Effect of surface stress on the asymmetric yield strength of nanowires

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While it is widely known that nanowires show strong size dependence on their elastic modulus and yield strength, the study on the asymmetric tensile and compressive yield strengths is scarce. In particular, the effect of the surface stress needs to be clearly revealed. In this paper, a theoretical framework is proposed to study the effect of surface stress on the elastic property and yield strength of nanowires. Both the surface residual stress and surface elasticity are taken into account, and the constraint of surface stress in the transverse direction is incorporated. For a representative aluminum nanowire with the decrease in the nanowire radius, the surface elasticity causes both the Young's modulus and Poisson's ratio to increase, and the surface stress causes the tensile yield strength to increase and the magnitude of compressive yield strength to decrease, leading to tension-compression asymmetry. The effect of surface elasticity is relatively small whereas the effect of transverse surface stress is important. © *2008 American Institute of Physics*.
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I. INTRODUCTION

With the rapid development of nanoelectromechanical systems, the mechanical properties of nanostructures, particularly nanowires, have attracted widespread interest. When the characteristic cross-section dimension gets much lower than microns, the ratio of the surface area and volume becomes more prominent, thus the nanowires are strongly influenced by their surface characteristics which lead to distinct mechanical properties compared with their bulk counterpart. This is known as the size effect.

In order to fulfill their promising applications, the size dependence of the mechanical properties of nanowires needs to be sufficiently understood. In essence, the atoms on the surface have different coordination numbers which cause the bonds of surface atoms to relax and affect the surface bond structure. The variation of surface energy leads to the formation of surface residual stress and elastic properties that are distinct from the core. In this paper, such behavior is termed as the surface stress effect. It is known that the surface stress plays a significant role on the elastic modulus of nanowires and nanofilms.[1–5]

The surface stress also has a profound effect on the yield strength of nanostructures.[6] Through molecular dynamics simulations on gold nanowires, Diao *et al.*[7] have discovered an intriguing phenomenon where the tensile and compressive yield stresses are not equal—such asymmetry does not exist in metal wires at the macroscopic scale which should be attributed to the surface stress effect. The asymmetric yield stress was also confirmed by Marszalek *et al.*[8] using atomic force microscopy. Through a simple continuum model, Chuang (Ref. 9) studied the effect of surface stress on the yield strength of a nanowire; however, only the axial component of the surface residual stress was considered. The surface elasticity was neglected and the asymmetry of yield strength was not discussed. It remains unclear how the critical components of surface stress, including the axial and transverse (lateral) surface residual stresses and surface elasticity, affect the asymmetry of yield strength of nanowires. This is the main objective of the present paper which will be elucidated through a surface model and theoretical framework.

II. SURFACE MODEL

According to the surface model introduced by Gurtin and Murdoch,[10] the surface stress is the summation of the surface residual stress and surface elasticity

$$\tau_{\alpha\beta} = \tau^0_{\alpha\beta} + k^s_{\alpha\beta\chi\lambda}\varepsilon^s_{\chi\lambda}. \tag{1}$$

In this paper, the Greek subscripts vary from $1\sim 2$ which are used to represent the in-plane surface properties, and Roman subscripts vary from $1\sim 3$ (for three-dimensional components). In the equation above, $\tau^0_{\alpha\beta}$ is the residual stress of an undeformed solid surface (and independent of deformation), $k^s_{\alpha\beta\chi\lambda}$ is the surface elastic moduli, and $\varepsilon^s_{\chi\lambda}$ is the surface strain. In most previous works, the surface elasticity [second term in Eq. (1)] is often neglected. The surface stress is related with the surface energy by[1]

$$\tau_{\alpha\beta} = \gamma\delta_{\alpha\beta} + \frac{\partial\gamma}{\partial\varepsilon^s_{\alpha\beta}}, \tag{2}$$

where γ is the excess free energy per unit area on the solid surface.

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Below the surface, the equilibrium and constitutive equations in the core of nanowire conform to that of the bulk counterpart

$$\sigma_{ij'j}=0, \quad \sigma_{ij}=C_{ijkl}\varepsilon_{kl}, \tag{3}$$

where σ_{ij} is the stress tensor, ε_{ij} is the strain tensor, and C_{ijkl} is the stiffness tensor. The surface stress and the core (bulk) stress satisfy the generalized Young–Laplace equation[11]

$$\sigma_{\alpha j}n_j+\tau_{\alpha\beta,\beta}=0, \quad \sigma_{ij}n_jn_i=\tau_{\alpha\beta}\kappa_{\alpha\beta}, \tag{4}$$

where n_j is the unit normal vector of the nanowire surface and $\kappa_{\alpha\beta}$ is the curvature tensor of the surface.

First, consider an undeformed nanowire without any surface stress, referred to as the reference configuration. A linear elastic surface with residual stress τ_{ij}^0 is then attached to the nanowire, and the nanowire will deform until it reaches a new stress balance state which is termed as the original configuration. Upon external axial load P, when the body force is neglected, the principle of minimum potential energy dictates[12]

$$\Pi = U_V(\varepsilon_{ij})+U_S(\varepsilon^s_{\alpha\beta})-Pu, \tag{5}$$

where U_V is the volume deformation energy, U_S is the surface energy, and u is the displacement from the reference configuration to the current (deformed) state. It should be emphasized during a real experiment that only the difference between the original and current configurations ($\bar{u}$) can be measured, which does not equal to u; the difference between u and $\bar{u}$ is caused by the surface stress, i.e., the difference between the reference and original states. Although u is used during the theoretical derivation in this paper, the final results (e.g., the yield strain) are presented in terms of $\bar{u}$ (by taking into account the difference between original and reference configurations) so as to connect more easily with real experiments.

III. CLOSED-FORM SOLUTION FOR NANOWIRE WITH CIRCULAR CROSS SECTION

The framework outlined above can be applied to nanostructures with arbitrary cross section and anisotropic materials. However, the results can be quite complicated for general cross-section geometry and material properties. In order to clearly reveal the intrinsic effect of surface stress via analytical closed-form solutions, we consider a nanowire with a circular cross section whose radius is R (see Fig. 1). Note that the ratio of surface area and volume is the smallest for circular cross section. We expect that the effect of surface is more prominent when other cross-section geometry is taken into consideration. When the nanowire is sufficiently long its end effect can be neglected, and thus a unit length of the nanowire can be investigated. We further assume that the

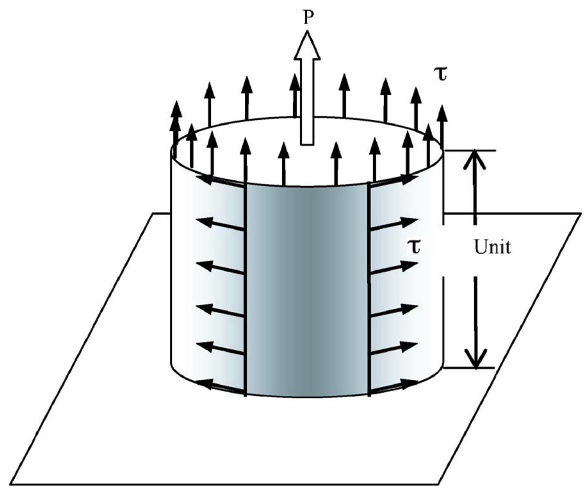

FIG. 1. (Color online) Schematic of a nanowire segment (of unit length) under uniaxial tension with surface stress τ.

properties of both core and surface are isotropic.[13,14] The core can be regarded as a subset of bulk material whose constitutive properties are

$$\sigma_{ij}=\lambda\varepsilon_{kk}\delta_{ij}+2G\varepsilon_{ij}, \tag{6}$$

where λ and G are the Lamé constants which are related with the Young's modulus E and Poisson's ratio ν as $\lambda=E\nu/[(1+\nu)(1-2\ \nu)]$ and $G=E/[2(1+\nu)]$. The surface properties are

$$\tau_{ij}=\tau_0\delta_{ij}+\lambda_s\varepsilon^s_{kk}\delta_{ij}+2G_s\varepsilon^s_{ij}, \tag{7}$$

where λ_s and G_s are surface moduli.

A cylindrical coordinate system (r,ϕ,z) is adopted (Fig. 1). Upon uniaxial loading, the magnitude of the displacement u equals to the axial strain ε_{zz} for the nanowire of unit length. For the present problem, the potential energy of nanowire consists of the following three parts:

$$U_V=\tfrac{1}{2}[\lambda\theta^2+2G(\varepsilon^2_{rr}+\varepsilon^2_{\phi\phi}+\varepsilon^2_{zz})]\pi R^2,$$

$$U_S=\tfrac{1}{2}[2\tau_0\theta_s+\lambda_s\theta_s^2+2G_s(\varepsilon^{s2}_{\phi\phi}+\varepsilon^{s2}_{zz})]2\pi R,$$

$$U_L=-Pu=-\varepsilon_{zz}\Sigma\pi R^2, \tag{8}$$

where $\theta=\varepsilon_{rr}+\varepsilon_{\phi\phi}+\varepsilon_{zz}$ and $\theta_s=\varepsilon^s_{\phi\phi}+\varepsilon^s_{zz}$ are the volumetric strain and surface area expansion, respectively. The strain components are $\varepsilon_{rr}=\varepsilon_{\phi\phi}$, $\varepsilon^s_{\phi\phi}=\varepsilon_{\phi\phi}|_{r=R}$, and $\varepsilon^s_{zz}=\varepsilon_{zz}|_{r=R}$. For circular cross section these quantities are uniform (i.e., $\varepsilon^s_{\phi\phi}=\varepsilon_{\phi\phi}$) but for a general section shape the strain field may be nonuniform. Σ is the applied stress (axial load per unit cross-section area). Under a constant external load Σ, the total system potential energy is a function of ε_{zz} and $\varepsilon_{\phi\phi}$ (since $\varepsilon_{rr}=\varepsilon_{\phi\phi}$ for a circular section and only two variables are independent).

The minimum of potential energy Π can be obtained by solving $\partial\Pi/\partial\varepsilon_{zz}=0$ and $\partial\Pi/\partial\varepsilon_{\phi\phi}=0$, and the strain components that respond to the external load Σ are

$$\varepsilon_{zz}=\frac{\Sigma(2\lambda+2G+\lambda_p+2G_p)-\dfrac{2\tau_0}{R}(\lambda+2G+2G_p)}{2G(3\lambda+2G)+\lambda_p(\lambda+6G)+2G_p(5\lambda+6G+4\lambda_P+4G_p)},$$

$$\varepsilon_{\phi\phi} = -\frac{\Sigma(\lambda+\lambda_p)+\dfrac{\tau_0}{R}(2G-\lambda+4G_p)}{2G(3\lambda+2G)+\lambda_p(\lambda+6G)+2G_p(5\lambda+6G+4\lambda_p+4G_p)}, \tag{9}$$

where $G_p = G_s/R$ and $\lambda_p = \lambda_s/R$.

From the above expressions, the residual strains ε_{zz}^0 and $\varepsilon_{\phi\phi}^0$ of the nanowire (in the original configuration with respect to the reference configuration) are obtained by letting the external load $\Sigma=0$. The real axial strain corresponding to the external load Σ is $\bar{\varepsilon}_{zz}=\varepsilon_{zz}-\varepsilon_{zz}^0$, which is also the strain measured from an experiment. The Young's modulus of the nanowire is obtained as $\bar{E}=d\Sigma/d\bar{\varepsilon}_{zz}$ under uniaxial loading

$$\bar{E} = \frac{2G(3\lambda+2G)+2G_p(5\lambda+6G)+2\lambda_p(6G+\lambda)+8G_p(G_p+\lambda_p)}{2\lambda+2G+2G_p+\lambda_p}. \tag{10}$$

The Poisson's ratio of nanowire is defined as $\bar{\nu}=-\bar{\varepsilon}_{rr}/\bar{\varepsilon}_{zz}$ upon uniaxial loading

$$\bar{\nu} = \frac{\lambda+\lambda_p}{2\lambda+2G+\lambda_p+2G_p}. \tag{11}$$

From the expressions of the Young's modulus and Poisson's ratio of nanowire, the surface residual stress τ_0 has no effect. Instead, these terms are influenced by the surface moduli, and hence the size effect.

Finally, the stress components in the core of nanowire can be obtained from the constitutive Eq. (6)

$$\sigma_{zz} = \frac{\Sigma[2G(3\lambda+2G)+\lambda_p(2G-\lambda)+2G_p(\lambda+2G)]-\dfrac{4\tau_0}{R}(G+G_p)(3\lambda+2G)}{2G(3\lambda+2G)+\lambda_p(\lambda+6G)+2G_p(5\lambda+6G+4\lambda_P+4G_p)},$$

$$\sigma_{\phi\phi} = -\frac{\Sigma[(\lambda+2G)\lambda_p-2\lambda G_p]+\dfrac{2\tau_0}{R}[(3\lambda+2G)(G+2G_p)]}{2G(3\lambda+2G)+\lambda_p(\lambda+6G)+2G_p(5\lambda+6G+4\lambda_p+4G_p)}. \tag{12}$$

In a bulk material, yielding occurs when the shear stress reaches critical on the slip plane. For nanowires, atomistic simulations by Diao *et al.*[7] found that the critical resolved shear stress (RSS) in the slip direction on the slip plane of the interior of nanowire is constant and size independent; thus, when a nanowire yields, its interior shear stress is a constant which may be applied as the criterion for nanowire yielding, i.e., when the applied loading and the surface stress make the RSS reach the critical value in the core. The core of nanowire still retains the bulk behavior, and it is convenient to assume that the critical RSS is symmetric for compression and tension (such that the effect of surface stress can be clarified), whose yielding condition can be effectively described by the von Mises criterion. In the present example, the nanowire subjects to an axisymmetric loading and the von Mises stress in the nanowire is

$$\sigma_e = |\sigma_{rr}-\sigma_{zz}|. \tag{13}$$

When the applied load is increased, the von Mises stress in the core gradually reaches its yield strength σ_y. At this moment, the nanowire is regarded as yielded and the critical applied stress is the yield strength of the nanowire under investigation. From Eqs. (12) and (13), after the equivalent stress is compared with σ_y, the yield strength (which is the critical value of the applied stress Σ) can be derived for uniaxial compression and tension of the nanowire, respectively,

$$\bar{\sigma}_{yC} = -\frac{(3\lambda+2G)(\sigma_y-\tau_0/R)+\chi\sigma_y}{3\lambda+2G+2G_p+2\lambda_p},$$

$$\bar{\sigma}_{yT} = \frac{(3\lambda+2G)(\sigma_y+\tau_0/R)+\chi\sigma_y}{3\lambda+2G+2G_p+2\lambda_p}, \tag{14}$$

where $\chi=3(\lambda_p+2G_p)+4Gp(\lambda_p+G_p)/G+\lambda(\lambda_p+10G_p)/(2G)$.

It should be emphasized that the closed-form solution Eq. (14) incorporates the effects from both the surface residual stress (in axial and lateral directions) and surface elasticity. During the nanowire deformation process, the surface generates a transverse constraint (Fig. 1) that varies with deformation which is also included in our analysis. The effects of surface residual stress and surface elasticity can now be analyzed.

The effect of surface elasticity on the yield strength of nanowire is symmetric with respect to compression and tension. However, the effect of surface residual stress is asymmetric and causes the overall asymmetry of compression-tension of the nanowire. If we neglect the surface elasticity terms in Eq. (14), the yield strength for compression and tension are $\bar{\sigma}_{yC}=\tau_0/R-\sigma_y$ and $\bar{\sigma}_{yT}=\sigma_y+\tau_0/R$, respectively. Thus, the difference between the magnitudes of the tensile and compressive yield strengths is $2\tau_0/R$. In Ref. 9, the transverse surface residual stress and the constraint by surface stress in the transverse direction were both neglected. By following the formulation in Ref. 9 the yield strength for

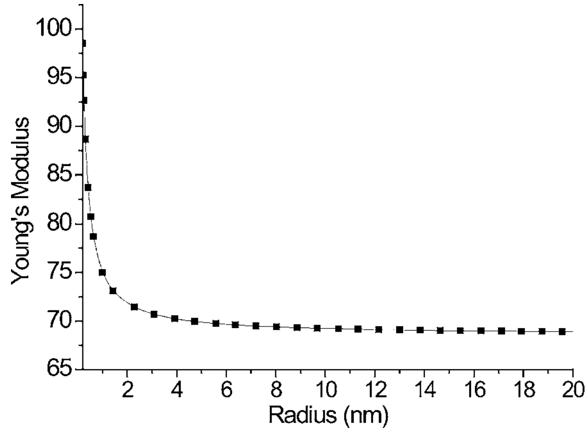

FIG. 2. Size (radius) dependence of the Young's modulus (GPa) of aluminum nanowires.

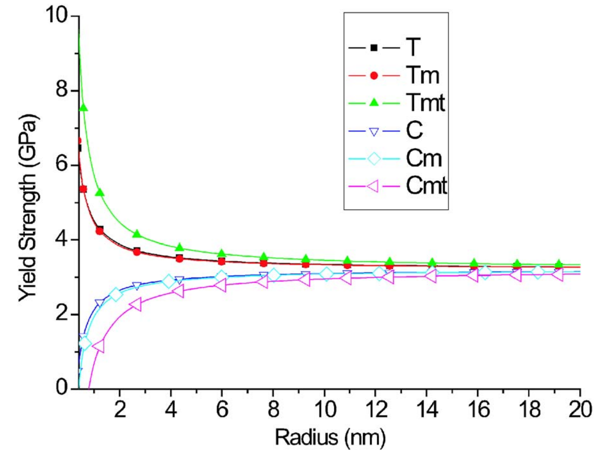

FIG. 4. (Color online) Size (radius) dependence of the magnitude of the yield strength of aluminum nanowires. T: computed tensile strength, Tm: tensile strength neglecting surface elasticity, Tmt: tensile strength neglecting both surface elasticity and transverse constraint by surface stress; C: computed compressive strength, Cm: compressive strength neglecting surface elasticity, Cmt: compressive strength neglecting both surface elasticity and transverse constraint by surface stress.

compression and tension can be derived as $\bar{\sigma}_{yC}=2\tau_0/R-\sigma_y$ and $\bar{\sigma}_{yT}=\sigma_y+2\tau_0/R$, respectively. Comparing with the current analysis, the previous work (Ref. 9) may have overestimated the effect of surface stress on the yield strength.

IV. REPRESENTATIVE RESULTS FOR ALUMINUM NANOWIRE

We now use the aluminum nanowire as an illustrative example. From previous experimental and numerical atomistic analyses, the effective parameters of the aluminum surface are the surface residual stress $\tau_0=1.25\ \mathrm{J/m^2}$,[1] the surface moduli $\lambda_s=6.8415\ \mathrm{N/m}$, and $\mu_s=-0.3755\ \mathrm{N/m}$.[4] The bulk parameters are $E=68.5\ \mathrm{GPa}$ and $\nu=0.35$ with an ideal von Mises yield strength $\sigma_y=3.2\ \mathrm{GPa}$.[15] We remark that, in general, these parameters depend on crystal orientation [these parameters are taken for loading direction (111)]. Since we have assumed isotropic material model in this study, these parameters only serve as the order-of-magnitude estimations that could illustrate the effects of surface stress.

First, we illustrate the effect of surface stress on the Young's modulus and Poisson's ratio according to Eqs. (10) and (11), respectively. The size dependences are given in Figs. 2 and 3, respectively. It is apparent that both Young's modulus and Poisson's ratio increase with the decrease of the radius of nanowire (R). It should be pointed out that the size dependence is related to certain surface properties which can be different if different surface properties are under investigation.

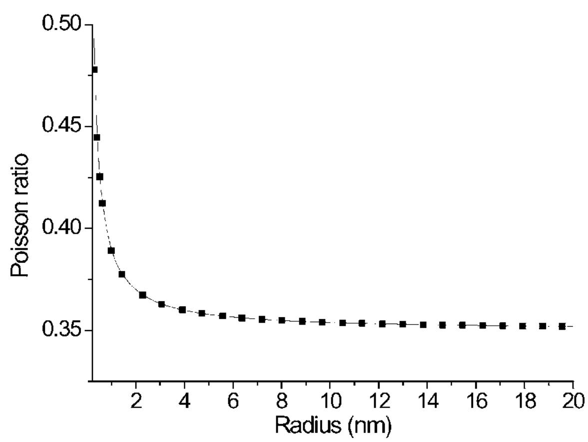

FIG. 3. Size (radius) dependence of the Poisson's ratio of aluminum nanowires.

Figure 4 shows the computed magnitude of the yield strength of aluminum nanowires, which is clearly size dependent and asymmetric in tension-compression. With the decrease of nanowire radius, the effect of surface stress on the yield strength becomes more significant, and the tensile yield strength is higher while the magnitude of the compressive yield strength is lower. For the current material under investigation, the surface elasticity has a relatively small effect on the yield strength, which is mainly attributed to the relatively small strain at yielding. For other materials and/or cross-section shapes, the effect of surface elasticity may be larger. The influence of the transverse surface stress is significant, and neglecting the transverse effect could significantly overestimate the surface effect.

The surface stress not only influences the yield strength of nanowires but also affects the yield strain. Upon yielding, the applied compressive and tensile strains are

$$\bar{\varepsilon}_{yC}=\bar{\sigma}_{yC}/\bar{E},$$

and

$$\bar{\varepsilon}_{yT}=\bar{\sigma}_{yT}/\bar{E}, \tag{15}$$

respectively. For the aluminum nanowire, the size dependence of the magnitude of yield strain is shown in Fig. 5. The yield strain also exhibits asymmetry in compression-tension. With the decrease of the radius of aluminum nanowire, the magnitude of compressive yield strain becomes smaller while the tensile yield strain becomes larger similar to the trend of yield stress. The yield strain is influenced by both the surface stress in the axial and transverse directions, and the effect of surface elasticity is relatively small for the current example of material and geometry.

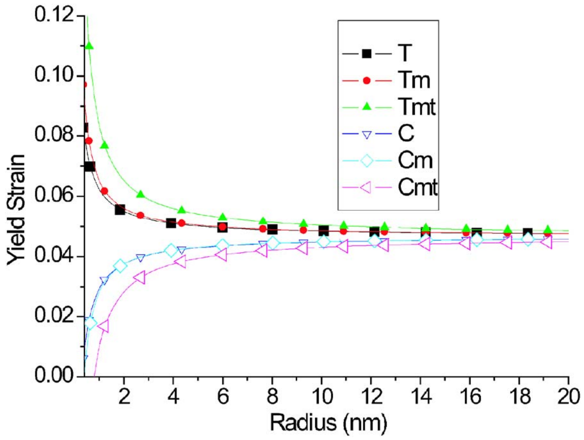

FIG. 5. (Color online) Size (radius) dependence of the magnitude of the yield strain of aluminum nanowires. T: computed tensile strain, Tm: tensile strain neglecting surface elasticity, Tmt: tensile strain neglecting both surface elasticity and transverse constraint by surface stress; C: computed compressive strain, Cm: compressive strain neglecting surface elasticity, Cmt: compressive strain neglecting both surface elasticity and transverse constraint by surface stress.

V. CONCLUSION

To summarize, we analyze the effect of surface stress on the elastic moduli and yield strength of nanowires by using a continuum surface model (assuming small deformation and linear elastic behavior). The effects from both the surface residual stress and surface elasticity are incorporated, as well as the transverse constraints. The surface stress has different effects on the elastic and yield properties of nanowires. For the elastic moduli of nanowires, the size dependence is solely due to the effect of surface elasticity while the surface residual stress has no effect. The magnitudes of yield strength and yield strain of nanowires are both size dependent and asymmetric in tension and compression, where the surface residual stress is responsible for the asymmetry. In the example of the yield strength of a representative aluminum nanowire, the effect of surface elasticity is relatively small; however, the constraint of surface stress in the transverse direction cannot be neglected. For other nanowire materials, the details of size dependence may be different depending on different surface properties.

In this study, a circular cross-section shape is adopted so as to obtain simple closed-form solutions, and we note that for other shapes the surface effect may be stronger. When the nanowire has a general cross-section shape or anisotropic, the framework established in this paper can be readily applied although the final solution will be much more complicated. The current study focuses on the yield stress based on the von Mises criterion. In fact, any critical stress can be defined (such as the Tresca stress, or a stress measure related with material failure) and substituted into the framework, and its size dependence and tension-compression asymmetry can be explored in a similar way.

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