Are surfaces elastically softer or stiffer?

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This letter addresses the issue of surface softening versus stiffening during elastic deformation. Using a combination of molecular statics and *ab initio* calculations, we show that a solid surface can be either softer or stiffer elastically than the corresponding bulk. Whether a particular surface is softer or stiffer depends on the competition between atomic coordination and electron redistribution (which sometimes is referred as bond saturation) on the surface. Taking Cu as an example, we demonstrate that the Young's modulus along $\langle 110 \rangle$ direction on $\{100\}$ surface is larger than its bulk counterpart; meanwhile, it is smaller along $\langle 100 \rangle$ direction on $\{100\}$ surface. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1682698]

Elastic constants near surfaces are different from their values in the bulk of solids. Usually, this difference is unessential for solids of macroscopic dimensions. In nanostructures, on the other hand, surface to volume ratio is large and this difference is pivotally important. Accompanying the emergence of nanotechnology, research effort has been focused on nanotubes. Understandably, much less effort has been on nanoplates and nanobeams (or nanorods), because of the difficulty in fabricating these structures.[1] However, it is eventually unavoidable that nanoplates and nanobeams will be present in various nanotechnologies. Mechanics, both statics and dynamics, in nanoplates and nanobeams can be different from that in their macro-counterparts. Some experiments show that surfaces are softer,[2] while others stiffer.[3] In contrast to the experimental investigations, simulations based on pair potentials consistently show that surfaces of plates are softer. Using harmonic potentials, Sun and Zhang conclude that the Young's modulus of nanoplates is only two-thirds of the corresponding bulk value,[4] indicating that the surface is softer. In a similar study based on Lennard-Jones potential, Van Workum and Pablo[5] arrive at the same conclusion. In an attempt to represent surface elastic properties in the continuum mechanics framework, Miller and Shenoy[6] show that effective elastic constants of a nanoplate approximately vary with the inverse of its thickness. They use atomistic simulations to confirm this dependence and to determine the proportionality constant. The simulation results indicate the possibilities of both surface softening and stiffening. But they give no account to the issue of when a surface may be elastically softer or stiffer. Another issue may be even more important—what is the physical reason for the softening and the stiffening?

In this letter, we address these two issues by using a combination of molecular statics and *ab initio* calculations. In the molecular statics calculations, we use Lennard-Jones[7] and embedded atom method (EAM) potentials[8] to describe the atomic interactions in the prototype materials, Cu. These potentials represent pair and many-body interactions, respec-

tively. The Lennard-Jones parameters in its 6-12 form are fit to the cohesive energy and lattice constant of Cu, and they are $\varepsilon = 0.2399$ eV, $\sigma = 0.2363$ nm. A sinusoidal function is multiplied[9] to the Lennard-Jones potential form so the cutoff distance is between the third and the fourth nearest neighbors in Cu (that is 0.477 nm). The EAM potential for Cu is developed by Mishin *et al.*,[10] and is transferable for a variety of structures including surfaces.[11] A typical simulation cell of nanoplates is shown in Fig. 1(a). Periodic boundary conditions are applied along the two horizontal $\langle 110 \rangle$ directions. Several atomic layers are removed along the vertical $\langle 100 \rangle$ direction to create a vacuum region so that the top and the bottom of the simulation cell represent two flat free surfaces. For a given vertical thickness, the simulation cell is fully relaxed to the local energy minimum. Along the two horizontal directions, we apply normal strains in the range of $[-1\%, 1\%]$. This strain range is meshed into 20×20 points. At each meshing point, all atoms are allowed to relax to the minimum energy corresponding to the horizontal strains; this is facilitated by the two free surfaces. For each strain along x direction, there is an energy minimum corresponding to a particular strain along y direction. The energy minimum as a function of strain along x is shown in Fig. 1(b). The corresponding energy–strain relationship $E(\varepsilon_x)$ gives the Young's modulus according to: $Y = (1/\Omega)[d^2 E(\varepsilon_x)/d\varepsilon_x^2]$. There is little ambiguity about second-order derivative of the energy with respect to strain ε_x at equilibrium position. However, the definition of nanoplate volume Ω deserves elaboration. As shown in Fig. 1(a), $\Omega = L_x L_y L_z$. The dimensions L_x and L_y refer to the horizontal dimensions of the simulation cell under no strain. Because of the free surfaces, a convention is necessary to define L_z.[12] We follow the convention that two neighboring layers equally share the space in between, and that the outmost layer has equal spacing from below and from above. The variation of layer spacing is only 4% of the bulk value. In contrast, the results of elastic constants are based on variations of several tens of percent, and the conclusions are therefore independent of the convention. Based on this convention, the Young's modulus can be calculated. Further, the Poisson's ratios along y as well as z directions are calculated and shown in the inset of Fig. 1(b). It is inter-

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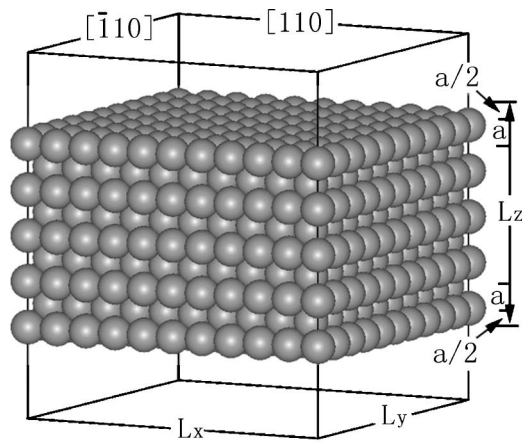
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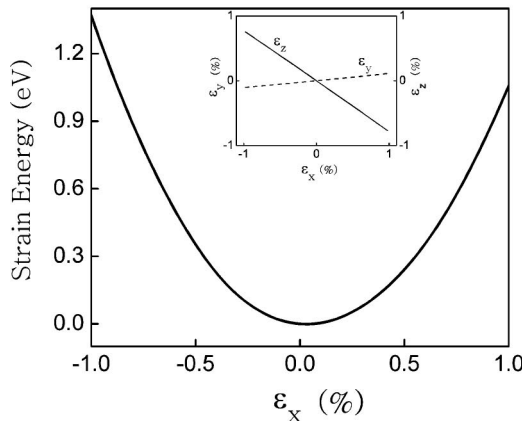
(b)

FIG. 1. (a) Schematic of simulation cell, and (b) the energy–strain curve $E(\varepsilon_x)$ based on the EAM potential; the inset shows strains along the other two directions, corresponding to Poisson's ratios of -0.11 along y and 0.78 along z.

esting that the x and y dimensions shrink and expand simultaneously, corresponding to a negative Poisson's ratio; this is a result of large relaxation along the z direction.

The calculated Young's modulus as a function of plate thickness is shown in Fig. 2. When only pair interactions are taken into account, the Young's modulus decreases as the plate becomes thinner; or the surface is softer, in agreement with previous studies using pair potentials.[4,5] In contrast,
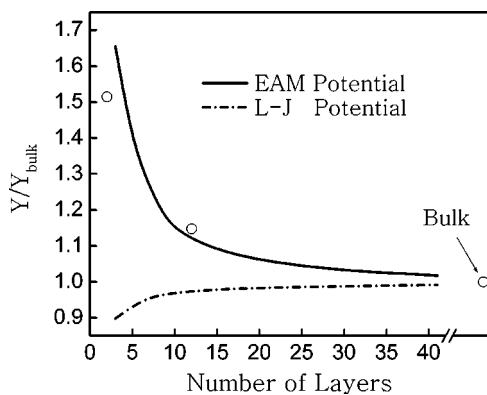

FIG. 2. Young's modulus as a function of thickness of the nanoplate based on EAM (solid line) and Lennard-Jones (dash dot line) potentials. The three circles represent *ab initio* results. The Young's modulus is normalized with respective to its bulk value.
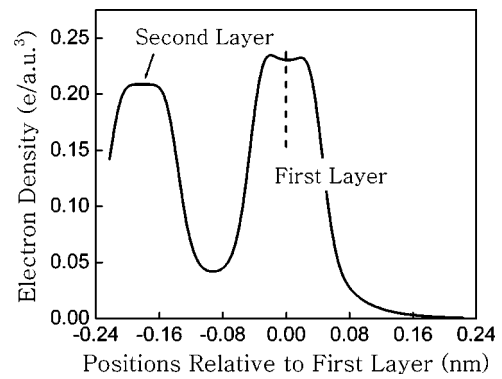

FIG. 3. Distribution of average electron density near the two surface layers in a 12-layer simulation cell.

when many-body interactions are also included as in the EAM potential, the Young's modulus increases as the nanoplate becomes thinner; or the surface is stiffer. This stiff phenomenon is in contrast to previous reports of nanoplates, and might appear counterintuitive as well. It is somewhat too simplistic to negate the calculations using pair potentials because of the simple form of the potential function. Rather, it is desirable to confirm this stiffening phenomenon and to understand why it happens.

The *ab initio* calculations provide an ideal tool for deeper insights. Using a similar setup of simulation cell while keeping the dimensions along x and y directions to be one lattice period, we calculate the Young's modulus for three different thicknesses of the plate: 2 layers, 12 layers, and infinite number of layers—that is bulk crystal. The calculations are based on the density functional theory, with the Perdew–Burke–Ernzerhof generalized gradient approximation[13] for the exchange–correlation potential. The electron–ion interaction is represented by an ultrasoft pseudopotential.[14] Monkhorst–Pack k-points sampling[15] is adopted for integrating over the Brillouin zones. The kinetic energy cutoff is 40 Ry in the wave function expansion using the plane wave basis set. Test calculations give the equilibrium lattice constant of Cu as $a = 0.367$ nm, in agreement with 0.362 nm from experiment.[16] The cohesive energy is found to be 3.49 eV, also in agreement with 3.54 eV from experiment.[17] For supercells of 2-layer, 12-layer, and bulk, the k space is meshed into $12 \times 12 \times 2$, $12 \times 12 \times 1$, and $12 \times 12 \times 8$ points, respectively. Convergence for each case is ensured through numerical testing. The atoms and the geometry of supercell are relaxed according to the Hellmann–Feynman forces and stresses.[18] Similar to the above-described molecular statics calculations, the *ab initio* calculations give an energy–strain relationship $E(\varepsilon_x)$; the second-order derivative in turn gives the Young's modulus. The *ab initio* results, as shown in Fig. 2, confirm that the surface is stiffer. Further, the electron density distribution, in Fig. 3, shows that electron density on the surface layer is higher. This electron redistribution gives rise to stronger bonding on the surface, and the surface stiffening effects.

To show whether the stiffening effects always dominate, we repeat the calculations for loading along $\langle 100 \rangle$ on $\{100\}$ surface and along $\langle 110 \rangle$ on $\{111\}$ surface; these are close-packed directions and close-packed surfaces. As shown in Fig. 4(a), when many-body interactions are taken into ac-
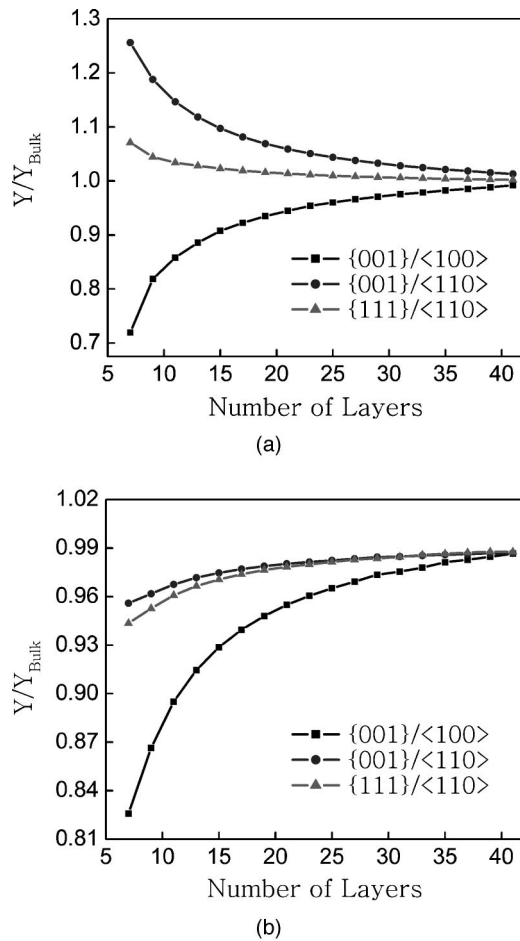
FIG. 4. Young's modulus as a function of thickness of the nanoplate based on (a) EAM and (b) Lennard-Jones potentials, for various surface/loading-direction combinations.

sume each atom interacts with its nearest neighbors only through elastic springs. Based on this simplified picture, the surface stiffness constant—defined as force over displacement—along $\langle 110 \rangle$ is 90% of its bulk value, and along $\langle 100 \rangle$ only 75%. The difference of the two softening effects is a result of different number and deformation of springs in the two loading directions. When the electron redistribution suffices to compensate for this reduction, the surface behaves stiffer; otherwise, the surface behaves softer, as shown in Fig. 4.

In summary, using a combination of molecular statics and *ab initio* calculations, we conclude that a surface may be softer or stiffer (or, equivalently a nanoplate can be softer or stiffer) than the corresponding bulk. The overall softening or stiffening depends on the competition between electron redistribution and the lower coordination on surfaces. Both the softening and stiffening effects will have major impacts on the mechanics of nanoplates.

count through the use of the EAM potential, both softening and stiffening are possible. On the other hand, when the many-body effects are absent [Fig. 4(b)], only softening is possible; in other words, surfaces are always softer. This comparison shows that the electron redistribution is not always sufficient to ensure surface stiffening. The softening factor competing against the electron redistribution effect is the atomic coordination. On surfaces, atomic coordination is low, and they tend to be softer. But the degree of this softening depends on the surface orientation and the loading direction. To demonstrate the different degrees of softening, consider {100} surfaces of Cu for different loading directions, $\langle 110 \rangle$ and $\langle 100 \rangle$. For simplicity of argument, we as-

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