# Conductance Oscillations in Squashed Carbon Nanotubes

C. Gómez-Navarro, J. J. Sáenz, and J. Gómez-Herrero

*Departamento Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain*

We report measurements on the radial electromechanical properties of single walled carbon nanotubes. By measuring the conductance of the nanotube, we show that a gap is opened while squashing the nanotubes and that during the deformation stages we observe at least two open-close cycles of the gap. We employ a novel experimental setup where an atomic force microscope tip is used both as an electrode and to induce radial deformations. In contrast with prior experiments reported, this technique allows direct probing of the local electronic structure of carbon nanotubes as they are radially deformed.

PACS numbers: 73.63.Rt, 73.22.−f

The ability of a material to change its conductance as a function of an external pressure is known as an electromechanical property. The search of solid state devices exhibiting this capability has been a major focus for material science. It has been demonstrated that the conductance of carbon nanotubes can be tuned by applying an external force [1–3]. It is well known that the electrical transport properties of carbon nanotubes critically depend on the geometrical structure of these molecules. If this geometry is perturbed, the result is a dramatic change of the conductance [4]. This unique capability of carbon nanotubes can be used to sense small displacements at high frequencies and opens new routes for nanoelectromechanical systems (NEMS) technology. However, the electromechanical properties of these fascinating structures are far from being clear enough for such applications.

In this Letter, we report experimental evidence of conductance oscillations in metallic single walled carbon nanotubes (SWNTs) as they are radially deformed. A phenomenological model is used to explain the experiments. According to this model, these oscillations should appear only if a cyclic opening and closing of the gap takes place in metallic tubes. The experiments are a first attempt to confirm the calculations carried out by Mehrez *et al.* [5], where gap cycles are predicted as the nanotube cross section is continuously deformed.

Most of the previous experimental approaches to measure the electromechanical properties of carbon nanotubes involved the deformation of a suspended nanotube with an insulating atomic force microscope (AFM) tip [1,2]. This experimental setup presents some drawbacks: It is difficult to implement, it does not discriminate between radial (squashing) and axial (stretching) electromechanical properties, and, as we shall illustrate, it masks the band-gap dependence as a function of the radial deformation because any gap opened along the tube would block the current flow. We have overcome these problems by measuring the conductance of a deformed nanotube lying on a hard insulating substrate, aiming exclusively at the radial electromechanical properties of SWNTs. In addition, the use of a metallized tip as a second electrode allows accurate

measurements of the SWNT band-gap structure since the opening of a gap along the nonuniform deformed region would not totally block the current flow. Our results will also help to elucidate the controversial theoretical situation surrounding this issue [5–9].

The experimental setup begins with a sample consisting on a random distribution of SWNTs deposited on an insulating substrate, with a macroscopic gold electrode made by masked thermal evaporation of gold. On these samples, molecules partially covered by the macroscopic gold electrode are easy to locate by imaging in noncontact dynamic mode [10] along the gold edge. Once a SWNT is selected, we use a metallized AFM tip as a second mobile electrode [11] [see the sketch in Fig. 1(a)]. We have designed an experimental procedure where we are able to measure the
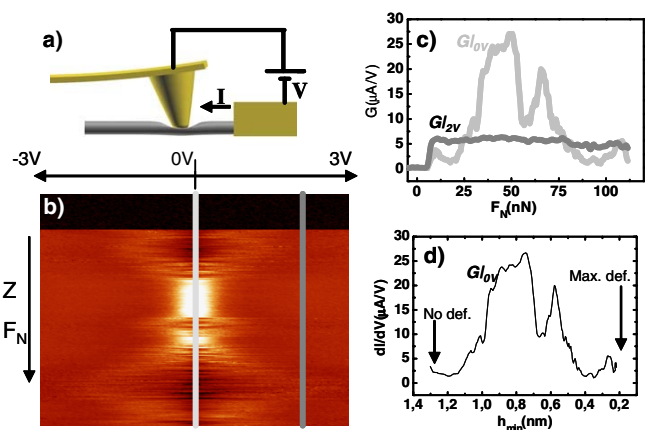


FIG. 1 (color online). Experimental results: Conductance vs deformation. (a) Scheme of the experimental setup. (b) Pseudo-color map of $G(Z, V)$ measured on a 1.3 nm diameter SWNT. The vertical axis is the $Z$ piezoelectric displacement and the horizontal axis is the bias voltage. Black corresponds to zero and white to 27 $\mu$A/V. The diamondlike structures indicate conductance oscillations. (c) Plot of the conductances $G|_{0\,V}$ (light gray) and $G|_{2\,V}$ (dark gray) as a function of the cantilever normal force obtained from $F = -kZ$, where $k$ is the cantilever force constant (3 N/m). (d) Conductance vs deformation plot obtained using the Hertz model for the data in (c).

current vs voltage (*I-V*) and differential conductance vs voltage (*G-V*) characteristics as the tip loading force is continuously increased [12]. The experiments are performed as follows: Once a spot along the length of the nanotube is selected, the tip is placed on top of the spot and the sample starts moving towards the tip; for each step of this movement, we apply a ramp of voltage to the tip and simultaneously measure the loading force ($F_N$), the current (*I*), and the differential conductance (*G*) of the nanotube. The differential conductance is measured using ac lock-in techniques. In contrast with other experimental approaches, our procedure allows us to measure simultaneous maps of these three magnitudes [$F_N(Z, V)$, $I(Z, V)$, $G(Z, V)$] as a function of the sample displacement towards the tip (*Z*) and the bias voltage (*V*), where *Z* is along the vertical axis and *V* is along the horizontal one [Fig. 1(b)].

In order to avoid bundles as much as possible, the experiments presented in this work have been performed on SWNTs with a measured height in the AFM topographic images, $h \leq 1,5$ nm. Only nanotubes presenting metallic characteristics (linear *I-V* at 0 V and a drop in conductance at high voltages [13]) have been selected. All the conductance versus deformation curves taken on different nanotubes present the same general tendency: For low loading forces, the *G* measured at 0 V ($G|_{0\,V}$) increases with the loading force due to electrical contact improvement [12] until $F_N \sim 50$ nN. At this critical load, the conductance presents a maximum, and increasing the load results in a $G|_{0\,V}$ drop. This drop is compatible with previous observations [1]. Surprisingly, in addition, we also observe peaks on the low voltage conductance as the load is linearly increased. An example of this is presented in Fig. 1; the data were obtained on a 1.3 nm height nanotube, compatible with a (10,10) chirality. In the $G(F, V)$ map [Fig. 1(b)], we observe diamondlike structures with a good symmetry along the 0 V white line that clearly indicate conductance oscillations, meaning that $G|_{0\,V}$ drops and grows as the nanotube is monotonically squashed. Figure 1(c) shows two profiles along the vertical lines in Fig. 1(b). The $G|_{0\,V}$ presents two marked peaks which are related with the low voltage structures present in Fig. 1(b). In addition to the high peaks, we observe small wiggles that, as can be seen in Fig. 1(b), depend on the loading and are also symmetrical with respect to the 0 V line. This symmetry indicates that both high peaks and wiggles are not noise but rather related with the actual details of the nanotube deformation and tip-nanotube contact. We shall discuss this point in greater detail in the forthcoming lines. In contrast, the high voltage conductance ($G|_{2\,V}$) remains constant as a consequence of the dissipation along the nanotube length [13]. It is worth noticing that, in similar experiments performed on multiwalled carbon nanotubes (MWNTs) and large gap SWNTs (data not shown), we have never observed low bias conductance variations, even for loads as large as 1 $\mu$N. On the contrary, these conductance oscillations are always present on metallic SWNTs, although their precise shape can change in consecutive experiments.

In order to estimate the maximum deformation of the SWNT induced in our experiments, we have used the results of the Hertz model [14] for a cylinder in contact with a spherical tip, where the deformation $\delta = h - h_{\min}$ [see Fig. 2(a) for notation] can be expressed as:

$$\delta = \left(\frac{9F_N^2}{16E_{\text{eff}}^2 R_{\text{tip}}}\right)^{1/3} Q(R_{\text{tip}}), \tag{1}$$

where $E_{\text{eff}}$ is the effective Young modulus and $Q$ is a geometric factor [15]. The tip radius $R_{\text{tip}} = 20$ nm is obtained from the apparent width *W* of the nanotubes on the topographic images and the deconvolution formula $R_{\text{tip}} = W^2/16R_{\text{SWNT}}$ [this leads to the *G* vs deformation curve depicted in Fig. 1(d)]. This calculated radius is compatible with the one provided by the manufacturer and is typical of most AFM tips. The large drop in the low bias conductance (at $F_N \sim 50$ nN) would then correspond to $\delta \approx 0.5$ nm, i.e., $h \approx 0.8$ nm [16], in agreement with the theoretical predictions for the opening of a band gap due to radial deformations in Ref. [5].

The theoretical works published so far on electromechanical properties of radially deformed nanotubes assumed a uniform cross section (i.e., like a nanotube squashed between two parallel plates). However, tip-induced deformations are certainly not uniform (see Fig. 2). The influence of this effect on the experimental conductance can be qualitatively understood in terms of the simplified model of the contact sketched in Figs. 2(b) and 2(c). In our model, the deformed nanotube region is divided in sections of fixed length $\Delta X$ (of the order of the Fermi wavelength) in which it is possible to define a *local band gap* $E[h(x)]$. The quantum resistance associated with each section would then be

$$R_i \approx \frac{1}{G_0}\left(\exp\left(\frac{E(h_i)}{2KT}\right) - 1\right), \tag{2}$$

where *KT* is the Boltzmann factor. The current flow towards the tip is modeled by including parallel contact resistances $R_{ci}(h)$ at each section. This contact resistance takes into account the electronic mismatch between the tube and the tip and, since the experiments are performed in air, the possible effect of a thin tunneling layer. The contact resistance should depend on the pressure distribution along the contact region, growing towards the less deformed sections. For simplicity, we assume it to be $R_{Ci} \approx R_0 - \alpha(d - h(x))^2$, where $R_0$, $\alpha$ are constant fitting parameters. We have also considered other possible dependences, and we find that the precise shape of $R_{ci}(h)$ is not critical and it does not modify the overall behavior of the conductance.

The equivalent circuit of the tip-nanotube contact is depicted in the inset in Fig. 2(c). By using the quantum addi-
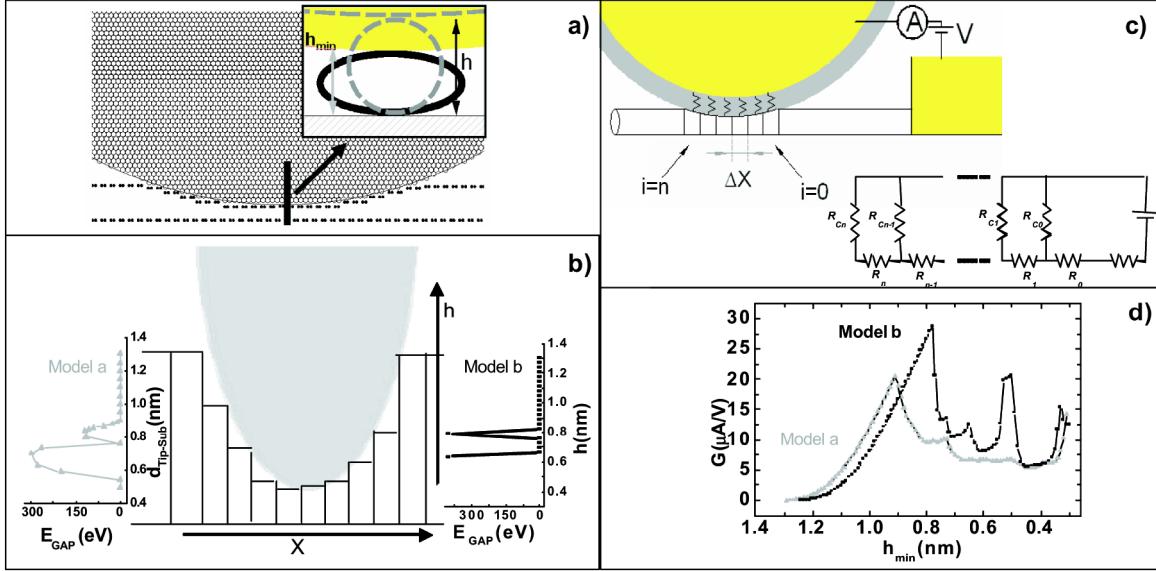
FIG. 2 (color online).   Extended contact region. (a) Atomistic scheme of the contact area between the tip and the nanotube. Inset: Schematic cross section of a tip deforming a SWNT, where we define the initial height $h$, the deformation $\delta$, and the effective height of the deformed nanotube $h_{min}$. (b) Schematic drawing of the nanotube tip contact area divided in sections perpendicular to the tube axis. Gray curve (model a): $E(h)$ obtained from Ref. [5]. Black curve (model b): $E(h)$ that leads to a good agreement with our experimental findings. According to our model and experimental setup, the measured $G$ is insensitive to the gap shape for $h < 0.6$ nm. (c) Geometry of the tip-nanotube contact region. The area corresponding to the interface has been divided in $n$ sections perpendicular to the tube axis. Each of these sections has an assigned intrinsic resistance ($R_i$) and contact resistance ($R_{Ci}$) with the tip. Inset: Circuit equivalent to the experimental situation considered in the model. (d) Conductances vs $h_{min}$ obtained with the models for the $E_{GAP}(h)$ curves depicted in (b). A very good agreement with the experimental findings is found for the $E(h)$ plotted in black (model b).

tion formula for series resistances $R_i' = R_{Ci} + R_i + R_{Ci}R_i$ (see Ref. [17] for a detailed explanation), the equivalent circuit can be solved in an iterative way, and the final equivalent resistance of the whole circuit is $R_{C0} = R_{equiv}$ and $G_{equiv} = 1/R_{equiv}$. Figure 2(d) represents the calculated conductance versus deformation, $G|_{0\,V}(h_{min})$, using the band-gap curves ($E[h]$) shown in Fig. 2(b). At low loads, before the band gap opens, the conductance increases with load, being roughly proportional to the contact area. The opening of a band gap under the tip leads to a first conductance drop. The electron transport is then dominated by the transmission probability of the sections that are closer to the macroscopic electrode. As the load increases, the conductance decreases further. The entrance of new sections (as the contact area increases) leads to small wiggles superimposed on the conductance curve. The closing of the band gap under the tip leads to sections of low resistance that shift again towards the edge of the contact as the load increases. When the low resistance section reaches the contact edge, the conductance presents a second peak. The size and shape of this second peak depend on the details of the $E(h)$ curve and the geometry of the contact. For example, the gray plot in Fig. 2(d), corresponding to the $G|_{0\,V}$ obtained using the $E(h)$ curve from Ref. [5] [model a in Fig. 2(b)], does not show a clear second peak. However, by using a slightly modified $E(h)$ curve [Fig. 2(b) (model b)], we obtain a conductance curve

[Fig. 2(d)] in good agreement with the experimental data shown in Fig. 1. In other words, the existence of two open and close cycles of the gap calculated in Ref. [5] does not necessarily lead to the appearance of peaks in the conductance (it depends on an incidental interplay from the contribution of the gap in the various sections under pressure). In contrast, within our model, the observed peaks in the conductance can only appear as a consequence of the existence of, at least, two open-close cycles in $E[h]$.

It is worth noticing that, according to Ref. [5], the gap structure critically depends on the details of the deformation path. This, together with changes in the geometry of the tip, could explain the variability observed in the experiments. We stress, however, that the physics of the conductance oscillations and not the quantitative agreement is indeed the central point of this work. This experimental situation is similar to that of the point contacts or the breaking junction experiments, where for each realization the measured conductance is different [18,19], depending on the precise conformation of the atoms on the nanometer neck, but with common features between the different realizations. As in the case of point contact experiments, atom rearrangement of the tip-nanotube junction could also be invoked to explain the conductance oscillations. However, a hypothesis based exclusively on atom rearrangement would predict conductance variations also for the case of MWNTs, large gap semiconducting tubes,
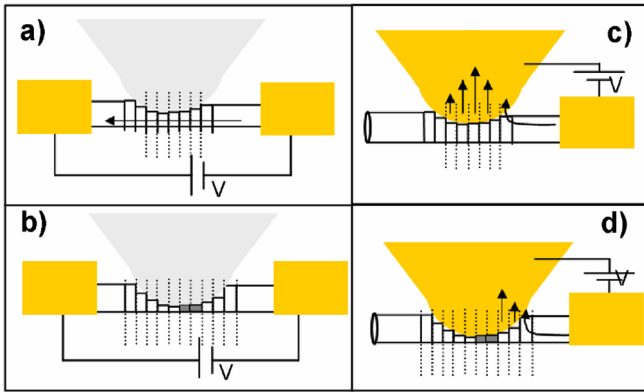
PHYSICAL REVIEW LETTERS

FIG. 3 (color online). Phenomenological model for a metallic tip. (a),(b) Two fixed electrodes and an insulating tip setup. In (b), a gap has opened by tip deformation: The current flow is blocked by the opened gap. (c),(d) Fixed electrode and a conducting tip setup. (e) is for the same deformation as in (b), but the current flow is possible through the outer sections of the contact area.

and high voltage conductance, but we have never observed either oscillations or a conductance drop in any of these three cases.

The signature of a band-gap opening in our conductance curves is very different from that observed on tubes deflected by an insulating tip. In particular, our measured conductance drop is lower than the 2 orders of magnitude jump reported previously [1]. This discrepancy is related to a fundamental difference between the experimental approaches. (In what follows, we will not consider the possible band-gap opening due to the longitudinal deformation induced by the stretching of the suspended tube in Ref. [1].) When the deformation is induced by an insulating tip, the opening of a gap, at any point along the deformed contact area, blocks the electron flow along the nanotube [see Figs. 3(a) and 3(b)] resulting on a dramatic drop of the conductance. The open-close cycle would then modulate the effective tunneling barrier leading to peaks superimposed on an exponentially dropping conductance. This exponential drop would make the conductance peaks difficult to observe. In contrast, in our experimental setup the electrons flow from the nanotube to the metallic tip (see Fig. 3). As discussed above, the opening of a gap under the tip apex induces a drop in the conductance, but there is a non-negligible current flowing to the tip through the less deformed regions of the contact. In this case, the opening and closing cycles of the band gap manifest themselves as conductance peaks.

In summary, we have reported measurements of the conductance of SWNTs under radial deformation. The experimental results, together with a phenomenological model, provide an understanding of the electronic structure of the tubes while being squashed. We find that a gap is opened before the tube is fully collapsed and that open-close cycles of the band gap are present during the radial deformation. Our fundamental findings clarify and simplify the situation described in previous works. Taken together, these results enable a better use of carbon nanotubes in NEMS.

[1] T. W. Tombler *et al.*, Nature (London) **405**, 769 (2000).
[2] E. D. Minot *et al.*, Phys. Rev. Lett. **90**, 156401 (2003).
[3] J. Cao, Q. Wang, and H. J. Dai, Phys. Rev. Lett. **90**, 157601 (2003).
[4] V. H. Crespi, M. L. Cohen, and A. Rubio, Phys. Rev. Lett. **79**, 2093 (1997).
[5] H. Mehrez *et al.*, Phys. Rev. B **71**, 155421 (2005).
[6] P. E. Lammert, P. H. Zhang, and V. H. Crespi, Phys. Rev. Lett. **84**, 2453 (2000).
[7] C. J. Park, Y. H. Kim, and K. J. Chang, Phys. Rev. B **60**, 10 656 (1999).
[8] J. Q. Lu *et al.*, Phys. Rev. Lett. **90**, 156601 (2003).
[9] O. Gülseren *et al.*, Phys. Rev. B **65**, 155410 (2002).
[10] P. J. de Pablo *et al.*, Phys. Rev. B **61**, 14 179 (2000).
[11] C. Gomez-Navarro *et al.*, Nat. Mater. **4**, 534 (2005).
[12] C. Gomez-Navarro, P. J. de Pablo, and J. Gomez-Herrero, Adv. Mater. **16**, 549 (2004).
[13] Z. Yao, C. L. Kane, and C. Dekker, Phys. Rev. Lett. **84**, 2941 (2000).
[14] K. L. Johnson, *Contact Mechanics* (Cambridge University Press, Cambridge, England, 1985).
[15] The Young modulus of the SWNT has been estimated from V. Lordi and N. Yao, J. Chem. Phys. **109**, 2509 (1998) to be 20 GPa, and the Young modulus of the tip has been considered to be the tabulated value for gold 80 GPa, the Poisson ratio of gold 0.4, and for SWNT 0.3. $Q$ is a geometric factor that accounts for the effective radius of the tip and nanotube.
[16] In order to compare $h$ and the atomistic lengths used in Mehrez *et al.,* we have to consider the atomistic size of the contacts, so the magnitude more suitable to be compared with the $h$ defined in our Letter is not the distance between the walls of the nanotube but the distance between the tip and the substrate, also defined in this reference.
[17] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, England, 1997).
[18] J. I. Pascual *et al.*, Science **267**, 1793 (1995).
[19] N. Agrait, J. G. Rodrigo, and S. Vieira, Phys. Rev. B **47**, 12 345 (1993).