

DOPING STATE OF MULTI-WALL CARBON NANOTUBE WIRES AND QUANTUM DOTS

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Abstract

Employing strong electrostatic gating (liquid-ion gating), the position of the Fermi energy E_F (relative to the charge-neutrality point) was determined in multi-wall carbon nanotubes (MWNTs). E_F is negative (hole doping) and amounts to $\approx -0.3\text{eV}$ for MWNTs in air. Evidence that water, and not oxygen, is the main source of doping has been found. As a consequence, the number M of occupied 1d-modes (not counting spin) is > 2 , i.e. $M \approx 10$. This is supported by the single-electron level spacing, deduced from observed single-electron charging effects (SET) at low temperature. The latter are dominated by co-tunneling processes, as we observe the Kondo effect. This provides evidence, that highly transmissive channels are present in MWNTs at low temperature, despite the ‘disorder’ observed in previous experiments.

1 Introduction

Carbon nanotubes (CNTs) are ideal model systems for the exploration of electrical transport in low dimensions.¹ Two sorts of nanotubes (NTs) exist: Single-wall and multi-wall NTs. An ideal (undoped) SWNT can be either metallic or semiconducting, but here, we only focus on metallic NTs. In these tubes, the current is carried by two modes,^a leading to a conductance of $4e^2/h$, provided backscattering is absent. Recent experiments have shown that scattering within metallic SWNT is weak. In a particular nice experiment the electrostatic potential drop along a voltage-biased NT was measured by using the tip of an atomic-force microscope as a probe.² For SWNTs, most of the potential drops at the contacts. In contrast, for MWNTs a considerable fraction of the potential drops along the tube, suggesting intrinsic scattering in MWNTs. A length dependent resistance was deduced before from electric resistance measurements on multiply contacted MWNTs.³ The typical value for the resistance per unit length is $R' = 5 - 10\text{k}\Omega/\mu\text{m}$. We mention, that there is one conflicting results: Frank *et al.*⁴ came to the conclusion that MWNTs are ballistic conductors even at room temperature.^b Seemingly compelling evidence for diffusive transport in MWNTs is provided by measurements of the magnetoresistance, both in parallel and perpendicular magnetic field.³ For example, the resistance modulation in parallel magnetic field can be described very well by the Altshuler-Aronov-Spivak (AAS) theory (weak-localization in a cylindrical conductor), which relies on *diffusive* transport.⁵ These experiments did also show that the electrical current is preferentially carried by the outermost tube, at least at low temperatures. Hence, a single nanotube is probed, albeit one with a large diameter of $d \approx 10 - 20\text{nm}$, which is about ten times larger than that of prototype SWNTs. As emphasized before, a metallic SWNT is characterized by only $M = 2$ 1d-modes, a property that should be independent of the diameter. How can we then reconcile the availability of only 2 modes for an ideal NT with the observation of diffusive motion. Diffusive transport requires $M \gg 1$. May it be that MWNTs are doped to a such a degree that $M \gg 1$?

By using a new gating technique (electrochemical gating), we have recently shown that MWNTs are indeed (hole-) doped.⁶ The number of 1d-modes is $\neq 2$, but rather $10 - 20$, see section 2. MWNTs are not single-mode, but rather few mode quasi-one-dimensional wires. Whether

^a If we refer to M modes, spin-degeneracy is not included.

^b Note, that ballistic transport is not expected in MWNTs at room temperature, because the energy-separation between 1d subbands is comparable to kT .

they are 1d diffusive, i.e. quasi-ballistic with a mean-free path l exceeding the circumference πd , or $2d$ diffusive ($l \leq \pi d$) is another question.

Taking $R' = (2Me^2l/h)^{-1} = 5\text{ k}\Omega/\mu$ (L is tube length), yields $l \approx 100\text{ nm}$ which is of order of the circumference. This simple estimate is in good agreement with measurements of the energy-dependent tunneling DOS $\nu(E)$. $\nu(E)$ is not structureless, as would be expected if $l \ll \pi d$, but shows features reminiscent of quantization into 1d-modes, albeit with some broadening.⁷

Recently, we have studied gate-induced conductance fluctuations in MWNTs at low temperatures and tried to compare the measurements with UCF theory. In the regime of thermally-induced averaging, i.e. for tubes which are much longer than the phase-coherence length l_ϕ and/or the thermal length l_T , the functional dependence is in agreement with theory. These data allow to deduce l_ϕ , which follows Nyquist-dephasing below $\approx 4\text{ K}$. However, when we approach the universal limit, i.e. if $L \approx l_\phi$, the temperature dependence of conductance fluctuations markedly deviates from standard theories. This has led us to study shorter tubes in more detail by measuring the differential conductance $G_d = dI/dV$ as a function of transport voltage V and gate voltage U_g in the fully coherent regime, i.e. for $l_\phi \sim L$. Displaying $G_d(U_g, V)$ in a greyscale plot helps to recognize the underlying physics. This is in particular true for single-electron charging effects which might be present simultaneously to quantum interference effects, both modulating the equilibrium conductance.

Single-electron charging effects (single-electron tunneling = SET), such as Coulomb blockade and Coulomb oscillations were observed in SWNTs from the beginning.⁸ However, in our own work on MWNTs we have never observed clear evidence of Coulomb blockade until now. We have argued that this absence is due to the low-ohmic contacts in our experiments, which are always of order $\lesssim 10\text{ k}\Omega$.³ In contrast, measurements on MWNTs with high-ohmic contacts ($> 10^6\ \Omega$) display the conventional features of single-electron charging effects.⁹ The evaporation of Au over the nanotubes, the method we prefer for fabricating contacts, leads to contact resistances that can be as low as $1\text{ k}\Omega$ at room temperature. This is low enough to suppress SET. At cryogenic temperature, however, contact resistances usually increase, so that SET may show up. In section 3 we present our first (and still rare) observation of SET in transport through a MWNT with ‘low-ohmic’ contacts. Since the coupling to the contacts is rather strong, the conductance is dominated by higher-order co-tunneling processes. These new data allow to extract the single-particle level spacing δE of the MWNT quantum dot. Similar to the result from electrochemical gating, the measured δE suggests that ≈ 10 modes are occupied.

2 Doping state of multi-wall carbon nanotubes

In order to determine the degree of doping in MWNTs (or other nanotubes) the position of the Fermi energy need to be determined. One possible approach is to measure the conductance as a function of a gate voltage U_g , which shifts the Fermi energy E_F . If the conductance G increases (decreases) with increasing E_F , the NT is n-doped (p-doped), see Fig. 1a. At, or in the vicinity of the charge-neutrality point (CNP), the number of modes is minimal. It is 2 for a metallic tube and zero for a semiconducting one.^c Hence, one expects to see a conductance minimum (or a resistance maximum) if E_F crosses the CNP. Ideally, for an undoped NT, E_F should lie at the CNP and the resistance maximum should appear at $U_g = 0$. If this maximum is observed at $U_g \neq 0$, the Fermi level is shifted due to some doping. In order to deduce E_F from the measured gate voltage, the electrochemical capacitance between gate and NT needs to be known. Conventional back gates (see Fig. 1b) have relatively low capacitance. Consequently Fermi-level shifts are small even for large applied gate voltages. In this case, the resistance maximum cannot be measured, and hence, the doping level cannot be determined. This problem is circumvented

^c At room temperature the 1d bandstructure in Fig. 1a is considerably smeared, so that no abrupt transitions are expected if E_F crosses a band onset.

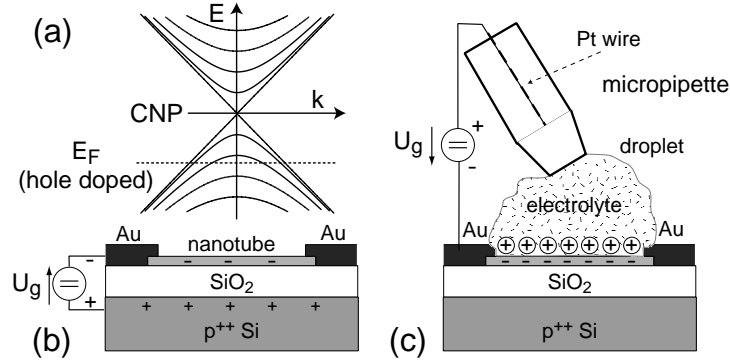


Figure 1: (a) Simplified 1d bandstructure of a metallic carbon nanotube. CNP, the charge neutrality point, refers to the position of the Fermi energy E_F of an undoped nanotube. The nanotube is hole (electron) doped if $E_F < CNP$ ($E_F > CNP$). E_F can be changed via the gate voltage U_g , conventionally applied to the substrate (backgate), as shown in (b). Much larger Fermi-energy shifts are possible through liquid-ion gating, (c). LiClO_4 (1 – 500 mM) was used as electrolyte.

in our approach, in which the coupling capacitance is made very large. We immerse the nanotube into an electrolyte through which gating is achieved, see Fig 1c. For details, see Ref. 6. Very large gate capacitances are possible due to the large double-layer capacitance of the electrolyte NT interface. This has an important implication: Because the double-layer capacitance is much larger than the electrochemical capacitance of the NT, the total capacitance (series connection of the two) is determined by the nanotube alone. Hence, there is a one-to-one correspondence between gate-voltage change ΔU_g and Fermi level shift ΔE_F , i.e. $\Delta E_F \cong \Delta U_g$.

Electrochemical gating is studied at room temperature on single MWNTs with lithographically defined Au contacts evaporated over the NTs. The nanotube-contact structure is fabricated on degenerately doped Si with a 400 nm thick SiO_2 spacer layer. The substrate can be used as a conventional backgate, Fig 1b. If, as outlined in Fig. 1c, a positive gate voltage U_g is applied, the NT-electrolyte interface is polarized by the attraction of cations. Consequently, the Fermi level increases in the NT to maintain charge neutrality.

An example for the dependence of the nanotube resistance on (electrochemical) gate voltage is shown in Fig. 2. A pronounced resistance maximum is seen at $U_g = 1\text{V}$, which we identify as the CNP. In order to reach the CNP the Fermi energy must first be raised by $\approx 1\text{eV}$. This suggests that the NT is considerably hole-doped at $U_g = 0$. There is, however, a time dependence (not shown).⁶ After immersion, the resistance maximum is observed at a smaller voltage of $\approx 0.3\text{eV}$. The position of maximum R then gradually moves to larger voltages to finally stabilize at 1 V in this example. Hence, the doping level increases in the electrolyte. Typical Fermi-level shifts in air (before immersion) amount to 0.3 – 0.5 eV.

Based on measurements of the electrical resistance of SWNTs in a controlled environment of different gases it was suggested that hole-doping is induced by oxygen.¹⁰ Our own experiments show that oxygen has an effect on the doping state of MWNTs. However, the effect is weak, as much larger doping shifts are seen in ambient air. An example is shown in Fig. 3. Here, we compare the evolution of the resistance of a MWNT at zero (back-) gate voltage when exposed to oxygen and air. Prior to exposure, the NT was annealed at 50C° in vacuum. As a consequence of added hole doping the resistance is seen to decrease. The decrease is much more pronounced for air than for oxygen. The resistance increases again in vacuum, nicely demonstrating that the oxidizing species are only weakly adsorbed. The strongest source of doping is most likely due to water, as large Fermi-level shifts can be induced by water vapour alone.

For the interpretation of previous electrical measurements, the net doping concentration Q_d and the Fermi-level shift for a ‘virgin’ MWNT in air are important. Typical values for the latter

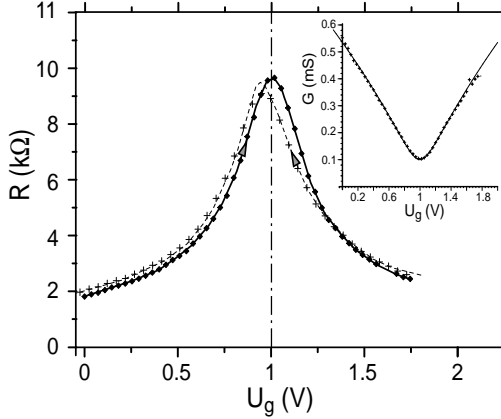


Figure 2: (Left) The typical evolution of the electrical resistance R of a single MWNT with gate voltage U_g measured in a 10 mM LiClO_4 electrolyte. Inset: Comparison of $G = 1/R$ (\bullet) with theory (full curve), see Ref. 6.

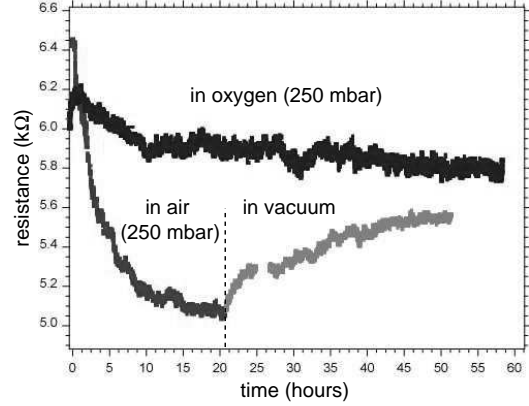


Figure 3: (Right) Doping induced change of the electrical resistance caused by the adsorption of (a) oxygen and (b) air. The nanotube was annealed before exposure. The resistance decrease is caused by increased hole-doping. Air (most likely water vapour) has a much bigger effect than pure oxygen.

are $0.3 - 0.5 \text{ eV}$. Comparing this with the average 1d subband spacing $\hbar v_F/2d$ ($\approx 33 \text{ meV}$ for a 10 nm diameter NT), we conclude that $M = 9 - 15$ subbands may contribute to the conductance instead of 2 for an ideal metallic NT. A doping-induced $E_F = 0.3 \text{ eV}$ corresponds to a doping concentration of $Q'_d/e \approx 2 \cdot 10^3 \mu\text{m}^{-2}$, or expressed per surface area to $Q_d/e \approx 0.7 \cdot 10^{13} \text{ cm}^{-2}$ giving approximately one elementary charge per 500 carbon atoms.

3 Multi-wall carbon nanotubes as quantum dots

As mentioned in the introduction single-electron tunneling (SET) such as Coulomb oscillations have been observed in MWNTs and SWNTs, provided the contacts were high-ohmic, i.e. $> 1 \text{ M}\Omega$.^{8,9} In the opposite limit of relatively low-ohmic contacts of order $\lesssim 10 \text{ k}\Omega$ charging effects have not yet been observed in transport through MWNTs. Though we have observed pronounced conductance oscillations as a function of gate voltage¹¹ and also as a function of magnetic field in the latter type of samples³, these cannot readily be assigned to charging effects, as the oscillations were strongly aperiodic. We have assigned these oscillations to quantum interference of non-interacting quasi-particles, with the interference being caused by the presence of randomly distributed scatterers. It may be that this interpretation need to be reconsidered, since we have recently observed SET effects in MWNTs low-ohmic contacts ($\lesssim 10 \text{ k}\Omega$).

In order to entangle SET from quantum interference it is useful to measure dI/dV as a function of gate voltage U_g and transport voltage V . The obtained greyscale plots greatly helps to recognize the underlying physics.

In small (semi) isolated objects, like our MWNT devices, transport may be blocked by Coulomb interaction (Coulomb blockade). This is the case, if the energy for adding a single electron to the tube (the single-electron charging energy $e^2/2C$) is larger than the thermal energy kT and if the object is only weakly coupled to external leads (contact resistance $\gtrsim h/2e^2$). Coulomb blockade is suppressed if the energy of two charge states are degenerate. For example, if $E(N) = E(N + 1)$, where $E(N)$ denotes the total ground-state energy of the NT with N electrons, an equilibrium current can flow via the sequence $N \rightarrow N + 1 \rightarrow N$. Such degeneracies can be induced by the gate voltage U_g and appear in the simplest possible model (constant interaction model) periodic in U_g . In SWNTs Coulomb blockade has been observed by several groups before.⁸ Until now, it was believed that MWNTs do not display Coulomb blockade because

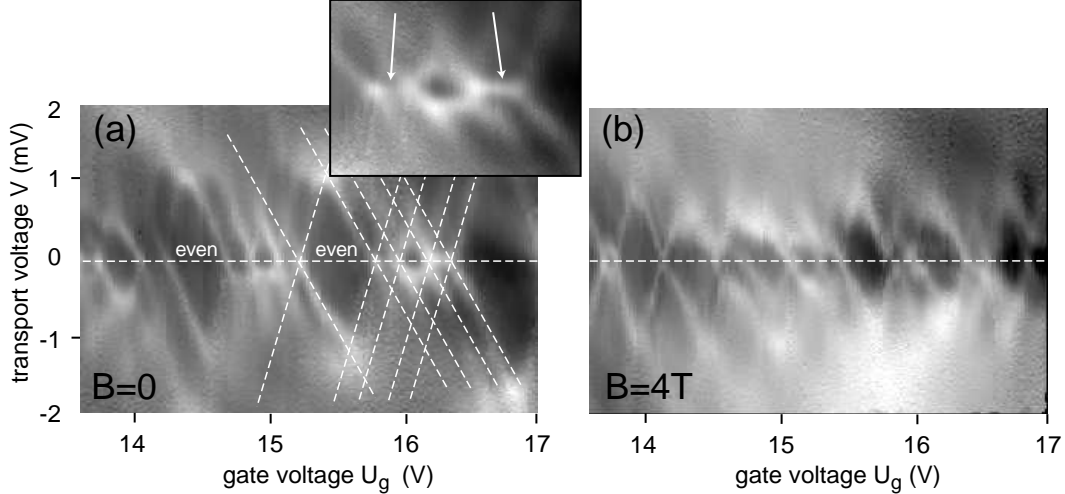


Figure 4: Differential conductance dI/dV as a function of transport voltage V (vertical) and gate voltage V_g (horizontal). White (black) corresponds to high (low) conductance. (a) was measured in zero magnetic field B and (b) in $B = 4$ T. The observed pattern is caused by single-electron charging effects. The inset shows a zoomed in portion of (a) in which two horizontal ridges (arrows) of high conductance are seen. These ridges are caused by the Kondo effect.

of low contact resistances. Recently, we have observed clear signatures of single-electron charging in a 300 nm long MWNT (distance between the contacts) with reasonably low-ohmic contacts (i.e. contact resistance $\lesssim h/2e^2$). An example is shown in Fig. 4 ($T = 270$ mK). In (a), measured for $B = 0$, a regular sequence is seen consisting of a large ‘diamond’ followed by three smaller ones.^d This pattern suggests a four-fold degeneracy of the single-electron states which we assign to spin degeneracy and an additional twofold orbital degeneracy. The latter may be caused by a peculiar degeneracy inherent to the graphite lattice, the so-called K, K’ degeneracy which originates from the presence of two identical carbon atoms per unit cell. If this interpretation is correct, this is quite amusing, because this basic feature has up to now not been seen in SWNTs.

Fig. 4b shows dI/dV measured at $B = 4$ T. Now, an irregular sequence is observed. It is well known that the K, K’ degeneracy is lifted in magnetic-field.

On the one hand, we do see clear signatures of Coulomb blockade suggesting low transparent contacts. On the other hand, the measured two-terminal resistance is low, of order of $h/2e^2$, suggesting highly (or intermediate) transparent contacts. Therefore, higher-order tunneling processes can play an important role in the electrical transport. A well known higher-order tunneling process is the Kondo effect, i.e. the dynamic screening of the spin on the dot due to exchange-correlation effects between the dot state and the electrodes. We observe the Kondo effect in a MWNT for the first time, see the features in Fig. 4., which are highlighted by arrows. At $V = 0$ and within the region of Coulomb blockade there are two ‘ridges’ of enhanced conductance. For the simplest filling scheme, i.e. $S = 0 \rightarrow 1/2 \rightarrow 0 \dots$, these ridges are expected to form in every second ‘diamond’ where the spin is $S = 1/2$. The Kondo effect has been observed before in SWNTs.¹²

The data in Fig. 4 allow to extract the single-particle level spacing δE . The large diamonds are large because an electron has to be added to a new level. The addition energy is therefore the sum of charging energy E_c and δE . Due to the fourfold degeneracy, the addition energy for the next three electrons is only E_c . Comparing the energies leads to a mean level spacing of $\delta E \approx 0.4$ meV. The 0d level spacing is predicted to be $\delta E = hv_F/2L$ for one mode, yielding 5.5 meV ($L = 300$ nm). The number of modes participating is therefore $M = 5.5/0.4 \approx 14$.

^d For other gate voltages the pattern can look quite different, not resembling SET effects at all.

Again we see that there are more than 2 modes occupied in MWNTs.^e

Since the measured two-terminal conductance $G \sim 2e^2/h$,^f the mean transmission probability T per mode is only 0.1 (here, we have taken $M = 10$). If all modes would have $T = 0.1$, co-tunneling effects like the Kondo effects could safely be neglected. Hence, there must be a distribution of transmission eigenvalues similar to that in many-mode diffusive wires. For the latter, random-matrix shows that the distribution is bimodal. Although we are dealing with a very small ensemble (only 10 modes), the distribution of transmission values is most likely bimodal, too. Though there are ≈ 10 modes available to accommodate charge, charge transport to the contacts is determined by only one mode (or a very small number of modes). If the mode with highest transmission probability has the appropriate T (not too low, but also not too high), the Kondo effect will show up.¹³ If T is larger, the observed conductance pattern can no longer be assigned to co-tunneling SET effects but rather reflects Fabry-Perot type interference.¹⁴

4 Conclusion

Multi-wall nanotubes in air are hole doped, most likely induced by the adsorption of water. Consequently, there are more than two 1d-modes occupied. A typical number is 10, not counting spin degeneracy. Estimates for the scattering mean-free path l vary widely in the literature and also among our own experiments. However, surprisingly many experiments suggests that the l is of order of the circumference of the tube. This may be a coincidence, but might also have a deeper reason: It was pointed out very early by White *et al.*¹⁵ that the mean-free path should grow with tube diameter d according to $l \propto d$, provided the number of scatterers per unit length is constant. On the other hand, if we assume that the source of scattering is a direct consequence of doping, the scattering density is proportional to the doping density which for a given environment can be taken to be constant. Therefore, the number of dopants per unit length (or the number of scatterers) grows linearly with d . The combination of both effects results in a diameter independent mean-free path. Another argument for a diameter-independent mean-free path in MWNTs was put forward by Egger and Gogolin.¹⁶

At low temperature, single-electron tunneling (SET) effects have been observed in MWNTs with low-ohmic contacts, i.e. $\lesssim 10 \text{ k}\Omega$. This has allowed to determine the single electron level spacing which appears to be consistent with the estimated number of occupied modes deduced from electrochemical gating. The presence of co-tunneling points to high transmission at the contacts. Even stronger: the prevailing absence of SET effects in MWNTs with $G \sim 2e^2/h$ suggests that at least one highly transmissive channel is present at low temperature.

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^e Note, that we have taken $v_F = 8 \cdot 10^5 \text{ m/s}$ to be constant in this estimate. This might be wrong because of the dispersion of higher subbands, lowering v_F .

^f $G \approx 2e^2/h$ is a typical value for all our MWNT devices with contact separation $L \approx 300 \text{ nm}$.

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