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Conductance of bulk samples of multiwall carbon nanotubes–metal junctions

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Abstract

Conductance as a function of voltage and temperature was measured in junctions made of bulk samples of multiwall carbon nanotubes and metal electrodes. A clear zero bias anomaly was observed at low temperatures. The experimental results were analyzed within existing models based on Luttinger liquid and disorder theories. We find that our results are well explained using the quasi-one-dimensional disordered model.

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The existence of depletion in the electronic tunneling density of states (TDOS) in carbon nanotubes have been recently a subject of great interest in experimental and theoretical studies. Experimentally, the depletion in the TDOS has been associated to the suppression of the conductance of carbon nanotubes at zero bias, and is generally termed as zero bias anomaly (ZBA).

There is a general agreement that the TDOS depletion in single wall carbon nanotubes (SWNT) is associated to electron–electron interaction leading to the so called Luttinger liquid (LL). Support for the LL model is based on theoretical considerations [1] and was confirmed by conductance measurements on metallic SWNT [2]. In addition, it has also been theoretically predicted a depletion in the electronic density of states by the opening of a pseudo gap, near the Fermi level, in bundles (or ropes) of SWNT due to the tube–tube interactions [3].

In the case of multiwall carbon nanotubes (MWNT), the explanation for the existence of ZBA is less clear, and there is controversy whether this system behaves as a LL or other microscopic mechanism that produces the anomaly. While some transport experiments on MWNT were explained in terms of a LL model [4,5]; other experimental results have been explained using localization theories in both one- and two-dimensional systems [6]. Lastly, in other approaches [7–9] dealing with LL theory, the role of disorder has been taken into account.

In this work, we present experimental studies performed in junctions made with MWNT bulk samples and metal electrodes. The results show a ZBA that evolves with temperature, and was analyzed with Luttinger and disordered theoretical models.

We used MWNT produced by arcing graphite rods without metal catalyst (MER Corporation). The as received material contains 25–35 wt% of MWNT (2–15 nm diameter, 5–10 graphite layers, and 1–10 μm long), the rest being other carbonaceous particles. In order to eliminate most of the carbonaceous particles, we used the selective oxidation by thermal annealing method, similar to that reported in Ref. [10]. It was found that with this method carbonaceous particles are etched by oxidation at a faster rate than carbon nanotubes [10]; but it is also known that the nanotubes are opened at the ends and that thinning through layer by layer starts from the ends [11].

The material was purified by thermal annealing in atmospheric blowing air at 600 °C, the time of the process

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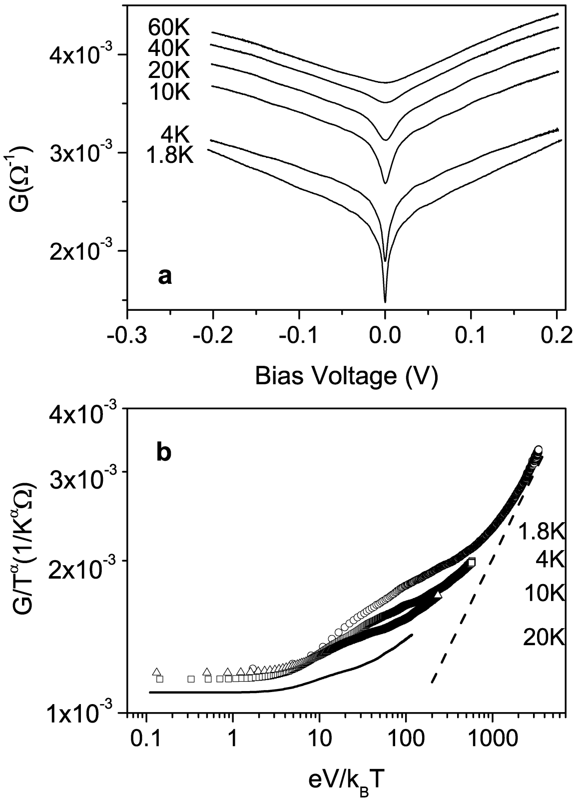

Fig. 1. (a) Plots of the differential conductance as a function of bias voltage at different temperatures. A zero bias anomaly develops and increases from high to low temperatures. (b) Scaled plot of G/T^{α} against $x = eV/k_BT$ for different temperatures with $\alpha = 0.35$, the dashed straight line is a guide to the eye and corresponds to x^{α}.

was adjusted to have ~25 wt% of the initial carbon powder mass. A small amount of dimethyl formamide (DMF) was added to about 5 mg of purified MWNT and mixed until a dense paste was obtained. Junctions were formed with an Al film electrode with thickness of about 2000 Å, thermally evaporated on a glass substrate to form a long stripe of 1.5 mm wide. The second electrode was obtained by carefully spreading the MWNT paste to form a 1.5–2 mm wide strip deposited crossing the aluminum film using a teflon spatula. The sample was heated at about 40 °C during a few minutes until the MWNT paste was dried. The junctions are formed by the intersection of the Al film and the strip of MWNT paste. By the method described above, we expect the MWNT sample to consist of many nanotubes accommodated in random directions and positions with multiple interconnections, and the carbon nanotubes having structural defects mainly due to the thermal annealing (necessary to purify the sample). Several junctions were characterized and studied at low temperatures by the standard four-probe modulation technique using a lock-in amplifier. With this technique we directly measured the differential resistance $R(V)$ versus bias voltage V and the differential conductance $G(V)$ is obtained as $1/R(V)$. For details about this technique see for example Ref. [12].

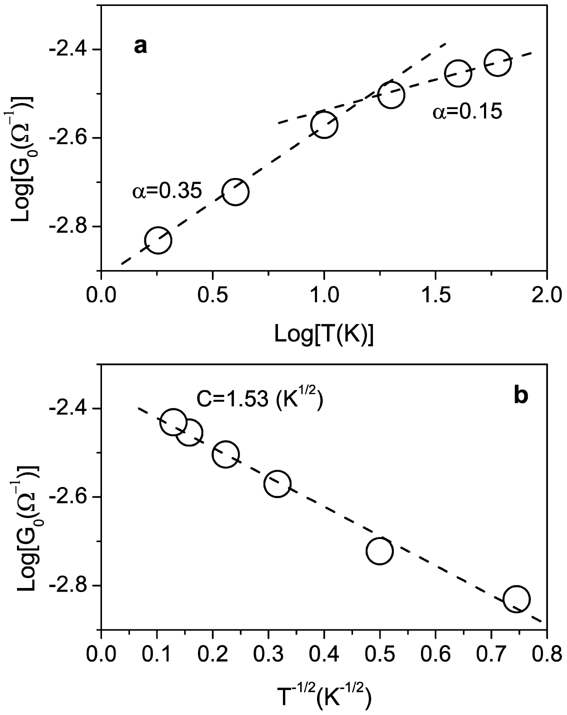

Fig. 2. Zero bias conductance G_0 as a function of temperature. (a) Fitting of data using the model $G_0 \sim T^{\alpha}$ (dashed straight lines) for low and high temperatures, with two values for α; 0.35 and 0.15, respectively. (b) Same data as in (a), but fitted now to $G_0 \sim \exp(-C/T^{1/2})$, with $C = 1.53K^{1/2}$ (dashed straight line).

Fig. 1(a) shows typical differential conductance curves versus bias voltage measured at different temperatures (T). The most important feature observed in our junctions is the ZBA that increases as the temperature decreases.

In order to analyze the obtained results, we first try the LL model. This model predicts a universal curve of the scaled conductance $G(V,T)/T^{\alpha}$ as a function of $x = eV/k_BT$ (k_B is the Boltzmann's constant and e, the electron charge); where the value of exponent α depends on whether the electrons tunnel into the bulk or at the end of the nanotubes, and it is related to the strength of the electron–electron interaction [1,2,4]. The universal curve has asymptotic behavior as $G(T) \sim T^{\alpha}$ for $x \ll 1$ and $G(V) \sim V^{\alpha}$ for $x \gg 1$. Fig. 2(a) shows the plots of zero bias conductances G_0 versus temperature in a log–log scale. It seems that in order to fit the results two α values are needed; $\alpha \sim 0.35$ for low temperatures, and $\alpha \sim 0.15$ for higher temperatures. As the ZBA conductance is well developed at low temperatures, we try to observe a universal behavior using $\alpha = 0.35$. In Fig. 1(b) we plot G/T^{α} against x for various temperatures in a log–log scale. It is clear from this figure that only the curves for low temperatures can be grouped together, but they do not collapse into an universal curve, this is evident

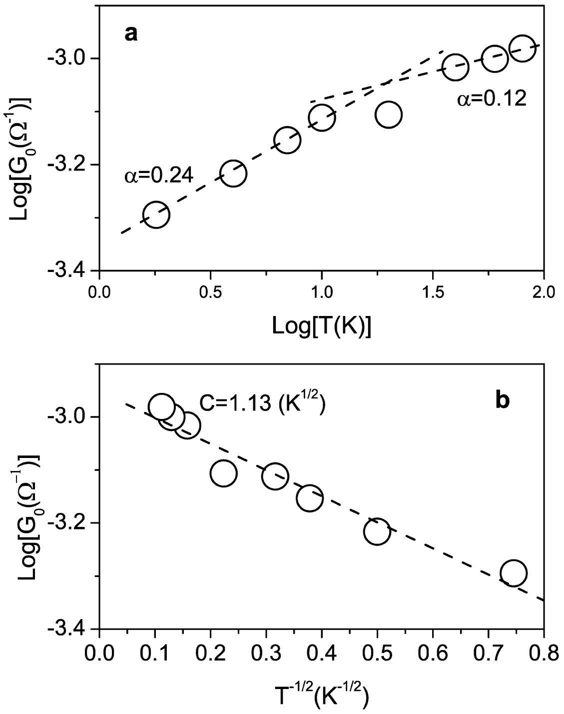

Fig. 3. Same plots as in Fig. 2 for another junction (a) fitting for low and high temperatures with $\alpha = 0.24$ and 0.12, respectively; (b) the fitting parameter is $C = 1.13K^{1/2}$.

for the curve at $T = 20$ K, which is well separated from the other. In Fig. 3(a) a plot of $\log(G_0)$ versus $\log(T)$ for another junction is presented, there, it seems that there is no unique value for α in the range of studied temperatures. According to these results we may conclude that the obtained data are far from an universal behavior within the LL model.

On the other hand, Krstić et al. [13] after analyzing the role of disorder in boron-doped MWNT concluded that a better account for their experimental data is given within a model where the MWNT are considered as a disordered quasi-one-dimensional conductor. Within this model, $G(T) \sim \exp(-C/T^{1/2})$, where C is a slowly varying temperature parameter [8] was interpreted as a measure of the degree of disorder introduced by the Boron doping in the MWNT [13]. Thermoelectric temperature dependence experiments on MWNT have also been explained in terms of electronic interactions in a disordered system, finding a temperature dependence of the conductance of the form $\sim \exp(-C/T^{1/2})$ at low temperatures [14].

In Figs. 2(b) and 3(b), a fit to our data of the two reported junctions is plotted in a $\log(G_0)$ versus $T^{-1/2}$ graph. It appears from these fittings that a better account of the experimental results is also obtained using the disorder model.

In the quasi-one-dimensional disordered conductor model [8] the electrons in the outermost shell of the MWNT can be scattered by impurities, lattice imperfections, and by the incommensurate lattice potential from the inner shells. The role of the disorder is very important since plasmons are scattered along the wire and this process makes the redistribution of the charge of the tunneling electron difficult, finally leading to suppression of TDOS. This model predicts a crossover from LL behavior at higher energies E (where TDOS scales as E^α), to another regime at lower energies where a strong suppression of TDOS at the Fermi level is expected following the form $\sim \exp(-C/T^{1/2})$, as a function of temperature. In the high energy regime and at very low temperatures ($x \gg 1$, in our notation) the model of Mishchenko et al. [8] predicts $G(V) \sim V^\alpha$; which appears to be consistent with our experimental results at the lowest temperature. There the experimental curve at 1.8 K tends asymptotically to the dashed straight line given by $\sim x^\alpha$ with $\alpha = 0.35$, as observed in Fig. 1(b).

In conclusion, we have observed a ZBA in junctions made up of bulk samples of MWNT and a metal. The experimental results are well accounted for by a quasi-one-dimensional disordered model, rather than the pure LL model.

Acknowledgements

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