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Geometric conservation laws for perfect Y-branched carbon nanotubes

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Abstract
Based on the integral theorems for mean curvature and Gauss curvature, geometric conservation laws for perfect Y-branched carbon nanotubes are presented. From the conservation laws, simple geometric regulations observed by spontaneous Y-branched carbon nanotubes are revealed, i.e. the angle between two neighbouring branches should be 120° and the radii of the three branches should be equal. These results coincide well with all experimental facts without exceptions. Possible applications of the geometric regulations to the design of super carbon nanostructures with self-similarities are predicted.

1. Introduction

Recently, geometric conservation laws [1] for three-way nanotube junctions [2, 3] are revealed. A three-way nanotube junction, with three lipid vesicles interconnected by three membrane nanotubes intersecting at a point (figure 1), may be formed through dynamic self-organizations of lipid molecules [2, 3]. Geometrically, this beautiful bionanostructure has been proved to observe very simple geometric regulations [1]. Surprisingly, such kind of geometric structures exist not only in biology but also in physics and material sciences. A very typical example is Y-branched carbon nanotubes [4–14]. Hence, the question may be asked: Do Y-branched carbon nanotubes also obey geometric conservation laws or what geometric regulations control their growth? To answer this question, similar ideas and procedures to those in [1] will be used.

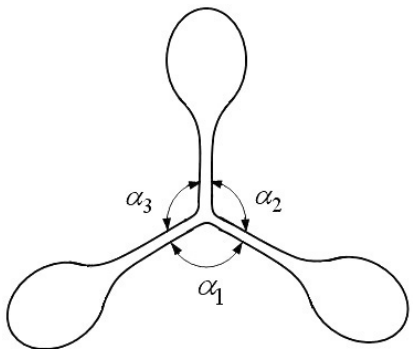

Figure 1. Smooth and closed curved surface formed from three vesicles and a three-way nanotube junction.

2. Methods and details

In this paper, perfect Y-branched carbon nanotubes will be studied. Here 'perfect' means that there are no defects such as dislocations or misconnected bonds. Geometrically such perfect structures may be idealized as globally smooth curved surfaces or two-dimensional (2D) Riemann manifolds. There are two reasons for this idealization: (a) it coincides with existing evidence [13]—a seamless and smooth transition has been found at the connecting locations between neighbouring branches of a perfect Y-branched carbon nanotube; (b) it makes differential geometry applicable and meaningful information about Y-branched carbon nanotubes available. To deal with the perfect Y-branched carbon nanotube correctly, a general smooth curved surface as shown in figure 2 is considered first. Let $\boldsymbol{n}$ be the outward unit normal of the surface and C be any smooth and closed curve drawn on the surface. At any point of the curve, let $\boldsymbol{t}$ be the unit tangent to the curve and along the positive direction of the curve. Let $\boldsymbol{m}$ be the unit vector tangential to the surface and normal to the curve, drawn outward from the region enclosed by C. Unit vectors $\boldsymbol{t}$, $\boldsymbol{n}$ and $\boldsymbol{m}$ form a right-handed system on curve C

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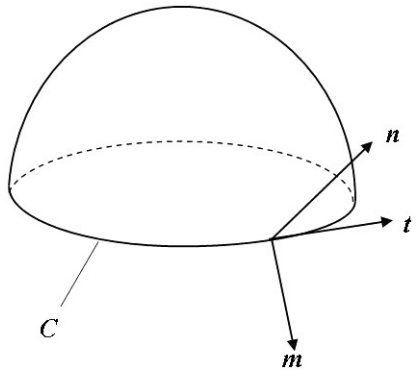

Figure 2. Schematic diagram of a curved surface with unit vectors $\boldsymbol{m}$, $\boldsymbol{t}$ and $\boldsymbol{n}$ at its boundary.

(figure 2) with the relation $\boldsymbol{m} = \boldsymbol{t} \times \boldsymbol{n}$ satisfied. On such a surface, integral theorems about two characteristic geometric quantities, i.e. the mean curvature $H = (c_1 + c_2)/2$ and Gauss curvature $K = c_1 c_2$ with c_1 and c_2 the two principle curvatures, will be specially focused. The first integral theorem in differential geometry is about the mean curvature H:

$$\oint_C \mathrm{d}\boldsymbol{s} = \int\int_A 2H\,\mathrm{d}\boldsymbol{A}. \tag{1}$$

The second one is about the Gauss curvature K [15]:

$$\oint_C \left(k_n \boldsymbol{m} + \tau_g \boldsymbol{t}\right) \mathrm{d}s = \int\int_A 2K\,\mathrm{d}\boldsymbol{A}. \tag{2}$$

Here $\mathrm{d}\boldsymbol{s} = \boldsymbol{m}\,\mathrm{d}s$ is the vector element with $\mathrm{d}s$ the length element along the curve C. $k_n = \frac{\mathrm{d}\boldsymbol{t}}{\mathrm{d}s} \cdot \boldsymbol{n}$ and $\tau_g = \frac{\mathrm{d}\boldsymbol{n}}{\mathrm{d}s} \cdot \boldsymbol{m}$ are respectively the normal curvature and the geodesic torsion at a point on the curve C. $\mathrm{d}\boldsymbol{A} = \boldsymbol{n}\,\mathrm{d}A$ is the element area vector in the normal direction of the curved surface and A is the area enclosed by C. Equations (1) and (2) lay the foundation of the conservation laws for perfect Y-branched carbon nanotubes.

Once equations (1) and (2) are applied to the perfect Y-branched carbon nanotube, a problem may not be avoided: How do we properly select the boundary curve C along which the line integrals are carried out? Here three principles are suggested. First, the line integrals should be easy enough to calculate. Second, they should include enough information about the geometric characteristics of the Y-branched carbon nanotube. Third, they should lead to simple conservation laws. According to these principles, we cut the three branches respectively along their cross sections (figure 3(a)). Thus a smooth and open curved surface A with three boundaries C_i $(i = 1, 2, 3)$ may be obtained (figure 3(b)). If the location of C_i is far enough from the junction, then the branch's shape near C_i may be treated as part of a circular cylindrical surface. Thus the unit vector $\boldsymbol{m}_i$ on C_i may be parallel to the axis of the branch and the line integrals will become

$$\oint_{C_i} \mathrm{d}\boldsymbol{s} = \boldsymbol{m}_i \int_0^{2\pi} r_i\,\mathrm{d}\theta = 2\pi r_i \boldsymbol{m}_i \tag{3}$$

$$\oint_{C_i} \left(k_n \boldsymbol{m} + \tau_g \boldsymbol{t}\right) \mathrm{d}s = \boldsymbol{m}_i \oint_{C_i} k_n \mathrm{d}s$$
$$= -\boldsymbol{m}_i \int_0^{2\pi} \mathrm{d}\theta = -2\pi \boldsymbol{m}_i, \qquad \left(\tau_g\right)_i = 0. \tag{4}$$

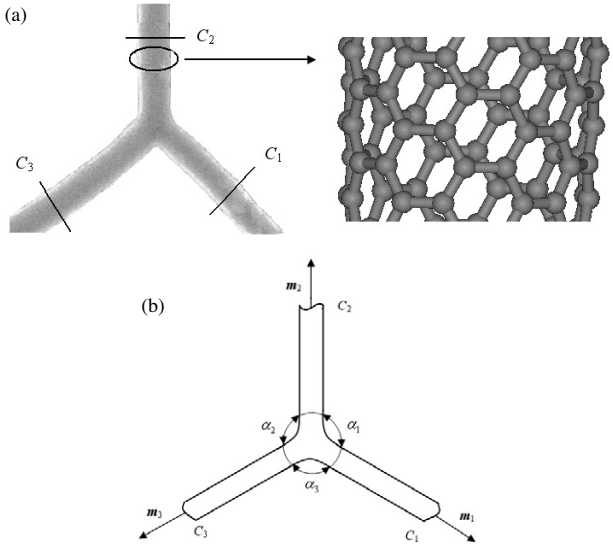

Figure 3. (a) Perfect Y-branched carbon nanotube with the three branches cut respectively along their cross sections. (b) Smooth and open curved surface with three boundaries, abstracted from the perfect Y-branched carbon nanotube in (a).

Here r_i is the radius of C_i. Finally, equations (1) and (2) may be changed into

$$\int\int_A H\,\mathrm{d}\boldsymbol{A} = \tfrac{1}{2}\sum_{i=1}^{3}\oint_{C_i} \mathrm{d}\boldsymbol{s} = \pi \sum_{i=1}^{3}(r_i \boldsymbol{m}_i) \tag{5}$$

$$\int\int_A K\,\mathrm{d}\boldsymbol{A} = \tfrac{1}{2}\sum_{i=1}^{3}\oint_{C_i} \left(k_n \boldsymbol{m} + \tau_g \boldsymbol{t}\right) \mathrm{d}s = -\pi \sum_{i=1}^{3} \boldsymbol{m}_i. \tag{6}$$

Equations (5) and (6) are the geometric conservation laws for perfect Y-branched carbon nanotubes. Of course these laws may not be valid for imperfect ones, because the basis for the assumption of a globally smooth curved surface is lost. Equation (5) means that the integral of the mean curvature H on the Y-branched carbon nanotube is determined not only by the directions but also by the radii of branches. Equation (6) implies that the integral of the Gauss curvature K on the Y-branched carbon nanotube is just related to the directions of branches.

3. Results and discussions

Technically there are different ways to produce branched carbon nanotubes, for example, 'forced' branching [4] in templates with branched nanochannels, spontaneous branching [5–12] and electron beam welding [16]. To evaluate the reasonability of equations (5) and (6), spontaneous Y-branched carbon nanotubes will be carefully investigated. From experiments [6, 7, 11, 14], it is found that a spontaneous Y-branched carbon nanotube usually has very regular geometry and the radius of each branch looks very uniform along the branch. Thus every branch may be further abstracted as a circular cylindrical surface A_i on which constant mean curvature ($H_i = \text{const.}$) and zero Gauss curvature ($K_i = 0$) are kept. If all three branches are long enough, then the following

integrals in which the contribution of the junction is omitted may be approximated:

$$\int\int_A H\,\mathrm{d}\boldsymbol{A} \approx \sum_{i=1}^{3}\left(\int\int_{A_i} H_i\,\mathrm{d}\boldsymbol{A}\right)$$

$$= \sum_{i=1}^{3}\left(H_i\int\int_{A_i}\mathrm{d}\boldsymbol{A}\right) = 0 \tag{7}$$

$$\int\int_A K\,\mathrm{d}\boldsymbol{A} \approx \sum_{i=1}^{3}\int\int_{A_i} K_i\,\mathrm{d}\boldsymbol{A} = 0. \tag{8}$$

Equations (5)–(8) together will give

$$\sum_{i=1}^{3}(r_i\boldsymbol{m}_i) = 0 \tag{9}$$

$$\sum_{i=1}^{3}\boldsymbol{m}_i = 0. \tag{10}$$

Equations (9) and (10) may lead to detailed information about the geometry of the spontaneous Y-branched carbon nanotube. Here equation (10) will be discussed first. Mechanically, equation (10) may be equivalent to the equilibrium equation for three unit forces. In mechanics, it is well known that the necessary and sufficient conditions for this equilibrium are: (a) the three unit forces intersecting at a point should remain on the same plane; and (b) the angle between two neighbouring forces should be 120°, i.e.,

$$\alpha_1 = \alpha_2 = \alpha_3 = 120^\circ. \tag{11}$$

Similarly, equation (9) may also be regarded as an equilibrium equation for three forces. With equation (11) satisfied, the necessary and sufficient condition for the equilibrium in equation (9) is that the radii of the three branches should be equal:

$$r_1 = r_2 = r_3 \tag{12}$$

Equations (11) and (12) are the geometric regulations for spontaneous Y-branched carbon nanotubes. From experiments, it may be confirmed that forced Y-branched nanotubes [7] have non-equal angle between branches but spontaneous ones possess structures with branches oriented at 120° [6, 7, 11, 14]. Therefore equation (11) coincides strictly with existing experiments. Besides, TEM images have shown that the radii of the three branches of a spontaneous Y-branched carbon nanotube are roughly the same [10, 11, 14]. Hence equation (12) also agrees well with experiments. Such coincidences support the validity of the geometric conservation laws in equations (5) and (6).

A spontaneous Y-branched carbon nanotube with equations (11) and (12) satisfied corresponds to a equilibrium state with both minimum energy and symmetric geometry as well. This judgment may be interpreted in detail as follows. For simplicity (but without losing generality), an arbitrary Y-branched carbon nanotube with junction S is supposed to grow in such a way that its three branches SA_i ($i = 1, 2, 3$) are connected exactly with three fixed points A_1, A_2 and A_3 on the plane (figure 4). The total elastic curvature energy of this Y-branched carbon nanotube may be written as

$$E = \sum_{i=1}^{3} E_i \tag{13}$$

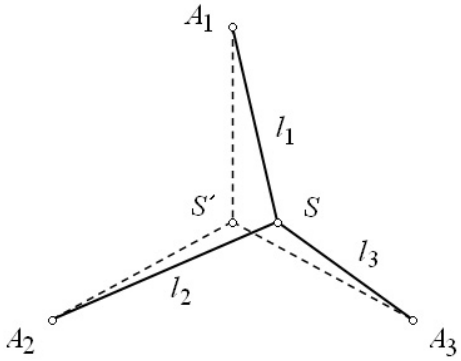

Figure 4. Y-branched carbon nanotube with three branches connecting with three fixed points.

where E_i is the ith branch's elastic curvature energy. Through a continuum limit treatment [17] to the potential given by Lenosky *et al* [18], the curvature elastic energy of a single layer curved graphite has been proved to be

$$E_s = \int\int_A [\tfrac{1}{2}k_c(2H)^2 + \bar{k}_1 K]\,\mathrm{d}A \tag{14}$$

where k_c and $\bar{k}_1$ are the bonding elastic constants. Once equation (14) is applied to the Y-branched carbon nanotube with $H_i = -1/2r_i$ and $K_i = 0$, one has

$$E_i = \frac{\pi k_c l_i}{r_i}. \tag{15}$$

Here l_i is the length of the ith branch. Suppose $r_1 = r_2 = r_3 = r$; then equations (13) and (15) will lead to

$$E = \frac{\pi k_c}{r}\sum_{i=1}^{3} l_i = \frac{\pi k_c l}{r} \tag{16}$$

where $l = \sum_{i=1}^{3} l_i$ is the total length of the three branches. The total potential energy F for an arbitrary Y-branched carbon nanotube is determined by $F = E + F_p$ with F_p the potential of external forces. However, for a spontaneous Y-branched carbon nanotube external forces do not exist and $F = E$ is met. Thus the equilibrium of the spontaneous Y-branched carbon nanotube will render F a minimum value $F_{min} = E_{min}$:

$$E_{min} = \frac{\pi k_c l_{min}}{r}. \tag{17}$$

Equation (17) clearly reveals that the spontaneous Y-branched carbon nanotube, at equilibrium and with minimum energy, is of minimum total length l_{min}. According to the theory of the Steiner minimal tree [19] in geometry, the necessary and sufficient condition for l_{min} is to set S as the Steiner point S' at which $\angle A_1S'A_2 = \angle A_2S'A_3 = \angle A_3S'A_1 = 120^\circ$ (figure 4). Therefore equation (17) includes the following information. (a) For a spontaneous Y-branched carbon nanotube at equilibrium, minimum energy means symmetric geometry, and vice versa. (b) Once a Y-branched carbon nanotube is grown spontaneously through dynamic self-organization, it tends to form automatically into a perfect geometry with low energy and high symmetry. In other words, the symmetric geometry described by equations (11)

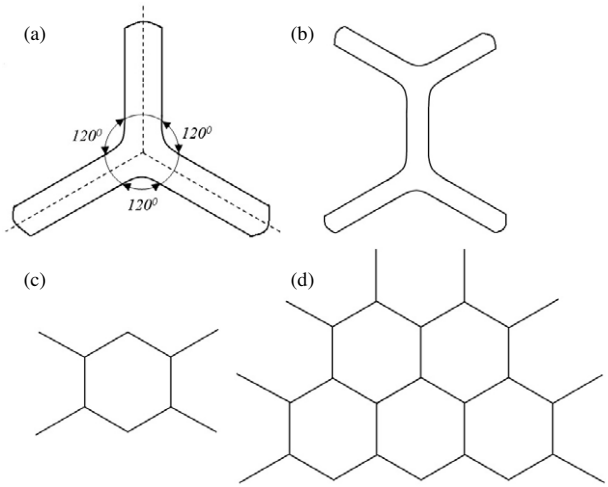

Figure 5. (a) Template with one symmetric Y-branched nanochannel. (b) Template with two symmetric Y-branched nanochannels. (c) Template with a network formed by four symmetric Y-branched nanochannels. (d) Template of a nanochannel network covered periodically with hexagonal cells.

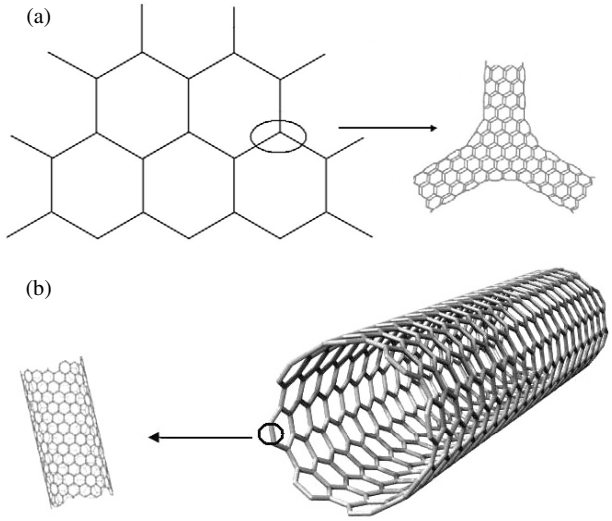

Figure 6. (a) Periodic network of hexagonal cells constructed by carbon nanotubes, grown from the template in figure 5(d). (b) Super carbon nanotube theoretically manufactured from the network of carbon nanotubes in (a).

and (12) is a 'natural' one to which a spontaneous branching process will approach with priority. (c) Any Y-branched carbon nanotube that diverges from the symmetric geometry may possess higher energy. In fact, any divergence needs external forces. For example, once a Y-branched carbon nanotube is grown through a template, the external forces caused by the template will force the nanotubes to grow along the channels. Finally the forced Y-branched carbon nanotube not only possesses non-symmetric structure such as curved branches, non-equal radii and non-equal angles, but also stores residual stresses or energies inside. In short, for spontaneous Y-branched carbon nanotubes at equilibrium, minimum energy and symmetric geometry are unitary.

To one's surprise, although the derivation processes are different, both the conservation laws in equations (5) and (6) and the geometric regulations in equations (11) and (12) for Y-branched carbon nanotubes are similar to those for three-way membrane nanotube junctions [1]. Why do these similarities exist? There are three reasons. First, Y-branched carbon nanotubes and three-way membrane nanotube junctions have similar geometries. Second, the major premises for the derivation processes, i.e. the integral theorems in equations (1) and (2), are the same. Third, the philosophies or beliefs for the two studies are the same: i.e. 2D Riemann manifolds instead of Euclidian spaces should be the natural choice of both the carbon nanoworld and the bionanoworld.

4. Potential applications

Equations (11) and (12) may be of potential applications in nanoscience and nanotechnology—they may provide inspirations for probing new carbon nanostructures. One possible carbon nanostructure is the periodic network of carbon nanotubes. As mentioned above, spontaneous branching has symmetry but no controllability, whereas forced branching has controllability but no symmetry. This may stimulate such an inspiration: Is it possible to design a forced branching process with both controllability and symmetry? The answer is positive: If a template with a symmetric Y-branched nanochannel is prepared (figure 5(a)), then the controllable forced branching with equations (11) and (12) satisfied will be equivalent to a symmetric spontaneous one. Extending this inspiration, one can have two symmetric Y-branched nanochannels interconnected (figure 5(b)). If four symmetric Y-branched nanochannels are connected in the way shown in figure 5(c), a hexagonal nanochannel network may be formed. Repeating the above procedures one can get a nanochannel network covered periodically with 'hexagonal cells' (figure 5(d)). From this template, a periodic hexagonal network constructed by carbon nanotubes may be grown (figure 6(a)). This is an interesting structure: it possesses low energy and high symmetry not only locally but also globally. Besides, it includes the first-level self-similarity—the similarity between the network of carbon nanotubes and the network of carbon atoms (or single layer graphite).

Another possible carbon nanostructure is the super carbon nanotube made from the network of carbon nanotubes in figure 6(a). In carbon nanoscience and technology, it is well known that a common carbon nanotube may be 'theoretically manipulated' by rolling up a single layer of graphite into a tube. Similarly, a super carbon nanotube may also be 'theoretically manufactured' by curling up the network of carbon nanotubes into a tube (figure 6(b)). Figure 6(b) also displays an interesting structure: it includes the second-level self-similarity—the similarity between the super carbon nanotube and the common carbon nanotube.

In organic worlds such as the bioworld, self-similarity is one of the most effective rules to create structures from a low level to a high one or from a smaller scale to a larger one. In inorganic worlds such as the carbon nanoworld, self-similarity seems also effective for designing new structures. Although the new carbon nanostructures above are just imaginary ones, they are reasonable—because they are designed according to self-similarity. What is more, at each level of self-similarity the

geometric regulations reflecting the principles of low energy and high symmetry are strictly observed. Once the new carbon nanostructures are realized, our understanding and knowledge about the carbon nanoworld may be enriched and deepened.

Except for the concept of self-similarity, the concept of the template also needs to be further annotated. In the above proposed manipulation process for super carbon nanotubes, the term 'theoretically' is used, because two technical difficulties exist: one is to roll up the planar network of nanotubes into a cylindrical one, and the other is to 'weld' the cylindrical network into a seamless tube. How do we overcome these difficulties? The answer is to give up the concept of 'planar template' and introduce the concept of 'circular cylindrical template'. In differential geometry, a circular cylindrical surface is a developable one that may be unrolled into a plane after it is cut along its generatrix. Hence, the nanochannel network in the planar template in figure 5(d) may be manipulated conformably on the surface of a circular cylinder, and then a circular cylindrical template may be made. From this template, the super carbon nanotube may be grown directly and 'practically'. Furthermore, if the concept of circular cylindrical template is extended into a more general one such as a 'curved template', then various super carbon nanostructures may be available. For example, super carbon nanotube cones may be formed from conic templates. From spherical templates, super carbon nanotube spheres with geometries similar to C_{60} may be created, though the spherical surface is not a developable one.

5. Conclusions

In short, perfect Y-branched carbon nanotubes should observe certain geometric conservation laws, and spontaneous ones should obey simple geometric regulations. These laws and regulations may enable us to understand better the formations of Y-branched carbon nanotubes, and may possibly be used to explore new carbon nanostructures with self-similarities.

Acknowledgment

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