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## Effective elastic properties of nanocomposites using a novel atomistic–continuum interphase model

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## ABSTRACT

We have introduced the concept of interphase and revised classical micromechanics to predict the effective elastic properties of heterogeneous materials containing nano-inhomogeneities. An interphase is described as an additional phase between the matrix and inhomogeneity whose constitutive properties are derived from atomistic simulations and then incorporated in a micromechanics model to compute effective properties of nanocomposites. This scale transition approach bridges the gap between discrete atomic level interactions and continuum mechanics. An advantage of this approach is that it combines atomistic with continuum models that consider inhomogeneity and interphase morphology. It thereby enables us to account simultaneously for both the shape and the anisotropy of a nano-inhomogeneity and interphase at the continuum level when we compute material's overall properties. In so doing, it frees us from making any assumptions about the interface characteristics between matrix and the nano-inhomogeneity.

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### 1. Introduction

Much of the recent research devoted to nanoscale science and to the development of various nanomaterials e.g. nanocomposites and nano-scale multilayer laminates [1,2] have suggested that they exhibit unusual thermo-mechanical, electrical, optical and magnetic properties as compared to conventional composites of similar constituents. The size-dependency of such properties has been mostly investigated in terms of surface/interface energy [3–5]. Such effects, however, are negligible except when the size range is in tens of nanometers, and if there is significant surface/interface-to-volume ratio. Thus, due to the large ratio of surface area to volume in nanosized objects, the behavior of surfaces and interfaces becomes a prominent factor controlling the mechanical properties of nanomaterials. Therefore in the case of nanocomposites the elastic properties of the interface-region (between the matrix and inhomogeneity), characterizing its stress–strain relationship, become very important and should be given due consideration while formulating their overall properties. There are different ways in which the properties of the interface can be defined. For example, if one considers an “interface” separating two otherwise homogeneous phases, the interfacial property may be defined either in terms of an *interphase*, or by introducing the concept of a dividing surface. While *interface* refers to the surface area between two phases, *interphase* corresponds to the volume defined by the narrow region sandwiched between the two phases but with different properties.

Considering *interphase* approach, where a single dividing surface is used to separate two homogeneous phases, the interface contribution to the thermodynamic properties is defined as the excess over the values that would obtain if the bulk

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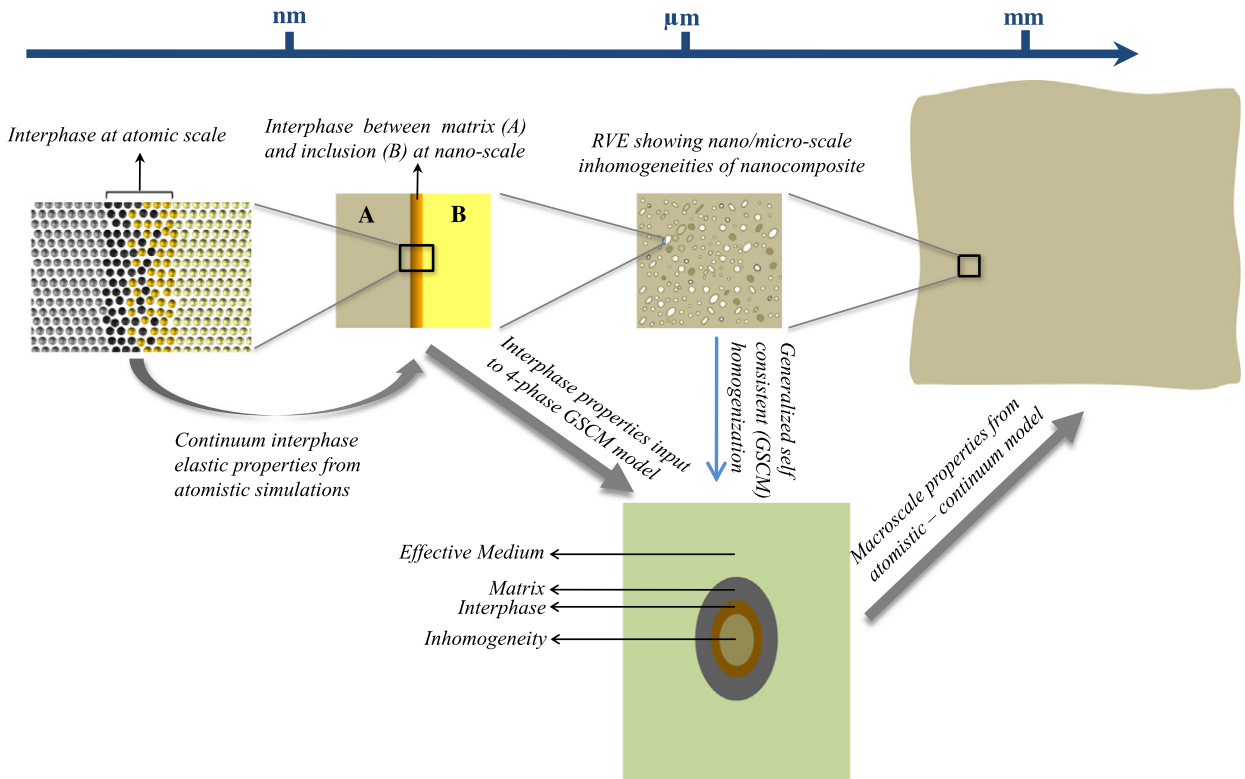
phases retained their properties constant up to an imaginary surface (of zero thickness) separating the two phases [3]. Several attempts [4–10] to analyze nanocomposites have been based on this viewpoint. Dingreville in his PhD work [11] developed the interfacial conditions for the displacement, strain and stress fields across the interface of bicrystalline materials. His work provided detailed computations of anisotropic interfacial elasticity which fully accounted for both in-plane and transverse deformations. Earlier, Shenoy [12] provided detailed anisotropic surface elastic constants for several single crystal fcc metals. More recently, Xia et al. [13] have explicitly incorporated surface elasticity in classical Euler–Bernoulli and Timoshenko models to study effective elastic modulus and the critical stress of microstructural buckling in nanoporous materials. Their results on gold nanoporous material reveal that both the elastic modulus and the critical buckling behavior exhibit a distinct dependence on the characteristic sizes of microstructures e.g. the ligament width. Although Shenoy [12] and Dingreville [14] formulated complete anisotropic surface/interface elasticity tensors, the solution of the full boundary value problem incorporating these anisotropic interface effects remains very complex to solve, and could not be analytically tractable for inhomogeneity-shapes other than spherical (or cylindrical in 2D). However, we note that finite element methods accounting for surface stress have been developed by various coworkers e.g. [15,16]. These computational methods with surface stress effect can be useful to analyze the elastic properties of nanostructured materials with complicated structures. Nonetheless, as pointed out by Brisard et al. [17], in contrast to the 2D surface/interface *stiffness* derived from the bulk elasticity tensor of the coated-phase of inhomogeneity, the surface/interface elastic tensor derived from atomistic simulations [12,14] are not necessarily positive definite. This makes analysis of a problem including surface/interface effects even more complex, and an inevitable assumption of positive definiteness of the 2D elasticity tensor is made as presented in Refs. [17,18].

Further, various micromechanical schemes have been proposed by several authors e.g. [19] and very recently Li et al. [1] developed a multi-interphase model for composites that could be used to characterize nanocomposites for various inclusion morphology, anisotropy, statistical distributions, etc. Marcadon et al. [20] also developed a model based on morphologically representative pattern-based approach which explicitly accounts for the interphase between the matrix and inhomogeneities of various morphologies and patterns. However these models need explicit properties characterizing the *interphase* volume between matrix and inclusion which, as mentioned above, cannot be provided by the interface assumption alone in every case. In models of nanocomposites, the type of interface is usually considered *a priori* to formulate their overall properties with imperfect coherent interfaces [5]. In contrast, by separately characterizing the interfacial region as an interphase in order to compute the effective properties of nanomaterials, we avoid making assumptions regarding the type of interface between the two constituents (see e.g. [21]). Another advantage of this approach is that it considers inclusion shape at the continuum level, thereby enabling both the nano-inhomogeneity and nano-interphase morphology to be simultaneously accounted for in computing the overall composite properties. Nonetheless, as mentioned by Li et al. [1], the interphase constitutes a main structural feature influencing the overall properties of composites (and particularly nanocomposites). Its explicit characterization is much more important in multi-phase composites with various inclusion shapes, orientations and spatial distributions. The nano-inhomogeneity shape is of importance when dealing with nano-platelet and nano-tube reinforcements. Obviously, in view of the small nature of interphase thickness, the use of atomistic simulations is necessary.

Considering the limitations of the coherent interface models used to characterize nanocomposites, we address the problems that arise using the *interphase* approach. In our previous study [22] we developed a scale transition framework (illustrated in Fig. 1), in which continuum interphase properties were explicitly computed from atomistic simulations which were then used to obtain the effective properties of the nanocomposite. These properties were obtained using the Eshelbian micromechanical scheme within the generalized self-consistent method. The methodology makes no assumption regarding the type of the interface (at continuum scale) between the matrix and the inhomogeneity. Previously, we used the framework to predict the isotropic elastic properties of aluminum with spherically shaped nano-voids. In this work, we extend it to obtain full anisotropic properties of single crystal aluminum with nano-voids. In this endeavor, the next section briefly states the problem we address. In Section 3 we describe the approach to determine the effective properties of the associated interphase from the atomistic simulations of the interfacial region by using Martin's inner elastic constants method [23]. Section 4 describes the micromechanical framework, drawn from Lipinski et al. [19] to compute the effective properties of the nanocomposite and finally, Section 5 presents numerical results to illustrate the effectiveness of the model.

## 2. Statement of the problem

Consider a representative volume element of a composite at the microscopic scale. The composite is considered to be homogeneous and anisotropic at the macro-continuum level; however it consists of a spatially uniform distribution of embedded inhomogeneities with nano-scale size distribution as shown in the schematic of Fig. 1. Clearly at the nano-continuum level the material becomes heterogeneous, consisting of three phases – two bulk phases of the matrix and inhomogeneity, and one of an interphase. The boundaries of the interphase are chosen to be at locations on either side of two bulk phases at which the properties do not vary significantly with position. This transition of the properties from one bulk value to the other may take place over a few layers of atoms [14]. In this article, this transition region is regarded as the interphase of thickness  $t$  which is chosen such that beyond this region the material property resembles the bulk property of the matrix on one side, and of the inhomogeneity on the other side of the interphase. We can consider the energy of the atoms compared with the per atom lattice energy to obtain the thickness of the interphase. For example, consider one



**Fig. 1.** Schematic of the scale transition framework employed in the work to compute effective elastic properties of nanocomposite from atomistic simulations.

of the simplest cases of a bicrystal with a symmetric tilt GB interface, e.g. GB interface in a Cu bicrystal with  $[1\ 0\ 0]$  tilt axis [24]. From the excess energy argument, it could be deduced that the interphase thickness is around 1 nm even for such simple systems. Real GB structures are more complex than simplified symmetric tilt GBs, let alone other interphases formed by different materials. Therefore in real materials the interphase thickness (and properties) are most likely more (and different) than what is expected from these ideal systems. Previous studies to model the behavior of nanocrystalline materials and nanocomposites that have to incorporate the volume fraction and thickness of the interphase considers this thickness to be around 1 nm. For example, Benkassem et al. [25] considered the width of the grain boundaries used in their modeling of nanocrystalline materials to be  $\sim 1$  nm, and Odegard et al. [26] in their continuum-based model of Polymer/SiO<sub>2</sub> nanocomposite have determined the interphase thickness between the SiO<sub>2</sub>/Polymer interface to be  $\sim 1.2$  nm using molecular simulations. Field quantities in the continuum framework such as stress, strain and strain energy density may all vary continuously across this region. It is quite apparent that as the size of the inhomogeneity reduces and its volume fraction increases, the ratio of the interphase to the bulk material volume increases and the interphase, therefore, exerts significant influence on the bulk macroscopic properties of the composite. Hence, an appropriate characterization of the interphase is of paramount importance while computing effective properties of the material. We obtain elastic property of the interphase from the atomistic simulation of the ensemble of atoms in equilibrium, where the ensemble is composed of the matrix and inhomogeneity phase with the interfacial region in the middle (see the first inset on the top-left in Fig. 1).

As the total energy of this discrete atomic structure can be written as the sum of energies associated with individual atoms, the second order elastic constants or the modulus tensor (first order elastic constants are identified with internal residual stress) can be written as the sum over all the atoms in the ensemble. It therefore enables the formulation of the elastic modulus associated with individual atoms, the average of which over a volume in the ensemble gives the elastic modulus of that region. This elastic modulus in general consists of two parts – the homogeneous part and the relaxation part. The homogeneous part can be evaluated using the method of homogeneous deformations [27]; however, the latter depends on the *inner displacements* of individual atoms as well. When a macroscopically uniform strain is applied to an ensemble consisting of non-equivalent or non-centrosymmetric atoms in crystalline systems (which are present in the interphase), the displacements of these atoms are different due to internal relaxation [14,23,27] compared to homogeneous deformation of equivalent atoms. Therefore, the total energy of the ensemble is dependent not only on the macroscopic strain, but also on the inner-relaxation of these atoms, which further affects the elastic modulus; the first order elastic constants or internal stress, however, remains unaffected. Hence, to compute effective elastic modulus of the interphase from atomistic simulations, we need to compute inner-relaxation associated with individual atoms under macroscopic uniform

loading. In this paper, we have adopted the methodology proposed by Martin [23] to compute internal displacement of every non-equivalent atom. These internal displacements are determined by using the usual equilibrium equations in which every atom in the ensemble under external deformation must experience zero force. Details of the approach are provided in the earlier work [22] which we briefly describe in the next section. This methodology was also adopted by Alber et al. [28] for a bicrystalline grain boundary type interface. They demonstrated that atoms near the interface display significantly different elastic properties compared to those in the bulk.

Note that if the composite contains nano-scale voids instead of nano-inhomogeneities, the region near the surface of the void, where the average of properties over a few atomic layers may be different from the bulk properties, is termed the *transition phase*; similar to surface/interphase, transition-phase/interphase are used interchangeably according to the type of the composite referred to. Once the property of the interphase is computed, it is then used in the 4-phase generalized self-consistent method by Lipinski et al. [19] to compute overall nanocomposite properties.

### 3. Interphase property

To evaluate the elastic properties of an interphase from a discrete medium viewpoint, we consider a given interface between two materials **A** and **B** (see second insert on the top in the Fig. 1). Using the methodology described in [22], the atomistic elastic constant for the interphase is obtained as:

$$C_{ijkl} = \frac{1}{\Omega} \sum_{p=1}^{L_N} \left( \Omega^p C_{ijkl}^{0p} - \sum_{q=1}^{L_N} G_{mn}^{pq} \cdot D_{mij}^p \cdot D_{nkl}^q \right) \quad (1)$$

here,  $L_N$  is number of sublattices,  $\Omega^p$  is the volume of sublattice  $p$  ( $\Omega = \sum_{p=1}^{L_N} \Omega^p$  and  $\Omega^p = \sum_{\alpha=p_1}^{p_N} \Omega^{(\alpha)}$ ; here  $p_1, \dots, p_N$  is the first and the last atom, all equivalent, associated with the sublattice  $p$ ) and  $C_{ijkl}^{0p}$  is the elastic constant of sublattice  $p(\alpha)$  without considering internal relaxation, such that  $C_{ijkl}^0 = \frac{1}{\Omega} \sum_{p=1}^{L_N} \Omega^p C_{ijkl}^{0p}$  and  $C_{ijkl}^{0p} = \frac{1}{\Omega^p} \sum_{\alpha=p_1}^{p_N} \Omega^{(\alpha)} C_{ijkl}^{0\alpha}$ . For more details regarding the definition of  $G_{mn}^{pq}$ ,  $D_{mij}^p$ ,  $L_N$ , etc. refer to [22].

Note that it is highly unlikely that the interphase between the matrix and the inhomogeneity would exhibit centrosymmetry that is similar to that of the bulk. As a consequence, its elasticity tensor, computed from the stated methodology, is not only different but could also display general anisotropy with 21 independent constants. Duan et al. [29], in their formulation of stress/strain concentration tensors for nanocomposites incorporating interface effects, have used elastic isotropic constitutive surface/interface description. Similar to Sharma et al. [4] they have noted that the interface elastic constants (similarly interphase constants for the present case) are functions of the complete set of crystallographic parameters of the surface/interface. However, computing stresses using full anisotropic elastic description of the interface is very complicated and certainly outweigh its usefulness. Sharma et al. [4] and Duan et al. [29] in their analysis of the effective properties of aluminum crystal with nano-voids have used two sets of isotropic surface properties of aluminum. Treatment of the problem taking general surface elastic properties, which are anisotropic can be very complicated and therefore, has not been explored in their analysis. We also note that in most nanocomposites, it is highly improbable if not impossible to have interphases (either naturally occurring additional *phase* near the interfacial region of matrix and inhomogeneities, or as a thin coating designed in composites with coated inhomogeneities) present in a particular crystallographic orientations. They generally tend to be *randomly oriented*. Although, studying randomly oriented anisotropic interphase is not strictly equivalent to studying equivalent isotropic interphase, orientation study (random or in specific distribution) adds to high degree of complexity which outweighs the usefulness.

In the present work, we have utilized the simplest possible Voigt–Reuss–Hill (VRH) approximation [30] to obtain isotropic interphase properties from general anisotropic properties. Obviously, one can use other averaging schemes or even one of several homogenization methods, e.g. self-consistent techniques to obtain average isotropic properties of the aggregates. But again one has to choose among various approximations, and it will not change the qualitative features of the predictions. Bhattachariya et al. [31], for example, have used the VRH approximation in their analysis of compressive brittle failure of several polycrystalline brittle ceramics and rocks, and the results of their model displayed excellent agreement with the experimental data. The average shear and bulk modulus of the interphase obtained using VRH approximation are used in the micromechanical framework described in the next section.

### 4. Effective properties of nanocomposites

Within the generalised self-consistent framework described in [22], the effective properties of the composite are given by

$$C^{eff} = c^{(3)} + \phi_1 (c^{(1)} - c^{(3)}) : A^{(1)} + \phi_2 (c^{(2)} - c^{(3)}) : A^{(2)} \quad (2)$$

where phases 1, 2, 3, 4 are the inhomogeneity, interphase, matrix and equivalent homogenized medium, respectively. The inhomogeneity, interphase and matrix are characterized by equatorial radii ( $a_1 \geq a_2 \geq a_3$ ) by  $(a_1^{(1)}, a_2^{(1)}, a_3^{(1)})$ ,  $(a_1^{(2)}, a_2^{(2)}, a_3^{(2)})$  and  $(a_1^{(3)}, a_2^{(3)}, a_3^{(3)})$ , respectively and elastic tensors by  $c^{(1)}$ ,  $c^{(2)}$ , and  $c^{(3)}$ . The unknown effective elastic constant tensor

of equivalent medium is represented by  $C^{eff}$ . The volume fraction of inhomogeneity, interphase and matrix are given as  $\phi_1 = a_1^{(1)} a_2^{(1)} a_3^{(1)} / a_1^{(3)} a_2^{(3)} a_3^{(3)}$ ,  $\phi_2 = (a_1^{(2)} a_2^{(2)} a_3^{(2)} - a_1^{(1)} a_2^{(1)} a_3^{(1)}) / a_1^{(3)} a_2^{(3)} a_3^{(3)}$ , and  $\phi_3 = 1 - \phi_1 - \phi_2$ , respectively, utilizing the framework from Lipinski et al. [19], where  $A^{(1)}$  and  $A^{(2)}$  are strain concentration tensors relating average strains of the inhomogeneity and the interphase, respectively, to the applied macroscopic strain. If we denote  $S_{ijkl}^{eff}$ ,  $S_{ijkl}^{(2)}$ , and  $S_{ijkl}^{(3)}$ , as Eshelby's tensor for ellipsoidal inclusion for effective medium, interphase and matrix, respectively, we can write these tensors in the component form as

$$A_{ijkl}^{(1)} = \left[ \phi_1 (I_{ijkl} + S_{ijmn}^{eff} \cdot [C^{eff-1}]_{mnpq} \cdot (c_{pqkl}^{(1)} - C_{pqkl}^{eff})) + \phi_2 (I_{ijkl} + S_{ijmn}^{eff} \cdot [C^{eff-1}]_{mnpq}) \cdot (c_{pqrs}^{(2)} - C_{pqrs}^{eff}) \cdot \omega_{rskl}^{(2/1)} + \phi_3 (I_{ijkl} + S_{ijmn}^{eff} \cdot [C^{eff-1}]_{mnpq}) \cdot (c_{pqrs}^{(3)} - C_{pqrs}^{eff}) \times \left( \frac{\phi_1}{\phi_1 + \phi_2} \omega_{rskl}^{(3/1)} + \frac{\phi_2}{\phi_1 + \phi_2} \omega_{rsvw}^{(3/2)} \cdot \omega_{vwkl}^{(2/1)} \right) \right]^{-1}$$

and

$$A_{ijkl}^{(2)} = \omega_{ijmn}^{(2/1)} \cdot A_{mnlk}^{(1)} \tag{3}$$

Here  $I_{ijkl}$  is the 4th order unit tensor  $\frac{1}{2}(\delta_{ik} \cdot \delta_{jl} + \delta_{il} \cdot \delta_{jk})$ .

Note that Eshelby's tensor is a function of the elastic properties of the solid (in this case they are effective medium, interphase and matrix for  $S_{ijkl}^{eff}$ ,  $S_{ijkl}^{(2)}$ , and  $S_{ijkl}^{(3)}$ , respectively) and the shape of the inhomogeneity. In the GSCM model, the inhomogeneity, interphase and the effective medium are considered to be homothetic, and therefore their shape, i.e. the ratio of semi-axes, remains the same. The effect of the shape of the inhomogeneity on the overall properties is reflected by virtue of Eshelby's tensor in the formulation.

For an anisotropic solid, Eshelby's tensor has to be computed numerically. From [32], Eshelby's tensor  $S$  is given by the following surface integral, parameterized on the surface of the unit sphere

$$S_{ijkl} = \frac{1}{8\pi} C_{mnlk} \int_{-1}^1 d\chi_3 \int_0^{2\pi} [G_{imjn}(\xi) + G_{jmin}(\xi)] d\omega$$

where

$$G_{ijkl}(\xi) = \xi_k \xi_l N_{ij}(\xi) / D(\xi) = \xi_k \xi_l (K_{kl}(\xi))^{-1}$$

$$\xi_i = \chi_i / a_i; \quad \chi_1 = \sqrt{(1 - \chi_3^2)} \cos \omega; \quad \chi_2 = \sqrt{(1 - \chi_3^2)} \sin \omega;$$

$$D(\xi) = \epsilon_{mnl} K_{m1} K_{n2} K_{l3}; \quad N_{ij}(\xi) = \frac{1}{2} \epsilon_{ikl} \epsilon_{jmn} K_{km} K_{ln}; \quad K_{ik} = S_{ijkl} \xi_j \xi_l \tag{4}$$

with  $\epsilon_{ijk}$  being the permutation tensor and  $C_{ijkl}$  the components of stiffness tensor. In some special cases e.g. for isotropic and transversely isotropic materials and for different values of  $a_i$  these equations can be obtained in closed form, and review of these results can be found in [32]. For the case of fully anisotropic material,  $S_{ijkl}$  is evaluated using the following Gaussian quadrature formula

$$S_{ijkl} = \frac{1}{8\pi} \sum_{p=1}^M \sum_{q=1}^M C_{mnlk} [G_{imjn}(\omega_q, \chi_{3p}) + G_{jmin}(\omega_q, \chi_{3p})] W_{pq} \tag{5}$$

where  $M$  refer to the Gaussian points used for integration (which is chosen to be 48 in this study) over  $\chi_3$  and  $\omega$ , and  $W_{pq}$  are the Gaussian weights.

Finally, tensors  $\omega^{(2/1)}$ ,  $\omega^{(3/1)}$  and  $\omega^{(3/2)}$  are given as follows,

$$\omega_{ijkl}^{(2/1)} = I_{ijkl} - S_{ijmn}^{(2)} \cdot [c^{(2-1)}]_{mnpq} \cdot (c_{pqkl}^{(2)} - c_{pqkl}^{(1)})$$

$$\omega_{ijkl}^{(3/1)} = I_{ijkl} - S_{ijmn}^{(3)} \cdot [c^{(3-1)}]_{mnpq} \cdot (c_{pqkl}^{(3)} - c_{pqkl}^{(1)})$$

$$\omega_{ijkl}^{(3/2)} = I_{ijkl} - S_{ijmn}^{(3)} \cdot [c^{(3-1)}]_{mnpq} \cdot (c_{pqkl}^{(3)} - c_{pqkl}^{(2)}) \tag{6}$$

Eqs. (2)–(6) present the complete sets of equations required to compute the effective elastic properties of nanocomposites for the anisotropic case of matrix, interphase and inclusion (and for their various morphologies as well). In the next section

**Table 1**  
Properties of the constituents used in the 4-phase GSCM model.

Inhomogeneity (void)	$\kappa = 0.0$	$\mu = 0.0$		
Matrix	$C_{11} = 111.4$ GPa	$C_{12} = 60.7$ GPa	$C_{44} = 31.8$ GPa	
Interphase	Surface A (111)		Surface B (100)	
	$t_1$	$t_2$	$t_1$	$t_2$
	$\kappa = 82.1$ GPa	$\kappa = 80.4$ GPa	$\kappa = 75.5$ GPa	$\kappa = 76.4$ GPa
	$\mu = 29.4$ GPa	$\mu = 29.3$ GPa	$\mu = 23.9$ GPa	$\mu = 26.1$ GPa

we present results for single crystal aluminum matrix containing nano-voids. We note that there are various theoretical frameworks developed for composites (with nano- and micron-scaled inhomogeneities) as mentioned in the previous section; however, there are few numerical results on nanocomposites other than for the case of an isotropic material with spherical nano-voids, and most simulations are conducted on aluminum with isotropic bulk and surface properties (see e.g. Duan et al. [29,33] and more recently Mogilevskaya et al. [9]). Chen et al. [34] and very recently, Mogilevskaya et al. [35] considered the case of transversely isotropic composites with reinforced periodic arrays of fibers extended to infinity in the transverse direction (2D plane strain case). They presented results for effective properties of composites with cylindrical cavities including the surface effects [34,35] and cylindrical fibres [35] (in 2D formalism, with isotropic properties of the constituents). Quang et al. [10] developed a framework for isotropic thermoelastic properties of nanocomposites with spherical inhomogeneities. In their model, the matrix and inhomogeneities are considered spherically transversely isotropic, and their formalism particularly catered to nanoparticles (spherically shaped) in semi-crystalline polymer matrix. They also considered the case of spherical nano-voids in polymer matrix to demonstrate the predictive capability of their model. However, due to the lack of appropriate surface properties needed for their computations, they used aluminum surface elastic properties in their analysis of polymer matrix with nano-voids without providing sound justifications. In the present work, we demonstrate the anisotropic elastic properties results on single crystal aluminum matrix with nano-voids. Most of the previously published work is conducted on nanoporous composites with isotropic matrix and interface elastic properties e.g. on nanoporous Al [5]. Here, we present results on effective elastic properties of similar nanoporous Al but by considering the Al matrix to be anisotropic.

Using the framework developed in [22], elastic properties of the transition phase required for predicting the effective properties of aluminum with nano-voids are given as

$$\bar{C}_{ijkl} = \frac{1}{V_0} \frac{\partial^2 U}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \Big|_{\varepsilon_{ij}=0} = C_{ijkl} + \frac{1}{t} Q_{ijkl} \tag{7}$$

where the non-zero values of  $Q_{ijkl}$  are given as

$$Q_{ijkl} = \Gamma_{\alpha\beta\kappa\lambda}^{(1)} \quad (i, j, k, l = 1, 2) \tag{8}$$

Here  $\Gamma$  represents surface elastic properties. Eqs. (7) and (8) indicate that for a bulk crystal with a planar surface, the effective properties of the transition region depend both on the surface elastic properties and the thickness of the region.

### 5. Results and discussions

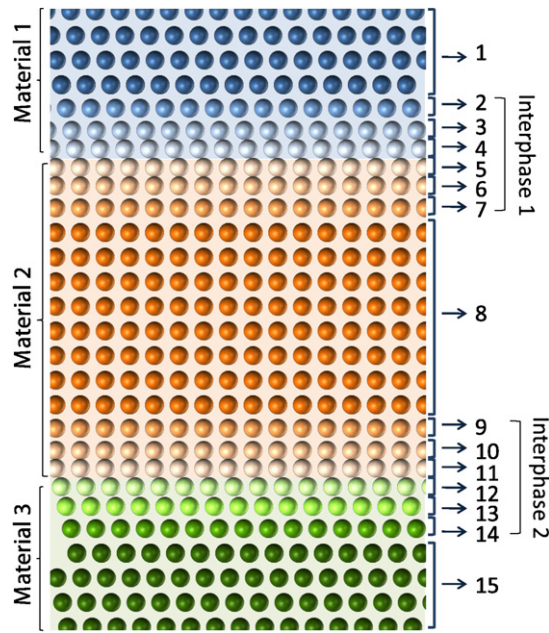
In this section, we present numerical results on single crystal aluminum matrix with nano-voids. The bulk elastic constants of aluminum are obtained from atomistic simulation using LAMMPS molecular dynamics code with EAM interatomic potential provided by Mishin et al. [36]. Using the Voight notation in  $\langle 1\ 0\ 0 \rangle$  crystallographic orientation,  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$  are 111.4 GPa, 60.7 GPa, and 31.8 GPa, respectively. The surface properties of the  $\{1\ 0\ 0\}$  and  $\{1\ 1\ 1\}$  aluminum surfaces are obtained from Miller et al. [37] and Sharma et al. [38] data from atomistic simulations.

- Surface **A** –  $\{1\ 1\ 1\}$  orientation:  $\kappa_s = 6.466$  N/m,  $\mu_s = -0.3755$  N/m
- Surface **B** –  $\{1\ 0\ 0\}$  orientation:  $\kappa_s = -2.7285$  N/m,  $\mu_s = -6.2178$  N/m

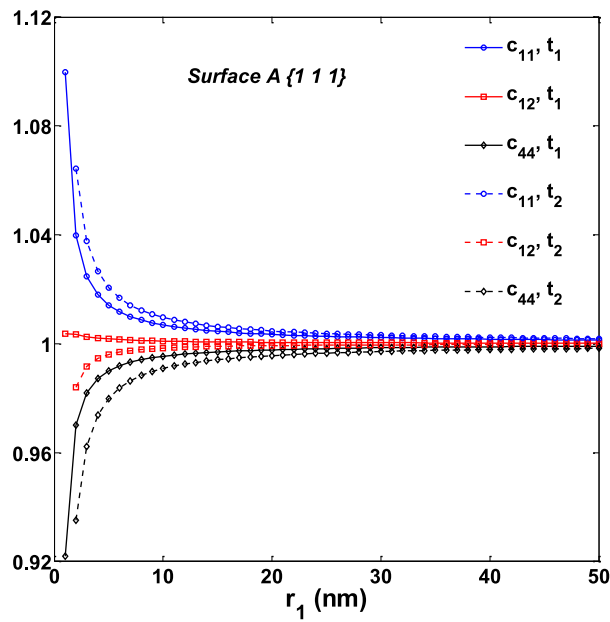
As stated previously, these surfaces are isotropic, so the surface stiffness tensor can be written in terms of  $\kappa_s$  and  $\mu_s$  as follows [3]:

$$\Gamma_{\alpha\beta\kappa\lambda}^{(1)} = \kappa_s \delta_{\alpha\beta} \delta_{\kappa\lambda} + \mu_s (\delta_{\alpha\kappa} \delta_{\beta\lambda} + \delta_{\alpha\lambda} \delta_{\beta\kappa} - \delta_{\alpha\beta} \delta_{\kappa\lambda}) \tag{9}$$

Therefore, using Eq. (9) for two surfaces – **A** and **B** – along with the bulk Al elastic properties in their respective crystallographic orientations, and putting them in Eqs. (2)–(3), we obtain the elastic constants of the transition phase surrounding the void as a function of its thickness  $t$ . For parametric evaluation, we will present results for two values of  $t$ :  $t_1 = 3(a/2)$ , and  $t_2 = 5(a/2)$ ; here  $a$  is the lattice constant of Al which is 4.05 Å. This results in the thickness of transition phase to be  $t_1 = 0.6075$  nm and  $t_2 = 1.0125$  nm, which are within the typical range [5]. An atom lying beyond this distance into the bulk from the surface typically does not experience the surface effect. We then follow the VRH averaging scheme to obtain



**Fig. 2.** Schematic of the multilayer metallic nanocomposite displaying interfacial regions at the atomic scale. Every non-equivalent atom is associated with a sublattice – 1 through 15; collection of sublattices near an interface forms the interphase as shown in the figure.



**Fig. 3.** Plots of normalized elastic properties as a function of void radius for A type transition phase.

the effective orientation-average isotropic properties (bulk and shear modulus) of the transition phase. Table 1 shows the elastic properties of the constituents used to compute the overall properties of the heterogeneous material within the GSCM framework. Note that the transition phase thickness is an intrinsic length scale in the system apart from the nano scale voids. As mentioned by Duan et al. [5], a material response containing nano-inhomogeneities is governed by the ratios of such intrinsic lengths to the characteristic length of the nano-size feature in the material, e.g., the radius of the nano-voids in the present case. In the present case changing the thickness of the transition phase around these nano-voids would alter its volume fraction, which is a function of the ratio of its thickness to void radius for a given void volume fraction. This in turn could influence the effective properties. This is relevant not only for the present case of heterogeneous materials with nano-voids, but also for nanocomposites with inhomogeneities of various morphologies. However, for the case of nano-voids note that the properties of the phase depend on its thickness as well.

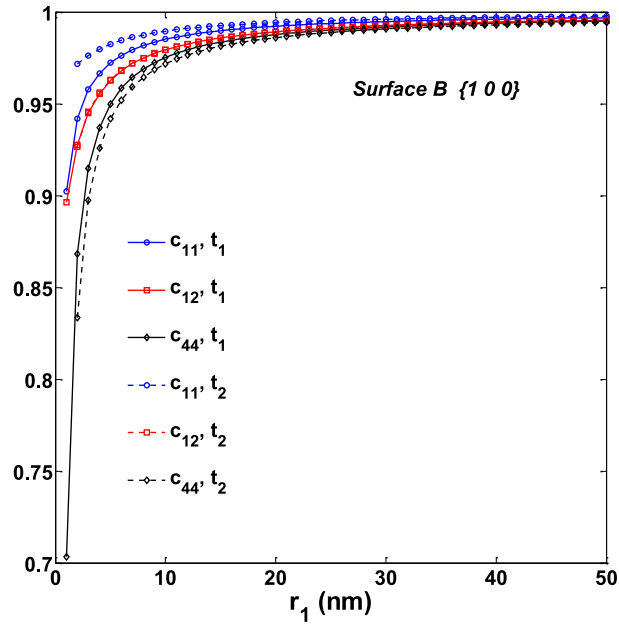


Fig. 4. Plots of normalized elastic properties as a function of void radius for **B** type transition phase.

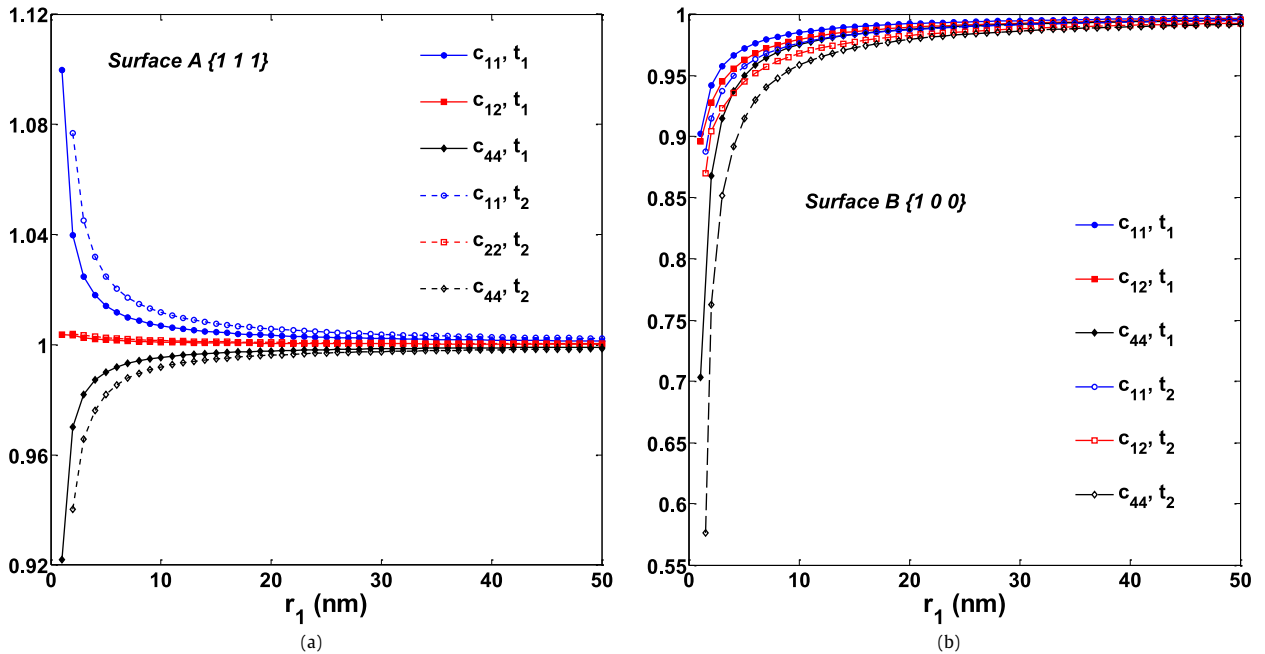
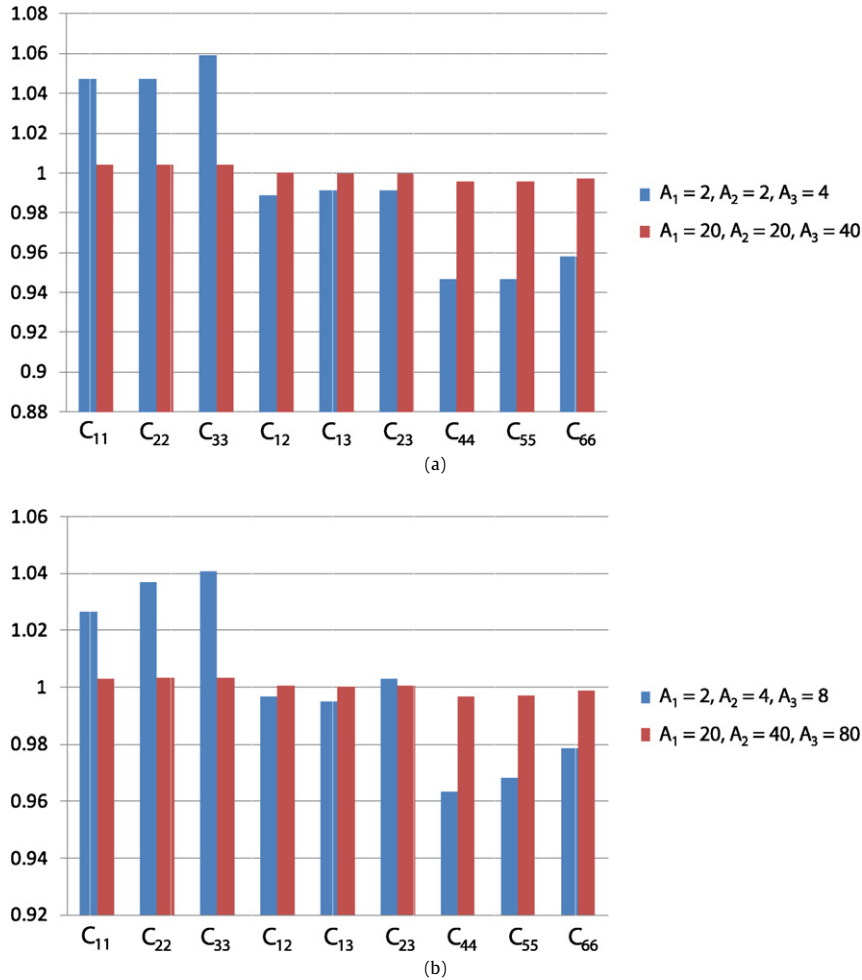


Fig. 5. Plots of normalized elastic properties with the void radius in which the properties of the transition phase are not allowed to vary with its thickness. Note the stronger effect of thicker transition phases (thickness  $t_2$ ) on the variation of bulk modulus with the void size compared with those shown in Figs. 3 and 4.

Figs. 3 to 5 present results obtained for spherical nano-voids in aluminum matrix for surfaces **A** and **B**, and for transition phase thickness  $t_1$  and  $t_2$ . Elastic constants shown in every plot are normalized by their respective elastic constants of nanoporous composites without surface effects. As the nano-voids are spherically shaped, their random distribution does not alter the anisotropy (which is cubic) of the single crystal. Figs. 2 and 3 show the variation of normalized  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  as a function of void radius for 30% void volume fraction with transition phases corresponding to **A** and **B** type surfaces, respectively. It is apparent from both plots that elastic constants  $C_{11}$ ,  $C_{12}$  and  $C_{44}$  are profoundly influenced by the surface effect ( $C_{11}$  and  $C_{44}$  more than  $C_{12}$ ) and are dependent on the void radius  $r_1$  for up to about 50 nm (normalized  $C_{11} = C_{12} = C_{44} = 1$  represent classical results without the surface effect and are independent of the radius  $r_1$ ). We note





**Fig. 6.** Bar-plots of normalized elastic constants of single crystal Al with (a) spheroidal shaped nano-voids, and (b) ellipsoidal shaped nano-voids. The voids volume fraction is 0.3 with 1.0125 nm of surface type **A** interphase thickness.

that the thickness of the interphase (parameterized as  $t_1$  and  $t_2$ ) governs its volume fraction for a given void size, and this in turn governs the properties of the nanocomposite. However, for the case of heterogeneous materials with nano-voids, the properties of the transition phase are affected by its thickness as well for a given surface orientation; the difference in the bulk and the transition phase properties becomes less as its thickness increases. Therefore, change in the properties tends to suppress the effect due to increase in the thickness of the transition phase. Hence, the effect of change of transition phase thickness is not as profound as expected in these cases. This is clearly observed in Fig. 5(a) and (b) which show the plot of normalized elastic constants of the material for **A** and **B** type transition phase whose properties are kept fixed i.e. independent of the thickness. Increasing the thickness affects the response of the material for both **A** and **B** type transition phase (much more profound for **B** type than for **A** type transition phase), compared with what is observed in Figs. 3 and 4. Finally, Fig. 6 shows a bar-plot of normalized elastic constants of single crystal Al containing spheroidal-shaped nano-voids with  $A_1 = A_2 \neq A_3$  (Fig. 6(a)) and ellipsoidal-shaped nano-voids with  $A_1 \neq A_2 \neq A_3$  (Fig. 6(b)). Volume fraction for both cases is 0.3, and normalization is with respect to their respective elastic constants of nanoporous composites without surface effects.

## 6. Conclusion

An interphase model for nanocomposites has been developed that bridges the gap between discrete systems (atomic level interactions) and continuum mechanics. Results from the atomistic simulations to obtain the continuum elastic properties of the interphase, are used in the Eshelbian micromechanical scheme within the generalized self-consistent method to obtain effective properties of nanocomposite. Contrary to the previous modeling schemes that utilize interface approach, the present methodology deals with a more general case of anisotropic elastic behavior with ellipsoidal inhomogeneities without making any assumptions regarding the type of interface between the two constituents. Simulations were conducted on single crystal Al with spherical nano-voids for two surfaces with different crystallographic orientations, and two transition phase

thickness, and also on a spheroidal and on an ellipsoidal shaped nano-voids in single crystal Al. Results clearly display the effect of the two types of surfaces on the effective bulk elastic property of the material particularly as the void size decreases as has been observed before [5,22]. To the best of authors' knowledge, such anisotropic elastic constants of nanoporous single crystal materials (or any other nanocomposites) by considering the anisotropic properties of the constituents have not been published before.

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