Nonlinear Resistance Dependence on Length in Single-Wall Carbon Nanotubes

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ABSTRACT

We report results of theoretical investigations of length dependence of electrical transport in single-wall carbon nanotubes. The structures investigated include straight nanotubes as well as nanotube multitapers of fixed and variable lengths. The nonlinear resistance as a function of the nanotube length obtained in our calculations supports the recent experimental findings and provides confirmation that this is an intrinsic feature of the nanotubes.

The discovery and large scale synthesis of single wall-carbon nanotubes (SWCN) have ignited research interest in their potential use as molecular wires.1–3 The unusual transport properties of molecular wires include such phenomena as ballistic transport and quantized resistance. Theoretical calculations have shown that the current vs voltage (I–V) characteristics of SWCNs depend sensitively on their diameter and chirality.4 Experimental studies of the nanotube resistance have yielded values much larger than theoretical predictions.5 The high resistance observed is generally attributed to a combination of contact resistance with the electrodes and the intrinsic resistance of the nanotube. More recently, experimentalists have managed to lower contact resistance by covering the ends of the nanotubes with metal electrodes.6,7 Direct measurement of intrinsic resistivity of individual nanotubes has been difficult owing to the difficulty associated with separating intrinsic resistance from the contact resistance. Recently, a general approach for intrinsic resistivity measurements of individual multiwalled carbon nanotubes has been reported.8 This technique was extended by de Pablo et al.9 to study the electrical transport properties of SWCN. The novel feature of their approach is that not only the resistance but also the I–V characteristics of the SWCN can be obtained. This enabled them to provide a full electrical characterization of the SWCN as a function of its length. Their results showed a nonlinear dependence of resistance on the length of the SWCN. Length-dependent conductance has also been reported for metal–semiconductor SWCN junctions.10 Experimental data of doped SWCNs have provided sufficient evidence that the presence of long-range disorder in these systems could justify the experimental findings.11 Based on these data it was proposed that disorder can break a semiconducting SWCN into a series of quantum dots with large barriers which dramatically reduce the conductance of the SWCN. Thus, it appears that both the L-dependence of the SWCN resistance, $R$, as well as the observed disorder-induced decrease of the conductance cannot be consistent with diffusive transport. Instead, a sequential tunneling through conducting parts of the nanotube was suggested.12,13 In the diffusive case, the conductance $G(E)$ can be approximated by the following equation: 

$$G(E) = \frac{4e^2}{h} \frac{l}{L}$$  

where $l$ is the average length of the conducting parts.
(approximately equal to the length of the mean free path) of a semiconducting nanotube of length \( L \).

As pointed out by de Pablo et al., their experimental results indicate that the nonlinear \( R \) vs \( L \) characteristic curve reflects an intrinsic feature of the SWCNs. This was attributed to the presence of nondissipative scattering centers, although the real cause of this behavior was not conclusive.

The nonlinear increase of \( R(L) \) can be attributed to weak localization effects, resulting from electron coherent scattering processes. Although weak localization has been proposed as the most probable reason for such a behavior, the possibility that conductivity in the diffusive regime may lead to the same behavior cannot be completely ruled out. Weak localization leads to an exponential increase of \( R(L) \), while a general nonlinear variation of \( R \) may be the signature of diffusive processes. These observations suggest the need for additional experimental works to provide a conclusive answer.

For finite SWCNs, the nonlinear \( R \) vs \( L \) dependence may be attributed to finite length effects. Results of the quantum potential—well problem (see appendix) can be used to show that density of the resonances of the transmission function, \( T(E) \), increases while the energy spacing between \( T(E) \) peaks decreases with the tube length. Also, it can be shown that the width of the \( T(E) \) resonances decreases as the tube length increases (see appendix). These potential—well results were also pointed out in other recent works. Orlikowski et al. have also found that there is no monotonic behavior of \( R(L) \) as a function of the tube length. Instead, \( R(L) \) exhibits dips when the tube length attains lengths \( L = 3M + 1 \), where \( M \) is the number of the unit cells of the SWCN.

While many of the findings are well justifiable by the potential-well picture, there are several other observed features that cannot be explained by this model. In particular, (i) the length-independent conduction gap found in the \((5,5)\)–\((10,0)\) SWCN-junction and; (ii) the decrease in the conductance value (at the Fermi energy, \( E_F \)), despite an increase in the junction-induced electron DOS at \( E_F \) as the nanotube length increases (in a metal-semiconductor nanotube-junctions). Some of these features have been attributed to the interplay between a gap opening in the metallic SWCN due to its finite length, the development of junction-induced states at \( E_F \), and the building up of a potential barrier due to charge transfer from metallic to the semiconducting tube. As pointed out in ref 10, the details of this interplay would depend on the specific nature of the constituent nanotubes.

In this letter, we present our results of theoretical calculations which confirm the nonlinear \( R \) vs \( L \) dependence for SWCNs and show it to be an intrinsic property of SWCN. Our theoretical method uses a unified approach that makes use of a tight-binding molecular-dynamics (TBMD) method in conjunction with a surface Green’s function matching (SGFM) method for obtaining structural relaxation as well as transport properties of the SWCNs using the same Hamiltonian. The TB Hamiltonian includes treatment of semiconductor and transition metal atoms and their hetero-systems. We make use of the full basis set for accuracy. This involves use of 4- and 9-orbital sets for semiconductor and transition metal atoms, respectively. Quantum conductivity calculations of SWCN are carried out using the SGFM method, which makes use of the same TB Hamiltonian. The SGFM method is based on a formalism for calculating transport properties proposed by Datta. The SGFM method has been used to obtain I–V characteristics of SWCNs in pristine form as well as in the presence of defects. In particular, I–V results obtained for SWCN Y-junctions using the SGFM method revealed asymmetric behavior and rectification, in complete agreement with experimental results on these systems.

We investigate the length dependence of SWCN transport properties by considering straight nanotubes as well as various nanotube tapers containing several tube junctions. All structures are fully relaxed using the TBMD scheme. Quantum conductivity calculations of each of the relaxed SWCNs is then carried out using the SGFM method.

We begin our study by considering a \((5,5)\) SWCN, as shown in Figure 1a. The dark colored carbon atoms on the left are in contact with the transition metal leads (not shown). These leads act as “fixed” contacts to the outside world. To obtain the length dependence of resistance we place the second (or “movable”) set of leads at regularly spaced intervals (shown in dark) along the length of the SWCN. The I–V characteristics are then calculated for length segments \( \xi, 2\xi, 3\xi, \) etc, where \( \xi \) is the shortest length (=12.3 Å). In Figure 1b we show the I vs V curves for different lengths of the nanotube. These curves are used to obtain R vs L dependence shown in the inset of Figure 1b, where \( R(L) \) values are plotted for three different values of the bias voltage. The nonlinear dependence of R on the tube length is evident in the figure. It should be noted, however, that due to the step features of the I–V curves (see top right inset) and the fact that for small tube lengths the current saturation value is obtained for small bias-voltages, the R(N) curves include superposition of additional finite length effects which lead to dips and peaks for certain \( N \) values and especially for small bias-voltages (see below). A more clear picture is obtained for values of bias-voltage which do not correspond to current—saturation values and/or major I–V steps. This is observed in Figure 1a (top left inset) for bias-voltage 1.0 V. The inset at the top right-hand side shows I–V characteristics near the origin for clarity. In the bottom inset we plot the Fermi energy \( (E_F) \) as a function of length.

We investigate the R vs L dependence further by considering the transport properties of SWCN multitapers, which consist of tube segments of different diameters joined together. Each junction between nanotube segments contains a pentagon–heptagon defect pair joined along the axis of the multitaper. In Figure 2 we show a SWCN \((6,0)\)–\((7,0)\)–\((8,0)\)–\((9,0)\)–\((10,0)\) multitaper. The ring of dark colored atoms at the junctions separates tube segments of different diameters. Each of the segments has the same length. The dark colored carbon atoms on the left are in contact with the transition metal leads (not shown). These leads act as “fixed” contacts to the outside world. The second (or “movable”) set of leads is put at one of the rings separating the tube junctions.
The taper in Figure 2 can be used to study the behavior of current as a function of the length of nanotube. This is accomplished by connecting the carbon atoms at the left end of the taper to the “fixed” metal leads, while allowing the “movable” leads to sweep through the junctions (indicated by dark colored atoms) as the currents are calculated. Our results for this setup are shown in Figure 3. As the figure shows, the tube length gives a pronounced nonlinear contribution to $I(L)$, in agreement with the results of Figure 1b.

The $L$-dependence of the tube resistance $R(L)$ (shown in Figure 1b) needs further attention. In the absence of doping and/or structural defects, the nonlinear dependence of $R = R(L)$ is clearly not attributable to either the diffusive result (eq 1) or the disorder effects. The nonlinear feature, therefore, be an intrinsic feature of the nanotubes and need to be investigated further. Our results lead us to support the conjecture that the behavior of $R(L)$ shown in Figure 1b is a finite length effect and can be well justified by the results of the quantum well potential (see appendix). Furthermore, a more careful inspection of the $R(L)$ dependence of Figure 1b reveals that for nanotube lengths commensurate with the $3M + 1$ feature, $R(L)$ exhibits a substantial dip for certain values of $M$ (where $M$ is an integer denoting the number of unit cells in the tube). In particular, this appears more pronounced for $V = 0.25$ V and for nanotube segments of lengths $2\xi$ and $5\xi$ ($\xi = 12.3$ Å). For these nanotubes, the tube length is commensurate with the $3M + 1$ feature with $M = 3$ and 8, respectively. This provides further support for the finite length effect in the nonlinear transport properties of the SWCN. The fact that for $V = 0.5$ V the dip is not well pronounced is due to the super-imposition of step-
features of the I–V curves (see top right inset of Fig. 1b). The step feature of the I–V curve is also reflected in the results of Figure 3 where a small dip (peak) is exhibited in the segment dependence I(N) [R(N)] of the multijunction. The step behavior combined with the decrease of the resonance widths in direct proportionality to the tube length may cause substantial changes as one samples the I–V curves.

In summary, we have carried out theoretical investigations of the length dependence of quantum conductance of carbon nanotubes by considering various nanotube structures that include straight tubes as well as nanotube multitapers of variable lengths. The nonlinear dependence obtained in our calculations supports the experimental findings of de Pablo et al. and provides evidence that this is an intrinsic feature of the nanotubes.

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Appendix

It is straightforward to show that for a 1-D potential well separated by vanishingly thin barriers from vacuum, the spacing between the resonance peaks of T(E) is proportional to 1/L² where L is the width of the well. (This is analogous to the Ramsauer–Townsend resonances resulting from constructive interference.) Within the same model, it can be easily shown that the resonance peaks of T(E) near the quasi-bound states of the potential-well located at energies E_n vary as

\[ T(E_n + \Delta E) = \frac{\Gamma_n^2}{\Gamma_n^2 + (\Delta E)^2} \]  

with \( \Gamma_n^2 \) proportional to 1/L².

References