

Effect of surfaces on the size-dependent elastic state of nano-inhomogeneities

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The effect of surface energies, strains, and stresses on the size-dependent elastic state of embedded inhomogeneities are investigated. At nanolength scales, due to the increasing surface-to-volume ratio, surface effects become important and induce a size dependency in the otherwise size-independent classical elasticity solutions. In this letter, closed-form expressions are derived for the elastic state of eigenstrained spherical inhomogeneities with surface effects using a variational formulation. Our results indicate that surface elasticity can significantly alter the fundamental nature of stress state at nanometer length scales. Additional applications of our work on nanostructures such as quantum dots, composites, etc. are implied. © 2003 American Institute of Physics.

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Classical elasticity does not admit intrinsic size dependence in the elastic solutions of inclusions and inhomogeneities. At nanolength scales, however, size effects often become prominent, the causes of which need to be explicitly addressed especially with an increasing interest in the general area of nanotechnology (and nanomechanics in particular). For structures with sizes >100 nm, typically, the surface-to-volume ratio is negligible and the effective properties are governed by classical bulk elastic strain energy through a fourth order elastic stiffness tensor (Young's modulus E , and Poisson ratio ν for isotropic materials). On the other hand, it is well known that surfaces and interfaces in solids behave differently from their bulk counterparts. The technological significance of surfaces is likely to be important in nanostructures due to their high surface-to-volume ratios, in quantum dots, nanocomposites, and other optoelectromechanical structures. The strain energy in these structures can be dramatically altered by surface effects and hence both their local and macroscopic properties.

In work, a pioneering Eshelby,¹ solved the general problem of the elastic state of an *inhomogeneity* containing *eigenstrains* located within a foreign material and subjected to an applied external stress. Here, inhomogeneities are defined as embedded objects with material properties differing from the surrounding host material or matrix while eigenstrains are stress-free strains such as lattice parameter mismatch, thermal expansion, inelastic strains, etc. Eshelby's work forms the backbone for analyzing several problems of interest in materials science, solid-state physics, and mechanics of composites. In its present form, Eshelby's formalism¹⁻³ does not include the effects of elastic surface properties (e.g., residual surface tension, surface moduli) of inhomogeneities and their elastic state as it is entirely based on bulk properties. At submicron inhomogeneity length scales the properties of the inhomogeneity surface/interface are expected to play a role in the determination of the nanoinhomogeneity elastic state. This increasing role of surface elasticity at smaller length scales induces a size effect in the otherwise classical size-

independent elastic solutions. Currently, no formulation exists which combines surface elasticity with Eshelby's formalism to analyze inhomogeneities with size-dependent surface effects. See, for example, comprehensive reviews by Mura³ and Mura *et al.*⁴ In this letter, we reformulate the inhomogeneity problem in terms of generalized energy functionals (rather than the stress-based approach of Eshelby),¹ permitting a simple way to include surface/interface effects.

A generic and mathematical exposition on surface elasticity has been presented by Gurtin and Murdoch.^{5,6} They have also presented simple applications of surface elasticity to the analysis of an isolated (unembedded) sphere, infinite cylinder, and square crystal under a residual surface tension loading.⁷ Recently, Miller and Shenoy⁸ have explored the effect of surfaces in isolated structural elements like nanoscale beams and plates. Their article, however, is not directed at inclusions or inhomogeneities. Cammarata, in particular, presents some example of surface effects in thin films.⁹ A method to solve the generalized inhomogeneity problem is proposed followed by an application to the problem of stress concentration near a nanovoid. Other applications of our work, i.e., (i) the determination of overall properties of composites with surface effects and (ii) the size-dependent interfacial corrections to strain state of quantum dots, will be discussed elsewhere.

The surface stress tensor, σ^{surface} , is related to the deformation dependent surface energy $\Gamma(\varepsilon_{\alpha\beta})$ by:

$$\sigma_{\alpha\beta}^{\text{surface}} = \tau_0 \delta_{\alpha\beta} + \frac{\partial \Gamma}{\partial \varepsilon_{\alpha\beta}}, \quad (1)$$

where, $\varepsilon_{\alpha\beta}$ is the 2×2 strain tensor for surfaces, $\delta_{\alpha\beta}$ represents the Kronecker delta for surfaces while τ_0 is the residual surface tension. The presence of surface stress gives rise to a nonclassical boundary condition, which in combination with the surface stress-strain relations and the equations of classical elasticity form a coupled system of field equations. Under the assumption that the surface adheres to the bulk without slipping, and in the absence of body forces, the equilibrium and constitutive equations for isotropic case can be summarized as:⁵⁻⁷

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In the bulk:

$$\sigma_{ij,j}^{\text{bulk}} = 0 \tag{2a}$$

$$\sigma_{ij}^{\text{bulk}} = C_{ijkl}\epsilon_{kl} = [\lambda \delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})]\epsilon_{kl}.$$

On the surface/interface:

$$\begin{aligned} \sigma_{\beta\alpha}^{\text{bulk}} n_\beta + \sigma_{\beta\alpha,\beta}^{\text{surface}} &= 0; & \sigma_{ji}^{\text{bulk}} n_j n_i &= \sigma_{\alpha\beta}^{\text{surface}} \kappa_{\alpha\beta} \\ \sigma_{\beta\alpha}^{\text{surface}} &= \tau^0 \delta_{\beta\alpha} + 2(\mu^s - \tau^0) \delta_{\beta\gamma} \epsilon_{\gamma\alpha} + (\lambda^s + \tau^0) \epsilon_{\gamma\gamma} \delta_{\beta\alpha}, \end{aligned} \tag{2b}$$

where, λ and μ are the Lamé constants for the isotropic bulk material. Isotropic interfaces or surfaces can be characterized by surface Lamé constants λ^s , μ^s (which render the surface energy deformation dependent)¹⁰ and residual surface tension, τ^0 (under unstrained conditions). Here, $\kappa_{\alpha\beta}$ represents the curvature tensor of the surface or interface, n_α is the normal vector on the interface or surface, and finally ϵ_{ij} is the infinitesimal strain tensor and σ_{ij} is the corresponding stress tensor. It is noted that only certain strain components appear within the constitutive law for surfaces due to the 2×2 nature of the surface stress tensor (i.e., strains normal to the surface are excluded). Thus, the Greek indices take on values 1 and 2 while Latin subscripts adopt values 1 through 3. Conventional summation rules apply unless otherwise noted.

We now consider a spherical inhomogeneity, of radius R_0 , located in an infinite matrix, and undergoing a dilatation eigenstrain (generally, but not necessarily, nonzero), i.e., $\epsilon_{11}^* = \epsilon_{22}^* = \epsilon_{33}^* = \epsilon^*$, and subjected to far-field triaxial stress σ^∞ . The bulk and surface elastic energy densities of an inhomogeneity-matrix system can be given as:

$$\Psi_\Lambda^{\text{bulk}} = \frac{1}{2} \lambda_\Lambda (\epsilon_{ii})^2 + \mu_\Lambda \epsilon_{ij} \epsilon_{ij} - 3K_\Lambda \epsilon^* \epsilon_{ii}; \tag{3a}$$

$$\Psi^{\text{surface}} = \int_{\text{surface}} dS \int_0^{\epsilon_{\alpha\beta}^s} \sigma_{\alpha\beta}^s d\epsilon_{\alpha\beta}^s, \tag{3b}$$

where, Λ represents either the inhomogeneity “I” or the matrix M, K_Λ is the bulk modulus ($=\lambda_\Lambda + 2\mu_\Lambda/3$), ϵ^* the eigenstrain which is finite in the inhomogeneity and zero outside of it. The superscript “s” is used to emphasize the surface terms. The free energy of the spherically symmetric system, in the presence of surface effects, can then be written as:

$$\begin{aligned} \Pi &= 4\pi \int_0^{R_0} r^2 \Psi_I^{\text{bulk}} dr + 4\pi R_0^2 \int_0^{\epsilon_{ij}^s} \sigma_{ij}^s d\epsilon_{ij}^s \\ &+ 4\pi \int_{R_0}^{R_\infty} r^2 \Psi_M^{\text{bulk}} dr. \end{aligned} \tag{4}$$

The Euler–Lagrange equations and the appropriate boundary conditions are obtained by setting the variation of the free energy to be zero, i.e., $\delta\Pi = 0$.

The spherically symmetric problem leads to a displacement field that is radially symmetric, i.e., $u = u(r)$. The corresponding infinitesimal strain components in spherical polar basis are:

$$\epsilon_{rr} = \frac{\partial u}{\partial r}; \quad \epsilon_{\theta\theta} = \epsilon_{\phi\phi} = \frac{u}{r}; \quad \epsilon_{\theta\theta}^s = \epsilon_{\phi\phi}^s = \frac{u}{R_0}. \tag{5}$$

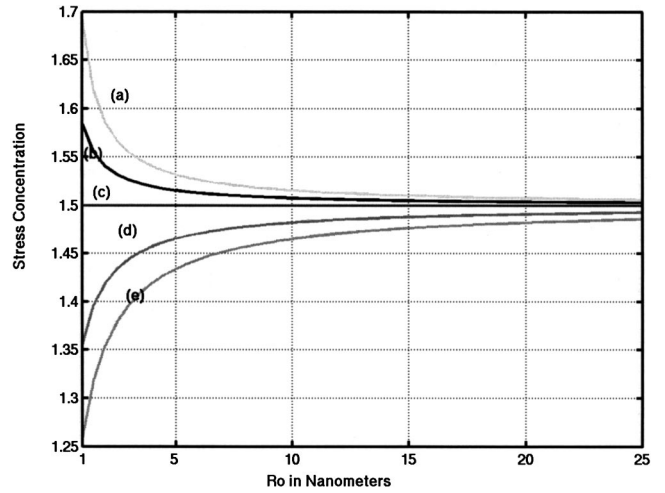


FIG. 1. Stress concentration as a function of surface properties and void radius. (a) Solution with surface modulus= $2K_s$, Al [1 0 0]; (b) solution with surface modulus=nominal K_s for Al [1 0 0]; (c) classical solution without surface effects, i.e., $K_s=0$; (d) solution with surface modulus = $2K_s$ Al [1 1 1] (e) solution with surface modulus=nominal K_s , Al [1 1 1].

Substituting, Eq. (5) in Eq. (4), using the constitutive Eqs. (2) and taking the variation of the total energy with respect to the displacement fields, we obtain¹¹: Eq. (6a): Euler’s equation for the integrand in both the inhomogeneity and matrix domains; Eq. (6b): the equilibrium of the bulk and surface forces at the interface; and Eq. (6c): the natural boundary condition:

$$r^2 \frac{\partial^2 u}{\partial r^2} - 2r \frac{\partial u}{\partial r} - 2u = 0, \tag{6a}$$

$$\sigma_{rr}^+ - \sigma_{rr}^- = \frac{2\sigma_{\theta\theta}^s}{R_0} \Big|_{r=R_0}, \tag{6b}$$

$$\sigma_{rr} \Big|_{r \rightarrow \infty} = \sigma^\infty. \tag{6c}$$

The general solutions to the differential equation of Eq. (6a) are simply, r and $1/r^2$. Using a linear combination of the general solutions to Eq. (6a), we can now write $u(r)$ as:

$$\begin{aligned} u(r) &= Ar + Br^{-2} \Big|_{r < R_0} \\ &Cr + Dr^{-2} \Big|_{r > R_0}, \end{aligned} \tag{7}$$

Where A, B, C, and D are constants to be determined from the boundary conditions and Eqs. (6b) and (6c). Two boundary conditions are immediately obvious: (i) at the center of the inhomogeneity $u(r)$ must approach zero and (ii) at points infinitely far away from the inhomogeneity, the stress field must approach the applied stress, i.e., $r \rightarrow \infty$, $\sigma \rightarrow \sigma^\infty$. These restrictions render $B=0$ and $C = \sigma^\infty / K_M = \epsilon^\infty$. Here, $K_M = \lambda_M + 2\mu_M/3$ is the matrix bulk modulus. Furthermore, displacements must be continuous, thus $u^+(r \rightarrow R_0) = u^-(r \rightarrow R_0)$ which gives $A = \epsilon^\infty + D/R_0^3$. Finally, the condition in Eq. (6b) is applied. The final solution is obtained as:

$$u(r) = \begin{cases} \frac{(3K_M + 4\mu_M)\varepsilon^\infty + 3K_I\varepsilon^* - 2\tau_0/R_0}{4\mu_M + 3K_I + 2K^s/R_0}, & r \leq R_0 \\ \varepsilon^\infty r + \left[\frac{(3K_M + 4\mu_M)\varepsilon^\infty + 3K_I\varepsilon^* - 2\tau_0/R_0}{4\mu_M + 3K_I + 2K^s/R_0} - \varepsilon^\infty \right] \frac{R_0^3}{r^2}, & r > R_0 \end{cases} \quad (8)$$

where $K_s = 2(\mu_s + \lambda_s)$ is introduced in this letter as the ‘‘surface modulus.’’ Strain can be obtained as derivatives [Eq. (5)] of $u(r)$ and the stresses, by using Eq. (2), can be expressed as:

$$\begin{aligned} r \leq R_0: \\ \sigma_{rr}(r) = \sigma_{\theta\theta}(r) = \sigma_{\phi\phi}(r) \\ = 3K_I \frac{(3K_M + 4\mu_M)\varepsilon^\infty + 3K_I\varepsilon^* - 2\tau_0/R_0}{4\mu_M + 3K_I + 2K_s/R_0}, \quad (9a) \end{aligned}$$

$$\begin{aligned} r > R_0: \\ \sigma_{\theta\theta}(r) = \sigma^{\phi\phi}(r) \\ = 2\mu_M \left(\frac{(3K_M + 4\mu_M)\varepsilon^\infty + 3K_I\varepsilon^* - 2\tau_0/R_0}{4\mu_M + 3K_I + 2K_s/R_0} - \varepsilon^\infty \right) \frac{R_0^3}{r^3} + 3K_M\varepsilon^\infty. \quad (9b) \end{aligned}$$

The stress component σ_{rr} can be derived similarly. Note that the surface effects enter the equations via K_s and τ_0 weighted appropriately by the curvature ($1/R_0$) of the inhomogeneity. Making R_0 arbitrarily large can trivially retrieve the classical solution. Interestingly, the stresses and strains in the inhomogeneity are uniform much like the classical case.¹

We will now present application of our work to the classical problem of stress concentration at a void. The expressions, though, are quite general and can be applied to any material property combinations.

For a void, $K_I = \mu_I = 0$, $\varepsilon^* = 0$, in Eq. (9). To determine the stress concentration, we let $r \rightarrow R_0$. The stress concentration is then given by:

$$S.C. = \frac{\sigma_{\theta\theta}}{\sigma_\infty} \Big|_{r=R_0} = 1 + \frac{1}{2} \left(\frac{1 - 2(\tau_0/\varepsilon^\infty + K_s)/3K_M R_0}{1 + K_s/2\mu_M R_0} \right). \quad (10)$$

In subsequent numerical results we set $\tau_0 = 0$, to study the effect of surface elastic constant, K_s . Effects of residual surface tension (which is closely related to the phenomenon of classical sintering) can be investigated through Eqs. (8)–(10). Furthermore, results can then be presented independent of loading conditions. Note that Eq. (10) trivially gives 1.5 as the stress concentration for the classical elasticity case when either surface modulus is small or void radius is relatively large (typically >25 nm). The numerical results are presented for aluminum using free-surface properties computed by previous researchers using the embedded atom method (EAM) molecular dynamics.⁸ The authors in Ref. 8 indicate different surface properties depending upon crystallographic orientation. Accordingly, we present numerical results for two different orientations one for which the surface moduli K_s is negative (surface [1 0 0]) while positive for the other [1 1 1]. The parameters as obtained from manipulation of data

from Ref. 9, are: [1 0 0], $\lambda_s = 3.48912$ N/m, $\mu_s = -6.2178$ N/m $\Rightarrow K_s = -5.457$ N/m, while for [1 1 1], they are: $\lambda_s = 6.842$ N/m, $\mu_s = -0.3755$ N/m $\Rightarrow K_s = 12.932$ N/m.

The stress concentration of the spherical cavity under hydrostatic tension is plotted as a function of the cavity radius R_0 in Fig. 1 for two different sets of surface properties (corresponding to [1 0 0] Al and [1 1 1] Al). To investigate a broader range of surface properties, curves of surface modulus twice that of Al [1 0 0] and Al [1 1 1] are also shown. As shown in Fig. 1, surface effects cause the stress concentration to reduce (increase) with decreasing pore size when $K_s > 0$ ($K_s < 0$). The classical case (without surface effects) corresponds to $K_s = 0$ and is, as expected, independent of pore size. Below a critical void radius the void will sinter. This effect, as mentioned earlier, is closely related to the residual surface tension and applied load and is not investigated here.

To summarize, we have reformulated the inhomogeneity problem to include the size dependent surface and interface effects on its elastic state. Our derived equations have several applications that are omitted here for the sake of brevity and will be discussed elsewhere. Quantum dots, which are often a few nanometers in size, have their optoelectronic properties severely affected by lattice mismatch related eigenstrains. It can be inferred from our work that in the traditional sizes of quantum dots (2–30 nm), surface effects are likely to influence the strain distributions and hence their optoelectronic properties. Our derived equations can be directly used to provide interfacial elasticity corrections to the size-dependent strain state of quantum dots [Eq. (8)]. Another application of this work is that surface effects can now be easily included in the determination of effective elastic properties of a composite. As shown by several authors (see, e.g., Nemat-Nasser and Hori¹²), effective bulk modulus of a composite is easily calculated once the single inhomogeneity solution is known [provided by our work in Eq. (9) for symmetric loading]. The effective properties will then, unlike the classical solutions, become size dependent.

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