THEORETICAL & APPLIED MECHANICS LETTERS **4**, 051009 (2014)

Surface effects on the persistence length of nanowires and nanotubes

Hua Liu,[1, a)] Hualong Song,[1, b)] Xiqiao Feng,[2, c)] Jialing Yang[1, d)]
[1)]*Institute of Solid Mechanics, Beihang University, Beijing 100191, China*
[2)]*AML and CNMM, Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China*

(Received 26 June 2014; revised 22 August 2014; accepted 27 August 2014)

Abstract Surface effects on the persistence length of quasi-one-dimensional nanomaterials are investigated by using the theory of surface elasticity and the core–shell model of nanobeams. A simple and unified expression is provided to determine the persistence length of nanowires and nanotubes with any regular polygonal cross-sections. It is demonstrated that surface effects have a distinct influence on the persistence length when the characteristic sizes of materials shrink to nanometers. This work is helpful not only for understanding the size-dependent behavior of nanomaterials but also for the design of devices based on nanotubes or nanowires.

 [doi:10.1063/2.1405109]

Keywords surface effect, persistence length, nanotube, nanowire

Quasi-one-dimensional nanomaterials such as nanowires and nanotubes hold great promise for many technologically important applications in, for instance, sensors, atomistic dust detectors, actuators, and oscillators in nanoelectromechanical systems and biotechnology.[1–3] The persistence length of a quasi-one-dimensional material is an important characteristic parameter quantifying the combined effect of flexural rigidity and thermal fluctuations of its conformation.[4,5] The persistence length of quasi-one-dimensional nanomaterials can be predicted by continuum models or atomistic simulations. Gittes et al.[6] estimated the persistence length by using the classical Euler–Bernoulli beam model, which ignores the shear and rotary effects and is appropriate for slender beams. When the length-to-thickness ratio is relatively small, the shear and rotary inertia effects should be taken into account. In this case, the Timoshenko beam model can be used to calculate the persistence length.[4] Recently, a nonlocal Timoshenko beam model[7] and a modified couple stress theory[8] were suggested to examine the size effect of the persistence length.

The material near the surfaces of a solid exhibits properties different from its interior. For macroscopic solids, the surface-to-bulk ratio is rather small and the surface effects can be ignored. When the characteristic sizes of materials shrink to nanometers, however, surface effects often play a significant role in the mechanical behaviour due to the large surface-to-bulk ratio. Both experimental measurements and atomistic simulations have evidenced that the physical, chemical, and mechanical properties of nanostructures are size-dependent.[9] To incorporate the effects of

[a)]Corresponding author. Email: liuhuarui@buaa.edu.cn.
[b)]Email: 1175618225@qq.com.
[c)]Corresponding author. Email: fengxq@mail.tsinghua.edu.cn.
[d)]Email: jlyang@buaa.edu.cn.

surfaces or interfaces, Gurtin and Murdoch[10] established a continuum model of surface elasticity, wherein the surface of a solid is treated as a layer of zero thickness adhering to the interior bulk without slipping.[11,12] As an extension of this theory, a core–shell model has been proposed, in which the surface has a finite thickness.[13,14] The models based on the concept of surface elasticity have been used to investigate the mechanical properties of various nanomaterials and nanodevices, e.g., nanoparticles, nanowires, nanobeams, and materials with nanosized voids or inclusions.[15] The results agree well with atomistic simulations and experiments.[16–18] In this letter, we will investigate the surface effects on the persistence length of quasi-one-dimensional nanomaterials such as nanowires and nanotubes. Based on the theory of surface elasticity and the core–shell model, an explicit expression will be given to predict the persistence length.

According to the classical Euler–Bernoulli beam model, the governing equation for a nanobeam reads

$$\kappa \mathrm{d}^4 w/\mathrm{d}x^4 = q(x), \tag{1}$$

where w is the transverse displacement of the nanobeam, $q(x)$ denotes the lateral loading, and $\kappa = EI$ is the flexural rigidity. Here, E is the Young's modulus of the bulk material and I denotes the second moment of area of the cross-section.

Furthermore, the thermodynamic behavior of one-dimensional nanostructures may be described by the worm-like chain model. Suppose that a worm-like chain has the same length, lateral loading, and boundary conditions as the nanobeam. Subjected to the lateral load $q(x)$, a chain with persistence length p and contour length L satisfies the following Langevin equation[7]

$$pk_{\mathrm{B}}T\,\mathrm{d}^4\bar{w}/\mathrm{d}x^4 = q(x), \tag{2}$$

where $\bar{w}$ is the transverse displacement of the worm-like chain, k_{B} is the Boltzmann's constant, and T is the absolute temperature. The persistence length can be determined by equating the deflections between the worm-like chain model and the beam model. Thus from Eqs. (1) and (2), the persistence length p without surface effects can be calculated by[6–8]

$$p = \kappa/(k_{\mathrm{B}}T). \tag{3}$$

In the absence of surface effects, however, the measured persistence length of a nanosized beam can be pronouncedly different from the value predicted by Eq. (3). This discrepancy is often attributed to the neglect of the size-dependent elastic properties of nanosized materials. Therefore, we here present a continuum model based on the theory of surface elasticity to reveal the surface effects on the persistence length of these nanostructures.

A one-dimensional nanostructure with length much larger than its thickness can be well modelled as a refined Euler–Bernoulli nanobeam with surface effects.[13] A core–shell model is used to consider the influence of surface elasticity. The hollow n-regular polygonal cross-section of a nanobeam is shown in Fig. 1, where R and r denote the external and internal radii of the circumcircles of the polygon, respectively. The thicknesses of the internal and external surface shells are assumed to be δ_{i} and δ_{e}, respectively. Their elastic constants may be different from the core,

which has the same elastic constants as the bulk material. Suppose that both the surface layers and the bulk of the nanostructure are isotropic, homogenous, and linearly elastic. By varying the number of sides, n, this core–shell model can well approximate the shapes of many nanowires and nanotubes observed in experiments and used in practical application.

For all values of n, the polar moment of inertia of a hollow n-regular polygon with respect to the origin o can be written as $I_p = n\left(R^4 - r^4\right)\sin 2\theta\,(2+\cos 2\theta)/12$, where $\theta = \pi/n$. Consider the symmetry of the n-regular polygon, the second moments of area of the cross-section, I_x and I_y, with respect to the x and y axes are given by $I_x = I_y = I = I_p/2 = C\left(R^4 - r^4\right)$, where $C = n\sin 2\theta\,(2+\cos 2\theta)/24$.

In the core–shell model in Fig. 1, the effective flexural rigidity κ^* of the nanobeam with surface effects is expressed as[19]

$$\kappa^* = EI_b + E_eI_e + E_iI_i, \tag{4}$$

where E_e and E_i denote the elastic moduli of the external and internal surface layers, respectively. It should be noted that E_e and E_i can either be larger or smaller than E. I_b, I_e, and I_i are the area moments of inertia of the bulk, the external, and internal surface layers, respectively. They are given by

$$I_b = C[(R-\delta_e\sec\theta)^4 - (r+\delta_i\sec\theta)^4], \tag{5}$$
$$I_e = C[R^4 - (R-\delta_e\sec\theta)^4], \tag{6}$$
$$I_i = I - I_b - I_e = C[(r+\delta_i\sec\theta)^4 - r^4]. \tag{7}$$

In the presence of surface effects, the governing equation of an Euler–Bernoulli nanobeam under bending becomes

$$\kappa^*\,\mathrm{d}^4w/\mathrm{d}x^4 = q(x). \tag{8}$$

Then from Eq. (2) and Eqs. (4)–(8), the persistence length with surface effects is derived as

$$p = \kappa^*/(k_BT) = [C/(k_BT)]\{E[(R-\delta_e\sec\theta)^4 - (r+\delta_i\sec\theta)^4] + E_e[R^4 - (R-\delta_e\sec\theta)^4] + E_i[(r+\delta_i\sec\theta)^4 - r^4]\}. \tag{9}$$

If the thicknesses of the surface layers are much smaller than R, the core–shell model reduces to the surface elasticity model proposed by Gurtin and Murdoch,[10] wherein the surface is modelled as a layer of zero thickness. The persistence length becomes

$$p = \kappa^*/(k_BT) = [C/(k_BT)][E(R^4 - r^4) + 4E_s(R^3 + r^3)\sec\theta], \tag{10}$$

where $E_s = E_e\delta_e = E_i\delta_i$ is the effective surface Young's modulus. For solid cross-sections, one can determine the persistence length by setting $r = \delta_i = 0$. The persistence length without surface effects can be obtained by letting $E_e = E_i = E$ in Eq. (9) or $E_s = 0$ in Eq. (10).

As an example, we first consider the persistence length of silver nanowires with solid cross-sections of square ($n = 4$), regular hexagonal ($n = 6$), and circular ($n \to \infty$) shapes. The material

constants are taken as $E = 76$ GPa, $E_s = 1.22$ N/m,[20] $k_B = 1.381 \times 10^{-23}$, and $T = 290$ K.[7] Assume that the surface layer has a thickness of the single atom diameter of silver, which is $D_0 = 0.35$ nm.[21] The persistence length can be predicted by Eq. (9) and the results are shown in Fig. 2. Herein, R/D_0 varies from 4 to 10. It is seen that for a given side number n, the effective flexural rigidity κ^* increases as the radius R increases, and thus the persistence length increases with the increase in R. For a specified R, the persistence length increases as the side number n increases.

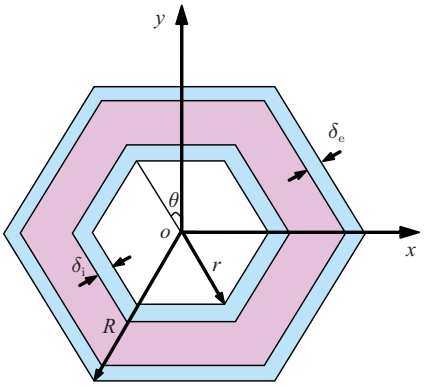

Fig. 1. The n-regular polygonal cross-section of a nanobeam.

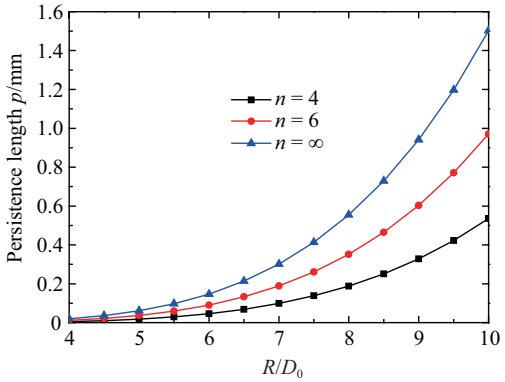

Fig. 2. Persistence length of nanowires with surface effects.

Figure 3 shows the variations of the absolute value of the fractional change in the persistence length as a function of R/D_0 for different cross-sections. η is defined as $|p_w - p_o|/p_o$, where p_w and p_o pertain to the persistence lengths with and without surface effects, respectively. For a given value of R/δ_e, among the square, regular hexagonal, and circular cross-sections, the surface effects on the persistence length are minimal for the circular nanowire and maximal for the square nanowire. This is due to the fact that the ratio of perimeter to area of the cross-section decreases with the increase of the side number n. As R increases, the surface effects become weaker and η decreases. Figure 4 shows the influence of surface layer thickness on the persistence length of a circular nanowire. The four curves correspond to four different values of δ_e, from the top to the bottom, $\delta_e = 0$, D_0, $2D_0$, and $3D_0$, respectively. As can be seen from Fig. 4, the influence of surface elasticity increases as the surface layer thickness increases.

Figure 5 shows the influence of the elastic modulus in the surface layer on the persistence length of a circular nanowire with $\delta_e = D_0$. The ratio E_e/E changes from 0.2 to 5, and R is specified as $6D_0$, $8D_0$, and $10D_0$, respectively. It is seen that the persistence length decreases as the elastic modulus of the surface layer decreases. For a thinner nanowire, this effect is more prominent.

Nanotubes with hollow cross-sections are typical quasi-one-dimensional materials as well. Recently, the surface effects on the vibrational frequency and wave dispersion characteristics of nanotubes have been investigated.[22–24] We here address the persistence length of nanotubes with different cross-sectional shapes. Equation (10) is employed to approximately predict the persistence length of nanotubes. Figure 6 shows the variations of η as a function of R/Δ for different cross-sections, where Δ denotes the thickness of the nanotubes and is taken as $\Delta = 0.5$ nm. Here,

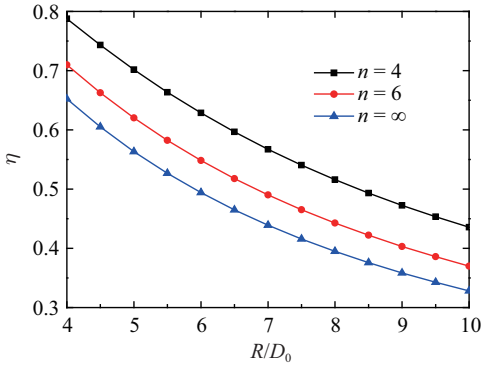

Fig. 3. Variations of η as a function of R/D_0 for nanowires with different cross-sections.

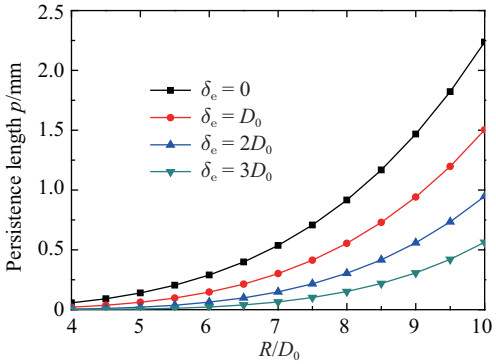

Fig. 4. Influence of surface layer thickness on the persistence length of circular nanowires.

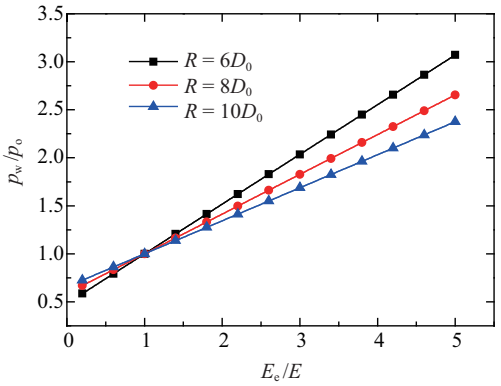

Fig. 5. Influence of the elastic modulus in the surface layer on the persistence length of circular nanowires.

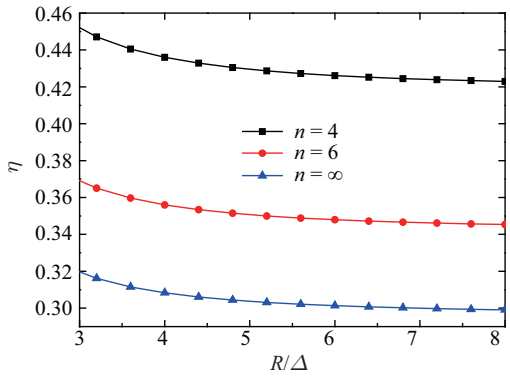

Fig. 6. Variations of η as a function of R/Δ for nanotubes with different cross-sections.

we take $E_s/E = 0.074\,1$ nm. Apparently, the surface effects on the persistence length of nanotubes follow traits similar to those for nanowires.

On the other hand, one can estimate the effective surface Young's modulus from Eq. (10), as long as the persistence length is measured. For example, the microtubules in living cells are self-assembled linear polymers which are hollow thin-walled cylindrical structures. The reported external and internal radii of microtubules are 12.5 nm and 7.5 nm, respectively, the bending rigidity $\kappa^* = 5 \times 10^{-24}$ N·m^2, the Young's modulus $E = 2$ GPa, and the persistence length $p = 1.248$ mm.[7] It is easy to verify that the reported bending rigidity κ^* is much lower than that estimated by the classic expression EI. Substituting these parameters into Eq. (10), one obtains the effective surface Young's modulus of microtubules as $-3.803\,6$ N/m.

In summary, a core–shell model based on the theory of surface elasticity has been presented to determine the persistence length of quasi-one-dimensional nanomaterials. Nanowires and nanotubes with any n-regular polygonal cross-sections are modelled as solid or hollow Euler–Bernoulli nanobeams with surface effects. The results demonstrate that surface effects should be taken into account in the prediction of the persistence length of nanomaterials. This model is also

applied in the determination of the effective surface Young's modulus of microtubules. It can be extended to nanowires with helical or other morphologies.[25] The work is helpful for interpreting the scale-dependent phenomena of nanostructures and the design of devices based on nanotubes or nanowires.

This work was supported by the National Natural Science Foundation of China (11472035 and 11432008) and 973 Program of MOST (2010CB631005 and 2012CB934001).

1. P. Zhou, C. W. Wu, X. D. Li. Three-point bending Young's modulus of nanowires. *Measurement Science & Technology* **19**, 115703 (2008).
2. J. S. Wang, Y. H. Cui, X. Q. Feng, et al. Surface effects on the elasticity of nanosprings. *Europhysics Letters* **92**, 16002 (2010).
3. J. Zhang. Surface effects on the buckling of nanowire networks. *Europhysics Letters* **99**, 56003 (2012).
4. F. Pampaloni, G. Lattanzi, A. Jonas, et al. Thermal fluctuations of grafted microtubules provide evidence of a length-dependent persistence length. *Proceedings of the National Academy of Sciences of the United States of America* **103**, 10248–10253 (2006).
5. L. Cademartiri, G. Guerin, K. J. M. Bishop, et al. Polymer-like conformation and growth kinetics of Bi_2S_3 nanowires. *Journal of the American Chemical Society* **134**, 9327–9334 (2012).
6. F. Gittes, B. Mickey, J. Nettleton, et al. Flexural rigidity of microtubules and actin filaments measured from thermal fluctuations in shape. *The Journal of Cell Biology* **120**, 923–934 (1993).
7. Y. W. Gao, F. M. Lei. Small scale effects on the mechanical behaviors of protein microtubules based on the nonlocal elasticity theory. *Biochemical and Biophysical Research Communications* **387**, 467–471 (2009).
8. Y. M. Fu, J. Zhang. Modeling and analysis of microtubules based on a modified couple stress theory. *Physica E: Low-Dimensional Systems & Nanostructures* **42**, 1741–1745 (2010).
9. D. W. Huang. Size-dependent response of ultra-thin films with surface effects. *International Journal of Solids and Structures* **45**, 568–579 (2008).
10. M. E. Gurtin, A. I. Murdoch. A continuum theory of elastic material surfaces. *Archive for Rational Mechanics and Analysis* **57**, 291–323 (1975).
11. P. Lu, L. H. He, H. P. Lee, et al. Thin plate theory including surface effects. *International Journal of Solids and Structures* **43**, 4631–4647 (2006).
12. C. W. Lim, L. H. He. Size-dependent nonlinear response of thin elastic films with nano-scale thickness. *International Journal of Mechanical Sciences* **46**, 1715–1726 (2004).
13. G. F. Wang, X. Q. Feng. Effects of surface elasticity and residual surface tension on the natural frequency of microbeams. *Applied Physics Letters* **90**, 231904 (2007).
14. C. Q. Chen, Y. Shi, Y. S. Zhang, et al. Size dependence of Young's modulus in ZnO nanowires. *Physical Review Letters* **96**, 075505 (2006).
15. J. X. Wang, Z. P. Huang, H. L. Duan, et al. Surface stress effect in mechanics of nanostructured materials. *Acta Mechanica Solida Sinica* **24**, 52–82 (2011).
16. R. E. Miller, V. B. Shenoy. Size-dependent elastic properties of nanosized structural elements. *Nanotechnology* **11**, 139–147 (2000).
17. R. Dingreville, J. Qu, M. Cherkaoui. Surface free energy and its effect on the elastic behavior of nano-sized particles, wires and films. *Journal of the Mechanics and Physics of Solids* **53**, 1827–1854 (2005).
18. K. B. Gavan, H. J. R. Westra, E. W. J. M. Drift, et al. Size-dependent effective Young's modulus of silicon nitride cantilevers. *Applied Physics Letters* **94**, 233108 (2009).
19. X. P. Zheng, Y. P. Cao, B. Li, et al. Surface effects in various bending-based test methods for measuring the elastic property of nanowires. *Nanotechnology* **21**, 205702 (2010).
20. J. He, C. M. Lilley. Surface effect on the elastic behavior of static bending nanowires. *Nano Letter* **8**, 1798–1802 (2008).
21. G. Ouyang, X. L. Li, X. Tan, et al. Size-induced strain and stiffness of nanocrystals. *Applied Physics Letters* **89**, 031904 (2006).
22. X. W. Lei, T. Natsuki, J. X. Shi, et al. Surface effects on the vibrational frequency of double-walled carbon nanotubes using the nonlocal Timoshenko beam model. *Composites Part B: Engineering* **43**, 64–69 (2012).
23. S. Narendar, S. Ravinder, S. Gopalakrishnan. Study of non-local wave properties of nanotubes with surface effects. *Computational Materials Science* **56**, 179–184 (2012).
24. B. Farshi, A. Assadi, A. Alinia-Ziazi. Frequency analysis of nanotubes with consideration of surface effects. *Applied Physics Letters* **96**, 093105 (2010).
25. Z. L. Zhao, H. P. Zhao, Z. Chang, et al. Analysis of bending and buckling of pre-twisted beams: A bioinspired study. *Acta Mechanica Sinica* **30**, 507–515 (2014).