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Twisting Carbon Nanotubes: A Molecular Dynamics Study.

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Abstract

We simulate the twist of carbon nanotubes using atomic molecular dynamic simulations. The ultimate twist angle per unit length and the deformation energy are calculated for nanotubes of different geometries. It is found that the big tube is harder to be twisted while the small tube exhibits higher ultimate twisting ratio. For multi-walled nanotubes, the zigzag tube is found to be able to stand more deformation than the armchair one. We observed the surface transformation during twisting. Formation of structural defects is observed prior to fracture.

Key words: carbon nanotubes, molecular dynamics, twist, NEMS

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1 Introduction

1 Carbon nanotube (CNT) is known as one of the strongest nanostructures cur-
2 rently known to mankind. This results from the high covalent energy of the
3 conjugated bonds between quasi- sp^2 carbon atoms. Their Young's moduli is
4 nearly 1 TPa and their ultimate stress can be up to 60 GPa [1, 2]. The thermal
5 conductivity of CNTs is also very high (about 4000 W/m.K) [3, 4]. This makes
6 them promising for future nanoelectromechanical systems (NEMS). Recently,
7 it has been reported that CNTs can be used as key rotational elements in

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8 a nanoactuator [5] and in an electromechanical quantum oscillator [6]. Their
9 potential application in ultra-high-density optical sweeping and switching de-
10 vices, bio-mechanical and chemical sensors or electromagnetic transmitters has
11 been mentioned [7]. Furthermore, it was shown by Jiang *et al.* [8] and Zhang *et*
12 *al.* [9] that multifunctional nanoyarns have been fabricated by twisting multi-
13 walled CNTs (MWCNTs) together.

14 Understanding the torsional behavior of CNTs for these promising applications
15 is a fundamental issue. In recent experimental studies, Williams *et al.* [10] mea-
16 sured the torsional constants of MWCNTs using atomic force microscopy force
17 distance technique and found that the MWCNTs become stiffer with repeated
18 deflection. Clauss *et al.* [11] presented atomically resolved scanning tunneling
19 microscopy images of twisted armchair single-walled CNTs (SWCNTs) in a
20 crystalline nanotube rope. Papadakis *et al.* [12] characterized nanoresonators
21 incorporating one MWCNT as a torsional spring, and found that inter-shell
22 mechanical coupling varies significantly from one tube to another.

23 The quantum conductance of CNTs depends strongly on their atomic struc-
24 ture, which can be changed by twisting [6]. The change of tube’s electronic
25 properties due to twist has been predicted in several theoretical studies [13, 14].
26 Recently, metal-semiconducting periodic transitions were reported in exper-
27 iments [6]. Moreover, Ertekin *et al.* [15] studied the ideal torsional strength
28 and stiffness of zigzag CNTs using first-principle calculations and found that
29 the strength of a MWCNT is about 20 times larger than that of an iron rod
30 of the same size. Wang *et al.* [16] calculated the shear modulus of CNTs using
31 molecular dynamics (MD). The mechanical integrity of SWCNTs was evalu-
32 ated by Shibutani *et al.* [17] with MD simulations. In this paper, we report
33 on the MD simulations computing the ultimate twist angle of CNTs at room
34 temperature. Related change in the deformation energy is also investigated.
35 The outline of this paper is as follows. The details about our computational
36 model will be presented in Section II. The results will be shown and discussed
37 in Section III. Then, we draw conclusions in Section IV. Analytical formulas
38 useful for the interatomic force calculation using the AIREBO potential are
39 given in Appendix.

40 2 Methods

41 To simulate the twisting of CNTs, we start with tubes fixed at one end by a
42 hypothetical substrate and relaxed in vacuum using a Nosé-Hoover thermostat
43 to reach equilibrium at 298 K. An imposed twist angle is then applied at the
44 other end by successive steps of 0.1 degree every 1000 fs. The positions of atoms
45 are updated at each iteration step (1fs) by using the leap-frog algorithm. In
46 the AIREBO potential [18, 19, 20], the total potential energy U^p of the system

47 is the collection of that of individual atoms:

$$U^p = \frac{1}{2} \sum_i \sum_{j \neq i} \left[V^R(r_{ij}) - b_{ij} V^A(r_{ij}) + V_{ij}^{L-J}(r_{ij}) + \sum_{k \neq i,j} \sum_{\ell \neq i,j,k} V_{kij\ell}^{tor} \right] \quad (1)$$

48 where V^R and V^A are the interatomic repulsion and attraction terms between
 49 valence electrons, for bound atoms i and j at a distance r_{ij} . The bond order
 50 function b_{ij} provides the many body effect depending on the local atomic en-
 51 vironment of atoms i and j . It is the key quantity which allows including the
 52 influence of the atomic environment of the bond (Huckel electronic structure
 53 theory). The long-range interactions are included by adding a parameterized
 54 *Lennard-Jones* 12-6 potential term V^{L-J} . V^{tor} presents the torsional inter-
 55 actions and depends on atomic dihedral angles. Note that the long-range van
 56 der Waals interactions between atoms in the same tube must be considered in
 57 the case of large deformation, to avoid an artificial cut-off energy barrier, as
 58 discussed in Ref. [2]. b_{ij} can be written as follows.

$$b_{ij} = \frac{1}{2} \left(b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi} + b_{ji}^{RC} + b_{ji}^{DH} \right) \quad (2)$$

59 where $b_{ij}^{\sigma-\pi}$ depends on the local coordination of i and j , and the bond angles,
 60 b_{ji}^{RC} represents the influence of possible radical character of atom j and of the
 61 π bond conjugations on the bond energy. b_{ji}^{DH} depends on the dihedral angle
 62 for C-C double bonds. Note that the value of b_{ij} is larger for a stronger bond.

$$b_{ij}^{\sigma-\pi} = \left[1 + \sum_{k(\neq i,j)} f_{ik}^c(\mathbf{r}_{ik}) \times G(\cos \theta_{ijk}) \exp(\lambda_{ijk}) + P_{ij} \right]^{-1/2} \quad (3)$$

63 where θ_{ijk} is defined as the angle between the vectors \mathbf{r}_{ij} and \mathbf{r}_{ik} . P_{ij} and
 64 $G(\cos \theta_{ijk})$ are a cubic and a fifth-order polynomial splines, respectively. The
 65 inter-atomic force is then calculated as the negative gradient of the total po-
 66 tential energy of the system. The formulation are presented in Appendix.

67 3 Results and Discussions

68 In this paper we studied the twist of various SWCNTs and of MWCNTs made
 69 of monochiral carbon layers, in which the interlayer distance is taken to be
 70 about 0.34 nm. The twisting angle θ is the angle between the initial position

71 of the outer wall and its deformed position, after an imposed rotation angle
72 at the free end, as shown in Fig. 1.

73 We next consider the surface change during the twisting. We observed that
74 periodic buckling waves appear on the tube surface when a tube is largely
75 twisted. The change of the helical shape of the CNT surface depends on the
76 tube radius. Fig. 2. shows the different shapes of three twisted chiral CNTs
77 prior to fracture. We can see that the buckling period is longer for big tubes
78 than for the small one. Furthermore, we find that the length of each buckling
79 period depends on the twisting angle and the tube radius. In our simulation,
80 the time step between each imposed deformation is taken to be long enough
81 (10000 step/degree) for letting the tubes have enough time to adapt to the
82 new deformation at one end. We note that, if we apply the deformation with
83 a higher rate (e.g. some degrees per *ps*), the fracture would occur earlier and
84 the buckling shape of the surface could be different.

85 Considering that the surface twisting can significantly change the electronic
86 properties of the tube [21], we present in Fig. 3 different shapes of the cross
87 section of a tube twisted to several twist angles. It can be seen that the section
88 remains circular when the deformation is relatively small. However, it deforms
89 to an ellipse when the deformation becomes important. Then, with increasing
90 twisting angle, this ellipse section rotates around the tube axis with an angular
91 momentum following the direction of deformation applied to the tube end.

92 How much twist deformation can a CNT sustain? To answer this question,
93 In Fig. 4, we show the fracture of a twisted SWCNT. We can see that when
94 $\theta = 596^\circ$, the honeycomb lattice of the tube is strongly deformed. The fracture
95 of the tube occurs very soon (some *ps*) after the appearance of the first defect.

96 In order to present general results from the here-studied short tubes, we define
97 the twist ratio as the twisting angle θ per unit length of CNTs. We plot in
98 Fig. 5 the ultimate value of the twist ratio (UTR) for 9 SWCNTs of a same
99 length but with different radii and chiralities. It can be seen that the UTR of
100 the small tubes is clearly higher than that of the big ones. We can also see
101 that the UTR of the zigzag tubes decreases faster than that of the armchair
102 tubes with increasing tube radius. We can conclude that a big tube can resist
103 better to twist than a small one.

104 To show further effect of the tube geometry, we define the deformation energy
105 of the tube as the change of the total potential energy of the CNT. It is an
106 important factor coupled to the tube's elastic constant. We plot in Fig. 6 the
107 torsion energy as a function of the twist ratio. We can see from Fig. 6 (a)
108 that the deformation energy of a big tube increases faster than that of a small
109 one, while the ultimate value of the deformation energy for a big tube is lower
110 than that for a small one. In Fig. 6 (b). we use the tubes of similar radii and

111 lengths to show that the deformation energy is almost independent of the tube
112 chirality. The increase ratio of deformation energy of the zigzag tube is slightly
113 higher than that of the chiral and the armchair ones. This corresponds to the
114 fact that the average axial bond strength of a zigzag SWCNT is slightly higher
115 than that of other tubes with similar sizes but differing chiralities [22, 23].

116 We study also the twist of multi-walled CNTs (MWCNTs), as demonstrated
117 in Fig. 7. It shows from two positions of observation how an armchair MWCNT
118 breaks under twist. We can see the appearance of buckling waves in both the
119 inner and outer layers when the tube is deformed, while the fracture occurs
120 first at the outer layer after the appearance of defects on its surface.

121 We show the ultimate twist ratio of MWCNTs in Table 1. It can be seen that
122 the UTR decreases with the number of carbon layers. The deformation energy
123 of a zigzag MWCNT is plotted in Fig. 8 (a). We can see that the energy per
124 atom of the outer layer during the deformation is much higher than that of
125 the inner layer. This can explain why the tubes are always broken from the
126 outer layer when they are largely twisted. We can also see that the van der
127 Waals interaction does not play a very important role in the total deformation
128 energy. In Fig. 8 (b), we can see the corresponding image of the failure of the
129 twisted tube.

130 4 Conclusions

131 In summary, the twist of CNTs has been simulated by using the MD method
132 based on the AIREBO potential. Surface transition from zigzag or armchair to
133 chiral type and periodic buckling waves were observed in our simulations. We
134 also observed the creation of defects and the fracture on the tube surface. The
135 cross section of SWCNTs is found to become an elliptic and rotates around
136 the tube center axis when the deformation is large enough. We calculated the
137 ultimate value of the twist ratio and the deformation energy for several types
138 of CNTs with different geometries. We find that the small tubes can be twisted
139 more than the big ones. The ultimate twist ratio of zigzag MWCNTs is higher
140 than armchair ones. Moreover, analytical formulas useful for the interatomic
141 force calculation using the AIREBO potential are given in Appendix.

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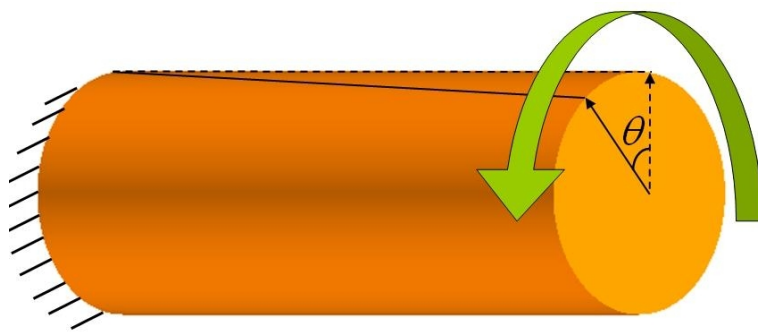


Fig. 1. (Color online) Schematic of the definition of the twisting angle θ . Imposed deformations are applied to one of the tube ends while another one is assumed to be fixed on a support.



Fig. 2. (Color online) Shape of three twisted chiral CNTs with a same length $L = 9.6\text{nm}$ and a same chiral angle $= 19.1^\circ$, prior to fracture at $\theta = 630^\circ$, 497° and 427° , respectively. Left: $(6, 3)$, $R = 0.31\text{nm}$; middle: $(14, 7)$, $R = 0.72\text{nm}$; right: $(20, 10)$, $R = 1.03\text{nm}$.

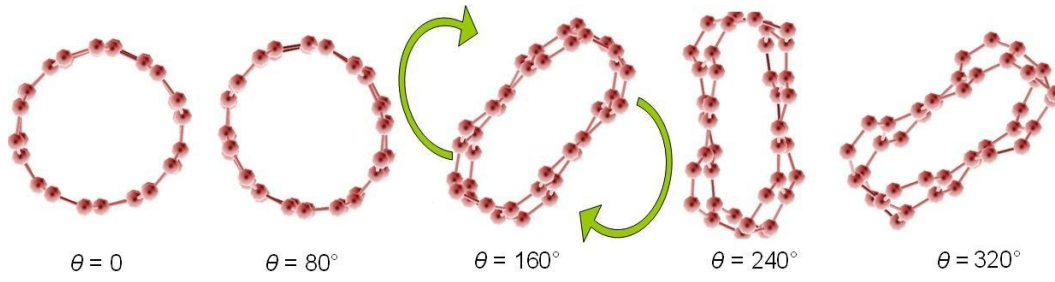


Fig. 3. (Color online) Cross section in the middle of a (5, 5) tube ($L = 9.5\text{nm}$) being twisted. The green arrows denote the direction of rotation.

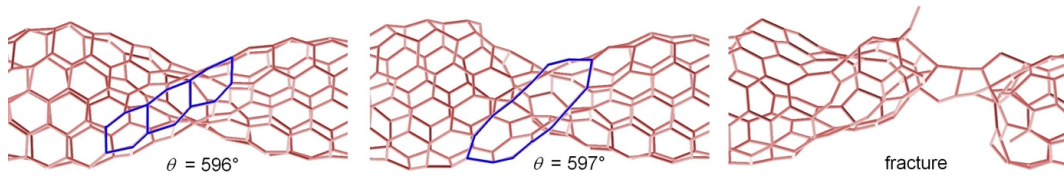


Fig. 4. (Color online) Fracture of a (5, 5) tube ($L = 9.5\text{nm}$) being twisted to fracture.

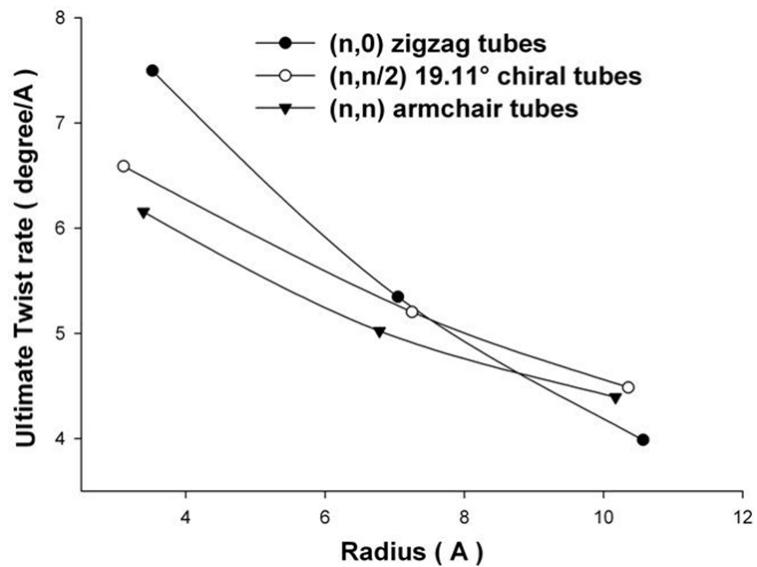


Fig. 5. Ultimate twist ratio versus the tube radius for 3 groups of tubes with different chiralities. Each group has 3 tubes with different radii. The length of all these tubes is fixed to 95 Å.

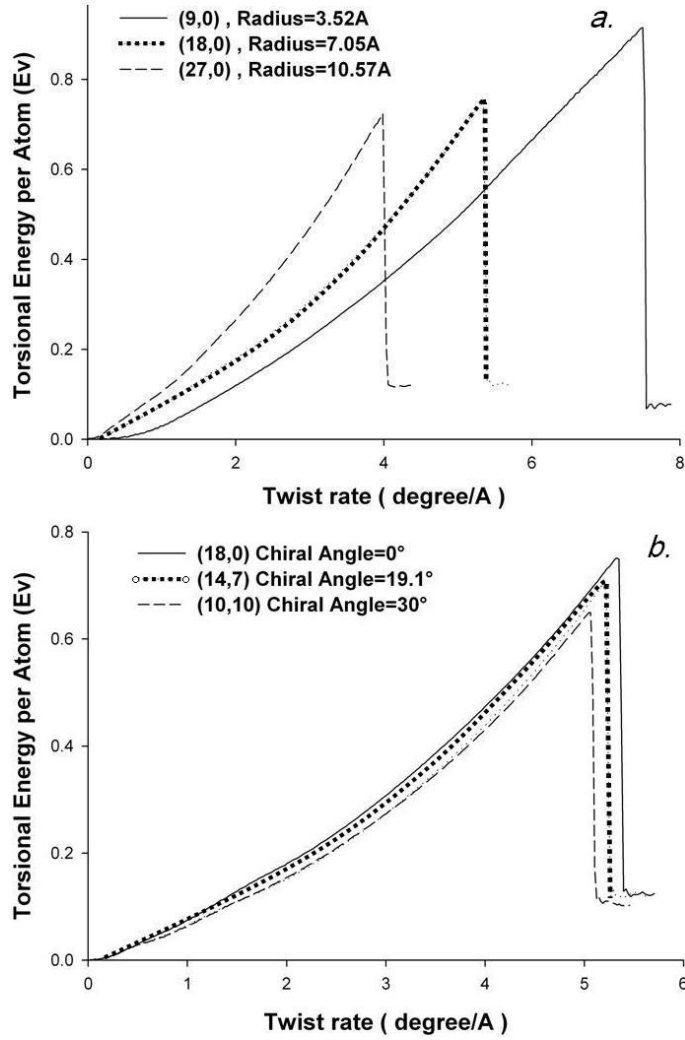


Fig. 6. Deformation energy versus the twist ratio for: (a) 3 zigzag tubes with the same length but with different radii, and (b) 3 tubes with almost the same length and radius but with different chiral angles. The deformation energy presented here is the value averages on all the atoms.

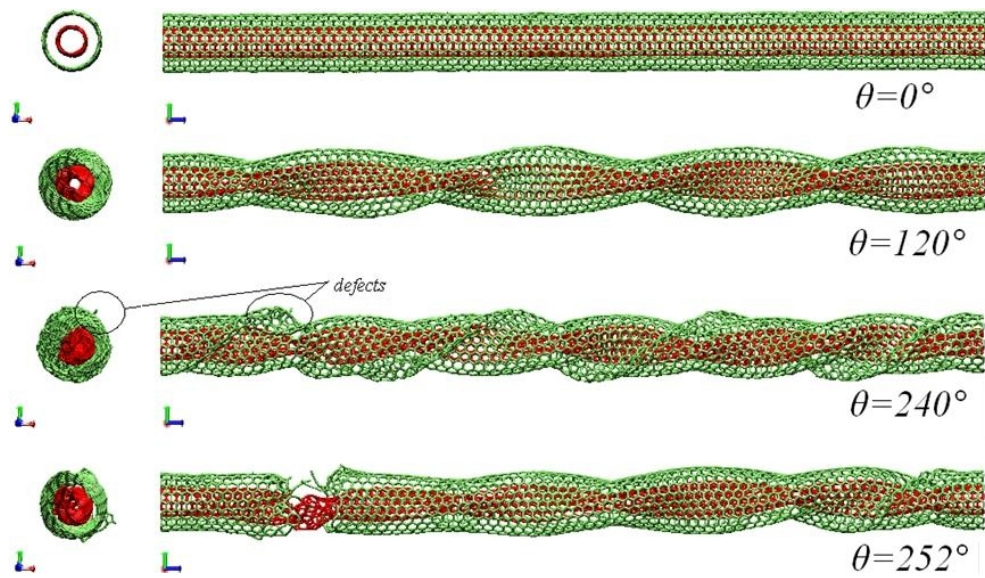


Fig. 7. (Color online) Fracture of an MWCNT (5,5)@(10,10) ($L = 194.3\text{\AA}$, $R = (3.39\text{\AA}@6.78\text{\AA})$)

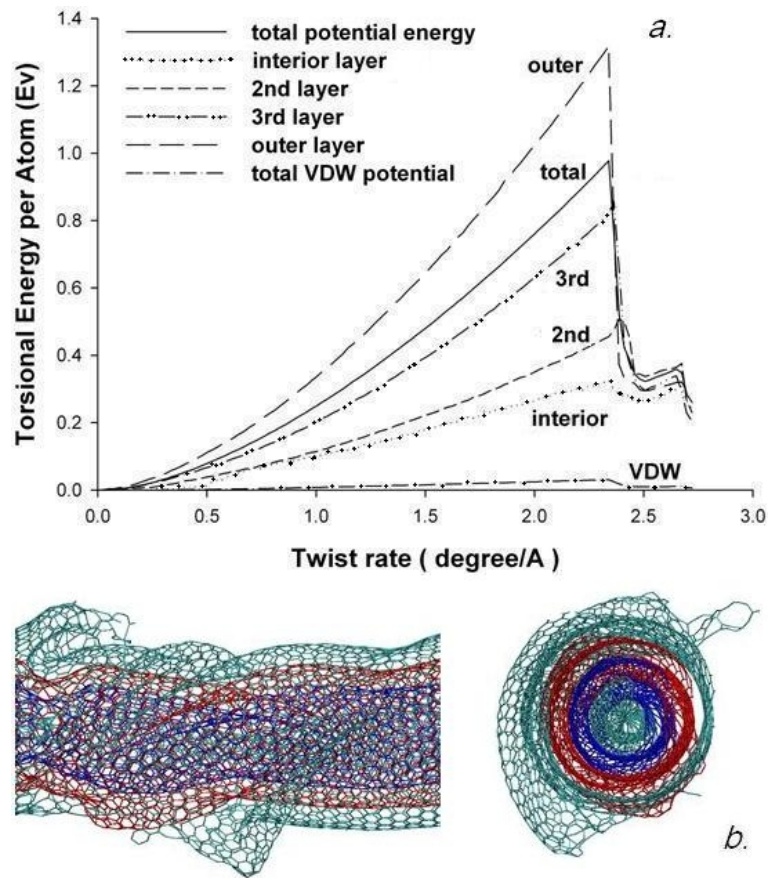


Fig. 8. (Color online) (a) Average deformation energy (per atom) vs. twist ratio for each layer in a MWCNT $(0,9)@(0,18)@(0,27)@(0,36)$ $L = 84.0\text{\AA}$. The deformation energy is the average value per atom. (b) Failure of this MWCNT being twisted. Top. side view. Bottom. cross-section view.

MWCNTs	UTR(degree/Å)
(5,5)@(10,10)	2.99
(5,5)@(10,10)@ (15,15) @ (20,20)	1.64
(5,5)@(10,10)@ ... @ 30,30)	0.96
(0,9)@(0,18)	3.66
(0,9)@(0,18)@ (0,27)@(0,36)	2.36
(0,9)@(0,18)@ ... @ (0,54)	1.55

Table 1

Ultimate twist ratio of MWCNTs with the same length about 200 Å.

¹⁴⁷ **Table**

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