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# Molecular Design and Mathematical Analysis of Carbon Nanotube Links

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**Abstract.** Similar to polyhedral links, carbon nanotube links are interlinked and interlocked knots with nanotube sharps. In this paper a novel constructional method is described based on the structure of carbon nanotube and the knowledge of polyhedral links. Two types of carbon nanotube links are introduced and analyzed: (5, 0) and (5, 5) carbon nanotube links, both being $D_5$ or $C_5$ symmetric. The model opens a door for molecular design and mathematical analysis on nanotube structures. By assigning an orientation to the links we analyze the mathematical properties of these oriented links. Our results show that both types of links are chiral. The recurrence formulae for the writhe, self-writhe, linking number and components of these links are also established.

## Introduction

Knot is one of the most elusive and intriguing questions in nature and mathematics. Knot theory[1-3] is a branch of algebraic topology that deals with knots and links. A knot is defined as a simple closed polygonal curve in 3-dimensional space, while a link is defined as a set of knotted loops all tangled up together[1-3]. Knots first received scientific attention in the 1880's when Lord Kelvin hypothesized that all matter was made of a substance called ether and that atoms are knots in the ether. Now the knot theory has been drawn into the applications of Chemistry, molecular biology, physics, and so on[3-12].

Carbon nanotubes are novel and interesting carbon material initially found by Iijima in 1991[13]. Due to its many unique electronic, mechanical and chemical properties, carbon nanotube has attracted great attention in recent years[14-17]. Although great progress has been made, some aspects of carbon nanotubes still need to be clarified and studied on. In this paper, knot theory is initially applied to the study of carbon nanotubes. Some results from knot theory can be used to distinguish different fullerene isomers and the fullerene graph can be transformed into the projection of an alternating knot or link[18]. Similarly carbon nanotube links can be obtained from carbon nanotubes. A new result has been achieved by the method of 'three-cross-curve and double-line covering'[19] applied to carbon nanotubes. Based on the perfect nanotubes structure we construct the carbon nanotube links model—interlinked and interlocked links with nanotube sharps. Novel topological model revealing another relationship between nanotubes and links has been established, which is different from that of fullerene study on knot theory before[18,20].

Molecular design and the tailored molecule are key challenges to synthetic chemists[21]. These two difficulties have blocked chemists from synthesizing the catenanes and knots for several decades. This new model provides a new pathway for controlling the molecular design and assembly of protein knots. The new molecular model of carbon nanotube links can be established based on the knowledge of polyhedral links[19] and the structures of HK97 capsid and clathrin. The study shows that the structure of bacteriophage HK97 capsid is topologically linked protein catenane[22]. While clathrin[23] forms a polyhedral lattice, a protein, plays a major role in the creation of vesicles in cells, whose is similar to the closed fullerene structures with 12 pentagons. This model opens a door for mathematical analysis of nanotubes structure. So far, we only know a little about this, but it certainly deserves more attention.

## Carbon nanotubes

Carbon nanotubes are molecular-scale tubes of graphitic carbon with outstanding properties. Generally speaking, they can be divided into single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) with regard to the carbon atom layers in the wall of the nanotubes[24]. SWNTs consist of a single, cylindrical graphene layer, while MWNTs consist of multiple graphene layers telescoped about one another. Carbon nanotubes are hollow cylinders of carbon atoms. Their appearance is that of rolled tubes of graphite, such that their walls are hexagonal carbon rings, and the ends of CNTs are domed structures of six-membered rings and capped by five-membered rings.

Carbon Nanotubes can be defined by vector $c_h$=n $a_1$+m $a_2$, where $a_1$ and $a_2$ are unit vectors, n and m are integers. A nanotube constructed in such a way is called a (n, m) carbon nanotube. Carbon nanotubes with n =m≠0 are armchair tubes, and zigzag tubes with n≠0, m=0[25]. Theoretical calculations are first used to predict the SWNTs due to their simple and ideal structures. Our research is also focused on SWNTs. We construct two classes of carbon nanotube links based on the structures of carbon nanotubes.

## Construction of carbon nanotube links

Our method of constructing carbon nanotube links is based on the knowledge of polyhedral links. We develop the 'three cross-curve and double-line covering' method in polyhedral links [19]. The method is as follows:

First, a three-dimensional carbon nanotube is deformed into a planar graph; then, a three-cross-curve and a double-line are used to cover a trivalent vertex of the graph, while a double-line is used to cover an edge on a bivalent vertex (see Fig. 1(b)), with the result of being a diagram of nanotube links; finally, the two-dimensional link is continuously deformed into the three-dimensional structure which results in an interlocked cage of carbon nanotube links created from the corresponding nanotubes. Furthermore, the links which we construct are alternating links, that is to say, these links possess a link diagram in which crossings alternate between underpasses and overpasses.

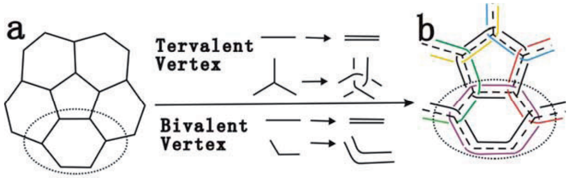


Fig. 1. Construction of the carbon nanotube links method.

An example to demonstrate how the above method works is given in Fig 2. The small three-dimensional (5, 0) carbon nanotube $C_{20}$ in Fig. 2a is continuously deformed into a planar graph as shown in Fig. 2b; then a two-dimensional $C_{20}$ link is constructed as in Fig. 2c, which can be called the reduced diagram of $C_{20}$ alternating link in knot theory, where there is no diagram has fewer crossing of the link; this two-dimensional link is continuously deformed into the three-dimensional structure as shown in Fig. 2d. Obviously, topological structure of the $C_{20}$ link is totally different from that of the $C_{20}$. The nanotube has $D_{5h}$ symmetry, whereas the link has $D_5$ symmetry[26]; the nanotube is a geometric solid bounded by 5 hexagons, whereas the link is composed of 5 hexagonal rings and 2 decagonal rings.

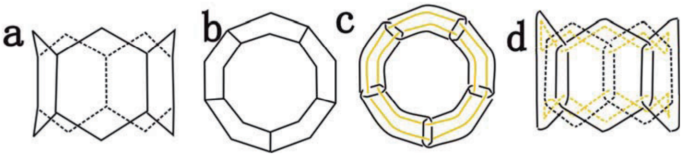


Fig. 2. The process of construction for the (5, 0) carbon nanotube $C_{20}$ link.

Polyhedral links are topological links with polyhedral shape which are linked by a collection of finitely separate closed curves. We improve the method of polyhedral links' construction and establish the method of carbon nanotube links' construction. Carbon nanotube links are new structures with nanotubes shapes. Interlocked (5, 0) carbon nanotube links and (5, 5) carbon nanotube links construct on the structure of (5, 0) and (5, 5) carbon nanotubes in the following.

## Construction of (5, 0) carbon nanotube links

(n, m) carbon nanotubes are zigzag nanotubes when n≠0, m=0. In terms of differences in end shapes, there are open-ended, semi-closed-ended and closed-ended carbon nanotubes. Starting from zigzag (5, 0) carbon nanotubes, we are going to construct three types nanotube links: (5, 0) open-ended, (5, 0) semi-closed-ended and (5, 0) closed-ended carbon nanotube links.

**1. (5, 0) open-ended carbon nanotube $C_{20+10n}$ links**

Considering (5, 0) open-ended carbon nanotubes, the number of C atom grows following the formula: N=20+10n (where N is the number of C atom, n=0, 1, 2, 3…). When n=0, there is the smallest (5, 0) open-ended carbon nanotube $C_{20}$ (Fig. 2a). The $C_{20}$ link is constructed by nanotube $C_{20}$ as shown schematically in figure 2d, which contains 7 components, 5 hexagonal rings and 2 decagonal rings respectively.

When n=1, 2, these two nanotubes are the $C_{30}$ and $C_{40}$ respectively. $C_{30}$ has 10 hexagonal faces and is $D_{5d}$ symmetric; $C_{40}$ has 15 hexagonal faces and is also $D_{5h}$ symmetric. Applying our conversion approach to these two nanotubes leads to two corresponding links. The $C_{40}$ link (Fig. 3b) consists of 10 hexagonal and 2 decagonal rings, and the $C_{50}$ link (Fig. 3d) consists of 15 hexagonal and 2 decagonal rings. They both possess the $D_5$ point group.

The components of (5, 0) open-ended carbon nanotube $C_{20+10n}$ links satisfy $C_n$= 7+5n. Moreover, the crossing of link's reduced diagram is 3 times in numbers vertices of degree 3 of the planar graph. Contrast to nanotubes' $D_{5h}$ symmetry, these links possess the $D_5$ point group.

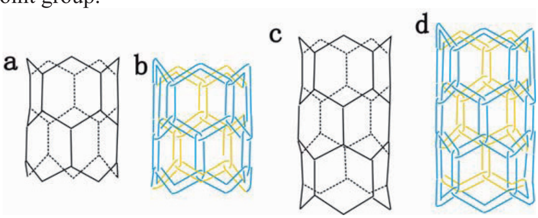


Fig. 3. (5, 0) open-ended carbon nanotubes and the relevant links: (a) (5, 0) carbon nanotube $C_{30}$; (b) (5, 0) carbon nanotube $C_{40}$; (c) (5, 0) carbon nanotube $C_{30}$ link; (d) (5, 0) carbon nanotube $C_{40}$ link.

**2. (5, 0) Semi-closed-ended carbon nanotube $C_{25+10n}$ links**

The number of C atom of (5, 0) Semi-closed-ended carbon nanotubes can be calculated by mathematical induction: N=10n+25(n=0, 1, 2, 3…). For example, when n=0, 1, 2, these three nanotubes are the $C_{25}$, $C_{35}$ and $C_{45}$ (Fig. 4a, c, e), which all have 6 pentagonal faces to form the cap, and 5, 10 and 15 hexagonal faces respectively. They all have $C_{5v}$ symmetry. With our conversion approach, these links (Fig. 4b, d, f) all contain 6 pentagonal and 1 decagonal ring and, at the same time, contain 5, 10 and 15 hexagonal faces respectively. The links possess the $C_5$ point group.

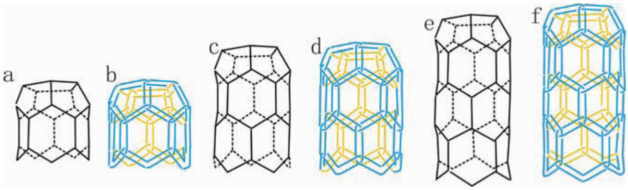


Fig. 4. (5, 0) Semi-closed-ended carbon nanotubes and links:

(a) $C_{25}$; (b )$C_{25}$link; (c) $C_{35}$; (d) $C_{35}$ link; (e) $C_{45}$; (f) $C_{45}$ link.

### 3. (5, 0) closed-ended carbon nanotube $C_{30+20n}$ links

The carbon nanotubes have $D_{5h}$ symmetry in which the formula of their C atom number is N=20n+30. These nanotubes can be viewed as cutting fullerene $C_{20}$ and adding cylindrical graphene layer inside, all of which have 12 pentagonal faces. When n=0, 1, 2, these three nanotubes are the $C_{30}$, $C_{50}$ and $C_{70}$ which have 12 pentagonal faces and 5, 10, 15 hexagonal faces respectively (Fig. 5a, c, e). The links in Fig. 5b, d, f all contain 12 pentagonal and 5, 10 and 15 hexagonal rings respectively, too. The crossing number of reduced knot diagram is 3 times the vertices number of the planar graph. The numbers of components in the links are the same as the faces on the nanotubes. Yet the links possess the $D_5$ point group. These structures with 12 pentagonal rings are similar to the structures formed when clathrin assembles into coats in vitro. The interlocked architectures are similar to clathrin triskelion too. So can these links exist as protein links?

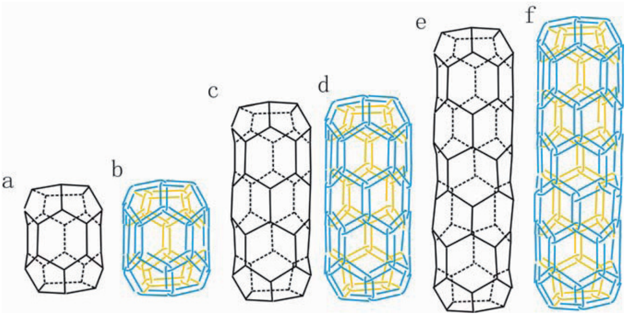


Fig. 5. (5, 0) closed-ended carbon nanotube $C_{30+20n}$ links:

(a) $C_{30}$; (b) $C_{30}$link; (c) $C_{50}$; (d) $C_{50}$ link; (e) $C_{70}$; (f) $C_{70}$ link.

**Construction of (5, 5) carbon nanotube links**

On armchair carbon nanotubes, carbon nanotude links on (5, 5) open-ended carbon nanotubes $C_{30+10n}$ (n=0, 1, 2, 3…) are constructed. When n=0, the small armchair carbon nanotube is $C_{30}$ with 5 hexagonal faces (Fig. 6a). The reduced diagram of $C_{30}$ link (Fig 6b) contains 5 hexagonal rings and 2 decagonal rings which are different from those of nanotube. The faces number of this kind nanotube satisfy $F_n$= 5+5n, while the number of links' components satisfies $C_n$= 7+5n =$F_n$+2. Contrast to nanotubes' $D_{5h}$ symmetry, these links possess the $D_5$ point group.

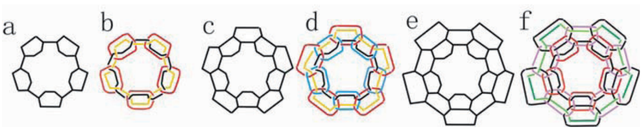


Fig. 6. (5, 5) open-ended carbon nanotubes and the links:

(a) $C_{30}$; (b) $C_{30}$link; (c) $C_{40}$; (d) $C_{40}$ link; (e) $C_{50}$; (f) $C_{50}$ link.

(5, 5) semi-closed-ended carbon nanotubes $C_{40+10n}$ (n=0, 1, 2, 3…) have 6 pentagonal faces forming the cap. The nanotubes have some faces satisfying $F_n$=16+5n. The links also have 6 pentagonal rings forming the cap and the number of links' components satisfying $C_n$=$F_n$+1. The nanotubes have $C_{5v}$ symmetry, while the links possess the $C_5$ point group. The $C_{40}$ and $C_{50}$ nanotubes and their relevant links are illustrated in Fig. 7.

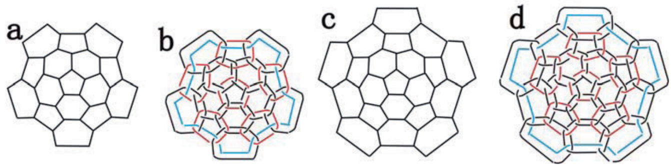


Fig. 7. (5, 5) semi-closed-ended carbon nanotubes and the links: (a) $C_{40}$; (b) $C_{40}$link; (c) $C_{50}$; (d) $C_{50}$ link.

The (5, 5) closed-ended carbon nanotubes have $D_{5h}$ symmetry with the C atom number N=80+20n. These nanotubes can be viewed as cutting fullerene $C_{60}$ and adding cylindrical graphene layer. All (5, 5) closed-ended carbon nanotubes have 12 pentagonal faces. The numbers of the components of links are the same as those of the faces of nanotubes ($F_n$=$C_n$=42+10n). The links possess the $D_5$ point group. Two (5, 5) closed-ended nanotubes $C_{80}$, $C_{100}$ and their links are in Fig. 8.

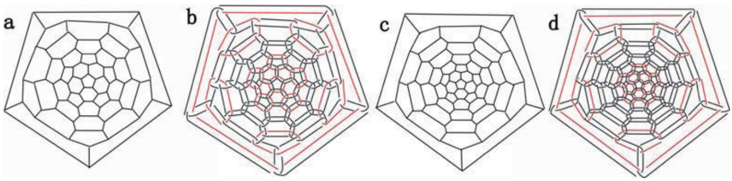


Fig. 8. (5, 5) closed-ended carbon nanotubes and the links: (a) $C_{80}$; (b) $C_{80}$link; (c) $C_{100}$; (d) $C_{100}$ link.

**Mathematical analyses of oriented carbon nanotube links**

When knot theory is used to analyze knotted or catenated molecules, oriented knots and links usually represent more faithfully those molecules that possess a natural orientation[27]. By assigning each component a direction to nanotube links, interesting and useful results of oriented carbon nanotube links are revealed. For a diagram of an oriented carbon nanotubes links, without loss of generality, we assign a clockwise orientation to each of its components. Before we move on, let us review the following basic definitions in knot theory first[1, 2, 27]:

**Definition 1** The *writhe* $w$ of an oriented link is the sum of the signs of the crossings of a minimal projection of the link. The sign convention commonly used is as follows:


**Definition 2** The *linking number l* of an oriented link is half the sum of the signs of the inter-component crossings of a minimal projection of the link.

**Definition 3** The *self-writhe s* of an oriented link is the sum of the signs of the intracomponent crossings of a minimal projection of the link.

**Definition 4** An oriented link L is *achiral* if it is equivalent to its mirror image, denoted by $L^*$. Otherwise, it is *chiral*.

The characteristics of orientated（5, 0）, (5, 5) carbon nanotube links are listed in table 1 and table 2. For each entry of Table 1, 2, columns 2, 3, 4, 5 list well-known numerical invariants of alternating oriented links, namely, the writhe *w*, the linking number *l* and the self-writhe *s*, the components of links. Recurrence formulae for all the invariants are developed. For example, the writhes of （5, 0） open-ended orientated carbon nanotube links follow the formula: $W_n$=10+30n. All numerical knot invariants can be figured out through the formulae without any troublesome calculation.

Chirality is an important notion not only in chemistry but also in knot theory. There are some general methods for establishing the chirality and achirality of topological links[27-32]. Detected by these methods, we study on the chirality of the links which we construct. Column 6 lists the chirality specifier[32] of these links. From the table we can see all the links are D specifier except (5, 0) carbon nanotube link $C_{30}$. Column 7 lists the chirality properties of the oriented links. Thereby, our study indicates all the links are chiral.

Table 1. Character of orientated（5, 0）carbon nanotube links.

| Carbon nanotubes link | | Writhe | Linking number | Self-writhe | Component | Chirality specifier | Chirality |
|---|---|---|---|---|---|---|---|
| Open-ended | $C_{20}$ | 10 | 5 | 0 | 7 | D | chiral |
| | $C_{30}$ | 40 | 20 | 0 | 12 | D | chiral |
| | $C_{40}$ | 70 | 35 | 0 | 17 | D | chiral |
| | … | … | … | … | … | … | … |
| | $N_n$=20+10n | $W_n$=10+30n | $L_n$=5+15n | 0 | $C_n$=7+5n | D | chiral |
| Semi-closed-ended | $C_{25}$ | 40 | 20 | 0 | 12 | D | chiral |
| | $C_{35}$ | 70 | 35 | 0 | 17 | D | chiral |
| | $C_{45}$ | 100 | 50 | 0 | 22 | D | chiral |
| | … | … | … | … | … | … | … |
| | $N_n$=25+10n | $W_n$=40+30n | $L_n$=20+15n | 0 | $C_n$=12+5n | D | chiral |
| Closed-ended | $C_{30}$ | 70 | 35 | 0 | 17 | D | chiral |
| | $C_{50}$ | 130 | 65 | 0 | 27 | D | chiral |
| | $C_{70}$ | 190 | 95 | 0 | 37 | D | chiral |
| | … | … | … | … | … | … | … |
| | $N_n$=30+20n | $W_n$=70+60n | $L_n$=35+30n | 0 | $C_n$=17+10n | D | chiral |

Table 2. Character of orientated（5, 5）carbon nanotubes links.

| Orientated carbon nanotubes | Link | Writhe | Linking number | Self-writhe | Components | Chirality specifier | Chirality |
|---|---|---|---|---|---|---|---|
| Open-ended | $C_{30}$ | －10 | －5 | 0 | 7 | L | chiral |
| | $C_{40}$ | 20 | 10 | 0 | 12 | D | chiral |
| | $C_{50}$ | 50 | 25 | 0 | 17 | D | chiral |
| | … | … | … | … | … | … | … |
| | $N_n$=30+10n | $W_n$=-10+30n | $L_n$=-5+15n | 0 | $C_n$=7+5n | D(n≥1) | chiral |
| Semi-closed-ended | $C_{40}$ | 50 | 25 | 0 | 17 | D | chiral |
| | $C_{50}$ | 80 | 40 | 0 | 22 | D | chiral |
| | $C_{60}$ | 110 | 55 | 0 | 27 | D | chiral |
| | … | … | … | … | … | … | … |
| | $N_n$=40+10n | $W_n$=50+30n | $L_n$=25+15n | 0 | $C_n$=17+5n | D | chiral |
| Closed-ended | $C_{80}$ | 220 | 110 | 0 | 42 | D | chiral |
| | $C_{100}$ | 280 | 140 | 0 | 52 | D | chiral |
| | $C_{120}$ | 340 | 170 | 0 | 62 | D | chiral |
| | … | … | … | … | … | … | … |
| | $N_n$=80+20n | $W_n$=220+60n | $L_n$=110+30n | 0 | $C_n$=42+10n | D | chiral |

## Conclusions

The topological approach to construct interlocked links has been described.

Meanwhile, new kinds of interlinked cages on the structure of nanotubes have been elaborated. The (5, 0) and (5, 5) single-walled carbon nanotubes are mainly discussed and the reduced alternating link diagrams are depicted in the paper. After constructing the number of crossing in diagrams is 3 times the number of vertices of degree 3 in the planar graph. However, the construction makes the symmetry debased: open-ended and closed-ended carbon nanotubes possess $D_{5h}$ symmetry, while corresponding links possess $D_5$ symmetry; semi-closed-ended carbon nanotubes possess $C_{5v}$ symmetry, while corresponding links possess $C_5$ symmetry. Mathematical characteristics of carbon nanotube links have also been analyzed. From our calculation we deduce the recurrence formulae of the writhe, linking number, self-writhe and components of the links, and conclude that the writhes of all the links are nonzero. Hence, the links are chiral because oriented links with chirality must have non-zero writhes. The construction of nanotube links makes the achiral nanotubes transform into chiral links.

Starting from the structure of nanotubes and the knowledge of biologic structure, our method produces a series of new links with $D_5$ or $C_5$ symmetry. The interlocked links can serve as molecular models, which provide a new idea for molecular design. The links can also help us understand the structure of nanotubes, such as the differences in numerical invariants of links referring the differences in nanotube molecules. In mathematics these links are helpful for making knot table, which are not yet completely clear in knot theory. In molecular topology building this model can help us analyze protein coat and molecular knots. Despite its preliminary character, the study indicates that the links are mathematical models for tubular structures of viral capsids: the open-ended and semi-close-ended carbon nanotube links correspond to virion's sharps of filament and bullet-shape. It is yet, still a challenge to synthesize and discover the links in organism.

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