Quantum Conductance Steps in Solutions of Multiwalled Carbon Nanotubes

A. Urbina

Departamento de Electrónica, Tecnología de Computadoras y Proyectos. Universidad Politécnica de Cartagena,
C/Doctor Fleming s/n, 30202 Cartagena, Murcia. Spain*

I. Echeverría

Department of Chemistry. University of Wisconsin-Madison, 1101 University Ave., Madison, WI 53706

A. Pérez–Garrido and A. Díaz–Sánchez

Departamento de Física Aplicada. Universidad Politécnica de Cartagena,
C/Doctor Fleming s/n, 30202 Cartagena, Murcia. Spain

J. Abellán

Departamento de Física. Universidad de Murcia, 30071 Murcia. Spain
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We have prepared solutions of multiwalled carbon nanotubes in Aroclor 1254, a mixture of poly-chlorinated biphenyls. The solutions are stable at room temperature. Transport measurements were performed using a scanning–tunneling probe on a sample prepared by spin–coating of the solution on gold substrates. Conductance steps were clearly seen. An histogram of a high number of traces shows maximum peaks at integer values of the conductance quantum $G_0 = 2e^2/h$, demonstrating ballistic transport at room temperature along the carbon nanotube over distances longer than $1.4 \mu m$.

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Since their discovery [1] theoretical calculations and experimental measurements suggest the enormous potential of carbon nanotubes as the building blocks of future molecular nanoelectronic devices [2, 3, 4, 5]. The electronic properties of carbon nanotubes depend strongly on their chirality and diameter. All armchair (n, n) nanotubes and those with $n - m$ multiple of three are metallic, the other ones are semiconducting with an energy gap inversely proportional to their diameter. This was confirmed experimentally by Wildoer and collaborators [6] using a scanning tunneling microscope (STM). They were able to obtain atomically resolved images and to perform local spectroscopy on their samples using the tip of the microscope as local probe.

Electronic transport measurements on individual single–wall carbon nanotubes (SWNT) deposited on metallic electrodes demonstrated their potential as molecular quantum wires [7, 8, 9]. Other researchers have done experiments on individually manipulated multiwalled nanotubes (MWNT): Langer and collaborators found effects of localization and universal conductance fluctuations at $T = 20mK$ [10], and Frank et al. found quantization of the conductance at room temperature [11]. In the absence of scattering, the momentum relaxation length and the localization length are much larger than the wire length, and the transport is ballistic. This is the case of carbon nanotubes in the absence of lattice defects, where the wavefunction of the electron is extended over the nanotube, and there are only two channels which contributes to the electronic transport giving $G = 2G_0$ (where $G_0 = 2e^2/h$ is the conductance quan-

tum) [2, 4]. If we consider elastic scattering, howewer the conductance of the system is described by the Landauer formula, which applies if the wavefunction can spread over the whole sample and is given by

$$G = \frac{2e^2}{h} M \mathcal{T} = \frac{2e^2}{h} \sum_{\alpha\beta}^{M} |t_{\alpha\beta}|^2,$$

where $\mathcal{T}$ is the transmission probability for a channel to go from one electrode to another. This probability is given by the sum over the number of channels, M, of transmission probabilities from α to β channel, $|t_{\alpha\beta}|^2$ (for a single–walled nanotube is $M = 2$). The elastic scattering affects the transmission probabilities and thereby reduces the conductance, which is no longer exactly quantized.

Molecular electronics based on the ensemble of thousands of nanoscale devices cannot be a real alternative to current microelectronics if the devices have to be individually manipulated using local probes. Some groups have tried a new approach using self–assembly of the macromolecules into controlled nets of devices or regular structures that could be later processed using nanolithographic methods, but carbon nanotubes have resisted this kind of treatment because of their difficulty to be diluted in appropriate solvents. Chen and collaborators studied both ionic and covalent solution–phase chemistry with concomitant modulation of the SWNT band structure [12], and Liu [13] and Vigolo [14] have prepared stable colloidal suspensions in water with the help of surfactants allowing for collective manipulation and orienta-

tion of the nanotubes. Howewer, the interaction between carbon nanotubes and their organic solvents or between carbon nanotubes and polymers in composites or other nanostructured materials is not yet fully understood.

We prepared our samples with purified arc–discharge soot material containing carbon nanotubes, which were first submitted to a sonication bath in 1,2–dichloroethane to unravel the material into nanotube bundles and single nanotubes. After evaporation of the 1,2–dichloroethane the remaining black powder was dissolved in a mixture of poly–chlorinated biphenyls (Aroclor 1254), using sonication and heat treatment to improve the dilution of the carbon material in the viscous solvent. Aroclor 1254 is a solvent of strong temperature–dependent viscosity. Whith our treatment, we arrived at an homogeneous dark solution of carbon nanotubes in Aroclor 1254 which is highly stable: no precipitation has been observed for months at room temperature. Scanning electron microscopy showed that our nanotubes have diameters ranging from 15 to 25nm, and lengths ranging form 0.8 to $2\mu m$, with a more or less Gaussian distribution centered at $1.4\mu m$. Our estimations of the critical density, d_c, for different solutions of carbon nanotubes with length $l = 1.5\mu m$, give the following values: if they were single walled (10,10) nanotubes, $d_c = 1.43\times10^{-6}g/cm^3$, if they were multiwalled with ten layers, then $d_c = 1.12 \times 10^{-5}g/cm^3$.

In order to prepare our samples for the transport measurements, we used a solution of density $c = 0.005g/cm^{-3}$ which is at least 10^3 times bigger than the overlaping concentration C^* of the nanotubes. The presence of overlaping in our samples is important to provide a percolative path between the nanotubes in solution and the gold substrate. We dropped the solution mentioned before on a gold substrate and then spin coated it to reach an homogeneous layer of about $0.5\mu m$. We used a scanning probe microscope (SPM) to make contact with the nanotubes and measure the conductance. The platinum tip was mechanically etched and mounted on a rigid STM piezo. We recorded the current as a function of time and tip distance to the sample. The applied bias voltage was kept fixed, so that conductance could be determined as a function of the position of the nanotube contact. We start the experiment with a coarse approach of the tip to the sample. Once electrical contact has been established, the tip is piezo controlled by the SPM and driven in and out cyclically. The vertical travel used is $2\mu m$. Data from sequences of 50 to 100 cycles were recorded automatically. When the tip makes contact with the sample, one nanotube can stick to it, remaining stuck while the tip cycles, and thus providing an electrical contact through the nanotube with the gold substrate, directly or through a percolative path with other nanotubes of the solution. While the tip is cycling, the contact of the nanotube with the tip remains constant, otherwise the nanotube contact with the substrate is changing while it is being lifted by
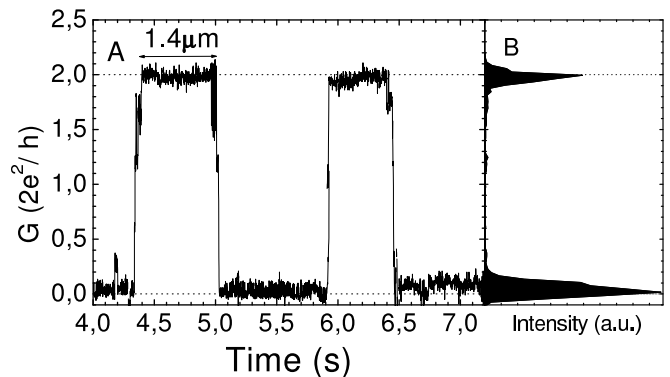

FIG. 1: A sequence of measurements of conductance versus time showing steps at $2G_0$, where G_0 is the conductance quantum $G = 2e^2/h$. Two steps of different length out of a sequence of more than fifty are shown. The histogram shows the persistence of the quantized value along the sequence, with a clearly defined peak at $2G_0$. The bias voltage between tip and substrate was $V_p = 10mV$.

the tip. When the tip retracts a distance larger than the length of the nanotube, the contact is broken and the conductance goes to zero. We can record sequences of more than fifty cycles, but usually it is difficult to reach more than seventy cycles without loosing contact with the nanotube.

In figure 1 we plot the conductance G versus time for a portion of a sequence in which two steps of different length are observed. This is representative of a high number of steps, which can be used to construct an histogram for every sequence, shown in figure 1B. The histogram is taken over the first fifty cycles. In this figure, a peak centered at the conductance value of $2G_0$ can be seen, along with the broadening expected from the noise in our measurement. Note that if the nanotubes behaved as diffusive conductors, we would expect the conductivity to vary as a function of the distance between the nanotube contact points to the substrate and the tip. Howewer, what we observe in our experiment is a series of plateaus, meaning that the conductivity remains constant for periods of time, which in our experiment are equivalent to tip displacements ranging from 0.8 to $1.4\mu m$. This can be explained by changes in the contact point between nanotube and substrate, which sometimes might even involve mechanical deformation (bending) of the nanotube. The value of the conductance remains fixed while the current path is changing, thus the nanotube behaves like a ballistic conductor. Furthermore, the conductance appears to be quantized, taking values only at even integer multiples of the conductance quantum G_0. This result suggests that the nanotube behaves like a quantum wire, with only two conductance channels. We find this to be true, regardless of the diameter and length of the nanotubes involved. We attribute the different plateau lengths observed to differences in the length of nanotube between
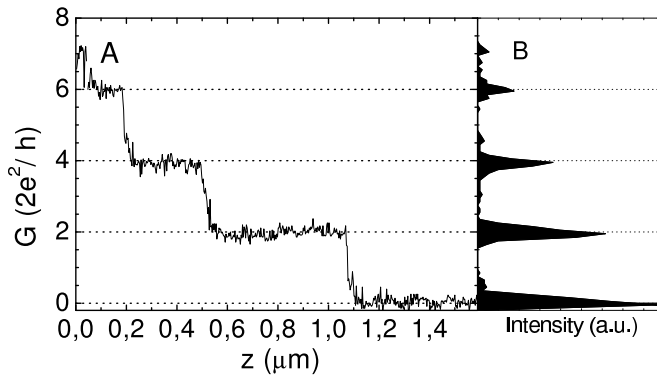
FIG. 2: In some of the sequences of conductance, three steps appeared at even integer values of the conductance quantum G_0. The conductance is plotted versus distance between tip and contact point with the sample. Two peaks are clearly seen in the histogram. A third peak is blurred by the noise. The bias voltage between tip and substrate was $V_p = 25mV$.

tip and substrate, which could be due to the adherence of a different nanotube or to a occasional displacement of the previously stuck one along the platinum tip. The presence of the solvent may enhance nanotube adherence to the tip. Howewer, as the contact heats up, the viscosity of the Aroclor decreases modifying the nanotube–tip structure in an unpredictable way. Nevertheless, the value of the conductance remains fixed at $2G_0$. The persistence of this value indicates that only the outer layer contributes to the electronic transport. The inner layers are isolated from the outer because the resistivity in the direction perpendicular to the tube axis is very high, as one could expect from similarities with graphite.

A second kind of results obtained with the same experimental procedure can be seen in figure 2. A series of steps at even integer values of the conductance quantum G_0 appears when the current along the nanotube is plotted versus the position of the tip. Since in single–walled metallic nanotubes only two channels contribute to electronic transport, we think that the new steps come from transport through other nanotubes. It is possible that two or more nanotubes get stuck to the tip, thus providing more than one connection, also ballistic and quantized, for the current between tip and substrate to flow. When the tip makes contact, sometimes the staircase begins with a step at a value of 4 and occasionally 6 G_0. When the tip begins to retrieve, the step remains fixed for a while and suddenly changes reducing to the next even integer value of G_0. We have never observed a step which changes in values higher than $2G_0$. This provides support to the idea that only the outer shell of the MWNT contributes, because if two (or more) consecutive metallic shells were contributing, it would provide a step of $4G_0$ (or higher) when this nanotube losses contact with the gold substrate. An histogram of twenty cycles is shown in figure 2B, showing peaks at even integer values.

Some of the observed steps present some slight but clear deviations from the quantized values, even after considering the noise of our measurements. This effect is more pronounced at the end of the step, when the current flows through longer distances along the nanotube. We attribute this deviation to the elastic scattering produced by structural defects of the nanotube atomic lattice, which affects the transmission coefficients and deviates the conductance from the quantized value as described by the Landauer formula. Our nanotubes were subjected to ultrasonic bath and this procedure could have produced some structural damage in the nanotubes. Such specific defects may affect the conduction at special energies werheas the transport remains unaffected for different energies.

An alternative explanation of the elastic scattering could be found in the interaction between shells of the multi–walled nanotube. The shell which is contributing to the electronic transport can be affected by its interaction with other shells, introducing an effective potential equivalent to structural disorder. Since we can not resolve the chirality of the successive shells of the MWNT, we could not study this effect. We think that the interaction between shells can be in part responsible for the discrepancy between our results and those found by S. Frank and coworkers (Ref. [11]). They found a quantized conductance at one unit of the conductance quantum G_0 instead of the expected $2G_0$. They attached a carbon fiber with protruding carbon nanotubes to a gold wire and used it as the tip of a scanning probe microscope. This fiber was found in the soft material inside the hardshelled deposit of an arc-discharge and no aditional treatment was performed to the fiber. We think that different shells of their MWNT can have electrical contact with the gold wire, increasing the intershell interaction even if only the outer shell have contact with the mercury melt. Recent theoretical works [15, 16] have studied the effect of intershell coupling and incommensurability in MWNT and they found that the mixing of quantum channels results in an enhanced contribution of backscattering and quantum interference effects which gives a quantum correction that reduces the conductivity. This effect could explain the different kinds of electronic transport reported for MWNT: ballistic, diffusive and even insulating behaviours. This may be the case of Ref. [11], but the exact reduction of one unit of the conductance quantum remains unexplained, unless the mechanism mentioned above eliminates only one of the two channels in the outer shell of the MWNT.

We also measured the current–voltage characteristics for some samples. When an electrical contact was obtained, we varied the bias voltage in a range between 0.1 and 1V. The I/V plot showed a linear behavior, which indicates that the nanotubes are indeed metallic. However, at higher voltages ($V \geq 0.6V$) we observed some instabilities even if there was no sign of current saturation,

those inestabilities may arise from the contribution of different subbands even if a single shell is contributing to transport. For a bias voltage of 1V, the current density is on the order of $J \sim 10^6 A cm^{-2}$, depending on the diameter of the nanotube. The dissipated power is $\sim 1 mW$. The electrical breakdown of the nanotube occurs at higher values of bias voltage, when the non linear regime is reached. It has been reported that for MWNT this breakdown occurs at powers of $300 \mu W$ [17]. The onset of saturation and the eventual breakdown are linked to a common dissipative process involving the excitation of phonons, temperature raising in the nanotube and a process of oxidation and loss of successive carbon shells. A simple heat transfer analysis, taking the nanotube as a solid cylinder with a bulk thermal conductivity of $\kappa = 3000 W m^{-1} K^{-1}$[18] gives for a nanotube of $1.4 \mu m$ long and 20nm in diameter a temperature $T = 1850K$, which is not possible, because nanotubes start to oxidate at $T \sim 1000K$. If we take other reported values such as $\kappa = 25 W m^{-1} K^{-1}$ [19], which possibly apply for nanotubes with more defects, or higher diameters, as is our case, the temperature would reach $T \sim 22000K$. Clearly heat is not dissipated in the nanotube, further supporting that the transport is ballistic.

In summary, we have prepared stable solutions of multiwalled carbon nanotubes in Aroclor 1254. Transport measurements using a scanning probe showed ballistic transport through distances longer than $1.4 \mu m$ and conductance steps at even integer values of the conductance quantum G_0.

* Electronic address: aurbina@upct.es

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