THREE-DIMENSIONAL STRUCTURE OF MULTILAYER CARBON NANOTUBES

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Introduction

In carbon materials, consisting of atoms of carbon in the sp2 bonded, layered structures will be formed [1,2]. As the characteristic of ordering degree of such structures it is accepted an average interlayer spacing d_{002}. By peculiarity of carbon materials: cokes, carbon fibres, particles of soot and other - difference of values of an average interlayer spacing from size, characteristic of graphite [1;2]. In multilayer nanotubes - new carbon materials, open Sumio Iijima in 1991, also fix intertubes d_{002} 0.34 - 0.36 nm, that there is more value, observable in structure of ideal of graphite - 0.3354 nm [3-5]. The reason of the given difference is not clear, therefore problem of the given work has made model analysis of three-dimensional structure of multilayer carbon nanotubes.

Formation nanotubes

The nanotube can be made by various ways: at a thermal deposition, oxidation, electrolytic synthesis, laser deposition and other methods [6]. There is no uniform opinion concerning the mechanism of formation of nanotubes [7], however the model formation of nanotubes is possible to consider as turn off process of a graphite plane in a tube (fig.1, 2).

The nanotubes depending on orientation of covalent bonds along an axis of a tube are characterized by various chirality, which is determined by two indexes (m, n), specifying compilations on axes x and y, corner between which makes 60° (fig.1). The indexes set the size of a layer and turn off direction. As the identical turn off direction can be given by various combinations of indexes (for example (2,1), (4,2), (6,3) and etc.), it is possible to determine the minimum values of indexes specifying a direction (m0, n0). Then any nanotube of such chirality can be given as (m0 * j, n0 * j), where j - number of periodic compilations, specifying the size of a turned off of a layer (j=1,2,…).

Two basic types of nanotubes of carbon - carbon bonds distinguished by orientation concerning an axis of a nanotube turn out of a graphite plane along turn off directions, set by indexes (j, j) and (j, 0). These structures name zigzag and armchair as configurations accordingly. The orientation of covalent bonds of a atomic plane along an axis of a nanotube for these structures is similar to orientation of bonds along an axis of carbon fibres, received from polyacrylenitrile and hydrated cellulose (PAN- and HC-structure) [8]. A degree of chirality of nanotubes conveniently to determine as:

$$k = n/m, \qquad (1)$$

area of definition of this parameter from 0 up to 1.

Admitting, that the bonds between atoms have constant length and = 0.1422 nm and that a nanotube is possible to receive by turn off of a plane, to which rigidly "sew" of bond between atoms, i.e. they are bent together with it on a surface of the cylinder. In this case the diameter of nanotubes can be found under the formula [6]:

$$D = \sqrt{m^2 + n^2 + mn}\,\frac{\sqrt{3}a}{\pi}. \qquad (2)$$

Intertubes distance between enclosed nanotubes of an identical chirality we shall find as:

$$d_{002} = \frac{D_{внеш} - D_{внутр}}{2}. \qquad (3)$$

Then using expression (2) and (1) we shall receive, that:

$$d_{002} = \frac{\sqrt{3}a}{2\pi}(j''-j')\sqrt{m_0^2 + m_0n_0 + n_0^2} \quad \text{or}$$

$$d_{002} = \frac{\sqrt{3}a}{2\pi}(j''-j')m_0\sqrt{1 + k + k^2}, \qquad (4)$$

where j' and j " - number of periodic compilations of a graphite layer along a direction, set by indexes (m0, n0), for internal and external tubes accordingly. Entering designation f = j"-j', where f = 1, 2, ... we receive, that intertubes distance for multilayer nanotubes are function of a degree of a chirality and difference in number of elementary compilations of an external and internal layer (fig.2). As the values of interlayer spacings d002 in carbon materials in an interval from 0.3354 nm till 0.36 nm [1-5], the size f should be those, that this condition was carried out. By computer simulation of various numbers of indexes of nanotubes specifying a chirality in a range from 1 up to 10000, is established, that there is total

16 values k for which at f=1 intertubes distance does not exceed 0.36 nm.

From these decisions completely to a condition of hit in a range d_{002} characteristic for carbon materials five cases (table 1) satisfy only. Thus, the formation of multilayer nanotubes of an identical chirality is possible for k=0 and 1 (armchair and zigzag of structure accordingly), and also at k=0.4, 0.6 and 0.8 Intertubes distances in such tubes are to constants and exceed 0.3354 nm - value of interlayer spacing, characteristic of graphite.

If the multilayer tube is made of tubes of a various chirality, intertubes distance d_{002} is not a constant (table 2). However and in this case it more value, characteristic of graphite, and varies in a rather wide interval (from d_{002} (min) up to d_{002} (max)). And the interval, in which value of intertubes distance changes, depends on what tube is taken as initial (table 3).

However the approximation of bent bonds is allowable only in the first approximation, actually the bonds remain direct. In this case the nanotubes will represent in section, perpendicular their axes, polygons, entered in circles (fig.3). Then, for example, for nanotubes of a chirality 0 diameters of circles it is possible to find under the formula:

$$D_{k=0} = \sqrt{3}a \Big/ 2\sin(\frac{\pi}{2j}) . \qquad (5)$$

Taking into account, that for nanotubes by a chirality 0 differences in number of elementary compilations of layers forming external and internal nanotubes should make f=9, the intertubes distances will be:

$$d_{002\_k=0} = 0.25\sqrt{3}a\left(\frac{1}{\sin\left(\frac{\pi}{2(j'+9)}\right)} - \frac{1}{\sin\left(\frac{\pi}{2j'}\right)}\right). \quad (6)$$

Their size corresponds to values, received on the formulas (4) only at large j' > 30, in the field of small values j' intertubes distances there is less than in approximation of bent bonds. A range of change d_{002} from 0.345 up to 0.3528 nm. For other types of multilayer nanotubes intertubes distances for small numbers of j' also there is less under the formula (4) and aspire to this limit at j' > 30.

The analysis of intertubes interactions

Thus, the intertubes distances are determined by geometry of formed tubes and have values, different from interlayer spacings, characteristic for graphite. However the mutual spatial arrangement of enclosed nanotubes is determined yet in two parameters, describing relative shift and rotation of tubes. To investigate energetically favourable values of these parameters it is possible by a method of atom - atom potential [9], finding energy van der Waals of interaction of two enclosed tubes and admitting, that each of atoms of an enclosed tube cooperates with each atom of an external tube with energy:

$$E = -Ar^{-6} + B\exp(-\alpha r), \qquad (7)$$

where r - distance between atoms. The factors of the equation A, B and α, determined on an empirical data are rather exact, set forces of intermolecular interaction in system carbon - carbon [9].

The modeling was carried out for enclosed nanotubes of an identical chirality (k=0 and k=1). It was supposed, that the enclosed tubes have infinite length. As the complete energy van der Waals of interaction of two enclosed nanotubes of the infinite size as is infinite, the account consist in search of specific energy of van der Waals bonds on an unit cell of an external nanotube (fig.2.(b)). The really complete energy of interaction of enclosed nanotubes will be equal to a sum of specific interaction energy of unit cells of one of nanotubes, therefore the minimum of complete energy will be in that case, when specific energy of interaction is minimum. The specific energy of interaction on an unit cell of a nanotube is necessary for finding as a sum of interaction energy of each atom of an elementary cell of an external nanotube with all atoms internal. In this case as turns out necessary to lead summation of infinite number composed. However fast decrease of energy of interaction with increase of distance allows to be limited by accounts of energy of interaction of fragments of tubes of the final size (for k=0 - 7 elementary cells of a nanotube (fig.2.(b)), for k=1 - 11 elementary cells of a nanotube). Really increase of length of an internal nanotube of the more specified above values results in change of specific energy of van der Vaals interaction less than on 0.1 %.

As intertubes distance is constant, dependent only from their diameter, the change specific energy of interaction was investigated depending on their relative shift along an axis of tubes on distances from 0 up to 1 period of compilation C:

$$C_{k=0.5} = \sqrt{3}a \ , \quad C_{k=0} = 3a \qquad (8)$$

with a step C/10, and also depending on a corner relative rotation φ. The corner φ changed from 0 up to 2θ (θ= 360/j" - corner, at which relative totation of two enclosed nanotubes again became equivalent to zero turn) with a step in 2 degrees.

The accounts were carried out for j " from 2 up to 100. Received data represented as power pictures, each point on which allows to determine specific energy of van der Waals interaction of two enclosed nanotubes at appropriate values of mutual shift and

rotation. Two typical power pictures, from 198 received, are resulted on figures 4 and 5.

In result carried out of computer accounts is established, that at relative shifts and rotation of enclosed tubes the energy of interaction changes unsignificantly (< 0.1 %). Are possible practically nonactivation relative displacement of enclosed nanotubes. For nanotubes with a chirality k=1 it is shifts along an axis of a tube (fig.4), and for nanotubes with k=0 - turns (fig.5). Thus, the relative arrangement of enclosed nanotubes arbitrary three-dimensional ordering in arrangement of carbon atoms is away. Apparently, just he causes similarity of X-rays diffraction diagram of multilayer nanotubes to X-rays diffraction diagram of turbostratic carbon, for which presence of an ordered arrangement of carbon atoms in layers and absence about in a mutual arrangement of layers is characteristic. However in case of nanotubes the difference of intertubes distance d_{002} from characteristic for graphite is caused by geometry of layers, braided in tubes, instead of minimum of energy of interlayer interaction as in a caseof soft carbon or carbon fibres [8, 10].

Conclusions

Probably, only five types of multilayer nanotubes, made of tubes of an identical chirality. Chiralities of tubes, appropriate to these types - 0, 0.4, 0.6, 0.8, 1. Intertubes distance d_{002} in such multilayer carbon nanotubes have the values 0.3528, 0.35927, 0.34842, 0.34174, 0.33948 nm accordingly.

In result of geometrical restrictions the intertubes distances in multilayer nanotubes, made of tubes of a different chirality, vary in a wide interval (from 0.3354 up to 0.345 nm) and exceed value of an interlayer spacing, characteristic of graphite.

At relative shifts and rotations of enclosed nanotubes the change of energy of bond is unsignificant, that causes absence three-dimensional ordering in a mutual arrangement of enclosed nanotubes and similarity of structure of multilayer nanotubes to structure of turbostratic carbon.

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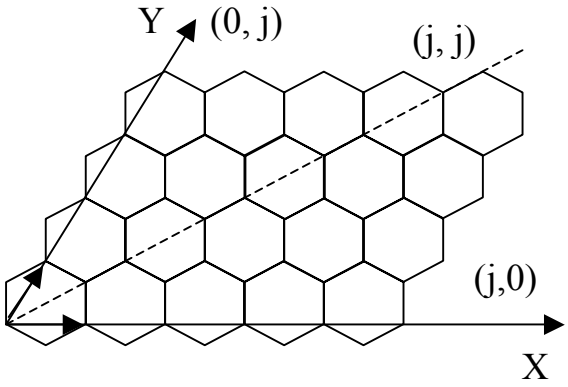
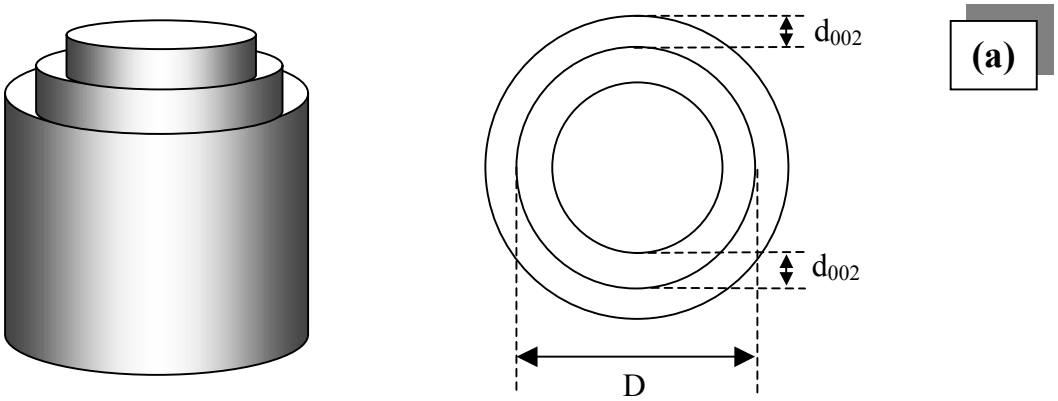


Fig.1. Formation nanotubes of a different chirality at turn off graphite layer in a direction set by indexes (m, n)



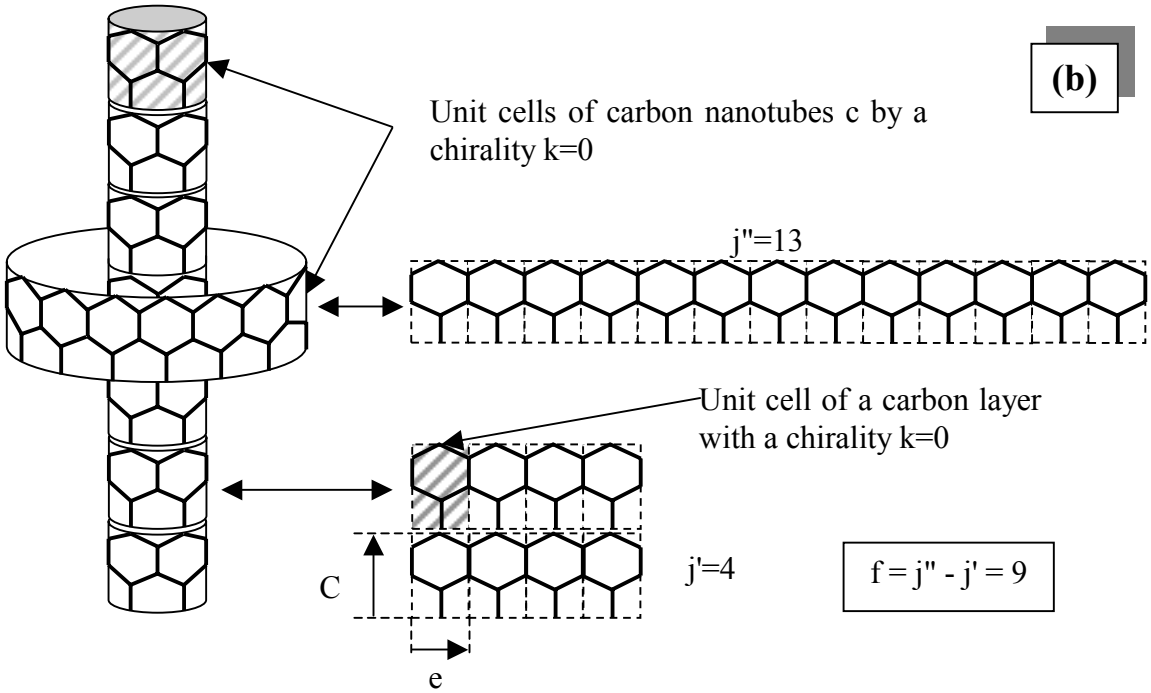


Fig.2. Multilayer carbon nanotubes: (a) the schematic image of three-layers carbon nanotube and its(her) sections; (b) illustration of computer simulation on an example of two-layers carbon nanotube with a chirality k=0 (armchair configuration).

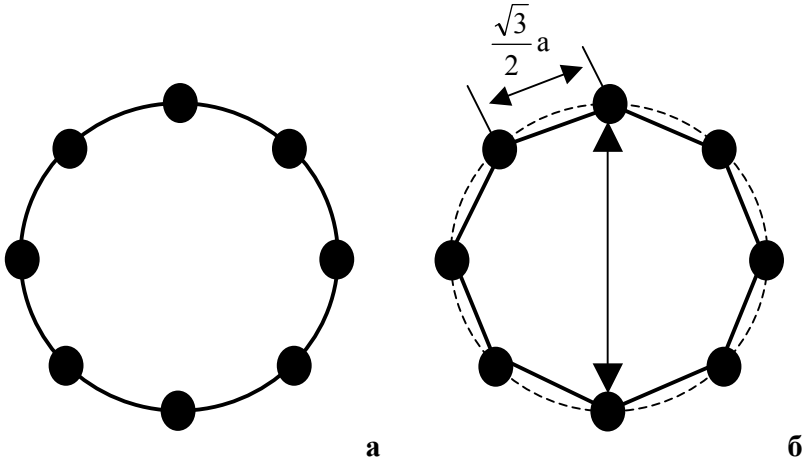


Fig.3. Schematic image of section of a carbon nanotube (4,0): (a) - approximation of curve bonds; (b) - interatomic bonds direct

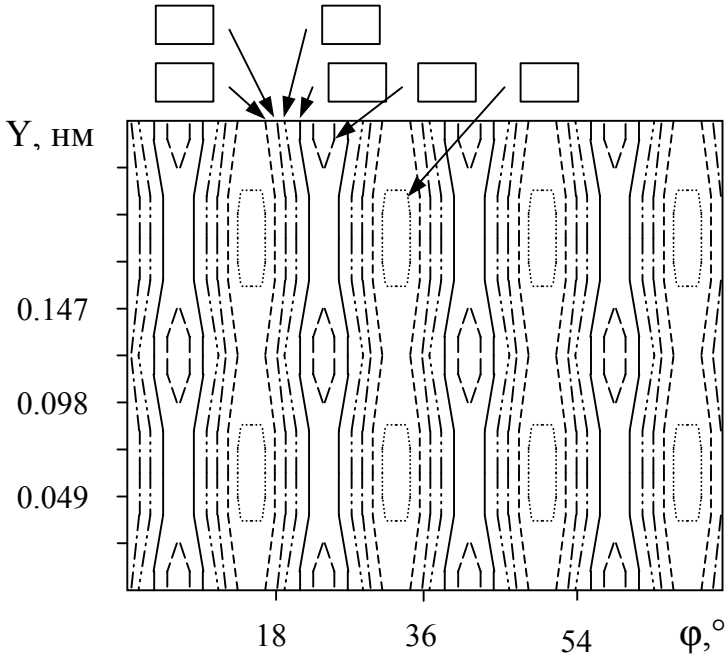


Fig.4. Change of specific energy of bond of two enclosed nanotubes, chirality k=0.5, diameter 0.679 nm and 1.358 nm depending on relative shift along an axis of a tube Y and relative turn. Energy of bond: 1 - -66261 J/mol; 2 - -66257 J/mol; 3 - -66253 J/mol; 4 - -66249 J/mol; 5 - -66245 J/mol; 6 - -66265 J/mol.

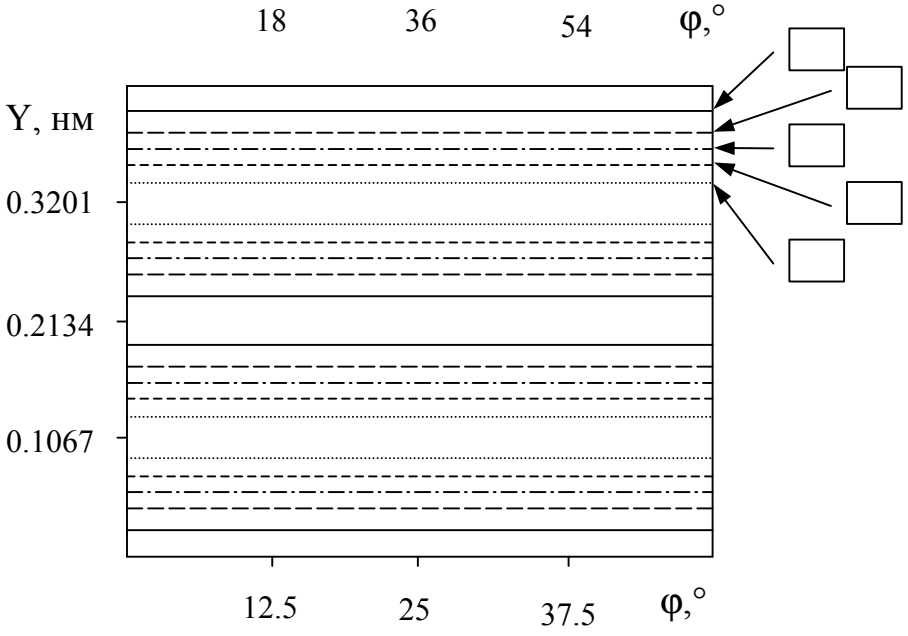


Fig.5. Change of specific energy of bond of two enclosed nanotubes of a chirality k=0, diameter 0.392 nm and 1.0976 nm depending on relative shift along an axis of a tube Y and relative turn. Energy of bond: 1 - -56127 J/mol; 2 - -56161 J/mol; 3 - -56195 J/mol; 4 - -56229 J/mol; 5 - -56263 J/mol

Table 1. Indexes of nanotubes, from which probably formation of multilayer nanotubes of an identical chirality and intertubes distance d_{002} in the appropriate multilayer nanotubes

№	m_0	n_0	$k=n_0/m_0$	d_{002}, nm (f=1)	d_{002}, nm ($f=f_0$)	f_0
1	1	0	0	0.03920	0.35280	9
2	2	1	1	0.06790	0.33948	5
3	5	1	0.4	0.17964	0.35927	2
4	5	2	0.8	0.17087	0.34174	2
5	10	3	0.6	0.34842	0.34842	1

Table 2. Possible structures of multilayer nanotubes, made of nanotubes of a different of a chirality (the first nanotube with the chirality k=0.5)

Nanotube number	m	n	k=n/m	D, нм	d_{002}, нм
1	4	2	1	0.35062	-
2	13	1	0,15384	1.02223	0.33580
3	21	6	0,57142	1.71231	0.34504
4	30	5	0,33334	2.38448	0.33608
5	36	15	0,83334	3.05765	0.33658
6	47	8	0,34042	3.73786	0.34010
7	55	12	0,43636	4.41351	0.33782
8	59	27	0,91526	5.08703	0.33676
9	71	19	0,53522	5.76236	0.33767
10	82	3	0,07318	6.43321	0.33542
11	84	34	0,80952	7.10473	0.33576
12	99	6	0,12122	7.77597	0.33562

Table 3. Range of change of intertubes distance d_{002} in multilayer nanotubes, consisting of 20 layers

The first nanotube				d_{002}(min), nm	d_{002}(max), nm
m	n	k=n/m	D, nm		
5	0	0	0.35062	0.33541	0.33730
10	0	0	0.78401	0.33548	0.34032
15	0	0	1.17602	0.33553	0.34378
20	0	0	1.56803	0.33540	0.33852
4	2	1	0.35062	0.33542	0.34504
8	4	1	0.70124	0.33549	0.34402
10	5	1	0.87655	0.33540	0.34280
12	6	1	1.05186	0.33542	0.33801