Nonlinear charging, and transport times in doped nanotubes junctions

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Abstract

The nonlinear capacitance in doped nanotube junctions is calculated self consistently. A negative differential capacitance is observed when the applied bias becomes larger than the pseudogap of the metallic armchair nanotube. For this device, one can deduce a relaxation time of about 0.1 femtosecond. Because of its negative differential resistance (NDR), a switching time of less than a fs, i.e. at least 3 orders smaller than present day switching times, can also be estimated. This effect is important in designing ultra fast nano-electronic components.

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Proposals for the calculation of the quantum capacitance of a mesoscopic system were put forth by Büttiker[1] and coworkers and later its full quantum version was derived by Zhao et al. [2], where the correction terms to the geometrical capacitance, unlike the result derived previously by Büttiker, could become negative due to effects such as quantum tunneling (a “leaky” capacitor). The work, mainly by Büttiker and coworkers[1], on mesoscopic systems has studied the RC relaxation time in the presence of an applied AC field. They had already noted that the true capacitance in a mesoscopic sample has contributions from two hypothetical capacitances put in series: the first being the geometric one caused by the Coulomb interaction which also persists in macroscopic samples. The second is a material-dependent effect caused by the filling of the (quantized) states of the system; it exists even for non-interacting electrons, and becomes negligible for large metallic systems where the density of states (DOS) at the Fermi level becomes large.

Experiments observing a negative value for the capacitance of a metal-carbon nanotube junction in the AC regime have been performed by Zhao et al. [3]. A non-classical capacitance was also measured by Hou et al. [5] in single electron spectroscopy of a double barrier tunnel junction. In their setup, for a small tip-cluster separation, the non-classical behavior (reduction) of the capacitance and the resistance was interpreted in terms of quantum tunneling of electrons. Theoretical works on the ac-response of one-dimensional systems have also been done. These models[4] use the Luttinger liquid theory, which is the effective low-energy theory of one-dimensional systems, to describe screening and ac response in homogeneous 1D quantum wires. It is not clear, however, whether at high biases such theories remain valid since the linear dispersion at the two ends of the junction is not the same anymore, and furthermore, in this paper, we are considering junctions of doped nanotubes.

In this work, we have a fully quantum mechanical theory explaining the decrease in C which is closely related to the electronic band structure of the tube. Also, from our calculations, the relaxation time of the nanotube junction is found to be extremely fast, of the order of a fraction of a femtosecond. Additionally, the switching time of this device is estimated to be of the same order as well. These features are central for the design of nanoscale devices, as the switching time issue is of paramount importance in making fast chips.

In the presence of a time-dependent applied bias, the quantum capacitance and transport times in doped junctions made of carbon nanotubes have been calculated in a self-consistent
manner. In our model, this junction can be made by a nanotube deposited on or embedded in two different materials. Depending on the material, this can induce transfer of electrons to or from the tube. We had previously studied the I-V characteristics of a nanotube junction in the DC case[6, 7] and found that the current is a non-linear function of the applied voltage. For semiconducting tubes, a rectifying behavior was observed, whereas metallic tubes displayed a negative differential resistance (NDR) specially for narrow tubes where the quantization of the transverse levels (pseudogap) is more significant. For an applied AC voltage, in addition to its resistance, the tube will also manifest its capacitive properties. Indeed there is a region of charge accumulation at the junction where, due to the difference in the chemical potentials on opposite sides of the junction, there will be diffusion of electrons from the donor into the acceptor region, and diffusion of holes into the donor region. It was previously shown[8] that the depletion-layer length of such a junction is of the order of a few carbon-ring separations. The doped nanotube junction can thus be viewed as a capacitor with a capacitance $C$ in parallel with a resistance $R$ if one assumes that the potential drop occurs in the junction region. The response time of this junction is usually controlled by the time $\tau_{\text{relax}} = RC$ where $R$ is the resistance of the junction. Hidden beneath the apparent simplicity of this expression is the quantum electron transport time across the junction. Our exact quantum calculation of $R[7]$ has incorporated this effect. In this work, we focus on the calculation of $C$ and show that it is a nonlinear function of the voltage whose differential value can become negative. Furthermore, from the I-V and the Q-V characteristics, a switching time is defined and estimated for this junction. In what follows, the model and the calculation method will be described.

We consider an infinite ideal (defectless) nanotube doped with two different dopants on its left and right. The doping can be realized by either inserting dopant atoms inside the tube, by depositing the tube on a substrate, or by embedding it in a host material. In both cases, there will be a charge transfer to or from the tube which will now acquire different electronic properties due to the addition of charge and the eventual shift in its Fermi level. It is assumed that there are no charged impurities present in the proximity of the junction, and therefore the effect of disorder is neglected in this study.

The junction problem is solved in the real space within a one $\pi$ orbital tight binding (TB) formalism. First the two isolated half tubes are treated, i.e. their surface Green’s function $(G_{00})$ in the tight-binding basis is calculated by using the renormalization method[9], as-
suming the effective onsite energies and chemical potentials known\textsuperscript{10}. Then the junction problem is solved by using the Green’s Function (GF) matching method\textsuperscript{11}. This is done self-consistently in the junction region, by adding to the Hamiltonian, a Coulomb interaction term (Hartree potential) due to both onsite and other sites extra charges. The onsite (Hubbard) term $U \approx 11\text{eV}$\textsuperscript{12} is about 4 times the hopping integral $t$. We must emphasize that the calculation of the transmission coefficient from which the two-terminal resistance of the junction is derived is an exact calculation within the self-consistent TB model.

A (3,3) and a (5,5) armchair nanotube\textsuperscript{13} were considered in this calculation as the nonlinear effects are more pronounced in small radius tubes. The junction region includes 8 unit cells and is of length $19.4\,\AA$. The onsite energies on the left and right tubes are respectively $U_L$ and $U_R$. The unit for energy or voltage is the hopping matrix element $t = 2.7\text{eV}$.

From the GF, one can compute the conductance, and the charge distribution in the junction region as a function of the applied bias. Thus both relations $Q(V)$ and $I(V) = \dot{Q}(V)$ can be obtained from this calculation. Fig. 1 shows the depletion charge profile of a (5,5) tube in the junction region which contains 8 layers (16 carbon rings). It was checked that increasing the number of layers did not change the amount of charge transfer on these layers\textsuperscript{8}. The depleted charge is calculated for two different dopings of $|U_L| = |U_R| = 0.1t$ and $0.5t$.

For large voltages, the charge-bias relation becomes nonlinear. The bandwidth of the local density of states (LDOS) in the junction region is larger than that of the bulk tube by the amount of the bias voltage. As a result, after the bias becomes greater than the pseudogap of the tube, the accumulated charge is reduced.

This nonlinear relation is displayed in Fig. 2 where the average charge is the sum of the charges on all rings on one side of the junction. For large biases, the charge on each side of the junction is not strictly zero but oscillates along the tube axis so that its average value becomes nearly zero. This oscillation plays an important role in determining the characteristics of the device since it causes the charge on one side of the capacitor to become small and yield a small switching time. The nonlinear $I(V)$ curve is also displayed in this figure.

We calculate the linear capacitance as the ratio of the charge induced on the two sides of the junction, divided by the applied voltage: $C = Q/V$. For small bias voltages, the
charge-bias relation is linear, and, assuming a hopping of 2.7 eV and the slope to be 0.55 electron/hopping, we obtain a capacitance of $2.8 \times 10^{-20} F$. This is comparable but smaller than the “geometrical” capacitance $C_g = \epsilon A/d \approx 3.6 \times 10^{-20} F$, where $A$ is the area of the nanotube (ring of circumference 21 Å and thickness 3.3Å), $d$ is the distance between the dipole layers (about 5Å) and $\epsilon = 3$ is the in-plane dielectric constant of graphite.

Taking the resistance $R$ to be $6.5 k\Omega$, we find a very fast relaxation time of $\tau \approx 0.2$ femto second. The resistance of a nanowire is always of the order of $h/2e^2 = 13 k\Omega$, and the capacitance is about $9 \times 10^{-12} A/d \approx 10^{-11} F = 10^{-20} F$, resulting always in a relaxation time of the order of $10^{-16}s$, or, including the dielectric constant, a fraction of a femto second. A smaller separation and sources of disorder may increase this value by an order of magnitude.

The fast relaxation time in junctions of nanowires comes about not only because the capacitance is very low but also because the resistivity is so small. Carbon nanotubes have a very small resistivity $\rho$, and furthermore, their resistance does not increase with length. We emphasize the resistivity of the junction is related but not the same as that of the carbon nanotube. It comes from a detailed sophisticated quantum transport calculation. That the magnitude is so small has not been perhaps emphasized enough previously. In general the resistance is inversely proportional to the area, $R \propto \rho/A$, whereas the capacitance is proportional to $A$. The time constant $RC$ is thus generally independent of $A$ no matter how small the device is! However, in the case of nanotubes only, the conductance of the tube is of the order of $2 \times 2e^2/h$ and thus independent of its cross sectional area.

From the knowledge of the relationship between the charge $Q(V)$ and the current $\dot{Q}(V)$ as a function of the bias, one can obtain the dynamics of this device. The slope at zero (small bias) is the relaxation time $\tau = RC$ already discussed. The other characteristic time which can be observed at biases where the NDR effect is seen is called the switching time. It is the time necessary for switching from ”zero” current (in the I-V valley) to its maximum value.

The switching time can be observed as the other characteristic time scale in the plot of charge versus current after the current has reached its maximum value. In Fig. it can be identified as the large, almost vertical slope seen on the right side of the s-shaped curve. According to our calculations, it is less than an order larger than the relaxation time ($\tau_{switching} \approx 4.5\tau_{relaxation}$ for the (3,3) tube). It is therefore still of the order of a femtosecond.
In general, the switching speed is enhanced if the peak to valley ratio of the NDR characteristic is large. Indeed this would stretch the curve in the $\dot{Q}$ direction, and therefore increase the denominator $\Delta \dot{Q}$, thereby reducing the switching time. As the device becomes comparable in size to the mean free path or larger, the resistance starts increasing with length, and both the relaxation time and the switching time increase. So for nanoscale systems where there is quantum coherence, one expects to obtain very fast devices capable of handling high switching speeds.

Inductive effects in this device have been neglected. The inductance $L$ for a device of size $l$ is of the order of $\mu_0 l$ and thus the impedance is about $L \omega \approx \mu_0 l \omega \approx 10 \Omega$ for a nanometer-length device at frequencies of $10^{16}$ Hz. This number is still a thousandth of the resistance of the junction, and therefore can be justifiably neglected.

There are three effects that can affect the relaxation: Impurity scattering, electron-phonon scattering and radiation. Carbon nanotubes have no impurities in their structure unless made on purpose. The electron mean free path being of the order of 1000 nm or more in nanotube ropes, it is very unlikely to find impurities within or near the junction which is of a much smaller size. Their potential is therefore very smooth and will not affect the properties of the electrons in the junction region.

Electron-phonon interactions will increase the resistance, but this increase is by a factor of the order of unity (see ref. [17] for example). The other effect which becomes important at such high frequencies is radiation. The radiated power is proportional to the second power of the acceleration of electrons which is itself quadratic in frequency. At high frequencies, one thus expects some power loss by radiation. The radiated power by a dipole is approximately $P = v^2 \omega^2 \beta$ with $\beta \approx \sqrt{\mu_0/\epsilon_0} e^2/c^2$. We assume that the shape or geometry of our device affects this coefficient by a factor of the order of one. The radiated power being quadratic in the velocity, one can associate a damping force to it: $F_{\text{damping}} = P_{\text{rad}}/v = -mv/\tau'$ with a relaxation time $\tau' = m/\beta \omega^2 = \sqrt{\epsilon_0/\mu_0 mc^2/\epsilon^2 \omega^2}$. This time should be compared to the relaxation time at frequencies of the order of $10^{16}$ Hz. A numerical substitution shows that $1/\tau' \approx 10^9$Hz $\ll 1/\tau \approx 10^{16}$ Hz. Thus, the relaxation time due to radiation does not depend much on the characteristics of the system except for the $\omega^2$ dependence, and radiation does not affect the relaxation time either.

In summary, we find that one can define two different time scales for such a junction displaying NDR and nonlinear charging properties: 1) the relaxation time (RC) which is
just the time necessary for the initially charged junction to discharge provided that the bias is small enough so that the device characteristics are linear; 2) the switching time which is the time needed for the voltage to transit from the NDR valley to the linear region. For the doped nanotube junction considered here, both times are very short because the resistivity of carbon nanotube is very low. This makes it attractive for possible practical applications.

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[10] The effect of the substrate or dopants is to transfer some charge to the tube. This modifies the onsite energies which we assume to be known for the two semi-infinite tubes. From this, the additional charge can be easily deduced without any need to perform a self-consistent calculation, if the onsite energies are uniform. At the junction, however, a self-consistent calculation needs to be performed in order to determine the charge and potential profiles, even if the two separated half tubes are treated non-selfconsistently.

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[14] $C_{\text{equivalent}}^{-1} = C_{\text{geometrical}}^{-1} + C_{\text{quantum}}^{-1} = \epsilon A/d + e^2 DOS(\mu)$. This relation, already explained in the introduction, explains why the real value of the capacitance of a nanodevice is always smaller than its geometrical value.
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FIG. 1: Charge transfer across the junction in a (5,5) armchair tube under the bias of 0 and 0.75 eV, for two different dopings of $U_{l,R} = 0.5$ and $U_{l,R} = 0.1$. The central cell contains a total of 8 layers or 160 atoms.
FIG. 2: $Q(V)$: Average charge ($e$) and $I(V)$: current in $2e/h \times t$ versus the applied bias (in $t$) for a (3,3) and a (5,5) nanotube with onsite energies of $-0.5t$ for the left and $0.5t$ for the right side tube. The residual dipole charge at zero bias at the interface due to doping has been subtracted in order to have curves passing through the origin.
FIG. 3: Phase space trajectory $(Q, \dot{Q})$ for both (3,3) and (5,5) tubes at $p_{doping}$ doping level. It is asymmetric due to the asymmetry caused by N-P doping.