Theoret. Appl. Mech., Vol.35, No.1-3, pp. 267–286, Belgrade 2008

Nanoparticles and the influence of interface elasticity

Changwen Mi **Demitris Kouris** *

Abstract

In this manuscript, we discuss the influence of surface and interface stress on the elastic field of a nanoparticle, embedded in a finite spherical substrate. We consider an axially symmetric traction field acting along the outer boundary of the substrate and a non-shear uniform eigenstrain field inside the particle. As a result of axial symmetry, two Papkovitch-Neuber displacement potential functions are sufficient to represent the elastic solution. The surface and interface stress effects are fully represented utilizing Gurtin and Murdoch's theory of surface and interface elasticity. These effects modify the traction-continuity boundary conditions associated with the classical continuum elasticity theory. A complete methodology is presented resulting in the solution of the elastostatic Navier's equations. In contrast to the classical solution, the modified version introduces additional dependencies on the size of the nanoparticles as well as the surface and interface material properties.

Keywords: Surface and interface effects, nanoparticles, eigenstrains, finite domain, micromechanics

1 Introduction

Crystal defects such as vacancies, interstitials, dislocations, grain boundaries and stacking faults are introduced when periodic arrangements of atoms or ions are not maintained. In the micromechanical study of solids, these defects have been often modeled as inclusions and inhomogeneities [1, 2]. Eshelby's inclusion and inhomogeneity theory [3, 4, 5] has been widely used to address

*Department of Mechanical Engineering, University of Wyoming, Laramie, WY 82071, U.S.A., e-mail: kouris@uwyo.edu

such problems and has served as the foundation of micromechanics. The validity of Eshelby's solution relies on the size of the ellipsoidal inclusion and inhomogeneity, i.e. the relative length scale of the semi-axes of the embedded ellipsoid, compared to the surrounding medium. The theory is appropriate when it models an unbounded substrate and the absolute size of the ellipsoidal inhomogeneity is relatively large (typically larger than 100 nanometers (nm)). In many practical applications, however, these two conditions are not satisfied, which necessitates the development of alternative methodologies.

In engineering applications such as the fabrication of ordered two- and three-dimensional quantum dots [6] and nano-composite materials [7, 8] the substrate phase has a finite size and the corresponding edge effects become considerable. As a result, modifications must be made to Eshelby's inhomogeneity theory to accommodate these boundary effects. In the last few decades, a number of researchers have contributed their efforts in investigating inclusion and inhomogeneity problems beyond the full-space geometry. Mindlin and Cheng [9] first studied the thermoelastic stress in a semi-infinite solid. Tsuchida et al. [10, 11, 12] derived three dimensional solutions for displacements and stresses in a thick plate with a spherical cavity under various loading conditions. The eigenstrain problems associated with finite domains have also been addressed by several authors [13, 14, 15, 16].

Inclusions and inhomogeneities with at least one dimension measured in nanometers are commonly referred to as nanoparticles. At such a small length scale, the elastic fields for both the nanoparticle and the encompassing medium depend on the absolute size of the particle [17, 18, 19]. The discovery originated from the distinct properties of the substrate/nanoparticle interface, compared to its associated bulk interior, which is then further strengthened by the convex-curvature effect of the interface. Actually, this phenomenon is not new and has been identified for a fluidic interface long time ago [20]; it is called Laplace-Young Effect therein. The associated Laplace-Young equation, $\Delta P = 2f/a$, describes the force balance condition across a spherical interface, separating two fluid phases. The pressure difference ΔP across the interface is equilibrated by twice the ratio of the fluid/fluid interface stress f over the fluid inclusion radius. A generalized version of the Laplace-Young Equation for interfaces separating two solid bodies, along with a constitutive equation relating the interface stress and interface strain tensors have been established by Gurtin, Murdoch and their co-authors [21, 22, 23]. These basic equations governing the mechanical behavior of solid surfaces and interfaces are referred to as the theories of surface and interface elasticity. The applications in nanomechanics include studies of inclusions and inhomogeneities embedded in infinite solids [17, 18, 19, 24, 25], semi-infinite elastic media [26, 27] and film substrates [28].

The objective of the present manuscript is to further extend this theoretical framework for a nanoparticle embedded in a finite spherical domain. Axially symmetric tension and eigenstrain loading are considered simultaneously. The Papkovitch-Neuber displacement potentials formulation [29], coupled with Gurtin and Murdoch's theory of surface and interface elasticity [21, 22, 23] yield an analytical solution. Compared to classical elasticity, Gurtin and Murdoch's formulation of elasticity has substantially increased the mathematical complexity and a curvilinear analysis for a Euclidean spherical interface becomes essential. The necessary mathematical background is addressed in the next section, along with a brief presentation of the method of displacement potentials. Gurtin and Murdoch's interface stress boundary conditions are utilized in Section 3 to derive the elastic states for the nanoparticle and the finite matrix. The closed-form solution for the case of centro-symmetric loading is given together with its classical version (without the influence of the interface stresses). A few numerical examples are presented in Section 4 to illustrate the effects of both the matrix/nanoparticle interface and the matrix outer surface. The last section presents the conclusions resulting from the analytical solution and the related numerical examples.

2 Displacement formulation and interface elasticity

We consider the inhomogeneity problem in a finite spherical domain. The geometry, definition of the coordinate system, material properties, and loading conditions are described in Fig. 1. A spherical nanoparticle of radius a is embedded at the center of a spherical substrate with radius b. For simplicity, both domains are treated as isotropic and linearly elastic solids. Their material properties are represented by the shear modulus G and Poisson's ratio ν, where the quantities denoted by an overbar refer to the inhomogeneity. Due to the symmetry of the problem, spherical coordinates (R, θ, φ) are preferred. Geometric relations associated with Cartesian coordinates (x, y, z) and the cylindrical system (r, θ, z) are also illustrated in Fig. 1. An axially symmetric tension field $(T_x = T_y, T_z)$ is applied along the outer boundary of the matrix. For the eigenstrain loading sustained by the inhomogeneity we consider a non-shear thermal expansion $(\varepsilon_x^* = \varepsilon_y^*, \varepsilon_z^*)$. The z-axis serves as the axis of symmetry for the applied loads. Following Gurtin and Murdoch's theory of linear surface and interface elasticity, both the matrix/nanoparticle interface $(R = a)$ and the outer boundary $(R = b)$ are treated as two-dimensional curvilinear thin films with an infinitesimal thickness. Three material constants, the residual interface stress (τ_0) and the Lamé constants (λ_0 and μ_0), represent

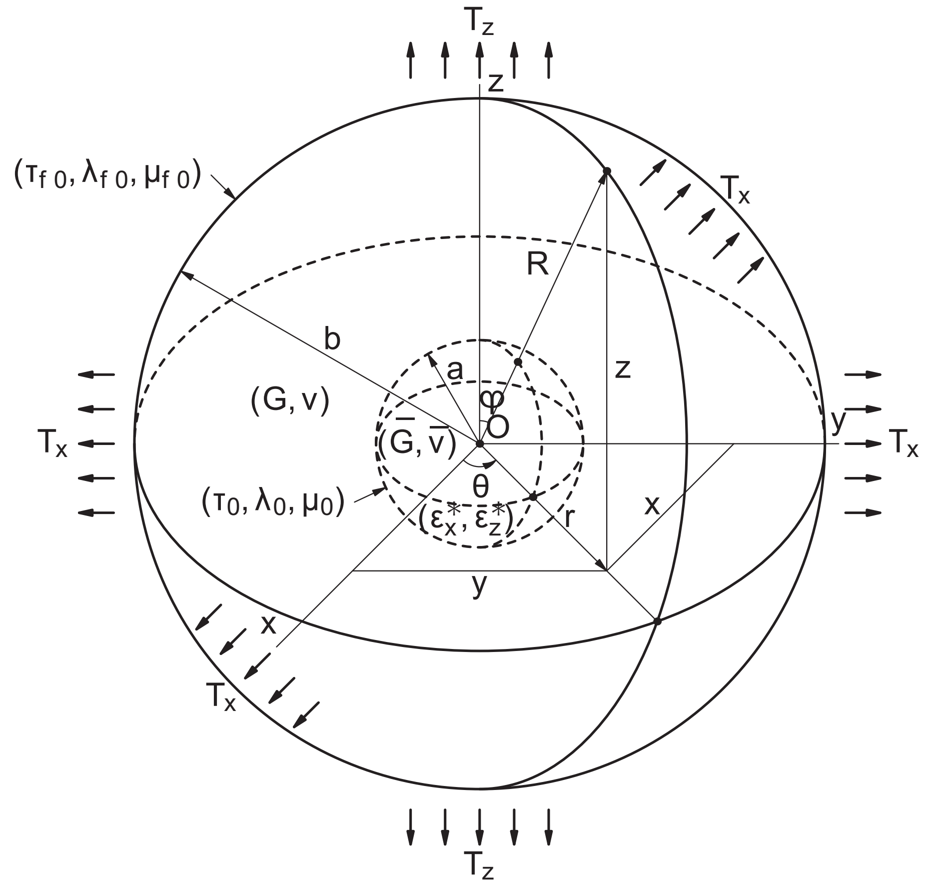

Figure 1: A spherical particle embedded in a finite spherical domain.

the properties of the interface. For the spherical outer boundary we use the same symbols, but with an additional subscript f.

In the absence of body forces, equations of equilibrium in terms of displacements for linearly elastic and isotropic materials are expressed as [29]:

$$\frac{1}{1-2\nu} u_{j,ji} + u_{i,jj} = 0, \tag{1}$$

where u_i represent the components of the displacement field and commas in subscripts denote partial differentiation. Einstein's summation rule over repeated indices is applicable unless otherwise stated. By convention, the Roman indices denote variables belonging to bulk domains and assume values from 1 to 3. The present problem is characterized by torsionless axisymmetry with respect to the z-axis. In such a simplified case, the displacement vector in equation (1) admits only two harmonic potential functions (ϕ_0 and ϕ_3) [29]. In terms of spherical coordinates (R, θ, φ), the displacement field assumes the form:

$$
\begin{aligned}
2Gu_R &= \frac{\partial \phi_0}{\partial R} - (3-4\nu)\,\mu\phi_3 + R\mu\frac{\partial \phi_3}{\partial R}, \\
2Gu_\varphi &= -\frac{\sqrt{1-\mu^2}}{R}\frac{\partial \phi_0}{\partial \mu} + \sqrt{1-\mu^2}\left(-\mu\frac{\partial \phi_3}{\partial \mu} + (3-4\nu)\,\phi_3\right),
\end{aligned} \tag{2}
$$

where $\mu = \cos\varphi$. Note that the azimuthal component of the displacements vanishes, since neither of the potentials is a function of the coordinate variable θ. Both ϕ_0 and ϕ_3 are harmonic functions and thus satisfy the three-dimensional Laplace equation. The most general spherical harmonics which are independent of θ are of the form [30]:

$$
\sum_{n=0}^{\infty}\left(A_n R^n + \frac{B_n}{R^{n+1}}\right)P_n\,(\mu), \tag{3}
$$

where A_n and B_n are coefficients and $P_n\,(\mu)$ denotes the Legendre polynomial of degree n.
In terms of the displacement field, the strain tensor is given by:

$$
\begin{aligned}
&\varepsilon_{RR} = \frac{\partial u_R}{\partial R},\;\; \varepsilon_{\theta\theta} = \frac{\mu u_\varphi}{R\sqrt{1-\mu^2}} + \frac{u_R}{R}, \\
&\varepsilon_{\varphi\varphi} = -\frac{\sqrt{1-\mu^2}}{R}\frac{\partial u_\varphi}{\partial \mu} + \frac{u_R}{R},\;\; 2\varepsilon_{R\varphi} = \frac{\partial u_\varphi}{\partial R} - \frac{u_\varphi}{R} - \frac{\sqrt{1-\mu^2}}{R}\frac{\partial u_R}{\partial \mu}.
\end{aligned} \tag{4}
$$

Hooke's law is expressed through:

$$
\frac{\sigma_{ij}}{2G} = \frac{\nu}{1-2\nu}\varepsilon_{kk}\delta_{ij} + \varepsilon_{ij},\;\; i,j = R,\theta,\varphi, \tag{5}
$$

where δ_{ij} denote the Kronecker delta operator.

Based on the basic solutions for spherical harmonics (3) and in view of the axial-symmetry properties of both the domain and the loading conditions (Fig. 1), we construct the general solution of the present problem via three sets of displacement potentials

$$
\phi_0 = \frac{\nu\,(T_x+T_z) - T_x}{(1+\nu)}R^2 P_2\,(\mu)\,,\;\; \phi_3 = -\frac{2T_x+T_z}{2\,(1+\nu)}RP_1\,(\mu)\,, \tag{6}
$$

$$
\phi_0 = G\sum_{n=0}^{\infty} A_n\frac{a^{2n+3}}{R^{2n+1}}P_{2n}\,(\mu)\,,\;\; \phi_3 = G\sum_{n=0}^{\infty} B_n\frac{a^{2n+3}}{R^{2n+2}}P_{2n+1}\,(\mu)\,, \tag{7}
$$

$$
\phi_0 = G\sum_{n=0}^{\infty} C_n\frac{R^{2n+2}}{a^{2n}}P_{2n+2}\,(\mu),\;\; \phi_3 = G\sum_{n=0}^{\infty} D_n\frac{R^{2n+1}}{a^{2n}}P_{2n+1}\,(\mu), \tag{8}
$$

for the finite spherical matrix ($a < R < b$), and an additional set

$$\phi_0 = \bar{G} \sum_{n=0}^{\infty} \bar{A}_n \frac{R^{2n+2}}{a^{2n}} P_{2n+2}(\mu), \quad \phi_3 = \bar{G} \sum_{n=0}^{\infty} \bar{B}_n \frac{R^{2n+1}}{a^{2n}} P_{2n+1}(\mu), \tag{9}$$

for the nanoparticle ($R < a$). Here all the spherical harmonic coefficients $A_n,\ B_n,\ C_n,\ D_n,\ \bar{A}_n$ and $\bar{B}_n$ have been normalized to be dimensionless through the shear moduli and the spherical nanoparticle size. These coefficients are to be determined using the boundary conditions. Equation (6) represents the axially symmetric tension field applied at the outer boundary of the spherical matrix (Fig. 1). The remaining three potential sets represent the disturbance due to the presence of the inhomogeneous particle and the eigenstrain field it sustains. Potential set (7) is a valid solution for an infinite domain containing a spherical cavity, while (8) and (9) correspond to finite spherical domains without any singularities. We need both (7) and (8) for the matrix, since a spherical layer may be viewed as a common region of the two domains just mentioned.

On the other hand, it is well recognized that surfaces and interfaces in solids exhibit a behavior different from the bulk phases. Different material constants are utilized to describe their thermodynamic and mechanical behavior. A surface can be viewed as a special case of an interface dividing an elastic solid and a vacuum phase. The theory of surface and interface elasticity was systematically established by Gurtin, Murdoch and their coauthors [21, 22, 23]. The basic equations include the definition for the interface strain tensor, the interface constitutive relation and the traction-discontinuity condition across the interface:

$$\mathrm{E}_{\alpha\beta} = \langle \varepsilon_{\alpha\beta} \rangle = \frac{1}{2} \Big((\nabla_{\mathrm{S}} \mathbf{u})_{\alpha\beta} + (\nabla_{\mathrm{S}} \mathbf{u})_{\beta\alpha} \Big), \tag{10}$$

$$\Sigma_{\alpha\beta} = \tau_0 \delta_{\alpha\beta} + 2(\mu_0 - \tau_0)\, \mathrm{E}_{\alpha\beta} + (\lambda_0 + \tau_0)\, \mathrm{E}_{\kappa\kappa} \delta_{\alpha\beta} + \tau_0 (\nabla_{\mathrm{S}} \mathbf{u})_{\alpha\beta}, \tag{11}$$

$$[\sigma_{ij}]\, n_j = -(\nabla_{\mathrm{S}} \cdot \mathbf{\Sigma})_i. \tag{12}$$

In this formulation, the interface strain ($\mathrm{E}_{\alpha\beta}$) is defined as the average value ($\langle\rangle$) of the two bulk stains projected onto the interface. In a manner analogous to its bulk counterpart (5), the interface constitutive equation (11) assumes a linear relationship between the interface strain and interface stress tensor, in terms of three interface constants (τ_0, λ_0 and μ_0). In contrast to the classical continuum elasticity, the traction field becomes discontinuous across the interface. The discontinuity (denoted by []) is mechanically balanced by the interface stress effects. As discussed in the introduction, equation (12) is basically a generalized version of the Laplace-Young equation [20]. As the condition is extended to solid interfaces, shear components emerges due to the ability of solids to sustain shear stresses. The Greek indices indicate field quantities defined on surfaces and assume values from 1 to 2.

In coupling the interface elasticity with the classical theory of elasticity, the primary challenges come from the evaluation of the interface gradient of the displacement vector ($\nabla_{\mathrm{S}}\mathbf{u}$) and the interface divergence of the interface stress tensor ($\nabla_{\mathrm{S}} \cdot \boldsymbol{\Sigma}$). According to Gurtin et al. [23], $\nabla_{\mathrm{S}}\mathbf{u}$ is a superficial tensor field. Upon operating on a vector field, the vector's components that are normal to the interface are annihilated. $\nabla_{\mathrm{S}} \cdot \boldsymbol{\Sigma}$ balances the traction discontinuity across the interface defined by the unit normal n_i. Its explicit expression in terms of the interface stress tensor is given as:

$$\begin{aligned} (\nabla_S \cdot \boldsymbol{\Sigma})_R &= -\frac{\Sigma_{\theta\theta} + \Sigma_{\varphi\varphi}}{R}, \\ (\nabla_S \cdot \boldsymbol{\Sigma})_\varphi &= \frac{1}{R}\left(\frac{1}{\sin\varphi}\frac{\partial \Sigma_{\varphi\theta}}{\partial\theta} + \frac{\partial \Sigma_{\varphi\varphi}}{\partial\varphi} + \cot\varphi\left(\Sigma_{\varphi\varphi} - \Sigma_{\theta\theta}\right)\right). \end{aligned} \tag{13}$$

The evaluation may be implemented as necessary at either the matrix/particle interface ($R = a$) or the matrix outer boundary ($R = b$). The elastic part of $\nabla_{\mathrm{S}} \cdot \boldsymbol{\Sigma}$ is due to potentials ϕ_0 and ϕ_3 in (6)-(9) and can be expressed in terms of them by substituting equations (2),(4),(10) and (11) into equation (13).

The boundary conditions at the matrix/particle interface include displacement continuity condition and the interface stress boundary condition (12). From equation (11), the interface stress depends on the interface strain and hence it depends on the bulk strain field through equation (10). Therefore, both the elastic strains and the non-elastic strains contribute to the interface divergence vector. As a result, the boundary conditions along the spherical interface ($R = a$) can be written in the following form:

$$(u_i)_{R=a} = (\bar{u}_i + u_i^*)_{R=a}, \quad (\sigma_{Ri} - \bar{\sigma}_{Ri})_{R=a} = -\left(\nabla_S \cdot \boldsymbol{\Sigma} + \nabla_S \cdot \boldsymbol{\Sigma}^*\right)_i, \quad i = R, \varphi, \tag{14}$$

where the vector components of the interface divergence are given implicitly by (13). The non-elastic part of the interface divergence vector ($\nabla_S \cdot \boldsymbol{\Sigma}^*$) can be obtained by substituting the eigenstrain field ($\varepsilon_x^* = \varepsilon_y^*$ and ε_z^*), (10) and (11) into equation (13):

$$\begin{aligned} (\nabla_S \cdot \boldsymbol{\Sigma}^*)_R &= -\frac{4G\chi_3}{3a}\left(\left(2\varepsilon_x^* + \varepsilon_z^*\right)P_0(\mu) + \left(\varepsilon_x^* - \varepsilon_z^*\right)P_2(\mu)\right), \\ (\nabla_S \cdot \boldsymbol{\Sigma}^*)_\varphi &= -\frac{2G\left(3\chi_0 - \chi_1\right)}{3a}\left(\varepsilon_x^* - \varepsilon_z^*\right)\sqrt{1-\mu^2}P_2'(\mu), \end{aligned} \tag{15}$$

where $P'_n(\mu)$ denotes the derivative of $P_n(\mu)$ with respect to its argument and the three interface length scale parameters are defined as:

$$\chi_0 = \frac{1}{4G}(\lambda_0 + 2\mu_0), \ \chi_1 = \frac{1}{4G}(\lambda_0 + \tau_0), \ \chi_3 = \chi_0 + \chi_1. \tag{16}$$

The corresponding non-elastic displacement components inside the nanoparticle are given by:

$$u_R^* = \frac{1}{3}R\left((2\varepsilon_x^* + \varepsilon_z^*) P_0(\mu) - 2(\varepsilon_x^* - \varepsilon_z^*) P_2(\mu)\right), \ u_\varphi^* = \frac{1}{3}R(\varepsilon_x^* - \varepsilon_z^*)\sqrt{1-\mu^2}P'_2(\mu). \tag{17}$$

The boundary condition at the matrix outer boundary ($R = b$) is represented by the traction discontinuity equation (12):

$$\begin{aligned}(\sigma_{RR})_{R=b} - \frac{2T_x + T_z}{3}P_0(\mu) + \frac{2(T_x - T_z)}{3}P_2(\mu) &= (\nabla_S \cdot \mathbf{\Sigma})_{fR}, \\ (\sigma_{R\varphi})_{R=b} - \frac{T_x - T_z}{3}\sqrt{1-\mu^2}P'_2(\mu) &= (\nabla_S \cdot \mathbf{\Sigma})_{f\varphi}.\end{aligned} \tag{18}$$

The additional subscript f in the divergence vector $(\nabla_S \cdot \mathbf{\Sigma})$ suggests that the evaluation of equations (13) should be made at the spherical surface ($R = b$).

3 Solution of the problem

The total displacements and stresses in the finite matrix are obtained by superposing equations (6)-(8), while those in the nanoparticle are given by equation (9) and the non-elastic displacement components (17). The total interface divergence vector at $R = a$ includes the contributions from equations (6)-(9) and the non-elastic part (15). The surface divergence vector at the matrix outer boundary $R = b$ is relatively simple and only due to potential sets (6)-(8). The geometric and loading symmetry result in the coefficients (A_n, B_n, C_n, D_n, $\bar{A}_n$ and $\bar{B}_n$) vanishing for $n \geqslant 2$. Therefore, only the first two terms ($n = 0, 1$) of the six series representations in equations (7)-(9) are needed for the final solution. Numerical calculations implemented for large n ($\geqslant 10$) confirm this conclusion.

Upon evaluating the displacements and stresses, enforcing the boundary conditions (14) and (18), and equating the coefficients preceding the Legendre polynomials ($P_0(\mu)$ and $P_2(\mu)$) and their derivatives ($P'_2(\mu)$) we obtain twelve independent linear algebraic equations leading to the unknown dimensionless coefficients (A_0, A_1, B_0, B_1, C_0, C_1, D_0, D_1, $\bar{A}_0$, $\bar{A}_1$, $\bar{B}_0$ and

$\bar{B}_1$). Solving these twelve linear equations yields the complete solution of the three-dimensional elastic problem under consideration. The displacements and stresses for the matrix and the particle are readily obtained by substitution of the dimensionless parameters. The explicit expressions for the solution, however, are quite lengthy and thus not included here. Instead, we choose to explore a few numerical examples for the case in Section 4. For the time being, we proceed to develop a closed-form solution for a special case corresponding to the centro-symmetric loading condition, i.e. ($T_x = T_y = T_z = T$ and $\varepsilon_x^* = \varepsilon_y^* = \varepsilon_z^* = \varepsilon^*$). Under this assumption, the solutions assume a much simpler form involving only six independent equations for six unknowns ($A_0, B_0, C_0, D_0, \bar{A}_0$ and $\bar{B}_0$), which yield:

$$\begin{aligned}
&A_0 = \rho_0 \frac{\tau_0}{aG} + \rho_{f0} \frac{\tau_{f0}}{bG} + \alpha_0 \frac{T}{G} + \xi_0 \varepsilon^*, \;\; B_0 = 0, \\
&C_0 = \frac{2\,(1-2\nu)}{3} D_0, \;\; D_0 = \rho_1 \frac{\tau_0}{aG} + \rho_{f1} \frac{\tau_{f0}}{bG} + \alpha_1 \frac{T}{G} + \xi_1 \varepsilon^*, \\
&\bar{A}_0 = \frac{2\,(1-2\bar{\nu})}{3} \bar{B}_0, \;\; \bar{B}_0 = \rho_2 \frac{\tau_0}{aG} + \rho_{f2} \frac{\tau_{f0}}{bG} + \alpha_2 \frac{T}{G} + \xi_2 \varepsilon^*.
\end{aligned} \tag{19}$$

where ρ_0, ρ_1, ρ_2, ρ_{f0}, ρ_{f1}, ρ_{f2}, α_0, α_1, α_2, ξ_0, ξ_1 and ξ_2 are dimensionless parameters. Their explicit expressions are given in the Appendix. A careful examination of equations (31)-(34) reveals that the surface and interface effects are not likely to influence the order of magnitude of these dimensionless constants. According to the atomistic calculations by Shenoy [31] and Mi et al. [32], the surface and interface material constants (τ_0, λ_0 and μ_0) are generally of the order of Newton per meter. Considering that the shear modulus of metal species is about a few tens of Gigapascal, then the length scale parameters in (16) and (35) are about the order of one-tenth nanometer. Therefore, the dimensionless (χ_3/a and χ_{f3}/b) are at least one order less than unity, provided that the embedded particle has a radius $> nm$. To conclude, the surface and interface elastic constants have negligible impact on the magnitude of these constants. However, the surface and interface stress effects enter the final solution through terms involving τ_0 and τ_{f0} in equation (19). These terms would otherwise vanish in the absence of surface and interface elasticity. The significance of the surface and interface effects can be measured by four dimensionless factors: τ_0/aT, τ_{f0}/bT, $\tau_0/aG\varepsilon^*$ and $\tau_{f0}/bG\varepsilon^*$. The first two are for the case of tension applied at $R = b$ while the latter two refer to eigenstrains inside the nanoparticle. As any of these significance factors approaches to unity, the surface and/or interface stress effects cannot be neglected and must be included in the final solution. It can be easily seen that the smaller the domain size, the more significant the surface and interface elasticity will become. From the above analysis, it is also apparent that the most important contribution of the surface and interface elasticity comes from the residual surface (τ_0) and interface stress (τ_{f0}).

With the solution of the dimensionless unknowns, as presented in equation (19), the non-zero components of the displacements and the stresses in the finite spherical matrix domain are given by:

$$\frac{u_R}{R} = \left(-\frac{1}{2}\frac{a^3}{R^3}\rho_0 - \frac{(1-2\nu)}{3}\rho_1\right)\frac{\tau_0}{aG} + \left(-\frac{1}{2}\frac{a^3}{R^3}\rho_{f0} - \frac{(1-2\nu)}{3}\rho_{f1}\right)\frac{\tau_{f0}}{bG} + \left(-\frac{1}{2}\frac{a^3}{R^3}\alpha_0 - \frac{(1-2\nu)}{3}\alpha_1 + \frac{(1-2\nu)}{2(1+\nu)}\right)\frac{T}{G} + \left(-\frac{1}{2}\frac{a^3}{R^3}\xi_0 - \frac{(1-2\nu)}{3}\xi_1\right)\varepsilon^*, \tag{20}$$

$$\frac{\sigma_{RR}}{G} = \left(\frac{2a^3}{R^3}\rho_0 - \frac{2(1+\nu)}{3}\rho_1\right)\frac{\tau_0}{aG} + \left(\frac{2a^3}{R^3}\rho_{f0} - \frac{2(1+\nu)}{3}\rho_{f1}\right)\frac{\tau_{f0}}{bG} + \left(\frac{2a^3}{R^3}\alpha_0 - \frac{2(1+\nu)}{3}\alpha_1 + 1\right)\frac{T}{G} + \left(\frac{2a^3}{R^3}\xi_0 - \frac{2(1+\nu)}{3}\xi_1\right)\varepsilon^*, \tag{21}$$

$$\frac{\sigma_{\theta\theta}}{G} = \frac{\sigma_{\varphi\varphi}}{G} = \left(-\frac{a^3}{R^3}\rho_0 - \frac{2(1+\nu)}{3}\rho_1\right)\frac{\tau_0}{aG} + \left(-\frac{a^3}{R^3}\rho_{f0} - \frac{2(1+\nu)}{3}\rho_{f1}\right)\frac{\tau_{f0}}{bG} + \left(-\frac{a^3}{R^3}\alpha_0 - \frac{2(1+\nu)}{3}\alpha_1 + 1\right)\frac{T}{G} + \left(-\frac{a^3}{R^3}\xi_0 - \frac{2(1+\nu)}{3}\xi_1\right)\varepsilon^*. \tag{22}$$

The corresponding displacements and stresses inside the spherical nanoparticle read:

$$\frac{\bar{u}_R + u_R^*}{R} = -\frac{(1-2\bar{\nu})}{3}\rho_2\frac{\tau_0}{aG} - \frac{(1-2\bar{\nu})}{3}\rho_{f2}\frac{\tau_{f0}}{bG} - \frac{(1-2\bar{\nu})}{3}\alpha_2\frac{T}{G} - \left(\frac{(1-2\bar{\nu})}{3}\xi_2 - 1\right)\varepsilon^*, \tag{23}$$

$$\frac{\bar{\sigma}_{RR}}{\bar{G}} = \frac{\bar{\sigma}_{\theta\theta}}{\bar{G}} = \frac{\bar{\sigma}_{\varphi\varphi}}{\bar{G}} = -\frac{2(1+\bar{\nu})}{3}\rho_2\frac{\tau_0}{aG} - \frac{2(1+\bar{\nu})}{3}\rho_{f2}\frac{\tau_{f0}}{bG} - \frac{2(1+\bar{\nu})}{3}\alpha_2\frac{T}{G} - \frac{2(1+\bar{\nu})}{3}\xi_2\varepsilon^*. \tag{24}$$

As expected, when the surface and interface stress effects are neglected, the solutions in equations (20)-(24) converge to the classical solutions of a spherical inhomogeneity, embedded concentrically inside a finite spherical domain:

$$\frac{u_R}{R} = \left(\frac{1}{2}\frac{N}{M}\frac{a^3}{R^3} + \frac{(1-2\nu)}{(1+\nu)}\frac{N}{M}\frac{a^3}{b^3} + \frac{(1-2\nu)}{2(1+\nu)}\right)\frac{T}{G} + \frac{\Gamma(1+\bar{\nu})}{M}\left((1+\nu)\frac{a^3}{R^3} + 2(1-2\nu)\frac{a^3}{b^3}\right)\varepsilon^*, \tag{25}$$

$$\frac{\sigma_{RR}}{G} = \left(-2\frac{N}{M}\frac{a^3}{R^3} + 2\frac{N}{M}\frac{a^3}{b^3} + 1\right)\frac{T}{G} + \frac{4\Gamma}{M}(1+\nu)(1+\bar{\nu})\left(-\frac{a^3}{R^3} + \frac{a^3}{b^3}\right)\varepsilon^*, \tag{26}$$

$$\frac{\sigma_{\theta\theta}}{G} = \frac{\sigma_{\varphi\varphi}}{G} = \left(\frac{N}{M}\frac{a^3}{R^3} + 2\frac{N}{M}\frac{a^3}{b^3} + 1\right)\frac{T}{G} + \frac{4\Gamma}{M}(1+\nu)(1+\bar{\nu})\left(\frac{1}{2}\frac{a^3}{R^3} + \frac{a^3}{b^3}\right)\varepsilon^*, \tag{27}$$

$$\frac{\bar{u}_R + u_R^*}{R} = \frac{(1-2\bar{\nu})}{2M}\left(3(1-\nu)\frac{T}{G} - 4(1+\nu)\left(1-\frac{a^3}{b^3}\right)\varepsilon^*\right) + \varepsilon^*, \tag{28}$$

$$\frac{\bar{\sigma}_{RR}}{\bar{G}} = \frac{\bar{\sigma}_{\theta\theta}}{\bar{G}} = \frac{\bar{\sigma}_{\varphi\varphi}}{\bar{G}} = \frac{3(1-\nu)(1+\bar{\nu})}{M}\frac{T}{G} + \frac{4(1+\nu)(1+\bar{\nu})}{M}\left(-1+\frac{a^3}{b^3}\right)\varepsilon^*, \tag{29}$$

where the common parameters M and N are given by:

$$M = (1+\nu)(2(1-2\bar{\nu}) + \Gamma(1+\bar{\nu})) - 2N\frac{a^3}{b^3},$$
$$N = (1+\nu)(1-2\bar{\nu}) - \Gamma(1-2\nu)(1+\bar{\nu}). \tag{30}$$

The solutions for other special cases can be derived in a straightforward manner. For example, the corresponding inclusion problem is solved by equating the material properties of the matrix to those of the inhomogeneity ($\Gamma = 1$ and $\bar{\nu} = \nu$) in equation (19) for the hydrostatic loading condition. In addition, the solutions for the inclusion and inhomogeneity problems associated with an infinite substrate, as studied in [17, 18, 19, 25], can be readily derived by extending the radius of the spherical matrix to infinity ($b \to \infty$).

4 Results and discussion

Numerical results were obtained to demonstrate the influence of the surface stress effects at the matrix outer boundary and the interface stress effects at the matrix/particle interface. In addition to the loading conditions, the governing parameters are the shear modulus of the matrix (G), shear moduli ratio (Γ), particle size (a), radius of the spherical matrix (b) and the material constants of the surface and interface (λ_0, μ_0, τ_0, λ_{f0}, μ_{f0} and τ_{f0}). Until recently, there has been a limited availability of these constants. Based on the embedded atom method (EAM), Shenoy [31] calculated the surface elastic tensor for seven fcc metals. The surface Lamé constants used in the constitutive equation (11) may be approximated from this tensor. More recently, Mi et al. [32] has extended this study to noncoherent metallic bilayers. Naturally, the interface Lamé constants are better described by the calculated interface elastic tensor. We chose to take advantage of this and simulate the present problem as a finite spherical silver matrix containing a nickel nanoparticle. The Ag/Ni interface material constants are derived from the interface elastic tensor for a close-packed {111} Ag/Ni interface [32]: $\lambda_0 = 1.82$ N/m, $\mu_0 = -0.54$ N/m, $\tau_0 = 0.40$ N/m. In a similar way, the silver matrix outer boundary is modeled as a free Ag surface oriented along {111} direction. The corresponding surface elastic constants are: $\lambda_{f0} = -2.07$ N/m, $\mu_{f0} = -0.96$ N/m, $\tau_{f0} = 0.95$ N/m. The shear moduli of both bulk domains are obtained from the stiffness constants for silver and nickel under room temperature [33]: $G = 15.15$ GPa, $\bar{G} = 50.4$ GPa. The nickel particle is actually a very hard inhomogeneity with $\Gamma \approx 3.33$. Without loss of generality, we keep Poisson's ratios of both domains equal, i.e. $\nu = \bar{\nu} = 0.3$.

Under the framework of the classical continuum theory of elasticity, the normalized solution of the inclusion and inhomogeneity problem is independent of the particle size. However, the surface and interface stress effects introduce dependencies on parameters in addition to the shear moduli ratio and the size ratio b/a, as presented in equations (20)-(24). Fig. 2 shows the distribution of the radial stress along the Ag/Ni spherical interface for four radii ratios. The loading condition corresponds to an axially symmetric tension field ($T_x = T_y = 50$ MPa and $T_z = 100$ MPa) applied at $R = b$ and a dilatational eigenstrain field ($\varepsilon_x^* = \varepsilon_y^* = \varepsilon_z^* = 1\%$). The size of the nickel particle has been fixed at $a = 10$ nm. Under these assumptions, the interface effects significance factors take values that are comparable to unity: $\tau_0/aT_z = 0.4$ and $\tau_0/aG\varepsilon^* = 0.26$. These numbers suggest that under the same loading conditions the disturbance due to surface and interface effects is significant only for nanosized particles. From Fig. 2, it is obvious that the effects of the surface ($R = b$) on the radial stress component are primarily a function of the matrix size (b). The most significant influence on the classical solution comes from the smallest matrix size ($b = 2a$). The same conclusion can be made for the radial stress sustained by the nickel particle, as shown in Fig. 3. It is worth noting from Figs. 2 and 3 that the traction continuity condition across the

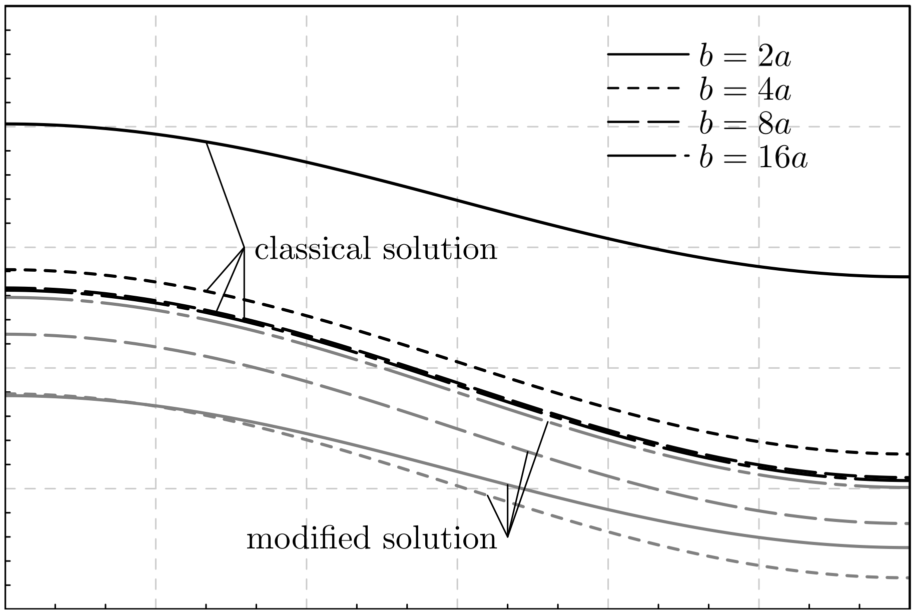

Figure 2: Distribution of radial stress along the matrix interface for $a = 10$ nm.

Ag/Ni interface, which is valid for the classical solution, is violated due to the influence of the surface and interface stress effects. To examine the stress distribution in the vicinity of the nanoparticle, calculations were carried out along three particular radial directions ($\varphi = 0,\ \pi/4,\ \pi/2$) for a nickel particle of radius 10 nm embedded in a silver matrix with $b = 40$ nm (Fig. 4). The same loading condition is assumed. As expected, stresses corresponding to the classical solutions are constant inside the nickel particle and converge to the applied tension field ($T_z,\ (T_z + T_x)/2,\ T_x$) toward the free surface along $\varphi = 0,\ \pi/4,\ \pi/2$ respectively. The traction discontinuity for the modified solutions is apparent at the Ag/Ni interface. The jump is balanced by the interface divergence of the interface stress. The three directions seem to have an equivalent dependence on the surface and interface elasticity.

One of the difficulties associated with the present problem is the large number of parameters. As seen from the expressions for surface and interface effects significance factors, the loading conditions may also strengthen or weaken the effects of surface and interface elasticity. For example, the stress concentration factor around a nanovoid embedded in an infinite substrate was found to depend significantly on the far-field tension [25, 34].

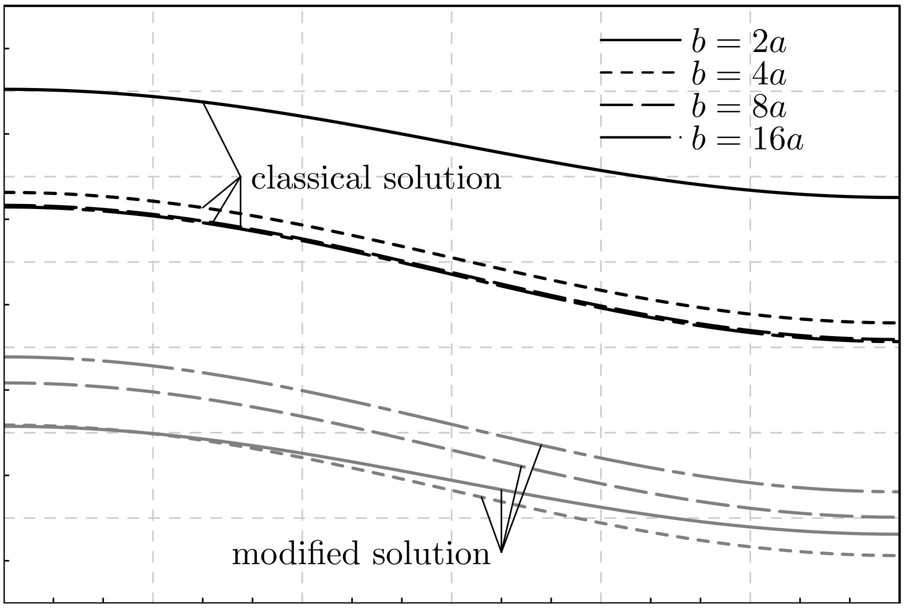

Figure 3: Distribution of radial stress along the particle interface for $a = 10$ nm.

5 Concluding Remarks

In this manuscript, the axisymmetric problem of a spherical nanoparticle embedded in a finite spherical elastic body is solved. The surface stress effects at the finite matrix outer boundary and the interface stress effects at the matrix/particle interface are fully represented by coupling Gurtin and Murdoch's surface and interface elasticity theory with the classical Papkovitch-Neuber displacement potentials methodology. The outer boundary of the matrix and the matrix/particle interface are simulated as two dimensional spherical thin films bordered with the bulk phases. These surfaces and interfaces have specialized material constants describing their mechanical response. When integrated with curvature effects, the surface and interface stresses substantially modify the elastic field predicted by the classical theory of elasticity. The significance of surface and interface effects can be principally described by the four significance factors: τ_0/aT, τ_{f0}/bT, $\tau_0/aG\varepsilon^*$ and $\tau_{f0}/bG\varepsilon^*$.

In addition to the closed form solutions for the case of centro-symmetric loading, several numerical examples are presented for an Ag/Ni system under axial symmetric tension applied at the outer boundary of the silver matrix and a dilatational eigenstrain field specified inside the nickel particle. Following the

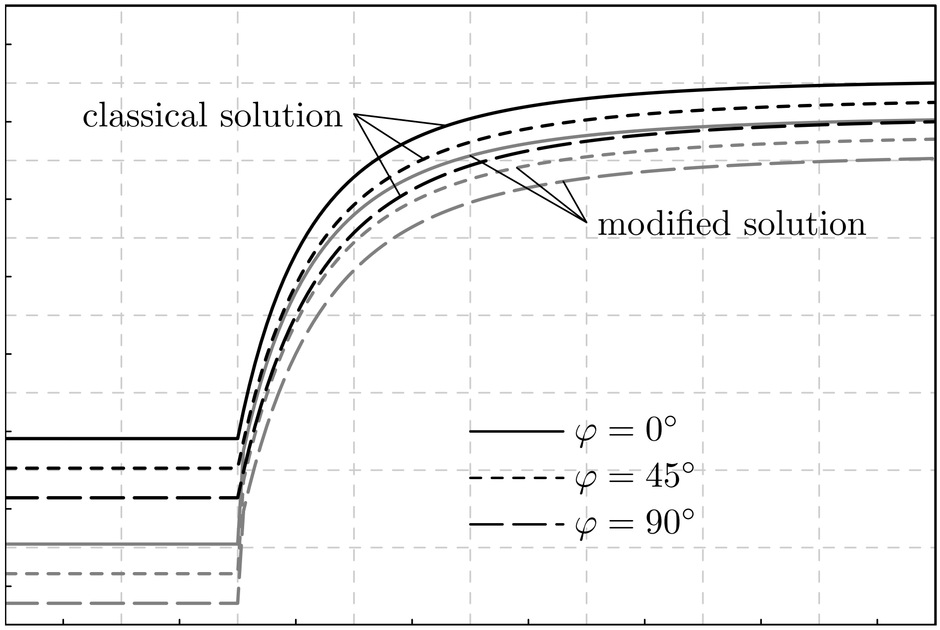

Figure 4: Stresses along three radial directions for $b = 4a = 40$ nm.

analytical and numerical studies, a few important observations can be made. The size-dependent property of the inclusion and inhomogeneity problem is verified. The solution depends not only on the radii ratio (b/a) but more importantly on the absolute size of the particle and matrix. If their sizes are measured in nanometers, the impact of surface and interface stress effects becomes significant. This conclusion may have implications on the fabrication of ordered nanostructures, since most of the associated structural elements are nanoparticles and quantum dots. The large surface-to-volume ratio yields a significant surface stress, which is in turn strengthened by the high curvature of the surface. Furthermore, the effect of the surface and interface elasticity strongly depends on the stiffness of the nanoparticle as well as the magnitude of the external loading.

References

[1] T. Mura, *Micromechanics of defects in solids*, Martinus Nijhoff, Hague, Netherlands, 1987.

[2] S. Nemat-Nasser and M. Hori, *Micromechanics: overall properties of heterogeneous materials*, North Holland, Amsterdam, 2nd ed., 1998.

[3] J. D. Eshelby, *The determination of the elastic field of an ellipsoidal inclusion and related problems*, Proceedings of the Royal Society of London **A241**(1957), 376-396.

[4] J. D. Eshelby, *The elastic field outside an ellipsoidal inclusion*, Proceedings of the Royal Society of London **A252**(1959), 561-569.

[5] J. D. Eshelby, *Elastic inclusions and inhomogeneities*, in Progress in Solid Mechanics, Edited by N. I. Sneddon and R. Hill, North-Holland, **2**(1961), 89-104.

[6] J. Tersoff, C. Teichert, and M. G. Lagally, *Self-organization in growth of quantum dot superlattices*, Physical Review Letters **76**(1996), 1675-1678.

[7] E. T. Thostenson, Z. Ren, and T.W. Chou, *Advances in science and technology of carbonnanotubes and their composites: A review*, Composite Science and Technology **61**(2001), 1899-1912.

[8] D-L Shi, X-Q Feng, Y-Y Huang, K-C Hwang, and H. Gao, *The effect of nanotube waviness and agglomeration on the elastic property of carbon nanotube-reinforced composites*, ASME Journal of Engineering Materials and Technology **126**(2004), 250-257.

[9] R. D. Mindlin and D. H. Cheng, *Thermoelastic stress in the semi-infinite solid*, Journal of Applied Physics **21**(1950), 931-933.

[10] E. Tsuchida, S. Togawa, I. Nakahara, and M. Kodama, *Stresses in a thick plate containing an eccentric spherical cavity under uniaxial tension*, Bulletin of the JSME **19**(1976), 838-848.

[11] E. Tsuchida, M. Nakamura, and I. Nakahara, *Stresses in an elastic thick plate with a spherical cavity under transverse bending*, Bulletin of the JSME **19**(1976), 849-856.

[12] E. Tsuchida and I. Nakahara, *Three-dimensional stress concentration around a spherical cavity in a thick plate under uniaxial tension*, Bulletin of the JSME **19**(1976), 1107-1114.

[13] N. Kinoshita and T. Mura, *Eigenstrain problems in a finite elastic body*, SIAM Journal on Applied Mathematics **44**(1984), 524-535.

[14] H. A. Luo and G. J. Weng, *On Eshelby's inclusion problem in a three-phase spherically concentric solid, and a modification of Mori-Tanaka's method*, Mechanics of Materials **6**(1987), 347-361.

[15] E. Krőner, *Modified Green's function in the theory of heterogeneous and/or anisotropic linearly elastic media*, In Micromechanics and Inhomogeneity, The Toshio Mura 65th Anniversary Volume, Edited by G. J. Weng, M. Taya and H. Abe, Springer, New York, 599-622, 1990.

[16] S. Li, R. A. Sauer, and G Wang, *The Eshelby tensor in a finite spherical domain: I theoretic formulations*, ASME Journal of Applied Mechanics **74**(2007), 770-783.

[17] J. W. Cahn and F. Larché, *Surface stress and the chemical equilibrium of small crystals. II. solid particles embedded in a solid matrix*, Acta Metallurgica **30**(1982), 51-56.

[18] P. Sharma, S. Ganti, and N. Bhate, *Effect of surfaces on the size-dependent elastic state of nano-inhomogeneities*, Applied Physics Letters **82**(2003), 535-537.

[19] P. Sharma and S. Ganti, *Size-dependent Eshelby's tensor for embedded nano-inclusions incorporating surface/interface energies*, Journal of Applied Mechanics-Transactions of the ASME **71**(2004), 663-671.

[20] A. W. Adamson, *Physical chemistry of surfaces*, John Wiley & Sons, 1982.

[21] M. E. Gurtin and A. I. Murdoch, *A continuum theory of elastic material surfaces*, Archives for Rational Mechanics and Analysis **57**(1975), 291-323; **59**(1975), 389-390.

[22] M. E. Gurtin and A. I. Murdoch, *Surface stress in solids*, International Journal of Solids and Structures **14**(1978), 431-440.

[23] M. E. Gurtin, J. Weissmüller, and F. Larché, *A general theory of curved deformable interfaces in solids at equilibrium*, Philosophical Magazine A **78**(1998), 1093-1109.

[24] H. Duan, J. Wang, Z. Huang, and Z. Luo, *Stress concentration tensors of inhomogeneities with interface effects*, Mechanics of Materials **37**(2005), 723-736.

[25] L. H. He and Z. R. Li, *Impact of surface stress on stress concentration*, International Journal of Solids and Structures **43**(2006), 6208-6219.

[26] C. Mi and D. A. Kouris, *Nanoparticles under the influence of surface/interface elasticity*, Journal of Mechanics of Materials and Structures **1**(2006), 763-791.

[27] D. A. Kouris and C. Mi, *Surface strain due to embedded epitaxial islands*, Surface Science **601**(2007),757-762.

[28] C. Mi and D. A. Kouris, *The role of interface stress for nanoparticles embedded in films*, JSME Journal of Solid Mechanics and Materials Engineering **1**(2007), 1219-1230.

[29] S. P. Timoshenko and J. N. Goodier, *Theory of elasticity*, 3rd ed., McGraw-Hill, New York, 1970.

[30] A. I. Lur'e, *Three-dimensional problems of the theory of elasticity*, Interscience Publishers, New York, 1964.

[31] V. B. Shenoy, *Atomistic calculations of elastic properties of metallic fcc crystal surfaces*, Physical Review B **71**(2005), 0941041-09410411.

[32] C. Mi, S. Jun, D. A. Kouris and S. Y. Kim, *Atomistic calculations of interface elastic properties in noncoherent metallic bilayers*, Physical Review B **77**(2008), 0754251-07542512.

[33] C. Kittel, *Introduction to solid state physics*, John Wiley & Sons, New York, 1996.

[34] C. Mi, *Nanoparticles under the Influence of Surface/Interface Elasticity*, Ph.D. Dissertation, University of Wyoming, 2006.

Appendix Dimensionless parameters in equation (19)

The various dimensionless parameters in equation (19) are defined by:

$$\begin{aligned}
\rho_0 &= \frac{2}{M}\left(1+\nu+2\left(1-2\nu\right)\frac{\chi_{f3}}{b}\right)\left(1-2\bar{\nu}\right),\\
\rho_1 &= \frac{6}{M}\left(1-\frac{\chi_{f3}}{b}\right)\left(1-2\bar{\nu}\right)\frac{a^3}{b^3},\\
\rho_2 &= \frac{3}{M}\left(1+\nu+2\left(1-2\nu\right)\frac{\chi_{f3}}{b}+2\left(1-\frac{\chi_{f3}}{b}\right)\left(1-2\nu\right)\frac{a^3}{b^3}\right),
\end{aligned} \tag{31}$$

$$\begin{aligned}
\rho_{f0} &= \frac{2}{M}\left(\left(1+\nu-4\left(1-2\nu\right)\frac{\chi_3}{a}\right)\left(1-2\bar{\nu}\right)-\Gamma\left(1-2\nu\right)\left(1+\bar{\nu}\right)\right),\\
\rho_{f1} &= \frac{3}{M}\left(2\left(1+2\frac{\chi_3}{a}\right)\left(1-2\bar{\nu}\right)+\Gamma\left(1+\bar{\nu}\right)\right),\ \rho_{f2} = \frac{9}{M}\left(1-\nu\right),
\end{aligned} \tag{32}$$

$$\alpha_0 = -\frac{1}{M}\Big((1-2\bar{\nu})\Big(1+\nu-4(1-2\nu)\frac{\chi_3}{a}\Big)-\Gamma(1-2\nu)(1+\bar{\nu})\Big),$$
$$\alpha_1 = \frac{3}{(1+\nu)M}\Big\{(1-2\nu)\Big(2(1-2\nu)\Big(1+2\frac{\chi_3}{a}\Big)+\Gamma(1+\bar{\nu})\Big)\frac{\chi_{f3}}{b}$$
$$-\Big(1-\frac{\chi_{f3}}{b}\Big)\Big((1-2\bar{\nu})\Big(1+\nu-4(1-2\nu)\frac{\chi_3}{a}\Big)-\Gamma(1-2\nu)(1+\bar{\nu})\Big)\frac{a^3}{b^3}\Big\},$$
$$\alpha_2 = -\frac{9}{2M}(1-\nu), \tag{33}$$

$$\xi_0 = -\frac{2\Gamma}{M}\Big(1+\nu+2(1-2\nu)\frac{\chi_{f3}}{b}\Big)(1+\bar{\nu}),\ \xi_1 = -\frac{6\Gamma}{M}\Big(1-\frac{\chi_{f3}}{b}\Big)(1+\bar{\nu})\frac{a^3}{b^3}, \tag{34}$$
$$\xi_2 = \frac{6}{M}\Big\{\Big(1+\nu+2(1-2\nu)\frac{\chi_{f3}}{b}\Big)\Big(1+2\frac{\chi_3}{a}\Big)-$$
$$\Big(1-\frac{\chi_{f3}}{b}\Big)\Big(1+\nu-4(1-2\nu)\frac{\chi_3}{a}\Big)\frac{a^3}{b^3}\Big\},$$

where

$$\Gamma = \bar{G}/G,\ \ \chi_{f0} = \frac{1}{4G}(\lambda_{f0}+2\mu_{f0}),\ \chi_{f1} = \frac{1}{4G}(\lambda_{f0}+\tau_{f0}),\ \chi_{f3} = \chi_{f0}+\chi_{f1}, \tag{35}$$

and

$$M = \Big\{\Big(1+\nu+2(1-2\nu)\frac{\chi_{f3}}{b}\Big)\Big(2\Big(1+2\frac{\chi_3}{a}\Big)(1-2\bar{\nu})+\Gamma(1+\bar{\nu})\Big)$$
$$-2\Big(1-\frac{\chi_{f3}}{b}\Big)\Big(\Big(1+\nu-4(1-2\nu)\frac{\chi_3}{a}\Big)(1-2\bar{\nu})-\Gamma(1-2\nu)(1+\bar{\nu})\Big)\frac{a^3}{b^3}\Big\}. \tag{36}$$

Submitted on December 2007, revised on April 2008.

Nanočestice i uticaj elastičnosti na interfejsu

Razmatra se uticaj napona na površi i interfejsu na elastično polje nanočestice potopljene u konačni sferni substrat. Ovde se ima u vidu aksijalno zatezno polje koje deluje na spoljnu granicu supstrata i nesmičuće uniformno polje usadne deformacije unutar čestice. Kao rezultat osne simetrije dve potencijalne funkcije pomeranja Papkovič-Nojbera su dovoljne da reprezentuju rešenje elastičnosti. Naponski efekti na površi i interfejsu su potpuno reprezentovani Gurtinovom i Mardokovom teorijom elastičnosti površi i interfejsa. Ovi efekti modifikuju granične uslove pridružene klasičnoj kontinualnoj teoriji elastičnosti. Kompletna metodologija rezultuje u elastostatičkom rešenju Navijeovih jednačina. U suprotnosti od klasičnog rešenja, modifikovana verzija uvodi dodatne zavisnosti od veličine nanočestica kao i materijalne osobine površi i interfejsa.

doi:10.2298/TAM0803267M Math.Subj.Class.: 74A50, 74A60, 74M25, 74B99