Energetics of Multilayered Carbon Tubules

J.-C. Charlier and J.-P. Michenaud

*Laboratoire de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, 1, Place Croix du Sud,
B-1348 Louvain-La-Neuve, Belgium*

(Received 26 October 1992)

We study the structure of nested multilayered systems composed of two infinite carbon tubules via density functional theory. The calculated *intertubule* distance is 3.39 Å, comparable to the recent measurement of 3.4 Å. In such a system, the energy gained by adding a new cylindrical layer around a central one is estimated to be 80% of the graphite dilayer binding energy. Low translation and rotation barriers suggest that carbon tubules of limited length could easily slide into or out of each other and rotate along the cylindrical axis. Comparison with graphite and hyperfullerenes is proposed.

Recently, a new form of graphitic carbon, best described as "needles" or "tubes," has been discovered by high-resolution transmission-electron microscopy [1] on the soot that results after an arc discharge between two carbon rods. It has also been synthesized in gram quantities [2]. A needle comprises multilayered coaxial cylinders (also called "carbon nanotubes" or "bucky tubes") centered on the needle axis. Each microtubule consists of a honeycomb network of carbon atoms (like in a single graphite sheet) rolled up into a cylinder with a diameter of a few Å. The unique structural characteristics of these multilayered microtubules can be connected with graphite and the recently discovered C_{60} solid [3].

Earlier theoretical studies of these small-radii graphene nanotubes focused on their electronic properties, predicting a metallic (more conducting than a planar graphite sheet at room temperature) or semiconducting behavior depending on their radii and the helical arrangement of the carbon hexagons [4-8]. In contrast, the lattice energetics of these structures have been reported later [9,10]. While theoretical studies have been devoted to single-layer graphene microtubule with diameters comparable to that of C_{60}, experimental observations have mainly involved specimens of two or more concentric shells of carbon sheets [1,11,12].

These theoretical papers concern finite or infinite single cylindrical carbon tubules of varying radii including a hypothetical smallest value equal to that of C_{60} ($r = 3.39$ Å). This limiting radius is reached when the elastic energy stored in bending the graphitic strip exceeds the energy recovered from stitching its dangling bonds along the tubule generator [13]. This smallest carbon nanotube which could be capped by two hemispheres of C_{60} has recently been discovered by Ajayan and Iijima [12] and Ugarte [14].

The aim of our study is to investigate the structural influence of a second tubule around a first one, using an *ab initio* theoretical method (self-consistent density-functional theory). The *interlayer* distance of these two tubules, a stacking effect induced by the presence of a surrounding tubule, and barriers to translation and rota-

tion are calculated based on energetics. An analog study has recently been established for hyperfullerenes [15] which are composed, like an imaginative "Russian doll," of a series of I_h-symmetric concentric giant fullerenes.

The smallest buckytube which possesses remarkable properties [8,16] such as metallicity, imposed by the perpendicularity of the tubule axis to the C-C bond [4,5], has been taken as the central cylinder of our bilayered system. This referential tubule, which exhibits the D_{5h} symmetry, is an achiral graphitic tube ($T_{1\perp}$) of infinite length [9], with ten carbon atoms ($n_{1\perp}$) around the circumference (cf. Fig. 1).

The distance and the position of the second tubule ($T_{2\perp}$) relative to the referential one ($T_{1\perp}$) have been optimized using the CORNING code [17] for total energy calculations. Density functional theory [18] (DFT) has been implemented within the local density approximation (LDA) [19] using the conjugate gradient algorithm [20], where diagonalization and self-consistency steps are done simultaneously. This method is an accurate tool for the study of the total energy of solids with no parametrization to experimental data and has been applied to bilayered carbon tubules where the atomic potentials plus core
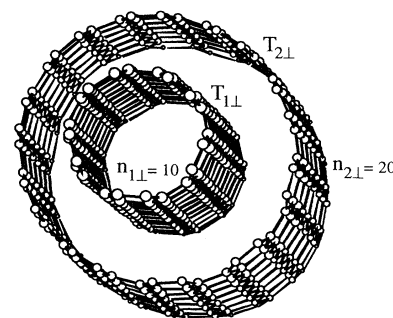

FIG. 1. Schematic representation of concentric bilayered carbon nanotubes. The centered referential tubule $T_{1\perp}$ was generated using a planar ring of ten carbon atoms ($n_{1\perp} = 10$) with the D_{5h} symmetry arranged in five pairs. The surrounding tubule $T_{2\perp}$ is a double-radius carbon cylinder ($n_{2\perp} = 20$).

electrons of carbon have been replaced by extended norm-conserving separable *ab initio* pseudopotentials [21]. A polynomial parametrization [22] of the exchange-correlation functional of Ceperley and Alder [23] has been used. The bilayered system composed by the $T_{1\perp}$ and $T_{2\perp}$ nanotubules has been placed in a periodically repeated supercell extended along directions perpendicular to the cylindrical axis and very thin in the axial one. The periodicity along this latter direction was fixed at $\sqrt{3}d$ where d is the bond length of a single-plane graphite (1.42 Å). Twenty carbons atoms of $T_{1\perp}$ are present in the supercell. A minimum distance of 5 Å was maintained between neighboring systems of tubules to prevent interactions due to the artificial periodic boundary conditions. Plane waves with maximum kinetic energies equal to 60 Ry (± 40000 plane waves) are included in the energetic study. The Brillouin zone integration on special point grids [24] from 1 to 5 special k points (in the direction of the tubule axis) have been studied in order to estimate convergence errors. The numbers of plane waves and special k points have been chosen to reach an accuracy of 5 meV/atom on the value of the total energy.

The study was performed by increasing the number of carbon atoms $(n_{2\perp})$ in the circumference of the surrounding tubule $(T_{2\perp})$ in order to minimize the energy per atom. A carbon hexagon was added at each step of the calculation [$+4$ (carbon atoms)/(unit cell)]. The symmetry of bilayered tubules does not generally require both cylindrical axes to coincide; but in the first series, the two axes were chosen to be nearly corresponding (quasicoaxial tubules). The energetic results for these bilayered systems are presented in Table I(a).

The integer $n_{2\perp}$ was varied from 12 to 22, and the bilayered tubules system with $n_{2\perp}$ equal to 20, has been found energetically the most stable. In that case, the two tubules are separated by an *interlayer* distance of 3.39 Å which is in good agreement with the recent experimental

TABLE I. Energy per atom for two quasicoaxial (a) and noncoaxial (b) tubules, relative to the referential monolayer tube $(n_{1\perp}=10)$ as a function of the *interlayer* distance. The first columns describe the bilayered system: $n_{1\perp}$, $n_{2\perp}$, and R [the corresponding *intertubule* distance (Å)—the smallest distance in case (b)]. The last column describes the energy (in eV/atom) obtained by the theoretical method.

Tubules	$n_{1\perp}$	$n_{2\perp}$	R	Energy
(a)	10	12	0.68	17.0088
	10	14	1.36	2.2187
	10	16	2.03	0.3510
	10	18	2.71	−0.0818
	10	20	3.39	−0.1348
	10	22	4.07	−0.1224
(b)	10	22	3.39	−0.1136

observation of 3.4 Å of Ebbessen and Ajayan [2]. The symmetry of this $(n_{1\perp}=10; n_{2\perp}=20)$ *optimal* carbon system requires concentricity of the two composing tubules (coaxial tubes).

A parallel study using the same theoretical method has been carried out for two isolated graphene sheets of natural graphite. The 3.39 Å value bears strong resemblance to the *interplanar* optimized distance of 3.34 Å obtained for this bilayered graphitic system, but is therefore smaller than the *interlayer* optimized spacing of 3.524 Å calculated for a double-layer hyperfullerene C_{60}/C_{240} [15].

In the bilayered *optimal* system of carbon tubules, the energy gained by adding the surrounding tubule $(n_{2\perp}=20)$ to the central referential one $(n_{1\perp}=10)$ is found to be 80% of the energy obtained, using the same technique, for the addition of an isolated graphitic plane to a single graphene sheet.

Such energetic gain also appears in spherical multishell fullerenes, where enhanced stability is observed for assemblies of fullerenes in an onionlike structure [25]. This stabilization due to the concentric stacking of double-layered C_{60}/C_{240} (14 meV/atom) and triple-layered $C_{60}/C_{240}/C_{540}$ (20 meV/atom) hyperfullerenes [15], where radii of these series increase by ± 3.5 Å, is therefore significantly smaller than our energetic gain of 48 meV/atom for the $(n_{1\perp}=10; n_{2\perp}=20)$ coaxial tubules.

Although the graphitic binding energy is weak [26], the multilayering phenomenon appears in nature for graphite as well as for carbon tubules [1,2] and onionlike hyperfullerenes [25].

The bilayered carbon cylinders are already more stable in comparison with the single tubule when the distance between the two tubules reaches a sufficient value $(n_{2\perp} \geq 18)$ [cf. Table I(a)] although theoretical calculations predict that a tubular structure is already energetically more favorable than a flat strip of carbon hexagons whose width is equal to the circumference [13].

Having determined a minimal energy structure in a series of tubules with varying diameters where the two cylindrical axes were nearly corresponding (quasicoaxial tubules), we address the question of tubules where the axis of the inner tubule does not coincide at all with that of the outer tubule (noncoaxial tubules). In the $(n_{1\perp}=10; n_{2\perp}=22)$ case, the referential tubule has been placed at a minimal distance of 3.39 Å away from the inside surface of the surrounding tubule, and the energy per atom has been calculated. As it can be seen in Table I(b), such a situation is less stable for the same carbon system than the previous one [Table I(a)] where the two tubules were nearly coaxial.

We now consider the diameter of the two $(n_{1\perp}=10; n_{2\perp}=20)$ coaxial tubules as fixed, and wonder about the remaining degrees of freedom needed to determine the geometry. In planar graphite, it is well-known that the layers can be arranged according to the *ABAB* stacking (natural graphite), *ABC* (rhombohedral graphite), or

AAA (simple hexagonal graphite)... [27], depending on the relative positions of the atoms in one layer with respect to the neighboring layers. Here, in order to generate different stacking, we consider translations and rotations of the outer tubule with respect to the inner one. A translation of **C**/2 (where **C** is the unit cell length along the tubule axis) has to be simultaneously followed by a $2\pi/60$ rotation, while keeping coaxial feature, to reach a different stacking structure as shown in Fig. 2. The stacking presented in (c) seems to be more *symmetric* than the other two equivalent ones (a) and (b). These distinctions arise exclusively for the special relationship between the number of hexagons in the circumference of each tubule such as the ratio of two to one (20:10) considered here for the optimal system.

Our first-principles results lead to an energy difference of ± 0.015 meV/atom between the two different stackings, in favor of the most symmetric one: (c). This value is smaller than our *absolute* accuracy but is likely mean-
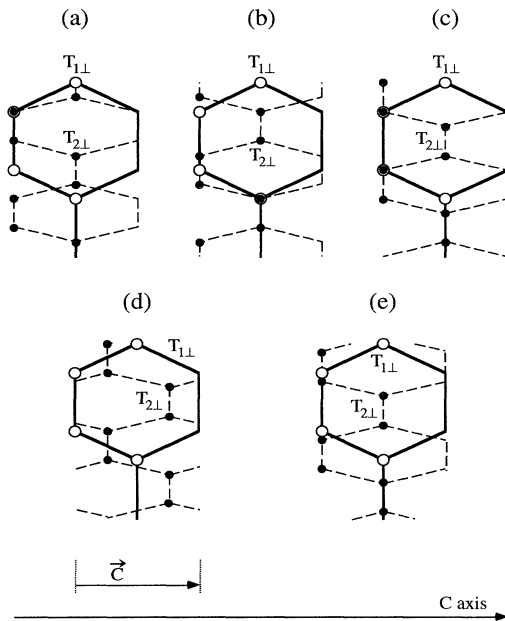
ingful when calculating the *relative* energy difference between two bilayered structures.

Estimates of translation and rotation barriers, which are respectively 0.23 and 0.52 meV/atom (in *absolute* value), have been calculated using the two structures (d) and (e) of Fig. 2. (d) corresponds to a **C**/4 translation while (e) is a $2\pi/120$ rotation of the $T_{2\perp}$ tubule; both starting from the most symmetric structure (c). In agreement with the *ab initio* barrier height for the transition path between the two stakings, the axial position of the carbon tubules relative to each other seems to intervene weakly in the structural energy. This result points out the possibility of free rotations and translations along the cylindrical axis for finite tubules. Such movements must be almost unhindered at room temperature. Identical motions for the inner shells of hyperfullerenes have been proposed by Yoshida and Osawa [15]. Their calculation reveals that a very low barrier to rotation (0.16 meV/atom) must be gone through in the C_{60}/C_{240} bilayered hyperfullerenes. However, only the core C_{60} can undergo concentric rotation because of its spherical shape while it is strongly hampered for larger shells because of their polygonal shape due to the presence of pentagons. This polygonal behavior does not appear in *purely cylindrical* (no pentagon) multilayered carbon tubules and does not affect the rotation of many independent finite tubes.

Although the translation is more relevant for cylindrical systems such as tubules than for spherical systems like hyperfullerenes, the energy increment due to a core shell displacement of 0.4 Å in C_{60}/C_{240} is less than 1.5 meV/atom, which suggests that an internal layer can oscillate over this distance about its equilibrium position rather smoothly [15]. This translation barrier is therefore significantly greater than our calculated result for the $(n_{1\perp}=10; n_{2\perp}=20)$ tubules and, again, points out the easy possibility of oscillating and sliding for multilayered tubules system.

In analogy with hyperfullerenes and solid C_{60} where buckyball molecules are freely rotating above a transition temperature (258 K) [28], we propose that graphitic microtubules of *limited length*, stabilized by their multilayered structure, could be considered as independent rotating and translating carbon cylinders which can easily slide into or out of each other. The finite size of the carbon tubules is taken into account in order to obtain a finite moment of inertia due to the rotation. Although carbon tubules seem to be often capped at their end and can also be bent [29], the translation properties could be relevant for the recently observed *open-end* nanotubes [30].

In conclusion, we found that a surrounding tubule, at a 3.39 Å distance from a central one, stabilizes the system by an energy of the same order as the one in graphite bilayering. Rotations and translations between finite carbon tubules have been suggested, on the basis of the first-principles results obtained for the stacking study of

FIG. 2. Relative positions of the referential $T_{1\perp}$ and the surrounding $T_{2\perp}$ tubules in the $n_{1\perp}=10$, $n_{2\perp}=20$ case obtained by projecting the two developed cylinders on a plane. The $T_{2\perp}$ carbon strip had previously been compressed (by a factor of 2) to reach a width equal to the circumference of $T_{1\perp}$. (a) Atomic positions of the two carbon tubules (white dots bonded by solid line: $T_{1\perp}$; black dots bonded by dashed line: $T_{2\perp}$), (b) equivalent to (a) structure after a **C**/2 translation of $T_{2\perp}$, and (c) new structure after a combination of a **C**/2 translation and a $2\pi/60$ rotation applied to $T_{2\perp}$. The (d) and (e) structures which correspond respectively to a **C**/4 translation and a $2\pi/120$ rotation of the $T_{2\perp}$ tubule starting from the most symmetric structure (c) are the middle points of two transition paths needed to calculate the respective barriers to translation and rotation. The tubule axial direction (*C* axis) is presented as well as the translation vector **C**.

these graphitic cylinders and compared to the shell mobility in hyperfullerenes. Finally, these multilayered carbon tubules may find an important industrial application in lubricants considering their cylindrical symmetry, rotating and translating properties, and resistance to compression in the direction perpendicular to the cylinder axis. These graphitic multilayered cylinders are also possible substitutes for carbon fibers currently used for their stiffness and are also a new candidate for a one-dimensional conductor [31].

[1] S. Iijima, Nature (London) 354, 56 (1991).

[2] T. W. Ebbessen and P. M. Ajayan, Nature (London) 358, 220 (1992).

[3] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) 318, 162 (1986); W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) 347, 354 (1990).

[4] J. W. Mintmire, B. I. Dunlap, and C. T. White, Phys. Rev. Lett. 68, 631 (1992).

[5] N. Hamada, S. Sawada, and A. Oshiyama, Phys. Rev. Lett. 68, 1579 (1992).

[6] K. Tanaka, K. Okahara, M. Okada, and T. Yamabe, Chem. Phys. Lett. 191, 469 (1992).

[7] M. S. Dresselhaus, G. Dresselhaus, and R. Saito, Phys. Rev. B 45, 6234 (1992).

[8] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, Mater. Res. Soc. Symp. Proc. 247, 333 (1992).

[9] G. B. Adams, O. F. Sankey, J. B. Page, M. O'Keeffe, and D. A. Drabold, Science 256, 1792 (1992).

[10] D. H. Robertson, D. W. Brenner, and J. W. Mintmire, Phys. Rev. B 45, 12592 (1992).

[11] S. Iijima, T. Ichiashi, and Y. Ando, Nature (London) 356, 776 (1992).

[12] P. M. Ajayan and S. Iijima, Nature (London) 358, 23 (1992).

[13] A. A. Lucas, Ph. Lambin, and R. E. Smalley, J. Phys. Chem. Soc. (to be published).

[14] D. Ugarte, Chem. Phys. Lett. (to be published).

[15] M. Yoshida and E. Osawa, Fullerene Science Technology 1, 55 (1993).

[16] K. Harigaya, Phys. Rev. B 45, 12071 (1992).

[17] D. C. Allan, Corning Inc., Corning, NY.

[18] P. Hohenberg and W. Kohn, Phys. Rev. B 136, 864 (1964); W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

[19] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989); W. E. Pickett, Comput. Phys. Rep. 3, 115 (1989).

[20] M. P. Teter, M. C. Payne, and D. C. Allan, Phys. Rev. B 40, 12255 (1989).

[21] M. P. Teter (unpublished).

[22] M. P. Teter (unpublished).

[23] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1981).

[24] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976); R. A. Evarestov and V. P. Smirnov, Phys. Status Solidi (b) 119, 9 (1983).

[25] D. Ugarte, Nature (London) 359, 707 (1992); D. Tomanek, W. Zhong, and E. Krastev (unpublished).

[26] S. B. Trickey, F. Müller-Plathe, G. H. F. Diercksen, and J. C. Boettger, Phys. Rev. B 45, 4460 (1992); L. A. Girifalco and R. A. Lad, J. Chem. Phys. 25, 693 (1956).

[27] See, for example, J.-C. Charlier, X. Gonze, and J.-P. Michenaud, Phys. Rev. B 43, 4579 (1991); J.-C. Charlier, J.-P. Michenaud, X. Gonze, and J.-P. Vigneron, Phys. Rev. B 44, 13237 (1991); J.-C. Charlier, J.-P. Michenaud, and X. Gonze, Phys. Rev. B 46, 4531 (1992); J.-C. Charlier, X. Gonze, and J.-P. Michenaud (to be published).

[28] A. Dworkin, H. Szwarc, S. Leach, J. P. Hare, T. J. Dennis, H. W. Kroto, R. Taylor, and D. R. M. Walton, C.R. Acad. Sci. Paris Ser. II, 312, 979 (1991); E. Grivei, M. Cassart, J.-P. Issi, L. Langer, B. Nysten, J.-P. Michenaud, C. Fabre, and A. Rassat (to be published).

[29] B. I. Dunlap, Phys. Rev. B 46, 1993 (1992).

[30] S. Iijima, P. M. Ajayan, and T. Ichihashi, Phys. Rev. Lett. 69, 3100 (1992).

[31] M. S. Dresselhaus, Nature (London) 358, 196 (1992); K. Tanaka, K. Okahara, M. Okada, and T. Yamabe, Chem. Phys. Lett. 191, 469 (1992).