

CARBON NANOCOILS: STRUCTURE AND STABILITY

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Abstract: We have constructed a model of single-wall helically coiled carbon nanotubes by means of graph theory and topological coordinates method. After obtaining three-dimensional coordinates of the atoms we proceed with the relaxation by successive application of the following methods: 1) harmonic approximation; 2) molecular mechanics based on the Brenner potential; and 3) density functional tight binding (DFTB). Finally, by DFTB and line group symmetry implemented POLSym code, we calculate total and cohesive energy of the obtained fully relaxed structures of CNCs.

Keywords: helically coiled carbon nanotubes, symmetry, topological coordinates, cohesive energy.

1. INTRODUCTION

Carbon nanocoils (CNCs) are experimentally observed by Zhang et al. in 1994 [2], shortly after being theoretically predicted by Ihara et al [1]. Their geometrical structure is usually described by four parameters: tubular diameter, pitch, inclination and diameter of a coil. Nowadays, CNCs synthesized by CVD method [3] have various helical and tubular parameters and regularly coiled structures have periodic incorporation of pentagons and heptagons into the basic hexagonal carbon network. Morphology of fabricated CNCs by this method can be controlled by synthesis conditions. Most of synthesized helically coiled carbon nanotubes are multiwall. Single wall CNCs are experimentally detected by Belgian group [4]. They reported geometrical parameters of the observed CNCs: pitch length, tubular diameter and overall diameter.

The atomic structure of regularly coiled carbon nanotubes consists of periodically inserted pentagons and heptagons into a slightly deformed basically hexagonal network. Many extraordinary physical properties, predicted for CNCs, present a motivation for their future investigation. They are presently being applied as: microwave absorbers, mechanical resonators, nanometer mechanical springs etc.

2. GEOMETRY AND SYMMETRY

Regularly coiled carbon nanotube can be imagined as a straight nanotube pulled onto helix.

Symmetry of CNCs is a line group from the first family $L^{(l)}=T_Q(F)C_l$ [5]. Elements of symmetry are rotation for $2\pi/Q$ around the helix axis followed by fractional translation along this axis. Symmetry group elements are the function of helical and tubular parameters. Geometrical parameters are divided into helical (radius of helix R , inclination angle χ or step of helix) and tubular (tubular radius ρ and monomer length a). Experimentally obtained results are usually presented with the following parameters: outer coil diameter $D=2(R+\rho)$ and tubular diameter $d=2\rho$. Fractional translation is the function of monomer length and inclination angle $F=a \sin\chi$, while the rotation angle depends on helix radius, monomer length and inclination angle $Q=2\pi R/a\cos\chi$ [6]. Calculations of physical properties become more efficient by implementing the symmetry of a system into the numerical code. All calculations are performed by POLSym.

3. STRUCTURAL MODEL OF HELICALLY COILED CARBON NANOTUBES (HCCNT)

Interatomic bounds are defined by nearest neighbors form pentagons, hexagons and heptagons. Pentagons and heptagons are regularly inserted into a slightly deformed basic hexagonal network. Periodically incorporated pentagons and heptagons induce curvatures. Pentagons are at the place of the positive Gaussian curvature, while the heptagons are at the place of negative Gaussian curvature closer to the helical axis. Physical properties and helical

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parameters of HCCNTs depend on the spatial distribution of pentagons and heptagons. In order to construct this model, topological coordinates method based on graph theory [7] is used. Fig.1 presents an illustration of two triple-connected tiling of the plane by pentagons (black fields), hexagons (white or bright gray fields) and heptagons (dark gray fields). Super cell vectors, obtained as the integer linear combination of the basis vectors, define parallelogram. Identification of the opposite edges of the parallelogram gives the graph of the torus. To obtain topological coordinates it is necessary to select appropriate eigenvalues and corresponding eigenvectors of the adjacency matrix [7,8]. Spatial distribution of pentagons or heptagons affects the helical parameters of the CNCs. A change of concentration and position of these 5,7-polygons is technically realized by graph manipulation, inserting stripes of hexagons vertically or horizontally. For instance, the right graph in Fig.1 is obtained from the left one by inserting two columns and two stripes of hexagons in such a way that heptagons are separated apart (becoming thus only next nearest neighbors). This reconstruction of graph gives a model of HCCNT which has greater helical and tubular radius and lower inclination angle than the model obtained from the left graph of Fig.2.

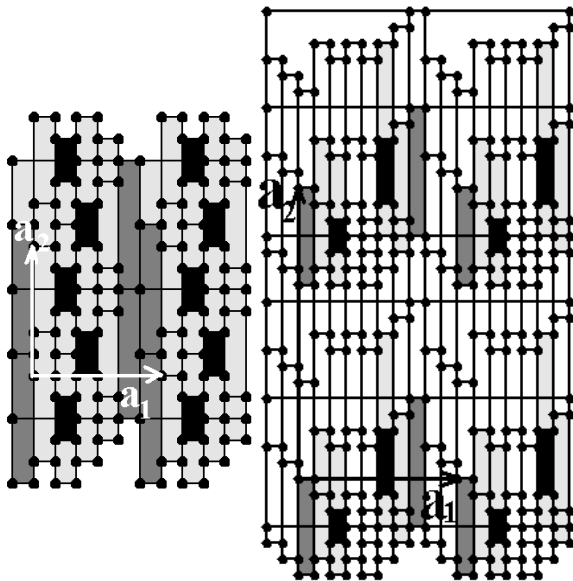


Figure 1. Triple-connected layers tiled with pentagons (black fields), hexagons (white or bright gray fields) and heptagons (dark gray fields). The right graph is obtained from left one by inserting columns (rows) of hexagons (white fields).

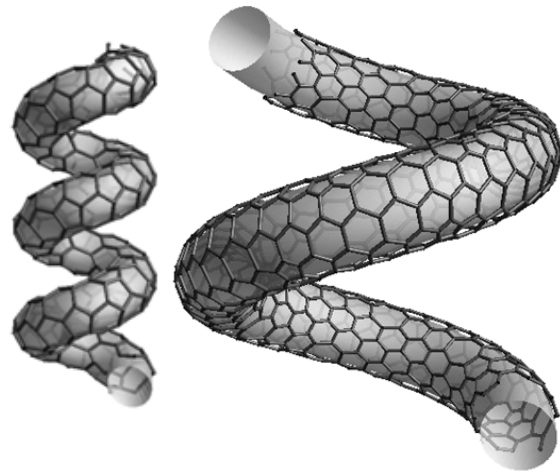


Figure 2. Models of HCCNT's obtained from upper graphs by applying method of topological coordinates. Parameters of these HCCNTs are: (left) $D=11.6 \text{ \AA}$, $d=4.1 \text{ \AA}$, $\chi=19^\circ$; (right) $D=31.1 \text{ \AA}$, $d=6.8 \text{ \AA}$, $\chi=16^\circ$

4. NUMERICAL RESULTS

All results are obtained numerically. Topological coordinates are used as initial atomic positions for relaxation which is performed in three stages. In the first step parameters: R , χ , ρ , ϕ_0 (relative position of tube end helix) and \mathbf{a} are relaxed according to harmonic potential (quadratic function of deviations between distance of the nearest neighbors and 1.42 \AA). The obtained parameters and cylindrical coordinates are further relaxed by molecular dynamic (MD), based on Brenner second-generation potential [9]. This empirical, short range interatomic potential for carbon can be written as a sum of nearest neighbor interactions:

$$V = \sum_i \sum_{j(>i)} [V_R(r_{ij}) - b_{ij} V_A(r_{ij})]. \quad (1)$$

The functions $V_R(r)$ and $V_A(r)$ respectively represent all interatomic repulsions and attractions from valence electrons. Empirical bond order function (b_{ij}) depends on dihedral angle and angle of the bonds between atoms i and k and atoms i and j . At last, five parameters R , χ , ρ , ϕ_0 and \mathbf{a} are relaxed within DFTB method. Presented results are obtained by relaxing two different classes of helically coiled carbon nanotubes. These classes differ by the number of horizontally inserted strips of hexagons into initial triple-connected graph and by the super cell vectors. HCCNTs of the same class have different number of columns of hexagons between the columns containing pentagons and heptagons.

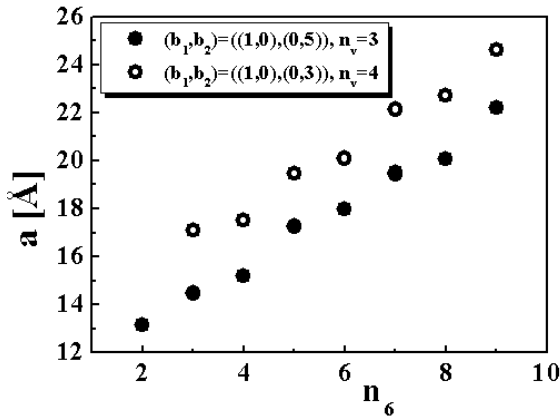


Figure 3. Monomer length as a function of graph parameter (number of columns of hexagons between heptagons and pentagons for two different classes).

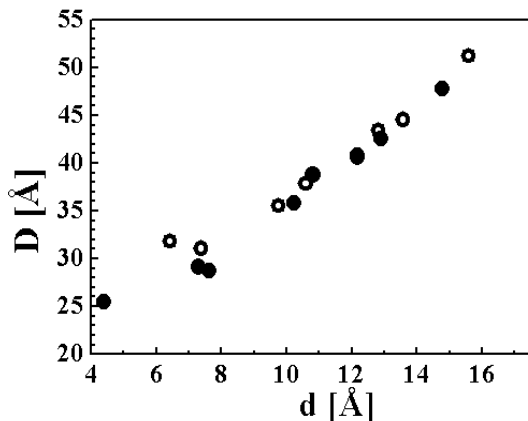


Figure 4. Outer coil diameter D vs. tubular diameter d .

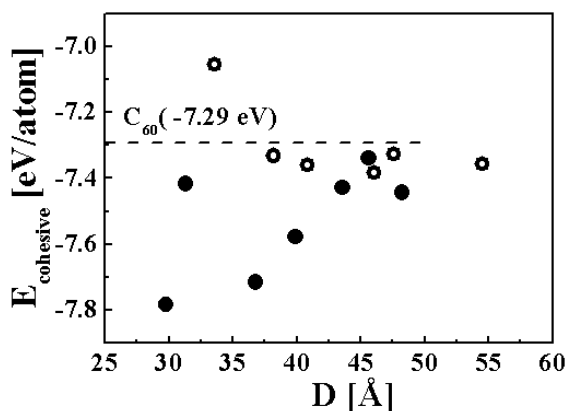


Figure 5. Cohesive energy of HCCNTs as a function of the outer diameter of the helix.

Monomer length increases linearly as the function of graph parameter, Fig.3. It is systematically shifted depending on the number of horizontally

added stripes of hexagons. Outer diameter is linear function of tubular diameter, Fig.4. These parameters are correlated by factor ~ 3.5 in both classes.

Total and cohesive energy are calculated by DFTB. In Fig.5 cohesive energy as function of outer diameter for the two classes is given. Cohesive energy as a function of outer diameter increases for the HCCNTs which belong to the class with lower concentration of hexagons per monomer. Most of relaxed HCCNTs in our sample are more stable than fullerene (cohesive energy of fullerene is -7.29 eV/atom) [10].

5. CONCLUSIONS

Standard numerical methods are inapplicable with the systems with large number of atoms. Symmetry based procedures enable reduction and application of calculations. Periodic incorporation of pentagons and heptagons induces curvature relaxed configuration. Helical parameters of CNCs depend on pentagons-pentagons distribution within basic hexagonal net. Model is energetically stable.

6. ACKNOWLEDGEMENTS

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УГЉЕНИЧНИ НАНО-КАЛЕМИ: СТРУКТУРА И СТАБИЛНОСТ

Сажетак: Израдили смо модел хеликално савијених једнослојних нанотуба уз помоћ теорије графова и методе тополошких координата. Након што смо добили тродимензионалне координате атома приступили смо релаксацији узаступном при-мјеном следећих метода: 1) хармонијском апроксимацијом; 2) молекуларном меха-ником на основу Бренеровог потенцијала; и 3) функционалом густине јаке везе (DFTB). На крају, уз помоћ DFTB-а и линијске групе симетрије имплементиране у POLSum кôд, израчунали смо укупну и кохезивну енергију добијених потпуно релак-сираних структура угљеничних нано-калема (CNCs).

Кључне ријечи: хеликално савијене угљеничне нанотубе, симетрија, тополо-шке координате, кохезивна енергија.

