Estimation of anisotropic elastic properties of nanocomposites using atomistic-continuum interphase model

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A R T I C L E   I N F O

Article history:
Received 26 October 2011
Received in revised form 2 April 2012
Available online 16 May 2012

Keywords:
Interphase model
Interface properties
Anisotropic nanocomposite
Atomistic simulations
Micromechanics

A B S T R A C T

We have revised classical micromechanics by accounting for the effect of interface to predict the effective anisotropic elastic properties of heterogeneous materials containing nano-inhomogeneities. In contrast to sharp interface between the matrix and inhomogeneity, we introduce the concept of interphase to account for the interfacial-stress effect at the nano-scale. The interphase's constitutive properties are derived from atomistic simulations and then incorporated in a micromechanics-based interphase 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.

1. Introduction and background

Recent advances in nanotechnology have led many investigations devoted to nanoscale science and to the development of various nanomaterials e.g. nanocomposites and nano-scale multilayer laminates (Benkassem et al., 2008; Demkowicz et al., 2008; Li et al., 2010). These nanomaterials are extremely interesting because they exhibit unusual mechanical, thermo-mechanical, electrical, optical and magnetic properties as compared to conventional composites or laminates of similar constituents, volume proportion and shape/orientation of reinforcement. Nanomaterials in general can be classified into two categories – first, if the characteristics length of the microstructure, e.g. grain size of a polycrystalline material, is in the nanometer range, it is called a nano-structured material; second, if at least one of the overall dimensions of a structural element is in the nanometer range, it may be called a nano-sized structural element. This may include nano-particles, nano-films and nano-wires (Alymov and Shorshorov, 1999; Dingreville et al., 2005). In this work, we describe nanocomposites as either bulk materials that consist of inhomogeneities with at least one dimension within the range of 1–100 nm, or as nano-scale structures with inhomogeneities. The latter case, of course, involves nano-scale inhomogeneities, since these inhomogeneities should be about one order smaller than the structure itself.

The size-dependency in the area of nanotechnology is well known and has been mostly investigated in terms of surface/interface energy, stress and strain (Dingreville et al., 2005; Duan et al., 2005b; Sharma and Ganti, 2004). 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 nanostructured materials. Coordination number of atoms near the surface is less than that of the bulk atoms, which correspondingly induces a redistribution of electronic charge altering the binding situation (Sander, 2003). As a result, the energy of these atoms is different from that of the atoms in the bulk. Similarly, atoms at (or near) an interface of two materials experience a different local environment than atoms in the bulk of the materials, and the equilibrium position and energy of these atoms are also different from those of the atoms in the bulk. Therefore in the case of nanocomposites the elastic properties of this interface-region 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 surface (and 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 interface 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 phases retained their properties constant up to an imaginary surface (of zero thickness) separating the two phases (Dingreville et al., 2005). In bimaterials, for example, there typically exist two distinct length parameters, namely the atomic spacing (lattice parameter) \( d \), and the radius of curvature of the interface \( D \), where \( D \) is generally several orders of magnitude greater than \( d \) for most of the problems of engineering interest. Thus, if one measures the characteristic length of these inhomogeneities by \( D \), the discrete atomic structure of the material is smeared (homogenized) into a continuum. Using this method, one can observe neither the atomic structure, nor the thickness of the interphase. One can only see that the properties jump from one bulk value to the other across the interface. Consequently, one may perceive that field quantities, such as stress and displacement, are discontinuous at the interface when measured by the mesoscopic length scale \( D \) (see Dingreville, 2007). Several attempts (Duan et al., 2005b; Huang and Sun, 2007; Lim et al., 2006; Mogilevskaya et al., 2008; Quang and He, 2007; Sharma and Ganti, 2004; Sharma and Wheeler, 2007) to analyze nanocomposites have been based on this viewpoint. Dingreville in his Ph.D. work (Dingreville, 2007) developed the interfacial conditions for the displacement, strain and stress fields across the interface of bi-crystalline materials. His work provided detailed computations of anisotropic interfacial elasticity which fully accounted for both in-plane and transverse deformations. Earlier, Shenoy (2005) provided detailed anisotropic surface elastic constants for several single crystal fcc metals. More recently, Xia et al. (2011) 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.

Within the linear elasticity framework, two models have been developed to characterize imperfect interfaces which, in a mathematically rigorous manner, are shown to be associated with limiting cases of thin-soft and thin-stiff interphases. First model is the spring-layer imperfect interface model (see e.g. Achenbach and Zhu, 1989; Benveniste, 1985; Duan et al., 2005c; Hashin, 2002; Qu, 1993) in which the traction is continuous across an interface and proportional to the displacement jump across it. The second model is the membrane-type imperfect interface model proposed by Gurtin and Murdoch (1975), which is more common for modeling the surface/interface effects in nanocomposites and nano-scale structures (see, e.g. Chen et al., 2007; Chen et al., 2007b; Dingreville et al., 2005; Duan et al., 2005b; Mitrushcenko et al., 2010; Mogilevskaya et al., 2010; Mogilevskaya et al., 2008; Quang and He, 2007; Quang and He, 2008; Sharma and Ganti, 2004; Sharma and Wheeler, 2007; Shenoy, 2002). This model uses the generalized Young–Laplace equation (Povstenko, 1993) representing equilibrium equation for the interface in solids, and a linear constitutive law of surface/interface elasticity. It stipulates that the displacement is continuous across an interface but the traction suffers a jump due to the presence of an interfacial tangential stress tensor proportional to the interfacial tangential strain tensor and related to the traction vector jump by the Young–Laplace equation. Therefore, by using either the spring type interface model or membrane type interface model, inevitable assumption of continuity of traction (with displacement discontinuity) or continuity of displacement (with traction discontinuity), respectively, is made. In practice, general interfaces can have both traction and displacement discontinuity at the same time which cannot be modeled using either interface approach. However, interphase approach presented in this work do not make any such assumptions.

Recently various solutions have appeared in the literature involving computation of Eshelby’s tensors, overall (or effective) thermoelastic properties, etc. for the nano-inclusion problems. These solutions assume an elastically isotropic surface/interface and spherical inhomogeneities, spherical voids (or cylindrical shaped in 2D) (Duan et al., 2005a; Mogilevskaya et al., 2010). Usually, such problems are solved utilizing an imperfect interface model representing a thin and stiff interphase. Therefore, not only the region around the interface (which constitutes the interphase between the matrix and inhomogeneity) is considered to be thin but also very stiff compared with either of the two phases. Such assumption never appears in the model using interphase approach as presented here. The methodology incorporating the surface/interface effect to obtain size-dependent effective elastic properties (Duan et al., 2005b), Eshelby’s tensor (Sharma and Ganti, 2004), or the stress distribution in the composite (Mogilevskaya et al., 2008) is based on the formalism proposed in the 1970s by Gurtin and Murdoch (1975), Gurtin et al. (1998). They provided a mathematical framework to incorporate surface stress and interfacial energy (which are obtained from atomistic simulations) into the continuum mechanics formulations.

If the phase between the inhomogeneity and the matrix is very thin and stiff compared to either material (which is often assumed in the above stated models of nanocomposites), the equilibrium equation of the finite-thickness interphase asymptotically yields a generalized Laplace equation linking the discontinuity of bulk stresses to the stresses within the thin coating (see e.g. Hashin, 2002). Using this, general expressions for the displacements in an infinite region containing a spherical inhomogeneity are obtained using methodology from Lur’e (1964) in terms of Legendre polynomial of second order. Although Shenoy (2005) and Dingreville and Qu (2008) 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). Although we note that finite element methods accounting for surface stress have been developed by various coworkers e.g. Gao et al. (2006), Yvonnet et al. (2008). These computational methods with surface stress effect can be useful to analyze the elastic properties of nano-structured materials with complicated structures. Nonetheless, as pointed out by Brisard et al. (2010), 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 (Dingreville and Qu, 2008; Shenoy, 2005) 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 Brisard et al. (2010), Quang and He (2008). This is another limitation of the interface approach which does not appear with the interphase approach presented here.

Further, various micromechanical schemes have been proposed by several authors e.g. Lipinski et al. (2006) and very recently by Li et al. (2010) developed a multi-interphase model for composites that could be used to characterize nanocomposites for various inclusion morphology, anisotropy, statistical distributions, etc. 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. Hence, either of the two interface approaches cannot be used in such micro-mechanical models but obtaining interphase properties using present approach is perfectly suited. Moreover, in models of nanocomposites, the type of interface is usually considered apriori to formulate their overall properties with imperfect coherent interfaces (Duan et al., 2005b). 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. Benveniste and Miloh, 2001). 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. (2010), the interphase constitutes a main structural feature influencing the overall properties of composites (and particularly nano-composites). 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, our objective is to address the problems that arise using the interphase approach. In our previous study (Paliwal and Cherkaoui, 2011) 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. The originality of this approach stems from the fact that this model is first of its kind to estimate elastic properties of composites with nano-scale heterogeneities by explicitly accounting for the inhomogeneity shape and size at the continuum scale, and also accounting for interfacial atomic structure from which the volume fraction and the elastic properties of the interphase are computed. In so doing, the model does not make any assumptions which are inevitably made by using interface approach as stated above. 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 of spherical, cylindrical, and ellipsoidal shape. 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 (Martin, 1975). Section 4 describes the micromechanical framework, drawn from Lipinski et al. (2006) to compute the effective properties of the nanocomposite and finally, Section 5 presents numerical results to illustrate the effectiveness of the model by comparing results from previous works.

2. Problem statement and interphase characterization

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

![Fig. 1. Schematic of the scale transition framework employed in the work to compute effective elastic properties of nanocomposite from atomistic simulations.](image-url)
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 (Dingreville and Qu, 2008). The interphase, therefore, has a finite volume and may be assigned thermodynamic properties in the usual way. Strictly speaking, in the framework of continuum mechanics an interface between two dissimilar materials may be considered as a region over which the material properties change gradually from the bulk property of one material to the other. In this paper, this transition region is regarded as the interphase of thickness \( t \). Therefore, \( t \) 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 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 (Spearot et al., 2008). From the excess energy argument, it could be deduced that the interphase thickness is around 1 nm (with 7–9 atomic layers on either side of the interface, or 15–19 total atomic layers (Spearot et al., 2008)) 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 nano-composites 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., 2008) considered the width of the grain boundaries used in their modeling of nanocrystalline materials to be ~1 nm, and Odegard et al. (2005) in their continuum-based model of Polymer/ SiO2 nanocomposite have determined the interphase thickness between the SiO2/ Polymer interface to be ~1.2 nm using molecular simulations. In both these cases, interphase properties are very different from both the inhomogeneity and the matrix.

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.

In order to characterize the interphase we regarded it as a magnified version of the region, consisting of a gap defined by the interatomic distance between atoms of the bulk phases. This region manifests itself as the interface at higher end of the nano to micro scale, and as an additional phase at lower scales. In order to study the effect of the interphase, we need to characterize it by its stiffness tensors and incorporate it, for example, in mechanistic models for composites in order to obtain its effective properties. The elastic property of the interphase is obtained 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 (Born and Huang, 1954); 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 (which are present in the interphase), the displacements of these atoms are different due to internal relaxation (Born and Huang, 1954; Dingreville and Qu, 2008; Martin, 1975) compared to homogeneous deformation of equivalent or centrosymmetric 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. We note that Dingreville and Qu (2009) have accounted for the internal relaxation to compute the interface elastic properties of a grain boundary type crystalline interface in a bicrystal. In these cases, atoms near the interface are of the same type but are not necessarily centro-symmetric. In their analysis, they however have made a simplifying assumption in which each atom carries the remote applied stress uniformly, including those at the interface. This results in uniform traction at each atomic site, which further results in Reuss-type lower bound computation of elastic properties. Such methodology may work well with homogeneous interfaces in the monoatomic ensemble. However, this may not be appropriate to compute internal-relaxation for atoms constituting interphases between two different materials (which is the case with nanocomposites), particularly when the resulting interface is not homogeneous and therefore when the stress for every atom is not equivalent to the macroscopic stress. In this paper, we have adopted the methodology proposed by Martin (1975) 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 next section. This methodology was later adopted by Alber et al. (1992) 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. (2006) to compute overall nanocomposite properties.

3. Atomistic and continuum description of the interphase

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 inset on the top in the Fig. 1). For a periodic system containing \( N \) equivalent, centrosymmetric atoms, the total energy \( E^{(s)} \) of the atom \( x \) is given by

\[
E^{(s)} = E^0 + \sum_{z \neq x} E(r^{xz}) + \frac{1}{N} \sum_{z \neq x} \sum_{y \neq z} E(r^{yz}, r^{yz}) + \ldots + \frac{1}{N^2} \sum_{z \neq x} \sum_{y \neq z} \sum_{w \neq z} E(r^{yz}, r^{zw}, r^{yz}, r^{zw}, \ldots, r^{ws})
\]

(1)
where \( r^{2} = \sqrt{(r_{x}^{2})^2 + (r_{y}^{2})^2 + (r_{z}^{2})^2} \) is the scalar distance between atom \( x \) and atom \( y \) and \( E \) is the interatomic potentials function, which may include pair potentials such as the Lennard–Jones potential as well as multi-body potentials such as the Embedded Atom Method (EAM) potentials. The total energy of this ensemble containing \( N \) such atoms is \( E = \sum_{i=1}^{N} E_{i}^{(0)} \). If one considers a single solid of infinite extent subjected to a macroscopically uniform strain field \( \varepsilon_{ij} \), Johnson (Johnson, 1972) demonstrated that the elastic stiffness tensor \( C_{ijkl}^{0} \) of the bulk crystal is

\[
C_{ijkl}^{0} = \frac{1}{\Omega} \frac{\partial^{2} E}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \frac{1}{\Omega} \sum_{x} N \frac{\partial^{2} E^{(0)}}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \frac{1}{\Omega} \sum_{x} N \frac{\partial^{2} E^{(0)}}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}}
\]

where \( \Omega \) is the volume of the structure, \( \Omega_{ijkl}^{(0)} \) is the volume of Voronoi polyhedron associated with atom \( x \) with \( C_{ijkl}^{0} \) defined as its atomic level elastic constants, \( r_{x}^{2} \) and \( r_{xy}^{2} \) is the scalar distance between atoms \( x \) and \( y \) in relaxed and deformed configurations, respectively, and \( F_{ij} \) is the deformation gradient from which macroscopic homogeneous Lagrange strain is defined as

\[
\varepsilon_{ij} = \frac{1}{2} (F_{ij} \cdot F_{ij} - \delta_{ij})
\]

However, when considering a periodic atomic ensemble containing non-equivalent atoms (e.g. the case of systems containing grain boundaries, interfaces, dislocation, interstitials) subjected to a macroscopically uniform deformation, internal relaxations occur in addition to the homogeneous deformation of the ensemble. In this case, Eq. (2) can be interpreted as a description of the homogeneous elastic response of the ensemble. To take into account the internal displacements, we use the methodology described by Martin (1975) where we associate every non-equivalent atom in the ensemble with a different sub-lattice. As is seen from a simple schematic of multi-layer metallic nanocomposite consisting of Materials 1, 2, and 3 in Fig. 2(a), there are 15 sublattices where each sublattice contains atoms that are equivalent to each other. Clearly, larger numbers of atoms are non-equivalent near the interface as could be interpreted from the figure, compared to those that are present in the bulk. Excess energy of atoms near the interfacial region could be used to deduce the thickness of the interphase as illustrated in Fig. 2(b). The figure shows a \( \sum_{5}(310)/[001] \) tilt GB interface in Cu obtained after energy minimization using conjugate gradient method, and per-atom excess energy profile (relative to their energy in the bulk) as a function of their Y-position. GB structural units are also shown in the plot, and the atoms are colored by their excess energy. Here, every atom in a periodic structure with same excess energy (they are equivalent atoms indicated with same color) constitutes a sublattice. Therefore, a sublattice is a union of each Voronoi polyhedra associated with equivalent atoms. For atoms in FCC lattice, they are rhombic dodecahedra but are not shown in the figure as their projection is complex to draw. It is apparent that the thickness of the interphase in this case is at least 1 nm with about 9 atomic layers on each side of the interface (see the shaded region in the graph). In real materials, the interphase could be thicker and its constituents could display wider range of excess energy of its constituents than shown for a symmetric tilt GB case. We also note that the equilibrium (or relaxed) configuration is considered as the reference configuration which is obtained using molecular static simulations. These relaxed atomic positions are required to compute interphase properties as presented later in this section. Once this initial reference configuration is obtained, no further atomicistic simulations are necessary.

The internal relaxation occurs between atoms in different sublattices (as they are non-equivalent), and equivalent atoms deform homogeneously with respect to each other in a sublattice. Every atom is associated with a sublattice which is denoted by \( p(x) \) for atom \( x \). The atomic level mapping between the undeformed, \( r_{x}^{0} \), and deformed, \( r_{x} \), configurations between atoms \( x \) and \( y \) belonging to sublattices \( p(x) \) and \( p(y) \), respectively is defined as

\[
r_{x}^{p} = F_{ij}^{p} r_{ij}^{(0)} + \frac{1}{2} \left[ F_{ij}^{p} \frac{1}{p_{\beta}} (\varepsilon_{ij}^{(0)} - \varepsilon_{ij}^{(p)}) \right]
\]

Here, \( \varepsilon_{ij}^{(0)} \) is the \( \beta \)-th component of the rotationally invariant internal displacement vector of the \( p(x) \) sublattice. Here, repeated subscript indices imply summation. Note that the internal displacement (in addition to homogeneous deformation) between equivalent atoms is zero. Due to the internal displacements of non-equivalent atoms, the strain energy is a function of these variables as well as in addition to the macroscopically applied strain \( \varepsilon_{ij} \). We now write the total inter atomic energy of the ensemble expanded in a Taylor series about \( (\varepsilon_{ij}^{(0)}, \varepsilon_{ij}^{(p)}) \) as

\[
\begin{align*}
\frac{1}{\Omega} (E - E_{\text{relaxed}}) &= C_{ijkl}^{0} \cdot \varepsilon_{ij} + \frac{1}{2} C_{ijkl}^{0} \cdot \varepsilon_{kl} \cdot \varepsilon_{ij} + \cdots + D_{ijkl}^{(p)(0)} \cdot \varepsilon_{ij}^{(p)} + D_{ijkl}^{(p)(p)} \cdot \varepsilon_{ij}^{(p)} \\
&\quad + D_{ijkl}^{(p)(p)} \cdot \varepsilon_{ij}^{(p)} \cdot \varepsilon_{kl}^{(p)} + \frac{1}{2} E_{ijkl}^{(p)(p)(p)} \cdot \varepsilon_{ij}^{(p)} \cdot \varepsilon_{kl}^{(p)} \cdot \varepsilon_{lm}^{(p)}
\end{align*}
\]

here, \( \Omega \) is the volume of the periodic ensemble, \( C_{ijkl}^{0} \) and \( C_{ijkl}^{0} \) are the familiar elastic constants in the absence of internal displacement, and \( D_{ijkl}^{(p)(0)} \), \( D_{ijkl}^{(p)(p)} \), \( E_{ijkl}^{(p)(p)(p)} \) and other coefficient of higher powers of \( \varepsilon_{ij}^{(p)} \) could be interpreted as the inner elastic constants, which are defined as

\[
\begin{align*}
D_{ijkl}^{(p)(0)} &= \frac{1}{\Omega} \frac{\partial^{2} E}{\partial \varepsilon_{ij}^{(p)2} \partial \varepsilon_{kl}} \\
D_{ijkl}^{(p)(p)} &= \frac{1}{\Omega} \frac{\partial^{2} E}{\partial \varepsilon_{ij}^{(p)} \partial \varepsilon_{kl}^{(p)}} \\
E_{ijkl}^{(p)(p)(p)} &= \frac{1}{\Omega} \frac{\partial^{2} E}{\partial \varepsilon_{ij}^{(p)} \partial \varepsilon_{kl}^{(p)} \partial \varepsilon_{lm}^{(p)}}
\end{align*}
\]

where, \( F^{2} \) and \( F^{4} \) are the position vectors of atom \( x \) in relaxed and deformed configurations, respectively. Here, \( p(x) \) is the position vector of the sublattice \( p \) in the relaxed configuration and can be interpreted as the position of a reference atom in a sublattice as suggested by Martin (1975). However, note that the interatomic potential used in these formulations is a function of the position vectors of the individual atoms constituting these sublattices, and not the position vectors of the sublattices themselves; these derivatives for this specific case of the embedded atom method potential (Daw and Baskas, 1984) are formulated in Appendix B.

Note that the internal displacement vectors are dependent on the applied macroscopic strain \( \varepsilon_{ij} \) and would assume values which minimize the total energy of the system under imposed deformation. Therefore, under equilibrium, every \( \varepsilon_{ij}^{(p)} \) (in what follows sublattices \( p(x) \), \( p(y) \),... are denoted as \( p, q, ... \) can be written as a function of \( \varepsilon_{ij} \) and can also be expanded in a Taylor’s series about \( \varepsilon_{ij} \) as

\[
\varepsilon_{ij}^{(p)} = A_{pq}^{(ij)} \cdot \varepsilon_{pq} + A_{pq}^{(ij)} \cdot \varepsilon_{pq} + A_{pq}^{(ij)} \cdot \varepsilon_{pq} + \cdots
\]

Substituting Eq. (9) in Eq. (5), we obtain

\[
E - E_{\text{relaxed}} = \sum_{p=1}^{n} \left[ (\Omega_{p}^{(p)} C_{ijkl}^{0} \cdot D_{ijkl}^{(p)(0)} \cdot A_{ijkl}^{(0)}) \cdot \varepsilon_{ij}^{(p)} + \sum_{k=1}^{n} \left[ \frac{1}{2} D_{ijkl}^{(p)(p)} \cdot A_{ijkl}^{(p)} + \sum_{l=1}^{n} \frac{1}{2} D_{ijkl}^{(p)(p)} \cdot A_{ijkl}^{(p)} \right] \cdot \varepsilon_{ij} \cdot \varepsilon_{kl} \right]
\]
where, $L_N$ is number of sublattices, $X_p$ is the volume of sublattice $p$ ($X = \sum_{p=1}^{L_N} X_p$ and $X = \sum_{p=p_1}^{p_N} X_p$); here $p_1, \ldots, p_N$ is the first and the last atom, all equivalent, associated with the sublattice $p$ and $C_{ijkl}$ is the elastic constant of sublattice $p(x)$ without considering internal relaxation, such that $C_{ijkl} = \frac{1}{L_N} \sum_{p=p_1}^{p_N} \Omega c_{ijkl}^{(p)}$ and $C_{ijkl} = \frac{1}{L_N} \sum_{p=p_1}^{p_N} \Omega c_{ijkl}^{(p)}$. Therefore, the elasticity tensor including the internal relaxation is given as

$$C_{ijkl} = \frac{1}{\Omega} \frac{\partial^2 E}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \bigg|_{\varepsilon_{ij}=\varepsilon_{kl}=0}$$

$$= \frac{1}{\Omega} \sum_{p=1}^{L_N} \left( \Omega c_{ijkl}^{(p)} + 2D_{ij}^{(p)} A_{ijkl}^P + D_{ij}^{(p)} A_{ijkl}^P + D_{ij}^{(p)} A_{ijkl}^P + D_{ij}^{(p)} A_{ijkl}^P + \sum_{q=1}^{L_N} E_{ijkl}^{(p)} \cdot A_{ijkl}^P \right)$$

Note that it may be easier to obtain homogeneous elasticity tensor $C_{ijkl}^{(p)}$ directly from atomistic simulation; however accurately computing inner relaxation vectors of every nonequivalent entity to obtain complete $C_{ijkl}$ is very tedious and difficult. For homogeneous interfaces, Dingreville and Qu (2009) had also presented a framework to compute such inner relaxation for further computing interface elastic constants. Similarly in our case, advantage of using sublattices is to obtain these critical inner relaxations particularly near the interfaces without substantially enhancing computational costs.

At equilibrium, the derivative of total energy with respect to the internal displacement vectors is zero. Therefore, by using the relation

$$\frac{\partial E}{\partial \varepsilon_{ij}} = D_{ij}^{(p)} + D_{ij}^{(p)} \varepsilon_{ik} + \cdots + E_{ijkl}^{(p)} \left( A_{ijkl}^P \varepsilon_{ik} + A_{ijkl}^P \varepsilon_{ik} + \cdots \right) + \cdots = 0$$

**Fig. 2.** (a) 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. (b) Structure of $\Sigma 5$ (310) [001] tilt GB interface in Cu after equilibration showing periodic GB structural units with atoms colored by their excess energy (left), and GB interface energy profile (right). Shaded region on the plot show the thickness of the interphase which is about 1 nm.
we can obtain coefficients \( A_{ij} \) used in the expansion of internal displacement vectors \( \zeta_i \). Using these coefficients along with Eqs. (6)–(8) in Eq. (11) we can obtain the elasticity tensor of the ensemble with non-equivalent atoms.

Eq. (12) is valid for any applied deformation; therefore, the coefficient of each power of \( q \) is zero as well. Thus

\[
D^p_i = 0, \quad D^q_{ij} + E^q_{ij} A^p_{ij} = 0
\]

defining an inverse \( G \) such that

\[
G^{pq} : E^{pq}_{ij} = \delta_{ik} \cdot \delta_{jr}
\]

we can obtain \( A^p_{ij} \) as

\[
A^p_{ij} = -G^{pq}_{ij} \cdot D^q_{ik}
\]

We note that before using these equations to obtain the overall stiffness tensor, the matrix representation of \( E^{pq}_{ij} \) is rank-deficient because the total energy depends on the difference \( c^{ij}_{ij} - c^{ij}_{ij} \) and not on \( c^{ij}_{ij} \) alone (see Appendix A for details on formulating \( E^{pq}_{ij} \) and removing rank deficiency).

Substituting Eqs. (13) and (15) in Eq. (11), the atomistic elastic constants are obtained as

\[
C_{ijkl} = \frac{1}{\Omega} \sum_{p=1}^{6} (\Omega \cdot G^{pq}_{ijkl} - \sum_{q=1}^{6} C^{pq}_{mn} \cdot D^p_{mj} \cdot D^q_{kl})
\]

Similarly, for individual sublattices, the elastic constants are

\[
C^p_{ijkl} = \left( C^{pq}_{ijkl} - \frac{1}{6} \sum_{q=1}^{6} C^{pq}_{mn} \cdot D^p_{mj} \cdot D^q_{kl} \right)
\]

Alber et al. (1992) has provided the expressions for \( D^p_{ij} \) and \( E^{pq}_{ij} \) for the case of the embedded atom method (Daw and Baskas, 1984) (EAM) interatomic potential; however, there is a minor error in their formulation of \( D^p_{ij} \), as the expression \( D^p_{ij} \) for Eqs. (B-6a) (Alber et al., 1992) is incorrect. We have provided a complete formulation for \( C^p_{ijkl} \) in Appendix B for EAM interatomic potential.

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. (2005a), in their formulation of stress/strain concentration tensors for nanocomposites incorporating interface effects, have used elastic isotropic constitutive surface/interface description. Similar to Sharma and Ganti (2004) 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. Moreover, in composites with randomly distributed inhomogeneities and anisotropic interphases with respect to their crystallographic orientations, one can obtain meaningful results by employing an isotropic description of their constitutive law using suitable orientation-averages of interphase properties. Sharma and Ganti (2004) and Duan et al. (2005a) in their analysis of the effective properties of aluminum crystal with nano-voids have used two sets of isotropic surface properties of aluminum. They used surface properties derived from the atomistic simulation results of Miller and Shenoy (2000) on \{100\} and \{111\} aluminum surfaces. However, elastic tensors characterizing the surface which does not exhibit threefold or higher symmetry (surfaces \{111\} and \{100\} have threelfold and fourfold symmetry, respectively see e.g. Dingreville et al. (2005), Shenoy (2005)) can in general be anisotropic (Buerger, 1963). 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 anisotropic 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 a simplest possible Voigt-Reuss-Hill (VRH) approximation (Hill, 1951) 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. Bhattacharya et al. (1998), 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.

If \( k_{AV} \) and \( g_{AV} \) denote the average bulk modulus and average shear modulus, respectively and \( k_V, g_V \) and \( k_s, g_s \) denote the corresponding Voight and Reuss bounds respectively, then from Hill (1951)

\[
9k_Y = (C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{31}) + 2C_{44},
\]

\[
15g_Y = (C_{11} + C_{22} + C_{33}) - (C_{12} + C_{23} + C_{31}) + 3(C_{44} + C_{55} + C_{66})
\]

\[
1/k_R = (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66})
\]

\[
15/g_R = 2(4(S_{11} + S_{22} + S_{33}) - 2(S_{12} + S_{23} + S_{31}) + 3(S_{44} + S_{55} + S_{66})
\]

Where the \( C_{ij} \) used are the usual 6 \( \times \) 6 matrix representation of the tensor of elastic constants. The average shear and bulk modulus of the interphase obtained from these equations are used in the micromechanical framework described in the next section.

4. Effective elastic constants of nanocomposites

Many micromechanical schemes have been successfully used to obtain effective elastic constants of heterogeneous solids. For a comprehensive exposition, one can refer to the monographs (Aboudi, 1991; Qu and Cherkaoui, 2006). In this paper, the single-coated inhomogeneities micromechanical scheme first developed by Cherkaoui et al. (1994) and later extended by Lipinski et al. (2006) for multi-coated inhomogeneities is used to compute the effective properties of the nanocomposite. The two-phase nanocomposite with interfacial effect is transformed to a three-phase nanocomposite. The detailed derivation of the effective elastic constants can be found in Lipinski et al. (2006); here we briefly present the necessary formulations.

Consider a representative volume consisting of a matrix phase, several ellipsoidal inhomogeneities and an interphase between them as shown in the schematic in Fig. 1 (see third inset from the top and first inset at the bottom). A perfect bond is assumed between the constituents. This composite is subjected to a homogeneous stress or strain

\[\text{Note that perfect bonding is assumed between matrix and interphase (S_i), and between the interphase and the inhomogeneity (S_j) i.e. } \sigma^{ij}_{ij} n^i = 0 \text{ and } \sigma^{ij}_{ij} n^j = 0 \text{ where superscript } p = 1, 2 \text{ represents interfaces } S_1 \text{ and } S_2, \text{ respectively and } [\ldots] \text{ represents discontinuity of the quantity at those interfaces.} \]
boundary condition. Within the GSCM framework, the problem presents itself as a four-phase composite model 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 \((a_1 > a_2 > a_3)\) by \((a_1^{(1)}, a_1^{(3)}, a_2^{(1)}, a_2^{(3)}, a_3^{(1)}, a_3^{(3)})\) respectively and elastic tensors by \(c^{(1)}, c^{(2)}\), and \(c^{(3)}\). The unknown effective elastic constant tensor of equivalent medium is represented by \(C^{\text{ef}}\). The volume fraction of inhomogeneity, interphase and matrix is given as \(\phi_1 = a_1^{(1)} a_1^{(3)} / a_1^{(2)} a_2^{(3)} a_3^{(2)}\), \(\phi_2 = a_2^{(1)} a_2^{(3)} / a_1^{(2)} a_2^{(2)} a_3^{(2)}\), and \(\phi_3 = 1 - \phi_1 - \phi_2\), respectively.

Utilizing the framework from Lipinski et al. (2006), the effective properties of the composite are given by

\[
C^{\text{ef}} = C^{(2)} + \phi_1 (C^{(1)} - C^{(2)}) + \phi_2 (C^{(2)} - C^{(3)}) + \phi_3 (C^{(3)} - C^{(2)})
\]

where \(A^{(1)}\) and \(A^{(2)}\) are strain concentration tensors representing average strains of the inhomogeneity and the interphase, respectively, to the applied macroscopic strain. If we denote \(S^{\text{ef}}\), \(S^{\text{int}}\), and \(S^{\text{mat}}\) as the Eshelby's tensor for ellipsoidal inclusion for effective medium, interphase and matrix, respectively, we can write these tensors in the component form as

\[
A^{(1)}_{ijkl} = \phi_1 \left( I_{ijkl} + S^{\text{int}}_{mnpp} \cdot C^{(1)}_{pppq} \right) + \phi_2 \left( I_{ijkl} + S^{\text{int}}_{mnpp} \cdot C^{(2)}_{pppq} \right) + O^{(2)} \phi_3 \left( I_{ijkl} + S^{\text{mat}}_{mnpp} \cdot C^{(3)}_{pppq} \right)
\]

and

\[
A^{(2)}_{ijkl} = O^{(2)}_{mnpp} \cdot A^{(1)}_{mnkl}
\]

Here \(I_{ijkl}\) is the 4th order unit tensor \(\frac{1}{3} (\delta_{ik} \cdot \delta_{jl} + \delta_{il} \cdot \delta_{jk})\).

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 \(S^{\text{ef}}, S^{\text{int}},\) and \(S^{\text{mat}}\) 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, the Eshelby's tensor has to be computed numerically. From Mura (1987), Eshelby's tensor \(S\) is given by the following surface integral, parameterized on the surface of the unit sphere

\[
S_{ijkl} = \frac{1}{8\pi} C_{mnkl} \int_0^{2\pi} \int_0^\pi \left[ G_{mnmp}(\zeta) + G_{mnmp}(\zeta) \right] d\zeta d\alpha
\]

where

\[
G_{mnmp}(\zeta) = \frac{\zeta}{a_1} N_{N_{ij}}(\zeta)/D(\zeta) = \frac{\zeta}{a_1} (K_{K_1}(\zeta))^{-1}
\]

\[
\zeta = \frac{\chi_1}{a_1}; \quad \chi_1 = \sqrt{1 - \chi^2}; \quad \chi_2 = \sqrt{1 - \chi^2}; \quad D(\zeta) = \epsilon_{mn} K_{mn} \epsilon_{mn} K_{mn}; \quad N_{ij}(\zeta) = \frac{1}{2} \left( \epsilon_{ai} \epsilon_{bj} \right) K_{mn} K_{mn}; \quad K_{K_1} = S_{ijkl} \zeta_j / \zeta_i
\]

with \(\epsilon_{jk}\) 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 \(a_1\) these equations can be obtained in closed form, and review of these results can be found in Mura (1987). For the case of fully anisotropic material, \(S_{ijkl}\) is evaluated using the following Gaussian quadrature formula

\[
S_{ijkl} = \sum_{p=1}^{M} \sum_{q=1}^{M} C_{mnkl} \left[ G_{mnmp}(\alpha_p, \chi_{lp}, \zeta_{lp}) \epsilon_{mn} K_{mn} \epsilon_{mn} K_{mn} \right] W_{pq}
\]

where \(M\) is the Gaussian points used for integration (which is chosen to be 48 in this study) over \(\chi_{lp}\) and \(\alpha_p, \epsilon_{mn} K_{mn} \epsilon_{mn} K_{mn}\) are the Gaussian weights.

Eqs. (20)–(24) present the complete sets of equations required to compute the effective elastic properties of nanocomposites for the general anisotropic case of matrix, interphase and inclusion (and for their various morphologies as well). It is noted here that residual stress (interfacial stress in relaxed reference configuration denoted by the coefficient of \(\epsilon_{ij}\) in Eq. (10) above) can very well be taken into account by including eigenstrain in the present framework. This would provide effective residual stress in nanocomposites and would be a subject of another study. In several studies by authors e.g. Duan et al. (2005a), Duan et al. (2005b), Duan et al. (2007a), Chen et al. (2007), Zhang and Wang (2007) residual surface stress has been neglected. It is considered to be a valid assumption as in residual stress is negligible compared with the stress due to surface elasticity in these materials. To numerically illustrate the features of the present framework and to compare it with previous methodologies, in the next section we present results for single crystal aluminum matrix containing nano-voids of spherical, cylindrical and ellipsoidal shape of various sizes and volume fractions. 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 nanovoids or aligned cylindrical nanoves, and most simulations are conducted on aluminum with isotropic bulk and surface properties (see e.g. Duan et al. (2005a), Duan et al. (2007b) and more recently Mogilevskaya et al. (2008)), Chen et al. (2007) and very recently, Mogilevskaya et al. (2010) 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 (Chen et al., 2007; Mogilevskaya et al., 2010) and cylindrical fibres (Mogilevskaya et al., 2010) in 2D formalism, with isotropic properties of the constituents). Quang and He (2007) developed a framework for isotropic thermoelastic properties of nanocomposites with spherical inhomogeneities. In their model, the matrix and inhomogeneities are considered spherical tranversely 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 of various shapes. We note that the framework proposed in this paper incorporates physics that accounts for general interfacial characteristics between materials with known
interatomic potential. Therefore, it is more appropriate for interfaces (e.g., composites with nanoinhomogeneities) compared to surfaces (e.g., voids). However, to the best of the authors’ knowledge there is no experimental or numerical data on composites with nanoinhomogeneities with known interatomic potential between the constituents; thus we are comparing the predictions of our model with previous work on aluminum with nano-voids. We, however, note that most of the previously published work is conducted by considering aluminum matrix to be isotropic unlike the present case where the matrix is anisotropic.

5. Transition phase between the void and the matrix

In the following, we consider a heterogeneous material with spherical voids of average radius \( r_v \) and volume fraction \( \phi_v \). Note that similar to the previous works (e.g. Sharma and Ganti, 2004), the nano-structural features in the material considered here are nano voids with an added transition phase of thickness \( t \) (described later in this section) surrounding the void; the surface of the void is considered to be traction free. We follow the methodology described in the previous section to incorporate the surface effects due to nano voids in computing the overall properties of the material. We note that in order to incorporate the surface effects in formulating the Escheby’s tensor (Duan et al., 2005a) or computing the average elastic properties of materials with spherical voids (Dingerville et al., 2005), the required surface elastic properties were obtained from atomistic simulations of isotropic planar surfaces. We use a similar formalism as follows. Consider a region of thickness \( t \) beneath the surface. As described in the previous section, within this layer, due to reduced coordination of atoms on the surface, and due to rearrangement of these atoms (and also few layers of atoms within the surface) to their new equilibrium positions compared to their initial position in the bulk crystal, the energy of these atoms is different from those in the bulk. Therefore, the elastic properties of this transition region differ from the regions in the bulk crystal (Dingerville, 2007). Although this region is very thin (only a few atomic layers, typically 0.5–1 nm (Dingerville et al., 2005)), its influence is particularly relevant where the nanoscale void size is small and is present in large volume fraction. In the present framework, we assume that this region manifests itself as a transition phase between the void and the matrix; this is analogous to the interphase between the matrix and inhomogeneity in nanocomposites. Similar to the surface elastic properties, the properties of the transition phase would be different for different crystallographic orientations. In order to formulate its effective properties, consider a bulk crystal with a free surface \( S_0 \) which is planar and homogeneous. We consider the equilibrium state (which includes the atomic relaxation in the transition region) as the reference zero-strain configuration. Since the surface is homogeneous,\(^2\) the inner-relaxation due to external loading throughout the region is zero i.e. \( \tilde{\epsilon}_0 = 0 \). Note that for this case, there are 2 sublattices - first one representing bulk material, and the second one representing the transition region with different elastic properties; however, as the reference configuration includes the surface relaxation achieved after equilibration, inner relaxation between the two sublattices is zero.

Corresponding to homogeneous strain \( \tilde{\epsilon}_0 \), total strain energy in the transition region of volume \( V_0 = A_0t \) can be written as

\[
U = U_{\text{bulk}}(\tilde{\epsilon}_0) + U_{\text{surface}}(\tilde{\epsilon}_0) \tag{25}
\]

where \( U_{\text{bulk}} \) is the total strain energy in the bulk with no surface effect, and \( U_{\text{surface}} \) is the free surface energy, which is a function of in-plane strain \( \tilde{\epsilon}_{xy}^2 = \epsilon_{xy}^2 \). Atoms in the transition region have higher energy because they are at the surface or they are present in its proximity compared to those in the bulk; \( U_{\text{surface}}(\tilde{\epsilon}_{xy}) \) represents this excess energy. Here the subscripts \( \alpha, \beta, \kappa, \gamma \) assume values 1, 2. Since \( \epsilon_{xy} \) is uniform, following the formalism used by Dingerville et al. (2005), we can write

\[
\tilde{\epsilon}_{xy}^2 = \tilde{\epsilon}_z \cdot \epsilon_{xy} \cdot \tilde{\epsilon}_y \tag{26}
\]

where \( \tilde{\epsilon}_i \) is the transformation tensor defined as \( \tilde{\epsilon}_i = \tilde{l}_i - \tilde{n}_i \tilde{n}_i \) where \( \tilde{l} \) is the identity tensor and \( \tilde{n} \) is the unit vector normal to the surface (which for the planar surface \( x_3 = 0 \), \( \tilde{n} = [0 \ 0 \ 1] \)). Therefore, we can write total strain energy up to second order in strain as

\[
U = V_0 \left[ \frac{1}{2} C_{ijkl}^{\text{bulk}} \cdot \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{kl} \right]
+ \frac{1}{2} \int_{S_0} G_{ij}^{(1)} \cdot \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} + \frac{1}{2} 
G_{ij}^{(1)} \cdot \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} + \frac{1}{2} \int_{S_0} Q_{ijkl} \cdot \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} + \frac{1}{2} \int_{S_0} \left( \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} - \tilde{l}_{ij} \cdot \tilde{l}_{ij} \right) \right] \, dS_0 \tag{27}
\]

Using Eq. (26) we can re-write the total energy as

\[
U = V_0 \left[ \frac{1}{2} C_{ijkl}^{\text{bulk}} \cdot \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{kl} \right]
+ \frac{1}{2} \int_{S_0} G_{ij}^{(1)} \cdot \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} + \frac{1}{2} \int_{S_0} Q_{ijkl} \cdot \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} + \frac{1}{2} \int_{S_0} \left( \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} - \tilde{l}_{ij} \cdot \tilde{l}_{ij} \right) \right] \, dS_0 \tag{28}
\]

We note that the effect of the surface morphology on the total strain energy is captured by the transformation tensor (for example, see Hirsh and Lothe (1982) for the ellipsoidal surface transformation tensor \( \tilde{l}_{ij} \)). Therefore, the effective elastic tensor of the transition region at equilibrium can be obtained as

\[
\tilde{\epsilon}_{ijkl} = \frac{1}{V_0} \frac{\partial U}{\partial \epsilon_{ij}} \bigg|_{\epsilon_{ij} = 0} = C_{ijkl} + \frac{1}{\tilde{T}} Q_{ijkl} \tag{29}
\]

where tensor \( Q_{ijkl} \) is defined as

\[
Q_{ijkl} = \int_{S_0} \left( G_{ij}^{(1)} \cdot \tilde{\epsilon}_{ij} + \frac{1}{2} \int_{S_0} Q_{ijkl} \cdot \tilde{\epsilon}_{ij} + \frac{1}{2} \int_{S_0} \left( \tilde{\epsilon}_{ij} \cdot \tilde{\epsilon}_{ij} - \tilde{l}_{ij} \cdot \tilde{l}_{ij} \right) \right] \, dS_0 \tag{30}
\]

Carrying out the above integral on the surface \( x_3 = 0 \) yields the non-zero values of \( Q_{ijkl} \) as

\[
Q_{ijkl} = \int_{S_0} Q_{ijkl} \, dS_0 \quad (i,j,k,l = 1, 2) \tag{31}
\]

Eqs. (29) and (31) 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. The properties obtained from these equations are used to characterize the transition phase between nano voids and matrix.

6. Results and discussions

In this section, we present numerical results on single crystal aluminum matrix with nano voids of spherical, cylindrical and ellipsoidal shape. 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. (1999). Using the Voight notation in (100) crystallographic orientation, \( c_{11}, c_{12}, \) and \( c_{44} \) obtained are 111.4 GPa, 60.7 GPa, and 31.8 GPa, respectively. The surface properties of the [100] and [111] aluminum surfaces are obtained from Miller and Shenoy (2000) and Sharma and Dasgupta (2002) data from their atomistic simulations. We are not presenting the atomistic simulations for...
this case to obtain surface properties, as they have already been adequately performed by these authors to obtain these properties.

- **Surface A** – (111) orientation: \( \kappa_A = 6.466 \text{ N/m} \), \( \mu_A = -0.3755 \text{ N/m} \)
- **Surface B** – (100) orientation: \( \kappa_B = -2.7285 \text{ N/m} \), \( \mu_B = -6.2178 \text{ N/m} \)

As stated previously, these surfaces are isotropic, so the surface stiffness tensor can be written in terms of \( \kappa_A \) and \( \mu_A \) as follows (Dingreville et al., 2005):

\[
\Gamma_{A(kl)}^{(1)} = \kappa_A \delta_{kk} \delta_{kl} + \mu_A (\delta_{kk} \delta_{kl} - \delta_{kl} \delta_{kk})
\]

(32)

Therefore, using Eq. (32) for two surfaces – A and B – along with the bulk Al elastic properties in their respective crystallographic orientations, and putting them in Eq. (31) and then in Eq. (29), 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 \( t \): \( t_1 = 3(a/2) \), \( t_2 = 5(a/2) \); 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 (Duan et al., 2005b). 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 presented in Eqs. (20) and (21) to obtain the effective orientation-averaged 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 described above in Section 3. 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. (2005b), 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 nanovoids in the present case. In the present case changing the thickness of the transition phase around these nanovoids 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 nanovoids noted that the properties of the phase depend on its thickness as well.

Figs. 3 and 4 present results obtained for spherical nanovoids 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 do not alter the anisotropy (which is cubic) of the single crystal. Fig. 3(a) and (b) 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 \( r_1 \) 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 \( r_1 \)). Insets in Fig. 3(a) and (b) show the VRH average of bulk \( (\kappa) \) and shear modulus \( (\mu) \) normalized by the respective values without the surface effects \( (\kappa_0) \) and \( \mu_0 \), respectively. These values, apparently follow very similar trend as the normalized bulk and shear modulus of isotropic nanoporous aluminum presented in our previous work (Palival and Cherkaoui, 2011). We note 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 tosuppress 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. Fig. 4(a) and (b) show the plot of the normalized \( C_{11}, C_{12} \) and \( C_{44} \) for surfaces A and B, respectively as a function of void volume fraction for different void sizes. An increase in the void volume fraction (for fixed void size) and/or a decrease in the void size (for a fixed void volume fraction) increases the volume fraction of a given transition phase. Therefore, surface effects become more pronounced with both an increase in the volume fraction of voids and a decrease in its radius. These are clearly demonstrated in the plots where all elastic constants display the following trend. As the void volume fraction increases, \( C_{11} \) increases, and \( C_{12} \) and \( C_{44} \) decrease compared with those without surface effect for A type phase. On the other hand, all the three decrease for B type phase with the increase in void volume fraction. This surface effect is more pronounced as the void size decreases.

Fig. 5(a)–(d) present plots of transverse bulk modulus (\( \kappa_T \)), longitudinal elastic modulus \( (E_L) \), and transverse \( (\mu_T) \) and longitudinal \( (\mu_L) \) shear modulus of aluminum single crystal with aligned cylindrical nanopores (which are aligned along z-axis and perpendicular to x-y plane) as a function of void radius for 20% void volume fraction. These plotted elastic properties are normalized by their respective values obtained without the surface effect. Note that due to the these cylindrical nanopores, the composite exhibits tetragonal anisotropy with six independent elastic constants; elastic properties presented in the plots can be expressed in terms of these constants as follows

\[
\kappa_T = C_{11} + C_{12} - 2C_{22}^2/C_{33}
\]

\[
E_L = C_{33} - 2C_{22}^2/(C_{11} + C_{12})
\]

\[
\mu_T = 2C_{66} \quad \mu_L = 2C_{44}
\]

Fig. 5(a) and (b) show plots of normalized longitudinal elastic modulus and normalized transverse bulk modulus, respectively. It is apparent from the figures that both elastic properties decreases (and increases) as the pore size increases for A-type (for B-type) transition phase. Therefore, composite becomes stiffer with A-type transition phase as these normalized elastic properties are greater than one, and becomes softer with B-type transition phase as the normalized properties are less than one. These results for transverse bulk modulus are in very good agreement with those obtained by Duan et al. (2007b) (results for longitudinal elastic modulus are not shown in their publication). However, we note here again that their results were obtained by considering isotropic aluminum matrix with aligned cylindrical nanopores, therefore their composite is transversely isotropic. Fig. 6(a) and (b) show the plots of normalized longitudinal and transverse shear modulus and both of them

| Table 1 Properties of the constituents used in the 4-phase GSCM model. |
|-----------------|-----------------|-----------------|
| **Inhomogeneity** | **\( \kappa = 0 \)** | **\( \mu = 0 \)** |
| **Matrix** | **C_{11} = 111.4 \text{ GPa}** | **C_{12} = 60.7 \text{ GPa}** | **C_{44} = 31.8 \text{ GPa}** |
| **Interphase** | **Surface A (111)** | **Surface B (100)** |
| **(void)** | **(void)** |
| **\( t_1 \)** | **\( t_2 \)** | **\( t_1 \)** | **\( t_2 \)** |
| **\( \kappa = 82.1 \text{ GPa} \)** | **\( \kappa = 80.4 \text{ GPa} \)** | **\( \kappa = 75.5 \text{ GPa} \)** | **\( \kappa = 76.4 \text{ GPa} \)** |
| **\( \mu = 29.4 \text{ GPa} \)** | **\( \mu = 29.3 \text{ GPa} \)** | **\( \mu = 23.9 \text{ GPa} \)** | **\( \mu = 26.1 \text{ GPa} \)** |


increases with the increase in the pore size for both, A- and B-type transition phase. Therefore, surface effect renders 'softer' shear modulus property in these composites compared with the classical results without the surface effect. Although, our results on normalized longitudinal shear modulus are in a very good agreement with Duan et al. (2007b), their transverse shear modulus is not in a good agreement with our results particularly for type-B surface (which refers to type-A transition phase in this study). Their results suggest a 'stiffer' ($\mu_T$) for B-type surface contrary to our results which suggest a 'softer' ($\mu_T$) compared with classical results. Note that the results presented in the work of Duan et al. (2007b) were obtained after imposing a remote strain field $\varepsilon_{xx} = -\varepsilon_{yy} = \varepsilon_T$ which amounts to a shear strain $\varepsilon_{xy} = \varepsilon_T$ as their composite was transversely isotropic (with x–y plane being the 'symmetric plane'). However, in our case imposing $\varepsilon_{xx} = -\varepsilon_{yy} = \varepsilon_T$ does not mean $\varepsilon_{xy} = \varepsilon_T$ as the composite exhibit tetragonal anisotropy; by imposing $\varepsilon_{xx} = -\varepsilon_{yy} = \varepsilon_T$ in our model results in the following modulus, $\mu_T = \frac{C_{11}}{C_0} C_{12}$ (which is the shear modulus $2C_{66}$ for transversely isotropic materials). Inset in Fig. 3 (d) show the variation of $\mu_T$ for A and B-type transition phase as a function of void radius, and the results are in a close agreement with the ones obtained by Duan et al. (2007b) i.e. A-type transition phase (B-type surface in the work of Duan et al. (2007b)) results in stiffer response and B-type transition phase, in softer response compared with the classical solution. Owing to such dependence of overall properties on surface elasticity, these nanoporous materials offer great potential for...
application in aerospace, aircraft and other transport industries. This is particularly because of their light weight and also because their effective modulus can be altered to become comparable to (or even exceed than) the non-porous counterparts by tuning their surface properties. This enable considerable reduction in the size and weight of structural elements without sacrificing their strength and other important physical properties. In such applications, specific stiffness i.e. stiffness-to-density ratio of a material is very important. For example, the ratio of specific longitudinal shear stiffness $\mu_l$ to that of the non-porous material ($\mu^*$) is given as

$$\frac{\mu_l}{\mu^*} = \frac{1}{1 - \phi_2 + \phi_1 \frac{\rho_2}{\rho_3} \left( \frac{\rho_1}{\rho_3} \right) \left( \frac{\phi_2}{\phi_3} \right) \mu_3}$$  \hspace{1cm} (34)

Similar equation can be written for other elastic properties as well. Here $\rho_2$ and $\rho_3$ denotes the density of the transition phase and of the matrix, respectively, and $t$, $r_1$ and $\phi_1$ denotes the transition phase thickness, void radius, and void volume fraction, respectively. Duan et al. (2007b) have demonstrated that the specific stiffness of these nanoporous materials can be made higher than the non-porous matrix material (Figs. 5 and 6 in the article for specific longitudinal shear modulus) by varying the porosity and transition phase characteristics, which in turn alters the mix-surface parameters $A$ and $B$ defined as (Duan et al., 2007b):

$$A = \frac{2}{(1 - \phi_2)} \frac{t}{r_1} \frac{\mu_2}{\mu_3}; \quad B = \frac{t}{r_1} \frac{\mu_3}{\mu_2}$$  \hspace{1cm} (35)

Here $\nu_2$ is the Poisson’s ratio of the transition phase. We have used the present framework to obtain a closed form solution of specific transverse shear modulus as a function of porosity and mixed surface parameter by considering aluminum matrix to be isotropic similar to Duan et al. (2007b). This can obviously be used for the anisotropic case, however results cannot be obtained in a closed
form and have to be solved numerically. Nonetheless, isotropic matrix assumption still allows us to demonstrate the capability of the interphase approach as with surface/interface used by Duan et al. (2007b) and other co-workers.

The coincident Hashin–Rosen bounds for the longitudinal shear modulus of a 4-phase composite cylinder assemblage (CCA) are given by the following relation (Herve and Zaoui, 1995):

\[
\frac{\mu_3}{\mu_1} = \frac{\mu_3 (r_2^2 - r_1^2)}{\mu_1 (r_2^2 + r_1^2)} + \frac{\mu_1 (r_1^2 + r_2^2)}{\mu_3 (r_2^2 + r_1^2)} + \frac{\mu_3 (r_2^2 - r_1^2)}{\mu_1 (r_2^2 + r_1^2)}
\]

This can also be written in terms of mix-surface parameters \(B\) as follows:

\[
\frac{\mu_3}{\mu_1} = \frac{1 - \phi_1 - 2\phi_2 + \phi_3}{1 + \phi_1 + 2\phi_2 + \phi_3} \left(2 + \frac{1}{2}\right) + B \left(1 + \phi_1 + 2\phi_2 + \phi_3\right) \left(2 + \frac{1}{2}\right)
\]

\[
\frac{\mu_3}{\mu_1} = \frac{1 - \phi_1 - 2\phi_2 + \phi_3}{1 + \phi_1 + 2\phi_2 + \phi_3} \left(2 + \frac{1}{2}\right) + B \left(1 + \phi_1 + 2\phi_2 + \phi_3\right) \left(2 + \frac{1}{2}\right)
\]

using Eqs. (34) and (37), the variation of \(\mu_3/\mu_1\) versus the void volume fraction and parameter \(B\) is plotted in Fig. 6. The parameters used are \(t/r_1 = 0.1\) and \(r_2/r_3 = 1\). These results are similar to the ones presented in Fig. 6 of Duan et al. (2007b) and suggest that \(\mu_3/\mu_1 > 1\) can be obtained for values of \(B\) which slightly depends on the void volume fraction. Also note that if the transition phase density is smaller than the matrix density, \(\mu_3/\mu_1\) values will be higher than shown in Figure 10. Here we reiterate that approach presented here is fundamentally different from the work of Duan et al. (2007b) who considered two phases with imperfect interfacial boundary conditions between them, where as we have an additional third interphase with perfect interfacial boundary conditions between them to obtain \(\mu_3/\mu_1\).

7. Conclusion

- An interphase model for elastic properties of nanocomposites has been developed that bridges the gap between discrete atomic level interactions and continuum mechanics. Results from the atomistic simulations to obtain the continuum elastic properties of the interphase, are used in the Eschelby micromechanical scheme within the generalized self consistent method to obtain effective properties of nanocomposites. 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 and cylindrical nano-voids for two surfaces with different crystalllographic orientations, and for two transition phase thickness. Simulations predicted anisotropic elastic constants for both types of nano-materials are new and to the best of authors’ knowledge, have never been reported before.
- Surface properties have profound effect on the effective elastic constants of nano-materials which is apparent from Figs. 2–9, particularly as the void size decreases and void volume fraction increases. Using interface approach, similar trend has been observed before for bulk and shear modulus of isotropic nanocomposites with spherical voids (Duan et al., 2005b).
- Results also suggest that surface effect could render ‘softer’ or ‘stiffer’ material response in these nano-composites compared with the classical results without the surface effect. These results (see Figs. 6–10) are in very good agreement with results from Duan et al. (2007b). However we note that Duan et al. (2007b) obtained their results by considering isotropic Al matrix as opposed to single crystal cubic assumed in this work.

Acknowledgements

The authors would like to acknowledge support from the Nanointerface project FP7NMP2007, a part of the 7th framework program by the European Commission under the Grant Agreement No. 214371.

Appendix A

The tensor \(E^{pq}\) is similar to the Hessian matrix used in the molecular mechanics simulations of atomic structures and presents the same symmetry i.e. \(E^{pq} = E^{qp}\), etc., except in this case it is defined for different sublattices. Representing \(E^{pq}\) in \(3L_x \times 3L_y\) matrix form \(E^{pq}_{3L_x \times 3L_y}\) we could define \(G = E^{pq}\) where \(G^{pq}\) is represented as \(G^{pq}_{3L_x \times 3L_y}\).

However, before computing \(G\) and further \(G^{pq}\), note that \(E^{pq}\) is rank deficient because for any solution \(\alpha\) of the equilibrium equations Eq. (12), \(\alpha' + C_i\) is also a solution. To remove these three dependent
freedoms, the matrix $E_{ij}^{pq}$ of $E_{(p-1)+3(q-1),j}$ is diagonalized. After diagonalization, taking the non-zero eigen values $\lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_{3(n-1)}$, and corresponding eigen vectors $v_1, v_2, v_3, \ldots, v_{3(n-1)}$ we can define $A$ and $V$ as
\[
A = \begin{pmatrix}
\lambda_1 & \cdots & 0 \\
\vdots & \ddots & \vdots \\
0 & \cdots & \lambda_{3(n-1)}
\end{pmatrix}
\]
(A1)
\[
V = (v_1, v_2, \ldots, v_{3(n-1)}); \quad V^TV = I
\]
where $I$ is identity matrix. Finally,
\[
E = VA^TV^T
\]
(A2)
and
\[
G_{ij}^{pq} = G_{(p-1)+3(q-1),ij}; \quad G = VA^{-1}V^T
\]
(A3)
is obtained and is used to compute $A_{ij}^{pq}$ in Eq. (15).

Appendix B

Consider a periodic ensemble of $N$ atoms, denoted by $x = 1, \ldots, N$. Let every atom is associated with a sublattice $p$, denoted by $\rho(x)$ for atom $x$, such that each sublattice contains atoms that are equivalent to each other and atoms in different sublattices are non-equivalent to each other. We denote the total number of sublattices as $L_{pq}$ which is $\leq N$. Under macroscopic homogeneous Lagrangian strain $\varepsilon_{ij}$ defined by Eq. (3), the square of the distance $s_{pq}$ between sublattices $p$ and $q$ can be obtained by using Eq. (4) as
\[
s_{pq}^2 = \rho_{i}^{p} \cdot \rho_{i}^{q} = \rho_{i}^{p} \cdot (2 \delta_{ij} + \varepsilon_{ij}) \cdot \rho_{i}^{q} + 2\left(\varepsilon_{ij} - \delta_{ij}\right) \cdot \rho_{i}^{p} \rho_{i}^{q}
\]
\[
\cdot \left[2\delta_{ij} + \varepsilon_{ij} \cdot \left(\varepsilon_{ij} - \delta_{ij}\right)\right]
\]
(B1)
If the inter-atomic potential characterizing the atomic interaction is given by EAM (Duan et al., 2005b), the total energy $E$ of the ensemble can be written as
\[
E = \frac{N}{2} \sum_{x=1}^{N} E(x) = \frac{N}{2} \sum_{x=1}^{N} \left(\frac{1}{2} \sum_{p=1}^{L_{pq}} V(\rho_{i}^{pq}) - f(\rho_{i}^{pq})\right)
\]
(B2)
here $R_{\rho}^{pq}$ is the distance between atom $x$ and $\beta$, and $V(R_{\rho})$ defines the repulsive pair-wise interaction energy between these two atoms. $f(\rho_{i}^{pq})$ represents the embedding energy to embed atom $\alpha$ into a local site with electron density $\rho_{\alpha}$, which is calculated as
\[
\rho_{\alpha} = \sum_{\beta=1}^{L_{pq}} \phi(\rho_{\beta}^{pq})
\]
(B3)
where $\phi(\rho_{\beta}^{pq})$ is the electron density at the location of atom $\beta$ due to atom $\alpha$. Here (and in Eq. (B2) above) $x_{1}$ and $x_{2}$ represents the first and the last interacting neighbor, respectively of atom $x$ covering all periodic images of other atoms within the cut-off distance, including the image ($s$) of $x$ itself. Therefore, we can write the elastic constant of sublattice $p$ with the help of atomic level elastic constant as follows (see Eqs. (2) and (10) above)
\[
C_{ijkl}^{pq} = \frac{4}{a^2 \rho_{\alpha}^2} \sum_{x=1}^{N} \sum_{x=x_{1}}^{x_{2}} \left\{ \frac{1}{2} V'(s_{\rho}^{pq}) - f'(\rho_{\alpha}^{pq}) \phi'(s_{\rho}^{pq}) \right\} \rho_{\alpha}^{pq} \rho_{\beta}^{pq} \phi'_{\beta}(s_{\rho}^{pq}) \phi'_{\beta}(s_{\rho}^{pq})
\]
\[
- f'(\rho_{i}^{pq}) \phi_{\beta}(s_{\rho}^{pq}) \phi_{\beta}(s_{\rho}^{pq}) \rho_{\alpha}^{pq} \rho_{\beta}^{pq}
\]
(B4)
here, the derivatives of $V$ and $f$ are taken with respect to $s_{\rho}^{pq}$. The following relationships are useful to obtain the formula shown above and in the equations presented later in the Appendix. At equilibrium i.e. $\rho_{i}^{pq} = \bar{\rho}_{i}^{pq}$
\[
\frac{\partial s_{pq}^{ij}}{\partial \varepsilon_{ij}} = 2\delta(\rho_{i}^{pq}, \rho_{i}^{pq})
\]
\[
\frac{\partial s_{pq}^{ij}}{\partial \varepsilon_{ij}} = 2\left(\delta(\rho_{i}^{pq}, \rho_{i}^{pq}) - \delta(\rho_{i}^{pq}, \rho_{i}^{pq})\right)
\]
\[
\frac{\partial s_{pq}^{ij}}{\partial \varepsilon_{ij}} = \frac{\partial s_{pq}^{ij}}{\partial \varepsilon_{ij}} = 0
\]
\[
\frac{\partial s_{pq}^{ij}}{\partial \varepsilon_{ij}} = 2\delta(\rho_{i}^{pq}, \rho_{i}^{pq}) - \delta\rho_{i}^{pq}(\rho_{i}^{pq}, \rho_{i}^{pq})\delta\rho_{i}^{pq}(\rho_{i}^{pq}, \rho_{i}^{pq})
\]
Here $\delta$ is the Kronecker delta function which is equal to one if the arguments are equal and zero otherwise. As shown in Eq. (19), the elastic constant due to internal relaxation of sublattice $p$ is given in terms of $E_{ij}^{pq}$ and $D_{ij}^{pq}$. With the help of Eq. (B5) and using Eqs. (7) and (8), we can obtain the following equations for $E_{ij}^{pq}$ and $D_{ij}^{pq}$
\[
E_{ij}^{pq} = E_{ij}^{pq}(\rho_{i}^{pq}) = \sum_{p=1}^{N} \sum_{q=1}^{N} \left\{ 2V'(s_{\rho}^{pq}) - 2f'(\rho_{i}^{pq}) \phi'(s_{\rho}^{pq}) \right\} \rho_{\alpha}^{pq} \rho_{\beta}^{pq} \phi'_{\beta}(s_{\rho}^{pq}) \phi'_{\beta}(s_{\rho}^{pq})
\]
\[
+ \left\{ V'(\rho_{i}^{pq}) - 2f'(\rho_{i}^{pq}) \phi'(s_{\rho}^{pq}) \right\} \delta_{\rho_{i}^{pq}, \rho_{i}^{pq}}
\]
\[
- 4f'(\rho_{i}^{pq}) \sum_{k=1}^{N} \phi'(s_{\rho}^{pq}) \rho_{\alpha}^{pq} \rho_{\beta}^{pq} \phi'_{\beta}(s_{\rho}^{pq}) \phi'_{\beta}(s_{\rho}^{pq})
\]
\[
- 4f'(\rho_{i}^{pq}) \sum_{k=1}^{N} \phi'(s_{\rho}^{pq}) \rho_{\alpha}^{pq} \rho_{\beta}^{pq} \phi'_{\beta}(s_{\rho}^{pq}) \phi'_{\beta}(s_{\rho}^{pq})
\]
(B5)
Here, $\delta_{\rho_{i}^{pq}, \rho_{i}^{pq}}$ is defined as $[\delta(\rho_{i}^{pq}, \rho_{i}^{pq}) - \delta(\rho_{i}^{pq}, \rho_{i}^{pq})]$. Therefore, using these equations along with those presented in Appendix A in Eq. (19), we can obtain relaxation part of elastic constant for every sublattice $p$.

References


