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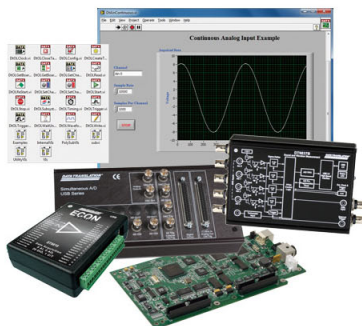
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Atomistic elucidation of the effect of surface roughness on curvature-dependent surface energy, surface stress, and elasticity

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It is well known that surface energy and the associated properties such as surface stress and surface elasticity have a significant effect on the physical behavior of nanostructures. In this letter, using a combination of atomistic simulations and a simple continuum model, we elucidate the role of surface roughness on the renormalization of surface stress, surface elastic constants, as well as the (generally ignored) term that represents the curvature dependence of surface energy (crystalline Tolman's length). We find, consistent with a recent theoretical prediction and in sharp contrast to few others, that the surface stress is negligibly impacted by roughness. However, even moderate roughness is seen to dramatically alter the surface elasticity modulus as well as the crystalline Tolman's length. We illustrate a simple application on the impact of roughness on nanosensors. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3695069>]

Surface effects, represented phenomenologically through “surface energy,” dramatically affect the physical properties and behavior of nanostructures. Some examples are elastic modulus,^{1–5} melting temperature,⁶ electromagnetic properties,^{7–9} self-assembly of nanostructures,¹⁰ defect nucleation,¹¹ among others. For more details, the reader is referred to review articles by Cammarata^{12,13} and references therein.

Surface energy effects are usually accounted for via the theoretical framework proposed by Gurtin and Murdoch.^{14,15} In their theory, surface is a zero-thickness deformable entity that is attached to the bulk and possesses a residual stress (the so-called “surface stress”) and surface elasticity (which is distinct from macroscopic bulk elasticity). In the original Gurtin-Murdoch theory, surface energy, as shown below, depends only on the surface strains. Let e_n be the outward unit normal to the surface, then we can define

$$I_s = \text{PIP}, \quad \text{P} = \text{I} - e_n \otimes e_n, \quad (1)$$

where P is the projection operator to the subspace orthogonal to e_n , I is the identity matrix, and I_s is the identity mapped to the tangential surface. So the Gurtin-Murdoch surface energy function is expressed as

$$\gamma = \gamma_0 + \tau_0 I_s \varepsilon_s + \frac{1}{2} C_0 \varepsilon_s^2. \quad (2)$$

Here, γ_0 is a constant unimportant to the objectives of the present work, $\varepsilon_s = \text{P}\varepsilon\text{P}$ is the surface strain that is the projection of the bulk strain ε on the tangential space to the surface, τ_0 is the residual surface stress, and C_0 is the surface elasticity modulus. It is worthwhile to note that a fair amount of literature (in some cases, justifiably) ignore surface elasticity (i.e., $C_0 = 0$). More recently, we have discussed a modified surface energy that, in addition to strain, also penalizes changes in curvature. This theory (based on the work of

Steigmann-Ogden^{16,17}) explained the observation that the effective elastic modulus of nanostructures under bending is significantly different than under stretching. This discrepancy between the elastic responses under bending vs stretching was a source of puzzlement since the conventional Gurtin-Murdoch theory predicts only a small difference between the two deformation modes. A simplified version of the curvature dependent surface energy can be written as

$$\gamma = \gamma_0 + \tau_0 I_s \varepsilon_s + \frac{1}{2} C_0 \varepsilon_s^2 + \frac{1}{2} C_1 \chi^2, \quad (3)$$

where χ is the curvature and C_1 is the Steigmann-Ogden material constant that penalizes surface energy upon changes in curvature. The details of the theory can be found in Steigmann-Ogden^{16,17} and Chhapadia *et al.*¹⁸ The constant C_1 can be also interpreted as Tolman's¹⁹ length for crystalline solids or alternatively can be used to assign a thickness for a surface ($t = \sqrt{C_1/C_0}$ can be argued to be related to the “definition” of surface thickness, see Chhapadia *et al.*¹⁸).

In this work, we address a simple question: What is the effect of roughness on the surface energy-related properties, e.g., τ_0 , C_0 , and C_1 ? Surfaces of real materials even for the most thoroughly polished ones will typically exhibit roughness. Alternatively, one may even consider intentionally nanostructuring the surface to design a tailored response. Recently, Weissmüller and Duan²⁰ theoretically predicted a large change in surface stress with roughness. In particular, they found a result that showed a switch in the sign of surface stress from positive to negative. Additionally, Ergincan *et al.*²¹ found that the cantilever curvature sensitivity decreases with increasing roughness. In contrast, our theoretical work²² appears to reach a different conclusion. Through a detailed theoretical calculation we concluded that the surface stress is hardly affected by surface roughness. In this paper, we carry out atomistic simulations of nano-cantilever beams of both flat and rough surfaces and assess the change in the surface stress τ_0 , the surface elastic constant C_0 , and Steigmann-Ogden material constant C_1 .

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We have chosen silver (Ag) nanowire as our model system and the calculations were (both tension and bending) performed using the LAMMPS (Ref. 23) molecular dynamics software. We simulate the interatomic interaction using embedded atom method (EAM) potential and the silver parameterization developed by Williams *et al.*²⁴

We consider two configurations. Both configurations are nanowires that are $\langle 100 \rangle$ axially oriented and have a square cross sectional area with side a and lateral nominal surfaces oriented in $[001]$ and $[010]$ directions. The first nanowire configuration is characterized by flat surfaces, while both the top and bottom surfaces of the second nanowire configuration are corrugated (Figure 1). The surface roughness is created such that it has zero mean value with the latter coinciding with the flat surface of the first configuration. The surface roughness profile has amplitude of 0.215 nm and wavelength of 1.636 nm and is kept the same while the thickness and width of the nanowires (a) are changed from 1.6 to 6 nm. Molecular static simulations are performed on the nanowire, and effective Young's elastic moduli of the nanowires are computed under both tension and bending.

The nanowires are initially created based on the silver atom configuration corresponding to a perfect face-centered cubic (FCC) bulk crystal. In order to consider the contribution of free surfaces, the boundary conditions in all directions are chosen to be non-periodic. The boundary conditions are selected as "shrink-wrapped"²³ which means that the position of the faces are not fixed and if an atom moves outside the face the position of the face is set so as to encompass the atoms in that dimension, no matter how far they move.

The nanowire geometry is then relaxed to a local minimum energy state at the absolute zero temperature using the conjugate gradient method. The atoms on or close to the surface change their equilibrium position during this process.

Tension loading: In order to determine the effective Young's modulus of the wire under tension, we followed the energy method proposed by Diao *et al.*³ One end of the nanowire is kept fixed, while the other end is strained axially up to 1.2%. The strain application is accomplished in six increments starting with zero and with an increment of 0.2%. Upon each incremental strain application, the free end is kept fixed and the nanowire is relaxed again. The change in the total potential energy of the system is equal to the work done due to the axial force that causes tensile strain,

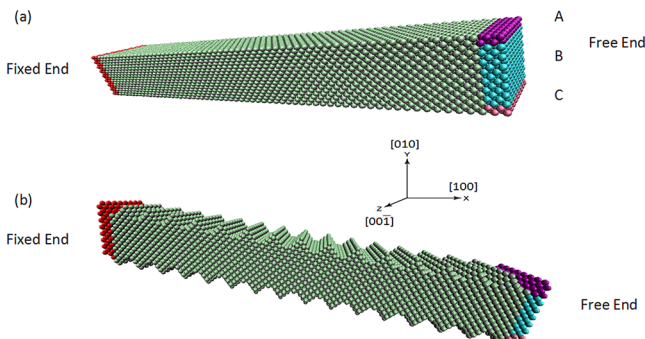


FIG. 1. (Color online) Schematic representation of the two nanowire configurations.

$$\Delta U = \int_0^{\Delta l} F d(\Delta l) = \int_0^{\epsilon} S \sigma l d\epsilon = \int_0^{\epsilon} V \sigma d\epsilon, \quad (4)$$

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. If σ and V be expanded in terms of strain ϵ , the change of total potential energy of the nanowire can be written in terms of elastic Young's modulus and strain³ as follows:

$$\frac{\Delta U}{V_0} = E \left[\frac{1}{2} \epsilon^2 + \frac{1}{3} \xi \epsilon^3 \right], \quad (5)$$

where V_0 is the initial volume of the nanowire, E is the Young's modulus before applying strain ($\epsilon = 0$), and ξ is a constant. From the atomistic simulations, we calculate the quantity $\frac{\Delta U}{V_0}$ at each loading step, which is then fitted as a cubic polynomial function of strain. Then the effective elastic modulus of the beam E_{eff} that includes the free surface effects is determined from the quadratic term coefficient.

Bending loading: Cantilever bending simulation method proposed by McDowell *et al.*²⁵ is performed on both nanowires with flat and rough surfaces. In our simulations, we consider a sufficiently long nanowire ($l/t > 8$) and keep the same aspect ratio with increasing nanowire thickness. Therefore, it is reasonable to ignore the shear forces created as a result of lateral deflection and only consider the bending moment effect. After initial relaxation, one end of the nanowire is held fixed and the free end is given an incremental downward displacement of 0.1 nm. The free end atoms are divided to three regions "A," "B," and "C" (Fig. 1). In each displacement increment, first, all the atoms in free end are displaced downward. Then atoms in region "A" are held fixed, and the nanowire is underwent energy minimization. Finally, the atoms in region "C" are held fixed and the nanowire is relaxed to the minimum energy state. This entire displacement–double relaxation cycle is repeated for a desired number of increments.

In continuum beam theory, for small deflections, the change in strain energy of a cantilever beam is obtained as²⁵

$$\Delta U = \int_0^l \frac{EI}{2} \left(\frac{\partial^2 \nu}{\partial x^2} \right)^2 dx, \quad (6)$$

where E is the Young's modulus, I is the moment of inertia, ν is the deflection as a function of x , and l is the length of the beam. In our simulation, for each bending increment, the deflection profile of the mid-plane that is a cubic polynomial of x is determined. Then change in strain energy and curvature data (which is the second derivative of deflection with respect to x) is fit to Eq. (6), and the effective Young's modulus E_{eff} is determined. The final Young's modulus is obtained as average of the values for the last three bending increments.

Figure 2 presents our results. As discussed in Chhapadia *et al.*,¹⁸ the elastic modulus in case of bending is less than (in absolute value) under tension. We observe that the wire with rough surface has a lower Young's modulus compared

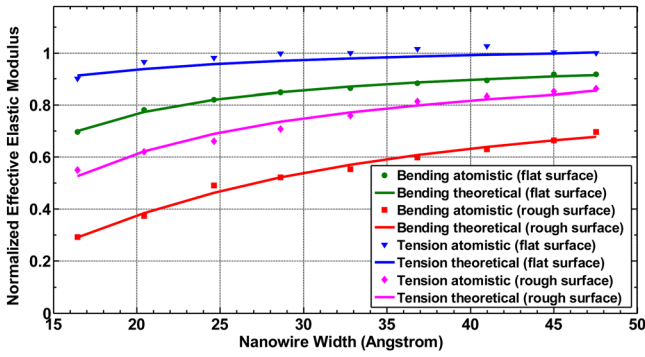


FIG. 2. (Color online) Normalized effective elastic modulus of nanowires with flat surface and rough surface.

to the wire with flat surface. Therefore, our simulation results prove that surface corrugation causes softening in the wire.

The continuum model that predicts the deviation of elastic property of a nanobar, E_{eff} , from that of conventional continuum mechanics, E , in tension can be expressed as²

$$\frac{E_{\text{eff}}}{E} = 1 + \frac{4C_0}{aE}, \quad (7)$$

where C_0 is the surface elastic constant proposed by Gurtin-Murdoch and a is the side of square cross section. In case of bending, this deviation is¹⁸

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

where C_1 is the Steigmann-Ogden material constant. Employing orthogonal least squares method, the coefficients C_0 and C_1 are determined by fitting the atomistic simulation data to the theoretical model (8). Moreover, surface stress τ_0 can be determined from the preliminary relaxation of the beam under the absence of external strain. Clearly,

$$4h\tau^0 + EA\varepsilon^* = 0, \quad (9)$$

where ε^* is the amount of compressive strain after initial relaxation and A is the cross section area of the beam. For wire with flat surface, the coefficients are obtained as $\tau^0 = 0.023096 \text{ eV/\AA}^2$, $C_0 = -0.168157 \text{ eV/\AA}^2$, and $C_1 = -3.181146 \text{ eV}$. Shenoy²⁶ also computed the elastic constants C_0 for the [100] surface orientations and found the constants to be negative for silver. For the wire with rough surfaces, these constants change to $(\tau^0)^{\text{eff}} = 0.01895$, $(C_0)^{\text{eff}} = -0.506521 \text{ eV/\AA}^2$, and $(C_1)^{\text{eff}} = 6.853007 \text{ eV}$. As is well-evident from the results, surface corrugation decreases the surface elastic constant C_0 by almost three times. Comparatively, as discussed earlier, there is only a modest change in the residual surface stress. This is in complete consistency with the theoretical results presented in our previous work.²² The theoretical expression predicts that

$$\begin{aligned} (\tau^0)^{\text{eff}} &= \tau^0 \left(1 - \frac{3}{4} \delta^2 \right), \\ (C_0)^{\text{eff}} &= C_0 - \delta^2 \frac{E}{k(1-\nu^2)} \frac{(9-8\nu)}{8(1-\nu)}, \end{aligned} \quad (10)$$

where k is the wave number, $\delta = \rho k$, ρ is the wave amplitude, and ν is the Poisson's ratio. This theoretical expression is

obtained with the key assumption of $\delta = \rho k \ll 1$. In other words, Eq. (10) is only approximately applicable to our case, nevertheless it is useful for making qualitative comparisons. Using a typical surface roughness of $\rho k = 0.2$, wave length of 10 nm and considering $\nu = 0.37$, $E = 50 \text{ GPa}$, $\tau^0 = 0.023096 \text{ eV/\AA}^2$, and $C_0 = -0.168157 \text{ eV/\AA}^2 = -2.69 \text{ N/m}$, we obtain the theoretical value of $(\tau^0)^{\text{eff}} = 0.02240 \text{ eV/\AA}^2$, $(C_0)^{\text{eff}} = -0.72177 \text{ eV/\AA}^2 = -11.5628 \text{ N/m}$. So the value of surface stress decreases by 3%. Also, the value of surface elastic constant decreases by more than four times in the presence of surface roughness—qualitatively consistent with the dramatic decrease observed in our simulations. In addition, it is observed that the roughness causes a large shift in the value of C_1 as well as a change in the sign.

What are the ramifications of rough surfaces in technological applications? Micro and nano-fabricated cantilevers are frequently used as highly sensitive chemical, biological, and mechanical sensors. One of the sensing mechanisms is to detect a shift in the resonant frequency subject to a stimuli. Lu *et al.*²⁷ have derived that the change in fundamental resonance frequency due to surface stress $\Delta\omega_{\text{stress}}$ in general can be expressed as

$$\frac{\omega_{\text{stress}}^2 - \omega_0^2}{\omega_0^2} = \frac{E_{\text{eff}} - E}{E}, \quad (11)$$

where ω_0 is the fundamental resonance frequency in absence of surface stress and ω_{stress} is the new resonance frequency with surface stress.

Since the surface roughness affects the effective elastic modulus of nanostructures (as we have already seen), we therefore expect a shift in the resonance frequency also. Chhapadia *et al.*¹⁸ for a 2 nm thick <100> axially oriented cantilever with flat lateral surfaces predicted that term in Eq. (11) is -0.22 . Considering a similar beam but with roughened surfaces identical to what we modeled in our atomistic simulations, the term in Eq. (11) becomes -0.61 . This simple example clearly indicates the enormous role roughness can play in the interpretation of sensing data.

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