Molecular structural mechanics applied to coiled carbon nanotubes

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**A B S T R A C T**

In this paper, mechanical properties of single-walled helically coiled carbon nanotubes are investigated by means of molecular structural mechanics method in ANSYS finite element code. To specify the geometry of coiled carbon nanotubes, a construction procedure is proposed which offers a full control over the morphology of the coiled nanotubes. In this construction approach, first a development map is drawn on a graphene sheet and then this graphene sheet is rolled to form a defected straight carbon nanotube; then, the sides of these defects are stuck together through a nonlinear analysis and finally, the straight carbon nanotube forms into coiled carbon nanotube. Using this construction procedure, several coiled nanotubes are built and their spring constants are calculated. It is shown that the spring constants found are in good agreement with those obtained from density function theory and tight-binding calculations reported in the literature. Moreover, in order to facilitate the simulation of those macroscopic systems which contain coiled carbon nanotubes, an equivalent continuum model is proposed and its mechanical properties are investigated. It is found that, as the tube diameter increases, both spring constant and shear modulus of the coiled carbon nanotube increase.

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**1. Introduction**

Soon after the discovery of carbon nanotubes (CNTs) in 1991 [1], the idea of their other morphologies emerged. These morphologies include coiled carbon nanotubes (CCNTs) [2–5], Y-branched carbon nanostructures [6–8], nanotori [3, 9–12], CNT knees [13, 14] and pointed CNTs, which have a sharp tip and cylindrical base [15].

Among these nanostructures, CCNTs have attracted considerable attentions in recent years, owing to their remarkable mechanical and electrical properties [16, 17], which come of their unique helical structures in combination with the CNTs unique characteristics. A CCNT can be geometrically viewed as a graphene sheet (single-walled) or nested graphene sheets (multi-walled) which are rolled and twisted to form a helically coiled nanotube. The existence of the helically CCNTs were first predicted in the early 1990s by molecular dynamics (MD) simulations [2, 3] and it was shown that these nanostructures are thermodynamically stable [18]. A few years later, their experimental fabrication and observation were reported [19].

CCNTs have numerous potential applications, for example because of their superelastic properties [20], they can be utilized as mechanical components such as nanosprings or as a promising reinforcement in advanced composites. Their coiled shapes would favor a better load transfer to the matrix and they would be better anchored in the matrix than in the case of ordinary straight nanotubes [16]. Moreover, because of the presence of heptagonal and pentagonal carbon rings in their structure, their electronic properties have significantly changed and are unlike the CNTs. They show semi-metallic character and as a result they have the possible application of being used as superconducting materials [4].

Despite numerous potential applications and remarkable properties of CCNTs, a few theoretical studies are conducted to examine these properties and most of the researches are devoted to the growth mechanism of these nanostructures [16]. The theoretical investigations lead us to a thorough understanding of detailed behavior of the nanostructures and help us to better utilize them in practical applications.

In theoretical mechanics approaches, different length scales require different theoretical methods. Computational chemistry and continuum mechanics are the best-known methods for investigation of microscopic and macroscopic properties, respectively. Nevertheless, nano-length scale of the nanostructures and their applications in macroscopic devices imply a large difference in the length scales involved, and demand new theoretical approaches due to the huge required computational tasks in atomistic methods and unsuitability of continuum mechanics. In order to overcome this issue several novel classical mechanics approaches have been proposed including shell [21], truss [22], beam [23] and special finite element models [24]. Among them, the molecular structural mechanics (MSM), in which bonds are simulated with accuracy.
Li and Chou [23] proposed the MSM method for investigation of mechanical properties of graphene sheet as well as shear and Young’s moduli of CNTs of different size and chirality. In [25], this method was used and van der Waals interactions were considered to investigate the buckling behavior of multi-walled and single-walled CNTs. They also employed this method to study the heat capacity of multi-walled CNTs [26] and specific heat of single-walled CNTs [27].

The numerous successful applications of the MSM method in a wide range of study fields, as well as its simplicity and accuracy, inspired us to adopt this method for analysis of CCNTs. In this paper, the MSM method is employed to construct and study CCNTs. In order to specify the geometry of the coiled nanotubes, a systematic approach is proposed, which offers a full control on the morphology of coiled nanotubes. In this approach, first a development map is drawn on a graphene sheet and then this sheet is rolled to form a defected straight CNT; finally the sides of defects are stuck together through a nonlinear analysis and the straight nanotube is formed into a CCNT. Using this construction procedure several CCNTs are built and their spring constants are obtained. It is shown that, these findings are in good agreement with those reported in literature [5]. Moreover, an equivalent continuum model is proposed and its mechanical properties are investigated.

2. Molecular structural mechanics theory

Fundamental to molecular mechanics (MM) is to mathematically model a molecule as a collection of balls (corresponding to atoms) held together by springs (corresponding to bonds) and to express the energy of a molecule in terms of the geometry, i.e. as a function of its resistance to bond stretching, bond bending and atom crowding [28,29]. The main advantage of MM is the low amount of required computational tasks which is seldom at the expense of accuracy. The possible pitfalls in using MM are discussed by Lipkowitz [30].

In MM methods, the total potential energy $U$, is generally expressed as

$$U = \sum U_i + \sum U_b + \sum U_o + \sum U_\text{vdw} + \sum U_\text{el}$$

where $U_i$, $U_b$, $U_o$, and $U_\text{vdw}$ are energy contributions from bond stretching, bond bending, dihedral bond torsion and out-of-plane torsion, respectively and $U_\text{vdw}$ and $U_\text{el}$ are nonbonded energies associated with Van der Waals and electrostatic interactions. The mathematical form of these terms and their parameters constitute a particular forcefield (this is the reason why MM methods are sometimes called forcefield methods).

For covalent systems, the main contributions to the total energetic come from the first four terms. In this paper a harmonic expression is adopted for bond bending and bond stretching from AMBER forcefield [31]; dihedral angle torsion and out-of-plane torsion are merged into a single harmonic form [23] and energy contributions from nonbonded interactions are neglected. Therefore,

$$U_i = K_r (r - r_0)^2 = K_r (\Delta r)^2$$
$$U_b = K_\theta (\theta - \theta_0)^2 = K_\theta (\Delta \theta)^2$$
$$U_o = U_\text{vdw} + U_\text{el} = K_\tau (\Delta \phi)^2$$

where $K_r$, $K_\theta$, and $K_\tau$ are bond stretching, bond bending and torsion force constants. Using the AMBER forcefield [31], the force constants used in this paper are $K_r = 46,900$ kcal/mole nm$^{-2}$, $K_\theta = 63$ kcal/mole rad$^{-2}$ and $K_\tau = 20$ kcal/mole rad$^2$. The parameters $\Delta r$, $\Delta \theta$, and $\Delta \phi$ represent the bond bending, bond stretching and dihedral torsion, respectively. The harmonic expression assumption for energy terms enables us to simulate the atomic interactions by means of simple linear elastic beam elements with the following governing equations.

$$U_i = \frac{1}{2} \frac{E A}{L} (\Delta L)^2$$
$$U_b = \frac{1}{2} \frac{E I}{L} (2x)^2$$
$$U_o = \frac{1}{2} \frac{G J}{L} (\Delta \beta)^2$$

Here $U_i$, $U_b$, and $U_o$ stand for energy contributions from axial loading, bending moment and torsional loading corresponding to bond stretching, bond bending and merged torsional potential energy terms of MM, respectively. The parameters $\Delta L$, $x$ and $\Delta \beta$ represent the beam stretching, angle variation of one beam and torsional angle variation, respectively. Beam elongation and torsion represent the bond stretching and merged torsion ($\Delta L = \Delta r$ and $\Delta \beta = \Delta \phi$) and the angle variation between two neighbor bonds of an atom equals twice angle variation of one beam $(2x = \Delta \theta)$. Therefore the stiffness parameters of the beam structure can be determined as

$$1 \frac{E A}{2 L} = K_r$$
$$1 \frac{E I}{2 L} = K_\theta$$
$$1 \frac{G J}{2 L} = K_\tau$$

This approach in which bonds are simulated with beams is referred to as MSM method.

3. Structural modeling and numerical simulations

3.1. Molecular structural mechanical model

To assess the suitability of present structural model and its parameters for analyzing CCNTs, straight CNTs, for which there is a wealth of literature [32–34], are examined first. Since the mechanical behavior of helical springs is considered to be mainly in response to torsion, in this verification, torsional stiffness of CNTs are examined and compared with available atomistic computational data. Moreover, the behavior of CNTs under axial loading condition is also examined. ANSYS commercial finite element code is used to model and analyze these two types of loadings and specify the associated stiffness parameters. Bonds are simulated with three-dimensional BEAM4 element.

In order to determine the geometry of the beam structure, a CNT is viewed as a rolled graphene layer with a radius of

$$r = \frac{b}{2 \pi} \sqrt{3(m^2 + mn + n^2)}$$

in which $m$ and $n$ are lattice translation indices and $b$ is the bond length for which a value of 0.1421 nm is adopted [35]. Fig. 1 illustrates the two types of boundary conditions corresponding to axial and torsional loading exerted on an (8,8) CNT.

Stiffness parameters for equivalent continuum models of armchair CNTs obtained from MSM, compared to those obtained from MD simulations reported in literature [32], are illustrated in Fig. 2. As shown in this figure, the shear moduli, which dominate the coiled CNTs behavior, as well as the Young’s moduli are in good agreement with MD simulations. This confirms the suitability of the employed molecular structural mechanics method and its
parameters for analyzing CCNTs. However, it should be mentioned that in [32] the force constant parameters were slightly different ($K_r = 70,000$ kcal/mole nm$^2$ and $K_h = 100$ kcal/mole rad$^2$) which explains the overestimation of the Young’s modulus in Fig. 2.

3.2. CCNT construction procedure

The first step towards studying coiled CNTs is to specify their geometry. Unlike straight CNTs, the construction procedure of coiled CNTs is not so straightforward. An essential difference between the helically coiled and straight CNTs is that the former must include pentagonal and heptagonal rings, whereas they are absent in the latter [2]. These ring patterns are also present in other types of carbon nanostructures and they are considered to be responsible for bending of straight CNTs. Pentagons form concave surfaces, while heptagons result in convex ones [36].

In order to construct a helical structure Ihara [2] tiled the optimized pattern of the rings of several nanotubes by cutting them into pieces and stretching them toward the fiber axis. Akagi et al. [4] drew a development map, including holes of pentagonal shape, on the surface of a perfect graphite layer. He stuck the sides of the holes together and then rolled the graphite layer to form the tube of the helix. Liu et al. [5] first individually introduced one pair of heptagons and one pair of pentagons in two sides of a CNT to form a basic segment and then assembled these segments to construct carbon nanocoil.

A systematic approach to form a CCNT should offer a full control on the geometric parameters of the produced coiled nanotube. In addition, it should be easy to understand and easy to make use of. For these purposes, we suggest to draw a development map, including hexagonal holes, on a graphene sheet. This sheet first is rolled to form a defected nanotube and then the two sides of each hole are stuck together to construct the coiled nanotube thorough a nonlinear analysis. Accordingly, in the proposed modeling method there are three steps towards constructing a coiled nanotube:

1. Introducing hexagonal holes in the perfect graphene sheet (Fig. 3a).
2. Rolling graphene sheet to form a defected CNT (Fig. 3b).
3. Sticking the two sides of each hole together to construct the CCNT (Fig. 3c).

Fig. 3 illustrates the three steps of the proposed modeling procedure towards constructing a CCNT. The same structure was previously built according to [2,4]. Ihara and Akai called it, 36I [6,10,4,1] coiled CNT and helix C360, respectively.

In the proposed modeling procedure, the hole edges meeting at acute angle define the two pentagonal carbon rings, placed in the outer sides of CCNTs, and the those meeting at obtuse angle form the heptagonal rings, placed in the inner sides of coiled CNTs. As illustrated in Fig. 3, four edges of each hole are equal in length and perpendicular to the bonds and the remaining two edges are also equal in length but tangent to the bonds. Thus, the length of tangent and perpendicular edges and consequently the dimensions of the holes can be specified based on only one vector. In addition, two vectors are needed to specify the two directions and offsets of the holes array.

Accordingly, the shape of the development map and thus, the geometry of the coiled nanotube is determined by three vectors: the hole vector $H$, which specifies the dimensions of the hexagonal holes, the arrangement vector $A$ and rolling vector $R$, which specify the arrangement of the holes formed in step one. In addition, the rolling vector $R$ represents the rolling direction and thus the tube diameter and chirality of the defected CNT, produced in step two. These vectors are illustrated in Fig. 3. They can be expressed in terms of basic vectors $a_1$ and $a_2$ as $(n,m)$ such that

$$V = na_1 + ma_2$$

The dimensions of the hexagonal holes compared to the tube diameter are the prominent factor in determining the angle at which the straight CNT is bent (bending angle). In the other words, the ratio of the length of the hole vector $H$ to the rolling vector $R$ determine the bending angle. A wide hole results in a bending angle of high value and consequently the produced coiled nanotube would have a polygonal shape from the top view, similar to CCNTs.
examined by Liu et al. [5]. Rolling vector \( R \) determines the tube diameter. The arrangement and hole vectors compared to the rolling vector, take part in specifying the pitch and the diameter of the coil.

Because of the large deformations involved in the third step, a nonlinear analysis is employed. Furthermore, in order to avoid convergence problems this nonlinear analysis is broken up into three to five nonlinear analyses, each with a smaller deformation.

Based on this modeling approach several CCNTs, similar to those examined by Liu et al. [5], are constructed as illustrated in Fig. 4. Among the wide variety of possible structures, here the CCNTs are constructed from defected \((n,n)\) armchair CNTs with widest possible holes and minimum possible pitch, and are called \((n,n)\) CCNTs [5]. The components of vectors \( R \), \( A \) and \( H \) corresponding to each coiled nanotube are expressed in terms of basic vectors \( a_1 \) and \( a_2 \), in Table 1.

4. Results and discussion

4.1. Mechanical properties of CCNTs

To specify the spring constant of these coiled CNTs, fixed boundary condition is applied to both ends of the coiled CNTs with the aim of more accurately simulating the experiments. This is more close to the real situation because clamps can effectively prevent coils from rotation [37].

We again made use of ANSYS commercial finite element code to simulate the structural model of the coiled CNTs and specify their spring constants. As shown in Fig. 4, a set of forces parallel to the coil axis (with a sum of 1 nN) is exerted to one end of each CCNT and the other end is set to be fixed. Spring constants \( k \) are calculated for one pitch.

\[
k = \frac{\text{force}}{\text{elongation}} \times \text{number of pitches}
\]

Here, elongation is measured by averaging the displacement of boundary atoms. Fig. 5 demonstrates the estimated spring constants from numerical analysis compared to those of density functional theory (DFT) and tight-binding (TB) calculations reported in literature [5]. As shown, the results obtained from present MSM method are in good agreement with those of atomistic calculations [5]. The results reveal that for this special class of CCNTs, the spring constant gradually increases with the tube diameter.

It should be noted that for the \((8,8)\) coiled CNT there is a significant inconsistency between the spring constant obtained from the present method and that presented in [5]. Unfortunately there is no experimental data for coiled CNT’s of this scale to assess the obtained results. Liu et al. did not present any explanation to justify this dramatic change in spring constant of \((8,8)\) CCNT and in addition they did not investigate the spring constant of CCNTs of larger diameters. It seems that such a huge increase in the spring constant of \((8,8)\) coiled CNT in the results reported by Liu, et al. would be inconsistent and the steady increase according to the results obtained in this study is more realistic.

4.2. Equivalent continuum model

In order to facilitate the examination of those macroscopic systems which contain coiled CNTs, it is beneficial to replace coiled CNTs with equivalent continuum models. As a first order estimation, a coiled CNT can be considered as a thin hollow torsional bar with the following governing equation

\[
k = \frac{Gt}{(R)^3} + \frac{G}{r} = C_g G
\]

in which \( k \), \( G \), \( t \), \( R \) and \( r \) are spring constant, shear modulus, wall thickness, coil radius and tube radius, respectively. The coefficient \( C_g \), which stands for the geometry of the CCNT, is introduced to investigate the contribution of geometry and stiffness of CCNT to the increase in spring constant. The tube radius is considered to be equal to the radius of corresponding straight CNT and the coil radius is measured as the difference of outer radius of the coil and tube radius. A value of 0.34 nm is adopted for the wall thickness. It should be mentioned that the measurement method may affect the shear modulus and geometry coefficient and thus measuring the geometry parameters based on another assumptions may cause slight differences. Based on this equation and measurements,
geometric parameters and spring constants are used to calculate shear moduli of equivalent continuum models for the CCNTs. For a more precise expression, the pitch angle and the curvature as well as the applied fixed boundary condition should be taken into account. Therefore, the modified spring constant can be expressed as follows \[ k_{\text{modified}} = \frac{1}{1 + \zeta_1 + \zeta_2} k \]

where \( \zeta_1 \) is the contribution from the spring geometry, while \( \zeta_2 \) is caused by the fixed boundary conditions. The parameter \( \zeta_1 \) can be expressed in terms of geometric parameters (the ratio of the tube radius to the coil radius \( r/R \), and the pitch length \( p \)) and Poisson’s ratio \( \nu \), as

\[ \zeta_1 = -\frac{3}{16} \left( \frac{r}{R} \right)^2 + \frac{3 + \nu}{2(1 + \nu)} p^2 \]

Huang [37] argued that if one takes \( \nu = 0.33 \), in the ordinary range of \( \nu \) (0.2 \( \leq \) \( \nu \) \( \leq \) 0.45) the error induced in \( \zeta_1 \) will not exceed \( \pm 7\% \). Thus in this paper a value of 0.33 is taken for \( \nu \) to calculate the modification factor \( \zeta_1 \). Moreover, our investigations as well as the theoretical results presented in [37] reveal that the boundary conditions have a little effect on the CCNTs spring constant. Therefore, here the modification factor \( \zeta_2 \) is neglected.

Accordingly, the unmodified and modified shear moduli and geometry coefficients of coiled CNTs as well as shear moduli of straight CNTs are calculated and illustrated in Figs. 6 and 7. As shown in these figures, the CCNTs shear moduli have a significant increase compared to those of straight CNTs.

Table 1
Arrangement, hole and rolling vectors for \((n,n)\) coiled CNTs examined in this paper.

<table>
<thead>
<tr>
<th>( n )</th>
<th>CCNT</th>
<th>( A )</th>
<th>( H )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>(5,5)</td>
<td>(-4.5)</td>
<td>(-4,-1)</td>
<td>(5,5)</td>
</tr>
<tr>
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<td>(6,6)</td>
<td>(-5.6)</td>
<td>(-5,-1)</td>
<td>(6,6)</td>
</tr>
<tr>
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<td>(-6.7)</td>
<td>(-6,-1)</td>
<td>(7.7)</td>
</tr>
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<td>(-8.9)</td>
<td>(-8,-1)</td>
<td>(9,9)</td>
</tr>
<tr>
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<td>(-9,-1)</td>
<td>(10,10)</td>
</tr>
<tr>
<td>11</td>
<td>(11,11)</td>
<td>(-10.11)</td>
<td>(-10,-1)</td>
<td>(11,11)</td>
</tr>
</tbody>
</table>

Fig. 4. (8,8) CCNT model constructed and subjected to axial load of 1 nN.

Fig. 5. Spring constants of \((n,n)\) CCNT obtained from present MSM method compared to those reported in the literature from density function theory (DFT) and tight-binding (TB) methods.

Fig. 6. Shear moduli of equivalent continuum \((n,n)\) CCNTs.
5. Conclusions

In this paper, mechanical properties of single-walled helically coiled CNTs are investigated. To specify the geometry of the coiled nanotubes a construction procedure is proposed. This construction procedure enables us to fully control both the morphology and dimensions of the coiled CNTs. Spring constants for several coiled CNTs are calculated. The results demonstrate that the spring constant increases steadily as the tube diameter enlarges. In addition, an equivalent continuum model is proposed and its shear modulus is investigated. According to the obtained results, the shear moduli of coiled CNTs show a significant increase with tube diameter, compared to the shear moduli of straight CNTs.

References