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Energy-equivalent inhomogeneity approach to analysis of effective properties of nanomaterials with stochastic structure

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ABSTRACT

A mathematical model based on the method of conditional moments combined with a new notion of the energy-equivalent inhomogeneity is presented and applied in the investigation of the effective properties of a material with randomly distributed nanoparticles. The surface effect is introduced via Gurtin–Murdoch equations describing the properties of the matrix/nanoparticle interface. The real system, consisting of the inhomogeneities and their surfaces possessing different properties and, possibly, residual stresses, is replaced by energy-equivalent inhomogeneities with modified bulk properties which incorporate the surface effects. The effective stiffness tensor of the material with so defined equivalent inhomogeneities is determined by the method of conditional moments. Closed-form expressions for the effective moduli of a composite consisting of a matrix and randomly distributed spherical inhomogeneities are derived for both the bulk and the shear moduli. Dependence of those moduli on the radius of nanoparticles is included in these expressions exhibiting analytically the nature of the size-dependence in nanomaterials. As numerical examples, nanoporous aluminum and nanoporous gold are investigated. The dependence of the normalized bulk and shear moduli of nanoporous aluminum (for two sets of surface properties) on the pore volume fraction (for different radii of nanopores) and on the radius of nanopores (for fixed volume fraction of nanopores) are compared to and discussed in the context of other theoretical predictions. Further, the normalized effective Young's modulus of nanoporous gold as a function of void volume fraction for various ligament radii is analyzed.

1. Introduction

The objective of this work is to investigate effective properties of composites with nanometer-scale randomly dispersed spherical inhomogeneities. They belong to a wider class of materials which, for example, may contain randomly distributed pores, inclusions, cracks, etc. of various sizes, shapes and orientations. Some of those materials are increasingly of interest in modern technological applications, and that often includes composites with randomly distributed spherical nanoparticles (Kickelbick, 2007; Ma and Kim, 2011; Wang and Weissmüller, 2013; Sarac et al., 2014).

It is commonly known that the conditions at the interface between the matrix and the inhomogeneities impact the overall properties of the composite. A thin layer along the interface between two dissimilar materials typically possesses properties which are different than those of the constituent materials on either side of it (Ma and Kim, 2011; Tserpes and Silvester, 2014). A significant residual interface stresses or interface cracks may be present as well (see, e.g., Gan, 2009). The influence of those interface features on the composite's overall properties depends on their kind and their intensities (or magnitude), as well as on some characteristics of the composite itself. Depending on the specific circumstances, they may decrease or increase the stiffness of the composite and appropriate interface models need to be used to capture those effects. If interfacial cracks are present, for example, the composite's overall properties may decrease appreciably – even if the inhomogeneities are well above the nanometer scale (Kim and Mai, 1998). On the other hand, changed material properties in a thin layer along the interface, or the residual interface stresses, have been found to meaningfully affect the overall material properties only if the size of the inhomogeneities is in the range of nanometers (see Buryachenko et al., 2005; He and Li, 2006; Lim et al., 2006; Wang and Weissmüller, 2013; Yang, 2004). The quantification of the effects which the changed interface properties have on the overall behavior of random

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nanocomposites is undertaken in this work. The interface model adopted here is that of Gurtin and Murdoch (1975, 1978), whereby the interface is treated as vanishingly thin layer with its own elastic properties (and, possibly, surface tension) coherently connected to the materials on either side. Although not valid universally, this model is adequate for many materials of practical interest and in recent years has been used quite extensively. Several authors modified the known deterministic micromechanical models and, using Gurtin and Murdoch's theory, introduced the surface elasticity and/or surface tension in analysis of random materials on the nanometer scale (see McBride et al., 2011, 2012; Javili et al., 2013 among others).

There are many prior publications addressing the same problem. Those most relevant to the ideas presented in this work are reviewed subsequently. It is important to underscore that this work differs in that the random nature of the analyzed composite is matched by the stochastic nature of the approach used to investigate it. Specifically, the stochastic method of conditional moments (MCM), developed earlier to analyze composites without the interface effects (Khoroshun, 1978; Khoroshun et al., 1990, 1992, 1993; Nazarenko et al., 2009), is extended here to include such effects. In fact, the present authors have used a preliminary extension in a previous work of theirs, Nazarenko et al. (2014), but the approach pursued there is too complex to obtain a complete characterization of the composite, but can rather be used to obtain the bulk modulus of the material. In the current work, the MCM is amended in a different way so as to account for the changed interface properties and obtain all properties of the composite. The idea is to, at a specific stage of the development, treat the inhomogeneities and their surfaces with different material properties as one energetic system and replace it by uniform, energy-equivalent inclusions. A similar approach was used in Chen et al. (2007) and Brisard et al. (2010), where the influence of surface stresses on the composite‘s effective properties are considered as a correction to the properties of the inclusions. Although not explicitly stated in their work (and, possibly, not intended), in fact, the approach of Duan et al. (2005) is also similar in the sense that the surface effects (as shown subsequently for bulk moduli in Section 4) appear only as a modification of the properties of inhomogeneities. As in the case of the previous results obtained using the MCM, closed-form formulas describing the effective properties are obtained also in this work.

The body of literature addressing the issue of surface effects in nanocomposites is growing at an increasing rate. The picture gleaned from the literature shows that virtually all of the existing publications employ deterministic techniques, even if analyzing composites with random microstructure. Two basic groups of techniques employed for this purpose can be identified. One is based on various forms of the self-consistent method (Willis, 1977), in which a deterministic solution for a single inclusion embedded in a homogeneous medium (Eshelby, 1957) is the main ingredient of the techniques, (see Chen et al., 2007; Duan et al., 2005; Sharma and Ganti, 2004, among others). The techniques belonging to the other group invariably employ some kind of computational approach to find elastic fields in the (randomly generated) repeating unit cell, the so-called representative cluster (Mogilevskaya et al., 2010a,b) or in a randomly generated representative volume element (see, e.g., Kushch et al., 2013), which are then post-processed in various ways to obtain the effective properties of the composite of interest (Kim and Mai, 1998; Kanit et al., 2003 among others). Such analysis is computationally very demanding, particularly in the case of realistic three-dimensional problems. In contrast, the statistical approach proposed herein is analytical and leads to the closed-form expressions defining the material's effective properties.

As mentioned earlier, this work is second in the sequence employing the method of conditional moments, a purely statistical approach, in analysis of surface effects in random nano-composites. The details of this work are arranged in the following order: To have a self-contained exposition of the material in the next Section some known aspects of the problem are reviewed: the governing equations of elasticity are cast in the form convenient for subsequent use in the context of the MCM, Gurtin–Murdoch description of the interface is inserted, and reference is made to the authors' previous results on the subject to justify the present approach. The idea of an energy-equivalent inhomogeneity is discussed in Section 3. It starts with the arguments after selection of the reference medium in the MCM, which is one of the critical aspects of the approach based on the notion of equivalent inhomogeneity. The description of equivalent inhomogeneity itself, which is the other critical aspect, is included at the end of Section 3. The development of the scalar and tensorial formulas for the effective properties resulting from the proposed approach is presented in Section 4. Sections 5 and 6 are dedicated to the discussion of the numerical results and to general comments on the proposed approach, respectively.

2. Problem statement

2.1. Governing equations

Consider a representative macro-volume V consisting of a matrix containing distributed nanoinhomogeneities. Then, the (properly evaluated) averaged macroscopic stresses $\bar{\boldsymbol{\sigma}}$ and strains $\bar{\boldsymbol{\varepsilon}}$ are related as follows

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

where $\mathbf{C}^*$ is the effective stiffness tensor. The objective of homogenization processes is to examine the effects of the properties of constituents, volume fraction, size, shape, orientation, and distribution of nanoinhomogeneities, as well as the effects of surface stresses, on the overall behavior of the composite, and to determine the effective stiffness tensor $\mathbf{C}^*$ as a function of those properties. This is also the goal in this work, but an important new aspect of it is that the nanoinhomogeneities are distributed randomly, as illustrated in Fig. 1. Given that such random materials may have (infinitely) many different realizations, the "proper" evaluation of $\bar{\boldsymbol{\sigma}}$ and $\bar{\boldsymbol{\varepsilon}}$ becomes a critical issue. In this regard, a very useful observation is that, under homogeneous loading, the stresses and strains in the representative volume constitute statistically homogeneous random fields satisfying the ergodicity condition. In probability theory it is proven that, under the condition of ergodicity, averaging over a representative volume (needed in Eq. (2.1)) and averaging over an ensemble of realizations (i.e., statistical averaging) lead to the same results (e.g., Gray, 2009; Gnedenko, 1962). Statistical averaging, which automatically takes into account the randomness of the material, is subsequently used in this work.

For any realization of linear elastic materials the problem of finding the effective stiffness tensor outlined in the previous paragraph requires the solution of the following set of equations

- Equations of equilibrium:

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

- Hooke's law:

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

- Linear kinematic relation:

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