Mechanical deformations and coherent transport in carbon nanotubes

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We have investigated the conductance of carbon nanotubes under mechanical distortions likely to occur when forming nanoscale electronic devices. Using a realistic tight-binding Hamiltonian, several structure-dependent classes of electrical behavior in deformed nanotubes have been discovered. Bending, defects, and tube-tube contacts are shown to strongly modify transport in individual nanotubes, and to induce, in some cases, metal-semiconductor transitions. These results provide a clear interpretation of recent experimental findings and suggest avenues for their use in devices. [S0163-1829(99)51748-7]

In recent years, carbon nanotubes (NT's) have emerged as potential candidates for novel components in miniaturized electronic devices. Their electronic and transport properties have been the subject of numerous experimental[1–3] and theoretical studies,[4–10] and there are examples of carbon nanotubes being used as actual components in a number of prototype devices such as rectifiers, actuators, and nanoswitches. Usually, the positioning of the individual nanotube on the circuit base can be attained via manipulation with a scanning probe tip,[11] or by utilizing strong adhesive forces between the NT and the substrate. These procedures are likely to introduce large mechanical deformations in the nanotube geometry, which will modify the electronic and transport behavior of the system. Despite the great interest in such manipulating procedures for designing novel nanostructured devices, a sufficient understanding of the effects of mechanical deformations on the electrical properties of carbon nanotubes is far from being achieved. In this work, we examine the coherent transport properties of mechanically deformed single-walled carbon nanotubes and discover several classes of electrical behavior in the distorted geometries. In particular, bent nanotubes, with no defects present, exhibit different electrical properties depending on their symmetry and diameter. In some cases, a metal-semiconductor transition is observed. Defective regions, likely to be present because of the local strain exerted in the manipulation process, reduce the conductance of the individual nanowire to an extent that is strongly dependent on the defect density per unit length. Tube-tube junctions are other essential structures in the design of nanotube-based devices. We show that the contact established between two individual nanotube tips is sufficient to ensure a certain degree of electron transmission. Our results explain a number of recent experimental results and suggest avenues for manipulating the quantum conductance of carbon NT's.

For the calculation of conductances in distorted nanotube geometries, we extended an efficient method for computing transport in extended systems[12] to a general configuration of a left-lead-conductor-right-lead (L-C-R). In the present case, the leads are ideal nanotubes, and the conductor is represented by a defective or distorted region. Briefly, using the Landauer approach the conductance is determined via the transmission function that can be written as[13–15]

$$\mathcal{T} = \mathrm{Tr}(\Gamma_L G_C^r \Gamma_R G_C^a),$$

where $G_C^{\{r,a\}}$ are the retarded and advanced Green's functions of the conductor, respectively, and $\Gamma_{\{L,R\}}$ are functions that describe the coupling of the conductor to the leads. The Green's function for the whole system can be explicitly written as[13]

$$G_C = (\epsilon - H_C - \Sigma_L - \Sigma_R)^{-1}, \qquad (1)$$

where Σ_L and Σ_R are the self-energy terms due to the semi-infinite leads.

Once the self-energy functions are known, the coupling functions $\Gamma_{\{L,R\}}$ can be easily obtained as[13]

$$\Gamma_{\{L,R\}} = i[\Sigma_{\{L,R\}}^r - \Sigma_{\{L,R\}}^a].$$

The expression of the self-energies can be deduced along the lines of Ref. 12 using the formalism of principal layers in the framework of the surface Green's function matching theory.[16] We obtain

$$\Sigma_L = H_{LC}^\dagger (\epsilon - H_{00}^L - (H_{01}^L)^\dagger \bar{T}_L)^{-1} H_{LC},$$
$$\Sigma_R = H_{CR} (\epsilon - H_{00}^R - H_{01}^R T_R)^{-1} H_{CR}^\dagger, \qquad (2)$$

where $H_{nm}^{L,R}$ are the matrix elements of the Hamiltonian between the layer orbitals of the left and right leads, respectively, and $T_{L,R}$ and $\bar{T}_{L,R}$ are the appropriate transfer matrices. The latter are easily computed from the Hamiltonian matrix elements via an iterative procedure.[12,17] Correspondingly, H_{LC} and H_{CR} are the coupling matrices between the conductor and the leads. The Hamiltonian matrix elements have been calculated using a realistic tight-binding model for carbon as parametrized by Charlier *et al.*[18] The nanotube geometries discussed in this work have been optimized via molecular dynamics simulations using an empirical many-body potential.[19] This potential has proven to reliably describe geometrical transformations in carbon nanotubes.[20]

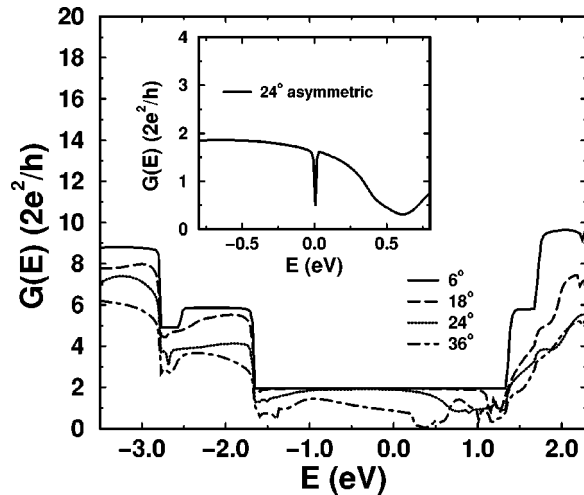We begin with the analysis of the electrical behavior of bent nanotubes. It has recently been observed[2] that in indi-

FIG. 1. Conductance of a symmetrically bent (5,5) armchair nanotube. Different curves correspond to different bending angles: 6°, 18°, 24°, and 36°, as shown in the legend. Inset: conductance of a (5,5) tube with an asymmetric bend of 24°. A pseudogap at the Fermi energy (always taken as reference) is clearly present, see text.
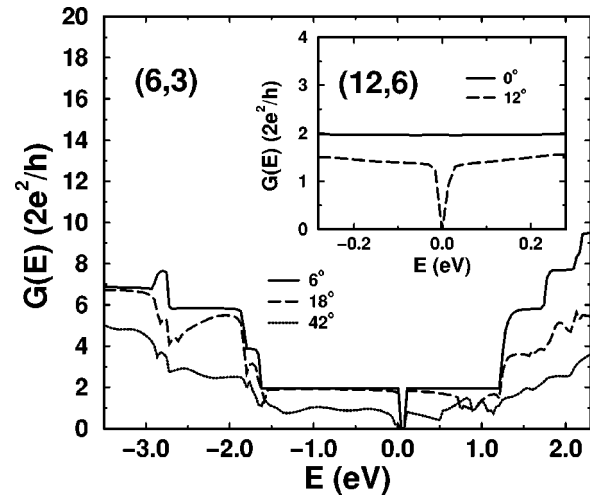
FIG. 2. Conductance of a bent (6,3) chiral nanotube. Different curves correspond to different bending angles: 6°, 24°, and 42°, as shown in the legend. Inset: conductance of a bent (12,6) chiral nanotube for $\theta = 0°, 12°$. The Fermi energy is taken as reference.

vidual carbon nanotubes deposited on a series of electrodes, three classes of behavior can be distinguished: (i) nonconducting at room temperature and below, (ii) conducting at all temperatures, and (iii) partially conducting. The last class represents NT's that are conducting at a high temperature, but at a low temperature behave as a chain of quantum wires connected in series. It has been argued that the local barriers in the wire arise from bending of the tube near the edge of the electrodes.

To address this issue, we have studied the effects of a general deformation in NT's of different symmetries and diameters. Single-walled carbon nanotubes may either be metallic or semiconducting depending upon their helicity, which is denoted by a pair of integers (n,m). In particular, they are predicted to be metallic if $n - m = 3q$ with q = integer.[21] While armchair NT's are always metallic, diameter plays an important role in modifying the electronic properties of chiral and zig-zag NT's. In particular, in small diameter NT's, the hybridization of s and p orbitals of carbon can give rise to the splitting of the π and π^* bands responsible for metallicity.[22] For example, $(3q,0)$ zig-zag nanotubes of diameters up to 1.5 nm are always small gap semiconductors, even in the absence of deformations, and can be assigned to the (i) class of behavior of Ref. 2, together with the naturally insulating NT's $(n - m \neq 3q)$.

In Fig. 1, we show the conductance of a (5,5) armchair nanotube ($d = 0.7$ nm) that has been symmetrically bent at angles $\theta = 6°, 18°, 24°, 36°$. θ measures the inclination of the two ends of the tubes with respect to the unbent axis. No topological defects are present in the geometry. For θ larger than 18°, the formation of a kink is observed, which is a typical signature of large-angle bending in carbon nanotubes.[23] Although armchair tubes are always metallic because of their particular band structure, the kink is expected to break the degeneracy of the π and π^* orbitals, thus opening a pseudogap in the conductance spectrum.[24] However, if the bending is symmetric with respect to the center of the tube, the presence of the kink does not drasti-

cally alter the conductance of the system,[25] since the accidental mirror symmetry imposed on the system allows the bands to cross. When this accidental symmetry is lifted, a small pseudogap (≈ 6 meV) occurs for large bending angles ($\theta \geq 24°$), see the inset of Fig. 1. The same calculations have been repeated for a (10,10) tube ($d = 1.4$ nm), and no pseudogap in the conductance spectrum has been observed even upon large-angle asymmetric bending. The formation of the pseudogap is thus triggered by the diameter of the nanotube, and our calculations indicate that for diameters $d > 0.7$ nm, the armchair tubes will keep their metallic character irrespective of the mechanical deformation and can be identified with the (ii) class of behavior in Ref. 2.

In Fig. 2, we present the conductance of a bent (6,3) chiral nanotube, for $\theta = 6°, 18°$, and 42°. Because of the relatively small diameter ($d = 0.6$ nm), the curvature induced breaking of degeneracy in the band structure opens a gap ($E_g \approx 0.1$ eV), clearly present in Fig. 2. The interesting result is that for large deformations ($\theta = 42°$) this gap is widened ($E_g \approx 0.2$ eV), increasing the semiconducting character of the nanotube. One can then expect that bending in a large diameter, metallic chiral nanotube will drive the system towards a semiconducting behavior via a reduction of the local curvature. This behavior is actually obtained for a larger diameter (12,6) chiral tube ($d = 1.2$ nm), as shown in the inset of Fig. 2. A bending-induced gap of ≈ 60 meV is opened at a relatively small angle (12°), whereas the NT was perfectly conducting prior to bending. This result demonstrates that local barriers for electric transport in metallic chiral NT's can occur with no defect involved, due to the microscopic deformations of the tube wall. Given the relatively small value of the energy gaps, these barriers will manifest themselves only at low temperatures, leading to the identification of these tubes with the (iii) class of behavior in Ref. 2.

Although bending itself can already bring a significant change in the electrical properties, defects are likely to form in a bent or a deformed nanotube, because of the strain that is exerted during the bending process.[26] It is now well estab-

TABLE I. Conductance in armchair nanotubes with point defects. (5-7-7-5) is the Stone-Wales defect; (5-7)-(7-5) corresponds to the onset of plastic behavior, the two (5-7) pairs separated by one hexagon row; (5-7-8-7-5) corresponds to the onset of brittle behavior, with the opening of a higher order carbon ring, see text. Units of $2e^2/h$.

	pristine	(5-7-7-5)	(5-7)-(7-5)	(5-7-8-7-5)
(5,5)	2.00	1.70	1.11	1.26
(10,10)	2.00	1.85	1.33	1.72

lished that a carbon nanotube under tension tends to release the strain via the formation of topological defects.[20] We have investigated how these defects affect the conductance of metallic armchair nanotubes of different diameters. Table I summarizes the results for (5,5) and (10,10) NT's under 5% strain, both pristine and in the presence of different topological defects: (i) a (5-7-7-5) Stone-Wales defect,[27] obtained via the rotation of the C-C bond perpendicular to the axis of the tube; (ii) a (5-7) pair separated from a second (7-5) pair by a single hexagon row, as in the onset of the plastic deformation of the nanotube;[20] (iii) a (5-7-8-7-5) defect, where another bond rotation is added to the original (5-7-7-5) defect, producing a higher order carbon ring (onset of the brittle fracture).[20] While strain alone does not affect the electronic transmission in both tubes, the effect of defects on conductance is more evident in the small diameter (5,5) NT, while it is less pronounced in the larger (10,10) NT. Our results for the (10,10) tube with a single (5-7-7-5) defect compare very well with a recent *ab initio* calculation.[28] If more than one (5-7-7-5) defect is present on the circumference of the NT, the conductance at the Fermi level is lowered: for the (10,10) NT it decreases from 2 $(2e^2/h)$ to 1.95, 1.70, and 1.46 $(2e^2/h)$ for one, two or three defects, respectively. The decrease in conductance is accompanied by a small increase in the DOS at the Fermi energy. This is due to the appearance of defect states associated with the pentagons and heptagons within the metallic plateau near the Fermi level. These localized states behave as point scatterers in the electronic transmission process and are responsible for the decrease in conductance.[29] This result confirms that in large diameter nanotubes, the key quantity in determining the electrical response is the density of defects per unit length. This is also in agreement with recent experimental results of Paulson *et al.*[3] for the electrical response of carbon nanotubes to strain applied with an AFM probe. As the AFM tip pushes the tube, the strain increases without any change in the measured resistance until the onset of a geometrical transition is reached. This corresponds to the beginning of a plastic/brittle transformation that releases the tension in the NT,[20] and coincides with a sharp yet finite increase in resistance. Since the onset of the plastic/brittle transformation that precedes breaking is associated with the formation of a region of high defect density,[20] the conductance at the Fermi energy is drastically reduced.

As the last example of conductance in nanotube structures, we have considered the tube-tube junction depicted in Fig. 3(a). Two open-ended (5,5) tubes have been put in contact with a small overlap region. The system was then annealed via a molecular dynamics simulation at a high tem-
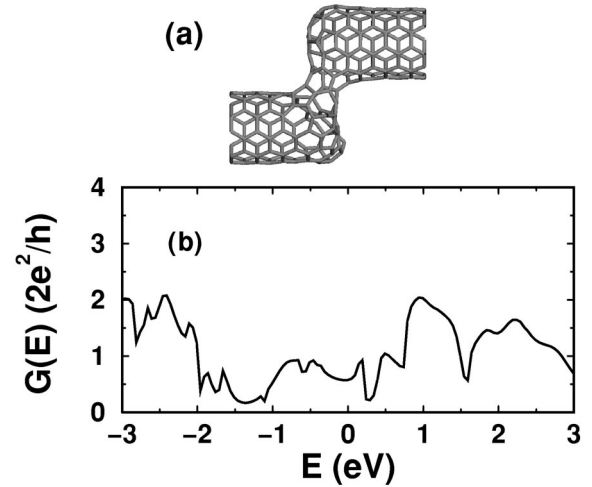

FIG. 3. The geometry (a) and the conductance (b) of an annealed contact between two open-ended (5,5) nanotubes. See text. The Fermi energy is taken as reference.

perature (3000 K) for ≈ 30 psec, after which the atoms were quenched to their ground state configuration. In the resulting geometry, the two ends bind together to form a small channel between the tubes, while the tips close in a partial hemisphere.[30] The conductance of the final structure is shown in Fig. 3(b). The small contact channel between the nanotubes enables electron transmission, although at a low level of conductance $(G(E_F) \approx 0.6(2e^2/h))$. This result does not change significantly if a larger overlap region is considered, provided that a transmission channel is formed in the process. This observation is consistent with the experimental findings of Ref. 3, where the ends of a tube previously broken by an AFM tip are put in contact with each other, reestablishing a finite resistance.

In summary, we have explored theoretically the coherent quantum conductance of various distorted geometries of carbon nanotubes. Bending, defects, and tube-tube contacts are shown to strongly modify the electrical behavior of individual nanotubes. Bent armchair tubes keep their metallic character for most practical purposes, even though an opening of a small symmetry-related pseudogap is predicted in small diameters ($d < 0.7$ nm) tubes. Metallic chiral nanotubes undergo a bending-induced metal-semiconductor transition that manifests itself in the occurrence of effective barriers for transmission, while bent zig-zag nanotubes are always semiconducting for the diameters considered in this study (up to 1.5 nm). Topological defects always increase the resistance of metallic nanotubes to an extent that is strongly dependent on their density per unit length. Finally, open-ended NT's that are put close to each other rebond and form conducting electrical contacts. Our calculations provide a clear interpretation of recent experimental results and suggest avenues for exploring the properties of specific nanotube structures in potential nanoscale electronic devices.

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