Surface deformation-dependent mechanical properties of bending nanowires: an ab initio core-shell model*

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Abstract An ab initio core-shell model is proposed to evaluate the surface effect in bending nanowires, in which the elastic modulus depends on the surface relaxation and deformation induced by external loading. By using first-principles calculations based on the density functional theory (DFT), the surface and bulk properties are calculated for Ag, Pb, and Si nanowires. The obtained theoretical predictions of the effective Young's modulus of nanowires agree well with the experimental data, which shows that the fixed-fixed nanowire is stiffened and the cantilevered nanowire is softened as the characteristic size of the cross section decreases. Furthermore, the contrastive analysis on the two kinds of nanowires demonstrates that increasing the nanowire aspect ratio would enhance the surface effect. The present results could be helpful for understanding the size effect in nanowires and designing nanobeam-based devices in nanoelectromechanical systems (NEMSs).

Key words surface effect, density functional theory (DFT), surface relaxation, surface stress, nanowire

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1 Introduction

As one of the most promising one-dimensional (1D) nano-sized materials, nanowires have attracted great interests due to their wide applications in miniature devices, e.g., sensors, actuators, transistors, probes, and resonators in nanoelectromechanical systems (NEMSs) and

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bio-technology^[1–7]. Similar to other nanomaterials, the mechanical properties of nanowires exhibit significant size-dependence, owing to the surface effect induced by a large surface-to-volume ratio^[8–10].

The surface effect has become a hotspot for nano-scaled bars and beams in NEMSs. By means of atomic force microscopy, the mechanical behaviors of nanowires with different boundary conditions have been revealed experimentally. Cuenot et al.^[11] firstly found that the elastic modulus of the Pd fixed-fixed nanowire increased with the decrease in its cross section diameter. Afterwards, similar experimental phenomena were observed in Ag^[12], CuO^[13], and Ni^[14] nanowires. At the same time, an oppositely size-dependent behavior of the elastic modulus was found for GaN^[15], Ag^[16], and Si^[17–18] cantilever nanowires. However, the classical elasticity theory is invalid to clarify the physical mechanism of the aforementioned interesting mechanical properties of nanowires. Therefore, it is necessary to propose a concise theoretical model to predict the bending response of nanowires.

The surface elasticity theory proposed by Gurtin and Murdoch^[19–20] has been widely adopted to develop elastic models for describing the surface effect in nanowires. Steigmann and Ogden^[21], Chhapadia et al.^[22], and Chiu and Chen^[23] improved the Gurtin-Murdoch (G-M) model by considering the surface flexural stiffness to analyze the relations between the surface effect and the bending nanowire curvature. Wang and Feng^[24] introduced a generalized Young-Laplace (Y-L) equation into the G-M model to characterize the surface effect induced by the surface stress on static bending nanowires. He and Lilley^[25] modified the above Y-L model to evaluate the surface effect on the dynamic bending of nanowires. Song et al.^[26] extended the Y-L model by considering the in-plane surface stress tangential to the cross section of the nanowire. Li et al.^[27] used the Y-L model to predict the surface effect in Timochenko nanobeams.

The most striking feature of the G-M theory is that the surface layer without thickness is described by a linearized constitutive law, in which the surface stress-strain relation is similar to the classical Hooke's law. Many surface elastic constants are created to describe the surface performance. In contrast to the G-M framework, Nix and Gao^[28] proved the nonlinear surface constitutive relation by an atomic interpretation. Sun et al.^[29–30] and Ou-Yang et al.^[31] further investigated the influence of surface strain on the surface elastic modulus of nanowires. Meanwhile, Diao et al.^[32] and Lee and Rudd^[33] revealed the relations between the bulk elastic modulus and the surface stress in nanowires by molecular dynamics (MD) simulations. Therefore, it is of great significance to quantitatively evaluate the effects of surface stress and strain on the elastic modulus of nanowires.

To investigate the mechanical mechanism of surface effects on the surface and bulk elastic moduli of nanowires, we propose an *ab initio* core-shell model for a nanowire consisting of a surface layer with an infinitesimal thickness and a core part (bulk material) based on the density functional theory (DFT). The model focuses on the dependence of surface deformation on the surface and bulk Young's moduli of the nanowire. It is well-known that the surface residual strain induced by the surface relaxation leads to alignment of atoms in the surface. The misfit dislocation of atoms between the surface and bulk of the nanowire would enhance the surface stress. Based on the potential energy principle, we further explore how the surface stress and strain induced by surface deformation affect Young's modulus of the nanowire. The obtained theoretical predictions of the mechanical behaviors of typical metallic and metalloid nanowires agree well with existing numerical results and experimental data. These findings provide insights into the fundamental physical mechanisms of stiffening and softening nanowires subjected to the concentrated force, and lay the ground for the optimal design in nanobeam-based devices of NEMSs.

2 Methodology

Because of the large surface-to-volume ratio, the effect of the nanowire surface phase becomes greater as the nanowire size decreases. The potential energy of a nanowire can be divided into

two parts, i.e., surface strain energy and bulk strain energy. Therefore, our nanowire model is regarded as a beam of a length L , including a core (bulk material) and a shell (surface layer). The shell component is coaxial with the core, and has an infinitesimal thickness t . The cross section of the nanowire can be rectangular with a height h and a width b ($b \geq t$) or circular with a diameter d (see Fig. 1) ($t \ll d$ or h). Then, the total potential energy function of such a nanowire is expressed as

$$U = U_c + U_s = S_c L \Phi(\varepsilon) + C_s L \gamma(\varepsilon), \quad (1)$$

where $\Phi(\varepsilon)$ and $\gamma(\varepsilon)$ represent the strain energy densities of the bulk material and the surface material, respectively. S_c is the cross-section area of the core, and C_s is the cross-sectional perimeter of the outermost layer in the surface.

Fig. 1 Ab initio core-shell model of nanowires: (a) cantilever nanowire; (b) fixed-fixed nanowire; (c) cross sections of the two kinds of nanowires; (d) and (e) schematic diagrams of supercells for surface relaxation of nanowires in the DFT (color online)

2.1 Effect of surface strain on the bulk elastic modulus

Assume that the nanowire has an idealized crystal structure. Then, we can define the surface residual strain induced by the surface relaxation as follows^[28,34]:

$$\varepsilon_r = \frac{a_r - a_0}{a_0} = \lambda - 1, \quad (2)$$

where a_0 and a_r denote the atomic spacings in the nanowire before and after surface relaxation, respectively. λ is the surface relaxation parameter.

As we know, the equilibrium configuration of a material usually corresponds to the lowest energy with zero-strain of the crystal lattices. Nevertheless, the lattice parameters of the surface layer accompanied with the lowest energy state tend to be different from those of the

bulk material due to the diverse of atomic arrangement in the surface and bulk crystals. Then, the bulk energy density $\Phi(\varepsilon)$ and the surface energy density $\gamma(\varepsilon)$ are expressed as

$$\Phi(\varepsilon) = \Phi_0 + \frac{1}{2}E_b\varepsilon^2, \quad (3a)$$

$$\gamma(\varepsilon) = \gamma_0 + \frac{1}{2}E_s(\varepsilon - \varepsilon_r)^2, \quad (3b)$$

where Φ_0 and γ_0 denote the lowest strain energy densities of the bulk material and the surface material, respectively. E_b and E_s represent the bulk Young's modulus and the surface layer Young's modulus, respectively. ε is the strain with respect to the equilibrium crystal lattice.

Substituting Eqs. 3(a) and 3(b) into Eq. (1) and employing the minimum potential energy principle ($\frac{\partial U}{\partial \varepsilon} = 0$) yield the following equilibrium strain ε^* of the undeformed nanowire by considering the effect of surface relaxation:

$$\varepsilon^* = \frac{\varepsilon_r}{\frac{S_c}{C_s} \frac{E_b}{E_s} + 1}. \quad (4)$$

Based on Sun's atomic model including bond order, bond length, and bond strength^[29–30], the modulus change ΔE induced by bond contraction or expansion can be expressed by $\Delta E/E_b = \lambda^{-m} - 3\lambda + 2$. Through mathematical derivations, the effective Young's modulus of the surface layer in the surface relaxation state $E_s^r (= \Delta E + E_b)$ is written as

$$E_s^r = E_b \left(\left(\frac{a_r}{a_0} \right)^{-m} - 3 \left(\frac{a_r}{a_0} \right) + 3 \right) = E_b (\lambda^{-m} - 3\lambda + 3), \quad (5)$$

where m is a parameter describing the dependence of bond length on the binding energy. $m = 4$ is for alloys or compounds, and $m = 1$ is for pure metals. Combining Eqs. (2), (4), and (5) yields

$$\varepsilon^* = \frac{\lambda - 1}{\frac{1}{\lambda^{-m} - 3\lambda + 3} \frac{S_c}{C_s} + 1}. \quad (6)$$

Then, the equilibrium strain is characterized as a function of the surface relaxation parameter λ and the characteristic size of the nanowire. The existence of this equilibrium strain ε^* has been revealed in previous literatures^[32–33], where ε^* is calculated by MD simulations.

Consider a nanowire with the initial configuration prior to surface relaxation. Then, the equilibrium strain ε^* rebalances as the intermediate configuration, and the length $L_r = (1 + \varepsilon^*)L$. If the nanowire is deformed from the equilibrium configuration by the strain ε_L under external loading, $\Delta L = \varepsilon_L L_r = (\varepsilon - \varepsilon^*)L$, where

$$\varepsilon_L = \frac{\varepsilon - \varepsilon^*}{1 + \varepsilon^*}. \quad (7)$$

Substituting Eq. (7) into Eq. (3a) yields the bulk energy density as follows:

$$\Phi(\varepsilon) = \Phi_0 + \frac{1}{2}E_b((1 + \varepsilon^*)^2\varepsilon_L^2 + 2\varepsilon^*(1 + \varepsilon^*)\varepsilon_L + (\varepsilon^*)^2).$$

Therefore, the effective Young's modulus contributed from the nanowire core is expressed as

$$E_{\text{eff}}^c = \frac{\partial^2 \Phi}{\partial \varepsilon_L^2} = (1 + \varepsilon^*)^2 E_b. \quad (8)$$

2.2 Effect of surface stress on the surface elastic modulus

The surface stress can be defined as an excess of the bulk stress in the nanomaterial near the surface, which is essentially induced by the difference between the properties of the nanomaterial near the surface and the nanomaterial away from the surface^[28]. According to the G-M theory, the relation between the surface stress and the strain of 1D nanomaterial in the axial direction is written as

$$\sigma = \sigma_0 + E_s \varepsilon, \quad (9)$$

where σ_0 is the surface residual stress, E_s is Young's modulus of the surface layer with surface deformation generated by the external force. The surface strain ε induced by the surface deformation can be represented as

$$\varepsilon = \frac{a - a_r}{a_r}, \quad (10)$$

where a is the surface atomic spacing related to the deformation, and ε is defined in the intermediate configuration after surface relaxation.

Since the variations of Young's moduli merely depend on the binding energy at the equilibrium bond length, and are independent of the particular form of the interatomic potential, the surface Young's modulus of the nanowire can be expressed as a function of the variation of the bond length induced by the surface deformation^[29–31,34] as follows:

$$\frac{E_s}{E_b} = \left(\frac{a}{a_0}\right)^{-m} - 3\frac{a}{a_0} + 3. \quad (11)$$

Performing mathematical derivations with $a_r = \lambda a_0$, we have $a = \lambda a_0(1 + \varepsilon)$, and

$$E_s = E_b((\lambda + \lambda\varepsilon)^{-m} - 3\lambda(1 + \varepsilon) + 3). \quad (12)$$

Substituting Eqs. (5), (12) and $\sigma_0 = E_s^r \varepsilon_r$ into Eq. (9) yields

$$\sigma = E_b(\lambda^{-m} - 3\lambda + 3)\varepsilon_r + E_b((\lambda + \lambda\varepsilon)^{-m} - 3\lambda(1 + \varepsilon) + 3)\varepsilon. \quad (13)$$

Therefore, the variable of surface energy can be written as

$$\Delta U_s = C_s(1 - \nu)\Delta L \cdot \sigma, \quad (14)$$

where ν is Poisson's ratio.

For a bending nanowire, the surface deformation ΔL is proportional to the square of the deflection under tangential loading or clamped-end three-point bending. Assume that a concentrated force F acts at the axial coordinate x_F . Then, we have^[11]

$$\Delta L = \int_0^{x_F} \left(\frac{\partial w(x)}{\partial x}\right)^2 dx, \quad (15)$$

where $w(x)$ is the bending deflection of the nanowire. In the case of a cantilever nanowire with F at $x = L$, the maximum deflection is $w_c^{\max} = FL^3/(3EI)$, and the function of the deflection curve is $w_c(x) = Fx^2(3L - x)/(6EI)$. In the case of F acting at the middle point of a fixed-fixed nanowire, the deflection equations are

$$w_c(x) = Fx^2(3L - 4x)/(48EI), \quad w_c^{\max} = FL^3/(192EI).$$

Hence, Eq. (15) can be rewritten as follows:

$$\Delta L = \begin{cases} \int_0^L \left(\frac{\partial w(x)}{\partial x} \right)^2 dx = \frac{6}{5} \frac{(w_c^{\max})^2}{L} & (\text{cantilever}), \\ \int_0^{L/2} \left(\frac{\partial w(x)}{\partial x} \right)^2 dx = \frac{12}{5} \frac{(w_f^{\max})^2}{L} & (\text{fixed-fixed}). \end{cases} \quad (16)$$

Then, a reaction force F_s in the bending nanowire induced by the surface stress is given by

$$F_s = -\frac{\partial U_s}{\partial w_{\max}} = \begin{cases} -\frac{12}{5} C_s (1-\nu) \frac{w_c^{\max}}{L} \cdot \sigma & (\text{cantilever}), \\ -\frac{24}{5} C_s (1-\nu) \frac{w_f^{\max}}{L} \cdot \sigma & (\text{fixed-fixed}). \end{cases} \quad (17)$$

Combined with $w_c^{\max} = FL^3/(3EI)$ and $w_f^{\max} = FL^3/(192EI)$, the effective Young's modulus contributed from the nanowire surface is expressed as

$$E_{\text{eff}}^s = \begin{cases} \frac{|F_s|}{w_c^{\max}} \frac{L^3}{3I} = \frac{4}{5} C_s (1-\nu) \frac{L^2}{I} \cdot \sigma & (\text{cantilever}), \\ \frac{|F_s|}{w_f^{\max}} \frac{L^3}{192I} = \frac{1}{40} C_s (1-\nu) \frac{L^2}{I} \cdot \sigma & (\text{fixed-fixed}), \end{cases} \quad (18)$$

where

$$I = \begin{cases} bh^3/12, & \text{rectangular cross section,} \\ \pi d^4/64, & \text{circular cross section.} \end{cases}$$

2.3 Effective elastic moduli of nanowires

Due to the coaxial structure of the surface layer material and the bulk material, the effective flexural rigidity of the core-shell model can be defined as

$$E_{\text{eff}} I = E_{\text{eff}}^c I_c + E_{\text{eff}}^s I_s. \quad (19)$$

Thus, the effective Young's modulus of a nanowire is written as

$$E_{\text{eff}} = \varphi E_{\text{eff}}^c + (1-\varphi) E_{\text{eff}}^s, \quad (20)$$

where

$$\varphi = I_c/I = \begin{cases} \left(1 - \frac{2t}{d}\right)^4 & (\text{circular}), \\ \left(1 - \frac{2t}{b}\right) \left(1 - \frac{2t}{h}\right)^3 & (\text{rectangular}). \end{cases} \quad (21)$$

Combining Eqs. (8), (19), and (20) yields

$$E_{\text{eff}} = \begin{cases} \varphi(1+\varepsilon^*)^2 E_b + (1-\varphi) \left(\frac{4}{5} (1-\nu) \frac{L^2}{I} \cdot \sigma \right) & (\text{cantilever}), \\ \varphi(1+\varepsilon^*)^2 E_b + (1-\varphi) \left(\frac{1}{40} (1-\nu) \frac{L^2}{I} \cdot \sigma \right) & (\text{fixed-fixed}). \end{cases} \quad (22)$$

With the increase in the characteristic size of the cross section (the diameter d for the circular cross section or the width b and height h for the rectangular cross section), the equilibrium strain

ε^* would approach zero according to Eq. (6). Therefore, E_{eff} in Eq. (22) will equal the bulk Young's modulus E_b when the characteristic size reaches the limit of the bulk material. From Eq. (22), it is noted that the effective Young's modulus of a nanowire depends not only on the characteristic size of the nanowire (e.g., the diameter d for the circular cross section or the width b and height h for the rectangular cross section) but also on the surface relaxation parameter and surface deformation relating to the loading boundary conditions, leading to the mechanical properties of the nanowire as those of nonlinear materials. The reason of this phenomenon could be interpreted as the nonlinear strain distribution induced by the atomic rearrangement of surface and external loading. As a rule, the surface relaxation of a nanomaterial will adjust the lattice length of atoms near the surface, which leads to a significant size effect in the nanomaterial owing to the large surface-to-volume ratio. Moreover, the surface stress induced by surface deformation will further stretch or compress the lattice length, while the bulk material is linearly elastic as the surface effect is weakened inside of the nanowire. When the characteristic size is small enough, the domination of the effective Young's modulus in Eq. (22) is the term referred to the surface stress, which obviously depends on the nonlinear strain distribution caused by the diverse loading boundary conditions on the surface. Therefore, the nonlinearly elastic properties of bending nanowires can be ascribed to the surface effect. In fact, similar conclusions have been revealed by MD simulations^[32,35–36], in which the numerical results of elastic moduli exhibit strong dependence upon the surface strains.

2.4 Determination of mechanical parameters by the DFT

As yet, the surface relaxation parameters of metals, alloys, and compounds are difficult to determine by experiments due to the spontaneous surface relaxation. Thus, many empirical formulas were adopted for the calculations^[32,37–38], in which a series of novel empirical coefficients were introduced into the theoretical model. To investigate the physical mechanism of surface relaxation, the first-principles method is used to predict the corresponding surface and bulk elastic constants.

The DFT calculations are conducted with the Vienna ab initio simulation package (VASP) based on a plane-wave-basis pseudo-potential method, in which the generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) function are introduced into the energy for exchange and correlation. In the present simulations, the total energy and residual force are converged to an accuracy of 10^{-5} eV and 10^{-1} eV/nm, respectively, while the energy cutoff is 450 eV. The Brillouin zone is represented by the Monkhorst-Pack special k-point meshes of $11 \times 11 \times 11$ for the bulk and $1 \times 1 \times 3$ for the nanowires.

The equilibrium lattice constants and relevant elastic constants are calculated for Ag, Pb, and Si in the bulk states. Ag, Pb, and Si are face-centered-cubic (FCC) crystals. The results of the lattice constants in accord with the least-energy of the respective materials are given in Table 1. With the numerical method proposed by Söderlind et al., the elastic constants of the above materials are determined (see Table 1). It can be noted that the theoretical predictions by the DFT agree well with the experimental data. The averaged bulk Young's modules and

Table 1 Equilibrium lattice constants (a), elastic constants (C_{11} , C_{12} , and C_{44}), Young's moduli (E), and Poisson's ratios (ν) of Ag, Pb, and Si obtained from first-principles calculations

Parameter	Ag		Pb		Si	
	Our model	Experiment	Our model	Experiment	Our model	Experiment
a/nm	0.408 6	0.409 ^[39]	0.496 6	0.495 ^[40]	0.545 3	0.543 ^[41]
C_{11}/GPa	121.2	131.5 ^[42]	40.6	45.5 ^[42]	159.6	165 ^[43]
C_{12}/GPa	100	97.3 ^[42]	49.2	45.4 ^[42]	56.5	63.9 ^[43]
C_{44}/GPa	40.7	51.1 ^[42]	12.1	19.4 ^[42]	76.7	79.6 ^[43]
E/GPa	78.5	79	15.4	16	160.7	169
ν	0.373	0.38 ^[44–45]	0.438	0.42 ^[44–45]	0.215	0.278 ^[43]

Poisson's ratio can be further calculated by the theoretical results of the elastic constants.

Based on the results of the bulk parts, the surface relaxation calculations of Ag, Pb, and Si nanowires are carried out. We adopt $4 \times 4 \times 4$ supercells along the [010] direction with more than 1.5 nm vacuum regions along the [100] and [010] orientations to avoid spurious interactions between periodic images. The central part is fixed to simulate the internal core section of the material, while the surface region is fully relaxed (see Figs. 1(d) and 1(e)). The result reveals that Ag and Pb experience lattice contraction in the process of surface relaxation while Si shows lattice expansion (see Table 2).

Table 2 Surface relaxation parameters of Ag, Pb, and Si

Parameter	Ag	Pb	Si
L_0/nm	1.430	1.733	2.037
L/nm	1.404	1.699	2.098
λ	-1.82%	-1.95%	3.06%

3 Results and discussion

To verify the accuracy of the ab initio core-shell model, the effective Young's moduli of Ag, Pb, and Si nanowires under cantilever and fixed-fixed boundary conditions are predicted.

3.1 Case of fixed-fixed nanowires

The effective Young's modulus E_{eff} of fixed-fixed nanowires is calculated by using fixed-fixed three-point bending tests, and the results are compared with the existing experimental data from Jing et al.^[46] for the Ag nanowire and Cuenot et al.^[11] for the Pd nanowire, respectively. As shown in Figs. 2 and 3, the curves of the normalized effective Young's modulus versus the diameter in our core-shell model agree well with the experimental results, even for the Ag nanowire with a diameter less than 40 nm and the Pd nanowire less than 80 nm, in which the effective Young's moduli would be twice as much as the corresponding bulk moduli. Both the theoretical predictions and the experimental data indicate that the bending stiffness of fixed-fixed nanowires is a function of the characteristic size and will be dramatically intensified owing to the surface effect. If the characteristic size of the cross section is large enough, the effective Young's modulus is equal to the bulk modulus.

Meanwhile, the comparisons between the present model and other theoretical models, e.g., Chhapadia's model^[22], Miller's model^[47], and Yao's model^[48], are also shown in Figs. 2 and 3. The effective elastic moduli in the above models are expressed as

$$E_{\text{eff}} = \begin{cases} E_b \left(1 + \frac{E_s I_{s1}}{E_b I} + \frac{D_s I_c}{E_b I} \right) & \text{(Chhapadia's model),} \\ E_b \left(1 + \frac{E_s I_{s1}}{E_b I} \right) & \text{(Miller's model),} \\ \frac{L}{192 \left(\frac{L}{4D_0 I_c} - \frac{\sqrt{E_b I + C_0 I_{s1}} \sinh(kL/4)}{(D_0 I_c)^{3/2} \cosh(kL/4)} \right)} & \text{(Yao's model),} \end{cases} \quad (23)$$

where E_s denotes the surface elastic modulus, and is taken as 1.22 N/m^2 for Ag and 8 N/m^2 for Pb^[18]. D_s is the surface bending modulus with a value of $0.344 \text{ N} \cdot \text{m}^2$ for Ag^[22]. C_0 and D_0 are terms associated with the surface energy density. The results show that the equations of the effective Young's modulus derived by Chhapadia et al.^[22] and Miller and Shenoy^[47] are only applicable to predict the experimental measurement with the nanowire diameter larger

Fig. 2 Normalized effective elastic modulus of the Ag fixed-fixed nanowire with respect to its diameter predicted by different models and experimental data (color online)

Fig. 3 Normalized effective elastic modulus of the Pb fixed-fixed nanowire with respect to its diameter predicted by different models and experiments data (color online)

than 65 nm for Ag and 85 nm for Pb. In contrast, the equation of Yao's model can successfully evaluate the surface effect on the elastic modulus of nanowires, while its solving process is much more complicated than the solving process in our model.

3.2 Case of cantilever nanowires

Besides Ag and Pd nanowires, Si nanowire is also a widely applicable nanostructure in sensing and actuating devices. Various cantilever bending experiments have been carried out for investigating the mechanical properties of Si nanowire, in which the cross section is treated as a rectangle with the width $b = 8 \mu\text{m}$ and the height h ranging from 40 nm to $1 \mu\text{m}$ ^[16–18]. The typical experimental data of Young's modulus by Sadeghian et al.^[17] are marked in Fig. 4 for examining the theoretical prediction of the cantilever Si nanowire with the present model. It is shown that the effective Young's modulus increases with the increase in the height of the cantilever nanowire, and approximates to the bulk Young's modulus as the height is beyond 300 nm. The conclusion suggests that the decrease in the characteristic size in the cantilever nanowire could weaken the bending stiffness, which has been found in experiments and numerical simulations as well^[16,39–40,49–51].

Fig. 4 Comparison of the normalized effective elastic modulus predicted by the present ab initio core-shell model and the experimental data obtained by Sadeghian et al.^[17] for the cantilever Si nanowire (color online)

3.3 Comparison of the two kinds of nanowires

On the basis of the analysis of theoretical predictions and experimental data, we find that the surface effect is always stiffening the fixed-fixed nanowire and softening the cantilever nanowire. The reason of this interesting phenomenon can be attributed to the nanowire curvature. For a fixed-fixed nanowire, an internal force with an opposite direction to that of external loading is induced by the deflection with a downward curvature, and acts as a resistance of external loading, which results in a smaller deflection than the classical one. As a result, the surface stress increases with the external force, as shown in Fig. 5(a). While an upward curvature in the cantilever nanowire would lead to an internal force with the same direction as that of external loading, yielding an ever-larger deflection than the classic one and thus leading to the dramatic decrease in the stress with increasing the external force, as shown in Fig. 6(a). The results in the insets of Figs. 5 and 6 indicate that the effect of the surface characteristic size could enhance the stiffening behavior of the fixed-fixed nanowire and the softening behavior of the cantilever nanowire. Meanwhile, the constitutive relations of the two kinds of nanowires are also given in Figs. 5(b) and 6(b). It is shown that the relation between surface stress and strain is approximatively linear for the fixed-fixed nanowire and nonlinear for the cantilever nanowire. As a result, the fixed-fixed nanowire is stiffened while the cantilever nanowire is softened by the surface effect as compared with the bulk counterparts in the same material.

Fig. 5 Case of Ag fixed-fixed nanowire: (a) surface stress σ (blue) and strain ε (red) as a function of the external force; (b) relation between surface stress and strain (color online)

Fig. 6 Case of Si cantilever nanowire: (a) surface stress σ (blue) and strain ε (red) as a function of the external force; (b) relation between surface stress and strain (color online)

Besides the surface characteristic size, the nanowire length is another dominant parameter to modulate the elastic behavior of two kinds of nanowires. Figure 7 shows the effective Young's modulus varying with the aspect ratio of both kinds of nanowires. It shows that the effective elastic modulus increases with the aspect ratio for the Ag fixed-fixed nanowire, while decreases with the aspect ratio for the Si cantilever nanowire. Moreover, not only the nanoscale characteristic sizes but also the length would show significant effects on the mechanical performance of nanowires, which has also been proved by Chen and Yao^[34] with employing a new theory for nanomaterials based on the surface-energy density. It must be noted that all these discussions of the length L are under the assumptions of small deformation and finite L or infinite effective Young's modulus and rigid nanowire.

Fig. 7 Effective elastic moduli of the Ag fixed-fixed nanowire and the Si cantilever nanowire predicted theoretically as a function of the diameter with different aspect ratios (L/d) (color online)

We believe that the agreement between the theoretical predictions by our model and the experimental results is credible, since there are no empirical data introduced in our theoretical approach. However, it is worth noting that the analysis of the mechanical behavior for the nanowires in the present paper is based on the Euler-Bernoulli beam theory, which ignores the shearing deformation in the cross section. Once the nanowire has a relatively small aspect ratio, our model should be improved to fit in the Timoshenko beam theory.

4 Conclusions

In the present paper, we show that the proposed ab initio core-shell model is a powerful method to address the highly size dependent problem of mechanical properties and performance in bending nanowires. The surface relaxation and deformation induced by external loading are taken into account for estimating the effective Young's moduli of Ag, Pd, and Si nanowires. The first-principles method is also adopted to calculate the surface and bulk properties of the above materials.

In contrast to the prediction of the classical beam theory, the surface effect of nanowires exhibits some unique mechanical properties, for example, the decrease in the characteristic size will stiffen fixed-fixed nanowires and soften cantilever nanowires. Furthermore, the mechanical behaviors of nanowires can be controlled by appropriate design of the aspect ratio. The larger the aspect ratio is, the larger the effective Young's modulus of the fixed-fixed nanowire is, but the smaller the effective Young's modulus of the cantilever one is.

Our model provides a novel point of view to explain the physical origin of the surface effect on the mechanical properties of nanostructures. First, the diverse of atomic arrangement in surface and bulk crystals leads to an equilibrium strain in the core part of a nanowire,

in which the effective Young's modulus contributed from the core is affected by the surface relaxation. Second, the surface stress induced by external loading will provide the required energy to elastically deform the surface. Therefore, for a nanowire, the tensile surface stress would enhance Young's modulus by decreasing the characteristic size, while the compressive surface stress would weaken Young's modulus by decreasing the characteristic size.

The present model can be applied in nanobeam-based devices of NEMSs with metals, alloys, or compound materials. The results can also promote the optimal design of the nanostructure of advanced materials for artificial intelligence engineering applications, e.g., flexible electronics devices and human health monitoring sensors.

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