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Curvature-dependent surface energy and implications for nanostructures

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ABSTRACT

At small length scales, several size-effects in both physical phenomena and properties can be rationalized by invoking the concept of surface energy. Conventional theoretical frameworks of surface energy, in both the mechanics and physics communities, assume curvature independence. In this work we adopt a simplified and linearized version of a theory proposed by Steigmann–Ogden to capture curvature-dependence of surface energy. Connecting the theory to atomistic calculations and the solution to an illustrative paradigmatic problem of a bent cantilever beam, we catalog the influence of curvature-dependence of surface energy on the effective elastic modulus of nanostructures. The observation in atomistic calculations that the elastic modulus of bent nanostructures is dramatically different than under tension – sometimes softer, sometimes stiffer – has been a source of puzzlement to the scientific community. We show that the corrected surface mechanics framework provides a resolution to this issue. Finally, we propose an unambiguous definition of the thickness of a crystalline surface.

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1. Introduction

Several types of nanostructures of various materials are observed to exhibit qualitatively different physical, mechanical and chemical behavior as compared to bulk state. A few examples among many others are that melting temperature can be severely suppressed in nanoparticles (Qi, 2005), Si quantum dots may exhibit optical activity not seen in its bulk form (Peng et al., 2006), and non-piezoelectric materials may be coaxed into behaving like one (Sharma et al., 2010). The afore-mentioned size-effects and others are often rationalized by invoking the concept of surface energy and the associated concepts of (residual) surface stress and superficial elasticity. Ranging from self-assembly (Suo and Lu, 2000), phase transformation (Diao et al., 2003), thin film growth (Freund and Suresh, 2003), to catalysis (Bertolini, 2000); surface energy based arguments have provided a framework to understand size-effects. The mechanics community, based on this concept, has heavily investigated the size-dependence of the elastic modulus of nanostructures. The turning point for research in surface mechanics appears to be the appearance of the paper by Miller and Shenoy (2000), who (predicated on the theory by Gurtin and Murdoch, 1975) presented both a method and the actual atomistic calculations of surface elastic constants of various materials and explored the consequences of surfaces on the size-dependency of elastic properties. Several works then followed: studies on inclusions (Sharma et al., 2003; Sharma and Ganti, 2004; Duan et al., 2005a, 2005b; He and Li, 2006; Tian and Rajapakse, 2007; Mi and Kouris, 2007), thin films and nanoparticles (Streitz et al., 1994; Dingreville et al., 2005), computational schemes, nanowires (Diao et al. 2003, 2004, 2006; Bar On et al., 2010),

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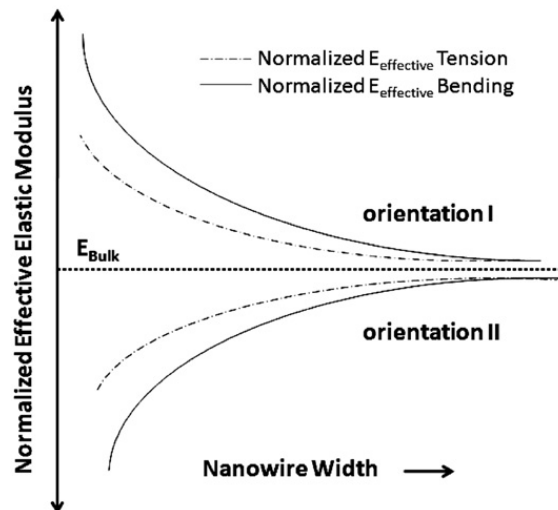


Fig. 1. Schematic showing the observation that the renormalized elastic modulus of a bent nanowire/beam is always greater than under tension (in terms of absolute value).

beams (Miller and Shenoy, 2000; Park and Klein, 2008; Jing et al., 2006), frequency modifications for sensing (Park and Klein, 2008; Wang and Feng, 2007), atomistic methods for computation of surface properties (Shenoy, 2005; Shodja and Tehrani, 2010; Mi et al., 2008) and composites (Mogilevskaya et al., 2008).

As far as the foundations of the theoretical frameworks of surface energy effects are concerned, Gurtin and Murdoch (1975, 1978) were the first to develop a rigorous mechanics based theoretical framework of surface elasticity. These works were later generalized to address interfaces also (Gurtin et al., 1998). Although not fundamentally different, a more materials science oriented viewpoint has been presented by Streitz et al. (1994). The reader is encouraged to refer to an excellent recent article by Cammarata (2009a, 2009b). An important series of paper was published by Huang and co-workers (e.g. Wang et al., 2010; Huang and Sun, 2006). While implicit in the original theory by Gurtin–Murdoch, it was not quite well-appreciated until the appearance of these works that residual surface stress can also impact overall elastic behavior (of nanostructures as well as composites). A few other recent review articles (Mogilevskaya et al., 2008, 2010; Ru, 2010; Schiavone and Ru, 2009) have also provided various clarifications regarding mis-concepts related to the Gurtin–Murdoch theory. The reader is also directed towards a recent tutorial article by Murdoch (2005), which particularly presents a clear exposition on the direct notation useful for surface mechanics.

The present work looks beyond the circumstances where the Gurtin–Murdoch theory applies and is an attempt to elucidate the important physical consequences of incorporation of curvature-dependence of surface energy. In the original Gurtin–Murdoch theory, surface energy depends only on the surface strains and any dependence on curvature is ignored—this notion is made clearer in Section 2.

There are two main motivations for this work:

- (1) The importance of curvature-dependence of surface energy became evident to us through publications by Steigmann and Ogden (1997, 1999) and personal communication with one of them. Steigmann and Ogden have pointed out that the Gurtin–Murdoch theory cannot be used for a compressive stress-state and in particular surface wrinkling or roughening – ostensibly a key application of the original Gurtin–Murdoch theory – cannot be handled properly within that framework. Steigmann and Ogden proposed a modified framework showing that incorporating curvature-dependent surface energy rectified the afore-mentioned issues. Steigmann–Ogden work has gone relatively unnoticed and nearly all the literature on surface mechanics is based on the Gurtin–Murdoch theory.¹ It is worth mentioning that for many problems we expect (intuitively) that the Steigmann–Ogden theory will only be a minor correction to the Gurtin–Murdoch’s but for certain problems there is no recourse but to use the former (e.g. wrinkling and bending deformation modes). The following questions remain: (a) what are the numerical values of the material parameters that characterize the Steigmann–Ogden theory and how can they be evaluated through atomistic calculations? (b) Setting the niceties of rigor aside, how important is the Steigmann–Ogden correction for some key applications of surface energy theory e.g. effective elastic modulus of nanostructures?
- (2) Several researchers (Miller and Shenoy, 2000; McDowell et al., 2008; Yun and Park, 2009) have observed that the effective elastic modulus of nanostructures under bending is significantly different than under homogeneous conditions. This has been a source of puzzlement since the Gurtin–Murdoch theory predicts negligible difference between the two states. Fig. 1

¹ Two important exceptions appear to be the works of Fried and Todres (2005) and Schiavone and Ru (2009). The former analyzes wrinkling type instability of a soft film subjected to the action of van der Waals force of a punch while Schiavone and Ru discuss the solvability of the Steigmann–Ogden theory in 2D context.

illustrates the observation. Further, the elastic modulus under bending is always found to be higher (in absolute value) as compared with under tension or compression. Again, this is not readily evident from the Gurtin–Murdoch theory. It is worth mentioning that gradient elasticity type theories cannot explain this. The typical elemental materials (without defects) on which atomistic calculations have been performed exhibit very low characteristic nonlocal length scales and indeed surface energy effects dominate—see for example Maranganti and Sharma (2007a, 2007b).

The outline of our paper is as follows. Section 2 presents the theory of curvature-dependent surface energy, stress and elasticity. We derive the effective elastic modulus of a cantilever beam in Section 3 and proceed to calculate the material constants of Steigmann–Ogden theory in Section 4. In Section 5, we present a discussion on the implications of this work for nanostructures. In particular we discuss three specific issues: (a) an explanation of the asymmetry of the elastic response under bending versus tension, (b) correction to the venerable Stoney’s formula (Stoney, 1909) and (c) a proposal for an unambiguous determination of surface thickness.

2. Theory of curvature-dependent surface energy, stress and elasticity

In this section, we primarily follow Steigmann and Ogden (1999) except that we have preferred the direct notation of Gurtin–Murdoch and therefore equations appear somewhat different. We have liberally used the formalism as well as notation in the work of Wang et al. (2010), in their representation of Gurtin–Murdoch’s work. Our derivation of the boundary conditions is somewhat different from that of Steigmann–Ogden.

Consider \mathbf{A}_0 , a smooth surface in the reference configuration (Wang et al., 2010) represented by parametric coordinates $\mathbf{R} = \mathbf{R}(\theta^1, \theta^2)$, where \mathbf{R} is the position vector of the points on the surface from the origin and (θ^1, θ^2) represents the curvilinear coordinates on the surface. Under deformation, the point \mathbf{R} will move to a point \mathbf{r} on the deformed surface \mathbf{A} . In Cartesian coordinate system, the covariant base vectors at \mathbf{R} are $\mathbf{A}_\alpha = \mathbf{R}_{,\alpha}$ ($\alpha=1,2$) in the reference configuration and $\mathbf{a}_\alpha = \mathbf{r}_{,\alpha}$ in the deformed configuration system. We assume that there is a linear transformation that maps a vector in the tangent plane of the undeformed surface into a vector in the tangent plane of the deformed surface. This mapping can be expressed by the surface deformation gradient $\mathbf{F}_S = \mathbf{a}_\alpha \otimes \mathbf{A}^\alpha$ in a two-dimensional space. In the above relation, \mathbf{A}^α are the contravariant base vectors at \mathbf{R} (Fig. 2).

The right and left Cauchy–Green tensors of the surface are defined as $\mathbf{C}_S = \mathbf{F}_S^T \cdot \mathbf{F}_S$ and $\mathbf{B}_S = \mathbf{F}_S \cdot \mathbf{F}_S^T$. Since \mathbf{C}_S and \mathbf{B}_S are symmetric and positive definite, we further define right and left stretch tensor on the surface $\mathbf{U}_S = \mathbf{C}_S^{1/2}$ and $\mathbf{V}_S = \mathbf{B}_S^{1/2}$. The surface deformation tensors \mathbf{C}_S and \mathbf{B}_S and their material derivatives are nonlinear in the displacement gradients and their consequent displacements. The linearized expressions of the surface deformation tensors under infinitesimal deformations are

$$\begin{aligned} \mathbf{C}_S &= \mathbf{I}_0 + 2\mathbf{E}_S \text{ and } \mathbf{B}_S = \mathbf{I} - 2\boldsymbol{\varepsilon}_S, \\ \mathbf{U}_S &= (\mathbf{C}_S)^{1/2} = \mathbf{I}_0 + \mathbf{E}_S \end{aligned} \tag{1}$$

where \mathbf{E}_S and $\boldsymbol{\varepsilon}_S$ are Green Lagrange strain tensors and \mathbf{I}_0 and \mathbf{I} are the identity tensors on the tangent planes of undeformed and deformed surface, respectively.

$$\mathbf{E}_S = \frac{1}{2}(\bar{\nabla}_{0S}\mathbf{u}_0 + \mathbf{u}_0\bar{\nabla}_{0S}), \quad \boldsymbol{\varepsilon}_S = \frac{1}{2}(\bar{\nabla}_S\mathbf{u} + \mathbf{u}\bar{\nabla}_S). \tag{2}$$

\mathbf{u}_0 is the displacement vector of a point on the surface in undeformed state and \mathbf{u} is the displacement vector in deformed configuration. $\bar{\nabla}_{0S}$ and $\bar{\nabla}_S$ are the gradient operators on the surfaces \mathbf{A}_0 and \mathbf{A} , respectively, and can be defined as $\bar{\nabla}_S\mathbf{u} = \nabla\mathbf{u} - \mathbf{n}(\mathbf{n} \cdot \nabla\mathbf{u})$, where \mathbf{n} is the unit normal vector of the surface after deformation. Under the Lagrangian description, surface Piola–Kirchhoff stress tensor of second kind (asymmetric) is given by the relation

$$\mathbf{T}_S = 2 \frac{\partial(J_2\gamma)}{\partial\mathbf{C}_S} \tag{3}$$

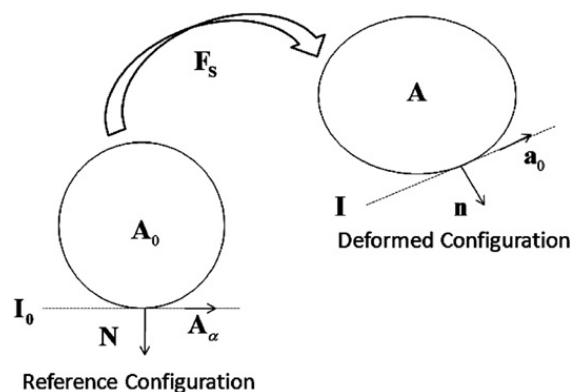


Fig. 2. Schematic representing the undeformed and deformed configuration of a surface.

where γ is the surface energy density and $J_2 = \det \mathbf{U}_S$ is the ratio between the area elements of before and after deformations. $(J_2\gamma)$ denotes the surface energy in the undeformed configuration. The relation between the first and second Piola–Kirchhoff stress is given as

$$\mathbf{S}_S = \mathbf{F}_S \cdot \mathbf{T}_S. \tag{4}$$

The surface deformation gradient can be written in the reference configuration as (Wang et al., 2010)

$$\mathbf{F}_S = \mathbf{I}_0 + \mathbf{u}_0 \bar{\nabla}_{0S} + \mathbf{F}_S^{(0)} \tag{5}$$

where $\mathbf{F}_S^{(0)}$ denotes the out-plane term of \mathbf{F}_S in the reference configuration. The reader is referred to the paper by Wang et al. (2010) for details of kinematic relations leading to derive this expression.

The surface strain energy functional may be formulated using the concepts of tensor functions and invariant theory (Truesdell and Noll, 1971). Principal invariants of a tensor \mathbf{A} , which are represented by $J_k(\mathbf{A}), (k=1, 2, \dots, n)$, are the coefficients of the following polynomial in λ

$$\det(\lambda \mathbf{I} + \mathbf{A}) = \lambda^n + J_1(\mathbf{A})\lambda^{n-1} + \dots + J_{n-1}(\mathbf{A})\lambda + J_n(\mathbf{A}). \tag{6}$$

In particular for any tensor \mathbf{A}

$$J_1(\mathbf{A}) = \text{tr} \mathbf{A}, \quad J_n(\mathbf{A}) = \det \mathbf{A}. \tag{7}$$

Steigmann and Ogden (1999) have used the formulation of surface energy density as proposed by Cohen and DeSilva (1966)

$$\gamma = \gamma(\mathbf{C}_S, \boldsymbol{\kappa}; \theta^1, \theta^2). \tag{8}$$

In the above relation \mathbf{C}_S is the right surface Cauchy–Green deformation tensor and $\boldsymbol{\kappa}$ is the curvature tensor and (θ^1, θ^2) are the parametric coordinates of the system. In general, for an isotropic body, the surface energy density is a functional of seven invariants. For our purposes, we consider only the first four invariants of the energy functional to formulate the surface energy density. These invariants are

$$\begin{aligned} J_1 &= \text{tr} \mathbf{U}_S \\ J_2 &= \det \mathbf{U}_S \\ J_3 &= (\text{tr} \boldsymbol{\kappa})^2 \\ J_4 &= \det \boldsymbol{\kappa} \end{aligned} \tag{9}$$

where \mathbf{U}_S is the right stretch tensor of the surface. We can simplify the expression for the invariants J_1 and J_2

$$J_1 = 2 + \text{tr} \mathbf{E}_S, \quad J_2 = 1 + \text{tr} \mathbf{E}_S + \det \mathbf{E}_S \tag{10}$$

where for small deformations $\det \mathbf{E}_S$ would be of higher order. For hyperelastic media, the surface energy density γ can be assumed to be some function of \mathbf{U}_S . In particular, for an isotropic surface, γ can be written as a function of the all the invariants of γ . Therefore representing in term of invariants

$$\begin{aligned} \gamma &= \gamma_0 + \gamma_1(J_1 - 2) + \gamma_2(J_2 - 1) + \gamma_3 J_3 + \gamma_4 J_4 + \gamma_{12}(J_1 - 2)(J_2 - 1) + \gamma_{13}(J_1 - 2)J_3 + \gamma_{14}(J_1 - 2)J_4 + \gamma_{23}(J_2 - 1)J_3 + \gamma_{24}(J_2 - 1)J_4 + \gamma_{34}J_3J_4 \\ &+ \frac{1}{2}(\gamma_{11}(J_1 - 2)^2 + \gamma_{22}(J_2 - 1)^2 + \gamma_{33}J_3^2 + \gamma_{44}J_4^2) + \dots \end{aligned} \tag{11}$$

Then from Eq. (3) we have

$$\begin{aligned} \mathbf{T}_S &= 2J_2 \frac{\partial \gamma}{\partial \mathbf{C}_S} + 2\gamma \frac{\partial J_2}{\partial \mathbf{C}_S} = 2J_2 \left[\frac{\partial \gamma}{\partial J_1} \cdot \frac{\partial J_1}{\partial \mathbf{C}_S} + \frac{\partial \gamma}{\partial J_2} \cdot \frac{\partial J_2}{\partial \mathbf{C}_S} \right] + 2\gamma \frac{\partial J_2}{\partial \mathbf{C}_S} \\ \text{as } \frac{\partial J_3}{\partial \mathbf{C}_S} &= \frac{\partial J_4}{\partial \mathbf{C}_S} = 0. \end{aligned} \tag{12}$$

Using the identities for any tensor \mathbf{A} (Holzapfel, 2000)

$$\frac{\partial \det \mathbf{A}}{\partial \mathbf{A}} = (\det \mathbf{A}) \mathbf{A}^{-T}, \quad \frac{\partial \text{tr} \mathbf{A}}{\partial \mathbf{A}} = \mathbf{I} \tag{13}$$

we can derive the second Piola–Kirchhoff surface stress tensor.

$$\begin{aligned} \frac{\partial J_1}{\partial \mathbf{C}_S} &= \frac{\partial J_1}{\partial \mathbf{U}_S} \cdot \frac{\partial \mathbf{U}_S}{\partial \mathbf{C}_S} = \frac{1}{2} \mathbf{U}_S^{-1} \\ \frac{\partial J_2}{\partial \mathbf{C}_S} &= \frac{\partial J_2}{\partial \mathbf{U}_S} \cdot \frac{\partial \mathbf{U}_S}{\partial \mathbf{C}_S} = \frac{1}{2} J_2(\mathbf{C}_S)^{-1} \\ \mathbf{T}_S &= 2 \frac{\partial (J_2 \gamma)}{\partial \mathbf{C}_S} = J_2 \frac{\partial \gamma}{\partial J_1} \mathbf{U}_S^{-1} + J_2 \left(J_2 \frac{\partial \gamma}{\partial J_2} + \gamma \right) \mathbf{C}_S^{-1} \end{aligned} \tag{14}$$

Using Eq. (1), (10) and (11) for small deformation, we have

$$J_2 \frac{\partial \gamma}{\partial J_1} \approx \gamma_1 + (\gamma_1 + \gamma_{11} + \gamma_{12}) \text{tr} \mathbf{E}_S + (\gamma_{13} J_3 + \gamma_{14} J_4) (1 + \text{tr} \mathbf{E}_S),$$

$$J_2 \left(J_2 \frac{\partial \gamma}{\partial J_2} + \gamma \right) \approx (\gamma_0 + \gamma_2) + (\gamma_0 + \gamma_1 + 3\gamma_2 + \gamma_{12} + \gamma_{22} + \gamma_3 (\text{tr} \mathbf{\kappa})^2 + \gamma_4 \det \mathbf{\kappa} + 3\gamma_{23} (\text{tr} \mathbf{\kappa})^2 + 3\gamma_{24} \det \mathbf{\kappa} + \gamma_{13} (\text{tr} \mathbf{\kappa})^2 + \gamma_{14} \det \mathbf{\kappa}) \text{tr} \mathbf{E}_S + ((\gamma_{23} + \gamma_3) (\text{tr} \mathbf{\kappa})^2 + (\gamma_{24} + \gamma_4) \det \mathbf{\kappa}). \quad (15)$$

Substituting Eq. (15) into Eq. (14) and simplifying the expression, the surface Piola–Kirchhoff stress of the second kind can be rewritten as

$$\mathbf{T}_S = (\gamma_0 + \gamma_1 + \gamma_2) \mathbf{I}_0 + (\gamma_0 + 2\gamma_1 + 3\gamma_2 + \gamma_{11} + \gamma_{22} + 2\gamma_{12}) (\text{tr} \mathbf{E}_S) \mathbf{I}_0 + (\gamma_1 - 2(\gamma_0 + \gamma_1 + \gamma_2)) \mathbf{E}_S + (\gamma_3^* (\text{tr} \mathbf{\kappa})^2 + \gamma_4^* \det \mathbf{\kappa}) \mathbf{I}_0 \quad (16)$$

where $\gamma_3^* = \gamma_{23} + \gamma_3$ and $\gamma_4^* = \gamma_{24} + \gamma_4$. In this expression of surface stress the last two terms $\gamma_3^* J_3$ and $\gamma_4^* J_4$ are nonlinear terms and (in this linearized theory) we discard those. The surface stress can be written as

$$\mathbf{T}_S = (\gamma_0 + \gamma_1 + \gamma_2) \mathbf{I}_0 + (\gamma_0 + 2\gamma_1 + 3\gamma_2 + \gamma_{11} + \gamma_{22} + 2\gamma_{12}) (\text{tr} \mathbf{E}_S) \mathbf{I}_0 + (\gamma_1 - 2(\gamma_0 + \gamma_1 + \gamma_2)) \mathbf{E}_S. \quad (17)$$

The linearized first Piola–Kirchhoff surface stress can be found using the relation given in Eq. (2), (4) and (5)

$$\mathbf{S}_S = (\gamma_0 + \gamma_1 + \gamma_2) \mathbf{I}_0 + (\gamma_0 + 2\gamma_1 + 2\gamma_2 + \gamma_{11} + \gamma_{22} + 2\gamma_{12}) (\text{tr} \mathbf{E}_S) \mathbf{I}_0 - (\gamma_0 + \gamma_1 + \gamma_2) \bar{\nabla}_{0S} \mathbf{u}_0 + \gamma_1 \mathbf{E}_S + (\gamma_0 + \gamma_1 + \gamma_2) \mathbf{F}_S^{(0)}. \quad (18)$$

Redefining constants, Eq. (18) may be rewritten in a more standard form as

$$\mathbf{S}_S = \tau_0 \mathbf{I}_0 + \lambda_0 (\text{tr} \mathbf{E}_S) \mathbf{I}_0 + 2\mu_0 \mathbf{E}_S + \bar{\tau}_0 \bar{\nabla}_{0S} \mathbf{u}_0 + (\gamma_0 + \gamma_1 + \gamma_2) \mathbf{F}_S^{(0)} \quad (19)$$

where τ_0 , λ_0 and μ_0 are the material constants of the surface. The above representation of surface stress resembles the definition of surface stress proposed by Gurtin and Murdoch (1975)

$$\mathbf{S}_S = \tau_0 \mathbf{I}_0 + \lambda_0 (\text{tr} \mathbf{E}_S) \mathbf{I}_0 + 2\mu_0 \mathbf{E}_S + \bar{\tau}_0 \bar{\nabla}_{0S} \mathbf{u}_0. \quad (20)$$

The surface Cauchy stress tensor can be determined by the following relation:

$$\boldsymbol{\sigma}_S = \frac{1}{J_2} \mathbf{F}_S \cdot \mathbf{T}_S \cdot \mathbf{F}_S^T. \quad (21)$$

Steigmann and Ogden (1999) have defined the surface moment stress \mathbf{M}_S , also known as edge traction, as

$$\mathbf{M}_S = 2 \frac{\partial (J_2 \gamma)}{\partial \mathbf{\kappa}}. \quad (22)$$

Essentially repeating the analysis of the preceding few pages, the surface moment stress can be written as

$$\mathbf{M}_S = 4\gamma_3 (\text{tr} \mathbf{\kappa}) \mathbf{I}_0 + 4(\gamma_3 + \gamma_{13} + \gamma_{23}) (\text{tr} \mathbf{E}_S \text{tr} \mathbf{\kappa}) \mathbf{I}_0. \quad (23)$$

The term $(\text{tr} \mathbf{E}_S \text{tr} \mathbf{\kappa})$ is a nonlinear contribution and accordingly discarded. We have then

$$\mathbf{M}_S = 4\gamma_3 (\text{tr} \mathbf{\kappa}) \mathbf{I}_0. \quad (24)$$

In summary, the constitutive equations we will use can be derived from the following simplified surface energy functional:

$$\gamma = \gamma_0 + \tau_0 \mathbf{E}_S + \frac{1}{2} C_0 \mathbf{E}_S^2 + \frac{1}{2} C_1 \mathbf{\kappa}^2 \quad (25)$$

where τ_0 is the residual surface stress, C_0 is the surface elastic constant (same as in Gurtin–Murdoch theory) and C_1 is the (new) Steigmann–Ogden material constant that reflects the penalty in surface energy upon changes in curvature.

We now proceed to outline the governing equations and boundary conditions. The picture below is a schematic of the bulk-surface system.

In Fig. 3 the surface is represented by S and the bulk volume and area are represented by V and \mathbf{A} , respectively. Let \mathbf{n} represent the outward unit normal to the surface, and \mathbf{t} be the unit vector tangential to the surface. Bulk stress is notated as $\boldsymbol{\sigma}^{bulk}$. At mechanical equilibrium the sum of all forces acting on the considered system must be identically zero. Using (Danov et al., 2010; Fried and Todres, 2005) force balance yields

$$\int_A (\mathbf{n} \cdot \boldsymbol{\sigma}^{bulk}) dS + \oint_L (\mathbf{t} \cdot \mathbf{S}_S) dL = 0. \quad (26)$$

Green's theorem gives us the following result:

$$\int_A \nabla_S \cdot \mathbf{S}_S dS = \oint_L (\mathbf{t} \cdot \mathbf{S}_S) dL. \quad (27)$$

Using Green's theorem on Eq. (26), we can simplify it to

$$\boldsymbol{\sigma}^{bulk} \cdot \mathbf{n} + \nabla_S \cdot \mathbf{S}_S = 0. \quad (28)$$

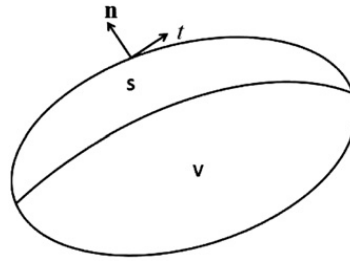


Fig. 3. Schematic of the surface and bulk representation for the equilibrium equations.

For equilibrium, the net moment of all acting forces should be identically zero (i.e.)

$$\int_A R \times (\mathbf{n} \cdot \boldsymbol{\sigma}^{bulk}) dS + \oint_L [R \times (\mathbf{t} \cdot \mathbf{S}_S) + \mathbf{t} \cdot \mathbf{M}_S] dL = 0. \quad (29)$$

Tensor identity gives us

$$R \times (\mathbf{n}_L \cdot \boldsymbol{\sigma}) = -\mathbf{n}_L \cdot (\boldsymbol{\sigma} \times R). \quad (30)$$

Using tensor identity and Eq. (28) we can simplify Eq. (29) in the following form:

$$\int_A R \times (\mathbf{n} \cdot \boldsymbol{\sigma}^{bulk}) dS + \oint_L [\mathbf{t} \cdot \mathbf{M}_S - \mathbf{t} \cdot (\mathbf{S}_S \times R)] dL = 0. \quad (31)$$

Applying Green's theorem, the above equation can be rewritten as

$$\int_A [R \times (\mathbf{n} \cdot \boldsymbol{\sigma}^{bulk}) + \nabla_S \cdot \mathbf{M}_S - \nabla_S \cdot (\mathbf{S}_S \times R)] dS = 0 \quad (32)$$

which gives us the following simplification:

$$R \times (\mathbf{n} \cdot \boldsymbol{\sigma}^{bulk}) + \nabla_S \cdot \mathbf{M}_S - \nabla_S \cdot (\mathbf{S}_S \times R) = 0. \quad (33)$$

Using the result from Eq. (28) we rewrite Eq. (33)

$$\nabla_S \cdot \mathbf{M}_S = \nabla_S \cdot (\mathbf{S}_S \times R) - R \times (\nabla_S \cdot \mathbf{S}_S) \quad (34)$$

The reader is also referred to Fried and Todres (2005) and Schiavone and Ru (2009) for alternative representations of the boundary conditions.

3. Predictions for a thin cantilever beam

Consider a thin cantilever beam loaded with a uniform lateral load $q(x)$ on top. The beam has longitudinal axis in x direction and vertical deflection in y direction (we assume a square cross section with side a without loss of any generality of our final qualitative results). Let $w(x)$ denote the deflection of the beam as a function of position x from the fixed end. Using the variational method, we will re-derive the equations governing beam bending theory considering surface free energy (25).

The axial and vertical displacements of the beam are approximated by

$$u_x = -y \frac{dw(x)}{dx}, \quad u_y = w(x). \quad (35)$$

For thin beams, we ignore the shear deformation of the beam. Therefore the bulk strains are

$$\varepsilon_{xx} = -y \frac{d^2w(x)}{dx^2}, \quad \varepsilon_{xy} = \varepsilon_{yy} = 0. \quad (36)$$

Liu and Rajapakse (2010) have shown that the effect of vertical stress σ_{yy} on beam deformation is very small and can be neglected. So, the relevant bulk stresses are

$$\sigma_{xx} = -Ey \frac{d^2w(x)}{dx^2}, \quad \sigma_{xy} = \sigma_{yy} = 0 \quad (37)$$

where E is the bulk Young's modulus. Also, the elastic surface with outward unit normal n_y has surface free energy represented by Eq. (25). We proceed by computing the total energy $U(w)$ of the cantilever beam by noting tangential surface strain as ε_{xx} and curvature as $d^2w(x)/dx^2$

$$U_{Bulk}(w) = \int_0^l \int_A \frac{1}{2} E \left(y \frac{d^2w(x)}{dx^2} \right)^2 dA dx \quad (38)$$

where A is the cross section area and l is length of the beam. Also, the surface energy is

$$U_{\text{Bulk}}(w) = \int_0^l \int_S \left[-\tau_0 y \frac{d^2 w(x)}{dx^2} + \frac{1}{2} C_0 y^2 \left(\frac{d^2 w(x)}{dx^2} \right)^2 + \frac{1}{2} C_1 \left(\frac{d^2 w(x)}{dx^2} \right)^2 \right] dS dx \quad (39)$$

where C_0 and C_1 are surface elastic modulus and Steigmann–Ogden constant, respectively, and S is the perimeter of the cross section. The potential energy of the external force is

$$U_q(w) = - \int_0^l q(x)w(x)dx. \quad (40)$$

Standard variational arguments require

$$\int_0^l \left[(EI + C_0 I^* + C_1 S^*) \left(\frac{d^2 w(x)}{dx^2} \frac{d^2 \delta w(x)}{dx^2} \right) - q(x) \delta w(x) \right] dx = 0 \quad (41)$$

where $I = \int_A y^2 dA$ is the moment of inertia of the beam cross section, $I^* = \int_S y^2 dS$ is the perimeter moment of inertia, and $S^* = \int_S n^2 dS$.

Using integration by part, the governing equation for bending of thin cantilever beam is obtained as

$$(EI + C_0 I^* + C_1 S^*) \frac{d^4 w(x)}{dx^4} - q(x) = 0 \quad (42)$$

Upon comparison with the classical Euler–Bernoulli beam equation with an “effective” elastic modulus, i.e.

$$E_{\text{eff}} I \frac{d^4 w(x)}{dx^4} - q(x) = 0. \quad (43)$$

We find the following:

$$\frac{E_{\text{eff}}}{E} = \frac{EI + C_0 I^* + C_1 S^*}{EI}. \quad (44)$$

In the case of a beam with square cross section of side a

$$I = \frac{a^4}{12}, \quad I^* = \frac{2a^3}{3}, \quad S^* = 2a \quad (45)$$

the effective elastic modulus is obtained as

$$\frac{E_{\text{eff}}}{E} = 1 + \frac{8C_0}{aE} + \frac{24C_1}{a^3 E} \quad (46)$$

It is worth pointing out that the asymmetrical term in the surface constitutive law and the dependence of elastic modulus on the residual stress should not be ignored in general (Mogilevskaya et al., 2008; Wang et al., 2010); however, it is justified in the present case for two reasons: (i) inclusion of that term makes no qualitative difference to our conclusions and (ii) while residual surface stress can be important for the stress-state, its impact on renormalized elastic modulus has been found to be small in recent works see for example (Liu et al., 2011).

We defer to Section 5 a discussion of the restriction on the values C_1 can take. We will simply state here that $\text{Sgn}(C_0) = \text{Sgn}(C_1)$. In other words, if surfaces tend to soften the material at the nanoscale (under tension); then under bending they will be even softer. The reverse is true as well: if the surfaces tend to stiffen the material under tension then under bending they will be stiffer. Following the similar analysis we also derive the renormalized effective elastic modulus of the wire under tension based on the Gurtin–Murdoch model

$$\frac{E_{\text{eff}}}{E} = 1 + \frac{2C_0}{aE} \quad (47)$$

Obviously, in computation of Eq. (47), the Steigmann–Ogden term does not enter. These expressions agree with prior work if C_1 is set to zero.

4. Atomistic calculations, computation of Steigmann–Ogden constants

We carried out the atomistic simulations of the nanowire using LAMMPS (Plimpton, 1995) molecular dynamics (MD) code. Embedded Atom Method (EAM) potential developed by Williams et al. (2006) was used for our simulations of Silver (Ag) nanowires. Molecular static simulations were performed on the nanowires with thickness ranging from 1.6 to 6 nm. We consider two configurations of the nanowire for our simulations. The first configuration corresponds to $\langle 100 \rangle$ axially oriented wire where the lateral surfaces are $[001]$ and $[010]$. The second configuration of the nanowire is chosen to be $\langle 110 \rangle$ axially and $[110]$ and $[001]$ along the lateral surfaces (Fig. 4).

Tension loading: We employed the method described by Diao et al. (2004) to determine the effective Young’s modulus of the wire under tension. The wire is non-periodic along the lateral surfaces but is periodic axially. The wire is initially

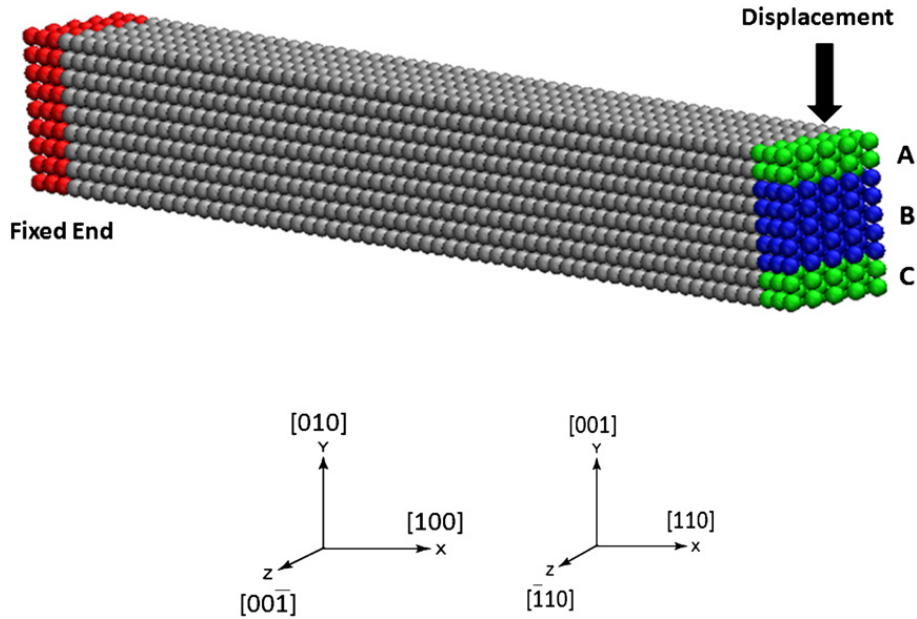


Fig. 4. Schematic representation of the orientations of nanowire. The bending experiment was performed with methodology given by McDowell et al. (2008).

relaxed using conjugate gradient method. The wire is then strained axially along X axis keeping Y and Z surface free. The wire is subjected to uniaxial loading at a given value of strain (0.2%). After application of the strain the wire is relaxed again using the conjugate gradient method. The change in the total potential energy of the system is attributed to the work done due to the force, which causes stretching

$$\Delta U = \int_0^{\Delta L} F d(\Delta L) = \int_0^{\epsilon} S \sigma L d\epsilon = \int_0^{\epsilon} V \sigma d\epsilon \quad (48)$$

where ΔU is the strain energy of the system, S is the cross section area of the wire after initial relaxation, F is the axial load applied which is balanced by the axial stress σ ($F=S\sigma$), $\epsilon=dL/L$ is the axial strain, and L and V are the length and volume of the nanowire, respectively. The silver nanowire is stretched to a total of 1.2% strain in X direction in 6 steps of 0.2%. The elastic modulus (Young's Modulus) is determined by the expansion of σ and V in (48)

$$\frac{\Delta U}{V_0} = E_{\text{eff}} \left[\frac{1}{2} \epsilon^2 + \frac{1}{3} \zeta \epsilon^3 \right] \quad (49)$$

where V_0 is the initial volume of the nanowire and ζ is a constant. E_{eff} is calculated by fitting strain energy data to applied strain data and determining the unknown constant.

Bending loading: Cantilever bending simulations were performed on the nanowire as described by McDowell et al. (2008). Non-periodic boundary conditions were imposed in all three directions of the nanowire and it is allowed to relax initially using conjugate gradient method. One end of the nanowire was fixed and the free end is given incremental downward displacement of 0.5 nm. The nanowire was relaxed twice after each displacement increment as described in the work of McDowell et al. (2008). Using classical beam theory and energetics from the molecular static simulations we determined the effective elastic modulus of the wire. The effective Young's modulus of the nanowire is given by the relation (Gere and Goodno, 2004)

$$\Delta U = \int_0^L \frac{E_{\text{eff}} I}{2} \left(\frac{\partial^2 v}{\partial x^2} \right)^2 dx \quad (50)$$

where L is the length, I is the moment of inertia and v is the beam deflection along the axial direction x . The curvature of the beam was determined from the profile of the beam after every strain increment as shown in (Fig. 5).

The deflection follows a cubic polynomial relation with axial position and therefore the curvature is a linear function. Fitting the strain energy data versus the curvature in Eq. (50) we determined the effective Young's modulus of the nanowire under bending.

Figs. 6 and 7 present our results. We observe stiffening effect for $\langle 110 \rangle$ axially oriented nanowire (Fig. 7) with decreasing width and the reverse for $\langle 100 \rangle$ axially oriented nanowire (Fig. 6). This could be attributed to larger number of atoms found in the similar dimension of wire as compared to $\langle 100 \rangle$ wire. Shenoy (2005) computed the effective elastic constants for the $[100]$ surface orientations and found the constants to be negative for Silver. Since the $\langle 100 \rangle$ axially oriented wire has four edges belonging to $[100]$ family of planes, the overall effect decreases the effective value

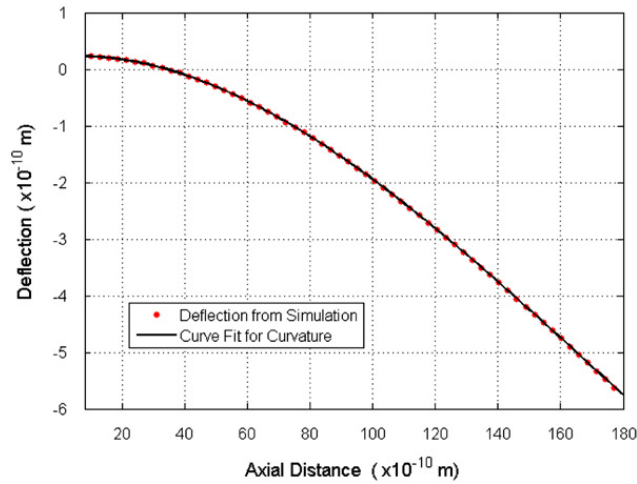


Fig. 5. Plot of deflection vs. axial distance to determine the curvature of bent beam.

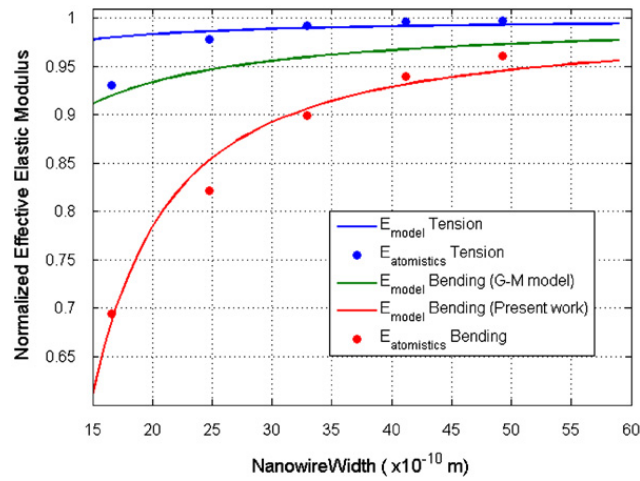


Fig. 6. Effective elastic modulus of $\langle 100 \rangle$ axially oriented nanowire.

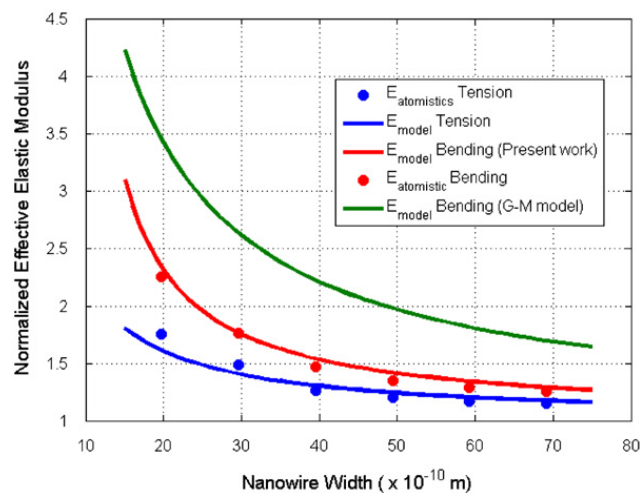


Fig. 7. Effective elastic modulus of $\langle 110 \rangle$ axially oriented nanowire.

thereby softening the wire. As already indicated in the Section 1 and evident in the work of Mcdowell et al. (2008), the elastic modulus is always (in absolute value) greater than under tension (regardless of whether it is a softening type of behavior or stiffening). Also evident is that the Gurtin–Murdoch theory is unable to explain these observations.

5. Discussion: asymmetry of elastic modulus under bending and tension, correction to Stoney's formula, and thickness of a crystalline surface

The renormalized effective elastic coefficient for the simulations was derived as

$$\frac{E_{\text{eff}}}{E} = 1 + \frac{8C_0}{aE} + \frac{24C_1}{a^3E}. \tag{51}$$

We used orthogonal least squares method to fit the atomistic simulation results to the theoretical model. The coefficients C_0 and C_1 were determined using the best curve fit obtained from least squares method. C_0 is determined from tension loading simulations alone (where by definition, the Steigmann–Ogden term is inactive). For Fig. 6 i.e. $\langle 100 \rangle$ axially oriented nanowire, the coefficients are: $C_0 = -0.37938 \text{ eV/\AA}^2$ and $C_1 = -42.3155 \text{ eV}$. For Fig. 7 i.e. $\langle 110 \rangle$ axially oriented nanowire, the coefficients are: $C_0 = 2.5227 \text{ eV/\AA}^2$ and $C_1 = 114.189 \text{ eV}$.

The key conclusion from our derivation of the effective elastic modulus of a bent beam is that the Steigmann–Ogden theory predicts a qualitatively different elastic modulus under bending than under tension. This is well-evident (at least qualitatively) in our atomistic calculations as well. Upon fitting the theoretical predictions to the atomistic calculations we can readily derive the constitutive parameter C_1 of the Steigmann–Ogden theory. It must be emphasized that the Gurtin–Murdoch theory cannot account for the difference.

Taking inspiration from shell-theory, we may now define the thickness of a surface as a ratio of the energy stored under bending to stretching:

$$t = \sqrt{\frac{C_1}{C_0}}. \tag{52}$$

This provides an unambiguous (and physically intuitive) means to define the thickness of a surface. For the two orientations we have analyzed, we obtain: $t_{\langle 100 \rangle} = 10.56$, and $t_{\langle 110 \rangle} = 6.73 \text{ \AA}$.

What is the importance of defining a surface thickness? The answer is rooted in history of surface energy theory. The Gurtin–Murdoch theory (and theories of capillarity in general) assumes a zero surface thickness. There is good reason for doing this dating back to Gibbs (1928). There is no clear physical way to decide where the surface terminates—in other words the choice of surface thickness is somewhat ambiguous and different researchers may justifiably choose slightly different thicknesses. The lack of flexural resistance in Gurtin–Murdoch theory indeed stems from the zero-thickness assumption. In principle, if conventional three-dimensional elasticity is used (with a finite thickness surface) then the need for the use of the (rather complex) Steigmann–Ogden theory is eliminated (in essence, the curvature-dependence of surface energy provides the flexural resistance and as per Eq. (52), a definition of surface thickness). However that requires an unambiguous determination of surface thickness for a crystalline surface—once this has been determined for a particular material (i.e. the Steigmann–Ogden constants), standard finite elements may be employed to assess effects of surface energy. We note that Park et al. (2006) have presented an all-numerical work on surface Cauchy–Born rule to handle surface effects in nanostructures. They use a finite thickness surface. In principle, if their choice of surface thickness is correct, their work incorporates the curvature-dependence correction.

It is also now clear why the elastic modulus under bending is always (in absolute value) greater than that under tension (i.e. stiffer or softer). Although a more rigorous thermodynamic argument is possible it is evident that given the physical interpretation in Eq. (52) C_1 must always be the same sign as C_0 .

We now turn to another possible application of the Steigmann–Ogden correction. Stoney's formula is frequently used to obtain the surface stress difference between two faces of a thin film or nanobeam. The surface stress difference may be caused due to adsorption or absorption on one face of the nanostructure. The difference in surface stress causes bending. The ensuing curvature is measured and related to the stress differential through the so-called Stoney's formula.

Considering only the first order terms in the definition of surface stress, we can simplify the surface stress on the upper and lower layer of a beam as

$$S_u = \tau_u + b_u \varepsilon_u, \quad S_l = \tau_l + b_l \varepsilon_l \tag{53}$$

In the above equation τ represents the residual surface stress in the upper layer with subscript u and lower surface layer with subscript l . b is the material constant associated with the surface strain ε for the respective surface layer $b_u = \lambda_{0u} + 2\mu_{0u}$, $b_l = \lambda_{0l} + 2\mu_{0l}$. Since the residual surface stresses on both the surfaces are different the beam undergoes axial as well as bending deformations. The strain induced in the beam due to these stresses can be written as

$$\varepsilon_0 = (z - h_n)/R \tag{54}$$

where h_n the height of neutral axis is from the lower surface and R is the radius of curvature.

Therefore the stress in the bulk is given by

$$\sigma_0 = E(z - h_n)/R \tag{55}$$

where E is the bulk modulus of elasticity. For the upper and lower surface layers the surface couple is given by

$$M_u = c_u(\text{tr}\kappa), \quad M_l = c_l(\text{tr}\kappa) \tag{56}$$

where κ , is the curvature of the cantilever and be expressed by the relation $\kappa = 1/R$, for pure bending assumption. Using the mechanical relations outlined in the earlier sections we write the equilibrium equations. First we balance the forces

$$\int_0^h \sigma_0(z) dz + \tau_u + b_u \varepsilon_u + \tau_l + b_l \varepsilon_l = 0. \quad (57)$$

which gives us

$$h_n = \frac{(R(\tau_u + \tau_l)/Eh) + (h/2) + (b_u/E)}{1 + ((b_u + b_l)/Eh)}. \quad (58)$$

Similarly balancing the moments about the lower surface we have

$$\int_0^h \sigma_0(z) z dz + h\tau_u + hb_u \varepsilon_u + (M_u + M_l) = 0. \quad (59)$$

This gives us

$$\frac{1}{R} = \frac{(\nabla\tau)h - 2(\tau_u b_l - b_u \tau_l)/E}{(Eh^3/6) + (h^2(b_u + b_l)/3) + ((2hb_u b_l)/E) + 2(c_u + c_l) + ((2(c_u + c_l)(b_u + b_l))/Eh)} \quad (60)$$

where $\nabla\tau = -(\tau_u - \tau_l)$.

The above equation can be rewritten as

$$\frac{1}{R} = \frac{6(\nabla\tau)}{Eh^2} + \frac{((12(\tau_u b_u - \tau_l b_l))/E) - ((72\nabla\tau b_u b_l)/E^2 h) - ((72\nabla\tau(c_u + c_l))/Eh^2) - ((72\nabla\tau(c_u + c_l)(b_u + b_l))/E^2 h^3)}{Eh^2(Eh^3 + 2h^2(b_u + b_l)) + ((12hb_u b_l)/E) + 12(c_u + c_l) + ((12(c_u + c_l)(b_u + b_l))/Eh)} \quad (61)$$

Alternatively

$$\frac{1}{R} = \frac{6(\nabla\tau)}{Eh^2} \left(1 + \frac{((2(\tau_u b_u - \tau_l b_l))/E\nabla\tau) - ((12b_u b_l)/E^2 h) - ((12(c_u + c_l))/Eh^2) - ((12(c_u + c_l)(b_u + b_l))/E^2 h^3)}{(Eh^3 + 2h^2(b_u + b_l)) + ((12hb_u b_l)/E) + 12(c_u + c_l) + ((12(c_u + c_l)(b_u + b_l))/Eh)} \right) \quad (62)$$

To make a clean comparison of Stoney's formula with and without Steigmann–Ogden correction, we ignore the strain dependent part of surface stress. We have already computed the values of the Steigmann–Ogden constant for two different surface orientations of a silver nanowire. Using an example of a 2 nm thick nanowire we find that

$$\frac{1}{R} = \frac{6(\nabla\tau)}{Eh^2} \left(1 - \frac{12(c_u + c_l)}{[Eh^3 + 12(c_u + c_l)]} \right) = \frac{6(\nabla\tau)}{Eh^2} (0.8279) \quad (63)$$

We see that the curvature of the nanowire changes by a value of 17.21% when we include the Steigmann–Ogden correction to the Stoney's formula.

6. Closing remarks

In this work, extending the claim made by [Steigmann and Ogden \(1999\)](#) we have highlighted the importance of the curvature-dependence of surface energy. In particular, this notion can readily explain the asymmetry in the renormalized elastic modulus of nanostructures under bending as compared to under tension. A simple connection to atomistics readily provides the evaluation of phenomenological constants that enter into the curvature-dependent surface energy theory providing an unambiguous definition of the so-called “thickness of a crystalline surface”. Several novel directions may be explored: impact of the “curvature-correction” on rough surfaces, Stoney's formula among others. We note again that nearly all work that has appeared on surface energy effects is predicated on the Gurtin–Murdoch theory. Indeed, for many such mechanics problems, Gurtin–Murdoch's theoretical framework should suffice. However, given our findings of the numerical values of the curvature-dependence of surface energy for some sample materials, problems that exhibit wrinkling, bending deformation modes in general or where unusually high curvature changes are expected should be revisited.

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