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Local and global instabilities in nanosize rectangular prismatic gold specimens

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ABSTRACT

We use molecular mechanics simulations with the tight-binding potential to study local and global instabilities in initially defect-free nanosize rectangular prismatic specimens of gold deformed in tension/ compression and simple tension/compression. Whereas in simple tension/compression atoms on end faces are constrained to move axially but are free to move laterally and the cross-sectional dimensions of end faces can change, in tension/compression all three components of displacements of atoms on end faces are prescribed and the cross-section of an end face does not change. The three criteria used to delineate local instabilities in a specimen are: (i) a component of second-order spatial partial derivatives of the displacement field has large value relative to its average value in the body, (ii) the minimum eigenvalue of the Hessian of the potential energy of an atom is negative, (iii) a relatively high value of the common neighborhood parameter. A specimen becomes globally unstable when its potential energy decreases noticeably with a small increase in its deformations. It is found that the three criteria for local instability are met essentially simultaneously at the same atomic position. Deformations of interior points of a specimen are different when it is deformed in simple tension/compression from those in tension/compression. It is found that the initial unloaded configuration (or the reference configuration) of the minimum potential energy has significant in-plane stresses on the bounding surfaces and non-zero normal stresses at interior points. This initial stress distribution satisfies Cauchy's equilibrium equations for a continuum. In deformations of a nanobar studied here, the yield stress defined as the average axial stress when the average axial stress vs. the average axial strain curve exhibits a sharp discontinuity depends upon the specimen size. It is shown possibly for the first time that deformations of the specimen are reversible if it is unloaded prior to yielding but have a permanent strain if unloaded after it has yielded. Because of residual stresses in the reference configuration, the average axial stress at yield in compression is nearly one-half of that in tension. The slope of the average axial stress vs. the average axial strain curve during unloading after it has yielded is the same as that during initial loading up to the yield point.

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1. Introduction

Mechanical properties of materials with one or more dimensions of the order of nanometers are of great interest due to the potential use of nanosize specimens as reinforcements in fabricating composites for structural applications and in the development of electrical, thermal and optical systems. Materials at the nanoscale have special features related mostly with the prominent influence of stresses induced in free surfaces and the residual stresses developed in the interior of the body.

The influence of surface and residual stresses can be important on the mechanical properties of a nanostructure. With a decrease in cross-sectional dimensions of a nanowire the interatomic spacing between atoms near the free surfaces decreases from that in a perfect crystal. The variation in the interatomic forces develops stresses in the specimen that may affect its response to subsequent loads. It has been observed in molecular mechanics/molecular dynamics (MM/MD) simulations that in-plane tensile stresses on the bounding surfaces generate compressive normal stresses in the interior of a nanowire [1,2].

Diao et al. [1] have used the modified embedded atom method (EAM) potential [3] to simulate tensile deformations of gold specimens of square cross-section oriented in the [1, 0, 0] and [1, 1, 1] crystallographic directions. They computed the effective Young's modulus *E* and Poisson's ratio *v* for different cross-sectional areas. For 3 nm thick nanowires oriented in the [1, 0, 0] direction, *E* equaled 42.3 GPa. We note that *E* for the bulk gold material also equals 42.3 GPa. However, for nanowires less than 1.83 nm thick *E* increased to 127 GPa. The local virial stress tensor computed in the initial unloaded relaxed or the reference configuration gave in-plane tensile stresses in nanowire's bounding surfaces and compressive stresses in the interior. For 2 nm thick wires, values of *E* at the four corners of the cross-section were 3.5 times of those at





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interior points. For nanowires in the [1, 0, 0] direction, the magnitude of the compressive stress at an interior point exceeded 1.6 GPa which is the yield stress in compression for a bulk material.

Gall et al. [4] have studied the effect of free surfaces in rhombic and multishell nanowires. The rhombic nanowires had [1, 1, 0] axis orientation and {1, 1, 1} side surfaces while the multishell wires were composed of a single atomic chain surrounded by a helix of six atoms. MD simulations of tensile loading using the EAM potential were performed until yield signified by a sharp discontinuity in the average axial stress-average axial strain curve. Young's modulus of a multishell wire was found to be greater than that of a rhombic nanowire. For a 0.7 nm diameter multishell wire the average axial yield stress and the average axial yield strain were 13 GPa and 14%, respectively. For a 2.2 nm diameter rhombic nanowire the average axial yield stress and the average axial yield strain were 3 GPa and 7%, respectively. Gall et al. [4] explained that the {1, 1, 1} surfaces contract without the application of an external load generating compressive stresses in the interior of the wire. The effect of surface stresses is negligible for macroscopic bodies but is significant for specimens of diameter less than 10 nm. They pointed out that the initially compressive stresses cause the experimentally observed asymmetry in the yield stress for small diameter specimens deformed in tension and compression. In a tension test after the external loads have overcome the internal compressive stress the wire fails due to a tensile stress reaching a limiting value. Although free surfaces contribute to the generation of internal compressive stresses that increase the strength of the structure under tension, points with high compressive stresses and other geometric irregularities are potential sites for the nucleation of instabilities.

Diao et al. [5] studied the effect of free surfaces on the yielding of gold nanowires and proposed that points where the resolved shear stress reaches a critical value are unstable points, and dislocations nucleate there. Isothermal MD simulations at 2 K of tensile and compressive deformations of gold specimens of square crosssection with [1, 0, 0] and [1, 1, 1] axial orientation were performed using periodic boundary conditions in the length direction which equaled three times the thickness of the nanowire. For [1, 0, 0] nanowires less than 2.45 nm in thickness some material points in the reference configuration had yielded. With an increase in the axial strain imposed upon the reference configuration of the 4 nm thick nanowire oriented in the [1, 0, 0] direction, the average axial yield strain and the average axial yield stress equaled \sim -4.8% and ~ -0.7 GPa, respectively, in compression, and $\sim 10\%$ and \sim 4 GPa, respectively, in tension. For the same nanowire oriented in the [1, 1, 1] direction the average axial yield stress in tension and compression was \sim 5 GPa. The yielding was attributed to the nucleation and propagation of {1, 1, 1} [1, 1, 2] partial dislocations from edges of the nanowires. The Schmidt factor for a bulk material at the onset of yield for the most favorable slip system in the [1, 0, 0] nanowire is larger in compression than that in tension causing the [1, 0, 0] nanowire to yield at a lower value of the axial stress in compression than that in tension. However, the Schmidt factor for the most favorable slip system in the [1, 1, 1] nanowire is larger in tension than that in compression but the residual compressive stresses counteract this effect producing an equal value of the yield stress in tension and compression. Even though Diao et al. [5] found that the critical resolved shear stress does not change appreciably with the cross-sectional area of the nanowire and that it can be used as a criterion for the nucleation of defects, Liu et al. [6] and Miller and Rodney [7] have stated that the slip system with the highest resolved shear stress is not always activated at the yield point.

Zhang et al. [2] using the linear elasticity theory considered effects of the surface and the initial stresses to find analytical expressions for the effective Young's modulus, strains, stresses, and the yield stress in tension/compression for an isotropic nanowire with a circular cross-section and unit length. They found that the effective Young's modulus and, in general, elastic constants of the nanowire do not depend upon the residual stresses. Assuming the von Mises yield criterion, they derived an expression for the yield stress in tension and compression which showed that the initial stress is responsible for the asymmetry observed in the yield stress in tension and compression. It was also found that the influence of elastic properties of the surface and of the initial stresses on the effective elastic properties of a nanowire and on the yield stress diminish with an increase in the radius of the nanowire. It seems that the assumptions of the material being isotropic and residual stresses being uniform are not realistic for a nanowire.

In the quest for determining the strength of materials at small scales, an important problem is the investigation of the material instabilities and the failure of the structures under external loads. A possibility is to assume that a structural element has failed when stresses or strains at a material point have just reached the level to make its deformations inelastic and the material point cannot return to its original state upon complete unloading of the structure. In an atomic system, the onset of an irreversible deformation is termed instability. Although atomic systems are discrete continuum concepts have been used to characterize the onset of irreversible deformations [6,10,11,16].

In a homogeneous continuous body, a strong singularity is associated with either the deformation gradient or the displacement becoming discontinuous across a surface passing through a material point (e.g., see Truesdell and Noll [8]). The singularity is called weak when both displacements and their first-order spatial derivatives are continuous but a second or a higher-order spatial derivative of the displacement is discontinuous at one or more points of the body. The initiation of instability at a point is synonymous with an acceleration wave not propagating through that point [9]. This is equivalent to the acoustic tensor evaluated at that point having a zero eigenvalue or a null determinant. van Vliet et al. [10] and Steinmann et al. [11], amongst others, have used it to characterize local instabilities in an atomic system.

The hypothesis of the acoustic tensor becoming singular at the onset of a local instability is equivalent to assuming that the matrix of instantaneous values of elasticities, defined as the second-order derivatives of the strain energy density with respect to the Green-St. Venant strain tensor, ceases to be positive-definite. In the phonon theory the acoustic tensor is called the dynamical matrix and is a discrete quantity. However, in continuum mechanics the acoustic tensor is defined at every point in the continuum and is a continuous function of the deformation gradient. For discrete systems Lu and Zhang [12] have used an atomistic counterpart of the continuum acoustic tensor, called the atomic acoustic tensor, to study the nucleation of local instabilities. It is equivalent to requiring that the energy of every atom in the system in equilibrium be convex for variations of position vectors of other atoms given by a mono-mode perturbation.

Energy principles have also been applied to the study of the stability conditions in atomic structures. The configuration of a system in equilibrium is globally stable if its potential energy in that configuration is the minimum. Kitamura et al. [13] studied delamination of a nanofilm from a substrate and found that the displacement at which the minimum eigenvalue of the Hessian of the potential energy of the system vanished equaled that at which the load–displacement curve became discontinuous (the displacement abruptly increased with an small increase in the applied load). The same criterion has been used to analyze strengths of thin films and cracked bodies [14].

Instabilities in an atomic system have also been studied by the normal mode analysis [15] which exploits symmetries of the system to reduce the number of degrees of freedom (d.o.f.). For a

system having no spatial symmetries, the normal mode analysis is equivalent to the method used by Kitamura et al. [13,14]. For a system having no symmetries, the reduction in the number of d.o.f. is not possible. The implementation of a criterion which includes all d.o.f. is prohibitive for a large system because of difficulties in finding an eigenvalue of a $N_a \times N_a$ sparse matrix, where N_a is the number of d.o.f. after the elimination of all prescribed displacements. Miller and Rodney [7] and Pacheco and Batra [16] have considered the Hessian of the potential energy of a subset of atoms to characterize a local instability.

Regions where deformations of an atomic system first become unstable have also been identified by using geometric measures of the local atomic structure. For example, for a face-centered cubic crystal Kelchner et al. [17] used the centrosymmetry parameter that measures relative positions between six pairs of nearest atoms situated on opposite sides of the atom whose centrosymmetric parameter is being calculated. Other quantities used include the slip vector [18], the atomic bond rotation angle [19], the common neighborhood parameter (CNP) [20], and invariants of the infinitesimal strain tensor [21]. Hartley and Mishin [22] computed the local deformation gradient by employing the least squares method and the Cauchy-Born rule, and used contour plots of components of the Nye tensor to identify screw and edge dislocations in a system of copper atoms. Since the integration of the Nye tensor over an area enclosed by Burger's circuit equals the Burger vector, Hartley and Mishin [22] asserted that this technique identifies well dislocations. Zimmerman et al. [18] used the slip vector for identifying dislocations and finding an approximation of Burger's vector

Here we use the tight-binding (TB) potential and MM simulations to study deformations of a system of gold (Au) atoms, and use (i) second-order partial derivatives with respect to space variables of the displacement field, (ii) the CNP, and (iii) eigenvalues of the Hessian of the local potential energy to characterize the onset of local instabilities. We also investigate whether or not these three criteria are met simultaneously at a point, and the permanent axial strain induced in the specimen subsequent to the complete removal of the applied load. Deformations simulated include tension/compression and simple tension/compression of prismatic specimens of different sizes and aspect ratios. Values of the firstand the second-order partial derivatives of displacement with respect to space variables are found by using the modified smoothed particle hydrodynamics (MSPH) method [23]. We find the local Hessian of the TB potential by considering the bond energy between an atom and other atoms included in its first shell of neighbors that contains atoms located within one atomic distance from it. The local instability criterion of the vanishing of an eigenvalue of the local acoustic tensor is not used here since in shear and simple shear deformations of a gold crystal Pacheco and Batra [16] found that it gives results inconsistent with those obtained by using the other criteria.

Values of the average Cauchy stress tensor are computed by using four definitions of the average stress tensor. The local Cauchy stress tensor is found with Hardy's method [24]. The von Mises stress and the maximum shear stress at atomic positions where instabilities were predicted by the vanishing of eigenvalues of the Hessian of the local energy are found to be much larger than their average values in the specimen. Unstable points (atoms) are located, in general, beneath free surfaces in zones of high stress gradients. The average axial yield stress is found to increase with a decrease in the specimen size but local stresses are found to be considerably high in certain zones in large samples.

The global instability of a system is characterized either by a sharp discontinuity in the average axial stress-the average axial strain curve or the strain energy density of the system ceasing to be a minimum. The latter is indicated by a 10-fold increase in the number of iterations required to find the configuration of the minimum potential energy.

The present work extends to tensile and compressive deformations our earlier work [16] on the analysis of local and global instabilities in three Au cubic specimens deformed in shear and simple shear. We also delineate effects of different boundary conditions on the end faces of prismatic specimens of aspect ratios (length/ width) varying from 1 to 20, and show the existence of permanent strains after a yielded specimen has been completely unloaded. However, there is no residual permanent strain left in a specimen unloaded from a configuration just before it yields.

2. Molecular mechanics simulations

2.1. Molecular mechanics potential

Interatomic potentials used to study mechanical deformations of a nanosize specimen include the Finnis–Sinclair potential [25], the embedded atom method (EAM) [26,27], the effective-medium theory [28], the glue models [29], and the tight-binding (TB) potential [30]. We use the TB potential to represent the internal energy and interatomic forces in an atomic system because it has been successfully used to characterize the mechanical behavior of Au nanowires [31-33]. Pu et al. [33] used three semi-empirical potentials, namely, the EAM potential [27], the glue model potential [29], and the TB potential [30], and compared results of MD simulations for a tension test on an Au cluster composed of 256 atoms. The accuracy of a potential was determined by comparing the potential energy in the reference configuration and the ultimate force at the breaking point with corresponding values from the Density Functional Theory (DFT). Predictions from the TB potential were found to agree well with the DFT results and the experimental data of Rubio-Bollinger et al. [34] for the force at the breaking point for an atomic chain of Au atoms.

The TB potential is given by

$$V^{(i)} = -\left(\sum_{\substack{j=1\\j\neq i}}^{N} \zeta^{2} \exp\left(-2D\left(\frac{r^{(ij)}}{r_{0}} - 1\right)\right)\right)^{1/2} + \sum_{\substack{j=1\\j\neq i}}^{N} M \exp\left(-\tilde{P}\left(\frac{r^{(ij)}}{r_{0}} - 1\right)\right).$$
(1)

In Eq. (1), $V^{(i)}$ equals the potential energy of atom *i*, *N* the total number of atoms in the system, r_0 the first-neighbor distance $(a_0/\sqrt{2}, \text{ where } a_0 \text{ is the lattice parameter})$, $r^{(ij)}$ the magnitude of the position vector between atoms *i* and *j*, and ζ , *D*, \tilde{P} and *M* are constants characterizing a material. These constants are obtained by minimizing an error function containing differences between the experimentally obtained material properties and predictions of the TB potential. For a FCC crystal in equilibrium at 0 K and oriented with the coordinate axes [1, 0, 0], [0, 1, 0] and [0, 0, 1], properties used in the fitting procedure for these constants are [30]: the cohesive energy V_c , the lattice parameter a_0 , the elastic constants, and the equilibrium equations. Values of material parameters for Au derived from the fitting procedure are:

 $M = 0.2061 \text{ eV}, \quad \zeta = 1.7900 \text{ eV}, \quad \tilde{P} = 10.2290,$ $D = 4.0360, \quad r_0 = 2.8850 \text{ Å}.$

Since $V^{(i)}$ given by Eq. (1) is essentially zero for $r^{(ij)} > 5.5$ Å, the summation in Eq. (1) is carried out for those values of j for which $r^{(ij)} < 6$ Å to reduce the computational cost. We note that the TB potential and its partial derivatives with respect to $r^{(ij)}$ are continuous at the cut off radius of 6 Å within the accuracy of the machine.

The potential energy V of a system of atoms equals the sum of the energy $V^{(i)}$ of all atoms in the system. That is

$$V = \sum_{i=1}^{N} V^{(i)}.$$
 (2)

The interaction force vector $\mathbf{f}^{(ij)}$ between atoms *i* and *j* equals the negative of the partial derivative of the potential energy with respect to $\mathbf{r}^{(ij)}$, or

$$f_{\alpha}^{(ij)} = -\left(\frac{\partial V^{(i)}}{\partial r^{(ij)}} + \frac{\partial V^{(j)}}{\partial r^{(ij)}}\right) \frac{r_{\alpha}^{(ij)}}{r^{(ij)}}.$$
(3)

Here and below, the index α ranges from 1 to 3, and $f_{\alpha}^{(ij)}$ equals the component of $\mathbf{f}^{(ij)}$ along the x_{α} -coordinate axis of a rectangular Cartesian coordinate system.

2.2. Stresses

For a system comprised of *N* atoms at 0 K, average values $\bar{\sigma}_{\alpha\beta}$ of components of the Cauchy stress tensor are computed from the relation

$$\bar{\sigma}_{\alpha\beta} = \frac{1}{2\Omega^{\mathrm{T}}} \sum_{i=1}^{N} \sum_{\substack{j=1\\ i\neq i}}^{N} f_{\alpha}^{(ij)} r_{\beta}^{(ij)},\tag{4}$$

where Ω^T equals the volume occupied by the system.

Hardy [24] proposed the following expression for the Cauchy stress tensor for a quasi-static problem:

$$\boldsymbol{\sigma} = -\frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1\\j\neq i}}^{N} \boldsymbol{r}^{(ij)} \otimes \boldsymbol{f}^{(ij)} \boldsymbol{B}^{(ij)}(\boldsymbol{R}),$$
(5)

where

$$B^{(ij)}(\boldsymbol{R}) \equiv \int_0^1 \Psi(\lambda \boldsymbol{r}^{(ij)} + \boldsymbol{r}^{(j)} - \boldsymbol{R}) d\lambda.$$
(6)

For the case where Ψ is a radial step function, $B^{(ij)}$ represents a fraction of the atomic bond between atoms *i* and *j* that is contained in a representative volume defined around each material point **R**. The function Ψ (units of this function are $1/L^3$) satisfies following conditions [35]:

(i) $\Psi(\mathbf{r}^{(i)} - \mathbf{R})$ has a global maximum at $\mathbf{r}^{(i)} = \mathbf{R}$. (ii) $\Psi(\mathbf{r}^{(i)} - \mathbf{R}) \to 0$ as $|\mathbf{r}^{(i)} - \mathbf{R}| \to \infty$. (iii) $\Psi(\mathbf{r}^{(i)} - \mathbf{R})$ is smooth and non-negative.

(iv) $\int_{\Omega} \Psi(r^{(i)} - R) d\Omega = 1.$

Zimmerman et al. [36] used Eq. (5) to compare the local Cauchy stress tensor with the local virial stress tensor and analyzed the influence of two different localization functions. Simple tensile deformation of a system of 3072 copper (Cu) atoms with energetics described by the EAM potential were analyzed using periodic boundary conditions on all bounding surfaces. Two bond functions, a radial step and a cubic spline, were used. The averaging volume $\Omega^{(i)}$ in Eq. (5) around each atomic position was taken to be a sphere of radius R_c . It was shown that the Cauchy stresses computed with the step function decreased to zero as R_c was increased, and fluctuations in the normal stress components were significant for R_c equal to the lattice parameter. However, the amplitude of these fluctuations was effectively suppressed to zero with the cubic spline function taken as the bond function.

2.3. Strains

Mott et al. [37] studied three dimensional (3D) deformations of an atomic system, and interpolated displacements using piecewise-linear continuous basis functions defined on a Delaunay tessellation of atomic positions. Falk [38] used the finite-difference method to compute infinitesimal strains using relative displacements between two neighboring atoms. Zimmerman et al. [39] used the least squares method to find displacement gradients from positions of atoms in the current and the reference configurations.

We employ the MSPH method [23] to compute the spatial distribution of the deformation gradient F and spatial gradients, G, of F from positions of atoms in the current and the reference configurations. The Cauchy–Born rule [40–42] states that for a crystal with a simple Bravais lattice, relative position vectors $\mathbf{r}^{(ij)}$ and $\mathbf{R}^{(ij)}$ between atoms i and j in the current and the reference configurations are related by $\mathbf{r}^{(ij)} = \mathbf{F}^{(i)} \mathbf{R}^{(ij)}$, where $\mathbf{F}^{(i)}$ is the deformation gradient at the position of atom i in the reference configuration. To partially account for non-local interactions in continuum mechanics, Kouznetsova et al. [43] also considered G in the kinematic description of the deformation. We use components of the tensor G, the second-order spatial derivatives of displacements, to characterize local instabilities in an atomic system.

While describing below briefly the MSPH method till Eq. (11), we use **X** and **X**⁽ⁱ⁾ to denote, respectively, position vectors of a generic point and point *i* in an Euclidean space. In the MSPH method, a continuously differentiable function $\varphi(\mathbf{X})$ (e.g., the position vector component $r_{\alpha}^{(i)}$) is first expanded in finite Taylor series. The three-term Taylor series approximation of $\varphi(\mathbf{X})$ at the point $\xi = (\xi_1, \xi_2, \xi_3)$ in the neighborhood of the point $\mathbf{X} = \mathbf{X}^{(i)} = (X_1^{(i)}, X_2^{(i)}, X_3^{(i)})$ is

$$\varphi(\boldsymbol{\xi}) \approx \varphi(\boldsymbol{X}^{(i)}) + \frac{\partial \varphi}{\partial X_{\alpha}^{(i)}} (\boldsymbol{\xi}_{\alpha} - X_{\alpha}^{(i)}) + \frac{1}{2} \frac{\partial^{2} \varphi}{\partial X_{\alpha}^{(i)} \partial X_{\beta}^{(i)}} (\boldsymbol{\xi}_{\alpha} - X_{\alpha}^{(i)}) (\boldsymbol{\xi}_{\beta} - X_{\beta}^{(i)}),$$
(7)

where $\partial \varphi / \partial X_{\alpha}^{(i)} = (\partial \varphi / \partial X_{\alpha})|_{\mathbf{X} = \mathbf{X}^{(i)}}$. To evaluate the function $\varphi(\mathbf{X})$ and its first- and second-order partial derivatives at the point $X^{(i)}$, we multiply both sides of Eq. (7) with a non-negative kernel function $W(|\mathbf{X} - \boldsymbol{\xi}|, h)$ of compact support, and by its first- and second-order partial derivatives, $W_{,\alpha}(|\mathbf{X} - \boldsymbol{\xi}|, h)$ and $W_{,\alpha\beta}(|\mathbf{X} - \boldsymbol{\xi}|, h)$; here $W_{,\alpha} = \partial W / \partial \xi_{\alpha}$ and $W_{,\alpha\beta} = \partial^2 W / \partial \xi_{\alpha} \partial \xi_{\beta}$, and h is the smoothing length which determines the size of the compact support of the kernel function W. The magnitude of h usually equals three times the atomic spacing. For a 3D problem one needs at least ten distinct points within the compact support of $W(|\mathbf{X} - \boldsymbol{\xi}|, h)$. We integrate the resulting equations with respect to ξ over the volume Ω_R^T occupied by the system in the reference configuration, employ the position $\mathbf{X}^{(i)}$ of point *i* as an integration point, and volumes associated with it as the corresponding weight to obtain a set of ten algebraic equations for $\varphi(\mathbf{X})$, $\varphi_{\alpha}(\mathbf{X})$ and $\varphi_{\alpha\beta}(\mathbf{X})$. Setting $\varphi(\mathbf{X}) = r_{\alpha}^{(i)}$ gives values of **F** and **G** at the point $X^{(i)}$. Unless the function $W(|X - \xi|, h)$ is a constant over its compact support, the influence of displacements of point *i* on values of **F** and **G** at the point $X^{(i)}$ occupied by the point *i* depends upon the relative values of $W(|\mathbf{X} - \boldsymbol{\xi}|, h)$ at points *i* and *j*. For a 3D problem, one needs to solve three systems of ten simultaneous linear algebraic equations to find **F** and **G** at a point. We recall that local instabilities are characterized by comparing the value of G at a point with its average value over the entire domain. Thus it is not necessary to estimate truncation errors in using the finite Taylor series (7) during the computation of G.

We use the following cubic spline function for W:

$$W(s) = \frac{1}{\pi h^3} \begin{cases} \left(1 - \frac{3}{2}s^2 + \frac{3}{4}s^3\right), s \le 1\\ \frac{1}{4}(2 - s)^3, 1 < s \le 2\\ 0, \text{ otherwise} \end{cases}$$
(8)

$$s = \frac{|\boldsymbol{X} - \boldsymbol{\xi}|}{h} = \frac{r}{h}.$$
(9)

From $F^{(i)}$ at the point $x^{(i)}$, we evaluate there the Almansi–Hamel strain tensor $\varepsilon^{(i)}$ from

$$\varepsilon_{\alpha\beta}^{(i)} = (1/2) \Big(\delta_{\alpha\beta} - (F^{-1})_{\phi\alpha}^{(i)} (F^{-1})_{\phi\beta}^{(i)} \Big), \tag{10}$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. The volume averaged value, \bar{e} , of this tensor for the system is defined by

$$\bar{\varepsilon}_{\alpha\beta} = \frac{1}{\Omega^T} \int_{\Omega^T} \varepsilon_{\alpha\beta}(x) d\Omega = \sum_{i=1}^N \frac{\Omega^{(i)}}{\Omega^T} \varepsilon_{\alpha\beta}^{(i)}, \tag{11}$$

where $\Omega^{(i)}$ and Ω^T equal, respectively, the volume assigned to point *i* and the total volume of the system in the deformed configuration.

We set $\Omega^{(i)}$ equal to the Voronoi volume associated with atom *i*. An approximation of the Voronoi volume is given by (e.g., see [33])

$$\Omega^{(i)} = \frac{4\pi}{3} a_i^3, \quad a_i = k_v \frac{\sum_{\substack{j=1\\j\neq i}}^{N_c} (r^{(ij)})^{-1}}{\sum_{\substack{j=1\\j\neq i}}^{N_c} (r^{(ij)})^{-2}}.$$
(12)

Here N_e equals the number of atoms in the neighborhood of atom *i* for which $r^{(ij)} \leq (\sqrt{3}/2)a_0, a_0$ is the lattice parameter, and we set the constant $k_v = 0.55$ found by computing the Voronoi volume of an atom at the centroid of the specimen, and equating it to the volume given by Eq. (11).

2.4. Average stresses

For a continuous body, the average value over volume Ω of the Cauchy stress tensor defined by

$$\bar{\sigma}_{\alpha\beta} = \frac{1}{\Omega} \int_{\Omega} \sigma_{\alpha\beta} d\Omega, \tag{13}$$

can be written as

$$\bar{\sigma}_{\alpha\beta} = \frac{1}{\Omega} \int_{\partial\Omega} \sigma_{\alpha\phi} x_{\beta} \hat{n}_{\phi} dS, \quad = \frac{1}{2\Omega} \int_{\partial\Omega} (t_{\alpha} x_{\beta} + t_{\beta} x_{\alpha}) dS, \quad (14)$$

where \hat{n} is a unit outward normal to the boundary $\partial \Omega$ of Ω , $t = \hat{n} \cdot \sigma$ is the surface traction, and we have used the divergence theorem and the balance of linear momentum with null body forces. Thus the average Cauchy stress tensor multiplied by the volume of the region occupied by the body equals the first moment of tractions acting on the bounding surfaces of the body.

For a discrete system, Eq. (14) can be written as

$$\bar{\sigma}_{\alpha\beta} = \frac{1}{\Omega^T} \sum_{i=1}^{N_b} x_{\beta}^{(i)} f_{\alpha}^{(i)},\tag{15}$$



Fig. 1. Schematics of the initial, the relaxed (reference), the unrelaxed deformed, and the current (deformed) configurations of an atomic system.

where N_b equals the number of atoms on the bounding surface of the region whose deformations are being studied.

Assuming that the volume assigned to each atom is the same, Eq. (4) becomes

$$\bar{\sigma}_{\alpha\beta} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2\Omega^{(i)}} \sum_{\substack{j=1\\j \neq i}}^{N} f_{\alpha}^{(ij)} r_{\beta}^{(ij)} = \frac{1}{N} \sum_{i=1}^{N} \omega_{\alpha\beta}^{(i)}$$
(16)

where

$$\omega_{\alpha\beta}^{(i)} = \frac{1}{2\Omega^{(i)}} \sum_{\substack{j=1\\j\neq i}}^{N} f_{\alpha}^{(ij)} r_{\beta}^{(ij)}$$
(17)

is the dipole force tensor [44]. However, for a finite size specimen, Eq. (16) is approximately valid since the volume assigned to an atom on the bounding surface equals ½ of that assigned to an atom in the interior of the body, and the volume of an atom at a vertex of the region equals 1/8th of that for an interior atom. For a system having a large number of atoms, Eqs. (4) and (16) will give



Fig. 2a. For the minimization of the total potential energy with the CG method and for three cubic samples of different sizes, variation with the number of iterations of the ratio of the total potential energy V_{ls} in the current iteration to the total potential energy V_l in the initial configuration.



Fig. 2b. For the minimization of the total potential energy with the CG method, variation with the number of iterations of the L_{∞} -norm of the gradient of the total potential energy of three cubic samples of different sizes.

Table 1

Values of the average axial stress and the average axial strain at the yield point for specimens with different L/H ratios deformed in tension and compression.

L/H Number of atoms		Tension		Compression	
		σ_{yy}^{yield} (GPa)	ε_{yy}^{yield} (%)	σ_{yy}^{yield} (GPa)	$arepsilon_{yy}^{yield}$ (%)
1	3430	7.317	9.597	-3.698	-7.789
3	9928	6.481	9.745	-1.783	-6.182
5	6787	6.344	9.809	-1.788	-6.764
10	32,671	6.256	9.883	-1.704	-5.460
20	65,883	6.242	9.942	-1.209	-3.245

essentially the same values of average stresses. However, for a small system with a large number of atoms on the bounding surfaces compared to those in the interior, average stresses computed from these two equations will differ.

2.5. Molecular mechanics simulations

We start numerical simulations by assigning the initial position vector $X_l^{(i)}$ of each atom in the system in a perfect lattice configuration (cf. Fig. 1). Without applying any external force, each atom is allowed to move freely till the potential energy of the system

has been minimized by using the conjugate gradient (CG) with warranted descent technique [45]. The minimization procedure is stopped when the magnitude of each component of the gradient of the internal energy at every atom in the system equals at most 1×10^{-8} eV/Å. The position vector of an atom in this relaxed configuration is denoted by $X_R^{(i)}$, and this configuration is taken as the reference configuration. This is similar in principle to annealing a macroscopic specimen before conducting a mechanical test. However, for a nanosize structure, this relaxation process may induce residual stresses whereas the annealing process is designed to eliminate them.

For three cubic specimens of Au oriented with crystallographic planes of the {1, 0, 0} family and different number of atoms Fig. 2a, b shows the variation with the number of iterations in the CG method of the total energy fraction and the norm of the gradient of the total potential energy during the minimization process. The energy fraction equals the ratio of the total potential energy V_{ls} in the current iteration to that (V_l) in the initial configuration. The general trend is that as the size of the sample increases the total potential energy fraction decreases. For the specimen with 3480 atoms the total potential energy in the relaxed configuration differs by ~0.37% from that in the initial configuration. A vanishing L_{∞} -norm of the gradient of the total potential energy is an



Fig. 3. Evolution with the average axial strain ε of the average values of components of the Cauchy stress tensor for the tension/compression tests for different *L*/*H* ratios. (a) σ_{vv} ; (b) σ_{xx} .



Fig. 4. Comparison of three measures of the Cauchy stress tensor for L/H = 10 in tension/compression tests; Eqs. (4) and (16) and the mechanics of materials approach (force/area).



Fig. 5. For L/H = 10, evolution with the average axial strain ε of the average values of the normal components of the Almansi–Hamel strain tensor for the tension/ compression tests. Curves for ε_{xx} vs. ε and ε_{zz} vs. ε overlap each other.

indication that all particles (atoms) in the specimen have reached their equilibrium positions. In general, the number of iterations needed to minimize the potential energy increases with an increase in the specimen size.

Subsequently, after each increment in the prescribed displacements of atoms on the end faces of the specimen, the total potential energy is minimized. The change in the potential energy of the system from that in the reference configuration equals the strain energy required to deform the body or the system of atoms. The process is continued till atoms on the end faces have been given the desired axial displacement.

In problems studied here, either an atom on a bounding surface has a displacement component prescribed or the corresponding component of the external force applied there is zero.

3. Instabilities in tensile and compressive deformations

We simulate tensile and compressive deformations of Au crystals having a square cross-section of side H = -37 Å and length L with the aspect ratio L/H varying from 1 to 20; the number of atoms in a specimen is listed in Table 1. Each specimen is oriented with the coordinate planes {1, 0, 0}, {0, 1, 0} and {0, 0, 1}. For the tension/compression tests, atoms in the reference configuration located on planes $Y = Y_{min}$ and $Y = Y_{max}$ are constrained from moving in the X- and the Z-directions while the Y-displacement is prescribed in increments of 0.25 Å. For the simple tension/compression tests, atoms on planes $Y = Y_{min}$ and $Y = Y_{max}$ have Y-displacement prescribed; those located on the centroidal line parallel to the X-axis also have null Z-displacements, and atoms located on the centroidal line parallel to the Z-axis also have null X-displacements. Thus all cross-sections of a specimen are allowed to expand or contract. Once a discontinuity in the strain energy density vs. the average axial strain curve is observed simulations are restarted from the immediately preceding displacement increment with the prescribed Y-displacement incremented by 0.1 Å. In all simulations, there are no external forces applied on the four lateral surfaces.

3.1. Average stresses and strains

3.1.1. Tension/compression

For different L/H ratios Fig. 3a and b shows the variation with the average axial strain ε (change in length per unit initial length)



Fig. 6. For different values of *L*/*H*, evolution with the average axial strain ε of the average value of σ_{yy} component of the Cauchy stress tensor for the simple tension/ compression tests.

of average values of σ_{xx} and σ_{yy} components of the Cauchy stress tensor computed using Eq. (4). It is observed that the variation with ε of the average σ_{yy} stress is the same for $L/H \ge 3$. For L/H = 1 all normal stresses are of the same order of magnitude showing a very different behavior as compared to that for samples having $L/H \ge 3$. For a square cross-section σ_{zz} equals σ_{xx} . Note that atoms on the end faces are constrained to move axially only; thus these cross-sections do not change. With an increase in L/H, the average values of σ_{xx} and σ_{zz} decrease and are nearly 1/10th of the average value of σ_{yy} . The average values of all shear stresses are negligible till discontinuities in the σ_{yy} vs. ε curve are observed. Subsequent to the occurrence of these discontinuities, values of local shear stresses are comparable to values of the local normal

Table 2

Values of the average axial stress and the average axial strain at the yield point for specimens with different L/H ratios deformed in simple tension and compression.

L/H	Simple tension		Simple compression	
	σ_{yy}^{yield} (GPa)	ε_{yy}^{yield} (%)	σ_{yy}^{yield} (GPa)	$arepsilon_{yy}^{yield}$ (%)
1	5.134	7.928	-2.498	-8.345
3	5.050	8.119	-1.784	-6.643
5	4.996	8.117	-1.810	-6.897
10	4.990	8.086	-1.671	-5.157
20	4.618	7.584	-1.387	-3.874



Fig. 7. For L/H = 10, comparison between different measures of the average Cauchy stress tensor in the simple tension/compression tests; Eqs. (4) and (16) and the mechanics of materials approach (force/area).



Fig. 8. For L/H = 10, evolution with the average axial strain ε of the average values of normal components of the Almansi–Hamel strain tensor for the simple tension/ compression tests. Curves for ε_{xx} vs. ε and ε_{zz} vs. ε overlap each other.

stresses in regions close to edges and vertices of the specimen. In Table 1 we have listed, for different values of L/H, average values of σ_{yy} and ε at yield identified by a sharp drop in the average axial stress for an infinitesimal increase in the average axial strain. Values of the average axial yield stress and the corresponding average axial strain for $L/H \ge 3$ for tension are ~6.2 GPa and ~9.8%, respectively. However, values of the average axial stress and the average axial strain at the yield point in compression for specimens with L/H = 1 and 20 differ noticeably from those for specimens with L/H = 3, 5 and 10. In compression, the magnitude of the average axial strain at yield from 7.8% to 3.2%; the higher values are for L/H = 1.

For the same L/H ratio asymmetry in the yield stress in tension and compression is apparent from values listed in Table 1 as was also found by Diao et al. [1] and Zhang et al. [2]. This asymmetry is attributed to initial stresses in the reference configurations of the specimens. The internal compressive stresses induced by the surface tension cause a local critical stress in compression to be reached at a smaller value of the average axial strain than that in an initially stress free specimen. Whereas the average axial stress vs. the average axial strain curve is essentially linear in tension that in compression is non-linear. For the specimen with L/H = 20, we have not examined closely details of deformation fields to ascertain if any other instability (e.g., buckling) initiated up to an average compressive axial strain of 3.245%.

Fig. 4 depicts σ_{yy} vs. ε curves by computing average values of stresses with definition (4) of the virial stress, Eq. (16) for the first moment of forces on bounding surfaces, and the mechanics of



Fig. 9. For L/H = 10, variation with the averaging length (L_g) in simple tension and compression of (a) the effective Young's modulus *E*, and (b) Poisson's ratio.

materials approach (force/area) in which forces along the Y-direction of atoms on an end face of the specimen have been considered. The three values are in good agreement with each other. Although they are used for the mechanical characterization of atomic systems the average values of the stress components do not give any information about its local values.

The evolution of the average values of normal components of the Almansi–Hamel strain tensor with the average axial strain ε (change in length per unit length) for a specimen with L/H = 10 is plotted in Fig. 5; curves for ε_{xx} vs. ε and ε_{zz} vs. ε overlap each other. The equality of ε and ε_{yy} suggests that, on the average, geometric non-linearities can be neglected up to the yield point. Normal strains in the transverse direction have opposite sign to that in the axial direction giving a positive value of Poisson's ratio. The averaged components of the shear strains are negligible. A similar behavior is observed for other specimens having $L/H \ge 3$.

3.1.2. Simple tension/compression

For different L/H ratios, Fig. 6 depicts the variation with ε of the average value of σ_{yy} component of the Cauchy stress tensor found by using Eq. (4). In agreement with results for the tension/compression simulations reported above, it is observed that the



Fig. 10. For L/H = 10, variation with the average axial strain ε of the average axial stress for loading and unloading paths in simple tension.



Fig. 11. For simulations with different values of L/H, variation with the average axial strain ε of the minimum eigenvalue of the local Hessian $H^{(i)}$ in simple tensile/ compressive deformations.

variation with ε of the average value of σ_{yy} is the same for specimens with $L/H \ge 3$. However, for the simple tension/compression simulations, the average values of σ_{zz} and σ_{xx} are negligible as compared to the average values of σ_{yy} . The applied boundary conditions allow atoms on the end faces to move freely in the *X*- and the *Z*-directions; consequently, edge effects are negligible and averaged values of σ_{zz} and σ_{xx} are very small.

As in the tension/compression tests the average values of all shear stresses are negligible up to the discontinuity in the σ_{yy} vs. ε curves. In Table 2 we have listed, for different *L*/*H* ratios, values of the average σ_{yy} stress and the average axial strain at the yield point. Values of the axial yield stress and the average axial strain at yield for $10 \ge L/H \ge 3$ for the simple tension case are ~5 GPa

and ~8%, respectively; the corresponding values for the tension test listed above are ~6.2 GPa and ~9.8%. In simple compression, a dependence of the average axial stress and the average axial strain at yield on the L/H ratio is also observed. For a given value of L/H, the yield stress in simple tension is higher than that in simple compression. Because of residual stress in the reference configuration, the difference in the yield stress in simple tension and simple compression cannot be attributed to the Bauschinger effect.

As evidenced from results exhibited in Fig. 7a good agreement between three measures of average stresses is found but in this case there is more scatter in the average stresses derived from the first moment of forces on bounding surfaces than that from the other two methods.



Fig. 12. For the simple compression test, distribution of the minimum eigenvalue of the local Hessian, the CNP and $\|G\|$ in the specimen with L/H = 10; (a) minimum eigenvalue, $\varepsilon = -5.15\%$; (b) minimum eigenvalue, $\varepsilon = -5.16\%$; (c) CNP on the mid-section X = 18 Å, $\varepsilon = -5.15\%$; (d) CNP, $\varepsilon = -5.16\%$; (e) $\|G\|$ on the mid-section X = 18 Å, $\varepsilon = -5.15\%$; (d) CNP, $\varepsilon = -5.16\%$; (e) $\|G\|$ on the mid-section X = 18 Å, $\varepsilon = -5.15\%$; (d) CNP, $\varepsilon = -5.16\%$; (e) $\|G\|$ on the mid-section X = 18 Å, $\varepsilon = -5.15\%$; (f) minimum eigenvalue, $\varepsilon = -5.16\%$; (g) atoms on the bounding surface have been removed to clearly depict values of the CNP at unstable points in the interior of the specimen.

For L/H = 10, the evolution of the average normal components of the Almansi–Hamel strain tensor with the average axial strain is plotted in Fig. 8. Curves for ε_{xx} vs. ε and ε_{zz} vs. ε overlap each other, and ε_{yy} is almost equal to ε till the specimen yields. Thus the effect of geometric non-linearities can be ignored until the yield point.

For an FCC material the effective Young's modulus E in the loading direction [0, 1, 0] is given by

$$E = \frac{\tilde{C}_{11}^2 + \tilde{C}_{12}\tilde{C}_{11} - 2\tilde{C}_{12}^2}{\tilde{C}_{11} + \tilde{C}_{12}}$$

where \tilde{C}_{11} and \tilde{C}_{12} are elastic constants in the stress-strain relation for an FCC metal written in Voigt's notation. From the elastic constants of Au at 0 K used to find values of constants in the TB potential, *E* in the Y-direction should equal 46.5 GPa. For the computation of *E* from results of the MM simulations a representative (or the gage) length L_g was defined around the mid-section of each specimen. The average axial stress–the average axial strain curves obtained by taking contributions of atoms inside the length L_g were used to find *E*. The simple tension/compression tests were performed up to $\varepsilon = 1\%$ and slopes of the stress–strain curves were computed by linear regression. For the specimen having L/H = 10, Fig. 9a shows the variation with L_g/a (recall that *a* is the lattice parameter) of *E* in simple tension and compression. For $L_g/a < 10$ the value of *E* varies between 46.8 GPa and 47.9 GPa; the difference



Fig. 13. For the simple tension test, distribution of the minimum eigenvalue of the local Hessian, the CNP and $||\mathbf{G}||$ in the specimen with L/H = 10; (a) minimum eigenvalue, $\varepsilon = 8.08\%$; (b) minimum eigenvalue, $\varepsilon = 8.15\%$; (c) CNP on the mid-section X = 18 Å, $\varepsilon = 8.08\%$; (d) CNP, $\varepsilon = 8.15\%$; (e) $||\mathbf{G}||$ on the mid-section X = 18 Å, $\varepsilon = 8.08\%$; and (f) $||\mathbf{G}||$ at unstable points, $\varepsilon = 8.15\%$; in Fig. (d) atoms on the bounding surface have been removed to clearly show values of the CNP at unstable points in the interior of the specimen.

between the maximum and the minimum values of *E* is only 2.3%. For $10 < L_g/a < 40$ the value of *E* equals ~47.1 GPa. For $L_g/a > 40$ a small increase in the values of *E* is found. Boundary effects are reflected in changes of the distribution of interatomic forces but their influence along the axial direction goes up to 1 or 1.5 times the specimen width in agreement with Saint-Venant's principle. The computed value, 47.1 GPa, of *E* in the *Y*-direction is 1.3% higher than the 46.5 GPa obtained from elastic constants of the material. This small difference in the computed and the expected values of *E* could be due to the fact that unstrained specimens in the reference configurations in our simulations had residual stresses but those used to fit constants in the TB potential had perfect lattice configurations and were stress free. Even though we have used average values of

axial stresses and axial strains in computing *E*, effects of residual stresses may have not been completely mitigated.

Recalling that the average values of σ_{xx} and σ_{zz} equal zero, we get the following expression for Poisson's ratio:

$$v = -\frac{\varepsilon_{xx}}{\varepsilon_{yy}} = \frac{\tilde{C}_{12}}{\tilde{C}_{11} + \tilde{C}_{12}}$$

For the specimen with L/H = 10, Fig. 9b exhibits the variation of v with L_g/a . For $10 < L_g/a < 30$, the computed value 0.478 of v agrees well with 0.453 obtained from values of \tilde{C}_{11} and \tilde{C}_{12} used to find constants in the TB potential.

We note that *E* and *v* can be computed from the average values of stresses and strains, and not from the plots of local values of σ_{yy} ,



Fig. 14. For the compression test, distribution of the minimum eigenvalue of the local Hessian, the CNP and $\|G\|$ in the specimen with L/H = 10; (a) minimum eigenvalue, $\varepsilon = -5.46\%$; (b) minimum eigenvalue, $\varepsilon = -5.52\%$; (c) CNP on the mid-section, X = 18 Å, $\varepsilon = -5.46\%$; (d) CNP, $\varepsilon = -5.52\%$; (e) $\|G\|$ on the mid-section, X = 18 Å, $\varepsilon = -5.46\%$; and (f) $\|G\|$ at unstable points, $\varepsilon = -5.52\%$; In Fig. (d) atoms on bounding surfaces have been removed to clearly show values of the CNP at unstable points in the interior of the specimen.

 ϵ_{yy} and ϵ_{xx} since the stress state locally is not that of uniaxial tension/compression.

In Fig. 10 we have plotted the average axial stress vs. the average axial strain during unloading from two configurations – one just before the drop in the average axial stress vs. the average axial strain curve and the other just after this drop. When the specimen is unloaded from the configuration just before the average axial stress drops noticeably, the average axial stress vs. the average axial strain curve during unloading overlaps that during loading suggesting that the specimen deformed elastically. However, when the specimen is unloaded from the configuration just after the severe drop in the axial stress, there is a residual average axial strain at zero average axial stress. It confirms that the specimen deformed plastically during the instant the average stress dropped, and the permanent average axial strain equals 4.5%.

3.2. Analysis of local instabilities

3.2.1. Simple tension/compression

For different values of L/H, Fig. 11 exhibits the evolution of the minimum eigenvalue of the local Hessian $H^{(i)}$ among all atoms in the system for simple tensile/compressive deformations. For sim-

а

b

C

ple compression, the minimum eigenvalue continuously decreases and remains positive until the strain level where the sharp drop in the average axial stress-the average axial strain curve occurs. The strain levels at which local instabilities, signified by the minimum eigenvalue of $H^{(i)}$ becoming negative, appear correspond to ε_{vv}^{yield} (see Table 2). No local instability occurred prior to this strain level. However, for simple tensile deformations, and for all values of L/Hconsidered here, a group of atoms in each of the eight corners of the sample become unstable at an average axial strain of $\sim 6\%$ when curves in Fig. 11 exhibit the first discontinuity. The minimum eigenvalue remains negative and continuously decreases up to \sim 8% average axial strain when the minimum magnitude of the negative eigenvalue drops noticeably; at this strain level the discontinuities in the average axial stress vs. the average axial strain curves also occur (cf. Fig. 6). Values of ε_{yy}^{vield} listed in Table 2 correspond to the initiation of the second sharp drop in the magnitude of the minimum eigenvalue of $H^{(i)}$. These local instabilities do not cause, on the average, permanent deformations since overall deformations are reversible as should be clear from results exhibited in Fig. 10.

For L/H = 10, Fig. 12 shows distributions of the minimum eigenvalue of $H^{(i)}$, the CNP parameter and ||G|| for the simple

Δu_x 0.002 0.001 0.001 0.001 0.000 -0.000 -0.001 -0.001 -0.001 -0.002 -0.002

> Δu, 0.045 0.037 0.029 0.020 0.012 0.004 -0.004 -0.029 -0.029 -0.037 -0.045

Δu_z 0.002 0.002 0.001 0.001



Fig. 15a. For the simple tension test, distributions of the changes in the components of the displacement field on the bounding surfaces at ε = 8.08% in the specimen with L/H = 10; (a) Δu_x ; (b) Δu_y ; (c) Δu_z (displacements in Å).

compression at $\varepsilon = \varepsilon_{yy}^{yield}$ and at ε slightly greater than ε_{yy}^{yield} . Negative eigenvalues of $\mathbf{H}^{(i)}$ occur at points located in planes {1, 1, 1} of high atomic density. The unstable atoms are not distributed symmetrically about the mid-section, Y = L/2, of the specimen (see Fig. 12b) possibly due to the asymmetry in the boundary conditions applied to the end faces and numerical truncation errors. Whereas atoms on one face are kept stationary, those on the other end face are displaced axially. Fig. 12d displays the distribution of the CNP at ε slightly greater than ε_{yy}^{yield} . The CNP equals either zero or has very small values at stable points but has large values at generally the same interior atomic positions where the local instability was predicted by the negative eigenvalues of $\mathbf{H}^{(i)}$. At $\varepsilon = \varepsilon_{yy}^{yield}$ values of the CNP parameter are negligible everywhere except at some points located on the bounding surfaces.

Fig. 12e and f exhibits the distribution of ||G|| at ε slightly higher than ε_{yy}^{yield} . High values of ||G|| occur at points close to the lateral surfaces and at points located near the end faces where displacements are prescribed. Values of ||G|| vanish at points in the interior of the specimen whose distance from the end faces exceeds ~37 Å,

i.e., the width of the sample. For $\varepsilon > \varepsilon_{yy}^{yield}$ high values of ||G|| occur at the same atomic positions where the minimum eigenvalue of $H^{(i)}$ is negative (cf. Fig. 12f) implying that deformations are highly inhomogeneous in the neighborhoods of atoms that have become unstable.

The sudden appearance of instabilities during an incremental axial strain of 0.01% suggests that either none of the three criteria used to characterize instability is robust enough to detect a gradual progression to an unstable state or the output time interval should have been considerably reduced. The latter option requires running the simulations several times with output at successively smaller intervals in order not to exceed the memory allocation in the computer. However, it has not been followed since for practical purposes instability strain within 0.01% is reasonably accurate.

Fig. 13 depicts, for L/H = 10, distributions of the minimum eigenvalue of $H^{(i)}$, the CNP and ||G|| for simple tensile deformations. At ε slightly less than ε_{yy}^{yield} there are very few atoms near the eight vertices of the specimen that have become unstable. However, at ε just greater than ε_{yy}^{yield} , several atoms have become unstable. The



Fig. 15b. For the simple tension test, distributions of the changes in the components of the displacement field at points where instabilities have initiated at ε = 8.15% in the specimen with L/H = 10; (a) Δu_x ; (b) Δu_y ; (c) Δu_z (displacements in Å).

distribution of unstable points has a serrated pattern along specimen's Y-centroidal line formed by atoms located on planes of high atomic density. The instabilities under compression and simple compression do not propagate through all of the specimen length. A similar serrated pattern was reported by Liang and Zhou [46] who performed MD simulations of tensile deformations of Cu nanowires at 300 K with specimens having the same crystallographic orientations as in the present work.

The distribution of unstable points predicted by the non-vanishing values of the CNP also coincides with that predicted by the minimum eigenvalue of the local Hessian (see Figs. 13b and 13d) becoming negative. The distribution of $||\mathbf{G}||$ depicted in Fig. 13e shows patterns symmetric with respect to the *Y*-centroidal line of the specimen. At $\varepsilon = \varepsilon_{yy}^{yield}$ values of $||\mathbf{G}||$ increase from almost zero at the centroidal line of the specimen to ~0.07 at atoms located on the traction free lateral surfaces. The regions of high values of $||\mathbf{G}||$ located at points close to the end faces of the specimen observed in compression and simple compression are not present in specimens deformed in tension. At $\varepsilon = \varepsilon_{yy}^{vield}$ high values of $\|\mathbf{G}\|$ occur at numerous points where the minimum eigenvalue of $\mathbf{H}^{(i)}$ is negative.

3.2.2. Tension/compression

Fig. 14 depicts, for L/H = 10, distributions of the minimum eigenvalue of $H^{(i)}$, the CNP parameter and ||G|| for the compressive deformations. The distributions of unstable points predicted by the minimum eigenvalue of $H^{(i)}$ becoming negative differ from those observed for simple compressive deformations shown in Fig. 13b. Similarly, the distribution of points in Figs. 14e and 12e with high values of ||G|| at $\varepsilon = \varepsilon_{yy}^{vield}$ for compression and simple compression are quite different. We recall that the only difference between the compressive and the simple compressive simulations is in the boundary conditions at the two end faces. Park et al. [47] performed MD simulations of tensile and compressive deformations of Au, Cu and Ni nanowires with different crystallographic orientations. However, their results cannot be compared with the present ones because of inertia effects included in [47].



Fig. 16a. For the simple compression test, distributions of the changes in the components of the displacement field on the bounding surfaces at $\varepsilon = -5.15\%$; (a) Δu_x ; (b) Δu_y ; (c) Δu_z (displacements in Å).

3.3. Displacements of atoms during instabilities

For simulations of the simple tension and the simple compression deformations of the sample with L/H = 10, we have plotted in Figs. 15a,b and 16a,b incremental displacements in going from the configuration just prior to the system yielding to the configuration in which it yields, and incremental displacements in going from the just yielded state to the immediately next configuration. In order to clearly show results incremental displacements of only unstable atoms are shown in Figs. 15b and 16b. Before yielding initiates displacements of atoms in the transverse directions equal nearly one-tenth of that (0.25 A) in the axial direction. However, in going from the just prior to the yielded state to the one just after vielding, several atoms that have become unstable undergo displacements in all three directions whose magnitude is of the order of the lattice parameter, i.e., 2 Å. Atoms with large X-incremental displacements are located on planes different from those with large Y-incremental displacements, and these two planes do not pass through the same material point. One can find the slip vector introduced by Zimmerman et al. [18] to deduce information on Burger's vectors and dislocations. The slip vector for an atom iequals the average of relative displacements of atom i with respect to those of its nearest neighbors; see Ref. [18] for details. It is clear that different groups of atoms are displaced significantly during yielding in simple tension and in simple compression. In simple tension, planes of unstable atoms are distributed along the entire length of the specimen, but in simple compression these planes are concentrated near the middle of the specimen.

3.4. Global instabilities

3.4.1. Tension/compression

Fig. 17a exhibits the variation with the average axial strain of the strain energy density. The σ_{yy} vs. ε curves show discontinuities at the same strain level where the energy density for the entire system decreases noticeably. The variation with ε of the strain energy density of the specimen with L/H = 1 is different from that for specimens with $L/H \ge 3$.



Fig. 16b. For the simple compression test, distributions of the changes in the components of the displacement field at points where instabilities have initiated at $\varepsilon = -5.16\%$; (a) Δu_x ; (b) Δu_y ; (c) Δu_z (displacements in Å).



Fig. 17a. Variation with the average axial strain ε of the strain energy density in tension/compression tests.



Fig. 17b. Variation with the average axial strain ε of the strain energy density in simple tension/compression tests.

3.4.2. Simple tension/compression

Results exhibited in Fig. 17b reveal that the variation with the average axial strain of the strain energy density for $3 \le L/H \le 20$ is essentially independent of the aspect ratio L/H in tension but not in compression. The average axial strain when the system becomes globally unstable in simple compression depends strongly upon the value of L/H. We note that in [48,49] the drop in the potential energy of a carbon nanotube for an infinitesimal increase in the incremental axial displacement is taken as the criterion for the tube to buckle.

4. Conclusions

We have used molecular mechanics simulations with the tightbinding potential to study local and global instabilities in initially defect-free nanospecimens of gold deformed in tension/compression, and simple tension/compression. The criteria used to delineate local instabilities are: (i) a component of second-order spatial partial derivatives of the displacement field having large values relative to its average value in the body, (ii) the minimum eigenvalue of the Hessian of the potential energy of an atom becoming non-positive, and (iii) a high value of the common neighborhood parameter. The system's configuration is said to be globally unstable when its potential energy density changes significantly with an infinitesimal increase in the average axial strain.

Conclusions from this work are:

- The three criteria for the initiation of a local instability are met essentially simultaneously at the same atomic positions.
- The average values of the Cauchy stresses derived from different definitions of the Cauchy stress tensor agree well with each other.
- The response of a specimen in tension and compression is very different. This can be attributed to the presence of non-uniformly distributed stresses in the reference configuration.
- Boundary conditions at the end faces affect the response of a specimen even when its aspect ratio is large.
- For specimens deformed in either tension or simple tension, the average axial strain at the initiation of local instabilities is noticeably less than that when the specimen yields or that when it becomes globally unstable.
- Atoms on the end faces do not become unstable. Furthermore, atoms that become unstable are located away from the end faces where essential boundary conditions are imposed.
- The average axial stress vs. the average axial strain curve up to the yield point is non-linear but deformations are elastic in the sense that the curve is reproduced during unloading. However, after the specimen has yielded (or has become globally unstable) there is a permanent axial strain induced in the specimen (~4.5% for L/H = 10). The slope of the average axial stress vs. the average axial strain curve during unloading is the same as that of the curve during loading.
- The average axial stress at yield in compression (or simple compression) is considerably less than that in tension (or simple tension).
- The local instabilities do not induce, on the average, plastic deformations and the average axial stress vs. the average axial strain curve is reproduced during unloading.

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References

- [1] J. Diao, K. Gall, M.L. Dunn, J. Mech. Phys. Solids 52 (2004) 1935-1962.
- [2] W. Zhang, T. Wang, X. Chen, J. Appl. Phys. 103 (2008) 123527.
- [3] M.I. Baskes, Phys. Rev. B 46 (1992) 2727-2742.
- [4] K. Gall, J. Diao, M.L. Dunn, Nano Lett. 4 (2004) 2431-2436.
- [5] J. Diao, K. Gall, M.L. Dunn, J.A. Zimmerman, Acta Mater. 54 (2006) 643-653.
- [6] Y. Liu, E. Van der Giessen, A. Needleman, Int. J. Solids Struct. 44 (2007) 1719– 1732.
- [7] R.E. Miller, D. Rodney, J. Mech. Phys. Solids 56 (2008) 1203-1223.
- [8] C. Truesdell, W. Noll, The Non-Linear Field Theories of Mechanics, second ed.,
- Springer-Verlag, 1992.
- [9] R. Hill, J. Mech. Phys. Solids 10 (1962) 1-16.
- [10] K.J. Van Vliet, J. Li, T. Zhu, S. Yip, S. Suresh, Phys. Rev. B 67 (2003) 104105.
- [11] P. Steinmann, A. Elizondo, R. Zunyk, Modell. Simul. Mater. Sci. Eng. 15 (2007) S271-S281.
- [12] J. Lu, L. Zhang, J. Mech. Mater. Strut. 1 (2006) 633-648.
- [13] T. Kitamura, Y. Umeno, N. Tsuji, Comput. Mater. Sci. 29 (2004) 499-510.

- [14] T. Kitamura, Y. Umeno, R. Fushino, Mater. Sci. Eng. A 379 (2004) 229–233.
- [15] S.V. Dimitriev, T. Kitamura, J. Li, Y. Umeno, K. Yashiro, N. Yoshikawa, Acta Mater. 53 (2005) 1215–1224.
- [16] A.A. Pacheco, R.C. Batra, J. Mech. Phys. Solids 56 (2008) 3116-3143.
- [17] C. Kelchner, S. Plimpton, J. Hamilton, Phys. Rev. B 58 (1998) 11085-11088.
- [18] J.A. Zimmerman, C.L. Kelchner, P.A. Klein, J.C. Hamilton, S.M. Foiles, Phys. Rev. Lett. 87 (2001) 165507.
- [19] Q.K. Li, M. Li, Appl. Phys. Lett. 88 (2006) 241903.
- [20] H. Tsuzuki, P.S. Branicio, J.P. Rino, Comput. Phys. Commun. 177 (2007) 518-523.
 [21] R. Pasianot, Z.Y. Xie, D. Farkas, E.J. Savino, Scr. Metall. Mater. 28 (1993) 319-324.
- [22] C.S. Hartley, Y. Mishin, Mater. Sci. Eng. A 400-401 (2005) 18-21.
- [23] G.M. Zhang, R.C. Batra, Comput. Mech. 34 (2004) 137-146.
- [24] R.J. Hardy, J. Chem. Phys. 76 (1981) 622-628.
- [25] M.W. Finnis, J.E. Sinclair, Philos. Mag. A 50 (1984) 45-55.
- [26] M.I. Baskes, M.S. Daw, Phys. Rev. B 29 (1984) 6443-6453.
- [27] F. Voter, S.P. Chen, in: R.W. Siegel, J.R. Weertman, R. Sinclair (Eds.), Mater. Res. Soc. Symp. Proc., vol. 82, Materials Research Society, Pittsburgh, 1987, p. 175.
- [28] K.W. Jacobsen, J.K. Norskov, M.J. Puska, Phys. Rev. B 35 (1987) 7423-7442.
- [29] F. Ercolessi, M. Parrinello, E. Tosatti, Philos. Mag. A 58 (1988) 213-226.
- [30] F. Cleri, V. Rosato, Phys. Rev. B 48 (1993) 22-33;
- S.P. Ju, J.S. Lin, W.J. Lee, Nanotechnology 15 (2004) 1221-1225.
- [31] W.J. Lee, S.P. Ju, S.J. Sun, M.H. Weng, Nanotechnology 17 (2006) 3253-3258.
- [32] J.S. Lin, S.P. Ju, W.J. Lee, Phys. Rev. B 72 (2005) 085448.

- [33] Q. Pu, Y. Leng, L. Tsetseris, H.S. Park, S.T. Pantelides, P.T. Cummings, J. Chem. Phys. 126 (2007) 144707.
- [34] G. Rubio-Bollinger, S.R. Bahn, N. Agrair, K.W. Jacobsen, S. Vieira, Phys. Rev. Lett. 87 (2001) 026101.
- [35] S. Root, R.J. Hardy, D.R. Swanson, J. Chem. Phys. 118 (2003) 3161-3165.
- [36] J.A. Zimmerman, E.B. Webb, J.J. Hoyt, R.E. Jones, P.A. Klein, D.J. Bammann, Modell. Simul. Mater. Sci. Eng. 12 (2004) S319–S332.
- [37] P.H. Mott, A.S. Argon, U.W. Suter, J. Comput. Phys. 101 (1992) 140-150.
- [38] M.L. Falk, Phys. Rev. B 60 (1999) 7062-7070.
- [39] J.A. Zimmerman, D.J. Bammann, H. Gao, Int. J. Solids Struct. 46 (2009) 238–253.
- [40] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Oxford, Clarendon, 1954.
- [41] J.L. Ericksen, Math. Mech. Solids 13 (2008) 199-220.
- [42] I. Stakgold, Quart. Appl. Math. 8 (1950) 169-186.
- [43] V. Kouznetsova, M.G.D. Geers, W.A.M. Brekelmans, Int. J. Numer. Methods Eng. 54 (2002) 1235–1260.
- [44] G.P. Potirniche, M.F. Horstemeyer, G.J. Wagner, P.M. Gullett, Int. J. Plast. 22 (2006) 257–278.
- [45] W.W. Hager, H. Zhang, SIAM J. Opt. 16 (2005) 170-192.
- [46] W. Liang, M. Zhou, Proc. Inst. Mech. Eng., Part C: J. Mech. Eng. Sci. 218 (2004) 599-606.
- [47] H.S. Park, K. Gall, J.A. Zimmerman, J. Mech. Phys. Solids 54 (2006) 1862-1881.
- [48] A. Sears, R.C. Batra, Phys. Rev. B 69 (2004) 235406.
- [49] A. Sears, R.C. Batra, Phys. Rev. B 73 (2006) 085410.