion) the system of algebraic equations in terms of component-average strains $\bar{\boldsymbol{\varepsilon}}_\nu$ is obtained (see [35,37]):

$$\begin{aligned}\bar{\boldsymbol{\varepsilon}}_\nu = \bar{\boldsymbol{\varepsilon}} + \mathbf{K}(\mathbf{x}^{(1)}-\mathbf{x}^{(2)}) * \left\{p_{\nu 1}(\mathbf{x}^{(1)}-\mathbf{x}^{(2)})\left[\tilde{\mathbf{C}}_1^0 : \left\langle \boldsymbol{\varepsilon}^{(2)} \middle|{}^{(2)}_{1}\right\rangle\right] + p_{\nu 2}(\mathbf{x}^{(1)}-\mathbf{x}^{(2)})\left[\mathbf{C}_2^0 : \left\langle \boldsymbol{\varepsilon}^{(2)} \middle|{}^{(2)}_{2}\right\rangle\right]\right\} \\ + 2\kappa\tau_0\mathbf{C}_\mathrm{c}^{-1} : \mathbf{S} : \overset{2}{\mathbf{I}}, \quad \nu \in \{1,\ 2\}. \end{aligned} \tag{2.18}$$

The last term on the right-hand side is taken from Nazarenko et al. [36], where the surface integral identical to the one present in Eq. (2.16) was processed using the MCM; $\mathbf{S}$ is the classical Eshelby tensor [9,34]. In addition, the following notations were introduced in Eq. (2.18)

$$\bar{\boldsymbol{\varepsilon}}_\nu = \left\langle \boldsymbol{\varepsilon}^{(1)} \middle|{}^{(1)}_{\nu}\right\rangle, \quad p_{\nu k}\left(\mathbf{x}^{(1)}-\mathbf{x}^{(2)}\right) = \overline{f}\left({}^{(2)}_{k}\middle|{}^{(1)}_{\nu}\right). \tag{2.19a}$$

and

$$\tilde{\mathbf{C}}_1^0 = \tilde{\mathbf{C}}_1 - \mathbf{C}_c, \quad \mathbf{C}_2^0 = \mathbf{C}_2 - \mathbf{C}_c. \tag{2.19b}$$

$p_{\nu k}(\mathbf{x}^{(1)} - \mathbf{x}^{(2)})$ on the right-hand side of Eq. (2.18) denotes the probability that point $\mathbf{x}^{(2)}$ belongs to the kth component, provided point $\mathbf{x}^{(1)}$ belongs to the νth component, and $\langle \boldsymbol{\varepsilon}^{(2)}|_k^{(2)} \rangle$ is the expectation value of the strain tensor at point $\mathbf{x}^{(2)}$, provided that point $\mathbf{x}^{(2)}$ belongs to the kth component.

If two-point probabilities $p_{\nu k}(\mathbf{x}^{(1)} - \mathbf{x}^{(2)})$ are specified and the implied integration performed, Eq. (2.18) is transformed to [36]:

$$\bar{\boldsymbol{\varepsilon}}_\nu = \bar{\boldsymbol{\varepsilon}} + K^{\nu 1} : \tilde{\mathbf{C}}_1^0 : \bar{\boldsymbol{\varepsilon}}_1 + K^{\nu 2} : \mathbf{C}_2^0 : \bar{\boldsymbol{\varepsilon}}_2 + 2\kappa\tau_0 \left(\mathbf{C}_c\right)^{-1} : \mathbf{S} : \overset{2}{\mathbf{I}}, \tag{2.20}$$

where

$$\mathbf{K}^{\nu k} = \mathbf{K}(\mathbf{x}^{(1)} - \mathbf{x}^{(2)}) * p_{\nu k}(\mathbf{x}^{(1)} - \mathbf{x}^{(2)}), \quad \nu, k \in \{1,\ 2\}\,. \tag{2.21}$$

The two-point conditional probabilities $p_{\nu k}\left(\mathbf{x}^{(1)} - \mathbf{x}^{(2)}\right)$ characterize shape and arrangement of inclusions.

The selection of the tensor of elastic moduli $\mathbf{C}_c$ (representing properties of the reference body) deserves some additional comments. If high-order multi-point probabilities are included in MCM [25,35], results obtained for effective properties of the composite are insensitive to the selection of $\mathbf{C}_c$. However, accuracy of the resulting effective properties depends on that selection (the more the degree of the moments in MCM is reduced). For the two-point approximation, it is best if the constant tensor $\mathbf{C}_c$ is selected as close to anticipated effective properties of the composite as possible. It is shown in [25,35–37] that for composites with closed inclusions (e.g., spheres or ellipsoids) a good choice for $\mathbf{C}_c$ is:

$$\mathbf{C}_c = \begin{cases} \bar{\mathbf{C}}, & \text{if } \mathbf{C}_1 \le \mathbf{C}_2 \\ \overline{\overline{\mathbf{C}}}, & \text{if } \mathbf{C}_1 \ge \mathbf{C}_2 \end{cases}, \tag{2.22}$$

with $\bar{\mathbf{C}} = c_1\mathbf{C}_1 + c_2\mathbf{C}_2$ and $\overline{\overline{\mathbf{C}}} = \left[c_1\mathbf{C}_1^{-1} + c_2\mathbf{C}_2^{-1}\right]^{-1}$, where $c_1 = V_1/[V_1 + V_2]$ and $c_2 = 1 - c_1$ denote the volume fractions of the inclusions and of the matrix.

3 Energy-equivalent inhomogeneity

3.1 The concept of energy-equivalent inhomogeneity

The idea of the energy-equivalent inhomogeneity is essentially tantamount to a two-stage homogenization. In the first stage, using energy equivalence, the individual inhomogeneity and its surface are replaced by an effective inhomogeneity ("homogenized"), which combines the properties of both. In the second stage, the effective inhomogeneity is perfectly interfaced with the matrix (no jumps in interfacial tractions and in displacements) and effective properties of the composite material evaluated. In the second stage, any homogenization approach (numerical or analytical) can be used. The approach is predicated on the expectation that the overall stiffness characteristics of the analyzed nanomaterials should remain essentially the same whether the stiffness provided by the interface is treated independently (as done in [36]) or lumped together with the original stiffness of the nanoinhomogeneities. With such modified stiffnesses of all nanoinhomogeneities, combining their original properties and those of their interfaces, the composite may be considered as standard, in which there is no need for an independent inclusion of the surface effects.

The advantage of the approach based on the notion of energy-equivalent inhomogeneity is that it bypasses all technical difficulties caused by the presence of independently treated interfaces, encountered for example in [36]. All formulas for effective properties of standard random heterogeneous materials (i.e., those not involving interfaces) that, for example, can be relatively easily developed using MCM [25,35] become then directly applicable to nanomaterials (i.e., involving interfaces), as long as properties of inhomogeneities are properly modified to include surface effects.

To find modified properties of energy-equivalent inhomogeneities, the standard homogenization procedure is followed. It is postulated that, for arbitrary average (thus constant) deformation describing displacements on the boundary of the inhomogeneity-surface system (which is the same as the surface of the inhomogeneity),

those modified properties render the elastic energy of the energy-equivalent inhomogeneity which is equal to the sum of energies of the unmodified inhomogeneity and its interface. Boundary displacements associated with the average (constant) strain result in the same (average) strain in the entire volume of the inhomogeneity. This conclusion, together with the observation that whether the last term of Eq. (1.1) is neglected this equation is identical to constitutive equations for elastic membranes (whose energy expression is readily available [10]), leads to the following expression describing energy equivalence if the last term in Eq. (1.1) is neglected:

$$\frac{1}{2}V_I(\bar{\boldsymbol{\varepsilon}}_1{:}\tilde{\mathbf{C}}_1{:}\bar{\boldsymbol{\varepsilon}}_1) = \frac{1}{2}V_I(\bar{\boldsymbol{\varepsilon}}_1{:}\mathbf{C}_1{:}\bar{\boldsymbol{\varepsilon}}_1) + E_S = \frac{1}{2}V_I(\bar{\boldsymbol{\varepsilon}}_1{:}\mathbf{C}_1{:}\bar{\boldsymbol{\varepsilon}}_1) + \frac{1}{2}\oint_S \boldsymbol{\varepsilon}_S{:}\mathbf{C}_S{:}\boldsymbol{\varepsilon}_S \mathrm{d}S. \tag{3.1}$$

In the above equation, $\tilde{\mathbf{C}}_1$ is the tensor of the modified properties to be found, $\mathbf{C}_1$ is the tensor of unmodified properties while $\mathbf{C}_S$ is the tensor of interface properties; V_I is the volume of the inhomogeneity and S its surface; $\bar{\boldsymbol{\varepsilon}}_1$ is the average (constant) strain tensor within the volume of the inhomogeneity and $\boldsymbol{\varepsilon}_S$ is the associated surface strain tensor. In [37,39], it is shown that for spherical and isotropic inclusions, and for isotropic surface properties expressed in Eq. (1.1), the tensor $\tilde{\mathbf{C}}_1$ is also isotropic and its Lame constants are

$$\tilde{\mu} = \mu_1 + \hat{\mu}_S, \tag{3.2a}$$

$$\tilde{\lambda} = \lambda_1 + \widehat{\lambda}_S, \tag{3.2b}$$

where μ_1 and λ_1 are the original Lame constants of the inclusion, while

$$\widehat{\lambda}_S = \frac{2}{5R_0}\left[\bar{\mu}_S + 3\bar{\lambda}_S\right], \quad \hat{\mu}_S = \frac{1}{5R_0}\left[7\bar{\mu}_S + \bar{\lambda}_S\right] \tag{3.3}$$

with $\bar{\lambda}_S = \lambda_S + \tau_0$, $\bar{\mu}_S = \mu_S - \tau_0$ appearing as a result of the surface contribution in Eqs. (3.1) and (1.1). It is also shown in [37,39] that if the nanomaterial is treated as standard nonhomogeneous material (i.e., without including additional surface effects), but with constants specified in Eq. (3.2), properties of the nanomaterial are retrieved with remarkably high accuracy.

The above development is quite natural if the last term of Eq. (1.1) is neglected. Inclusion of the complete Eq. (1.1) within the framework of the energy-equivalent inhomogeneity is outlined in the next subsection, with some supporting derivations presented in "Appendix". The development presented there not only defines the contribution of that term, but also reveals that the justification of that contribution is, in fact, very analogous to the justification leading to the energy expression used in Eq. (3.1) and in [36].

3.2 Contribution of the surface gradient of displacement field to the energy of equivalent inhomogeneity

3.2.1 Evaluation of the surface gradient of the displacement field

The outstanding issue that needs to be addressed is how to modify the surface contribution in Eq. (3.1) in order to account for the surface gradient of displacements in Eq. (1.1). To this end, the surface gradient of the displacement field is evaluated first.

It is again assumed that the strains $\bar{\varepsilon}_1$ an inhomogeneity is subjected to are constant. Under those conditions, neglecting an additive constant vector, displacements of the surface of that inhomogeneity are expressed as

$$\mathbf{u}(\xi^\Lambda) = \bar{\boldsymbol{\varepsilon}}_1 \cdot \mathbf{r}(\xi^\Lambda), \tag{3.4}$$

where $\mathbf{r}(\xi^\Lambda)$ is the position vector of a point on that surface which is locally parameterized by ξ^Λ, $\Lambda \in \{1,\ 2\}$. Consequently (cf. [22]),

$$\nabla_S\mathbf{u} = \mathbf{u}_{,\Delta} \otimes \mathbf{G}^\Delta = [\bar{\boldsymbol{\varepsilon}}_1 \cdot \mathbf{G}_\Delta] \otimes \mathbf{G}^\Delta = \bar{\boldsymbol{\varepsilon}}_1 \cdot \left[\mathbf{G}_\Delta \otimes \mathbf{G}^\Delta\right] = \bar{\boldsymbol{\varepsilon}}_1 \cdot \overset{2}{\mathbf{I}}_S, \tag{3.5}$$

where $\mathbf{G}_\Delta = \mathbf{r}_{,\Delta}$ are vectors of the natural basis associated with the parameterization $\boldsymbol{\xi}^\Delta$ (tangent to the surface) and $\mathbf{G}^\Delta$ are vectors of the dual, or reciprocal, basis also tangent to the surface) satisfying $\mathbf{G}_\Delta \cdot \mathbf{G}^\Lambda = \delta^\Lambda_\Delta$ with δ^Λ_Δ being the "Kronecker delta".

3.2.2 Surface energy accounting for the surface gradient of the displacement field

The formula for the surface strain energy expression accounting for all terms of Eq. (1.1) is best deduced by exploring the *symmetric weak formulation* of the surface equilibrium equations. Those equations are described by Eq. (2.5a$_2$) or, equivalently, by Eq. (2.5b) which, for convenience, is rewritten as:

$$\mathrm{div}_S\, \boldsymbol{\sigma}^u_S + \mathbf{b} = \mathbf{0}, \tag{3.6}$$

where $\mathrm{div}_S\boldsymbol{\sigma}^u_S$ is the surface divergence of the deformation-related part of the surface stress tensor defined in Eq. (2.5c) and $\mathbf{b}$ is a three-dimensional vector combining interaction with the surrounding medium and $2\tau_0\kappa\mathbf{n}$ isolated in Eq. (2.5b). The *(nonsymmetric) weak form* of Eq. (3.6) is expressed by

$$\oint_S \mathbf{v}\cdot\left[\mathrm{div}_S\boldsymbol{\sigma}^u_S + \mathbf{b}\right] \mathrm{d}S = \mathbf{0}, \tag{3.7}$$

that should be satisfied for any *test function* $\mathbf{v}$ continuous over the surface S. Considering the general formula for the surface divergence operator, the above equation can be rewritten in the more explicit form

$$\oint_S \mathbf{v}\cdot\left[\boldsymbol{\sigma}^u_{S,\Delta}\cdot\mathbf{G}^\Delta + \mathbf{b}\right] \mathrm{d}S = \mathbf{0}. \tag{3.8}$$

Subsequent transformation is accomplished by converting integration over the surface S to integration over the two-dimensional space of parameters ξ^Λ, denoted here by S_0. Then, the first term of Eq. (3.8) is written as

$$\begin{aligned}\oint_S \mathbf{v}\cdot\mathrm{div}_S\boldsymbol{\sigma}^u_S \mathrm{d}S &= \oint_{S_0} \mathbf{v}\cdot\left[\boldsymbol{\sigma}^u_{S,\Delta}\cdot\mathbf{G}^\Delta\right]\sqrt{g}\mathrm{d}\xi^1\mathrm{d}\xi^2 = \oint_{S_0}[\sqrt{g}\mathbf{v}\otimes\mathbf{G}^\Delta]{:}\boldsymbol{\sigma}^u_{S,\Delta}\mathrm{d}S_0 \\ &= \left\{\oint_{S_0}\left[\left(\sqrt{g}\mathbf{v}\otimes\mathbf{G}^\Delta\right){:}\boldsymbol{\sigma}^u_S\right]_{,\Delta} - \left[\sqrt{g}\mathbf{v}\otimes\mathbf{G}^\Delta\right]_{,\Delta}{:}\boldsymbol{\sigma}^u_S\right\}\mathrm{d}S_0,\end{aligned} \tag{3.9}$$

where

$$\sqrt{g} = \sqrt{\begin{vmatrix}\mathbf{G}_1\cdot\mathbf{G}_1 & \mathbf{G}_1\cdot\mathbf{G}_2\\ \mathbf{G}_2\cdot\mathbf{G}_1 & \mathbf{G}_2\cdot\mathbf{G}_2\end{vmatrix}}. \tag{3.10}$$

Upon application of the divergence theorem to the first term in the second line of Eq. (3.9) one obtains

$$\oint_S \mathbf{v}\cdot\mathrm{div}_S\boldsymbol{\sigma}^u_S\mathrm{d}S = \oint_{\partial S_0}\sqrt{g}\mathbf{v}\cdot\boldsymbol{\sigma}^u_S\cdot\left(\mathbf{G}^\Delta\overset{0}{n}_\Delta\right)dL - \oint_{S_0}\left[\sqrt{g}\mathbf{v}\otimes\mathbf{G}^\Delta\right]_{,\Delta}{:}\boldsymbol{\sigma}^u_S\mathrm{d}S_0, \tag{3.11}$$

in which ∂S_0 is the boundary of S_0 and $\overset{0}{n}_\Delta$ denotes the unit vector located in S_0 and normal to ∂S_0. In view of the fact that surfaces of the inhomogeneities are closed, the boundary term in Eq. (3.11) vanishes and the weak formulation of Eq. (3.8) takes the form

$$\oint_{S_0}\left(\sqrt{g}\mathbf{v}\otimes\mathbf{G}^\Delta\right)_{,\Delta}{:}\boldsymbol{\sigma}^u_S\mathrm{d}S_0 = \oint_S \mathbf{v}\cdot\mathbf{b}\mathrm{d}S. \tag{3.12}$$

Further transformation of the left-hand side of the above equation is performed to deduce the needed expression for the surface strain energy

$$\oint_{S_0}\left[\sqrt{g}\mathbf{v}\otimes\mathbf{G}^\Delta\right]_{,\Delta}{:}\boldsymbol{\sigma}^u_S\mathrm{d}S_0 = \oint_{S_0}\left[\sqrt{g}_{,\Delta}\mathbf{v}\otimes\mathbf{G}^\Delta + \sqrt{g}\mathbf{v}_{,\Delta}\otimes\mathbf{G}^\Delta + \sqrt{g}\mathbf{v}\otimes\mathbf{G}^\Delta_{,\Delta}\right]{:}\boldsymbol{\sigma}^u_S\mathrm{d}S_0. \tag{3.13}$$

Considering that

$$\mathbf{G}^{\Delta}_{,\Lambda} = -\Gamma^{\Delta}_{\Lambda\Sigma}\mathbf{G}^{\Sigma} + B^{\Delta}_{\Lambda}\mathbf{n}, \tag{3.14}$$

where $\Gamma^{\Delta}_{\Lambda\Sigma} = \mathbf{G}_{\Lambda,\Sigma}\cdot\mathbf{G}^{\Delta}$ are Christoffel symbols and $B^{\Delta}_{\Lambda} = \mathbf{G}^{\Delta}_{,\Lambda}\cdot\mathbf{n}$ are (mixed) components of the surface curvature tensor, one has

$$\mathbf{G}^{\Delta}_{,\Delta} = -\Gamma^{\Delta}_{\Delta\Sigma}\mathbf{G}^{\Sigma} + B^{\Delta}_{\Delta}\mathbf{n}. \tag{3.15}$$

Furthermore, the definition of $\sqrt{g}$ provided in Eq. (3.10) leads to

$$\sqrt{g}_{,\Delta} = \frac{1}{\sqrt{g}}\Gamma^{\Sigma}_{\Sigma\Delta}g = \Gamma^{\Sigma}_{\Sigma\Delta}\sqrt{g}. \tag{3.16}$$

As a result, from Eqs. (3.15), (3.16) and (3.13) one obtains

$$\oint_{S_0}\left[\sqrt{g}\mathbf{v}\otimes\mathbf{G}^{\Delta}\right]_{,\Delta}:\boldsymbol{\sigma}^{\mathrm{u}}_{\mathrm{S}}\mathrm{d}S_0 = \oint_{S}\left[\nabla_{\mathrm{S}}\mathbf{v} + B^{\Delta}_{\Delta}\mathbf{v}\otimes\mathbf{n}\right]:\boldsymbol{\sigma}^{\mathrm{u}}_{\mathrm{S}}\mathrm{d}S. \tag{3.17}$$

Substitution of Eqs. (3.17) and (2.5c) into Eq. (3.12) results in the weak formulation of the surface equilibrium equations

$$\oint_{\mathrm{S}}\left[\nabla_{\mathrm{S}}\mathbf{v} + B^{\Delta}_{\Delta}\mathbf{v}\otimes\mathbf{n}\right]:\left[2\bar{\mu}_{\mathrm{S}}\boldsymbol{\varepsilon}_{\mathrm{S}} + \bar{\lambda}_{\mathrm{S}}\mathrm{tr}\left(\boldsymbol{\varepsilon}_{\mathrm{S}}\right)\mathbf{I}_{\mathrm{S}} + \tau_0\nabla_{\mathrm{S}}\mathbf{u}\right]\mathrm{d}S = \oint_{S}\mathbf{v}\cdot\mathbf{b}\mathrm{d}S, \tag{3.18}$$

where $\bar{\lambda}_{\mathrm{S}} = \lambda_{\mathrm{S}} + \tau_0$ and $\bar{\mu}_{\mathrm{S}} = \mu_{\mathrm{S}} - \tau_0$.

To interpret the above result more clearly, the vector $\mathbf{v}$ is now resolved with respect to the local vector basis

$$\mathbf{v} = v_{\Delta}\mathbf{G}^{\Delta} + v_{\mathrm{n}}\mathbf{n}. \tag{3.19}$$

Then, the surface gradient [22] of the displacement field can be evaluated more specifically

$$\begin{aligned}
\nabla_{\mathrm{S}}\mathbf{v} = \left[v_{\Lambda}\mathbf{G}^{\Lambda} + v_n\mathbf{n}\right]_{,\,\Delta}\otimes\mathbf{G}^{\Delta} &= \left[v_{\Lambda,\Delta}\mathbf{G}^{\Lambda} + v_{\Lambda}\mathbf{G}^{\Lambda}{}_{,\Delta} + v_{n,\Delta}\mathbf{n} + v_n\mathbf{n}_{,\Delta}\right]\otimes\mathbf{G}^{\Delta}\\
&= v_{\Lambda,\Delta}\mathbf{G}^{\Lambda}\otimes\mathbf{G}^{\Delta} + v_{\Lambda}\left[-\Gamma^{\Lambda}_{\Delta\Sigma}\mathbf{G}^{\Sigma} + B^{\Lambda}_{\Delta}\mathbf{n}\right]\otimes\mathbf{G}^{\Delta}\\
&\quad + v_{n,\Delta}\mathbf{n}\otimes\mathbf{G}^{\Delta} - v_n B_{\Lambda\Delta}\mathbf{G}^{\Lambda}\otimes\mathbf{G}^{\Delta}\\
&= v_{\Lambda}\|_{\Delta}\,\mathbf{G}^{\Lambda}\otimes\mathbf{G}^{\Delta} + v_{\Lambda}B^{\Lambda}_{\Delta}\mathbf{n}\otimes\mathbf{G}^{\Delta} + v_{n,\Delta}\mathbf{n}\otimes\mathbf{G}^{\Delta} - v_n B_{\Lambda\Delta}\mathbf{G}^{\Lambda}\otimes\mathbf{G}^{\Delta}\\
&= \left[v_{\Lambda}\|_{\Delta} - v_n B_{\Lambda\Delta}\right]\mathbf{G}^{\Lambda}\otimes\mathbf{G}^{\Delta} + \left[v_{\Lambda}B^{\Lambda}_{\Delta} + v_{n,\Delta}\right]\mathbf{n}\otimes\mathbf{G}^{\Delta}\\
&= \boldsymbol{\varepsilon}_{\mathrm{S}} + \boldsymbol{\omega}_{\mathbf{n}} + \boldsymbol{\omega}_{\mathrm{S}},
\end{aligned} \tag{3.20}$$

where the symmetric part of the tensor $\left[v_{\Lambda}\|_{\Delta} - v_n B_{\Lambda\Delta}\right]\mathbf{G}^{\Lambda}\otimes\mathbf{G}^{\Delta}$ is denoted by $\boldsymbol{\varepsilon}_{\mathrm{S}}$ and represents the surface strain tensor, the skew-symmetric part of that tensor is denoted by $\boldsymbol{\omega}_{\mathbf{n}}$ and represent rotation about normal to the surface and $\left[v_{\Lambda}B^{\Lambda}_{\Delta} + v_{n,\Delta}\right]\mathbf{n}\otimes\mathbf{G}^{\Delta} = \boldsymbol{\omega}_{\mathrm{S}}$ represents rotation about a vector tangent to the surface.

Remark At this point, it is possible to precisely identify the difference between the complete surface gradient of displacements specified in Eq. (3.20) and that of Huang and Sun [21]. For axi-symmetric loading considered in [21] $\boldsymbol{\omega}_{\mathbf{n}} = \mathbf{0}$, but $\boldsymbol{\omega}_{\mathbf{n}} \neq \mathbf{0}$. So, in their analysis the Authors of [21] neglected $\boldsymbol{\omega}_{\mathrm{S}}$ which makes $\nabla_{\mathrm{S}}\mathbf{v}$ symmetric. However, when $\nabla_{\mathrm{S}}\mathbf{v}$ is symmetric $\nabla_{\mathrm{S}}\mathbf{v} = \boldsymbol{\varepsilon}_{\mathrm{S}}$ and the last term of Eq. (1.1) can be combined with the second term on its right-hand side. Effectively, that completely removes the last term of Eq. (1.1) (cf. [8,21]) and, with a small modification of the parameter multiplying $\boldsymbol{\varepsilon}_{\mathrm{S}}$ (by adding τ_0 to it), all methods developed for the incomplete Gurtin–Murdoch model [i.e., without the last term in Eq. (1.1)] become applicable, as remarked in [36].

Considering the symmetry properties just described, and symmetries of various tensors present in the definition of the surface stress tensor of Eq. (2.5c), one concludes that the integrand on the left-hand side of Eq. (3.18) may be transformed as follows

$$\nabla_{\mathrm{S}}\mathbf{v}:\left[2\bar{\mu}_{\mathrm{S}}\boldsymbol{\varepsilon}_{\mathrm{S}} + \bar{\lambda}_{\mathrm{S}}\,\mathrm{tr}\left(\boldsymbol{\varepsilon}_{\mathrm{S}}\right)\mathbf{I}_{\mathrm{S}}\right] + \tau_0\nabla_{\mathrm{S}}\mathbf{v}:\nabla_{\mathrm{S}}\mathbf{u} = 2\bar{\mu}_{\mathrm{S}}\boldsymbol{\varepsilon}_{\mathrm{S}}(\mathbf{v}):\boldsymbol{\varepsilon}_{\mathrm{S}}\left(\mathbf{u}\right) + \bar{\lambda}_{\mathrm{S}}\,\mathrm{tr}\left(\boldsymbol{\varepsilon}_{\mathrm{S}}\left(\mathbf{v}\right)\right)\,\mathrm{tr}\left(\boldsymbol{\varepsilon}_{\mathrm{S}}\left(\mathbf{u}\right)\right) + \tau_0\nabla_{\mathrm{S}}\mathbf{v}:\nabla_{\mathrm{S}}\mathbf{u}. \tag{3.21}$$

The three terms in the above result are the only bilinear terms with respect to $\mathbf{v}$ and $\mathbf{u}$ in Eq. (3.18), which implies that the appropriate form of the surface energy is [12]

$$E_S = \frac{1}{2}\oint_S \left[2\bar{\mu}_S \boldsymbol{\varepsilon}_S{:}\boldsymbol{\varepsilon}_S + \bar{\lambda}_S \,\mathrm{tr}\,(\boldsymbol{\varepsilon}_S)^2 + \tau_0 \nabla_S \mathbf{u}{:}\nabla_S \mathbf{u}\right] \mathrm{d}S. \tag{3.22}$$

The first two terms of the above integrand are identical to the one present in the surface integral of Eq. (3.1) and in [37]. Thus, the last term of Eq. (3.22) represents the surface gradient of the displacement field. The expression of Eq. (3.22) can be made still more specific if the expanded version of the result present in Eq. (3.5) is taken into account. This is done in the next section where the working formula for properties of the energy-equivalent inhomogeneity is also presented. Here, the reader attention is directed to the fact that, when a weak formulation of the nonlinear equations of mechanics is linearized, a term analogical to the last term of Eq. (3.21) appears. In the finite element discretization of such linearized weak form that term leads to the so-called geometric stiffness matrix, while the remaining terms result in the "material stiffness matrix" (e.g., Stolarski et al. [42,43]).

3.2.3 Constitutive tensor of the energy-equivalent inhomogeneity

While the development presented in the preceding section is general, in the sense that no restriction was imposed on the surface vector fields $\mathbf{u}$ and $\mathbf{v}$, evaluation of properties of the energy-equivalent inhomogeneity assumes averaged (constant) strains within inclusions. Thus, the surface gradient of displacements is defined by Eq. (3.5). It is clear, however, that both the surface gradient of displacements and the surface strain tensor vary from one point of the surface to another.

Considering that $\boldsymbol{\varepsilon}_S = \overset{4}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1$ where $\overset{4}{\mathbf{I}}_S = \mathbf{G}_\Delta \otimes \mathbf{G}_\Lambda \otimes \mathbf{G}^\Delta \otimes \mathbf{G}^\Lambda$ is the rank four surface identity tensor; that $tr\,(\boldsymbol{\varepsilon}_S) = \overset{2}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1 = \bar{\boldsymbol{\varepsilon}}_1 : \overset{2}{\mathbf{I}}_S$ where $\overset{2}{\mathbf{I}}_S = \mathbf{G}_\Delta \otimes \mathbf{G}^\Delta$ is rank two surface identity tensor; and accounting for Eq. (3.5), the surface energy of Eq. (3.22) is transformed as follows

$$\begin{aligned} E_S &= \frac{1}{2}\oint_S \left[2\bar{\mu}_S \boldsymbol{\varepsilon}_S{:}\boldsymbol{\varepsilon}_S + \bar{\lambda}_S \,\mathrm{tr}\,(\boldsymbol{\varepsilon}_S)^2 + \tau_0 \left(\bar{\boldsymbol{\varepsilon}}_1 \cdot \overset{2}{\mathbf{I}}_S\right) : \left(\bar{\boldsymbol{\varepsilon}}_1 \cdot \overset{2}{\mathbf{I}}_S\right)\right] \mathrm{d}S \\ &= \frac{1}{2}\oint_S \left[2\bar{\mu}_S \bar{\boldsymbol{\varepsilon}}_1 : \overset{4}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1 + \bar{\lambda}_S \bar{\boldsymbol{\varepsilon}}_1 : \overset{2}{\mathbf{I}}_S \otimes \overset{2}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1 + \tau_0 \left(\boldsymbol{\varepsilon}_S + \bar{\varepsilon}_{1[\mathbf{n}\Delta]} \mathbf{n} \otimes \mathbf{G}^\Delta\right) : \left(\boldsymbol{\varepsilon}_S + \bar{\varepsilon}_{1[\mathbf{n}\Lambda]} \mathbf{n} \otimes \mathbf{G}^\Lambda\right)\right] \mathrm{d}S \\ &= \frac{1}{2}\oint_S \left[(2\bar{\mu}_S + \tau_0)\, \bar{\boldsymbol{\varepsilon}}_1 : \overset{4}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1 + \bar{\lambda}_S \bar{\boldsymbol{\varepsilon}}_1 : \overset{2}{\mathbf{I}}_S \otimes \overset{2}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1 + \tau_0 \left(\bar{\varepsilon}_{1[\mathbf{n}\Delta]} \mathbf{n} \otimes \mathbf{G}^\Delta\right) : \left(\bar{\varepsilon}_{1[\mathbf{n}\Lambda]} \mathbf{n} \otimes \mathbf{G}^\Lambda\right)\right] \mathrm{d}S. \end{aligned} \tag{3.23}$$

This last formula is then put in the following form

$$\begin{aligned} E_S = \frac{1}{2}\oint_S \Bigg[& (2\bar{\mu}_S + \tau_0)\, \bar{\boldsymbol{\varepsilon}}_1 : \overset{4}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1 + \bar{\lambda}_S \bar{\boldsymbol{\varepsilon}}_1 : \overset{2}{\mathbf{I}}_S \otimes \overset{2}{\mathbf{I}}_S : \bar{\boldsymbol{\varepsilon}}_1 \\ & + \frac{\tau_0}{2} \bar{\boldsymbol{\varepsilon}}_1 : \left(\mathbf{n} \otimes \mathbf{G}_\Delta \otimes \mathbf{n} \otimes \mathbf{G}^\Delta + \mathbf{G}_\Delta \otimes \mathbf{n} \otimes \mathbf{G}^\Delta \otimes \mathbf{n}\right) : \bar{\boldsymbol{\varepsilon}}_1 \Bigg] \mathrm{d}S. \end{aligned} \tag{3.24}$$

In the transition from Eqs. (3.23) to (3.24) the property $\bar{\varepsilon}_{1[\mathbf{n}\Delta]} \mathbf{n} \otimes \mathbf{G}^\Delta = \bar{\boldsymbol{\varepsilon}}_1 : \left[\mathbf{n} \otimes \mathbf{G}_\Delta \otimes \mathbf{n} \otimes \mathbf{G}^\Delta\right]$ and symmetry of $\bar{\boldsymbol{\varepsilon}}_1$ has been taken into account. The last result for E_S and energy equivalence expressed by Eq. (3.1) leads to the effective moduli of equivalent inclusion:

$$\tilde{\mathbf{C}}_1 = \mathbf{C}_1 + \frac{1}{V_I}\oint_S \left[(2\bar{\mu}_S + \tau_0)\, \overset{4}{\mathbf{I}}_S + \bar{\lambda}_S \overset{2}{\mathbf{I}}_S \otimes \overset{2}{\mathbf{I}}_S + \frac{\tau_0}{2}\left(n \otimes \mathbf{G}_\Delta \otimes \mathbf{n} \otimes \mathbf{G}^\Delta + \mathbf{G}_\Delta \otimes \mathbf{n} \otimes \mathbf{G}^\Delta \otimes \mathbf{n}\right)\right] \mathrm{d}S. \tag{3.25}$$

If the curvilinear coordinates ξ^{Λ} introduced to parameterize the surface of inclusions are orthogonal (as can easily be done for spherical or ellipsoidal inclusions, for example), the unit vectors $\bar{\mathbf{G}}_{\Delta} = \frac{\mathbf{G}_{\Delta}}{|\mathbf{G}_{\Delta}|} = \bar{\mathbf{G}}^{\Delta} = \frac{\mathbf{G}^{\Delta}}{|\mathbf{G}^{\Delta}|}$ can be substituted for $\mathbf{G}_{\Delta}$ and $\mathbf{G}^{\Delta}$ in the above equation and its last term can be rewritten in the form:

$$\begin{aligned}\mathbf{K}_{\nabla} &= \frac{\tau_0}{2V_I}\oint_{\mathrm{S}}\left[\mathbf{n}\otimes\bar{\mathbf{G}}_{\Delta}\otimes\mathbf{n}\otimes\bar{\mathbf{G}}^{\Delta}+\bar{\mathbf{G}}_{\Delta}\otimes\mathbf{n}\otimes\bar{\mathbf{G}}^{\Delta}\otimes\mathbf{n}\right]\mathrm{d}S\\ &= \frac{\tau_0}{2V_I}\oint_{\mathrm{S}}\left[\mathbf{n}\otimes\bar{\mathbf{G}}_1\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_1+\mathbf{n}\otimes\bar{\mathbf{G}}_2\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_2+\bar{\mathbf{G}}_1\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_1\otimes\mathbf{n}+\bar{\mathbf{G}}_2\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_2\otimes\mathbf{n}\right]\mathrm{d}S.\end{aligned} \tag{3.26}$$

Evaluation of the components of the above tensor is illustrated in "Appendix".

4 Effective properties

4.1 Tensor form of effective properties

For two-point probabilities $p_{\nu k}(\mathbf{x}^{(1)}-\mathbf{x}^{(2)})$ characterizing composites with randomly distributed spherical inclusions, the algebraic operators $\mathbf{K}^{\nu k}$ of Eq. (2.21) can be represented by [25,36]

$$\mathbf{K}^{\nu k} = [\delta_{\nu k} - c_k]\,\mathbf{L}, \tag{4.1}$$

where $\mathbf{L}$ has the following form

$$\mathbf{L} = 2b\overset{4}{\mathbf{I}} + a\overset{2}{\mathbf{I}}\otimes\overset{2}{\mathbf{I}}, \tag{4.2}$$

with

$$a = \frac{\lambda_{\mathrm{c}}+\mu_{\mathrm{c}}}{15\mu_{\mathrm{c}}[\lambda_{\mathrm{c}}+2\mu_{\mathrm{c}}]}, \quad b = -\frac{3\lambda_{\mathrm{c}}+8\mu_{\mathrm{c}}}{30\mu_{\mathrm{c}}[\lambda_{\mathrm{c}}+2\mu_{\mathrm{c}}]}, \tag{4.3}$$

and with λ_{c}, μ_{c} being the Lamé constants of the reference medium [25].

Taking into account Eq. (4.3), the system of linear algebraic equations (2.16) reads

$$\bar{\boldsymbol{\varepsilon}}_1 = \bar{\boldsymbol{\varepsilon}} + c_2\mathbf{L}\colon\left[\tilde{\mathbf{C}}_1^0\colon\bar{\boldsymbol{\varepsilon}}_1 - \mathbf{C}_2^0\colon\bar{\boldsymbol{\varepsilon}}_2\right] + 2\kappa\tau_0\mathbf{C}_{\mathrm{c}}^{-1}\colon\mathbf{S}\colon\overset{2}{\mathbf{I}}. \tag{4.4}$$

It is noted that $\kappa = -1/R_0$ for spheres, where R_0 is their radius [36].[1] It is also noted that an isotropic rank four tensor $\mathbf{C}_{\mathrm{c}}$ can be written in terms of its Lamé constants

$$\mathbf{C}_{\mathrm{c}} = 2\mu_{\mathrm{c}}\overset{4}{\mathbf{I}} + \lambda_{\mathrm{c}}\overset{2}{\mathbf{I}}\otimes\overset{2}{\mathbf{I}}. \tag{4.5}$$

Additionally, for isotropic spherical inclusions

$$\mathbf{S}\colon\overset{2}{\mathbf{I}} = \frac{1+\nu_{\mathrm{c}}}{3[1-\nu_{\mathrm{c}}]}\overset{2}{\mathbf{I}}, \tag{4.6a}$$

and

$$\mathbf{C}_{\mathrm{c}}^{-1}\colon\overset{2}{\mathbf{I}} = \frac{1}{3K_{\mathrm{c}}}\overset{2}{\mathbf{I}}, \tag{4.6b}$$

in which ν_{c} is the Poisson ratio and K_{c} is the bulk modulus of the reference medium (see [36,37]). Taking into account Eqs. (4.6a,b) and recognizing that $\bar{\boldsymbol{\varepsilon}} = c_1\bar{\boldsymbol{\varepsilon}}_1 + c_2\bar{\boldsymbol{\varepsilon}}_2$, $\bar{\boldsymbol{\varepsilon}}_2$ can be eliminated from Eq. (4.4) to obtain

$$\bar{\boldsymbol{\varepsilon}}_1 = \left[\overset{4}{\mathbf{I}} - \mathbf{L}\colon\mathbf{C}_2^0\right]\colon\bar{\boldsymbol{\varepsilon}} + \mathbf{L}\colon\tilde{\mathbf{C}}'\colon\bar{\boldsymbol{\varepsilon}}_1 - \frac{2\tau_0}{9R_0K_{\mathrm{c}}}\left[\frac{1+\nu_{\mathrm{c}}}{1-\nu_{\mathrm{c}}}\right]\overset{2}{\mathbf{I}}, \tag{4.7}$$

[1] The minus sign is due to the assumption that the vector $\mathbf{n}$ normal to the interface is pointing away from the inhomogeneities.

where

$$\tilde{\mathbf{C}}' = \tilde{\mathbf{C}}_4 - \mathbf{C}_\mathrm{c}, \quad \tilde{\mathbf{C}}_4 = c_1\mathbf{C}_2 + c_2\tilde{\mathbf{C}}_1. \tag{4.8}$$

The new tensors $\tilde{\mathbf{C}}'$ and $\tilde{\mathbf{C}}_4$ defined in the above equation are isotropic, can be characterized by two Lame constants or, equivalently, by $\tilde{K}'$, $\tilde{\mu}'$ and $\tilde{K}_4$, $\tilde{\mu}_4$, respectively.

Equation (4.7) yields the average strain in inclusions $\bar{\varepsilon}_1$ in terms of the overall average strains $\bar{\varepsilon}$ and τ_0. This result, in combination with the relationship $\bar{\boldsymbol{\varepsilon}} = c_1\bar{\boldsymbol{\varepsilon}}_1 + c_2\bar{\boldsymbol{\varepsilon}}_2$, provides an analogical relationship for $\bar{\varepsilon}_2$ in terms of $\bar{\varepsilon}$ and τ_0. Substitution into the macrostresses $\bar{\boldsymbol{\sigma}} = c_1\tilde{\mathbf{C}}_1{:}\bar{\boldsymbol{\varepsilon}}_1 + c_2\mathbf{C}_2{:}\bar{\boldsymbol{\varepsilon}}_2$ leads to the constitutive equation for the macrovolume

$$\bar{\boldsymbol{\sigma}} = \mathbf{C}^*{:}\bar{\boldsymbol{\varepsilon}} - \frac{2c_1\tau_0}{9R_0K_\mathrm{c}}\left[\frac{1+\nu_\mathrm{c}}{1-\nu_\mathrm{c}}\right]\tilde{\mathbf{C}}_3{:}\left[\overset{4}{\mathbf{I}} - \mathbf{L}{:}\tilde{\mathbf{C}}'\right]^{-1}{:}\overset{2}{\mathbf{I}}, \tag{4.9}$$

in which $\mathbf{C}^*$ is the effective stiffness tensor (cf. Eq. (2.1)) given by

$$\mathbf{C}^* = c_1\tilde{\mathbf{C}}_1 + c_2\mathbf{C}_2 + c_1\tilde{\mathbf{C}}_3{:}\left[\overset{4}{\mathbf{I}} - \mathbf{L}{:}\tilde{\mathbf{C}}'\right]^{-1}{:}[c_2\mathbf{L}{:}\tilde{\mathbf{C}}_3], \tag{4.10}$$

with $\tilde{\mathbf{C}}_3 = \tilde{\mathbf{C}}_1 - \mathbf{C}_2$.

4.2 Scalar form of effective properties

As indicated on many occasions in the preceding sections, the tensors entering the tensorial formula for effective properties of the composite are all isotropic. Under those conditions, closed-form scalar expression for effective bulk and shear moduli can be extracted from Eq. (4.10) in the manner detailed in [36]:

$$K^* = c_1\left[K_1 + \hat{K}_\mathrm{S}\right] + c_2K_2 + \frac{9c_1c_2K\left[K_1 - K_2 + \hat{K}_\mathrm{S}\right]^2}{1 - 9K\left[c_1K_2 + c_2\left(K_1 + \hat{K}_\mathrm{S}\right) - K_\mathrm{c}\right]}, \tag{4.11}$$

$$\mu^* = c_1\left[\mu_1 + \hat{\mu}_\mathrm{S}\right] + c_2\mu_2 + \frac{4c_1c_2b\left[\mu_1 - \mu_2 + \hat{\mu}_\mathrm{S}\right]^2}{1 - 4b\left[c_1\mu_2 + c_2\left(\mu_1 + \hat{\mu}_\mathrm{S}\right) - \mu_\mathrm{c}\right]}. \tag{4.12}$$

In this expression K_1, μ_1 and K_2, μ_2 are bulk and shear moduli of inclusions and matrix, respectively; K_c and μ_c are bulk and shear moduli of the selected reference medium; K depends on a and b of Eq. (4.3) and, therefore, on properties of the reference medium as well. Expressions defining $\hat{K}_\mathrm{S}$ and $\hat{\mu}_\mathrm{S}$ are

$$\hat{K}_\mathrm{S} = 2\frac{\left[2\bar{\mu}_\mathrm{S} + 2\bar{\lambda}_\mathrm{S} + \tau_0\right]}{3R_0}, \tag{4.13}$$

$$\hat{\mu}_\mathrm{S} = \frac{7\bar{\mu}_\mathrm{S} + \bar{\lambda}_\mathrm{S} + 5\tau_0}{5R_0}, \tag{4.14}$$

and they constitute an additional contribution of surface effects to the bulk and shear moduli of equivalent inhomogeneities. Derivation of these formulas is outlined in "Appendix".

It should be noted that taking $K_\mathrm{c} = K_2$ and $\mu_\mathrm{c} = \mu_2$ in Eq. (4.11) the resulting expression for effective bulk modulus coincides with the one presented in [26]. As observed in that paper, when the surface residual stresses vanish that expression coincides also with that of Duan et al. [7]. This is in agreement with findings presented in [37]. However, as shown (for example) in [35], the choice of matrix as the reference medium is not optimal from the viewpoint of the MCM approach.

5 Numerical comparisons and discussion

Nanoporous aluminum, for which numerical results are available, is a very good material for evaluating our approach. Porous materials exhibit strong surface effects, and their use for comparison is more likely to expose attributes or flaws of the approach.

We consider a composite material consisting of an aluminum matrix with properties $K_2 = 75.2$ GPa and $\nu_2 = 0.3$ containing spherical cavities ($\mu_1 = K_1 = 0$). The free surface properties are those presented by Miller and Shenoy [31]. In their article, two sets of surface properties are used, corresponding to surfaces oriented along two different crystallographic directions: A for surface [100]: $\lambda_S = 2.92025$ N/m; $\mu_S = -5.64893$ N/m; $\tau_0 = 0.56887$ N/m and B for surface [111]: $\lambda_S = 5.93126$ N/m; $\mu_S = 0.53524$ N/m; $\tau_0 = 0.910737$ N/m, and both are used in the present work.

The variation of the normalized bulk modulus $K^*/K_{\rm cl}$ with void volume fractions calculated by the MCM in combination with the equivalent inclusion approach (short dash line for surface A and dash line for surface B) for spherical cavities of radius $R_0 = 5$ nm is shown in Fig. 2. The subscript "cl" represents results for the classical solution, i.e., without surface effects. For comparison, the normalized bulk modulus for the same material obtained without accounting for surface gradient of displacements (solid line for surface A and dash dot line for surface B) is also shown in Fig. 2. The normalized bulk moduli obtained with and without accounting for the surface gradient of displacements are very similar for all volume fractions of pores. As expected, this numerical illustration indicates that the influence of the surface gradient of displacements is insignificant for bulk moduli.

The variation of the normalized shear modulus $\mu^*/\mu_{\rm cl}$ with void volume fractions calculated by the method of conditional moments in combination with the equivalent inclusion approach (dot line for surface A and dash line for surface B) for spherical cavities of radius $R_0 = 5$ nm is shown in Fig. 3. The normalized shear moduli for the same material obtained without regards for the surface gradient of displacements (solid line for surface A and dash dot line for surface B) are also shown in Fig. 3. Influence of the surface gradient of displacements is distinguishable for the pore volume fractions greater than $c_1 \approx 0.25$, depending on the case. Although this influence must depend on relative values of all parameters describing the problem, it (expectedly) appears to particularly depend on the magnitude of the residual stress τ_0. While for surface A, the influence of the surface gradient of displacements on shear modulus is rather small (and comparable to that for the bulk modulus), for surface B it is significant. In the case of surface B, where the value of residual stresses τ_0 is about twice the residual stresses of surface A, the influence of the surface gradient of displacements approximately equals that of all the remaining terms of Eq. (1.1).

For the sake of comparison with the results obtained in [26], the normalized bulk modulus $K^*/2\mu_2$ of nanoporous material with the matrix possessing properties of aluminum is presented in Fig. 4 as a function of the residual stress τ_0; the void volume fraction was taken to be $c_1 = 0.5$ and $\lambda_S = \mu_S = 0$. The results of [26] were obtained on basis of the representative unit cell, with both simple cubic structure and quasi-random arrangement of inclusions. The analogous results for the shear modulus μ^*/μ_2 are shown in Fig. 5. As seen,

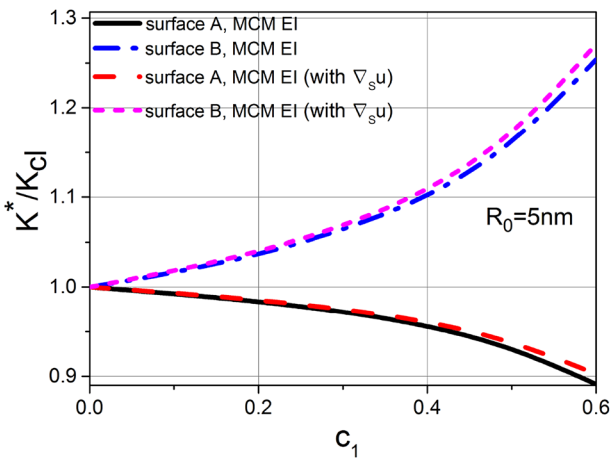

Fig. 2 Dependence of bulk modulus $K^*/K_{\rm cl}$ for nanoporous aluminum on void volume fraction c_1; radius of spherical cavity $R_0 = 5$ nm

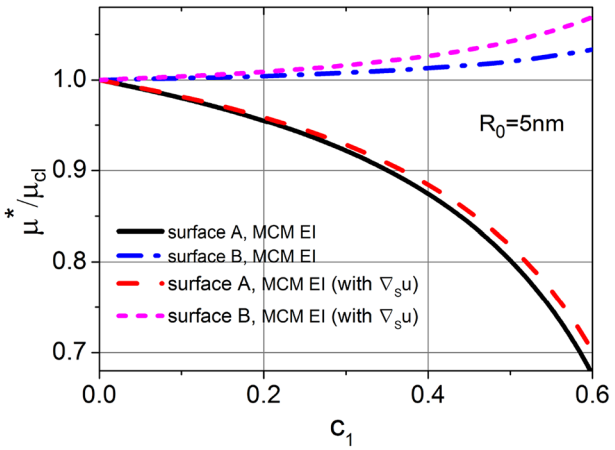

Fig. 3 Dependence of shear modulus $\mu^*/\mu_{\rm cl}$ for nanoporous aluminum on void volume fraction c_1; radius of a spherical cavity $R_0 = 5$ nm

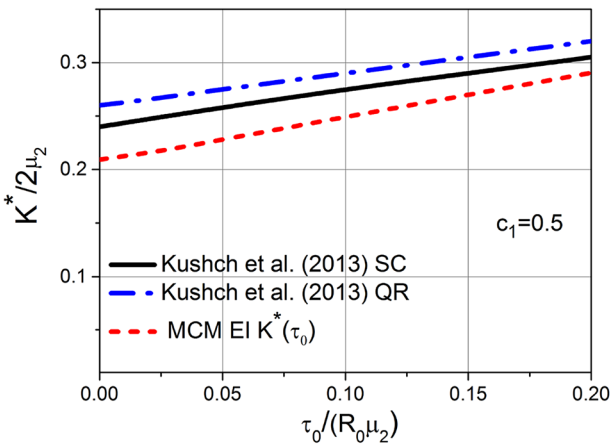

Fig. 4 Dependence of bulk modulus $K^*/2\mu_2$ for nanoporous aluminum, on surface residual stresses τ_0; void volume fraction $c_1 = 0.5$. *SC* simple cubic structure, *QR* quasi-random structure

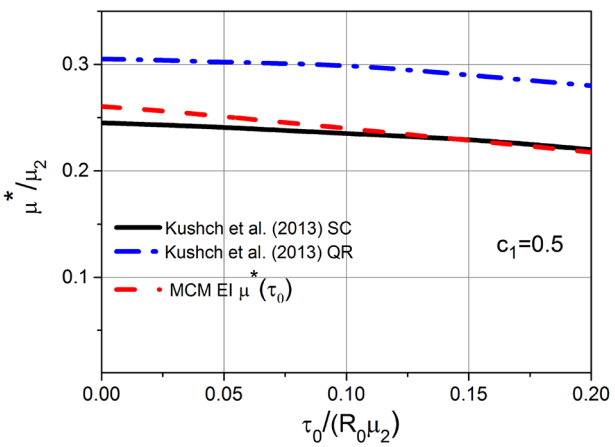

Fig. 5 Dependence of shear modulus μ^*/μ_2 for nanoporous aluminum on surface residual stresses τ_0; void volume fraction $c_1 = 0.5$. *SC* simple cubic structure; *QR* quasi-random structure

tendencies and numerical values for the results calculated by radically different methods (both in terms of the approach and the required effort) are quite similar. For the shear modulus, the results obtained in this work are closer to those obtained in [26] for the cubic structure arrangement of pores, not for the quasi-random arrangement. In both cases, the influence of residual stresses is positive for the bulk modulus (in the sense that the bulk modulus increases with increasing residual stresses) and negative for the shear modulus. Comparison with results obtained in [26] shows that the closed-form formulas provided in this work are in a good agreement. This is remarkable considering vastly different modeling assumptions, significantly different computational effort (in favor of the approach used here), and the fact that a closed-form results could be provided in this work.

6 Conclusions

A mathematical model, employing the recently introduced concept of the energy-equivalent inhomogeneity in combination with the MCM [37,39], has been generalized to introduce surface effects described by the complete Gurtin–Murdoch equations [12,13]. The focus was on accounting for the last term in Eq. (1.1) (the surface gradient of displacements) in the definition of the energy-equivalent inhomogeneity. As discussed in the introduction, this term can be relatively easily introduced in some numerical analysis methods [e.g., [26]], but its full inclusion in approaches aiming at development of closed-form expressions for effective properties of nanocomposites has been lacking. Only partial inclusion of the last term in Eq. (1.1) has been discussed in the previous publications. The approach based on a recent and new notion of energy-equivalent inhomogeneity employed in this work facilitates a straightforward inclusion of the complete Gurtin–Murdoch equation in the previously developed closed-form expressions for effective properties of nanomaterials. The model was further combined with the method of conditional moments and used to evaluate effective properties of materials with randomly distributed nanoparticles.

The properties of the energy-equivalent inhomogeneity are determined based on the derived definition of surface energy which includes the surface gradient of the displacement field. To this end, the standard energy-based homogenization scheme is employed. This requires application of displacements on the inhomogeneity-interface boundary which is consistent with the average strain in the system (composed of the inhomogeneity and the interface), solution of the problem (which in this case is trivial) and evaluation of the system energy. The resulting effective inhomogeneity can be used with any valid homogenization procedure (analytical or numerical) to determine effective properties of the nanomaterial at hand. However, it is of particular value if such properties are sought directly, without knowledge of the local strain and stress fields, since, till now, methods of that sort have not been able to include the complete Gurtin–Murdoch model of the interface.

As a numerical illustration, nanoporous aluminum is studied.

The effective bulk and shear moduli of nanoporous aluminum have been analyzed for varying volume content of nanocavities accounting for the surface gradient of displacements. The size effect introduced due to the contribution of the residual stresses and elasticity on the matrix/nanoparticles interface in nanoporous aluminum is accounted for in the expressions for effective bulk and shear moduli. It has been shown that the influence of the Gurtin–Murdoch type surface gradient of displacements is insignificant for the bulk moduli in the elastic region. For shear moduli, the surface gradient of displacements becomes essential for high pore volume fraction. Comparison with numerical results of Kushch et al. [26], which are based on the precise solution of the differential equations of the problem, shows that proposed approach is comparable in accuracy and can be successfully used for particulate nanomaterials. This agreement is particularly remarkable considering that it involves comparison between a highly elaborate solution of the governing differential equations with relatively simple closed-form formulas provided herein.

To conclude, it is worth mentioning that the definition of the energy-equivalent inhomogeneity is general and can be used in case of inhomogeneities of other shapes than spherical, e.g., ellipsoidal or cylindrical. It can very naturally be combined with the MCM and appears to be potentially amenable for inclusion of other than Gurtin–Murdoch interface models. The important characteristic of the proposed approach is its ability to provide closed-form expressions for effective properties of nanocomposites. Closed-form results are important, especially if the influence of different problem parameters needs to be explored.

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Appendix: Surface contribution to properties of the energy-equivalent inhomogeneity accounting for the surface gradient of the displacement field

For illustration of some technical details, $\mathbf{K}_\nabla$ of Eq. (3.26) is evaluated in this appendix. In addition to $\mathbf{K}_\nabla$, the contribution of surface effects to properties of equivalent inhomogeneity includes two other terms present in Eq. (3.25); however—recognizing the difference in the scalar multiplier of the first term—these two terms are in all aspects identical to those present in [37]. Evaluation of all three terms is reduced to evaluation of integrals very similar to those presented below.

Assuming that inhomogeneities are spheres of radius R_0 (which in some cases is a good approximation for inhomogeneities of other shapes [24]) and using spherical coordinate system, $\mathbf{K}_\nabla$ of Eq. (3.26) is described by

$$\mathbf{K}_\nabla = \frac{3\tau_0}{8\pi R_0}\int_0^\pi\int_0^{2\pi}\left[\mathbf{n}\otimes\bar{\mathbf{G}}_1\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_1+\mathbf{n}\otimes\bar{\mathbf{G}}_2\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_2+\bar{\mathbf{G}}_1\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_1\otimes\mathbf{n}+\bar{\mathbf{G}}_2\otimes\mathbf{n}\otimes\bar{\mathbf{G}}_2\otimes\mathbf{n}\right]\times\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta. \tag{A.1}$$

As done in [37], Cartesian components of that tensor are obtained by evaluating all dyadics present in the integrand of Eq. (A.1) in terms of Cartesian components of the vectors they contain and by integration of the resulting formulas. This leads to the following nonvanishing components of $\mathbf{K}_\nabla$

$$K_{\nabla(1111)} = \frac{3\tau_0}{8\pi R_0}\int_0^\pi\int_0^{2\pi}\left[\cos^2\varphi\sin^2\varphi\sin^2\theta+\cos^4\varphi\sin^2\theta\cos^2\theta+\cos^2\varphi\sin^2\varphi\sin^2\theta+\cos^4\varphi\sin^2\theta\cos^2\theta\right]\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta=\frac{2\tau_0}{5R}, \tag{A.2a}$$

$$K_{\nabla(1122)} = K_{\nabla(1133)} = \frac{3\tau_0}{8\pi R_0}\int_0^\pi\int_0^{2\pi}\left[-2\cos^2\varphi\sin^2\varphi\sin^2\theta+2\cos^2\varphi\sin^2\varphi\sin^2\theta\cos^2\theta\right]\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta=-\frac{\tau_0}{5R_0}, \tag{A.2b}$$

$$K_{\nabla(1212)} = \frac{3\tau_0}{8\pi R_0}\int_0^\pi\int_0^{2\pi}\left[\cos^4\varphi\sin^2\theta+2\cos^2\varphi\sin^2\varphi\cos^2\theta\sin^2\theta+\sin^4\varphi\sin^2\theta\right]\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta=\frac{4\tau_0}{5R_0}, \tag{A.2c}$$

$$K_{\nabla(2112)} = \frac{3\tau_0}{8\pi R_0}\int_0^\pi\int_0^{2\pi}\left[-2\cos^2\varphi\sin^2\varphi\sin^2\theta+2\cos^2\varphi\sin^2\varphi\cos^2\theta\sin^2\theta\right]\sin\theta\,\mathrm{d}\varphi\mathrm{d}\theta=-\frac{\tau_0}{5R_0}. \tag{A.2d}$$

As explained in [37], the shear modulus is related to the sum of the above components (not to two different values of $K_{\nabla(1212)}$ and $K_{\nabla(2112)}$ individually)

$$K_{\nabla(1212)}+K_{\nabla(2112)}=\frac{4\tau_0}{5R_0}-\frac{\tau_0}{5R_0}=\frac{3\tau_0}{5R_0}. \tag{A.3}$$

Consequently, the contribution of $\mathbf{K}_\nabla$to bulk and shear moduli of the effective inhomogeneity is

$$\widehat{K}_\nabla = K_{\nabla(1111)}+K_{\nabla(1122)}+K_{\nabla(1133)}=\frac{2\tau_0}{5R_0}-\frac{\tau_0}{5R_0}-\frac{\tau_0}{5R_0}=0, \tag{A.4}$$

$$\hat{\mu}_\nabla = \frac{1}{2}\left[K_{\nabla(1212)}+K_{\nabla(2112)}\right]=\frac{3\tau_0}{10R_0}. \tag{A.5}$$

To obtain total contribution of surface effects to bulk and shear moduli of the equivalent inhomogeneity, it is first noted that without the surface gradient of the displacement field those contributions are given in Eq. (3.3). This result, combined with $K = \lambda + \frac{2}{3}\mu$, and with the fact that $2\bar{\mu}_S$ in Eq. (3.22) is replaced by $2\bar{\mu}_S + \tau_0$ in Eq. (3.25), and with the observation that contributions of Eqs. (A.4) and (A.5) are additively combined with the remaining two contributions (cf. Eq. 3.25), the total surface contributions are obtained

$$\hat{K}_S = 2\frac{\left[2\bar{\mu}_S + 2\bar{\lambda}_S + \tau_0\right]}{3R_0}, \tag{A.6}$$

$$\hat{\mu}_S = \frac{7\bar{\mu}_S + \bar{\lambda}_S + 5\tau_0}{5R_0}. \tag{A.7}$$

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