A Modified Energy Method for Stress-Free of Armchair Single-Walled Carbon Nanotubes

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Abstract. In this paper, the geometric analysis of armchair-shaped single-walled carbon nanotubes (SWCNTs) without external loading is carried out by energy method. Carbon nanotubes are thin-walled cylinders made of monolayer graphene. Based on the theory of molecular mechanics, an improved mechanical model was proposed to predict the energy of armchair carbon nanotubes (CNTs) under stress-free conditions, and the diameter of CNTs was estimated according to the principle of minimum energy. The results show that the diameter obtained by the improved model is larger, but basically consistent with that obtained by conformal mapping. The inversion energy term is added to the modified model, and the inversion energy term related to atomic curvature is characterized by the conization angle. It can be seen from the error that the inversion energy of carbon nanotubes can not be neglected in the stress-free state, especially in the case of small diameter.

Introduction

In 1991, Lijima discovered multi-walled carbon nanotubes (MWCNTs) when he observed hard deposits formed by evaporation of graphite cathode arc using high resolution electron microscopy [1]. As quasi-one-dimensional nano-materials, carbon nanotubes (CNTs) have attracted wide attention from scholars in different fields due to their unique atomic structure and physical and chemical properties, such as high elastic modulus, excellent conductivity and good adsorption capacity [2-6]. There are many methods to study carbon nanotubes, including experiment, simulation and theoretical calculation. Although the MD method has been widely used to simulate the properties of nanostructured materials, it is a complex and time-consuming method, especially for a large number of atomic systems. Therefore, continuum mechanics seems to be a good method to study the properties of carbon nanotubes. Another modeling method is based on atomic continuum technology, which has the unique advantage of describing the atomic structure characteristics in the continuum framework. It can reduce the computational requirements while using appropriate atomic constitutive relations [7].

Therefore, it is necessary to develop an energy method to analyze the mechanical properties of carbon nanotubes at atomic scale. Considering that carbon nanotubes are rolled cylindrical graphite sheets, we extend the classical structural mechanics theory to the modeling of carbon-graphite sheets by calculating Young's modulus of C-C bond of Euler beam at atomic scale. In this paper, graphene sheets are curled into carbon nanotubes without longitudinal and transverse stresses. Because of the curvature effect, the mechanical and physical properties of the structure will change after rolling two-dimensional sheet metal into three-dimensional tube. In cylindrical coordinates, considering the curvature effect, the angle between adjacent bonds in armchair carbon nanotubes carbon cycle is different from that of graphite sheets. According to the AMBER potential, the pyramidation angle of the p-orbital direction of carbon atoms based on POAV technique is proposed [8], and the inverse energy term related to the atomic curvature is described.
**Interatomic Potential of Armchair CNTs**

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:

\[
U = \sum U_r + \sum U_\theta + \sum U_\varphi \\
= \frac{1}{2} \sum K_r (\Delta \theta)^2 + \frac{1}{2} \sum K_\theta (\Delta \theta)^2 + \frac{1}{2} \sum K_\varphi (\Delta \varphi)^2
\]

(1)

where \(U_r\), \(U_\theta\) and \(U_\varphi\) are the bonding energy associated with bond stretching and inversion, respectively. \(K_r\), \(K_\theta\) and \(K_\varphi\) are the stretching constants, bending force constants and inversion force constants. In this paper, the three constants are \(K_r = 652\, nN/\text{nm}\), \(K_\theta = 0.876\, nN/\text{nm}\) and \(K_\varphi = 4.65\, nN/\text{nm}\), respectively [8, 9].

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:

\[
U = \frac{1}{2} \sum K_\theta (\Delta \theta)^2 + \frac{1}{2} \sum K_\varphi (\Delta \varphi)^2
\]

(2)

**Initial Diameter for Armchair 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 [8], the change of angle for the inversion energy can be showed as Fig. 1. The simple relations among these angles are derived as:

\[
\tan \psi = \frac{\cos (\theta_i/2) \sin \left(\frac{\pi}{2n}\right)}{1 + \cos (\theta_i/2) \cos \left(\frac{\pi}{2n}\right)}
\]

(3)

\[
\Delta \varphi = \tan^{-1} \left( \frac{\cos (\theta_i/2) \sin \left(\frac{\pi}{2n}\right)}{1 + \cos (\theta_i/2) \cos \left(\frac{\pi}{2n}\right)} \right)
\]

(4)

where \(\theta_i\) is the bond length, \(n\) is the chiral vectors of armchair carbon nanotubes.
According to the principle of minimum energy $\left[\frac{\partial U(D)}{\partial D}\right]_{\Omega_b} = 0$, the unmodified AMBER potential can be expressed as [9]:

$$4nK_o \left( \frac{\Delta \theta_2}{\Delta \alpha} \frac{\partial \Delta \theta_2}{\partial \alpha} + 2\Delta \theta_1 \frac{\partial \Delta \theta_1}{\partial \alpha} \right) + 6nK_\psi \frac{\partial \Delta \psi}{\partial \alpha} = 0$$

(5)

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

$$D = \frac{a_o}{\sin \frac{\pi}{2n}} \sqrt{1 + \sin^2 \alpha + 2\sin \alpha \cos \frac{\pi}{2n}}$$

(6)

where $a$ is the bond length and $a = 0.142\text{nm}$.

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

$$2\left( \alpha - \frac{\pi}{6} \right) + \left( \Delta \theta_1 - \Delta \omega \frac{3K_m}{2K_o} \frac{\partial \Delta \omega}{\partial \Delta \theta_1} \right) \frac{\partial \Delta \theta_1}{\partial \alpha} = 0$$

(7)

where
\[ \Delta \theta_1 = \arccos \left[ -\sin \alpha \cos \frac{\pi}{2n} \right] - \frac{2\pi}{3} \]

(8)

\[ \Delta \theta_2 = \frac{\pi}{3} - 2\alpha \]

(9)

The expression (7) is a nonlinear equation of \( \alpha \), which was solved numerically by the Newton method. Once \( \alpha \) 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 [9] and the relative error taking \( D_m \) as the reference solution are included to get an insight into the difference.

**Results and Discussion**

As shown in Table 1, the diameter obtained by the modified method is slightly higher than that obtained by the conformal mapping and the unmodified method. This difference may be related to the pre-energy stabilization effect, which tends to expand transversely. The smaller the diameter is, the more obvious the prophase effect is. The diameter of armchair carbon nanotubes is different from that of zigzag carbon nanotubes, which is closely related to the structure of carbon nanotubes. The diameter obtained by the modified method is larger than that obtained by the uncorrected method. This is because the modified method adds an inversion energy term. As shown in Figure 3, the angle obtained by the correction method is small. The same result can be seen in conjunction with equation (6). In addition, in the case of small diameter, because of the large curvature of small diameter carbon nanotubes, the influence of inversion energy is particularly obvious. However, with the increase of pipe diameter, this effect will gradually decrease, and the same trend is shown in Table 1.

| n   | \( \alpha \)[rad] | \( \alpha_m \)[rad] | \( D \)[nm] | \( D_m \)[nm] | \( D_t \)[nm] | E[\%] | \( \varepsilon_1 \)[\%] | \( \varepsilon_2 \)[\%] |
|-----|------------------|------------------|----------|----------|----------|------|----------------|----------------|
| (4, 4) | 4 | 0.5375 | 0.5431 | 0.5514 | 0.5531 | 0.5424 | 1.6322 | 1.9346 | 0.3074 |
| (5, 5) | 5 | 0.5327 | 0.5375 | 0.6853 | 0.6872 | 0.6780 | 1.0652 | 1.3388 | 0.2765 |
| (6, 6) | 6 | 0.5300 | 0.5339 | 0.8197 | 0.8215 | 0.8215 | 0.2191 | 0.2191 | 0.2191 |
| (10, 10) | 10 | 0.5260 | 0.5277 | 1.3597 | 1.3611 | 1.3560 | 0.2721 | 0.3747 | 0.1029 |
| (15, 15) | 15 | 0.5246 | 0.5255 | 2.0365 | 2.0375 | 2.0340 | 0.1228 | 0.1718 | 0.0491 |
| (20, 20) | 20 | 0.5242 | 0.5247 | 2.7139 | 2.7147 | 2.7120 | 0.0700 | 0.0995 | 0.0295 |

\( D, D_m \) and \( D_t \) are the diameter associated to the unmodified method, modified method and conformal mapping, respectively. \( \varepsilon \) represents the relative error of unmodified method taking \( D \) as the reference solution, \( \varepsilon_1 \) represents the relative error of modified method taking \( D_m \) as the reference solution, \( \varepsilon_2 \) represents the relative error of modified and unmodified method.
Figure 3. The $\alpha$ angle varies with the chiral vector of the armchair carbon nanotubes.

As can be seen from Table 1 and Figure 4, the relative error of diameter obtained by the modified method is larger than that obtained by the unmodified method due to the increased influence of the inversion energy term and the influence of small tubule diameter. With the increase of tube diameter and curvature, the effect of inversion energy decreases and the relative deviation decreases. The modified numerical results are more valuable because the pre-energy and inversion energy of armchair CNTs are not negligible in the unstressed state, especially in the case of small diameter ($d<1\text{nm}$).

Figure 4. Relative error against diameter obtained by modified method (armchair, AMBER)

**Conclusion**

An improved energy method based on molecular structural mechanics is proposed in this paper. When the armchair carbon nanotubes are in a stress-free state, the binding angle of carbon nanotubes will change when the graphene plate is bent. The results show that the effect of inversion energy on the diameter of armchair carbon nanotubes can not be ignored, especially in the case of small diameter. The armchair carbon nanotubes described in this paper are similar in zigzag and chiral carbon nanotubes. This study will provide more accurate basis for experiment and theoretical simulation.
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