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Optimum diameter of small single-wall carbon tori

Shumin Zhao *, Shengli Zhang, Minggang Xia, Erhu Zhang, Xianjun Zuo

Department of Applied Physics, Xi'an Jiaotong University, Xi'an 710049, China

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Abstract

In this Letter we study the optimum diameter of stable small single-walled carbon nanotube (SWNT) tori based on the minimum of their free energy. A simple continuum model is used to calculate the free energy of SWNT tori, from which their thermodynamic stability is investigated. The small toroidal nanotubes are stabilized because of the competition between deformation energy and entropy. We use this to derive the optimal diameter of small SWNT torus and our calculations show that a tube with a diameter of 1.4 nm can be bent to form a stable torus with a toroidal diameter ≈ 34 nm.

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With their unique electronic and mechanical properties, carbon nanotubes are of great interest for the fabrication of new classes of advanced materials [1–3]. Recently, rings of single-walled carbon nanotubes have been synthesized experimentally [4–9]. Under ultrasonic irradiation, straight SWNTs can fold and bundle to form SWNT rings of 20–2000 nm in size. They could be ideal systems for studying electronic, magnetic and even superconductive properties in perfectly circular quantum wires [10–15], making the further investigation of the formation and structure of toroidal SWNTs well worth the effort.

More recently, Han [16] and Huhtala et al. [17,18] have studied the toroidal carbon nanotube's structures under different bending strain conditions by large-scale molecular dynamics simulations. Also, nanotoroidal structures based on carbon nanotubes have been studied in the past [19–24]. The geometrical structure, electronic structure and energy were investigated by means of a tight-binding and semiempirical quantum chemical approach [25–28]. A simple estimate shows that the critical radius of an elastic torus made from a $(10, 10)$ nanotube is approximately 90 nm [29]. However, many tori of smaller

* Corresponding author.
E-mail address: mixi@263.net (S. Zhao).

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radius than the critical ring radius have been found experimentally [15]. Here, our investigation provides a theoretical study of the optimum tori radius of an individual small SWNT torus using the continuum model.

In this Letter, an approach to the free energy of individual toroidal SWNTs is given analytically to understand the formation mechanism. This is a continuation of our earlier work [30], in which we studied ring formation of single-walled carbon nanotubes in ropes. In the present Letter, our purpose is to study in more detail the free energies of the ring SWNTs by investigating the structures of individual toroidal SWNTs in terms of the continuum limit of their free energies. The toroidal SWNT is formed when a straight single nanotube bends and its two ends are connected. Tubes under study include circular and polygonal tori, formed by bending (n, n) tubes and by bending tubes with defined diameters which have topological pentagonal–heptagonal defects.

Note that carbon tori grows from initial straight SWNTs with fixed radii. This is supported by the experimental observations of Liu et al. [4] and Martel et al. [8,9], in which the size of the observed rings is restricted to a well-defined diameter range ($r \sim 7$ Å). The formation energy of the toroidal SWNT is the deformation energy E_d of the graphite layers. Therefore, the free energy F of the toroidal SWNT is expressed as follows:

$$F = E_d - TS, \tag{1}$$

where T is the synthesis temperature and S stands for the entropy of the tube. Continuum models have been proved by some studies to be a good description of carbon nanotubes. Based on an SWNT coiling model and using a continuum model, the thermodynamically stable ring diameter of ring SWNTs in a rope was calculated [30]. In fact, it has been suggested that the toroidal nanotubes are stabilized by the competition between deformation energy and entropy. Here, our investigation provides theoretical support for this proposition in case of single tori SWMNTs.

The deformation energy E_d of a curved graphite layer has been proposed in terms of a 2-dimensional lattice [31]. In the continuum approximation, the deformation energy is expressed as follows [32–34]:

$$\begin{aligned} E_d = {} & \frac{1}{2}\oint D\big[(2H)^2 - 2(1-\nu)K\big]\,dA \\ & + \frac{1}{2}\oint \frac{C}{1-\nu^2} \\ & \times \big[(\varepsilon_x+\varepsilon_y)^2 - 2(1-\nu)\big(\varepsilon_x\varepsilon_y - \varepsilon_{xy}^2\big)\big]\,dA, \end{aligned} \tag{2}$$

where H is the mean curvature, K is the Gaussian curvature, ε is the in-plane strain, and x and y are local coordinates. Here the bending rigidity $D = 1.2$ eV A^2 [31], the in-plane stiffness $C = 59$ eV and the Poisson ratio $\nu = 0.34$ [34]. The first term in Eq. (2) expresses the curvature elastic energy of the graphite layers, and the second term represents the stretching energy of the SWNT. This deformation energy has been applied in the study of fullerenes clusters [35,36] and in the study of SWNT helicity and MWNT formation [32–38].

As we have modeled ring SWNTs as tori, they can be parametrized in Cartesian coordinate $\mathbf{Y} = \{\cos\theta(R - r\cos\phi), \sin\theta(R - r\cos\phi), r\sin\phi\}$, where R denotes the toroidal radius and r is the radius of the tube. The parametric variables θ and ϕ both range from 0 to 2π. Using the parametric representation, we derive the mean curvature $H = 1/2[\cos\phi/(r\cos\phi - R) + 1/r]$, and the differential area element $dA = \sqrt{g}\,d\theta\,d\phi = r(R - r\cos\phi)\,d\theta\,d\phi$. According to differential geometry [39], the Gaussian curvature K contributes a topological invariant given by $\int K\,dA = \chi$, where χ is the Euler characteristic for a surface. For simplicity, we consider a toroidal SWNTs loaded with uniform axial stresses when $r \ll R$—i.e., the case of $\varepsilon_y = -\nu\varepsilon_x$ and $\varepsilon_{xy} = 0$. Applying these to the deformation energy, we obtain the deformation energy for ring SWNTs as follow:

$$E_d = \frac{2\pi^2 DR}{r\sqrt{1-(r/R)^2}} + 2C\pi^2 Rr\varepsilon_x^2, \tag{3}$$

in which we have applied the zero Euler characteristic for a torus ($\chi = 0$).

Next, we will study the entropy of individual toroidal SWNTs. According to the specific structure of individual toroidal SWNTs, the entropy is the summation of structure entropy and the mixing entropy. For a toroidal SWNT with torus radius R and tube radius r, its total area is $A = 4\pi^2 Rr$. Since the number of carbon atoms per unit area is

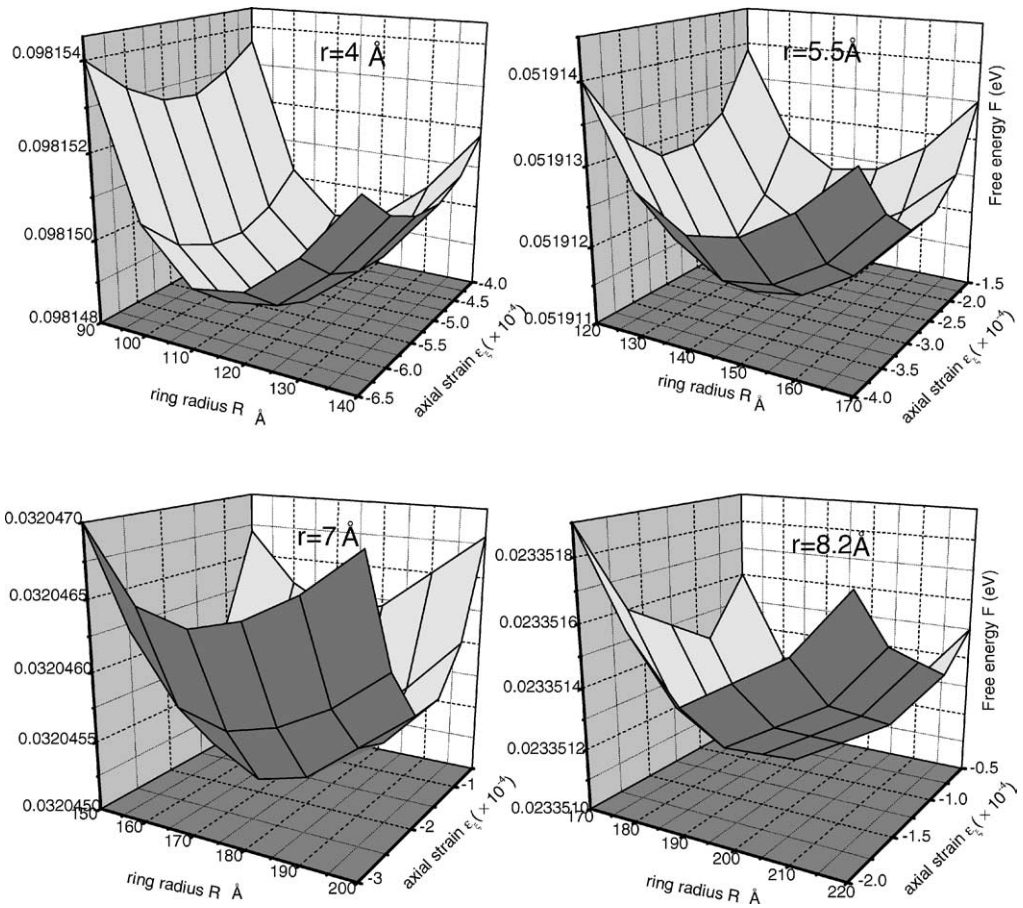

Fig. 1. The free energy per atom of circular tori relative to straight tubes as function of torus radius R and the axial strain ε_x. The synthesis temperature of ring SWNTs $T = 1500$ K.

$n_\sigma = 4/(3\sqrt{3}a^2)$, the total number of carbon atoms is given by $N = 16\pi^2 Rr/(3\sqrt{3}a^2)$, where $a = 1.421$ Å. From the definition of entropy, one has the structure entropy of toroidal SWNT $S_s = k_B \ln \Omega$, where k_B is the Boltzmann constant. Under the continuum approximation, the structure entropy of a toroidal SWNT becomes [30]

$$S = k_B \ln\left(4\pi^2 \frac{Rr}{a^2} + \frac{\sqrt[4]{3}}{\sqrt{2}}\pi \frac{\sqrt{Rr}}{a} - 6\right). \tag{4}$$

Since there are pentagonal–heptagonal defects in the ring SWNT, the mixing entropy should be taken account of. Suppose there are M_{57} carbon pentagons in the network of carbon hexagons of the ring SWNT. Using the Brag–Williams theory [40], we can derive the mixing entropy $S_m = k_B M[-x \ln x - (1 - x)\ln(1 - x)]$, where M stands for the total number of carbon polygons (hexagons, pentagons and heptagons) and $x = 2M_{57}/M$ is the ratio of the number of pentagons and heptagons to that of polygons. Generally, the number of the pentagons and heptagons is far less than that of the hexagons. Since each hexagon includes two carbon atoms, the number of the polygons, M, is approximately half of the number of carbon atoms, i.e., $M \simeq N/2$. Then we have

$$S_m = \frac{8\pi^2 Rr}{3\sqrt{3}a^2} k_B\big[-x \ln x - (1 - x)\ln(1 - x)\big]. \tag{5}$$

Using the deformation energy (3), entropy (4) and (5), the free energy per atom of the toroidal SWNT can

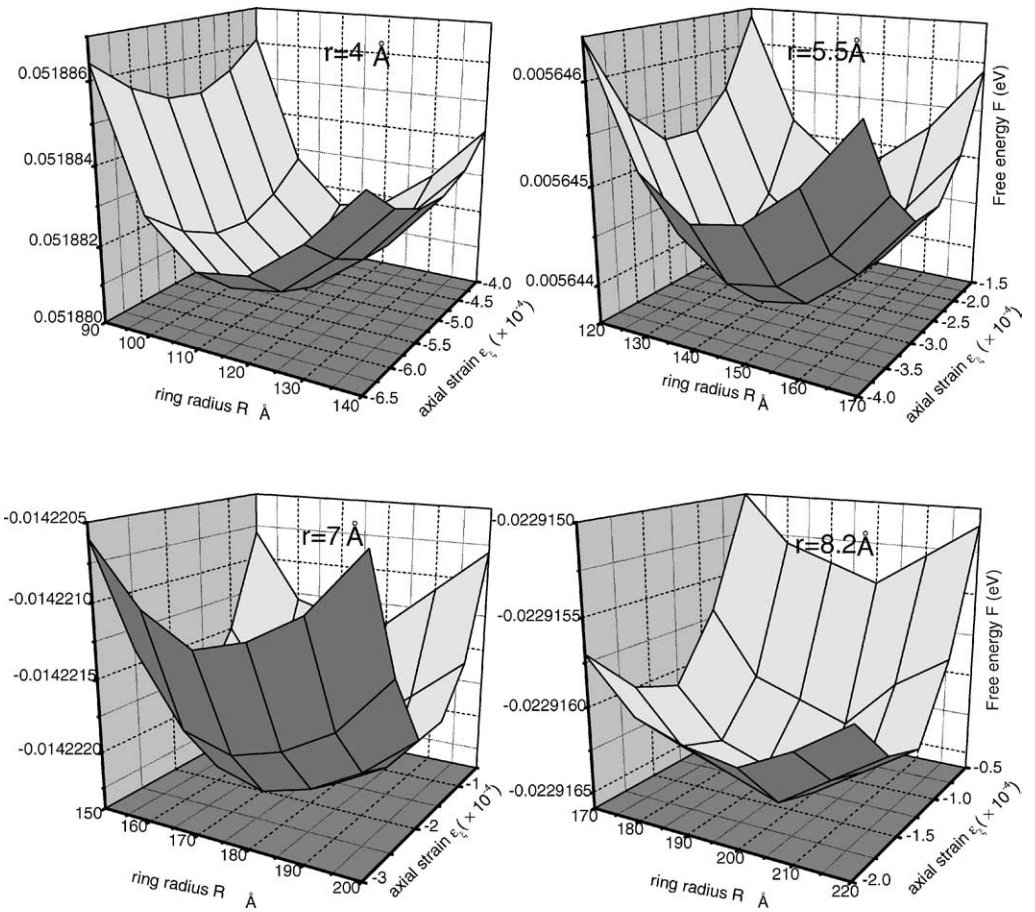

Fig. 2. The free energy per atom of polygonal tori relative to straight tubes as function of torus radius R and the axial strain ε_x. The synthesis temperature of ring SWNTs is $T = 1500$ K and the ratio $x = 0.5$.

subsequently be expressed as

$$\begin{aligned} F &= \big[E_d - T(S_s + S_m)\big]/N \\ &= \frac{1}{N}\left\{\frac{2\pi^2 k_c R}{r\sqrt{1-(r/R)^2}} + 2C\pi^2 Rr(\varepsilon_x)^2 \right. \\ &\quad - k_B T \ln\left(4\pi^2\frac{Rr}{a^2} + \frac{\sqrt[4]{3}}{\sqrt{2}}\pi\frac{\sqrt{Rr}}{a} - 6\right) \\ &\quad \left. - k_B T\frac{8\pi^2 Rr}{3\sqrt{3}a^2}\big[-x\ln x - (1-x)\ln(1-x)\big]\right\}, \end{aligned} \tag{6}$$

where T stands for the synthesis temperature of toroidal SWNTs. The simplest form of the circumferential strain is $\varepsilon_y = (r - r_0)/r_0$, where r is the current tube radius and r_0 is the original tube radius. Similarly, the axial strain can be defined as $\varepsilon_x = (R - R_0)/R_0$, in which R is the tori radius at strain and R_0 is the original tori radius.

Using Eq. (6) we can study the optimal structure of a toroidal SWNT which is determined by the equilibrium condition $\delta F = 0$, exactly the equilibrium shape of the SWNT is determined by minimizing the free energy per atom.

From the Gauss–Bonnet theorem [39], we know that a torus can only be covered with hexagons. There are no topological defects in this kind of torus—the circular torus ($x = 0$). It has been found experimentally that carbon nanotubes grow from an initial tubular nucleus with fixed radius [41]. Therefore, we consider these circular tori with fixed tube radius, e.g., (n, n) tubes with $n = 6,\ 8,\ 10$ and 12 (tube radius $r_0 =$

4, 5.5, 7 and 8.2 Å), respectively. The free energies of these four circular tori are shown in Fig. 1. The free energy per atom of a torus is a function of the torus radius R and the axial strain ε_x. The free energy per atom reaches its minimum when $R = 120,\ 140,\ 170$ and 190 Å with $\varepsilon_x = -5.0 \times 10^{-4},\ -2.7 \times 10^{-4},\ -1.7 \times 10^{-4}$ and -1.3×10^{-4}, respectively. Therefore we can obtain the optimal tori radii $R = 120,\ 140,\ 170$ and 190 Å, respectively. These torus radii are consistent well with the experiment data [10,15]. The optimal torus radius of other circular torus can also been investigated similarly.

Except for circular tori, we also study polygonal tori formed by tubes with topological pentagonal–heptagonal defects ($x \neq 0$). For the same reason as circular tori, i.e., carbon nanotubes grow from an initial tubular nucleus with fixed radius [41], the free energy per atom is also a function of the torus radius R, axial strain ε_x and the ratio x. From Eq. (6), we find that the free energy is minimum only when the ratio $x = 0.5$ for the arbitraty torus radius and axial strain. Therefore the stable conformation of a toroidal SWNT is found by the minimum of its free energy per atom with respect to the torus radius R and the axial strain ε_x of the toroidal SWNT when $x = 0.5$. For comparison with the results of circular tori, we set $r = 4,\ 5.5,\ 7$ and 8.2 Å, respectively. The free energies per atom versus the tori radii R and the axial strains ε_x are plotted in Fig. 2. It can been seen that the optimum tori radii occur at $R = 120,\ 140,\ 170$ and 190 Å with $\varepsilon_x = -5.0 \times 10^{-4},\ -2.7 \times 10^{-4},\ -1.7 \times 10^{-4}$ and -1.3×10^{-4}, respectively, which correspond to the minima of the free energies per atom ($\delta F = 0$). The remarkable result is that the polygonal tori with topological pentagon–heptagon defects have lower energies than the circular tori, and are also energetically more stable. Therefore, based on energy concerns, we conclude that polygonal tori are more favourable since their energies are lower.

In conclusion, we have studied small toroidal SWNTs of two different structures, circular and polygonal. We have explained some experimental observations of SWNTs in terms of their free energies, which consist of deformation energy and the entropy of toroidal nanotubes. Optimal structure of the toroidal SWNTs is reached when a balance is reached between these two energies. The optimal tori diameter for small toroidal SWNTs has also been derived. The toroidal structures which we studied are of (n, n)-chirality and have torus diameters of approximately 24, 28, 34 and 38 nm which correspond to tube lengths of 76, 88, 106 and 120 nm. For our simulations, the number of atoms ranges from 7233 to 23 452. Our calculations show that a tube with a diameter of 1.4 nm can be bent to form a stable torus with a toroidal diameter ≈ 34 nm.

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References

[1] S. Iijima, Nature (London) 354 (1991) 36.
[2] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1998.
[3] M.S. Dresselhaus, G. Dresselhaus, Ph. Abouris, Carbon Nanotubes Synthesis, Structure, Properties, and Applications, Springer-Verlag, Berlin, 2001.
[4] J. Liu, et al., Nature (London) 385 (1997) 780.
[5] J. Liu, et al., Science 280 (1998) 1253.
[6] M. Ahlskog, et al., Chem. Phys. Lett. 300 (1999) 202.
[7] M. Sano, et al., Science 293 (2001) 1299.
[8] R. Martel, et al., Nature (London) 398 (1999) 299.
[9] R. Martel, et al., J. Phys. Chem. B 101 (1999) 7551.
[10] H. Watanabe, et al., Thin Solid Films 438–439 (2003) 462.
[11] R.C. Haddon, Nature 388 (1997) 31.
[12] J. Rollbuintsov, Physica B 280 (1996) 483.
[13] H.R. Shea, R. Martel, Ph. Avouris, Phys. Rev. Lett. 84 (2000) 4441.
[14] K. Sasaki, Phys. Rev. B 65 (2002) 155429.
[15] A. Latge, C.G. Rocha, L.A.L. Wanderley, M. Pacheco, P. Orellana, Z. Barticevic, Phys. Rev. B 67 (2003) 155413.
[16] J. Han, Chem. Phys. Lett. 282 (1998) 187.
[17] M. Huhtala, et al., Comput. Phys. Commun. 146 (2002) 30.
[18] M. Huhtala, et al., Comput. Phys. Commun. 147 (2002) 91.
[19] B.I. Dunlap, Phys. Rev. B 46 (1992) 1933.
[20] S. Itoh, S. Ihara, J. Kitakami, Phys. Rev. B 47 (1993) 1073.
[21] S. Ihara, S. Itoh, J. Kitakami, Phys. Rev. B 47 (1993) 12908.
[22] S. Itoh, S. Ihara, Phys. Rev. B 48 (1993) 8323.
[23] J.K. Johnson, B.N. Davidson, M.R. Pederson, J.Q. Broughton, Phys. Rev. B 50 (1994) 17575.
[24] J.C. Greer, S. Itoh, S. Ihara, Chem. Phys. Lett. 222 (1994) 621.
[25] R. Setton, N. Setton, Carbon 35 (1997) 497.
[26] A. Ceulemans, L.F. Chibotaru, P.W. Fowler, Phys. Rev. Lett. 80 (1998) 1861.

[27] D.H. Oh, J.M. Park, K.S. Kim, Phys. Rev. B 62 (2000) 1600.
[28] S.A. Bovin, L.F. Chibotaru, A. Ceulemans, J. Mol. Catal. A: Chem. 166 (2001) 47.
[29] V. Meunier, Ph. Lambin, A.A. Lucas, Phys. Rev. B 57 (1998) 14886.
[30] S.-L. Zhang, et al., Phys. Rev. B 68 (2003) 245419.
[31] T. Leonosky, et al., Nature (London) 355 (1992) 333.
[32] Z.-C. Ou-Yang, Z.B. Su, C.L. Wang, Phys. Rev. Lett. 78 (1997) 4055.
[33] B.I. Yakobson, C.J. Brabec, J. Bernholc, Phys. Rev. Lett. 76 (1996) 2511.
[34] Z.-C. Tu, Z.-C. Ou-Yang, Phys. Rev. B 65 (2002) 233407.
[35] S.-L. Zhang, S.-M. Zhao, J.-Y. Lu, M.-G. Xia, Phys. Rev. B 61 (2000) 12693.
[36] S.-L. Zhang, Phys. Lett. A 285 (2001) 207.
[37] S.-L. Zhang, Phys. Rev. B 65 (2002) 235411.
[38] M.T. Yu, T. Kowalewski, R.S. Ruoff, Phys. Rev. Lett. 86 (2002) 87.
[39] M.P. do Carmo, Differential Geometry of Curves and Surfaces, Prentice–Hall, Englewood Cliffs, NJ, 1976.
[40] P.M. Chaikin, T.C. Lubensky, Principles of Condensed Matter Physics, Cambridge Univ. Press, Cambridge, UK, 1995.
[41] P. Zhang, V.H. Crespi, Phys. Rev. Lett. 83 (1999) 1791 and references therein.