Journal of Mathematical Chemistry Vol. 38, No. 2, August 2005 (© 2005)
DOI: 10.1007/s10910-005-5410-z

On the number of Kekulé structures in capped zigzag nanotubes

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Received 23 February 2005; revised 25 March 2005

Two theoretical formulae for the number of Kekulé structures in general capped zigzag nanotubes are established: one of which is by using the techniques of the transfer matrices, the other involves the eigenvalues of the transfer matrix which reveals the asymptotic behaviour of this index. In effective, according to the symmetric aspect of the tubule, the order of the transfer matrix could be notably decreased. As an application, the closed expressions for four types are given out and the relevant numerical results for those of length up to 50 are listed.

KEY WORDS: Kekulé structure, capped zigzag nanotube

1. Introduction

Kekulé structures (perfect matchings) in benzenoid hydrocarbons was systematically studied in the previous work of chemists (for an example, see Cyvin and Gutman [1] for details). The number of Kekulé structures in benzenoid hydrocarbons is both theoretically and practically an interesting parameter [2]. Various techniques and methods have been developed to calculate this index. For physicists, the enumeration of perfect matchings in some cases are equivalent to the dimer problem of the rectangle lattice graph on the plane, which had been solved by Kasteleyn [3].

Following the experimental discovery of carbon nanotube [4–6] and the theoretical prediction of the existence of boron-nitride nanotubes, the index Kekulé count of nanotubes has become interesting objects of research.

Theoretically to say, an open-ended nanotube is mathematically a hexagonal system embedded in a cylinder and a capped nanotube consists of an open-ended nanotube capped at its ends by two hemispherical (trivalent and two-connected polygonal system) caps. For examples, the caps in a capped carbon

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nanotube are composed of hexagons and (12) pentagons while, in a Boron-Nitride nanotube, the caps are composed of hexagons and (6) squares.

Sachs, Hansen and Zheng have done some significant works on Kekulé counts in the open-ended nanotubes and gave out, in particular, the closed formula for a special capped carbon fullerene tubule which consists of an untwisted (or called zigzag in some other literatures) tubule capped at its ends by two halves of a pentagon-dodecahedron [7]. For the hexagonal system embedding on the torus, Klein bottle and the capped near-benzenoid nanotube (or called the cylindrical near-benzenoid graph in their article), Klein and Zhu established the analytical formulae, in terms of transfer matrix and self-avoiding walk system, to this index. In [8], Lin and Tang set up a recurrence algorithm to the Kekulé count for two types of the boron-nitride zigzag nanotubes and gave out the numerical results for those of length up to 8. From their numerical results, Lin et al. also observed that the Kekulé counts increase exponentially with respect to the length of the tubule. In [9], the present authors dealt with the capped armchair nanotubes.

In this paper, we focus our attention on the Kekulé counts for the (single-wall) capped zigzag nanotubes. Two theoretical formulae for general capped zigzag nanotubes are established: one of which is by using the techniques of transfer matrices, the other involves the eigenvalues of the transfer matrices. The study shows that the maximum eigenvalue of the transfer matrix reveals the asymptotic behaviour of the Kekulé counts: the number of Kekulé structures in capped zigzag nanotubes increase exponentially with respect to the length of the tubule. This yields a theoretical proof to the observation of Lin et al. mentioned above. In effective, according to the symmetric aspect of the nanotube, the order of the transfer matrix could be notably decreased. As an application, the closed expressions for four types are given out and the relevant numerical results for those of length up to 50 are listed.

2. Transfer matrix

An open-ended (single-wall) nanotube, or tubule for short, is a part of some regular hexagonal tessellation of a cylinder. Two types of such tubules, namely the 'zigzag' (or 'untwisted') and 'armchair' (or 'fully twisted') in nanotube terminology received much attention in previous literatures. In fact, zigzag and armchair are two extreme patterns of the twisted tubules (see [7, 10] for details). The zigzag tubule [7, 8, 10] is constructed by starting from a suitable rectangular section cut from the honeycomb lattice as shown in figure 1(a) in which two edges of each hexagon are parallel to the axis y: each dangling bond at the left-side ($x = 0$) is identified to the corresponding (with equal-y axis) dangling bond at the right-side ($x = w$). The number h ($h \geqslant 1$) and w measure the length and the circumference of the tubule (in Figure 1(a), we have $h = 13$ and $w = 6$),

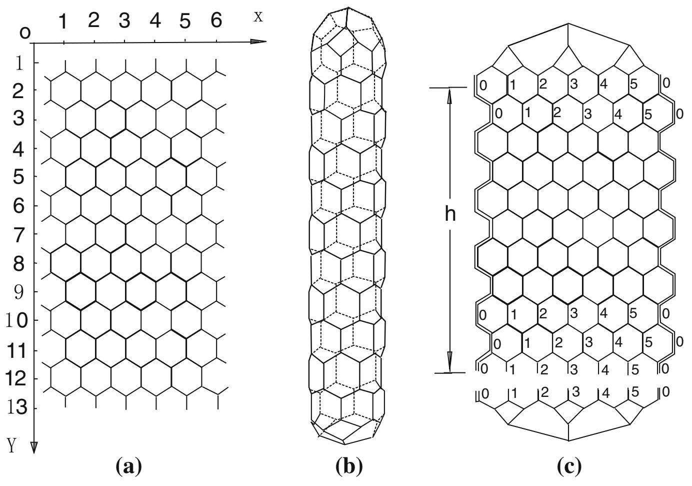

Figure 1. (a) A rectangular section cut from the honeycomb lattice; (b) a capped zigzag nanotube; (c). draw a semi-capped tubule and a cap in a planar mode.

respectively. In the following, the layers of a tubule of length h are always numbered by $1, 2, \ldots, h$, in an order from the top to the bottom, respectively.

The capped zigzag tubule [8,10] $T_h(C, C')$ is constructed by adding two suitable caps (i.e., the trivalent and two-connected polygonal system with some dangling bonds on its boundary) C and C' to the upper and lower open ends of an open-ended zigzag tubule of length h, respectively (i.e., identifying the corresponding dangling bonds of the open tubule with that of the two caps C and C'). To be convenient, we will call a tubule with exactly one end capped with a cap C a semi-capped tubule and denote it by $T_h(C)$. Therefore, a capped tubule $T_h(C, C')$ could be considered to be constructed by joining a cap C' to the semi-capped tubule $T_h(C)$. One can see that the structure of a capped tubule $T_h(C, C')$ is determined uniquely by the way how to join C' with $T_h(C)$. Some examples of caps are shown in figure 2 and a capped tubule $T_h(C_4, C_4)$ is shown in Figure 1(b). For the further information of caps, we may refer to [8,11,12]. Let

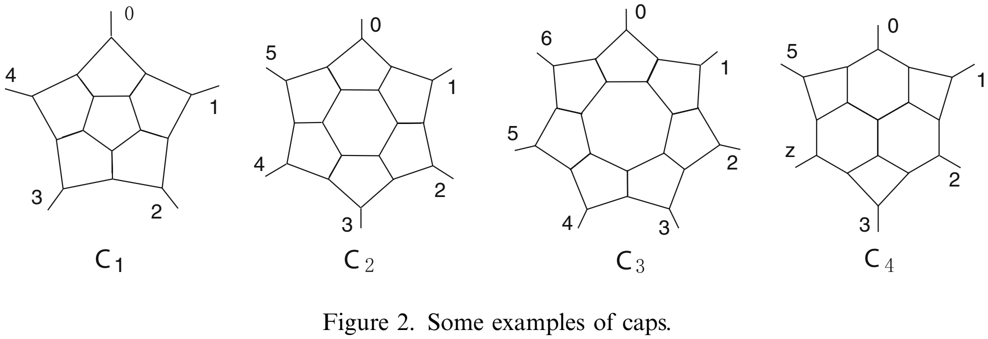

Figure 2. Some examples of caps.

us draw a semi-capped tubule $T_h(C)$ and a cap C' in a planar mode as shown in figure 1(c).

In the following, when we speak of the bonds in a layer, we always mean the vertical bonds. For a Kekulé structure M of $T_h(C, C')$, a bond e is said to be a double bond if $e \in M$. It could be observed that there is exactly one double bond between two successive double bonds of the previous layer. So for any Kekulé structure M, the number of double bonds in each layer are the same. Let the bonds in each layer be numbered by $0, 1, 2, \ldots, w$ as illustrated in figure 1(c). For a layer j and a subset $\{x_1, x_2, \ldots, x_k\} \subseteq \{0, 1, 2, \ldots, w-1\}$, denote by $x_1x_2, \ldots, x_k$ the double-bond structure (or shortly, D-B structure) when the jth layer has exactly k D-B, numbered by $x_1, x_2, \ldots, x_k$, respectively. With no loss of generality, we always assume that $x_1 < x_2 < \cdots < x_k$. Arrange all the possible $\binom{w}{k}$ D-B structures in a suitable order, say the lexicographic order:

$$X_1 = 012\cdots(k-2)(k-1), \quad X_2 = 012\cdots(k-2)k,$$
$$X_3 = 012\cdots(k-2)(k+1), \ldots, X_{\binom{w}{k}} = (w-k)(w-k+1)\cdots(w-1).$$

Consider the distribution of the double bonds in two neighboring, say the pth and $(p+1)$th, layers. A D-B structure X' in the pth ($p \in \{0, 1, 2, \ldots, h-1\}$) layer is called a successor of the D-B structure X in the $(p+1)$th layer if X' may immediately follow X. For an example, let $w = 5$ and let the DB-structure $X = 134$, then all the successors of X are 013, 023, 134 and 234 as illustrated in figure 3. The following result is immediate.

Proposition 1. $x'_1x'_2\cdots x'_k$ is a successor of $x_1x_2\cdots x_k$ if and only if

1. When $p+1$ is odd, $x_i \leqslant x'_i \leqslant x_{i+1}-1$ for each $i = 1, 2, \ldots, k-1$, and $x_k \leqslant x'_k \leqslant w-1$ or
   $x_{i-1} \leqslant x'_i \leqslant x_i - 1$ for each $i = 2, \ldots, k$, and $0 \leqslant x'_1 \leqslant x_1 - 1$;
2. When $p+1$ is even, $x_i + 1 \leqslant x'_i \leqslant x_{i+1}$ for each $i = 1, 2, \ldots, k-1$, and $x_k + 1 \leqslant x'_k \leqslant w-1$ or
   $x_{i-1} + 1 \leqslant x'_i \leqslant x_i$ for each $i = 2, \ldots, k$, and $0 \leqslant x'_1 \leqslant x_1$.

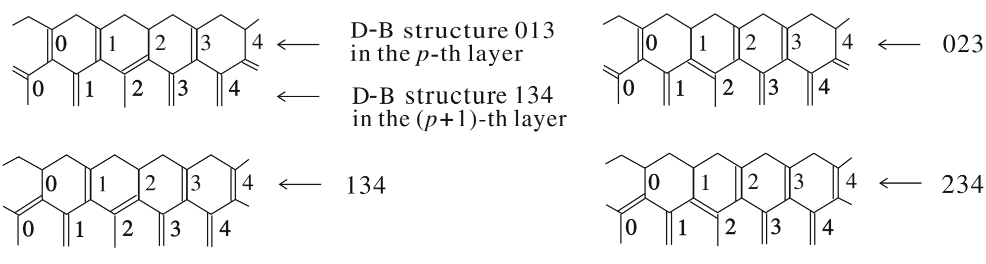

Figure 3. The D-B structure 134 in the $(p+1)$th layer and its successors.

For a D-B structure X, let $k_h(C, X)$, or $k_h(X)$ if no confusion can occur, be the number of Kekulé structures in the semi-capped tubule $T_h(C)$, when the hth layer has D-B structure X. In particular, $k_1(C, X)$ is the number of Kekulé structures in the cap C when the dangling bonds of C has the D-B structure X.

For a cap C, we may treat it as a graph including its w dangling bonds. Consider the automorphism group Aut(C) of C. Two D-B structures $x_1x_2 \dots x_k$ and $x'_1x'_2 \dots x'_k$ of the dangling bonds of C are called equivalent if there is a permutation π on $\{1, 2, \dots, k\}$ and an automorphism $\rho \in \mathrm{Aut}(C)$ such that

$$\rho(x_{\pi(i)}) = x'_i, i = 1, 2, \dots, k.$$

In this way, the D-B structures of the dangling bonds of C with cardinality k may be partitioned into some equivalence classes, say $\mathcal{X}_1, \mathcal{X}_2, \dots, \mathcal{X}_s$. For an example, the equivalence classes of the D-B structures of C_4 with cardinality 2 (see figure 2) are

$$\mathcal{X}_1 = \{01, 12, 23, 34, 45, 05\}, \mathcal{X}_2 = \{02, 24, 04\}, \mathcal{X}_3 = \{03, 14, 25\}, \mathcal{X}_4 = \{13, 35, 15\}.$$

From the above definition, one can see that if two D-B structures X and X' are in the same equivalence class, then $k_1(X) = k_1(X')$. It can be observed that $\mathcal{X}_1, \mathcal{X}_2, \dots, \mathcal{X}_s$, are also the equivalence classes of the D-B structures for each odd layer of $T_h(C)$.

Choose an arbitrary representative D-B structure, say $X_{\alpha(i)}$ ($\alpha(i) \in \{1, 2, \dots, \binom{w}{k}\}$), from each $\mathcal{X}_i, i = 1, 2, \dots, s$, respectively. Define the s-dimensional vector $\mathcal{V}_h^k(C)$ for odd h to be

$$\mathcal{V}_h^k(C) = (k_h(X_{\alpha(1)}), k_h(X_{\alpha(2)}), \dots, k_h(X_{\alpha(s)})).$$

Taking the role of C by $T_2(C)$ and repeating the same discussion as above, we get an equivalence classes, say $\mathcal{Y}_1, \mathcal{Y}_2, \dots, \mathcal{Y}_t$, for the D-B structures with cardinality k of the second layer of $T_2(C)$. It can also be observed that $\mathcal{Y}_1, \mathcal{Y}_2, \dots, \mathcal{Y}_t$, are the equivalence classes of the D-B structures for each even layer of $T_h(C)$.

Similarly, choose an arbitrary representative D-B structure, say $X_{\beta(i)}$ ($\beta(i) \in \{1, 2, \dots, \binom{w}{k}\}$), from each $\mathcal{Y}_i, i = 1, 2, \dots, t$, respectively. Then $\mathcal{V}_h^k(C)$ for even h is defined analogously to be the t-dimensional vector:

$$\mathcal{V}_h^k(C) = (k_h(X_{\beta(1)}), k_h(X_{\beta(2)}), \dots, k_h(X_{\beta(t)})).$$

For two representative D-B structures $X_{\alpha(i)}$ and $X_{\beta(i)}$, Let $\mathcal{S}_i$ and $\mathcal{S}'_i$ be the sets of all successors of $X_{\alpha(i)}$ and $X_{\beta(i)}$, respectively. With this notation and recalling that if two D-B structures X and X' are in the same equivalence class then $k_1(X) = k_1(X')$, when h is odd it can be seen that

$$k_h(X_{\alpha(i)}) = \sum_{X \in \mathcal{S}_i} k_{h-1}(X) = \sum_{j=1}^{t} \sum_{X \in \mathcal{S}_i \cap \mathcal{Y}_j} k_{h-1}(X) = \sum_{j=1}^{t} k_{h-1}(X_{\beta(j)}) \cdot |\mathcal{S}_i \cap \mathcal{Y}_j|.$$

Similarly, when h is even, we have

$$k_h(X_{\beta(i)}) = \sum_{X\in\mathcal{S}'_i} k_{h-1}(X) = \sum_{j=1}^{s} \sum_{X\in\mathcal{S}'_i\cap\mathcal{X}_j} k_{h-1}(X) = \sum_{j=1}^{s} k_{h-1}(X_{\alpha(j)}) \cdot |\mathcal{S}'_i \cap \mathcal{X}_j|.$$

In terms of transfer matrix [12,13], the above discussion implies the following result.

Proposition 2. $\mathcal{V}_h^k(C)$ could be expressed by the following recurrence relation

$$\mathcal{V}_h^k(C) = \mathcal{V}_{h-1}^k(C) M_h^k,$$

where the transfer matrix M_h^k is of order $t \times s$ if h is odd; or $s \times t$ if h is even. Furthermore, the entry $t_{i,j}$ at the (i, j)-position of M_h^k equals

$$t_{i,j} = \begin{cases} |\ \mathcal{Y}_i \cap \mathcal{S}_j\ |, & \text{when } h \text{ is odd,} \\ |\ \mathcal{X}_i \cap \mathcal{S}'_j\ |, & \text{when } h \text{ is even.} \end{cases}$$

The above proposition also indicates that $M_l^k = M_h^k$ if l and h have the same parity. So it would be convenient to rewrite M_h^k generally by M_e^k (resp., M_o^k), when h is even (resp., odd). Thus,

$$\mathcal{V}_h^k(C) = \begin{cases} \mathcal{V}_{h-1}^k M_o^k = \mathcal{V}_{h-2}^k (M_e^k M_o^k) = \cdots = \mathcal{V}_1^k (M_e^k M_o^k)^{h-1/2}, & \text{when } h \text{ is odd,} \\ \mathcal{V}_{h-1}^k M_e^k = \mathcal{V}_{h-2}^k (M_o^k M_e^k) = \cdots = \mathcal{V}_2^k (M_o^k M_e^k)^{(h/2)-1}, & \text{when } h \text{ is even.} \end{cases} \tag{1}$$

According to the connecting mode between $T_h(C)$ and the cap C', the D-B structure X of $T_h(C)$ corresponds to a D-B structure, say X^*, of C'. More precisely, let $T_h(C, C')$ be constructed from $T_h(C)$ and C' by identifying the dangling bonds $0, 1, 2, \ldots, w-1$ of $T_h(C)$ with the dangling bonds $q, q+1, q+2, \ldots, q+w-1$ mod w of C', respectively and let $X = x_1x_2\cdots x_k$. Then $X^* = (x_1+q)(x_2+q)\cdots(x_k+q)$ mod w. Furthermore, we define

$$\mathcal{X}_i^* = \{X^* : X \in \mathcal{X}_i\}.$$

For a D-B structure X in the h-th layer of $T_h(C, C')$, let $k_h(C, C', X)$ denote the number of the Kekulé structures in $T_h(C, C')$ in which the hth layer of $T_h(C)$ has the D-B structure X. One can verify that

$$k_h(C, C', X) = k_h(C, X) k_1(C', X^*).$$

Let

$$k_h(C, C', \mathcal{X}_i) = \sum_{X\in\mathcal{X}_i} k_h(C, C', X).$$

Let $\mathcal{X}_1, \mathcal{X}_2, \ldots, \mathcal{X}_s$ and $\mathcal{X}'_1, \mathcal{X}'_2, \ldots, \mathcal{X}'_{s'}$ be the equivalence classes of the hth layer of $T_h(C)$ and the dangling bonds of C', respectively. For any $\mathcal{X}_i \in \{\mathcal{X}_1, \mathcal{X}_2, \ldots, \mathcal{X}_s\}$, define

$$\mathcal{V}_1^k(C')/\mathcal{X}_i = \sum_{j=1}^{s'} |\mathcal{X}'_j \cap \mathcal{X}_i^*| \cdot k_1(C', X'_j),$$

where X'_j is the representative D-B structure of $\mathcal{X}'_j$.

Recall that if two D-B structures X and X' are in the same equivalence class, then $k_p(C, X) = k_p(C, X')$ for any $p \in \{1, 2, \ldots, h\}$. So we have

$$\begin{aligned} k_h(C, C', \mathcal{X}_i) &= \sum_{X \in \mathcal{X}_i} k_h(C, C', X) = \sum_{X \in \mathcal{X}_i} k_h(C, X) k_1(C', X^*) \\ &= k_h(C, X_i) \cdot \sum_{X \in \mathcal{X}_i} k_1(C', X^*) = k_h(C, X_i) \cdot \left(\sum_{j=1}^{s'} \sum_{X \in \mathcal{X}'_j \cap \mathcal{X}_i^*} k_1(C', X) \right) \\ &= k_h(C, X_i) \cdot (\sum_{j=1}^{s'} |\mathcal{X}'_j \cap \mathcal{X}_i^*| \cdot k_1(C', X'_j)) = k_h(C, X_i) \cdot \mathcal{V}_1^k(C')/\mathcal{X}_i, \end{aligned}$$

where X_i and X'_j are the representative D-B structures of $\mathcal{X}_i$ and $\mathcal{X}'_j$, respectively.

Let

$$\mathcal{V}_1^k(C')/\mathcal{V}_h^k(C) = (\ \mathcal{V}_1^k(C')/\mathcal{X}_1, \mathcal{V}_1^k(C')/\mathcal{X}_2, \ldots, \mathcal{V}_1^k(C')/\mathcal{X}_s\ ).$$

Then by (1), we have the following result.

Proposition 3. The number of Kekulé structures in $T_h(C, C')$ is

$$\begin{aligned} K_h(C, C') &= \sum_{k=1}^{w} \sum_{i=1}^{s} k_h(C, C', \mathcal{X}_i) = \sum_{k=1}^{w} \sum_{i=1}^{s} k_h(C, X_i) \cdot \mathcal{V}_1^k(C')/\mathcal{X}_i \\ &= \begin{cases} \sum\limits_{k=1}^{w} \mathcal{V}_1^k(C)(M_e^k M_o^k)^{h-1/2}(\mathcal{V}_1^k(C')/\mathcal{V}_1^k(C))^{\mathrm{T}}, & \text{when } h \text{ is odd,} \\ \sum\limits_{k=1}^{w} \mathcal{V}_2^k(C)(M_e^k M_o^k)^{(h/2)-1}(\mathcal{V}_1^k(C')/\mathcal{V}_2^k(C))^{\mathrm{T}}, & \text{when } h \text{ is even.} \end{cases} \end{aligned} \tag{2}$$

For some tubules, for examples, $T_h(C_i, C_i), i \in \{1, 2, 3\}$, the odd layer and the even layer may have the same equivalence classes partition and the same transfer matrix, which implies that (2) could be simplified to be

$$K_h(C, C') = \sum_{k=1}^{w} \mathcal{V}_1^k(C)(M_e^k)^{h-1}(\mathcal{V}_1^k(C')/\mathcal{V}_1^k(C))^{\mathrm{T}}. \tag{3}$$

If the number of vertices in the upper cap is odd (resp., even), then the term for even (resp., odd) k in the summations (1), (2) and (3) will vanish.

Finally, consider the Boron-Nitride zigzag nanotube $T = T_h(C, C')$. Recall that all the polygons on the caps of T are of even sides and therefore, all the polygons on T are of even sides. So, in terms of graph theory, T is a bipartite graph. Colour the vertices in the upper cap C by using two colors, say black and red, such that any two adjacent vertices have distinct colors. Then it can be observed that the end vertices of the dangling bonds of C must have the same color. Since for any Kekulé structure M, each double bonds in M matches exactly one black vertex and one red vertex, so the dangling bonds of C contains exactly $k = |r - b|$ double bonds which do not depend on the choice of M, where b and r are the numbers of the black and red vertices, respectively. This also implies that each layer of T contains exactly $k = |r - b|$ double bonds. Thus, the formula (2) would be simplified further to be

$$K_h(C, C') = \begin{cases} \mathcal{V}_1^k(C)(M_e^k M_o^k)^{(h-1/2)}(\mathcal{V}_1^k(C')/\mathcal{V}_1^k(C))^{\mathrm{T}}, & \text{when } h \text{ is odd,} \\ \mathcal{V}_2^k(C)(M_e^k M_o^k)^{(h/2)-1}(\mathcal{V}_1^k(C')/\mathcal{V}_2^k(C))^{\mathrm{T}}, & \text{when } h \text{ is even.} \end{cases} \tag{4}$$

3. An algebraic formula

In this section, we will establish an other expression to the number of Kekulé structures in which the characteristic polynomial of the transfer matrix is involved. We firstly assume that h is odd. Let the characteristic polynomial of the transfer matrix $M_e^k M_o^k$ be

$$p(\lambda) = \lambda^s - d_1\lambda^{s-1} + d_2\lambda^{s-2} - \cdots + (-1)^s d_s, \tag{5}$$

where the coefficient d_i $(1 \leqslant i \leqslant s)$ is the sum of all main minors of order i in the determinant $\det(M_e^k M_o^k)$.

By (1), from a standard result on simultaneous relations, each entry $k_h(X_j)$ of $\mathcal{V}_h^k(C)$ satisfies a common recurrence relation [13], i.e.

$$k_h(X_j) = \sum_{i=1}^{s} (-1)^{i+1} d_i k_{h-2i}(X_j). \tag{6}$$

Let $\xi_1, \xi_2, \cdots, \xi_p$, $|\xi_1| \geqslant |\xi_2| \geqslant \cdots \geqslant |\xi_p|$, be the roots of (5) (i.e., the eigenvalues of the matrix $M_e^k M_o^k$) with multiplicity $m_1, m_2, \ldots, m_p$, respectively. Then by standard techniques in recursive relation (see [14] for details), we have

$$k_h(X_j) = \sum_{i=1}^{p} (a_{i1}^j h^{m_i-1} + a_{i2}^j h^{m_i-2} + \cdots + a_{im_i}^j)\xi_i^{h-1/2}, \tag{7}$$

where $a_{it}^j, i = 1, 2, \ldots, p; t = 1, 2, \ldots, m_p$, are coefficient which could be determined by $k_i(X_j), i = 1, 3, \ldots, 2s - 1$, and hence could be calculated from (1).

Combining with (2), we get an other expression, by words of eigenvalue, to the number $K_h(C, C')$:

$$K_h(C, C') = \sum_{k=1}^{w} \sum_{j=1}^{s} \left((\mathcal{V}_1^k(C')/\mathcal{X}_j) \sum_{i=1}^{p} (a_{i1}^j h^{m_i-1} + a_{i2}^j h^{m_i-2} + \cdots + a_{im_i}^j) \xi_i^{(h-1/2)} \right). \tag{8}$$

Similarly, when h is even we have (the discussion is similar and is omitted)

$$K_h(C, C') = \sum_{k=1}^{w} \sum_{j=1}^{t} \left((\mathcal{V}_1^k(C')/\mathcal{Y}_j) \sum_{i=1}^{p} (a_{i1}^j h^{m_i-1} + a_{i2}^j h^{m_i-2} + \cdots + a_{im_i}^j) \xi_i^{(h/2)-1} \right). \tag{9}$$

The above two algebraic formulae (8) and (9) also provide a way to view the asymptotic behaviour to the number $K_h(C, C')$ which indicates that, in general, the number of Kekulé structures in capped zigzag nanotubes increase exponentially with respect to the length h.

Theorem 1.

$$K_h(C, C') \sim h^{m_1-\delta} \xi^{h/2}, \quad \text{as } h \to +\infty,$$

where ξ is the eigenvalue of greatest modulus among all the matrices $M_e^k M_o^k$ (or $M_3^k M_e^k$), $k = 1, 2, \ldots, w$, satisfying

(1). $\mathcal{V}_1^k(C')/\mathcal{V}_1^k(C) \neq (0, 0, \ldots, 0)$ (or $\mathcal{V}_1^k(C')/\mathcal{V}_2^k(C) \neq (0, 0, \ldots, 0)$); and

(2). $\delta = \max\{l : a_{1l}^j \neq 0, j = 1, 2, \ldots, t(\text{or } s); l = 1, 2, \ldots, m_1\}$.

4. Examples

As applications of the previous two sections, in this section we will deduce the value $K_h(C_i, C_j)$ for the caps illustrated in figure 2. To this end, we will work mainly with $T_h(C_1, C_1)$ and give out the closed expression and numerical results (for those of length up to 50) for all the tubules with the caps shown in figure 2. With no loss of the generality, we always assume that the bond $i, i = 1, 2, \ldots, w$, in the first layer of the upper part is joined to the bond i in the dangling bonds of the upper cap (for an example, see figures 1(c) and 2).

According to the relevant position of the two caps C_1 and C_1 at opposite side ends of the tubule, there is essentially one kind of available structures for $T_h(C_1, C_1)$. Since the number of vertices in C_1 is odd, so the number k in the summation (2) must be odd.

Case 1. $k = 1$. The D-B structures in each layer has exactly one equivalence class $\{0, 1, 2, 3, 4\}$ and therefore the transfer matrix is the 1×1 matrix of all 1's: $M_o^1 = M_e^1 = (1)$. By a direct calculating, we have $\mathcal{V}_1^1(C_1) = (5)$ (the one-dimensional row vector) and $\mathcal{V}_1^1(C_1)/\mathcal{V}_1^1(C_1) = (25)$. So when $k = 1$, the total number of Kekulé structures is (see (2))

$$\mathcal{V}_1^1(C_1) \cdot (M_e^1)^{h-1} \cdot \mathcal{V}_1^1(C_1)/\mathcal{V}_1^1(C_1) = 5^{h+2}.$$

Case 2. $k = 3$. In this case, by a direct observation, the equivalence classes of D-B structures in the odd layer and the even layer are the same:

$$\mathcal{X}_1 = \mathcal{Y}_1 = \{012, 123, 234, 034, 014\};\ \ \mathcal{X}_2 = \mathcal{Y}_2 = \{013, 124, 023, 134, 024\}.$$

Furthermore, it is easy to verify that $M_e^3 = M_o^3$.

Choose 012 and 013 as the representative D-B structures of $\mathcal{X}_1$ and $\mathcal{X}_2$, respectively. The set of all successors of 012 and 013 are $\mathcal{S}_1 = \{012, 013, 014\}$ and $\mathcal{S}_2 = \{013, 014, 023, 024\}$, respectively. So by Proposition 2, we have the transfer matrix

$$M_e^3 = M_o^3 = \begin{pmatrix} |\mathcal{X}_1 \cap \mathcal{S}_1| & |\mathcal{X}_1 \cap \mathcal{S}_2| \\ |\mathcal{X}_2 \cap \mathcal{S}_1| & |\mathcal{X}_2 \cap \mathcal{S}_2| \end{pmatrix} = \begin{pmatrix} 2 & 1 \\ 1 & 3 \end{pmatrix}.$$

It is easy to calculate that $\mathcal{V}_1^3(C_1) = (k_1(012), k_1(013)) = (2, 1)$ and

$$\mathcal{V}_1^3(C_1)/\mathcal{V}_1^3(C_1) = (5 \times 2, 5 \times 1) = (10, 5).$$

So by (3), the total number of Kekulé structures with $k = 3$ is

$$\mathcal{V}_1^3(C_1) \cdot (M_e^3)^{h-1} \cdot (\mathcal{V}_1^3(C_1)/\mathcal{V}_1^3(C_1))^{\mathrm{T}} = (2, 1) \begin{pmatrix} 2 & 1 \\ 1 & 3 \end{pmatrix}^{h-1} \begin{pmatrix} 10 \\ 5 \end{pmatrix}.$$

Case 3. $k = 5$. In this case, it can be seen easily that there is only one Kekulé structure.

So by (3), the number of Kekulé structures in $T_h(C_1, C_1)$ is

$$K_h(C_1, C_1) = \mathcal{V}_1^1(C_1) \cdot (M_e^1)^{h-1} \cdot (\mathcal{V}_1^1(C_1)/\mathcal{V}_1^1(C_1))^{\mathrm{T}} + \mathcal{V}_1^3(C_1) \cdot (M_e^3)^{h-1} \cdot (\mathcal{V}_1^3(C_1)/\mathcal{V}_1^3(C_1))^{\mathrm{T}} + 1 = 5^{h+2} + (2, 1) \begin{pmatrix} 2 & 1 \\ 1 & 3 \end{pmatrix}^{h-1} \begin{pmatrix} 10 \\ 5 \end{pmatrix} + 1.$$

Our next step is to deduce the algebraic formula of the form (8) for $K_h(C_1, C_1)$.

The characteristic polynomial of $A = \begin{pmatrix} 2 & 1 \\ 1 & 3 \end{pmatrix}$ is

$$P(\lambda, A) = \lambda^2 - 5\lambda + 5 = \left(\lambda - \frac{5 + \sqrt{5}}{2}\right)\left(\lambda - \frac{5 - \sqrt{5}}{2}\right).$$

Table 1
The closed expressions of $K_h(C_i, C_i)$, $i = 1, 2, 3, 4$.

tubule	$K_h(C_i, C_i)$
$T_h(C_1, C_1)$	$1 + 5^{h+2} + (2,1)\begin{pmatrix}2 & 1\\ 1 & 3\end{pmatrix}^{h-1}\begin{pmatrix}10\\ 5\end{pmatrix}$ $= 1 + 5^{h+2} + 5 \times (\frac{5}{2} + \frac{\sqrt{5}}{2})^h + 5 \times (\frac{5}{2} - \frac{\sqrt{5}}{2})^h$
$T_h(C_2, C_2)$	$1 + 2^{h+3} + (3,4,5)\begin{pmatrix}2 & 2 & 2\\ 2 & 4 & 4\\ 1 & 2 & 3\end{pmatrix}^{h-1}\begin{pmatrix}18\\ 24\\ 15\end{pmatrix} + (2,1,0)\begin{pmatrix}2 & 1 & 0\\ 1 & 2 & 2\\ 0 & 1 & 2\end{pmatrix}^{h-1}\begin{pmatrix}12\\ 6\\ 0\end{pmatrix}$ $= 2 + 2^{h+4} + ((112 + 64\sqrt{3}) \times 2^{h-1} + 7 + 4\sqrt{3})(2 + \sqrt{3})^{h-1}$ $+((112 - 64\sqrt{3}) \times 2^{h-1} + 7 - 4\sqrt{3})(2 - \sqrt{3})^{h-1}$
$T_h(C_3, C_3)$	$1 + 7^{h+2} + (3,2,4,3)\begin{pmatrix}2 & 1 & 1 & 0\\ 2 & 4 & 2 & 4\\ 1 & 1 & 3 & 3\\ 0 & 2 & 3 & 5\end{pmatrix}^{h-1}\begin{pmatrix}21\\ 28\\ 28\\ 21\end{pmatrix}$ $+(2,1,0)\begin{pmatrix}2 & 1 & 0\\ 1 & 2 & 1\\ 0 & 1 & 3\end{pmatrix}^{h-1}\begin{pmatrix}14\\ 7\\ 0\end{pmatrix}$ (the second expression is too tedious and is omitted here)
$T_h(C_4, C_4)$ (Type 1)	$(4,8,8,6)\begin{pmatrix}10 & 16 & 18 & 16\\ 8 & 16 & 16 & 12\\ 9 & 16 & 19 & 16\\ 8 & 12 & 16 & 16\end{pmatrix}^{\frac{h-1}{2}}\begin{pmatrix}24\\ 24\\ 24\\ 18\end{pmatrix}$ when h is odd $= 6 \times 4^{h-1/2} + (291 + 168\sqrt{3})(28 + 16\sqrt{3})^{h-1/2} + (291 - 168\sqrt{3})(28 - 16\sqrt{3})^{h-1/2}$ $(28, 52, 60, 32)\begin{pmatrix}7 & 8 & 9 & 3\\ 16 & 28 & 32 & 16\\ 9 & 16 & 19 & 9\\ 3 & 8 & 9 & 7\end{pmatrix}^{\frac{h}{2}-1}\begin{pmatrix}12\\ 42\\ 24\\ 12\end{pmatrix}$ when h is even $= (2172 + 1254\sqrt{3})(28 + 16\sqrt{3})^{h/2-1} + (2172 - 1254\sqrt{3})(28 - 16\sqrt{3})^{h/2-1}$
$T_h(C_4, C_4)$ (Type 2)	$(4,8,8,6)\begin{pmatrix}10 & 16 & 18 & 16\\ 8 & 16 & 16 & 12\\ 9 & 16 & 19 & 16\\ 8 & 12 & 16 & 16\end{pmatrix}^{h-1/2}\begin{pmatrix}24\\ 18\\ 24\\ 24\end{pmatrix}$ when h is odd $= -6 \times 4^{h-1/2} + (291 + 168\sqrt{3})(28 + 16\sqrt{3})^{h-1/2} + (291 - 168\sqrt{3})(28 - 16\sqrt{3})^{h-1/2}$ (The value is the same as that of Type 1 when h is even)

So for the D-B structure 012, we have

$$k_h(012) = A_1\left(\frac{5+\sqrt{5}}{2}\right)^{h-1} + A_2\left(\frac{5-\sqrt{5}}{2}\right)^{h-1}, \tag{10}$$

where A_1, A_2 are coefficient, which could be determined by the initial condition of $k_h(012)$. For example, from

Table 2
The numerical results of $K_h(C_i, C_i)$, $i = 1, 2, 3, 4$.

h	$k_h(C_1, C_1)$	$k_h(C_2, C_2)$	$k_h(C_3, C_3)$	$k_h(C_4, C_4)$(Type 1)	$k_h(C_4, C_4)$(Type 2)
1	151	272	673	588	576
2	701	1782	4901	4344	– the same as Type 1, herein
3	3376	12740	38711	32448	after 32400
4	16501	93654	317864	242016	–
5	81251	694928	2675401	1806528	1806336
6	401876	5174118	22952189	13483392	–
7	1993751	38576900	200041031	100641792	100641024
8	9912501	287790246	1766636593	751197696	–
9	49359376	2147549072	1577299975×10	5607017472	5607014400
10	246062501	1602752348×10	1420811630×10^{2}	4185133670×10	–
11	1227656251	1196236735×10^{2}	1288981957×10^{3}	3123826360×10^{2}	3123826237×10^{2}
12	6128671876	8928558289×10^{2}	1175975363×10^{4}	2331655692×10^{3}	–
13	3060859375×10	6664264589×10^{3}	1077601707×10^{5}	1740371504×10^{4}	1740371499×10^{4}
14	1529171875×10^{2}	4974236787×10^{4}	9908269470×10^{5}	1299030974×10^{5}	–
15	7641308594×10^{2}	3712806706×10^{5}	9134323628×10^{6}	9696099191×10^{5}	9696099189×10^{5}
16	3819007813×10^{3}	2771271364×10^{6}	8437762723×10^{7}	7237266962×10^{6}	–
17	1908908203×10^{4}	2068503133×10^{7}	7806270265×10^{8}	5401969602×10^{7}	5401969602×10^{7}
18	9542385742×10^{4}	1543951022×10^{8}	7230457585×10^{9}	4032085003×10^{8}	–
19	4770413086×10^{5}	1152420457×10^{9}	6703039330×10^{10}	3009589219×10^{9}	3009589219×10^{9}
20	2384924414×10^{6}	8601782366×10^{9}	6218252628×10^{11}	2246387975×10^{10}	–
21	1192360132×10^{7}	6420457382×10^{10}	5771447007×10^{12}	1676726811×10^{11}	1676726811×10^{11}
22	5961431348×10^{7}	4792294489×10^{11}	5358794074×10^{13}	1251525930×10^{12}	–
23	2980582056×10^{8}	3577017250×10^{12}	4977081237×10^{14}	9341516714×10^{12}	9341516714×10^{12}
24	1490242684×10^{9}	2669922004×10^{13}	4623564470×10^{15}	6972602999×10^{13}	–
25	7451038513×10^{9}	1992856906×10^{14}	4295862613×10^{16}	5204421731×10^{14}	5204421731×10^{14}
26	3725455974×10^{10}	1487488643×10^{15}	3991880926×10^{17}	3884633265×10^{15}	–
27	1862705091×10^{11}	1110276637×10^{16}	3709755288×10^{18}	2899529743×10^{16}	2899529743×10^{16}
28	9313442618×10^{11}	8287217635×10^{16}	3447811027×10^{19}	2164238463×10^{17}	–
29	4656691338×10^{12}	6185663452×10^{17}	3204532118×10^{20}	1615409581×10^{18}	1615409581×10^{18}
30	2328334826×10^{13}	4617042056×10^{18}	2978537796×10^{21}	1205758126×10^{19}	–
31	1164163490×10^{14}	3446207107×10^{19}	2768564474×10^{22}	8999901178×10^{19}	8999901178×10^{19}
32	5820803253×10^{14}	2572284003×10^{20}	2573451508×10^{23}	6717617692×10^{20}	–
33	2910396491×10^{15}	1919978918×10^{21}	2392129754×10^{24}	5014098106×10^{21}	5014098106×10^{21}
34	1455196387×10^{16}	1433091774×10^{22}	2223612193×10^{25}	3742573778×10^{22}	–
35	7275975214×10^{16}	1069674263×10^{23}	2066986098×10^{26}	2793495098×10^{23}	2793495098×10^{23}
36	3637985175×10^{17}	7984157392×10^{23}	1921406359×10^{27}	2085093127×10^{24}	–
37	1818991707×10^{18}	5959456209×10^{24}	1786089718×10^{28}	1556334698×10^{25}	1556334698×10^{25}
38	9094955353×10^{18}	4448198671×10^{25}	1660309713×10^{29}	1161664033×10^{26}	–
39	4547476525×10^{19}	3320180689×10^{26}	1543392181×10^{30}	8670778385×10^{26}	8670778385×10^{26}
40	2273737846×10^{20}	2478216604×10^{27}	1434711233×10^{31}	6471957096×10^{27}	–
41	1136868772×10^{21}	1849766056×10^{28}	1333685614×10^{32}	4830734541×10^{28}	4830734541×10^{28}
42	5684343314×10^{21}	1380684180×10^{29}	1239775389×10^{33}	3605709349×10^{29}	–
43	2842171460×10^{22}	1030556702×10^{30}	1152478915×10^{34}	2691338098×10^{30}	2691338098×10^{30}
44	1421085659×10^{23}	7692179944×10^{30}	1071330065×10^{35}	2008842104×10^{31}	–

Table 2 *(Continued)*

h	$k_h(C_1, C_1)$	$k_h(C_2, C_2)$	$k_h(C_3, C_3)$	$k_h(C_4, C_4)$(Type 1)	$k_h(C_4, C_4)$(Type 2)
45	7105428034×10^{23}	5741521275×10^{31}	9958956683×10^{35}	1499420159×10^{32}	1499420159×10^{32}
46	3552713924×10^{24}	4285529822×10^{32}	9257731460×10^{36}	1119182443×10^{33}	–
47	1776356928×10^{25}	3198763007×10^{33}	8605883332×10^{37}	8353691483×10^{33}	8353691483×10^{33}
48	8881784517×10^{25}	2387589212×10^{34}	7999934557×10^{38}	6235280209×10^{34}	–
49	4440892214×10^{26}	1782120850×10^{35}	7436652590×10^{39}	4654076508×10^{35}	4654076508×10^{35}
50	2220446091×10^{27}	1330193111×10^{36}	6913032717×10^{40}	3473849998×10^{36}	–

$$\mathcal{V}_h^3(C_1) = \mathcal{V}_1^3(C_1) \cdot (M_e^3)^{h-1} = (2, 1) \begin{pmatrix} 2 & 1 \\ 1 & 3 \end{pmatrix}^{h-1},$$

we have $k_1(012) = 2, k_2(012) = 5$ and therefore, $A_1 = A_2 = 1$. This means that

$$k_h(012) = \left(\frac{5+\sqrt{5}}{2}\right)^{h-1} + \left(\frac{5-\sqrt{5}}{2}\right)^{h-1}.$$

Similarly, we have

$$k_h(013) = \left(\frac{1}{2} + \frac{\sqrt{5}}{2}\right)\left(\frac{5+\sqrt{5}}{2}\right)^{h-1} + \left(\frac{1}{2} - \frac{\sqrt{5}}{2}\right)\left(\frac{5-\sqrt{5}}{2}\right)^{h-1}.$$

Therefore, by (8), the number of Kekulé structures in $T_h(C_1, C_1)$ is

$$\begin{aligned} K_h(C_1, C_1) &= 1 + 5^{h+2} + 10k_h(012) + 5k_h(013) \\ &= 1 + 5^{h+2} + 5 \times \left(\frac{5}{2} + \frac{\sqrt{5}}{2}\right)^h + 5 \times \left(\frac{5}{2} - \frac{\sqrt{5}}{2}\right)^h \end{aligned}$$

To end the paper, the closed expressions of $K_h(C, C)$ for the caps shown in figure 2 are shown in table 1 and the relevant numerical results for those of length up to 50 are listed in table 2.

For $T_h(C_2, C_2)$ and $T_h(C_3, C_3)$, there are essentially one kind of available structures, respectively. For $T_h(C_4, C_4)$, there are essentially two different kinds of available structures, namely Type 1 and Type 2: In Type 1, the dangling bond $i, i = 0, 1, 2, 3, 4, 5,$ of the lower cap C_4 is joined to the bond i in the hth layer of the semi-tubule $T_h(C_4)$; in Type 2, the dangling bond $i, i = 0, 1, 2, 3, 4, 5,$ of the lower cap C_4 is joined to bond $i + 1$ (mod 6) in the hth layer of the tubule.

Acknowledgment

This work is supported by natural science foundation of Fujian province (F0210011)

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