Novel Polygonized Single-Wall Carbon Nanotube Bundles

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We have synthesized novel crystalline ropes of "polygonized" single-wall carbon nanotubes (SWCNTs). The tubes exhibit rounded-hexagonal cross sections in contrast to the earlier observations of nearly circular tubes. To investigate the structural characteristics of the lattice of SWCNTs we have performed extensive molecular-dynamics simulations. We find several metastable structures of the lattice characterized by different tube cross sections, hexagonal, rounded-hexagonal, and circular, and increasing cell volume. The competition between different tube shapes as a function of tube diameter is analyzed and compared to experiments.

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A thorough understanding of the properties of single-wall carbon nanotubes [1,2] (SWCNTs) requires the knowledge of their geometrical structure. In most studies, cylindrical tubes with circular cross sections are assumed with the implicit justification that this is the shape which minimizes the strain energy of free, isolated tubes. However, it has been shown that the tubes may deform elastically, without destroying the honeycomb arrangement of the carbon atoms on the tube surface, when they interact either with the substrate in which they are deposited [3] or with other tubes [4,5] (crossing tubes, bundles, etc.). In this Letter we present compelling experimental and theoretical evidence that tubes in a bundle may deform from the ideal circular cross section of isolated tubes to a polygonized, hexagonal cross section.

The properties of the deformed tubes may change substantially with respect to the properties of the corresponding circular tubes. Assuming a circular cross section of the tubes in bundles would then be a poor approximation in some cases and could even lead to wrong predictions. For instance, the metallic or semiconducting character of the tubes is predicted to change (band gap modification) after radial deformations giving rise to tubes with elliptical [6] or polygonized cross sections [7]. Tubes with different cross sections exhibit different σ^*-π^* hybridization and consequently different electronic properties, namely, a different metal/insulator character [8]. One would also expect changes in the phonon spectrum of deformed tubes [9] which would have relevant implications in the interpretation of the Raman [10,11] and infrared spectra of the tubes.

Single-wall carbon nanotubes may (and in most cases they do) self-organize into crystalline bundles [12,13], i.e., a set of a few to a few hundred aligned tubes arranged in a two-dimensional triangular lattice in the plane perpendicular to their common axes. Tubes in a bundle interact through van der Waals–type attractive forces similar to the ones which hold together the graphene layers in graphite. The intertube interaction could prompt elastic structural changes in the bundled tubes, e.g., faceting of the tubes. Some indirect evidences of faceting have been observed in multiwall carbon nanotubes (MWCNTs) [4]. Here we present a direct experimental observation of faceting in bundles of SWCNTs. It is, then, of the greatest interest to elucidate the structural features of the nanotubes under interaction conditions either with the substrate or with other tubes. In this paper we also focus on the theoretical study of lattices and bundles of SWCNTs.

Crystalline bundles of monodisperse SWCNTs with tube diameters D of approximately 17 Å have been produced by CO_2 laser ablation. Figure 1 shows a high resolution transmission electron microscopy (HRTEM) image of the transversal section (perpendicular to the common axes of the tubes) of a bundle consisting of at least a hundred tubes. From the HRTEM image it is apparent that the tubes depart from the circular shape and develop facets parallel to one another between adjacent tubes. This is, to the best of our knowledge, the first direct observation of a lattice of tubes with polygonized (hexagonal) cross sections. The hexagonal symmetry of the individual tubes is compatible with the two-dimensional triangular symmetry of the lattice. Polygonization of tubes with diameters of about 17 Å was not expected from previous theoretical studies [5]. Simulations of $(n, 0)$ tubes found the onset of tube polygonization for much higher diameters ($D \geq 25$ Å). The finding of bundles of polygonized tubes is also in contrast to previous observations of tubes with almost circular cross section [14]. Our finding, then, opens up the question of what is the equilibrium configuration of a lattice of aligned tubes and the possibility of the existence of several metastable structures depending on the growth conditions.

In order to shed some light on this problem we have simulated the structural features of triangular lattices of monodisperse armchair and zigzag SWCNTs as a function of the diameter of the individual tubes. The thermal

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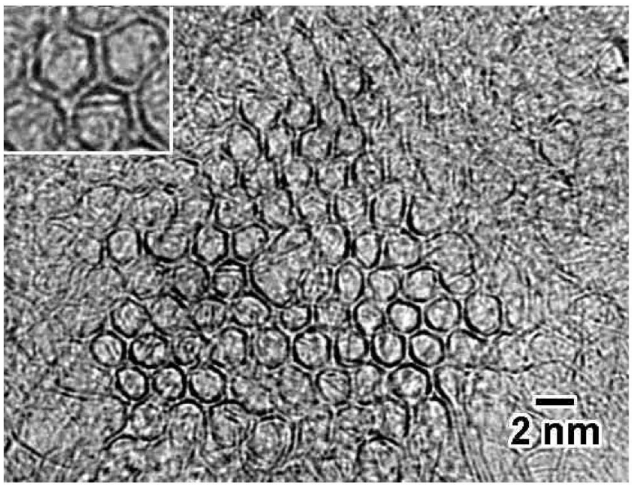

FIG. 1. HRTEM image of a lattice of polygonized tubes produced by CO_2 laser ablation.

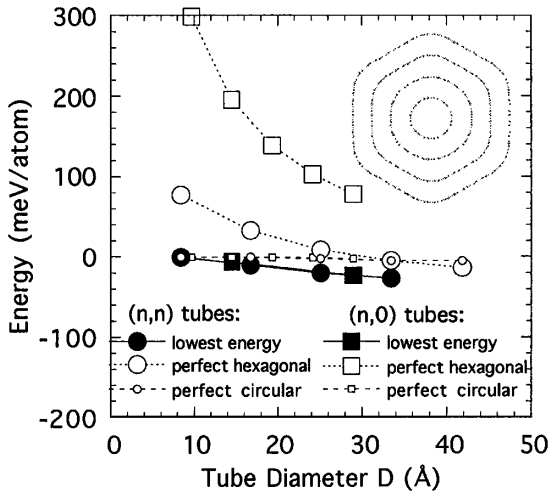

FIG. 2. Energy of the lattice with respect to isolated tubes. Lowest energy tubes are nearly circular for low D and almost hexagonal for large D. The inset shows, superimposed, the structures of the lowest energy (n, n) tubes.

quenching procedure [15] has been extensively applied to obtain possible metastable structures of the lattice of tubes (restricted to the triangular symmetry) and, eventually, the equilibrium configuration of the lattice.

The interatomic interactions between carbon atoms in the lattice of tubes are mimicked by a reliable and computationally efficient potential consisting in two terms: (i) the short-range Tersoff's potential and (ii) a long-range many-body potential. The short range Tersoff's potential [16] appropriately describes the covalent bond in diamond and graphite. This potential has been successfully applied to the study of fullerenes and tubes. In particular, it produces the R^{-2} (where R is the tube radius) behavior of the strain energy of SWCNTs. A long-range many-body potential describes the interaction between graphene layers in graphite [17]. This term accounts for the attractive interaction between the tubes and is, consequently, responsible for the formation of bundles.

The binding energy of a lattice of perfect circular tubes (with respect to isolated tubes) is very small (see Fig. 2). Its value ranges from about 0.5 meV/atom for tube diameters of 8 Å to a saturation value of about 5.5 meV/atom for diameters of 42 Å. The reason for these small values (as compared to the interaction energy between graphene layers in graphite [18]) is the lack of plano-parallel facing surfaces between adjacent tubes. A way of optimizing the interaction between tubes is, then, to deform the tubes introducing planar facets lying parallel to each other between adjacent tubes, i.e., considering tubes with polygonized cross sections (the optimal shape is the hexagon which complies with the two-dimensional triangular symmetry of the lattice). The intertube interaction energy in a lattice of perfect hexagonal tubes is 1 order of magnitude larger than in a lattice of circular tubes, a fact that favors faceting. However, the energy cost for deforming the tubes is high for tubes in the size range considered here. The *deformation* energy opposes polygonization of tubes. This energy decreases with increasing tube diameter and, eventually, its magnitude becomes lower than the intertube interaction energy of hexagonal tubes. As a consequence, lattices of hexagonal armchair and zigzag tubes are more stable than the corresponding lattices of circular tubes for tube diameters larger than 34 and 50 Å, respectively. These values for the onset of polygonization are too high, as compared with the size ($D = 17$ Å) of the polygonized tubes found in the experiment, since only perfect hexagons have been considered so far.

The actual shape of the tubes comes out from a delicate balance between the attractive intertube graphitic interaction and the intratube deformation energy. The relaxations, restricted to triangular lattices, yield not only the equilibrium configuration of the lattice but also several metastable structures characterized by different tube cross sections and unit-cell volume. The unit-cell volume correlates with the shape of the tubes. The smallest volume corresponds to the lattice of "nearly" hexagonal tubes, whereas the lattice of "almost" circular tubes has the largest volume. There is also an intermediate volume lattice structure formed by hexagonal tubes with rounded corners. The lowest energy configuration of the lattice progresses from *circular* to *hexagonal* tubes with increasing tube diameter. The relative stability of the different structures is also a function of pressure. There are some indirect evidences [10,11,19] of a pressure induced phase transformation from circular to hexagonal tubes, at about 1.5–1.7 GPa, for small tubes ($D < 14$ Å). Very recent measurements [19] of the mechanical deformation of (14 Å) tubes under hydrostatic pressure suggest that the tubes might be slightly faceted even at zero pressure, although polygonization becomes more noticeable for higher pressures, as expected.

The cell parameter of the triangular lattice is given by the tube width (i.e., the tube diameter in the case of

circular tubes and 2 times the apothem in the case of hexagonal tubes) plus the intertube spacing, which is found to be approximately equal to the interlayer separation in graphite. Since the radius of a circular tube is larger than the apothem of the corresponding hexagonal tube, the cell parameter of the lattice of *hexagonal* tubes is about 5%–7% smaller than the one of *circular* tubes. Correspondingly, the density of the lattice of *hexagonal* tubes is about 9%–16% larger than the one of *circular* tubes.

The lowest energy configuration of a lattice of tubes with $D \leq 17$ Å corresponds to *nearly circular* tubes. This would explain why all previous observations of bundles in this size range show tubes with circular cross sections. However, the metastable structure formed by *rounded-hexagonal* tubes is very close in energy; it is only 0.6 and 2.8 meV/atom above the equilibrium *circular* configuration for (12,12) and (18,0) tubes, respectively. This "novel" lattice configuration supports the observed bundle shown in Fig. 1. Some deformation is apparent in the experimental tubes. Because of the formation conditions and the large diameter of the tubes, such deformation is unavoidable. However, the polygonized structure of these bundled tubes is undisputable. For $D \geq 25$ Å the lattice of polygonized tubes becomes more stable than the one of circular tubes [5]. We have found the same value of the polygonization onset for the relaxed lattices of armchair and zigzag tubes, which correlates with the independence of the elastic properties of CNTs on chirality [20]. From our simulations we conclude that polygonization can be observed, under the proper conditions, in tubes as small as $D = 17$ Å, although it should be observed more frequently in bundles of tubes of larger diameters. These conclusions are in agreement with all the experimental evidence up to date.

For a more stringent comparison of theory and experiment we have simulated the TEM images which would be obtained from the theoretical lattice structures. Figure 3 shows the simulated images, focused in the plane perpendicular to the tube axes, for a lattice of (12,12) tubes with circular, hexagonal, and rounded-hexagonal cross sections, respectively. The TEM image of the *rounded-hexagonal* tubes correlates unambiguously with the experimental HRTEM image shown in Fig. 1.

We have also studied how the polygonization effect is modified in bundles consisting of a small number of tubes, e.g., one central tube plus six tubes surrounding it completely. We find, in agreement with the images obtained in finite bundles, that the central tube polygonizes completely whereas the surface tubes adopt a hybrid shape formed by half an hexagon (facing inward to the bundle) and half a circumference (facing outward to the bundle) (see Fig. 4). A similar hybrid model should apply for the surface tubes of larger bundles.

A number of potential applications of carbon nanotubes rests upon their extraordinary mechanical properties. One might expect a different mechanical behavior for different lattice structures. In what follows we concentrate on

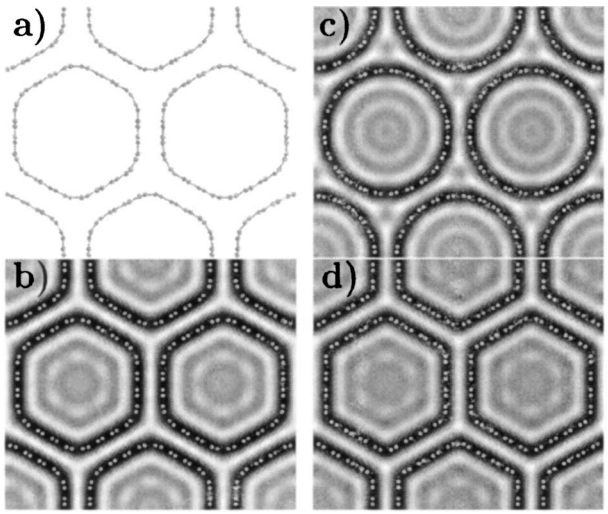

FIG. 3. Simulated TEM images of the plane perpendicular to the tube axes for a lattice of (12,12) tubes with (b) rounded-hexagonal (c) circular and (d) hexagonal cross sections. (a) The atomic positions for configuration (b).

the study of the compressibility of the lattice in the plane perpendicular to the tube axis. Figure 5 shows the two-dimensional bulk modulus (B) for the perfect hexagonal, perfect circular, and the lowest energy equilibrium lattices. B increases as a function of tube diameter in all cases. The steep rising of B for the perfect hexagonal lattice is caused by the structural rigidity of the basic units (hexagonal tubes) together with a high intertube interaction energy. Relaxation of the lattice produces a lowering of B and of its slope. The lattice of tubes behaves as a very peculiar material since the decrease in the lattice density with increasing tube diameter does not produce a corresponding lowering in the bulk modulus B. The compressibility $(1/B)$ of the lattice of (12,12) tubes in its ground state (nearly circular) is 2.5 times the compressibility of graphite in the direction perpendicular to the graphitic planes (both calculated using

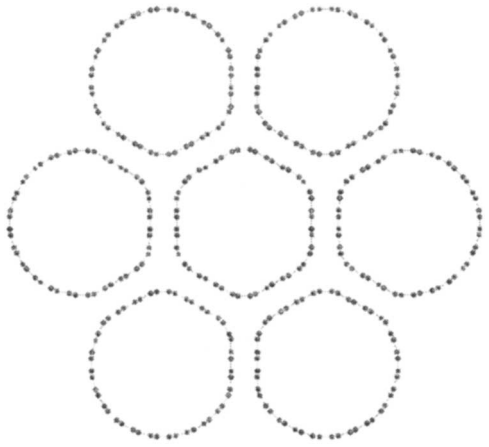

FIG. 4. Proyection of the atomic positions, in a plane perpendicular to the tube axes, of the hybrid configuration (partly polygonized) of a finite bundle of (12,12) tubes.

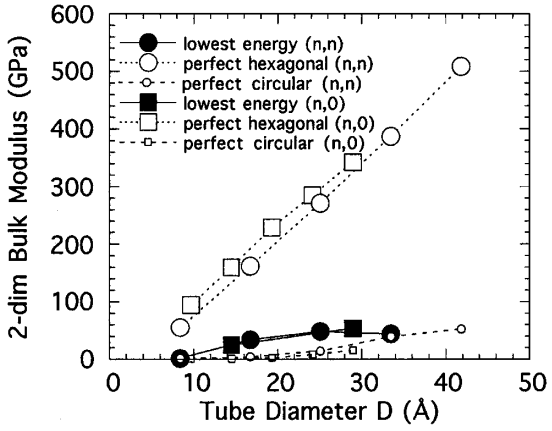

FIG. 5. Two-dimensional bulk modulus in the plane perpendicular to the tube axis of the perfect hexagonal, perfect circular, and lowest energy lattices as a function of tube diameter.

the present model). However, the compressibility of the rounded polygonized metastable structure (not shown in Fig. 5), which should be compared to the experimental lattice shown in Fig. 1, is only 1.4 times the compressibility of graphite, which improves the agreement with the available experimental data [21].

In summary novel crystalline ropes of polygonized SWCNTs have been found. The intertube wall-wall interaction is the driving force which prompts the elastic deformation of the tubes from circular to hexagonal cross sections. Molecular-dynamics simulations of triangular lattices of tubes produce several metastable configurations. For tube sizes similar to the experimental ones ($D = 17$ Å) the equilibrium configuration of the lattice corresponds to *circular* tubes. However, the lattice of *rounded-hexagonal* tubes is very close in energy and exhibits a TEM pattern in good agreement with the experimental HRTEM image of polygonized tubes. The polygonized lattice presents reduced compressibility with respect to the circular one, what could be relevant for applications relying on the mechanical properties of the tubes. As the technology for controlling the tube diameters becomes available, systematic studies on crystalline ropes of SWCNTs will, certainly, offer new insight on the evolution, as a function tube diameter, of the structure and properties of these fascinating lattices.

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