

Ordered phases of fullerene molecules formed inside carbon nanotubes

Miroslav Hodak* and L. A. Girifalco

Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 12 December 2002; published 28 February 2003)

A simulated annealing method was used to study the minimum energy configurations of C_{60} molecules inside carbon nanotubes. Simulations for over 50 nanotubes with radii from 6.27 Å to 13.57 Å showed that ten different phases exist in this size range. Both chiral and achiral phases were found. The achiral phases consist of layers of stacked polygons rotated by an angle of $360/(2k)$ relative to each other, where k is an integer. The chiral phases consist of multistranded helices. Tubes of larger radii, each of the (n,n) type, were also studied; these also exhibited helical and polygonal-layered phases. For tubes larger than (24,24), C_{60} molecules can be at the tube center as well as at the wall. The effects of multiwalled versus single-walled tubes were shown to be small. The phase structure is very sensitive to the tube radius and is different from that for the packing of hard spheres.

DOI: 10.1103/PhysRevB.67.075419

PACS number(s): 61.48.+c, 61.43.Bn

The filling of single-walled carbon nanotubes with molecules has received increasing attention since such filling was first observed.^{1–15} The cylindrical constraint produces structures in the tube that differ substantially from those in the bulk. Iodine, for example, forms helical chains inside single-walled carbon nanotubes (SWNT's),⁷ $AgCl_{1-x}I_x$ forms metastable one-dimensional wurzite crystals,¹⁴ and one-dimensional potassium iodide forms crystals with lattice spacings different than in the bulk.⁴ Also, a molecular dynamic simulation of water inside nanotubes showed the existence of a variety of phases that do not exist in the bulk ice.¹⁶

In this paper, we present the first systematic study of the phases of molecules of any kind inside nanotubes as a function of nanotube radius. Previous theoretical investigations in this area have only considered a few nanotube types chosen *a priori*; here we systematically investigate all nanotubes with radii less than that of the (20,20) nanotube. Our goal is not only to identify all phases, but also to make comparisons with the packing of hard spheres into a cylinder to investigate differences between the structures that maximize packing efficiency and those that give minimum energy.

To identify minimum energy configurations of C_{60} molecules inside carbon nanotubes, we used the simulated annealing (SA) method.¹⁷ Two potential energy functions are required for this calculation: that for the interaction of two C_{60} molecules, and that for the interaction of a C_{60} molecule with the wall of an infinitely long tube. Both of these are van der Waals interactions and the calculation is greatly simplified by using the surface-continuum approximation, which has been very successful in many other studies.^{18–25} The interaction between two C_{60} molecules is given by the Girifalco potential.²⁶ The potential function for the interaction between a C_{60} molecule and a tube cannot be obtained analytically. However, the results of numerical calculation based on Eq. (10) in Ref. 18 are well represented by the equation

$$V(x) = A + B \left(\frac{1}{(x-d)^3} - \frac{1}{(x+d)^3} \right) + C \left(\frac{1}{(x-d)^9} - \frac{1}{(x+d)^9} \right), \quad (1)$$

where x is the distance of the molecule from the tube axis, A , B , and C are constants determined from a least squares fit to the numerical calculation, and d is the difference between the radii of the nanotube and the C_{60} molecule. The values of these constants for several nanotubes are shown in Table I. For tube radii less than 7.3 Å, the potential has a minimum at the center of the tube, while for larger radii the minimum is shifted towards the wall.

The number of C_{60} molecules used in the simulations varied from 20 for narrow tubes up to over 100 for wide tubes. In the simulations, the molecules were confined to a nanotube with given radius and length. The nanotube length was taken to be 20–30 % greater than the length occupied by the same number of C_{60} molecules in the lowest energy structure found for the C_{60} molecules inside a nanotube with a smaller radius. Two types of starting configurations were used: random and the structure obtained from the simulation for the smaller nanotube radius. The starting temperature was chosen to be 1000–1500 K; our previous calculations show that at these temperatures C_{60} molecules are quite mobile inside nanotubes.^{27,28} To ensure that the obtained phases are independent of boundary conditions we used both periodic and closed end boundary conditions. This means that for each nanotube radius at least four simulations were run. Typically, all these simulations yielded the same structure and energy for a given nanotube radius. In all simulations we performed, no external pressure was applied. All together, the simulations were run for over 50 tubes in the radius range of 6.27 Å to 13.57 Å.

The resulting phases and their properties are listed in Table II and displayed in Figs. 1 and 2. For the narrowest tubes that can accommodate C_{60} molecules (radius 6.27 Å,

TABLE I. Constants for nanotube- C_{60} molecule interactions.

Nanotube	Radius (Å)	A (eV)	B (eV Å ³)	C (eV Å ⁹)	d (Å)
(10,10)	6.79	-2.79	20.16	-13972.2	3.24
(15,15)	10.18	-0.20	41.76	-9842.2	6.63
(20,20)	13.57	-0.05	38.65	-8743.5	10.02
(25,25)	16.96	-0.02	35.79	-7905.6	13.41

TABLE II. Phase behavior of C_{60} molecules inside nanotubes for nanotubes with radius $r < 13.57$ Å.

Radius (Å)	Phase	Chirality	Can be reduced to single helix?
6.27–7.25	linear chain	achiral	
7.25–10.8	zigzag	achiral	N/A
10.8–11.15	double helix	chiral	yes
11.15–11.4	layers of 2 molecules	achiral	N/A
11.4–12.05	triple helix	chiral	yes
12.05–12.45	layers of 3 molecules	achiral	N/A
12.45–13.0	layers of 2 molecules	achiral	N/A
13.0–13.3	4-stranded helix	chiral	yes
13.3–13.5	4-stranded helix	chiral	no
13.5–14.05	layers of 4 molecules	achiral	N/A

Ref. 19), the molecules form a linear chain and they adopt a zigzag structure when the radius is increased to 7.25 Å. This remains stable until the radius is increased to 10.8 Å, at which point a double-helix structure appears. The double helix can be algebraically described as a single helix.

For a radius of 11.15 Å, the structure consists of two-molecule layers. Further increases in radius show that chiral and achiral structures alternate except for the transition at 12.45 Å. The reason for this exception is that at the tube radius of 12.45 Å it is energetically favorable to form an achiral structure consisting of two-molecule layers. This is similar to the phase observed for radii 11.15–11.4 Å, with the interlayer distance decreased to 5 Å, which gives 10 Å for the distance between two molecules in next-adjacent layers and each C_{60} molecule has six nearest neighbors, just as

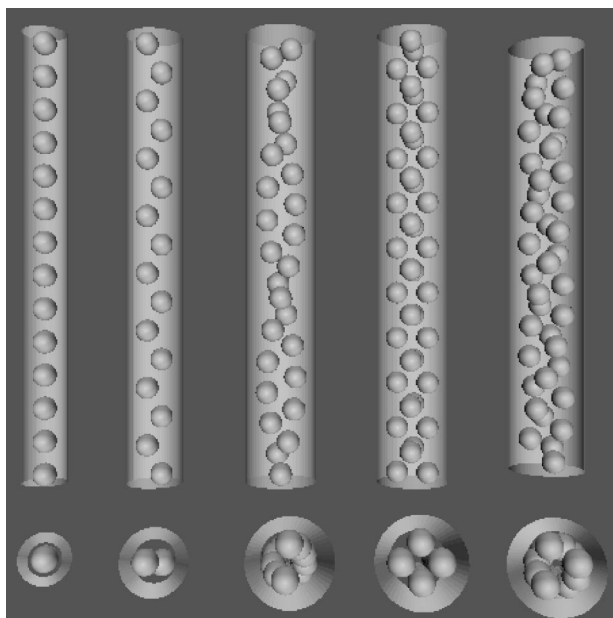


FIG. 1. Phases of C_{60} molecules: the single chain phase [(10,10) tube], the zigzag phase [(13,13) tube], double-helix phase (tube with radius 10.96 Å), the phase of two-molecule layers (tube with radius 11.33 Å), and triple helix [(17,17) tube], from left to right.

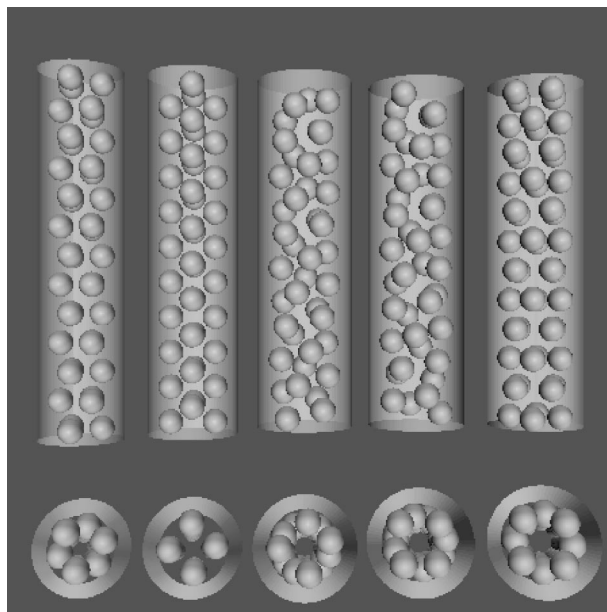


FIG. 2. Phases of C_{60} molecules: the phase of three-molecule layers, the phase of two-molecule layers, two chiral phases of 4 strands and an achiral phase of 4 molecules. For nanotubes with radii 12.21 Å, 12.89 Å, 13.23 Å, 13.33 Å, and 13.57 Å, from left to right.

in the case of the achiral triplet configuration. This makes a large contribution to the stability of the achiral layer structure.

When the radius is increased to 13.0 Å, a four-strand chiral phase forms that can be reduced to a single helix just as is the case for the double and triple helices formed at lower tube radii. But when the radius is increased to 13.3 Å, a new four-strand helical structure forms that is not reducible to a single helix. Figure 2 shows that the two four-strand phases look very much alike. But the two structures differ in that for the one, which cannot be reduced to a single helix, the molecules are arranged in groups of four and the nearest neighbor distances within a group are different from the nearest neighbor distances for molecules between groups. Such phases have been observed for cylindrical packing of hard balls.²⁹ Our results show that small changes in tube radii can result in major differences in phase structure.

Calculations for tubes with radii larger than 13.5 Å were restricted to (n,n) tubes with $n = 20$ to 29. For tubes smaller than $n = 24$, all C_{60} molecules are at the same distance from the tube axis, forming a cylindrical shell on the inside wall. For (24,24) and larger tubes, the shell is large enough to accommodate molecules at its center. These molecules form an independent structure inside the fullerene shell. The structures formed by internal molecules are similar to those for C_{60} molecules inside tubes with small radii (linear chain to double helix), but these structures show some deviations from ideal molecular positions. This is due to the potential from the fullerene shell, which is not symmetric in either radial or axial directions. Also, end effects due to the finite size of the shell affect the arrangement of internal molecules.

TABLE III. Phases of C_{60} molecules inside nanotubes.

Type	Radius (Å)	Structure of C_{60} shell	Internal layer
(21,21)	14.25	5-stranded helix	
(22,22)	14.93	pentagonal layers	
(23,23)	15.61	6-stranded helix	
(24,24)	16.28	6-stranded helix	linear chain
(25,25)	16.96	hexagonal layers	linear chain
(26,26)	17.64	7-stranded helix	single helix
(27,27)	18.31	heptagonal layer	single helix
(28,28)	19.00	8-stranded helix	double helix
(29,29)	19.68	octagonal layers	double helix

The structures and their properties for (n,n) tubes with $n = 21$ to 29 are listed in Table III and some of them are shown in Fig. 3.

For large tubes, it is important to consider the effect of multiwall nanotubes. It can be expected that adding nanotube walls stabilizes the circular cross section³⁰ and makes the nanotube more resistant to deformations due to internal fullerene molecules or interactions with other nanotubes in a rope.³¹ Our calculations of the energetics of multiwalled systems show that adding concentric nanotubes increases the binding energy of C_{60} to the nanotube wall by about 15%, while the position of the energy minimum changes only by 0.05 Å for tubes larger than (20,20). Also, the second tube is the most important. Increasing the number of walls beyond two has essentially no effect on the nanotube- C_{60} potential. This is shown in Fig. 4 for a C_{60} molecule inside a multiwalled nanotube with the smallest wall having a diameter of a (26,26) nanotube. Simulations for multiwall tubes larger than (20,20) show that the cylindrical shell of molecules on the inside tube wall is affected only by a small increase in its radius, and that a molecule at the tube center is favored en-

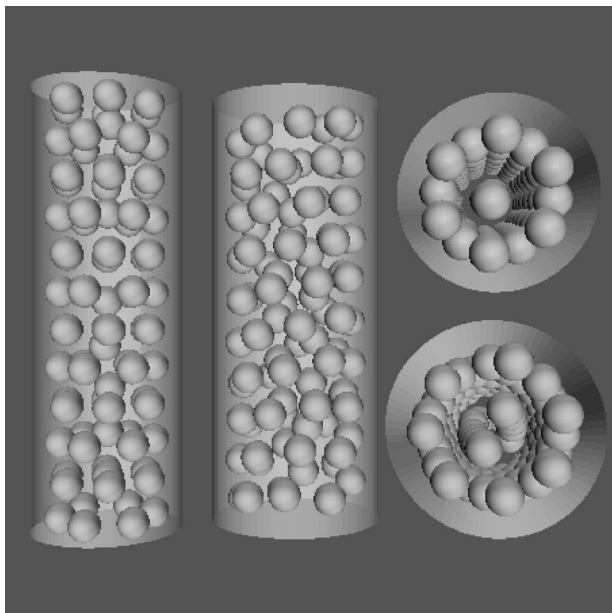


FIG. 3. Phases of C_{60} molecules inside (25,25) (left and top right) and (28,28) (middle and bottom right) nanotubes.

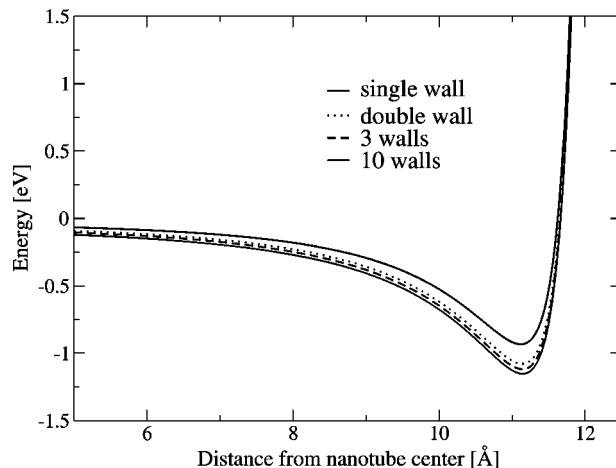


FIG. 4. Potential between C_{60} molecule and a multiwalled nanotube as a function of distance from nanotube axis for 1- (single-wall nanotube), 2-, 3-, and 10-walled nanotubes. The smallest nanotube is (26,26).

ergetically (relative to a molecule at the inside wall) only for (24,24) and (25,25) tubes. In all cases changes to the fullerene shell were limited to a small change of its radius.

Our study sheds light on three important effects: the breaking of chiral symmetry, the packing of hard spheres in a cylinder, and the formation of lattices on a cylindrical surface. Our simulations demonstrate that the existence of chirality depends on the value of the tube radius.

The packing of hard spheres into cylinders has been studied by Pickett *et al.*²⁹ Their results (for spheres with diameters equal to the separation between two C_{60} molecules at the minimum of the interaction) is a first order approximation to the study presented here. For a range of tube radii up to that at which a three-molecule layer appears, Pickett *et al.* identified nine phases. (Note that our definition of phase differs somewhat from theirs. They labeled only six structures in this range as phases, but also identified achiral configurations of singlets, doublets, and triplets, which they did not count as separate phases.) Our simulations found only six phases in this range. The origin of this difference is that, for hard spheres, achiral states can exist only for single values of the tube radius, while we find them stable over a range of radii. Also, Pickett *et al.* find three chiral phases that cannot be described as a single helix, while we find only one.

The origin of the differences of the SA results from hard sphere packing is that the molecules need not maintain a fixed distance between them so they can shift positions as needed to minimize the energy. The hard sphere model can be used to derive a simple rule for tube radii at which achiral phases are expected to form. For a sphere of radius R , n spheres can be arranged on the surface of a cylinder if its radius r is given by

$$r = R \left(1 + \sqrt{\frac{2}{1 - \cos(2\pi/n)}} \right). \quad (2)$$

For C_{60} molecules in nanotubes, the sphere radius is just half the distance between molecules at their potential energy

minimum. Also, to get the correct nanotube radius, one has to add 1.49 Å to the geometric radius of the tube because of the van der Waals repulsion between the molecule and the tube. The formula then gives tube radii of 11.5 Å, 12.3 Å, and 13.6 Å for achiral phases with layers of 2, 3, and 4 molecules, respectively. Comparison with the values in Table II shows that these values are correct for the 3- and 4-molecule layers, and is only a slight overestimate for the 2-molecule layer.

The relation of the lattice on a cylinder to that on a plane is straightforward since a cylinder can be formed by rolling up a plane. Indeed, unrolling the structures from the SA results gives close packed two-dimensional configurations, as expected from pairwise potentials. Actually, small deviations from close packing were found in several cases. The reason for this is that wrapping a plane of close packed spheres into a cylinder can only be done for a discrete set of radii, whereas there is no restriction on tube radius in our calculation.

Interestingly, packing hard spheres on cylindrical surfaces has its manifestation in several biological effects such as

growing leaves of plants or the structure of some bacteria and has been extensively studied.^{32,33}

In conclusion, simulations of C₆₀ molecules inside nanotubes show how the structure changes as a function of tube radius. Both helical structures and layered structures were found. A comparison to the case of packing of hard spheres shows substantial differences between the two cases. Because of the high binding energy of molecules to the tube wall, no configurations resembling a three-dimensional close packed bulk phase was found. In this study, we focused on the structural properties only. But as one can imagine, other properties of fullerene-filled nanotubes also change with changing fullerene configuration. For example, the phonon modes will be different for the linear and zigzag configurations. As a result, thermal conductivity will be different in the two configurations. Thus it should be possible to tune properties of filled nanotube materials by changing the radii of the host nanotubes.

We gratefully appreciate support for M.H. through the National Science Foundation Grant No. 98-02560.

*Electronic address: hodak@seas.upenn.edu

- ¹J. Sloan, J. Hammer, M. Zwiefka-Sibley, and M. L. H. Green, *Chem. Commun. (Cambridge)* **3**, 347 (1998).
- ²B. W. Smith, M. Monthieux, and D. E. Luzzi, *Nature (London)* **396**, 323 (1998).
- ³J. Sloan, D. M. Wright, H. G. Woo, S. Bailey, G. Brown, A. P. E. York, K. S. Coleman, J. L. Hutchinson, and M. L. H. Green, *Chem. Commun. (Cambridge)* **8**, 699 (1999).
- ⁴R. R. Meyer, J. Sloan, R. E. Dunin-Borkowski, A. I. Kirkland, M. C. Novotny, S. R. Bailey, J. L. Hutchinson, and M. L. H. Green, *Science* **289**, 1324 (2000).
- ⁵J. Sloan *et al.*, *Chem. Phys. Lett.* **329**, 61 (2000).
- ⁶C. G. Xu *et al.*, *Chem. Commun. (Cambridge)* **24**, 2427 (2000).
- ⁷X. Fan, E. C. Dickey, P. C. Ecklund, K. A. Williams, L. Grigorian, R. Buczko, S. T. Pantelides, and S. J. Pennycook, *Phys. Rev. Lett.* **84**, 4621 (2000).
- ⁸A. Kuznetsova, J. T. Yates, J. Liu, and R. E. Smalley, *J. Chem. Phys.* **112**, 9590 (2000).
- ⁹Z. L. Zhang, B. Li, Z. J. Shi, Z. N. Gu, Z. Q. Xue, and L. M. Peng, *J. Mater. Res.* **15**, 2658 (2000).
- ¹⁰J. Mittal, M. Monthieux, H. Allouche, and O. Stephan, *Chem. Phys. Lett.* **339**, 311 (2001).
- ¹¹B. W. Smith, D. E. Luzzi, and Y. Achiba, *Chem. Phys. Lett.* **331**, 137 (2000).
- ¹²K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara, and S. Iijima, *Phys. Rev. Lett.* **85**, 5384 (2000).
- ¹³K. Suenaga, T. Tence, C. Mory, C. C. Colliex, H. Kato, T. Okazaki, H. Shinohara, K. Hirahara, S. Bandow, and S. Iijima, *Science* **290**, 2280 (2000).
- ¹⁴J. Sloan, M. Terrones, S. Nufer, S. Friedrichs, S. R. Bailey, H. G. Woo, M. Ruhle, J. L. Hutchinson, and M. L. H. Green, *J. Am. Chem. Soc.* **124**, 2116 (2002).
- ¹⁵J. Sloan, S. J. Grosvenor, S. Friedrichs, A. I. Kirkland, J. L. Hutchinson, and M. L. H. Green, *Angew. Chem. Int. Ed. Engl.* **41**, 1156 (2002).
- ¹⁶K. Koga, G. T. Gao, H. Tanaka, and X. C. Zeng, *Nature (London)* **412**, 802 (2001).
- ¹⁷S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, *Science* **220**, 671 (1983).
- ¹⁸L. A. Girifalco, M. Hodak, and R. S. Lee, *Phys. Rev. B* **62**, 13 104 (2000).
- ¹⁹M. Hodak and L. A. Girifalco, *Chem. Phys. Lett.* **350**, 405 (2001).
- ²⁰M. C. Abramo, C. Caccamo, D. Costa, and G. Pellicane, *Europhys. Lett.* **54**, 468 (2001).
- ²¹V. I. Zubov and C. G. Rodrigues, *Phys. Status Solidi B* **222**, 471 (2000).
- ²²M. M. G. Alemany, C. Rey, O. Dieguez, and L. J. Gallego, *J. Chem. Phys.* **112**, 10 711 (2000).
- ²³L. Henrard, E. Hernandez, P. Bernier, and A. Rubio, *Phys. Rev. B* **60**, R8521 (1999).
- ²⁴I. O. S. Tamaki, N. Ide, and K. Kojima, *Jpn. J. Appl. Phys., Part 1* **37**, 6115 (1998).
- ²⁵J. Song and R. L. Cappelletti, *Phys. Rev. B* **50**, 14 678 (1994).
- ²⁶L. A. Girifalco, *J. Phys. Chem.* **96**, 858 (1992).
- ²⁷L. A. Girifalco and M. Hodak, *App. Phys. A* (to be published).
- ²⁸M. Hodak and L. A. Girifalco (unpublished).
- ²⁹G. T. Pickett, M. Gross, and H. Okuyama, *Phys. Rev. Lett.* **85**, 3652 (2000).
- ³⁰T. Hertel, R. E. Walkup, and P. Avouris, *Phys. Rev. B* **58**, 13 870 (1998).
- ³¹J. Tersoff and R. S. Ruoff, *Phys. Rev. Lett.* **73**, 676 (1994).
- ³²R. O. Erickson, *Science* **181**, 705 (1973).
- ³³L. S. Levitov, *Pis'ma Zh. Eksp. Teor. Fiz.* **54**, 542 (1991) [*JETP Lett.* **54**, 546 (1991)].