Introducing a twist in carbon nanotubes

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A simple model based on rotational distortion of carbon atoms between adjacent layers running perpendicular to the tube axis, without altering the hexagonal motifs is proposed for constructing coiled carbon nanotubes.

Keywords: Coiled carbon nanotubes, defects in nanotubes, molecular mechanics

CARBON is a fascinating element. It exists in different allotropic forms that give rise to its versatile behaviour. In the amorphous form it is powdery in nature and black in colour. It becomes the hardest substance known and has a shining appearance in the allotropic form of diamond. Catenation, the self-linking property of carbon atoms is responsible for much of organic chemistry. The role of carbon clusters and carbon clouds in the interstellar region and in atmosphere remains to be understood[1]. The discovery of fullerene[2], a new form of carbon, was perhaps a serendipity. But it led to a number of other fundamental discoveries. Fullerenes of various sizes and shapes have been reported subsequently. It would be fair to say that the discovery of carbon nanotubes in 1991 was a by-product of the fullerene production process[3].

Carbon nanotubes can be thought to be formed by the rolling of graphite layers. The rolling of a single layer of graphite results in a single-walled carbon nanotube (SWCNT), whereas the rolling of more than one layer around a central axis produces multi-walled carbon nanotubes (MWCNT). Depending on the way of rolling of graphene sheets (as shown in Figure 1), nanotubes of different types, viz. armchair, zig-zag and chiral could be produced. They can be represented using the method given by Hamada et al.[4] For example, to realize an (n, m) nanotube, one has to move n times $\mathbf{a}_1$ from the selected origin and then m times $\mathbf{a}_2$. On rolling the graphite sheet these points coincide to form the (n, m) nanotube. Thus armchair, zig-zag and chiral nanotubes can be represented as (n, n), $(n, 0)$ and (n, m) respectively.

Like many solids, carbon nanotubes are not devoid of defects. Such defects in carbon nanotubes at the intramolecular junction, formed by interposing one or more topological pentagon/heptagon defects in the hexagonal structure between two nanotube segments of different helicity was predicted first theoretically[5] and observed later experimentally[6]. Depending on the orientation in the hexagonal network, the pentagon–heptagon pairs can cre-

ate a small deformation in the nanotube. It is considered to be a local defect in a straight nanotube.

Defects in nanotubes can be produced by controlled electron irradiation, for example. This causes atom removal and creates vacancies, which cluster into large holes in the structure. Molecular simulations have shown that such nanotubes undergo surface reconstruction and non-hexagonal rings such as squares, pentagons, heptagons and octagons so formed disappear finally through Stone–Wales mechanism and lead to five-, six-, and seven-membered rings[7]. Coalescence and welding of carbon nanotubes have also been reported[8]. Welding of nanotubes creates molecular junctions of various geometries like X, Y and T[9,10]. These defects in carbon nanotubes seem to be responsible for the changes in many of their properties.

The mechanical properties of carbon nanotubes have been discussed extensively in the last one decade. The Young's modulus and tensile strengths of carbon nanotubes are very high compared to that of steel. Reinforcement of these carbon nanotubes can be done to fully exploit the above tensile strengths by the coiling of the tubes. Many models have been proposed for these coiled nanotubes. Recently, Szabó et al.[11] reported the inclusion of impurities like N and S atom and non-hexagonal rings causing the coiling of carbon nanotubes. The folding of haeckelite sheets, which are made up of pentagon, hexagon and heptagons, has also been predicted. All the proposed models explain either the local defect in the straight nanotube or the non-uniform coils of carbon nanotube. Due to the lack of proper experimental results, the structures of these coils are not yet completely revealed in the atomic scale.
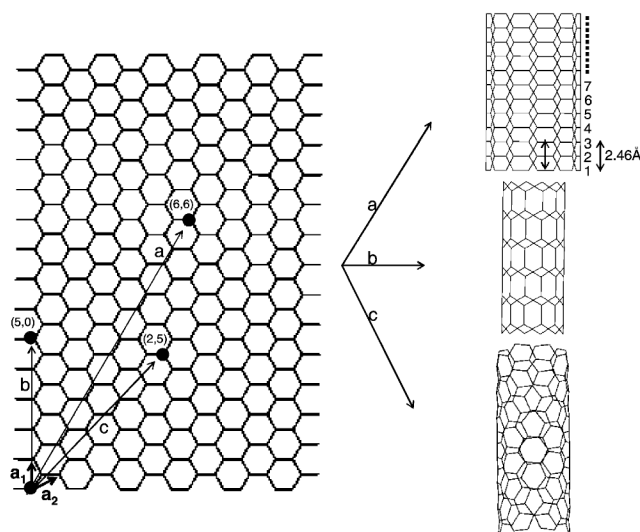

Figure 1. Rolling of a graphite layer to form single-walled carbon nanotubes of (a) armchair, (b) zig-zag and (c) chiral type. The numbering in the case of the armchair nanotube shows the numbering of the layers running perpendicular to the tube axis as described in the text.

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In the present paper, a simple model for constructing uniformly coiled carbon nanotubes is proposed. It retains the hexagonal motifs, but introduces twists by a gradual rotational distortion between adjacent layers of carbon atoms.

A careful examination of the carbon nanotube structure reveals that it is made up of repeating layers of carbon atoms. For example, Figure 2 *a* illustrates the formation of a (6, 6) carbon nanotube from the basic layer of carbon atoms. The odd numbered layers repeat with an interlayer separation of 2.46 Å (see Figure 1). Similarly, the even numbered layers repeat with the same distance and the entire single walled carbon nanotube is formed.

To introduce a twist in an otherwise 'straight' nanotube, a different strategy is called for. Carbon atoms of the second layer undergo a rotational distortion from their original positions by any small angle (θ) and the shift moves on a helix of desired radius. Continuous distortion followed by a repetition of these layers generates the coiled nanotube as shown in Figure 2 *b*. The geometry of the coiled carbon nanotube thus constructed is optimized by molecular mechanics method using universal force field (UFF) adopted in the Gaussian suite of programs[12]. The coiled carbon nanotube thus obtained with a 1° shift between successive layers is reproduced in Figure 3.
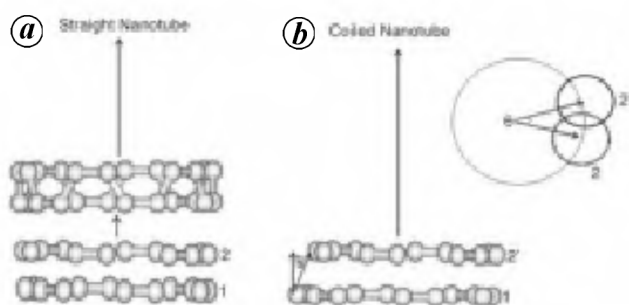

Figure 2. Schematic representation for the formation of (*a*) straight carbon nanotubes and (*b*) coiled carbon nanotubes from a repetition of the basic layer of carbon atoms.
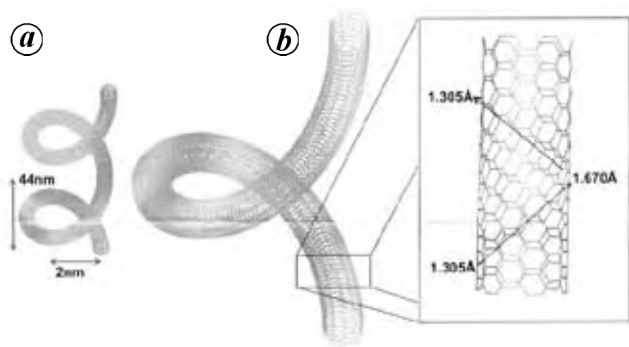

Figure 3. Optimized geometry of (*a*) a carbon nanotube coil and (*b*) one pitch of the coil, along with the magnified portion of a part of the coil.

The pitch of the resultant coil is ~44 nm and the radius is 2 nm. There are 4320 carbon atoms per pitch. It is interesting to note the variation in the distance between adjacent carbon atoms of the hexagons on the surface of the coil. The C–C bonds in the 'inner' side of the coils are slightly compressed (1.305 Å) and those in the 'outer' side are slightly stretched (1.67 Å), when compared to the C–C distance of 1.421 Å in a 'straight' nanotube. Understandably, this gradation in the distance as we move from the inner surface to the outer surface reverses as we move on to the inner side again. It can be seen that after a regular interval the pattern would repeat itself. Here, the changes in bond length between carbon atoms are not negligible and may not be favourable under normal conditions. In such case, either it can form (go back to) straight carbon nanotube or break into nanotubes with local defect and act like a metastable system. However, coils formed by rotational distortion of very small angle (<<1°) between successive layers may be energetically favourable as the contraction and elongation between carbon atoms are less. The formation of such coils will be more feasible especially, as the height and the number of the pitch(es) increase. Due to the limitation of the program the present study restricts us to select a rotational distortion of 1 degree and two pitches. Like in the formation of nanotubes of various chiralities, the studies on the role of catalyst in the formation of coiled carbon nanotube will be interesting.

Szabó *et al.*[11] have studied the statistical distribution of coiled carbon nanotubes. From a three-dimensional plot of the number of coils, pitch and diameter of all the experimentally reported carbon nanotube coils, it was observed that there were some stability islands in which the number of coils are more for a range of diameter and pitch values. They occur in the region of 50–70 nm pitch and 20–60 nm diameter. Our model is flexible enough to achieve this range with less than 1° distortion between successive layers.

In summary, a simple model based on a slight shifting of carbon atoms between adjacent layers of carbon atoms running perpendicular to the tube axis, without altering the hexagonal motifs has been proposed for the construction of coiled carbon nanotubes. The same approach can be used to construct other nanocoils.

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Molecular tensegrity: predicting 1,3–X– – –X distance in gas-phase MX_n ($n \leq 4$) compounds from atomic sizes

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This article extends an earlier definition[1] and use of molecular tensegrity for obtaining quantitatively the 1,3-non-bonded distances in gas-phase MX_2 compounds to nearly 160 gas-phase MX_n ($n \leq 4$) inorganic compounds (including those of transition metal elements), once a transferable 'core' atomic size is specified. The simple principles behind this methodology (involving only linear equations), its quantitative character, its transparency, its portability and its generality account very simply for molecular geometry in such compounds without requiring earlier theoretical methodologies. We also establish clear distinction in the prescription for obtaining the 1,3-distance when M is an atom of a metallic or insulating element.

Keywords: Atomic size, gas phase, molecular tensegrity, non-bonded distance.

THE Fuller notion[2] of tensegrity structures has structural elements that are held together by compressive and tensile elements that balance each other. Such a notion is ex-

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pected to hold for all length scales, as a general principle. Fuller–Snelson tensegrity structures using (incompressible) struts and (tensile) cables describe well the qualitative features of the role of cell and tissue architecture in the dynamics of complex biological systems[3]. A 'molecular tensegrity'[4] that determines, say, the mechanical stability of the structure of isolated gas-phase MX_2 has recently been proposed, taking advantage of a free-atom-like $\mu = 0$ condition[5,6] in which atoms in molecules may be treated independent of each other. The molecular tensegrity structure is obtained from simple mechanical relationships between atomic sizes that contribute to interatomic distances 'without requiring to know the (quantum) mechanics of the way the $\mu = 0$ state is reached from a $\mu \neq 0$ state'.

For an isolated MX_n molecule, the mutual influences of 1,2-bonded (attractive) M–X distance, d_{M-X}, and 1,3-non-bonded (repulsive) X– – –X distances, d_{X-X}, is expressed (eq. (3)) as a tensegrity factor (similar to the tolerance factor in solids[7,8]) that forms the quantitative basis for molecular tensegrity. 1,2-Interatomic distance, d_{MX}^{n0}, has been expressed as[5,9] an universal function of 'core' (small compared to interatomic distances) empirical[9] atomic sizes, r_G as

$$d_{MX}^{n0} = CR_0^+(M)/F_S(M) + CR_0^-(X)$$
$$= [C_0^+ r_G(M) + D_0^+]/F_S(M) + C_0^- r_G(X) + D_0^-, \quad (1)$$

with $CR_0^\pm = C^\pm r_G + D_0^\pm$, and $C_0^+ = 2.24$, $C_0^- = 2.49$, $D_0^- = 111$ pm and $D_0^+ = -37$ pm. The term[10] $F_S(M)$ is associated[10] with decrease in atomic sizes or bond lengths due to the presence of n_v 'unsaturated' valence electrons. We take[10] $F_S = 1$ ($n_v = 0$) for all M except for transition metal MX_3 ($n_v = 1$) and MX_4 compounds ($n_v = 2$). The superscript, $\pm$, refers to charge-transfer states CR_0^+ and CR_0^- in (eq. 1). The size $CR_0(X)$ is close to the ionic radii in solids[9] and is different from the van der Waals' radius[11], $r_{VDW} \neq CR_0(X)$. The non-bonded distance, d_{XX}^{00} is expected to be

$$d_{XX}^{00} = 2KCR_0^-(X). \quad (2)$$

Unless otherwise mentioned, we take $K = 1$ hereafter. Equations (1) and (2) are required to define an ideal 'tensegrity' factor[4], $t_{n0}^\pm$, as

$$t_{n0}^\pm = d_{MX}^{n0}/d_{XX}^{00}. \quad (3)$$

We have expressed an experimental quantity[4] F_S (obs) as

$$F_S \text{(obs)} = d_{XX} \text{(obs)}/d_{XX}^{00} \equiv d_{XX} \text{(obs)}/2CR_0^-(X). \quad (4)$$

A plot of F_S (obs) vs $t_{n0}^\pm$ (Figure 1) for all gas-phase MX_2, MX_3 and MX_4 compounds[12,13] ($X =$ atom of insulating element) two nearly linear relationships of the type

$$F_S \text{(obs)} = A - Bt_{n0}^\pm \quad (5)$$

are obtained (Figure 1) which we refer to as type I and type II. From the ratios of the two slopes in Figure 1 we