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Molecular statics simulations of buckling and yielding of gold nanowires deformed in axial compression

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Abstract

We use molecular statics simulations with the embedded atom method potential to delineate yielding (material instability) and buckling (structural instability) in gold nanowires deformed axially in compression. It is found that both local (stacking faults) and global instabilities occur when the gold nanowire yields but only global instabilities occur when the nanowire buckles. Furthermore strong surface effects reorient the lattice structure which significantly increases Young's modulus in the axial direction and cause a nanowire of relatively small slenderness ratio (e.g., 14) to buckle. Upon complete unloading of the nanowires, the average axial stress and the total potential energy revert to their values in the reference configuration for the nanowires that buckled but not for the one that yielded. © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Buckling; Yielding; Gold FCC lattice; Surface effects; Inhomogeneity

1. Introduction

Gold (Au) nanowires have been experimentally produced by contact of a metal surface with a scanning tunneling microscope [1,2] and also from thin films [3,4]. They have potential applications in nanotechnology due to their capacity for biomolecule functionalization [5,6], high conductivity [7] and distinct optical properties [8]. However, nanowires have a large (surface area)/volume ratio as compared to bulk materials and their structural properties can be quite different from those of bulk materials. For example, Gall et al. [9] have observed that for an Au nanowire the magnitude of the tensile yield stress is much larger than that of the compressive yield stress. Furthermore, for a $\langle 1 0 0 \rangle$ initial crystal orientation and cross-sectional area less than 4 nm², surface stresses alone cause Au nanowires to transform from a face-centered-cubic (FCC) structure to a body-centered-tetragonal (BCT) structure [10]. It has also been experimentally found that the free surface energy could increase the apparent in-plane bi-axial modulus of a metal film [11].

Besides surface effects, one should also consider defect nucleation when investigating an atomic system. Continuum level concepts and instability criteria have been extended to the nanoscale level to identify or to predict the onset of instability in an atomic system. An instability criterion in continuum mechanics (see, e.g., [12]) is expressed as a strong ellipticity condition which ensures the uniqueness of the solution of equations governing static deformations of a homogeneous elastic body. The loss of strong ellipticity indicates that an acceleration wave [13] cannot propagate or a local bifurcation [14] becomes admissible in a homogeneous deformation field. Several approaches have been suggested to extend the continuum-scale criterion to the nanoscale (e.g., see [15-23]). Kitamura et al. [17,18] postulated that an atomic system becomes globally unstable when the minimum eigenvalue of the Hessian of its potential energy vanishes. Instabilities in an atomic system have also been studied by the normal mode analysis [19] which exploits symmetries of the system to reduce the number of degrees of freedom. For a system having no spatial symmetries, the normal mode analysis is

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equivalent to the method used in [17,18]. To reduce the computational cost, some researchers have proposed local instability criteria. For example, van Vliet et al. [16] developed the Λ criterion based on Hill's [13] theory, and Lu and Zhang [22] the equivalent mono-mode convexity condition. These researchers investigated the positive-definiteness of the atomistic counterpart of the continuum acoustic tensor. Recently, Miller and Rodney [21], Delph et al. [20], Pacheco and Batra [33] and Batra and Pacheco [38] used a criterion based on the non-positive value of an eigenvalue of the Hessian of a group of atoms surrounding the atom whose instability is being studied.

Here we use molecular statics (MS) simulations with the embedded atom method (EAM) potential to study deformations of an Au nanowire deformed in axial compression. In Section 2, we briefly describe the EAM potential and how numerical simulations are conducted. We discuss the two types of instabilities in Section 3 by analyzing the loading and the unloading curves, geometric indicators related to atom positions and local instability criteria. The role of surface effects in the compression of Au nanowires is discussed in Section 4, and conclusions of the work are summarized in Section 5.

2. Molecular statics (MS) simulations

We use the freely available open-source code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [24,25] to conduct MS simulations of Au nanowire



Fig. 1. (a) Perfect lattice, and (b) the relaxed configurations of a 20.4 Å × 408 Å × 20.4 Å Au lattice. (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

deformed in axial compression. As shown in Fig. 1, an Au nanowire with dimensions $h \times l \times h$ is compressed along the x_2 -axis, where the x_1 -, the x_2 - and the x_3 -axis are aligned along the [0 0 1], [0 1 0] and [0 0 1] directions of an FCC lattice, respectively. We start numerical simulations by assigning the initial position of each atom in the system in a perfect lattice configuration (cf. Fig. 1a) and then minimize the potential energy of the system by the Polak-Ribiere conjugate gradient method. The minimization involves an outer iteration loop that sets the search direction along which coordinates change. It is followed by an inner iteration using a line search algorithm evaluating forces and energies several times to set new coordinates. We set the maximum number of outer iterations and the maximum number of force/ energy evaluations to be very large so that the relaxation process will cease only when the change in the energy between two successive outer iterations is less than $1.0e^{-16} \text{ eV/Å}$. Fig. 1b depicts the relaxed configuration of the system with the starting perfect lattice shown in Fig. 1a. Differences between the two configurations can be observed when the surface area to volume ratio of the system is large, e.g., 0.20 Å⁻¹ for the 20.4 Å \times 408 Å \times 20.4 Å Au nanowire shown in Fig. 1. In order to compute strains we take the relaxed configuration as the reference configuration.

We compress the Au nanowire by fixing atoms on the bottom layer of the lattice and axially moving downwards atoms on the top surface. After each 0.1 Å increment in the prescribed axial displacement the potential energy of the system is minimized to obtain an equilibrium configuration of nanowire. Shrink-wrapped boundary conditions are used in all three directions, i.e., no atoms are allowed to enter the atomic system from the opposite side. Interactions among Au atoms are modeled by the EAM potential [26,27]. The EAM assumes that the density of the electron gas can be approximated by the sum of electron densities from surrounding atoms, and adds a repulsive term to account for the core-core interactions. The total binding energy of a collection of atoms is given by the sum of energies for each atom. That is,

$$\Phi = \sum_{\alpha} E^{\alpha},\tag{1}$$

$$E^{\alpha} = \frac{1}{2} \sum_{\beta} \phi(r^{\alpha\beta}) + F'\left(\sum_{\beta} \rho'(r^{\alpha\beta})\right).$$
⁽²⁾

The function $\phi(r^{\alpha\beta})$ represents the core–core repulsion, F' is the embedding function, and $\rho'(r^{\alpha\beta})$ is the contribution to the electron density at the site of atom α from atom β . Here and below, Greek superscripts refer to atom number, Latin subscripts to components of a tensor with respect to a rectangular Cartesian coordinate system, and summations only on Latin repeated indices are implied.

3. Analysis of buckling and yielding

We perform MS simulations on the following three Au nanowires:

Nanowire1:20.4 Å × 408 Å × 20.4 Å(l/h = 20),containing12,161 atoms.Nanowire2:40.8 Å × 816 Å × 40.8 Å(l/h = 20),containing88,421 atoms.Nanowire3:40.8 Å × 2040 Å × 40.8 Å(l/h = 50),containing220,721 atoms.

As discussed below, we found that nanowires 1 and 3 buckled but nanowire 2 yielded. In this section, we study details of these two instabilities by comparing deformations of the specimens during loading and unloading, and changes in the lattice geometry. Effects of surface stresses in nanowire 1 will be discussed in Section 4.

3.1. Loading and unloading of nanowires

3.1.1. Definition of atomic stress and strain

A commonly used definition of stress tensor in atomistic studies is the virial stress that is based on a generalization of the virial theorem of Clausius [28] for gas pressure. It has two parts; one part is associated with the motion of atoms across a fixed spatial surface through a point and postulates that this motion of atoms 'exerts' forces on the surface. The other part of the virial stress arises from interatomic forces. Considering these two effects Lutsko [29] has derived an expression similar to the virial stress by applying the continuum equation of the balance of linear momentum to an atomic system, and averaging computed stresses over the volume of the continuum region perceived to equal the region occupied by the atomic system. Some investigators do not agree with contributions from the kinetic terms to Lutsko's definition of the stress tensor (e.g., see [30-32]). However, kinetic terms do not appear in MS simulations in which the temperature of all atoms is assumed to be steady and equal 0 K, and atoms are assumed to move rather slowly so as not to affect their temperatures. Therefore, the average Cauchy stress $\bar{\sigma}$ in a region of volume Ω can be written as:

$$\bar{\boldsymbol{\sigma}} = \frac{1}{2} \sum_{\alpha} \frac{J^{\alpha} \Omega^{\alpha}}{\Omega^{*}} \left[\sum_{\beta \neq \alpha} \frac{\partial \phi(r^{\alpha\beta})}{\partial r^{\alpha\beta}} \frac{\mathbf{r}^{\alpha\beta} \otimes \mathbf{r}^{\alpha\beta}}{r^{\alpha\beta}} \right], \tag{3}$$

where $\Omega^* = \sum_{\alpha} J^{\alpha} \Omega^{\alpha}$ is the volume of the atomic system after deformation, $J^{\alpha} = \det \mathbf{F}^{\alpha}$, Ω^{α} equals the volume associated with atom α in the reference configuration, $\phi(r^{\alpha\beta})$ is the energy of the atomic system, \otimes denotes the tensor product between two vectors, and the deformation gradient \mathbf{F}^{α} at the position of atom α can be found from positions of atoms in the current and the reference configurations either by the least squares interpolation or by using the modified smooth particle hydrodynamics (MSPH) method (e.g., see [33,39]). In Eq. (7) $\mathbf{r}^{\alpha\beta} = \mathbf{r}^{\beta} - \mathbf{r}^{\alpha}$ gives the relative position of atom β with respect to that of atom α , and for radially symmetric potentials such as pairwise potentials found by the EAM with the potential energy of a system of atoms depending only on the interatomic distance, the interatomic force $\mathbf{f}^{\alpha\beta}$ exerted on atom α by atom β is assumed to be given by

$$\mathbf{f}^{\alpha\beta} = \frac{\partial \phi(r^{\alpha\beta})}{\partial \mathbf{r}^{\alpha\beta}} = \frac{\partial \phi(r^{\alpha\beta})}{\partial r^{\alpha\beta}} \frac{\mathbf{r}^{\alpha\beta}}{r^{\alpha\beta}}.$$
 (4)

Thus in MS simulations, the local Cauchy stress σ^{α} in the equivalent continuum structure at the point that corresponds to atom α can be written as:

$$\boldsymbol{\sigma}^{\alpha} = \frac{1}{2\Omega^{\alpha}} \sum_{\beta(\neq\alpha)} \mathbf{r}^{\alpha\beta} \otimes \mathbf{f}^{\alpha\beta}.$$
 (5)

We use the Cauchy–Born rule to define the deformation gradient F^{α} through the relation

$$\mathbf{r}^{\alpha\beta} = \mathbf{F}^{\alpha}\mathbf{R}^{\alpha\beta},\tag{6}$$

where atom β is adjacent to atom α , and $\mathbf{R}^{\alpha\beta} = \mathbf{R}^{\beta} - \mathbf{R}^{\alpha}$ is the vector between atoms α and β in the reference configuration. The method of least squares is used to find \mathbf{F}^{α} , i.e., we minimize the function Θ defined by

$$\Theta = \sum_{\beta} \left| \mathbf{r}^{\alpha\beta} - \mathbf{F}^{\alpha} \mathbf{R}^{\alpha\beta} \right|^{2}$$
$$= \sum_{i=1}^{3} \sum_{\beta} \left(r_{i}^{\alpha\beta} - F_{ik}^{\alpha} R_{k}^{\alpha\beta} \right)^{2}, \quad i, j, k = 1, 2, 3.$$
(7)

We set

$$\frac{\partial \Theta}{\partial F_{ij}^{\alpha}} = \sum_{\beta} 2 \left(r_i^{\alpha\beta} - F_{ik}^{\alpha} R_k^{\alpha\beta} \right) R_j^{\alpha\beta} = 0, \tag{8}$$

to obtain a system of nine simultaneous equations whose solution is

$$F^{\alpha}_{ij} = \frac{\Delta^{\alpha}_{ij}}{\Delta^{\alpha}},\tag{9}$$

where

$$\Delta^{\alpha} = \begin{vmatrix}
\sum_{\beta} R_{1}^{\alpha\beta} R_{1}^{\alpha\beta} & \sum_{\beta} R_{1}^{\alpha\beta} R_{2}^{\alpha\beta} & \sum_{\beta} R_{1}^{\alpha\beta} R_{3}^{\alpha\beta} \\
\sum_{\beta} R_{2}^{\alpha\beta} R_{1}^{\alpha\beta} & \sum_{\beta} R_{2}^{\alpha\beta} R_{2}^{\alpha\beta} & \sum_{\beta} R_{2}^{\alpha\beta} R_{3}^{\alpha\beta} \\
\sum_{\beta} R_{3}^{\alpha\beta} R_{1}^{\alpha\beta} & \sum_{\beta} R_{3}^{\alpha\beta} R_{2}^{\alpha\beta} & \sum_{\beta} R_{3}^{\alpha\beta} R_{3}^{\alpha\beta}
\end{vmatrix},$$
(10)

and Δ_{ij}^{α} is calculated by replacing the *j*th column of Δ^{α} with the vector $\left[\sum_{\beta} r_i^{\alpha\beta} R_1^{\alpha\beta} - \sum_{\beta} r_i^{\alpha\beta} R_2^{\alpha\beta} - \sum_{\beta} r_i^{\alpha\beta} R_3^{\alpha\beta}\right]^T$.

With \mathbf{F}^{α} and $\boldsymbol{\sigma}^{\alpha}$ known we can compute other stress and strain tensors by using continuum mechanics relations amongst them.

3.1.2. Loading and unloading curves

In Fig. 2, we have plotted the average axial stress $\bar{\sigma}_{22}$ vs. the average axial strain $\bar{\epsilon} = (l - l_0)/l_0$ for the three nanowires deformed in axial compression; l and l_0 equal, respectively, lengths of a nanowire in the present and the references configurations. In these and other Figures, the compressive axial stress and the compressive axial strain are taken as positive. Initially, the average axial stress



Fig. 2. Average axial stress vs. average axial strain for axial compression of the three Au nanowires. These plots show that instabilities ensue at the average axial strains of 0.022, 0.027 and 0.010, respectively, for nanowires with dimensions 20.4 Å × 408 Å × 20.4 Å (nanowire 1), 40.8 Å × 816 Å × 40.8 Å (nanowire 2), and 40.8 Å × 2040 Å × 40.8 Å (nanowire 3) after monotonic increases of average axial stresses with average axial strain during the initial stage. (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

monotonically increases with an increase in the average axial strain but the average axial stress abruptly decreases when the average axial strain reaches 0.022, 0.027 and 0.010, respectively, for nanowires 1, 2 and 3. This sudden drop in the axial stress indicates the occurrence of instabilities in atomic systems. Figs. 3 and 4 depict, respectively,



Fig. 3. Average axial stress vs. average axial strain curves during loading and unloading of the three Au nanowires deformed in axial compression. For nanowires with dimensions 20.4 Å \times 408 Å \times 20.4 Å (nanowire 1), and 40.8 Å \times 2040 Å \times 40.8 Å (nanowire 3), the average axial stresses "recover" to their values in the reference configurations with the removal of the compressive load; while inelastic deformations occurred in the nanowire with dimension 40.8 Å \times 816 Å \times 40.8 Å (nanowire 2). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)



Fig. 4. Total potential energy change vs. average axial strain curves during loading and unloading of the three Au nanowires deformed in axial compression; curves for nanowires 1 and 3 are coincident. For nanowires with dimensions 20.4 Å × 408 Å × 20.4 Å (nanowire 1), and 40.8 Å × 2040 Å × 40.8 Å (nanowire 3), the total potential energy "recovers" to its value in the reference configuration with the removal of the compressive load; while irreversible change occurred in the nanowire with dimensions 40.8 Å × 816 Å × 40.8 Å (nanowire 2). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

evolutions of the axial stress and the change in the potential energy of the system with an increase in the axial compressive strain. Results exhibited in Fig. 4 imply that the discontinuity in the total potential energy vs. the axial strain curve also indicates the onset of instability in the atomic system.

For nanowires 1 and 3 the average axial stress and the total potential energy "recover" to their values in the reference configurations with the removal of the compressive load accomplished by slowly moving atoms on the top surface to their positions in the reference configuration. These results coupled with the deformed shapes of nanowires shown in Figs. 6 and 7 suggest that the nanowires buckled. However, for nanowire 2, neither the average axial stress nor the total potential energy revert to their values in the reference configuration with the removal of imposed axial displacement implying thereby that inelastic deformations occurred in the nanowire; accordingly we interpret the sudden drop in the axial stress and the potential energy of nanowire 2 as the onset of yielding. Recall that our simulations are displacement controlled rather than load controlled and that is why there is a residual axial compressive stress rather than a residual permanent strain.

3.2. Centrosymmetry parameter (CSP) and inhomogeneity parameter (IHP)

We now examine if changes in the CSP proposed by Kelchner et al. [34], and the IHP introduced herein help characterize buckling and yielding instabilities for nanowires 2 and 3. Deformations of nanowire 1 will be elabo-



Fig. 5. Distributions of the CSP in the 40.8 Å × 816 Å × 40.8 Å Au nanowire (a) just before instability; (b) soon after instability; (c) just before instability without surface atoms; and (d) immediately after instability without surface atoms (units: Å²). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)



Fig. 6. Distributions of the CSP in the 40.8 Å \times 2040 Å \times 40.8 Å Au nanowire (a) just before the onset of instability and (b) immediately after the initiation of instability. Surface atoms have been removed to clearly show the distribution of the CSP (units: Å²). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)



Fig. 7. Distribution of the inhomogeneity parameter in the 40.8 Å \times 816 Å \times 40.8 Å Au nanowire (a) just before the wire yielded and (b) immediately after the wire yielded. (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

rated upon in Section 4 due to its large surface area to volume ratio.

The CSP for an atom is defined by

$$CSP = \sum_{i=1}^{6} |\mathbf{r}_i + \mathbf{r}_{i+6}|^2$$
(11)

where \mathbf{r}_i and \mathbf{r}_{i+6} are vectors or bonds corresponding to the six pairs of opposite nearest neighbors in the FCC lattice. The 12 nearest-neighbor vectors for each atom are first determined in the perfect FCC lattice. The CSP measures departure from centrosymmetry in the immediate vicinity of an atom and is used to determine if the atom is near a defect. For reference, the CSP equals zero for atoms in a perfect Au lattice, 24.9 \AA^2 for surface atoms, 8.3 \AA^2 for atoms in an intrinsic stacking fault, and 2.1 Å² for atoms halfway between FCC and HCP sites, i.e., in a partial dislocation. These values assume that the nearest neighbor distance does not change in the vicinity of these defects [34]. Since one compares relative values of the CSP before and after the nucleation of instabilities, there will be no effect in using these for identifying points where instabilities have occurred.

In Figs. 5 and 6, we have displayed distributions of the CSP in configurations just before and immediately after the nanowire 2 yields and the nanowire 3 buckles. Note that values of the CSP for surface atoms are always very large. Accordingly, we have deleted atoms in the three outermost layers in plots of Figs. 5c,d and 6a,b. It is clear that there is a noticeable increase in the CSP when the wire yields but there is no significant increase in the CSP when it buckles.

Said differently, the yielding of Au nanowires is closely related to the intrinsic stacking faults, while no local dislocations originate when the Au nanowire buckles.

The CSP [34] also indicates the onset of dislocations in an FCC system, and needs to be modified for use in other lattices. Furthermore, it cannot be applied to amorphous materials. Therefore, we introduce the IHP based on values of the deformation gradient for an atomic system. We hypothesize that local instabilities initiate where the deformation is highly heterogeneous, i.e., values of one or more components of \mathbf{F}^{α} are locally very large as compared to their values at neighboring points. Accordingly, an IHP is defined by the following expression:

$$\Gamma^{\alpha} = \frac{\sum_{\beta} |\mathbf{r}^{\alpha\beta} - \mathbf{F}^{\alpha} \mathbf{R}^{\alpha\beta}|}{\sum_{\beta} |\mathbf{R}^{\alpha\beta}|}.$$
(12)

We note that the definition of Γ^{α} is independent of the lattice structure, and hence is applicable to FCC, BCC and HPC lattices and also to an amorphous material. Unlike the CSP, surface defects do not influence much values of the IHP. The distribution of the IHP exhibited in Fig. 7 suggests that the IHP is greater than 0.1 in regions containing stacking faults.

As depicted in Figs. 7 and 8, variations of the IHP and the CSP are similar to each other just before and immediately after the onset of instabilities. These suggest that during yielding of the Au nanowire, deformations become highly heterogeneous locally in some groups of atoms. However, such is not the case during the buckling of Au nanowire.

3.3. Acoustic tensor and local Hessian matrix

The equilibrium configuration of a system of N discrete atoms with external forces acting on it is stable if the potential energy Φ of the system is the minimum with respect to arbitrary small virtual displacements of atoms from their equilibrium positions [35]. The system potential energy when expanded in terms of the virtual displacements can be written as

$$\Phi = \Phi_0 + \sum_{\alpha=1}^{N} \sum_{i=1}^{3} \left(\frac{\partial \Phi}{\partial \bar{u}_i^{\alpha}} - f_i^{\alpha} \right) \bar{u}_i^{\alpha} + \frac{1}{2} \sum_{\alpha,\beta=1}^{N} \sum_{i,j=1}^{3} \frac{\partial^2 \Phi}{\partial \bar{u}_i^{\alpha} \partial \bar{u}_j^{\beta}} \bar{u}_i^{\alpha} \bar{u}_j^{\beta},$$
(13)

where Φ_0 is the potential of atoms when they are all located in their initial equilibrium positions, and \bar{u}^{α} is the virtual displacement of atom α . The second term on the right hand side of Eq. (13) vanishes because the system is in equilibrium. Thus the stability condition can be written as

$$\sum_{\alpha,\beta=1}^{N}\sum_{i,j=1}^{3}\frac{\partial^{2}\Phi}{\partial\bar{u}_{i}^{\alpha}\partial\bar{u}_{j}^{\beta}}\bar{u}_{i}^{\alpha}\bar{u}_{j}^{\beta}>0,$$
(14)

which requires that the matrix $\left[\frac{\partial^2 \Phi}{\partial u_i^x \partial u_j^{\beta}}\right]$ be positive definite. This stability condition is equivalent to requiring that all long wavelength acoustic lattice waves have positive



Fig. 8. Distribution of the inhomogeneity parameter in the 40.8 Å \times 2040 Å \times 40.8 Å Au nanowire (a) just before the wire buckled and (b) immediately after the wire buckled. (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

energies. Moreover, the satisfaction of this requirement insures the decay with time of small phonon disturbances [35].

The inequality (14) has been satisfied by Kitamura et al. [17,18] and Miller and Rodney [21] by requiring that the minimum eigenvalue of the global Hessian matrix be positive. Components of the Hessian matrix equal second order differentials of the total potential energy with respect to coordi-

nates of atoms, $\left[\frac{\partial^2 \phi}{\partial r_i^a \partial r_j^\beta}\right]$. However, this is difficult to apply to a large atomic system due to the excessive computational resources needed. Therefore, a local instability criterion is used instead, which involves checking the positive-definite-

ness of the local Hessian matrix of each atom [33], i.e.,

$$\partial^2 \Phi^{\alpha}$$

$$H_{3\gamma+i,3\delta+j}^{\alpha} = \frac{\partial}{\partial r_i^{\gamma} \partial r_j^{\delta}},$$
(15)

where $1 \leq \gamma$, $\delta \leq N_f$ and N_f equals the number of atoms within the cut-off distance of atom α .

In Figs. 9 and 10, we have exhibited the non-positive minimum eigenvalue of the local Hessian matrix just before and immediately after yielding or buckling of the Au nanowires. The local Hessian matrix is positive definite almost everywhere before instabilities initiate in the Au lattice, but becomes non-positive definite in zones of stacking faults identified by rather large values of the geometric parameters CSP and IHP. Recall that these stacking faults form only when the Au nanowire yields. However, the local Hessian matrices remain positive definite even after the Au nanowire has buckled.

On the continuum scale, the decay of small wavelike disturbances forms the basis for the strong ellipticity condition of Hill [13]. The strong ellipticity condition is equivalent to the Wallace criterion for a sufficiently large domain, and has been extended to the atomic level by van Vliet et al. [16] and Lu and Zhang [22]. That is, an atom is stable in the present position if and only if all

$$Q_{ij}^{\eta} = \sum_{\alpha,\beta=1}^{N} \sum_{\gamma,\delta=1}^{N} \left(\mathbf{r}^{\alpha\beta} \cdot \mathbf{n} \right) \frac{\partial^2 \Phi^{\eta}}{\partial r_i^{\alpha\beta} \partial r_j^{\gamma\delta}} \left(\mathbf{r}^{\gamma\delta} \cdot \mathbf{n} \right), \tag{16}$$

where $|\mathbf{n}| = 1$ are positive.

In Figs. 11 and 12, we have plotted non-positive minimum eigenvalues of the local acoustic tensor just before and immediately after yielding or buckling of the Au nanowires. The local acoustic tensor is positive definite almost everywhere except at atoms on edges before instabilities ensue but becomes non-positive around the area of stacking faults identified by relatively large values of the geometric parameters CSP and IHP. However, the local acoustic tensor for atoms in the Au lattice, except for atoms near the edges, remains positive definite during the buckling of the Au nanowire.

Nanowires 2 and 3 have the same cross-section but different length. For l/h = 20, local instabilities (stacking faults) cause the Au nanowire to yield, while for l/h = 50, the Au nanowire buckles before any local instabilities initiate. For both buckling and yielding instabilities, the average axial stress vs. the axial strain curve and the total potential energy vs. the axial strain exhibit discontinuities. Since the average axial stress and the total potential energy



Fig. 9. Non-positive minimum eigenvalues of the local Hessian matrix for the 40.8 Å \times 816 Å \times 40.8 Å Au nanowire (a) just before the onset of instability and (b) immediately after the onset of instability (units: eV/Å²). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)



Fig. 10. Non-positive minimum eigenvalues of the local Hessian matrix for the 40.8 Å \times 2040 Å \times 40.8 Å Au nanowire (a) just before the onset of instability and (b) immediately after the onset of instability (units: $eV/Å^2$). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

return to their initial values when axial loads on the buckled nanowire are removed, we conclude that only structural instabilities occur instead of the material instabilities appearing during the yielding of nanowires.

4. Surface effects

During the minimization of the potential energy in going from a starting configuration with a perfect lattice to the



Fig. 11. Non-positive minimum eigenvalues of the local acoustic tensor for the $40.8 \text{ Å} \times 816 \text{ Å} \times 40.8 \text{ Å}$ Au nanowire (a) just before the onset of an instability and (b) immediately after the initiation of instability (units: eV). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

reference configuration, a tensile axial stress is induced at points on the four lateral bounding surfaces of the nanowire. This is equilibrated by a compressive axial stress at interior points. In the reference configuration, the magnitude of the induced compressive axial stress can be estimated as $4\tau h/A$, where τ is the average axial surface stress along the x_2 -direction on the bounding surfaces, his the width of a nanowire, and A is the area of cross-section. In an equilibrium configuration, the resultant axial force on a cross-section vanishes.

The compressive surface stress can be expressed as a linear function of the axial surface strain ε_{22} as follows [36] $\tau = \tau^0 + S\varepsilon_{22}$, (17)

where τ^0 is the surface axial stress in the reference configuration and S is the surface elastic modulus. The average axial stress can be approximated as

$$\bar{\sigma}_{22} = 4(\tau_0 + S\bar{\varepsilon}_{22})h/A + E_2\bar{\varepsilon}_{22},\tag{18}$$

where E_2 equals Young's modulus for the bulk material in the axial direction and $\bar{\varepsilon}_{22}$ the average axial strain. The effective Young's modulus along the x_2 -direction is given by

$$\overline{E}_2 = E_2 + 4Sh/A. \tag{19}$$

For the EAM potential being used here, E_2 and S equal 35.2 GPa and -0.901 eV/Å², respectively [37], therefore $\overline{E}_2 < E_2$ and \overline{E}_2 of different Au nanowires of the same cross-section will be the same. It is clear from the plots of the average axial stress vs. the average axial strain curves given in Fig. 1 that \overline{E}_2 , which equals the slope of these curves, has the same value of 18.4 GPa for nanowires 2 and 3 with 40.8 Å × 40.8 Å cross-section and it is close to the theoretical value of 21.0 GPa calculated from Eq. (19).

However, for nanowire 1 \overline{E}_2 equals 87.1 GPa which is much greater than the value of E_2 due to the phase transformation in the 20.4 Å × 20.4 Å Au nanowire because of its small cross-sectional area. Fig. 13 shows cross-sections of the central region of the unrelaxed and the relaxed 20.4 Å × 408 Å × 20.4 Å nanowire as seen from the x_1 direction. Only two adjacent lattice planes of atoms are shown as the lattice planes repeat in an ABAB stacking sequence and atoms in the A and the B planes are shown as open and filled circles, respectively. After relaxation, the contraction of dimension in the x_2 -direction and expansion of dimensions in the x_1 - and the x_3 -directions change the structure of the wire from the original FCC with lattice parameters of a = 4.08 Å to BCT with lattice parameters



Fig. 12. Non-positive minimum eigenvalues of local acoustic tensor of 40.8 Å \times 2040 Å \times 40.8 Å Au nanowire (a) just before the onset of instability and (b) soon after the onset of instability (units: eV). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

 $a' = 4.08/\sqrt{2}$ Å = 2.88 Å. This reorientation phenomenon was also reported by Diao et al. [10] who used the modified EAM potential.

For nanowires 1 and 3, the buckling load cannot be predicted well by the Euler buckling theory which might be due to the large residual axial stress in the reference configuration, as shown in Fig. 14. A quantitative analysis of this problem is left for a future study.

Sears and Batra [40,41] found that the Euler buckling theory predicts well the axial strain at buckling in single-wall carbon nanotubes provided that the length/diameter is large.



Fig. 13. Phase transformation in the 20.4 Å \times 408 Å \times 20.4 Å wire (a) unrelaxed and (b) relaxed configurations of the wire.



Fig. 14. Axial stress distribution in the reference configuration of the $20.4 \text{ Å} \times 408 \text{ Å} \times 20.4 \text{ Å}$ Au wire. (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)



Fig. 15. For the 20.4 Å \times 408 Å \times 20.4 Å Au nanowire without surface atoms, distributions of the CSP and the IHP in two different configurations; (a and c) just before instability; (b and d) soon after instability (units: Å²). (For interpretation of the references to colours in this figure, the reader is referred to the web version of this paper.)

The reorientation of the lattice structure and the induced residual stress in the reference configuration result in very large values of the CSP and the IHP when the 20.4 Å × 408 Å × 20.4 Å nanowire buckles; cf. Fig. 15. Furthermore, the minimum eigenvalues of the local Hessian matrix and the acoustic tensor being positive are not good indicators of the stability of an Au nanowire if its surface area to volume is large (i.e., the cross-sectional dimensions of a nanowire are small).

5. Conclusions

We have used MS simulations with the EAM potential to study deformations of three gold nanowires having dimensions: $20.4 \text{ Å} \times 408 \text{ Å} \times 20.4 \text{ Å}$ with 12,161 atoms, $40.8 \text{ Å} \times 816 \text{ Å} \times 40.8 \text{ Å}$ with 88,421 atoms and $40.8 \text{ Å} \times 816 \text{ Å} \times 40.8 \text{ Å}$ with 88,421 atoms and 40.8 $\text{Å} \times 816 \text{ Å} \times$

2040 Å \times 40.8 Å with 220,721 atoms. The results of this work are summarized below.

- (1) Nanowires of the same cross-section (40.8 Å \times 40.8 Å) but of different lengths show two types of instabilities. One is yielding in which both local (stacking faults) and global instabilities can be observed for l/h = 20; while for l/h = 50, buckling precedes local instabilities and the average axial stresses and the total potential energy is fully recovered during complete unloading of the specimen. One may say that the buckling phenomenon is synonymous with structural instabilities, and material instabilities accompany yielding.
- (2) For the 20.4 Å \times 408 Å \times 20.4 Å nanowire, strong surface effects reorient the lattice structure, which greatly increases Young's modulus and also causes

the nanowire to buckle even when l/h = 20 (in the reference configuration, this ratio is approximately 14).

- (3) Relatively large values of the inhomogeneity parameter (IHP) indicate where local instabilities ensue. The IHP is independent of the lattice structure and can be applied to an amorphous structure.
- (4) Strong surface effects should be considered when using geometric parameters (CSP and IHP) and local instability criteria (the minimum eigenvalues of the local Hessian matrix and the acoustic tensor must be positive for stability) to characterize local instabilities.

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