Contacts, non-linear transport effects and failure in multi-walled carbon nanotubes

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Abstract. Pristine arc-produced multi-walled carbon nanotubes are contacted to liquid mercury \textit{in situ} in a transmission electron microscope. The conductance \(G(V)\) for all tubes increases with increasing bias voltage \(V\). This is related to the electronic density of the nanotubes. Similar \(G(V)\) behaviour is observed for HOPG-graphite contacted in air with Hg, with \(dG(V)/dV \sim 0.3G_0\). Variations observed in the conductance are related to nanotube–Hg contact effects. For tubes barely touching the Hg surface, the conductance is low (typically \(G(V = 0) \sim 0.1–0.5G_0\)); \(G(V)\) may maximize around \(V = 1.5–2\) V or continue to increase linearly depending on the MWNT–Hg contact. For good contacts the maximum low-bias conductance is \(1G_0\). Non-conducting tubes are observed having a low-bias conductance smaller than \(10^{-3}G_0\). High-voltage tube failure usually occurs at the contact with Hg for clean tubes, or at tube defects. An important phenomenon is the formation of a Hg bubble near the contact nanotube–Hg surface when the nanotube is negatively biased, under high bias current conditions, indicating the heating effect of hot electrons injected into the mercury.

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1. Introduction

Electronic transport in carbon nanotubes is non-trivial as evidenced by the wide variety of mechanisms that have been proposed to describe it [1]–[7], even though the basic electronic structure has been known for more than a decade [8, 9]. For example, in early work, multi-walled carbon nanotubes (MWNTs) were classified as three-dimensional or two-dimensional diffusive conductors [1, 10]. Measurements on lithographically contacted nanotubes found that the electronic transport was complex and varied from one tube to the next, involving among other things serpentine electronic trajectories [2]. In contrast, our earlier work [4] found remarkable uniformity in the transport at room temperature, which led us to conclude that the transport is one-dimensional. Our experiments were the first to demonstrate ballistic transport in any nanotube. These conclusions were drawn from several observations, including the propensity of the conductance to be quantized in units of the conductance quantum ($G_0 = 2e^2/h = (13 \text{ k}\Omega)^{-1}$), the very weak dependence of the conductance on the length of the nanotube and the extremely large current densities that the nanotubes could sustain. Our more recent (room-temperature) measurements have demonstrated that the intrinsic resistance of MWNTs is very small: in particular, for a nanotube of length $L$, the typical intrinsic resistance per unit length, $R/L < 100 \Omega \mu\text{m}^{-1}$ [11]. The intrinsic resistance of a typical MWNT of a few $\mu\text{m}$ long is much smaller than $1/G_0$ shows that it is a ballistic conductor [12, 13]. Consequently, the dissipation occurs at the contacts. Part of this resistance is due to the quantum mechanical aspects of the electronic coupling of a collision-free one-dimensional conductor to a metal contact, which gives quantized conductances [12, 14]. The other part is due to scattering at the metal–nanotube interface, which reduces the transmission coefficient [12, 14].

While recently a consensus appears to have been reached that under favourable conditions, SWNTs are ballistic conductors [6, 7, 15], there is still some controversy surrounding MWNTs, some concluding that they are diffusive conductors [1, 5, 10, 13, 16], and others that they are ballistic conductors [4, 11, 17, 20]. Transport in MWNTs was shown to be phase coherent over distances of order 1 $\mu\text{m}$ [18, 19]. Discrepancies can be partly traced to variations in nanotube production and preparation methods. In fact, catalytically produced
MWNTs [21] may be so defective that neither individual layers are distinguished; they may not even have an interior cavity. Many of these graphitic structures should rather be classified as nanoscopic graphite fibres. Nevertheless, they are collectively called nanotubes, causing considerable confusion, since the transport properties vary considerably. The MWNTs described here are (essentially) defect-free multilayered straight tubular graphitic structures produced using the catalyst-free high temperature carbon-arc method [22].

The contacting method also may cause a variety of transport behaviours. Several layers may be connected at the contact itself either intentionally, by breaking open the tube ends, or by potential damage due to heat or irradiation treatment. Also contact has been realized to a clean and largely undoped inner layer through tunnelling to a semiconducting outermost disorder and doped layer [18]. Transport may also be affected due to interaction with a substrate.

In this paper we address high bias voltage effects of essentially defect-free suspended nanotubes and effects of nanotube to metal contacts on the transport. As already discussed extensively [4, 11], the room temperature conductance of clean nanotubes is essentially independent of the dipping length $L_D$ for large $L_D$ and on distances up to a few $\mu$m ($L_D$ is the length of the nanotube that is in contact with the mercury). In fact, as a clean MWNT is brought in contact with liquid mercury, the conductance initially jumps to a finite value, then increases with $L_D$ in a rounding until it reaches a plateau. We have demonstrated [11] that for clean tubes the typical residual slope on the plateau is small (this is the intrinsic resistance per unit length of the tube $R/L < 100 \, \Omega \, \mu$m$^{-1}$). We have shown that the entire variation of the conductance with $L_D$ can be attributed to the contact itself, so that the conductance is essentially of the form $G^{-1} = G_t^{-1} + G_{\text{contact}}^{-1} = G_t^{-1} + R^*/L_D$ (more precisely a tip conduction can be also included so that the contact conductance can be written as $G_{\text{contact}} = G_{\text{tip}} + L_D/R^*$). The typical mercury to nanotube contact resistance $R^*$ is in the range 0.1–1 k$\Omega$ $\mu$m$^{-1}$. Because of the low intrinsic resistance of the clean suspended MWNT, we expect the conductance of tubes making a small contact with liquid metal to be mostly determined by the contact contribution. Therefore, the geometry of the contact and the dipping length on a small scale (determined by the nanotube contact resistance) are decisive.

2. Experimental methods

The MWNTs are produced in a pure carbon arc in a pristine He environment at a pressure of about 0.5 bar [22]. A fibrous soft sooty material deposits on the cathode, composed of fibres that are typically 1 mm long and 0.1 mm wide. The fibres are composed of densely packed MWNTs, typically 10 $\mu$m long and 5–30 nm in diameter [4, 11, 17]. Nanotubes protrude from the fibre, to which they are found to make good electrical contact. The fibres are connected to metal leads with silver adhesive, to make contact with the protruding nanotubes and to bypass complex and potentially damaging lithography procedures. The contacted nanotubes are used in a variety of experiments to investigate metal–nanotube contact properties.

*In situ* transmission electron microscope (TEM) experiments are performed by attaching a fibre to a moving stage so that it can be manipulated (translated and rotated) in the field of view of the microscope. In this way a protruding nanotube can be brought near to or into contact with an opposing electrode so that current can pass through the nanotube. More than 50 MWNTs have been individually measured. Various counter electrodes are used.
Figure 1. Conductance $G = I/V$ as a function of bias voltage $V$ for a clean MWNT connected on one side to its pristine fibre and on the other side to liquid Hg in air from $V = -4.0$ to $+4.0$ V. Note the striking symmetry and the essentially perfect linearity of $G(V)$. This is a robust property of the nanotubes studied in these experiments. The current at $V = 4$ V corresponds to $I = 620 \mu\text{A}$. Inset: $G(V)$ of a nanotube for various depths, $L_D$, of the nanotube submerged into the Hg: 50, 200, 400 and 700 nm for open circles, full circles, open squares and full squares respectively.

such as flame-annealed gold electrodes or liquid metal (typically mercury) electrodes. In this configuration, current versus voltage measurements are made, typically by sweeping the voltage at a rate of the order of 1 Hz between two preset voltages (typically from $-3$ to $+3$ V). The tube is grounded and the voltage is applied to the opposing electrode.

Similar experiments are also performed in air, where the nanotube fibre is attached and manipulated using the scanning mechanism of a Park Instruments Autoprobe SPM. This of course does not allow the visual inspection of the nanotube that is measured but allows more data to be accumulated.

Finally, for comparison we have also measured the current–voltage characteristics of a Hg droplet touching an HOPG (Highly Oriented Pyrolytic Graphite) surface. The transport characteristics of these contacts resemble those of the nanotube–liquid metal contacts.

3. Results

3.1. $G(V)$ properties in air

Figure 1 shows typical conductance $G = I/V$ versus voltage for an MWNT in air that is connected to a carbon fibre on one side, and immersed in liquid mercury at the other side. For this MWNT [11], the conductance is near $G_0$ at low bias, which is the maximum $G(V = 0)$ value we have measured for a single MWNT. The conductance increases essentially linearly with increasing applied voltage with a slope $dG(V)/V = 0.5G_0/V$ and is symmetrical around

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Figure 2. Conductance $G(V)$ versus $V$ for an MWNT contacted to Hg in situ in the TEM for successive voltage sweeps from $0\,V \rightarrow V_{\text{max}} \rightarrow -V_{\text{max}} \rightarrow 0\,V$. The low-bias conductance is initially low (at a). When the bias voltage reaches 1.5 V the conductance jumps abruptly (b). A stable linear pattern develops for many sweeps (c). The bias voltage sweep range is then increased, which induces a change (d) in the conductance. The new pattern (e) is stable. After again increasing $V_{\text{max}}$, $G(0)$ increases again and the stable characteristic (f) was obtained. Next the conductance attains a maximum. The bias voltage sweep range was increased to 3 V, and the nanotube failed at $V = 2.9\,V$.

zero bias. In the inset, $G(V)$ is plotted up to $\pm 1\,V$ for various depths of the tube submerged into Hg (50–700 nm). The $G(V)$ characteristic is remarkably constant for this MWNT which is in good contact with Hg as shown by the large $G(0)$ value. The increase in $G(V)$ has been related to the density of states in the nanotube [11]. Nanotubes typically fail for applied voltages in the range from 2.5 to 4 V. The increase with increasing bias voltage is a universal feature of all the nanotubes we have measured. These properties have been reported in [4, 11]. Variation in the linear behaviour is observed at higher voltages, as presented below.

3.2. In situ measurements of variable contacts

Figure 2 shows transport of a carbon nanotube measured in the TEM. The distance from contact to contact measured along this 16 nm diameter nanotube was $0.8\,\mu m$. Only a small segment of the nanotube and its tip contacted the Hg surface in the course of this measurement. The MWNT was slightly bent due to the stress. The conductance is measured as a function of voltage continuously, where the voltage is swept at a rate of 2 Hz spanning the voltage range from $-V_{\text{max}}$ to $+V_{\text{max}}$ with $V_{\text{max}} = 1.6$ to 2.4 V. The pattern evolves in time as the contact of the MWNT with the Hg surface changes due to drift. Hence the differences from one sweep to the next primarily reflect slight changes in the contact of the nanotube with the Hg.
The initial conductance was quite low (figure 2(a)). When the bias voltage reached 1.5 V the conductance jumped abruptly (figure 2(b)) from about $0.1G_0$ to $0.22G_0$. A stable pattern developed for many sweeps (figure 2(c)). Both the slope ($\sim0.13G_0/V$) and the zero-bias conductance, $G(0) \sim 0.07G_0$ gradually increased slightly. After about 20 sweeps, the bias voltage sweep range was increased, which induced a change in $G(V)$ figures 2(d) and 2(e): $G(0) \sim 0.22G_0$; $dG/dV \sim 0.2G_0/V$. The patterns remain remarkably symmetric. While the observed change in the conductance was probably due to a change in the contact geometry (caused by the increased bias voltage), this change was too small to be noticed (i.e. $< 50\,\text{nm}$). After further increasing the bias voltage sweep range the conductance increases, $G(0) \sim 0.52G_0$, $dG/dV \sim 0.2G_0/V$ (figure 2(f)); however, now the conductance attains a maximum: $G(1.6\,\text{V}) = 0.77G_0$. Although the conductance decreases above $\sim1.5\,\text{V}$ in this case, the current $I = V \cdot G$ continues to increase but at a lower rate. The $G(V)$ pattern is stable. Subsequently, the bias voltage sweep range was expanded to $\pm3\,\text{V}$, and the nanotube failed at $V = 2.9\,\text{V}$ 2. At that point $G(2.9\,\text{V}) = 0.6G_0$. The failure occurs near the Hg contact (where some contamination was also observed).

The TEM observations presented in figure 3 are instructive. The nanotube is 10 nm in diameter of which a length of 2.5 $\mu$m spans the distance from the fibre to Hg. In figure 3(a), the nanotube was slightly bent at the tip where it contacted Hg, causing an angle of about $45^\circ$ with the Hg surface. Initially, contact with Hg was small and the nanotube did not appear to penetrate through the Hg surface. In this configuration the conductance $G(0) \sim 0.15G_0$ with a slope $dG/dV \sim 0.05G_0/V$, maximizing at $2.3\,\text{V}$: $G(2.3\,\text{V}) = 0.27G_0$, and decreasing at higher applied voltages. This pattern was reproducible and stable. When the fibre was pushed closer to the Hg surface (figure 3(b)), the geometry abruptly changed. This change was consistent with the nanotube submerging by $\sim1\,\mu\text{m}$ below the Hg surface, as expected when the pressure of the nanotube exceeds the Hg surface tension. At this point the conductance increased to $G(0) = 0.48G_0$ with a slope $dG/dV \sim 0.2G_0/V$. In this configuration the conductance did not maximize up to bias voltages of $2.2\,\text{V}$. The current at 2 V is about $140\,\mu\text{A}$, with no sign of saturation, which is significantly higher than the maximum of $25\,\mu\text{A}$ measured in single wall nanotubes [23]. The earlier configuration was reproduced by retracting the fibre, giving similar $G(V)$ behaviour as before, displaying a maximum conductance.

The nanotube was then further retracted to produce a small contact giving rise to the $G(V)$ of figure 3(c). As for figure 3(a), $G(0)$ is small and $G(V)$ maximizes. The nanotube was retracted slightly further, producing $G(V)$ in figure 3(d). The contact area was so small that the nanotube drifted out of contact at the next voltage sweep, causing $G(V) = 0$. Contact spontaneously re-established at $G(V = 2.8\,\text{V})$ (figure 3(e)), which coincides with the previous voltage sweep (figure 3(d)). The nanotube then failed ($V_{\text{bias}} = 3\,\text{V}, G(3\,\text{V}) = 0.12G_0$) at the contact with Hg, obliterating a fraction of the nanotube at the Hg contact.

$G(V)$ behaviour of this MWNT is representative of many tubes we have measured that have small contacts with the Hg. Note in particular the variation in $G(0)$, which ranges from 0.01 to $0.5G_0$, the range of $dG(V)/dV$ which is always symmetrical and positive up to at least $\pm1.5\,\text{V}$, the fact that a maximum $G$ is observed in some of the scans but not in others. Most strikingly, as seen in figures 3(f)–(h), when the tube makes a small contact with Hg some curves intercept others. Since only the contact with the Hg surface varied, the observed variations should be ascribed to the contact properties.

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Figure 3. Conductance $G(V)$ versus $V$ for a nanotube (10 nm diameter, 2.5 $\mu$m long) contacted to Hg in situ in the TEM. (a) Initially, the contact to the Hg is small and the nanotube appears to bend over the Hg surface. (b) After the fibre is pushed closer to the Hg surface, the contact geometry is more consistent with the nanotube submerging for $\sim 1 \mu$m below the Hg surface. (c) The tube is retracted to produce a small contact, and retracted slightly further in (d). In (e) the contact area was so small that the nanotube drifted out of contact, causing $G(V) = 0$. Contact spontaneously reestablished at $G(V = 2.8 \text{ V})$, which coincides with the previous voltage sweep (d). The nanotube then failed ($V_{\text{bias}} = 3 \text{ V}, G(3 \text{ V}) = 0.12G_0$) at the contact with the Hg. (f)–(h) Summary of the $G(V)$ characteristics observed at small contact for the same tube. Note, in particular, the variation in $G(0)$, the range of $dG(V)/dV$, the $G(V)$ shape variation and the fact that some curves intercept others. Since only the contact with the Hg surface varied, the observed variations should be ascribed to the contact properties.
3.3. Non-conducting MWNT

Figure 4 is an example of the conductance of a highly resistive MWNT. The tube, clean and straight, was 6 µm long. It was submerged straight into Hg by at least 1 µm. Great care was taken to make contact with a clean spot of Hg. At a certain point a clear meniscus was formed at the tip touching the Hg surface. The conductance is low \( G(0) = 10^{-3} G_0 \) and increases very slightly with voltage according to \( \frac{dG}{dV} = 9 \times 10^{-3} G_0 / V \).

In two cases, a conducting MWNT contacted the Hg. The conductance was \( G(0) \sim 0.6 \) and \( \sim 0.1 G_0 \) respectively. The conductance increased with increasing bias voltage and maximized at 1.5 and 2.5 V respectively. The tube failed about 1 V above the maximum of \( G \) and the remaining stem was re-contacted to Hg. But this time the conductances were very low \( (G(0) \sim 10^{-3} G_0) \) and the stem eventually failed at a voltage above 7 V. These observations are related to the semiconducting nanotubes produced by Collins et al [24]. Further examples of non-conducting nanotubes are given below.

3.4. In situ observations of nanotube failure

Observations of nanotube failure at high currents are summarized in figure 5. Clean defect-free conducting MWNTs typically fail at the Hg contact, at a bias voltage ranging from \( V_{\text{bias}} = 2.5 \) to 4 V, for both positive and negative polarities. It is remarkable that we have never observed nanotubes failing at the fibre contact. Highly resistive nanotubes have also been observed to fail at the Hg contact.

Defective MWNTs typically fail at the defect. A defective nanotube has a higher than usual resistance, which is ascribed to scattering at the defect, leading to a large potential drop at the defect, and likely (but not necessarily) to dissipate at the defect. Figure 5(b) and (c) shows TEM picture before and after failure for one MWNT with a kink and two contaminated
Figure 5. (a) Failure of many tubes in parallel at the contact with the Hg resulting in the ‘cut grass’ appearance. This corresponds to the typical failure of clean tubes as explained in the text. (b)–(e) Before and after in situ TEM images of contacted nanotubes and their failure at high currents. (b), (c) One MWNT with a kink and two contaminated nanotubes, showing that the failure occurred at the defects. (d), (e) High resolution images of the failure of a clean nanotube showing that only the outer layer is affected, which corresponds to the current flow pattern in these tubes.

MWNT, showing that the failure occurred at the defects. Occasionally, tubes were observed to fail somewhere along the tube, although no obvious defects were observed. This resulted in two tapered endings, with one protruding from the liquid mercury.

The high resolution image of a nanotube in figure 5(d) and (e) shows how the nanotube surface (possibly only a single layer) was disrupted at the end of the nanotube that contacted the metal electrode (gold in this case) due to the high current, giving it the molten appearance. Similar shedding of the outer layer is also observed for field emitting nanotubes under high current conditions.

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Figure 6. TEM picture of a Hg bubble stabilized at the contact of a nanotube to the Hg with a voltage of $\sim 1.5$ V. The shape appears to be a spherical segment with a radius of 0.5 µm. This phenomenon occurs when the nanotube is negatively biased with respect to the Hg, when only the tip of the nanotube touches the surface under high current conditions.

The TEM image of figure 5(a) clearly illustrates the failure of many MWNTs which contacted the Hg after the bias voltage was ramped from 0 to 8 V. This resulted in the ‘cut grass’ appearance. (At some point a Hg bubble was formed which made contact with the tubes; the phenomenon is described in detail below.) This observation indicates that most of the power is dissipated at the Hg contact.

3.5. Hg bubble formation

One of the most spectacular in situ observations is the formation of a Hg bubble-shape feature near the contact of a nanotube to the Hg surface. This phenomenon occurs when the nanotube is negatively biased with respect to the Hg, when only the tip of the nanotube touches the surface under high-current conditions. The Hg bubble can be stabilized by appropriately adjusting the voltage. In the case of figure 6, a bubble of radius $\sim 0.5$ µm was kept stable for a bias voltage of 1.5 V (current $\sim 0.14$ mA). When the bias voltage is swept, then the bubble emerges and submerges synchronizing with the applied voltage, similar to a rising and setting moon. The bubble has been seen to burst after which a new one forms. A bubble is not formed when the nanotube is positively biased. The fact that the bubble is spherical suggests that it is indeed liquid Hg. This is further strengthened by the observation of a meniscus at the nanotube–Hg contact. Furthermore, the bubbles are conducting, since such a bubble caused the failure of the nanotubes in figure 5(a).

This phenomenon appears to occur only for specific small contacts to the Hg. The 10 nm diameter MWNT contacting the Hg contact produced bubbles for positive $V$ (i.e. nanotube negatively biased with respect to the Hg). $G(V)$ is shown in figure 7(a). In figure 7(b), the tube had drifted away, causing the conductance, and consequently the current, to decrease for
Figure 7. Conductance $G(V)$ versus $V$ for a tube (10 nm diameter) in contact with Hg. (a) Hg bubbles are formed. (b) The tube drifted away, causing the conductance to decrease. The bubbling phenomenon stopped. After pulling the tube out, contact was reestablished in (c). No bubble was observed even for higher bias voltage and current than in (a), indicating the influence of the nature of the contact. In all cases, note the symmetry of the conductance versus polarity.

The same bias voltage. The bubbling phenomenon stopped. After reapproaching the tube to the Hg, contact was reestablished in figure 7(c), but this time no bubble formation was observed even for higher bias voltage and current than in figure 7(a). Note that even when the bubbles are formed (figure 7(a)), $G(V)$ is symmetric with respect to $V = 0$.

3.6. Experiments with a small Hg droplet touching an HOPG surface

Deeper insight into the nature of the contact is obtained in the following experiments. Here we attached a small Hg droplet to a fine wire, which was manipulated in air using a scanning probe microscope (SPM). Hence the droplet was brought into contact with a freshly cleaved HOPG surface, and the conductance was measured as a function of the applied voltage, as for the nanotube experiments above. The contact area of the droplet to the graphite surface can be adjusted using the SPM positioning mechanism: at first contact, the conductance is small, when the droplet is lowered further, then the conductance increases. Even though the contact area is not calibrated, these experiments can provide important insights into the properties of very small metal contacts to graphitic systems.

Here we concentrate on the conductance as a function of voltage. As shown in figure 8, the conductance increases with increasing voltage. The increase is monotonic, essentially linear and reminiscent of the Hg–MWNT properties discussed above. The patterns are remarkably symmetric (a slight asymmetry is sometimes observed, that causes $|dG/dV|$ to be slightly lower for the negatively biased Hg tip compared to the positively biased Hg tip).
Figure 8. Conductance $G(V)$ versus $V$ for an HOPG sample contacted to a droplet of liquid Hg in air, for several different contacts (the larger the contact, the greater $G(V = 0)$). As for MWNT the conductance increases with increasing voltage. The increase is monotonic, essentially linear and remarkably symmetric.

When $G(V = 0) > G_0$, then the pattern approximately scales with $G(V = 0)$: $(dG(V)/dV)/G(V = 0) \sim 0.3/V$. For $G(V = 0) < G_0$ the slope appears to be relatively constant: $(dG(V)/dV) \sim 0.3G_0/V$.

4. Discussion

The results presented here demonstrate several interesting properties of nanotube–metal contacts. A MWNT is composed of nested SWNTs; as for graphite, the interlayer coupling is weak, hence the properties of MWNTs are closely related to those of SWNTs [21]. Nanotubes are either conducting or non-conducting. In general, only one in three layers is conducting. Hence if a MWNT is found to conduct, then the outer layer is conducting and the next layer is usually non-conducting. Transport in MWNTs has been shown to be confined to the outer layer [4, 25]. A nanotube stem that remains after a conducting MWNT fails, was observed not to conduct.

Conducting layers have two metallic subbands, which should give rise to a conductance of $2G_0$. These subbands cause a constant density of states spanning the pseudogap (about $1\,\text{eV}/D$, where $D$ is the diameter in nm). The density of states is V-shaped, rising approximately linearly with increasing (decreasing) energy above (below) the gap. The density of states of a nanotube evolves to that of a graphene sheet by increasing the diameter (which decreases the gap; a graphene sheet is a zero gap semiconductor for which, as for nanotubes, the density of states increases linearly with increasing energy). Similarity of contacts to these two systems is probably caused by the similarity of electronic structures.

We have observed highly resistive MWNTs ($\leq 10^{-3}G_0$). Note that these resistance values could not be ascribed to diffusive scattering in a conducting tube for this would require
resistance of at least 2 MΩ µm⁻¹, which is more than two orders of magnitude higher than diffusive MWNTs [13]. Some of these tubes can hold off bias voltages > 2 V and even up to 8 V, which is in any case very much greater than the gap. This suggests that there is a Schottky barrier at the semiconducting nanotube–Hg interface [26] (the work function of Hg is 4.48 eV compared to an estimated 4.7 eV for a SWNT [27]). When a non-conducting nanotube breaks down at high voltages, then the failure occurs at the nanotube–metal contact. It is reasonable to assume that the breakdown of the metal–nanotube Schottky barrier initiates the failure. This is probably initiated by a tunnelling current that causes local heating, which in turn produces thermionic electron emission [7]. The current is enhanced, ultimately destroying the nanotube. In any case, non-conducting multi-walled nanotubes are remarkably good insulators, even though \( k_B T \) is of the same order as the energy gap.

We next address the rise in the conductance with increasing applied bias voltage. This is a robust feature, observed in all of the contacts we have made to nanotubes. Note that this property has not been reported by other groups. In fact, the only report on the conductance for MWNTs at large bias voltages by Collins et al [24] shows a uniform decrease in the conductance with increasing bias voltage, in contrast to our findings. Moreover, in their case, the nanotubes appear to fail in the middle of the tube. Single-wall carbon nanotubes have been reported [23] to show a saturation in the current starting around \( V_{bias} = 1 \) V (ascribed to the production of longitudinal phonons).

The \( G(V) \) properties of HOPG and conducting MWTNs are remarkably similar. In fact, \( G(V) \) on HOPG has been previously measured by Agrait et al [28] using a tungsten STM tip in contact with HOPG. They also found an increase in the conductance with increasing \( V_{bias} \). The increase in the conductivity in that case has been ascribed to the linear increase in the density of states with increasing and decreasing applied voltage. We have also concluded that the increased conductance in MWNTs is due to the increased density above and below the Fermi level [11]. Moreover, it is likely that for graphite the contact conductance is essentially determined by the top layer, since the \( c \)-axis resistivity is about five orders of magnitude higher (≈10 Ω cm) than the basal plane resistivity (≈100 µΩ cm). A full report on the contact conductances of various liquid metal contacts to HOPG in UHV will be published later [29].

In the literature, \( I–V \) characteristics have also been measured for MWNTs in the low temperature, low bias-voltage range (typically < 50 mV). For high tunnelling resistance junctions, the tunnelling conductance of MWNTs increases as a function of bias voltage, which is often taken as a signature of electron–electron interaction [30, 31]. This increase could be successfully described [31] by the environmental quantum fluctuation theory, in which the tube acts as an effective transmission line connected by tunnel junctions to reservoirs. The \( G(V) \) increase was also discussed in the framework of the Luttinger liquid theory, which could be also connected to the environmental quantum fluctuation theory with the same transmission line analogy [30, 31]. Our measurements are done in very different experimental conditions: room temperature, high bias voltage and low contact resistance (for tube immersed in Hg the measured contact resistance was \( R^* = 0.1–1 \) kΩ µm [11], it can be larger if only the tube tip is in contact), so that we do not expect to observe these effects.

The \( G(V) \) properties for Hg–nanotube contacts show variations that are due to the contacts and not due to the properties of the nanotubes themselves. This is clear from variations in \( G(V) \) when only the contact geometry is changed (figures 2 and 3). First the value of the conductance at low bias voltage increases with increasing contact area, in agreement with our
previous measurements [11] and in accordance with the calculation of SWNTs in contact with a metal along its circumference [32, 33]. The same is observed for HOPG (figure 8). There are several cases where $G(V)$ curves for the same nanotube intercept each other, which can only be explained in terms of the contact properties, which appear to affect not only the $G(0)$ but also, to some degree, the slope $dG/dV$. This appears most clearly when $G(0) \ll 1G_0$, i.e. when the measured two-point conductance is most probably dominated by the contact contribution. Hence, the contacts themselves cannot be characterized only by the contact area since then it is difficult to understand how two curves can intercept. In fact, we have observed that $G(V)$ for nanotubes that appear to rest on the surface tend to exhibit a maximum near $V = 2\, V$, while nanotubes that penetrate the surface, tend not to exhibit a maximum, suggesting that details of the contact to the Hg affect the shape of $G(V)$. This property is reminiscent of the differences in the electronic tunnelling properties into nanotubes according to whether the tube is end-contacted or side-contacted [34]. A poorer contact is predicted for end-contacted nanotubes to Al since the $\pi$ states preferentially couple to the metal states, as found also for the cylindrical contact geometry [33], whereas both $\pi$ and $\pi^*$ states couple equivalently for side contacts. It is worth noting that in this case the two $\pi$ and $\pi^*$ channels do not mix at low bias, which is consistent with ballistic transport (see also [32]).

The failure modes of MWNTs shed light on the heat dissipation processes. Undamaged nanotubes tend to fail at the Hg contact, suggesting that most of the heat is dissipated there. Nanotubes with defects tend to fail at the defect. Curiously, we have not observed nanotubes to fail at the contact with the fibre. This contact can be considered to be composed of multiple nanotube–nanotube contacts. In a previous publication [11] we argued that the transmission coefficient of this contact was probably about $\frac{1}{2}$ which explains the ‘missing’ quantum. We observe that well-contacted MWNTs have one quantum of conductance rather than two, as expected from the band structure. On the other hand, this explanation could imply that more heat is dissipated at the fibre contact than at the metal contact, since the transmission coefficient of the metal contact would then be $1$ and $\frac{1}{2}$ for the fibre contact. Hence, $\frac{2}{3}$ of the power $W = I^2R$ would be dissipated in the fibre contact and $\frac{1}{3}$ in the Hg contact. On the other hand, if the reduced transmission at the fibre contact is caused by elastic processes (which is likely), then this argument does not hold. In fact, the heat may be distributed far from the contact point of the nanotube with the fibre. Also, the contact nanotube–fibre can be viewed as a multiple contact so that the power is dissipated over a distance along the tube.

The formation of Hg bubbles is one of the most intriguing effects that we have observed in these experiments. It occurs when the contact of the nanotube is relatively small under high-current conditions and only when the nanotube is negatively biased with respect to the Hg. Once the bubble is formed (which appears like a rising and setting moon), the size of it above the Hg surface can be varied continuously by adjusting the bias voltage. The asymmetry with respect to bias is very important and indicates that the direction of the current matters. However, as seen in figure 7, there is no asymmetry in $G(V)$ of the tube making contact. Therefore, we believe the phenomenon is related to an unusual heating effect. Apparently, when electrons are injected into the Hg, then the temperature near the nanotube increases enough to locally vaporize the Hg. In contrast, when the electrons flow into the nanotube, this does not happen. The driving force to pull the bubble partially out might be of electrostatic origin. This scenario is consistent with ballistic transport, where the electrons are accelerated into the Hg due to the potential drop (which is of the order of $V_{bias}$) at the nanotube–Hg

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interface. These electrons rapidly dissipate their energy in the metal causing local heating. When the bias is reversed, the electrons are accelerated as they enter the nanotube due to the potential drop at the interface. If the mean free path is larger than the nanotube length (as in ballistic transport) then no energy is dissipated in the nanotube, and it will not heat up. Hence, an asymmetry in the heat dissipation (but not in $G(V)$) is expected in ballistic transport.

On the other hand, nanotube failure is observed at the Hg interface for both positive and negative bias. It may be that failure is not only due to heating but also due to electromigration and electrical breakdown effects, due to the large electric fields (of the order of $V_{bias}/D$, where $D$ is the contact interface thickness and it is of atomic dimensions).

5. Summary and conclusion

We have compiled a wide range of observations of metal-contacted nanotubes in order to provide an overview for several of the processes that are involved. High contact resistances are observed when the contact area is small, which also affects the $G(V)$ behaviour.

For all conducting nanotubes we find that $G(V)$ increases with increasing bias voltage: $\frac{dG}{dV_{bias}} \sim 0.3G_0/V$ for $V_{bias} < 2$ V. In some cases (apparently when the nanotube ‘floats’ on the Hg), $G(V)$ maximizes and then decreases; in other cases (apparently when the nanotube submerges), $G(V)$ does not maximize.

An increase in the conductance with increasing $V_{bias}$, is observed in both Hg–nanotube contacts and also in Hg–HOPG contacts. This strongly indicates that the density of states dominates $G(V)$. The maximization of $G(V)$ mentioned above is probably due to kinematic effects related to electron injection at the contact.

Conducting nanotubes fail for $V_{bias}$ in the range 2.5–4 V. Failure typically occurs at the Hg contact or at defects, but not at the fibre contact. This property is consistent with ballistic transport through the nanotube, where all the dissipation and the voltage drop occurs at the contact.

Highly resistive nanotubes can stand off voltages of more than 2 V, and they eventually fail at the Hg contact. These voltages are much greater than the expected typical band-gap (of the order of 0.1 eV).

From the failure properties it appears that only the outer layer participates in the transport, consistent with previous measurements.

The formation of Hg bubbles for negatively biased nanotubes, indicates that hot electrons are injected into the Hg under those conditions, which cause local heating of the Hg at the interface. The absence of this effect for positively biased nanotubes is remarkable, and demonstrates an asymmetry in the heat dissipation (which is consistent with ballistic transport). On the other hand, we observe that $G(V) \sim G(−V)$. It is curious that no asymmetry is observed here as an indirect consequence of the heat dissipation asymmetry.

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