Size-dependent elasticity of nanowires: Nonlinear effects

Haiyi Liang and Moneesh Upmanyu

Simulation and Theory of Atomic-scale Material Phenomena, Materials Science Program, Engineering Division,
Colorado School of Mines, Golden, Colorado 80401, USA

Hanchen Huang

Department of Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

We employ a molecular statics approach based on embedded-atom-method interatomic potentials to study the elasticity of copper nanowires along [001], [110], and [111] crystallographic directions. Self-consistent comparison with the bulk response clearly shows that the overall nanowire elasticity is primarily due to nonlinear response of the nanowire core. While the surface-stress-induced surface elasticity modifies the behavior for ultrathin nanowires, their contribution is always considerably smaller than that due to nonlinear elasticity of the nanowire core. More importantly, for all three orientations, the surface is softer than an equivalently strained bulk, and the overall nanowire softening or stiffening is determined by orientation-dependent core elasticity.

I. INTRODUCTION

Decreasing characteristic dimensions of materials often leads to qualitatively different behavior. Such size effects gain relevance in several classes of emerging nanoelectromechanical systems (NEMS), where the mechanical properties of the structural members need to be well characterized in order to control their functionality.[1–3] Several studies have demonstrated that size effects are especially important for elastic properties of nanoscale thin films[4,5] and metallic nanowires.[6,7] Since the surface area to bulk ratio is quite significant in such systems, the surface stress is implicated in most size effects.[8,9] For example, molecular dynamics (MD) simulations using embedded-atom-method (EAM) interatomic potentials have shown that nanowires and nanoplates of tungsten oriented along the [111] direction are softer compared to the bulk.[10] These size effects have also been reported in free-standing metal thin films. MD simulations of EAM copper thin films have shown that the film softens along the ⟨001⟩ direction and stiffens along the ⟨110⟩ direction.[6,11] Similar trends have also been observed in MD simulations of Al thin films.[12]

In this paper, we focus on the size-dependent elasticity of copper nanowires. Various theories have been put forth to explain the opposing trends in size effects. Almost all continuum analyses have been restricted to isotropic, linear elasticity.[12] These approaches assume a surface modulus distinct from the bulk, and then develop the overall response by considering the surface as a separate layer with a predetermined thickness. Size-dependent surface modulus is then considered to be the dominant effect that determines the elasticity of nanowires.[4,12–14] *Ab initio* calculations report a correlation between redistribution of electron density across the surface layers and the elasticity of the nanowires. Specifically, the form of the orientation-dependent electronic redistribution can result in a soft or hard surfaces.[6] Recently, Villain *et al.* have shown that the size effects can induce atomic

decohesion on the surface, and the resultant surface stresses modify the equilibrium lattice parameter on the surfaces.[10] In some cases, the surface stresses can be large enough to even initiate phase transformations.[7]

Since the surface stresses are quite large at the nanoscale, nonlinear modifications to elasticity of nanowires cannot be ignored. In fact, it is well known that for free-standing nanoscopic structures, surface stress alone will induce prominent compressive strains at the surface which are well beyond the linear elastic regime.[7,10,15,16]

In this computational study, we focus on quantifying the contribution of nonlinear elastic effects on overall elastic response of nanowires. We employ molecular statics simulations to investigate the size effect on the Young's modulus of copper nanowires, and also extract the relative contributions of surface and nanowire "core" elasticity. Below, we first describe the methodology and computational cell geometries used to simulate the orientation-dependent elasticity of nanowires, as well as the orientation-dependent bulk response. Comparisons between the nanowire and bulk elasticity are presented to facilitate determination of the relative contributions of surface and nanowire core (bulk) elasticity, and then the main conclusions are summarized.

II. SIMULATION METHOD

We have performed molecular static simulations for square cross-section nanowires with side lengths ranging from 1.2 to 14.0 nm. The side length is defined as the averaged width along Y and Z axes after relaxation. Three orientations are simulated (see Fig. 1) [001], [110], and [111] nanowires. The lateral surfaces associated with all three nanowires are shown in Fig. 1. Periodic boundary conditions are applied along the X axis, and the lateral surfaces are free. The EAM copper interaction potential developed by Mishin *et al.* is employed in all simulations.[17] The potential reproduces several important properties of Cu, including cohesive
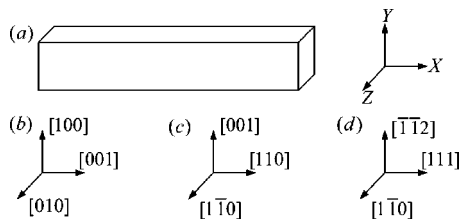
FIG. 1. Schematic illustrating the simulation cell used to study the elasticity of nanowires. The X axis is the strained direction and is subject to periodic boundary conditions. Surface normal to Y and Z directions are traction free. (b)-(d) indicate the orientations of the lateral surfaces associated with the simulated [001], [110], and [111] nanowires.

energy, elastic constants, formation energy of point defects, stacking fault energy, unstable stacking fault energy, and (most importantly) surface energy.

The entire simulation cell is initially relaxed using the conjugate gradient method. Thus, the nanowire is allowed to explore surface configurations which minimize its energy locally. Our choice of nanowire lateral surfaces ensures that the nanowire is bounded by low-index planes, such that the assumed lateral surfaces are not drastically different from those corresponding to the global minimum surface configuration. Nevertheless, it must be noted that the global minimum lateral surface configuration cannot be determined using such a simplistic energy minimization technique. However, this is not the focus of the study, and furthermore, we do not expect the inaccuracies in the surface stresses to drastically affect the balance between surface stress and nanowire core elasticity.

The nanowire is strained along the X axis in the range -5.0% to 1.0% and incremented at $\pm 0.05\%$. The conjugate gradient method is again employed to determine the energy minimum following each strain step. The Young's modulus is evaluated as $Y = 1/V\, d^2U/d\epsilon^2$, where U is the total system (interaction) energy, ϵ is the strain, and V is the instantaneous volume of nanowire. Note that the reported equilibrium strain is determined with respect to the equilibrium length of nanowire at the local energy minimum. The volume of the nanowire is also determined at this minimum—the length is well-defined, while the cross-sectional area is based on distances between the outermost parallel layers.

III. RESULTS AND DISCUSSION

Figure 2 shows the compressive strain as a function of nanowire thickness for each of the three nanowires. The strain increases rapidly at small thicknesses, indicating the presence of a (tensile) surface stress. The behavior is quite similar for the [110] and [111] nanowires, while the increase in strain is particularly dramatic for the [001] nanowires. The fact that the nanowire surfaces are intrinsically strained is also apparent from the inset of Fig. 3, a plot of the minimum strain energy versus thickness of [001] nanowires. Evidently, thinner nanowires have a larger equilibrium compressive strain at their local energy minimum, while the bulk is unstrained due to the absence of a surface (for the simulation
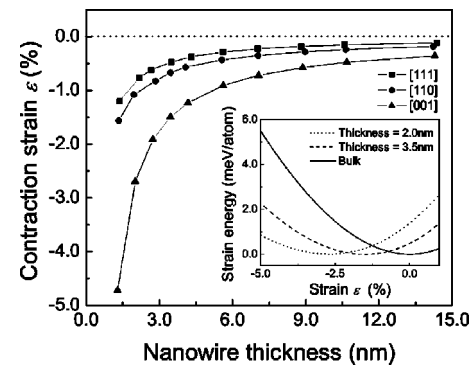

FIG. 2. The simulated equilibrium compressive strain ϵ as a function of nanowire thickness. (Inset) Strain energy per atom vs strain for [001] nanowires and the corresponding bulk.

scheme employed for the bulk simulations, see below). This trend is also observed in [110] and [111] nanowires (not shown).

In order to ascertain if the resultant compressive strains are within the linear elastic regime for bulk copper, we self-consistently extract the stress-strain curves for bulk copper by eliminating the surfaces associated with the nanowires. A uniaxial strain is applied along the X axis, while keeping the lateral directions periodic and stress free. The molecular static simulations are performed at constant pressure via concomitant changes in computation cell volume. In this manner, we eliminate the surface elasticity contributions and simulate the stress-strain response of bulk copper. Evidently, the stress-strain response quickly becomes non-Hookean for strains in excess of -1%, and the Young's modulus for each of the three nanowire orientations is now a function of strain. The leading-order strain dependence can be expressed as $Y(\epsilon) = Y_o + (dY/d\epsilon)\epsilon$, where Y_o and $dY/d\epsilon$ are constants. Performing quadratic fits to the stress-strain curves for strains $\epsilon \gtrsim -5\%$, we get

$$[001] \rightarrow Y_o = 67.1\ \mathrm{Nm}^{-2}, \quad \frac{dY}{d\epsilon} = 278.8\ \mathrm{Nm}^{-2}$$

$$[110] \rightarrow Y_o = 130.1\ \mathrm{Nm}^{-2}, \quad \frac{dY}{d\epsilon} = -1286.8\ \mathrm{Nm}^{-2}$$

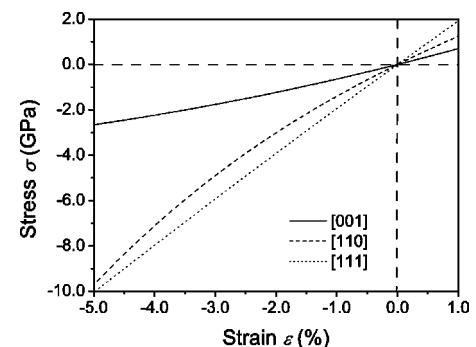FIG. 3. Stress-strain response of bulk copper for uniaxial strains applied along [001], [110], and [111] orientations.
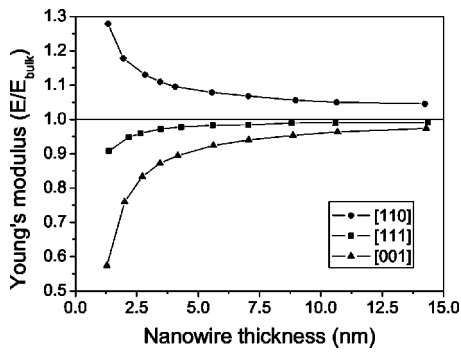
FIG. 4. Thickness dependence of Young's moduli for [001], [110], and [111] nanowires.

$$[111] \rightarrow Y_o = 193.5 \text{ Nm}^{-2}, \quad \frac{dY}{d\epsilon} = -113.5 \text{ Nm}^{-2}.$$

Thus, the Young's modulus along the [001] orientation decreases with compressive strain, while the opposite is true for the [110] and [111] orientations. It must be emphasized that this bulk response is in agreement with previous *ab initio* calculations on strained bulk copper,[18] and also the bulk response extracted using EAM potentials of a different variety.[19] In particular, the onset of the nonlinearities occurs roughly at the same threshold strain values as in our results.

Having extracted the bulk response, we are now in a position to determine the relative contributions of surface stress and core elasticity on the overall elastic response of the nanowire. In order to ascertain the dominant effect, we first extract nanowire Young's moduli, at equilibrium contraction of the nanowires and along each of the three orientations, and then compare these values with those of the bulk strained along the corresponding orientation. Nanowire thickness (and therefore equilibrium compressive strain) dependence of the normalized Young's moduli E/E_b is shown in Fig. 4. Both [001] and [111] nanowires exhibit softening, while the [110] nanowire stiffens. This is consistent with the prior simulations on copper thin films[11] and nanowires.[6] More importantly, the variations of nanowire Young's moduli with thickness (and therefore compressive strain) are quite similar to the strain-dependent bulk response extracted in the nonlinear elastic regime (Fig. 3). This is strongly suggestive of the fact that the compressive strain associated with the nanowires is mostly due to the nonlinear elastic deformation of the nanowire core.

The extent of core nonlinear elasticity contribution to overall nanowire elasticity can be further quantified by considering the *in toto* elastic response to be a superposition of surface and core contributions. Their relative contribution is now simply a function of the surface area to volume ratio of the nanowire. Due to the surface stress, elasticity of the atoms lying on the outmost layers is modified compared to that of the nanowire core.[7,16] For the sake of simplicity, we can assume that the atoms in the outmost layer constitute the surface atoms, and the remaining atoms form the nanowire core. Then, core elasticity should exert a decisive influence on thicker nanowires, as the surface to volume ratios are relatively smaller and the effects of surface stresses are neg-
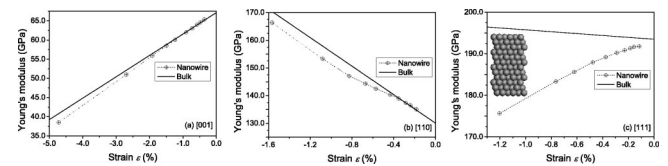

FIG. 5. Strain dependence of the bulk and nanowire Young's moduli for (a) [001], (b) [110], and (c) [111] orientations. [Inset in (c)] Longitudinal view of the [111] nanowire showing the stepped nature of the nanowire surface.

ligible. For example, for ~ 14 nm thick nanotubes, surface layer atoms constitute 4.9%, 4.2%, and 4.8% of [001], [110], and [111] nanowires, respectively. If the nonlinear core elastic effects are generally negligible, then we expect that these thicker nanowires should recover the bulk Young's moduli. Clearly, that is not the case, as shown in Fig. 4. The nanowire Young's moduli are quite different from their bulk counterparts. More importantly, surface stress effects, which now account for a mere 5% deviation from the bulk moduli, cannot account for the difference between the bulk and nanowire Young's moduli. Our results unambiguously show that the nonlinear elasticity of the core region has a dominant effect on the Young's moduli and overall nanowire elasticity.

This conclusion is further supported by plots of the strain dependence of Young's moduli of both nanowire and the bulk, for each of the three nanowire orientations [Figs. 5(a)–5(c)]. At large nanowire thicknesses or small strains, the agreement between Young's moduli of the [001] and [110] nanowires and the correspondingly strained bulk is quite good. In both cases, the agreement extends to thinner nanowires, well past the linear elastic regime associated with the bulk response. For thin nanowires, the difference between the nanowire and bulk Young's moduli are evident. Here, the surface area to volume ratios are considerably larger -43.8%, 37.5%, and 44.4% for [001], [110], and [111] nanowires, respectively. Evidently, the deviations are due to the increasing effect of surface elasticity. However, this contribution is still considerably smaller than that due to the nonlinear elasticity of the nanowire core. Interestingly, the Young's modulus of [111] nanowires decreases with compressive strain and the reverse trend is observed in the bulk [Fig. 5(c)]. The bulk stiffens slightly, a 3.5% increase in the Young's modulus until a strain of -1.2%. On the other hand, the nanowire softens substantially. Admittedly, the softening is perhaps artificially exaggerated as the lateral surfaces associated with this nanowire orientation are stepped (inset of Fig. 5). The overestimate in the nanowire volume is proportional to the step height and results in enhanced softening at small thicknesses.

IV. DISCUSSION AND CONCLUSIONS

For all three nanowire orientations, the nanowire Young's modulus is smaller than that of bulk copper strained to an equivalent compressive strain. Thus, *the nanowire surface is always softer than the (equivalent) bulk*. The decohesion of the surface atoms is due to decrease in their coordination, and the extent of surface softening depends on strain-induced

surface rearrangments. For the [110] nanowires, the nearest-neighbor atoms align along the X axis, on the $(0\bar{1}0)$ and (001) directions. In [001] nanowires, the nearest neighbors align at 45° angles on the (100) and (010) planes. The [111] nanowire scenario is qualitatively different—the atom interactions on the $(1\bar{1}0)$ surface are inherently suppressed, and the spacing between $(1\bar{1}0)$ surface atoms along the strain axis (X direction) is greater than the EAM potential cutoff—their interactions are negligible.

In summary, the surface elasticity effects for [001] and [110] copper nanowires result in moderate deviations from the bulk behavior, and their effects are negligible for the [111] nanowires. Comparing the orientation-dependent elastic response of the copper nanowires with that of bulk copper, we conclude that it is the nonlinear elasticity within the nanowire cores that has a dominant effect on the size-dependent softening or stiffening of nanowires. The implications of these conclusions are quite broad in that they are not just limited to copper nanowires. In material systems with large surface stresses, the size-dependent elasticity of their nanowires will be profoundly affected by the bulk (and in all probability, nonlinear) elasticity. Therefore, a fundamental understanding of the nonlinear bulk response of these material systems is critical for predicting the mechanical properties of ultrathin, crystalline (metallic, ceramic) nanowires.

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