Energy Method for Stress-Free Zigzag Single-Walled Carbon Nanotubes

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Abstract: In this paper, the geometry of zigzag single walled carbon nanotubes without any external loading is analyzed via an energy procedure. Carbon nanotubes (CNTs) are thin walled cylinders made from single sheets of graphene. Based on the theory of molecular mechanics, a modified mechanical model is proposed to predict the energy of unstressed zigzag carbon nanotubes (CNTs), and the diameter of CNTs is estimated according to the principle of minimum energy. The results show that the diameter obtained by the modified model is larger, but basically consistent with that obtained by conformal mapping. The inversion energy term is added to the modified model, in which the pyramidalization angle is used to characterize the inversion term energy associated with the curvature at an atom. According to the errors, the inversion energy can not be neglected in the stress-free state of carbon nanotubes, especially in the case of small diameter.

1. Introduction

Since its discovery in 1991 [1], carbon nanotubes (CNTs) have attracted extensive attention from many researchers because of their unique structure and excellent performance. As a carbon isotope, carbon nanotubes (CNTs) have unique one-dimensional hollow structure and very low density, which determine their mechanical, electrical and adsorption properties that other materials cannot match [2]. In material science and engineering, nanotube reinforced composites and polymers have shown wide potential applications. Their main structural properties are the ultimate longitudinal stiffness and tensile strength [3, 4]. In the experimental aspect, various experimental techniques, including atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectroscopy, have been used to directly measure Young's modulus of CNT. Despite the obvious scattering in the reported data, the Young's modulus of CNT is still on the order of 1 TPa [5-8]. In the theoretical research of carbon nanotubes, many methods and models have been developed to simulate the mechanical properties of carbon nanotubes. Among them, the most widely used theoretical mechanics method is molecular mechanics. Nowadays, many improved molecular mechanics models have been developed, which greatly improves the calculation accuracy of the mechanical properties of carbon nanotubes [9-11].

In this paper, graphene sheets are curled into carbon nanotubes without longitudinal and transverse stresses. Due to the curvature effect, after the two-dimensional sheets are rolled into a three-dimensional tube, intrinsic properties of the structure will be changed, such as mechanical and physical characteristics. In cylindrical coordinates, on account of the curvature, the included angles between the adjacent bonds in a carbon cycle of SWCNTs are different from those of graphite sheets. According to AMBER potential, the pyramidalization angle of p-orbital direction of carbon atoms based on POAV technique is proposed in this paper to describe the inversion energy term related to atomic curvature.

2. Interatomic Potential

In this paper, the initial diameter is calculated based on the minimum potential energy. The potential energy used is AMBER potential. AMBER potential can be expressed by the following equation:

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$$U = \sum U_\rho + \sum U_\theta + \sum U_\omega$$
$$= \frac{1}{2}\sum K_\rho (\Delta \mathrm{b})^2 + \frac{1}{2}\sum K_\theta (\Delta\theta)^2 + \frac{1}{2}\sum K_\omega (\Delta\theta)^2 \quad (1)$$

where U_ρ, U_θ and U_ω are the bonding energy associated with bond stretching and inversion, respectively. K_ρ K_θ and K_ω are the stretching constants , bending force constants and inversion force constants. In this paper, the three constants are $K_\rho = 652nN/nm$, $K_\theta^{300} = 0.876nNnm$ and $K_\omega = 4.65nNnm$, respectively [12, 13].

Since the longitudinal stiffness of covalent bonds is significantly higher than angular stiffness between two neighboring covalent bonds, the lengthening of covalent bonds from the planar graphene sheet to the nanotube has been neglected. So the Eq. (1) can be simplified as:

$$U = \frac{1}{2}\sum K_\theta (\Delta\theta)^2 + \frac{1}{2}\sum K_\omega (\Delta\theta)^2 \quad (2)$$

3. Initial Diameter for Zig-Zag Nanotubes

The definitions of the bond stretch and bond angle variation are clear, but there is little agreement to treat the inversion term. According to the method of Shen and Li [14], the change of angle for the inversion energy can be showed as Figure 1. The simple relations among these angles are derived as:

$$\tan\omega = \frac{\sin\theta_2 \sin\left(\frac{\pi}{2n}\right)}{1-\cos\theta_2} \quad (3)$$

$$\Delta\omega = \tan^{-1}\left(\frac{\sin\theta_2 \sin\left(\frac{\pi}{2n}\right)}{1-\cos\theta_2}\right) \quad (4)$$

where θ_2 is the bond length, n is the chiral vectors of zigzag carbon nanotubes.

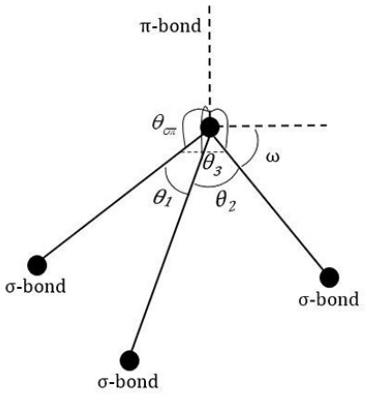

Figure 1 The representation of the bond angle of carbon nanotubes.

According to the principle of minimum energy $\left[\partial U(\mathrm{D})/\partial D\right]_{D_0} = 0$, The unmodified AMBER potential can be expressed as [12]:

$$nK_\theta\left(2\Delta\theta_2\frac{\partial\Delta\theta_2}{\partial\alpha}+4\Delta\theta_1\frac{\partial\Delta\theta_1}{\partial\alpha}\right)=0 \tag{5}$$

α is angle included from each oblique bond and the transversal plane, angle relationship as shown in Figure 2. The relationship between α and D is as follows:

$$D=\frac{a_0\cos\alpha}{\sin\dfrac{\pi}{2n}} \tag{6}$$

where a_0 is the bond length and a_0=0.142nm.

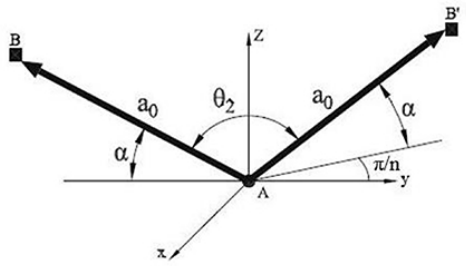

Figure 2 Angle relationship of zigzag carbon nanotubes.

The modified total energy can be obtained from Eqs. (1)-(4). Therefore, the modified AMBER potential based on the principle of minimum energy is:

$$4\left(\alpha-\frac{\pi}{6}\right)-\left(2\Delta\theta_2-\Delta\omega\frac{K_\omega}{K_\theta}\frac{\partial\Delta\omega}{\partial\Delta\theta_2}\right)\frac{\partial\Delta\theta_2}{\partial\alpha}=0 \tag{7}$$

where

$$\Delta\theta_1=\alpha-\frac{\pi}{6} \tag{8}$$

$$\Delta\theta_2=\arccos\left[\sin^2\alpha\left(1+\cos\frac{\pi}{n}\right)-\cos\frac{\pi}{n}\right]-\frac{2\pi}{3} \tag{9}$$

The expression (7) is a nonlinear equation of α, which was solved numerically by the Newton method. Once α is obtained and substituting in (6), the diameters of modified energy method can be obtained. Likewise, the diameters D_t calculated with the conformal mapping [15] and the relative error taking D_m as the reference solution are included to get an insight into the difference.

4. Results and Discussion

As has been shown in Table 1, our obtained diameters D_m are slightly higher than those obtained from the conformal mapping and unmodified method. This difference is probably related to the stabilization effect of the preenergy, which tend to expand transversally the nanotube. The smaller the diameter is, the higher effect of the preenergy is found. And the diameter obtained by the modified method is larger than that obtained by the unmodified method. This is because the modified method adds an inversion energy term. As can be seen from Figure 3, the angle α obtained by the modified method is smaller. The same result can also be seen in combination with Eq. (6). Otherwise, the effect of inversion energy is especially obvious in the case of small diameter, because the curvature of small diameter carbon nanotubes is larger. However, with the increase of pipe diameter, this effect will gradually reduce, and the same trend can be seen in Table 1.

Table 1 Comparison of parameters obtained by modified and unmodified methods.

	n	α(rad)	α_m(rad)	D(nm)	D_m(nm)	D_t(nm)	ε(%)	ε_1(%)	ε_2(%)
(4, 0)	4	0.4406	0.4374	0.3356	0.3361	0.3132	6.6746	6.8134	0.1488
(5, 0)	5	0.4685	0.4489	0.4100	0.4140	0.3914	4.5366	5.4589	0.9662
(6, 0)	6	0.4848	0.4659	0.4854	0.4902	0.4697	3.2344	4.1820	0.9792
(10, 0)	10	0.5094	0.5009	0.7925	0.7962	0.7829	1.2114	1.6704	0.4647
(15, 0)	15	0.5173	0.5133	1.1807	1.1834	1.1743	0.5505	0.7690	0.2282
(20, 0)	20	0.5200	0.5178	1.5706	1.5726	1.5658	0.3056	0.4324	0.1272

D, D_m and D_t are the diameter associated to the unmodified method, modified method and conformal mapping, respectively. ε represents the relative error of unmodified method taking D as the reference solution, ε_1 represents the relative error of modified method taking D_m as the reference solution, ε_2 represents the relative error of modified and unmodified method.

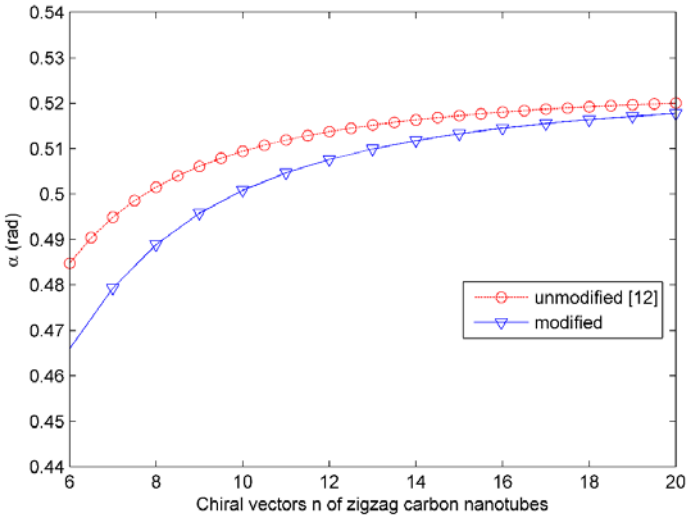

Figure 3 The α angle varies with the chiral vector of the zigzag carbon nanotubes.

As can be seen from Table 1 and Figure 4, the relative error of the diameter obtained by the modified method is larger than that of the uncorrected method, because of the increase of the energy term and the effect of the preenergy on the diameter of the small tube. With the increase of tube diameter, the effect of inversion energy is gradually weakened, so the relative deviation is gradually reduced. The modified numerical results are more valuable because the pre-energy and the inversion energy of the CNTs are not negligible in the unstressed state, especially in the small diameter of the CNTs (D<1nm).

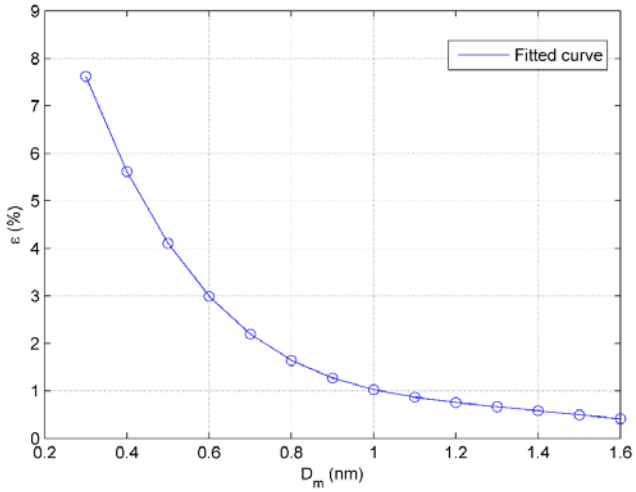

Fig. 4 Relative error against diameter obtained by modified method (Zigzag, AMBER)

5. Conclusion

In this paper, a modified energy method is proposed. When zigzag carbon nanotubes are in stress-free state, the bond angle of carbon nanotubes will change when graphene sheets are bent due to curvature. The inversion energy term is added to the modified method and the results show that the effect of inversion energy on the diameter of zigzag carbon nanotubes cannot be neglected, especially under small diameter. The zigzag carbon nanotubes introduced in this paper also have such effects in armchair and chiral carbon nanotubes. The effects and differences of these effects will continue to be studied in the future.

Acknowledgements

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