Induced and intrinsic superconductivity in carbon nanotubes

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Abstract

Metallic single wall carbon nanotubes have attracted considerable interest as 1D quantum wires combining a low carrier density and a high mobility. It was believed for a long time that low temperature transport was exclusively dominated by the existence of unscreened Coulomb interactions leading to insulating behaviour at low temperature. However, experiments have also shown evidence of superconductivity in carbon nanotubes. We distinguish two fundamentally different physical situations. When carbon nanotubes are connected to superconducting electrodes, they exhibit proximity-induced superconductivity strongly dependent on the transmission of the electrodes. On the other hand, intrinsic superconductivity was also observed in suspended ropes of carbon nanotubes, in doped or very small diameter individual tubes. These experiments indicate the presence of attractive interactions in carbon nanotubes which overcome Coulomb repulsion at low temperature and enable investigation of superconductivity in a 1D limit never explored before.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single wall carbon nanotubes (SWCNTs) are constituted by a single graphene sheet wrapped into a cylinder. The Fermi surface of graphene is very particular, it is reduced to six discrete points at the corners of the first Brillouin zone [1]. As a result, depending on their diameter and their helicity which determine the boundary conditions of the electronic wave functions around the tube, SWCNTs can be either semiconducting or metallic. When metallic they have only two conducting channels [2, 3]. The minimum resistance of a single wall nanotube in good contact with normal electrodes is thus $R_Q/2$, where $R_Q = h/(2e^2) = 12.9 \text{k}\Omega$ is the resistance quantum.

It has been shown that these two conduction modes of carbon nanotubes are only very weakly coupled by electron interactions. SWCNTs are thus expected to exhibit electronic properties similar to systems presenting 1D conducting ladders with very small transverse coupling. In such 1D systems electron–electron interactions have been shown to determine the low temperature properties, with a non-Fermi liquid behaviour characteristic of a Luttinger liquid (LL) state [4, 5] with collective low energy plasmon-like excitations giving rise to anomalies in the single particle density of states. Proof of the validity of LL description with repulsive interactions in SWCNTs was given by the measurement of a resistance diverging as a power law with decreasing temperature, extrapolating to an insulating state at zero temperature [6]. However, in these experiments the nanotubes were forming tunnel junctions with the measuring leads. The low temperature transport, corresponding to $k_B T < E_C$, is dominated by Coulomb blockade, where $E_C = e^2/C$ of the order of 10 K is the charging energy of the nanotube of capacitance $C$.

In contrast it is also possible to investigate transport through carbon nanotubes in good contacts with metallic and possibly superconducting electrodes. Individual metallic tubes with a room temperature resistance between 10 and 40 kΩ were obtained either using the nano-soldering technique developed by Kasumov et al [8] or by burying the tube ends over a large distance under metallic electrodes fabricated with electron beam lithography [9, 10]. The increase in resistance is only logarithmic at low temperature and low bias in stark contrast to the behaviour of tubes with tunnel contacts. This finding is consistent with the theoretical results obtained on LLs between normal reservoirs [11] showing that the resistance of a ballistic tube on perfect contacts is insensitive to interactions and given by $R_Q/2 = 6.5 \text{k}\Omega$ at all temperatures, as for an ideal two channel conductor.

In between these two extreme regimes of strong Coulomb blockade, where the nanotube behaves as a quantum dot and
ballistic transport, and where the nanotube behaves as a wave guide of conductance close to 2 conductance quanta, there is also an interesting regime at intermediate transmission between the electrodes and the tube. This happens when the number of electrons on the nanotube is odd, with the formation of a strongly correlated Kondo resonant state where the magnetic moment of the highest occupied level is screened by the spins of the electrons in the contacts [12]. Finally, when the carbon nanotubes are in good contact with superconducting electrodes, it is possible to induce superconductivity and observe supercurrents, as was first investigated in ungated suspended devices [13, 14] and then explored in gated devices with evidence of a strong modulation of subgap conductance, depending on the transmission.

More surprising, intrinsic superconductivity was also observed in suspended ropes of carbon nanotubes and recently in doped individual tubes. These experiments indicate the presence of attractive interactions in carbon nanotubes which overcome Coulomb repulsion at low temperature.

The paper is organized as follows:

– The next section is devoted to proximity induced superconductivity starting with experiments on ungated suspended carbon nanotubes performed a few years ago in our group, which also offer the possibility of an investigation of transverse vibration modes. We also discuss more recent experiments on gated tubes (performed by several groups including ours) which lead to tunable Josephson junctions and the possibility to observe the competition between Kondo and Josephson physics.

– The third section is devoted to intrinsic superconducting fluctuations observed by our group at sub-kelvin temperatures in suspended ropes of carbon nanotubes. We discuss the various parameters which influence this superconductivity, like the invasive character of the normal contacts, the number of tubes and disorder within a rope, and finally the suspended character of the tubes. Magnetization experiments on similar samples reveal a small but detectable Meissner effect difficult to observe because of residual catalytical magnetic particles in the tubes. We finally discuss recent experiments performed by other groups showing evidence of superconducting fluctuations at much higher temperatures, above 10 K, in very small diameter doped carbon nanotubes.

2. Proximity induced superconductivity in carbon nanotubes

A normal metal in good contact with macroscopic superconducting leads is in the proximity effect regime: superconducting correlations enter the normal metal over a characteristic length \( L_N \) which is the smallest of either the phase coherence length in the normal metal \( L_\phi \) or the thermal length \( L_T \). Both lengths, of the order of a few micrometres, can be much greater than the superconducting coherence length \( \xi \) of the superconducting contacts. This effect was extensively investigated in mesoscopic wires made of noble metals [15–17] connected to massive superconducting electrodes. These so-called SNS junctions exhibit a Josephson effect like tunnel junctions, i.e. a supercurrent at zero bias. The maximum low temperature value of the supercurrent (critical current) in such SNS junctions of normal state resistance \( R_N \) is related to the superconducting gap \( \Delta \) by \( \pi \Delta / e R_N \) in the short junction limit \( L \ll \xi \) [18, 19], and \( \alpha E_c / e R_N \), with \( \alpha \) a numerical factor of the order of 10, in the limit of long junctions \( L \gg \xi \) where \( E_c = h / \tau_0 \) and \( \tau_0 \) is the typical traversal time of charge carriers through the junction [16]. Probing the proximity effect in a normal wire connected to superconducting electrodes and in particular the existence of a Josephson current constitutes a powerful tool for the investigation of phase coherent transport through this normal wire.

Inspired by these ideas several transport experiments were performed on individual (SWCNTs) connected to superconducting electrodes. These experiments probe not only the conduction of SWCNTs but also the coherent nature of the transport from the observation proximity induced superconductivity below the superconducting transition temperature of the electrodes. This is of particular interest in these 1D systems where the existence of low energy many-body electronic excitations is predicted.

2.1. First observation of supercurrents in ungated suspended SWCNTs

Proximity induced superconductivity was first observed in suspended carbon nanotubes mounted on Ta/Au electrodes [13] which are a bilayer (5 nm Ta, 100 nm Au) with a transition temperature of the order of 0.4 K. This value is strongly reduced compared with the transition temperature of bulk tantulum (4 K) due to the large thickness of gold relative to tantalum. Tubes were soldered with a laser pulse on low resistive metallic contacts across a slit etched in a silicon nitride membrane. This technique enables both the realization of contacts with a transmission probability of carriers between the nanotube and the electrodes close to unity and a good characterization of the samples by transmission electron microscopy. The temperature dependence of the low current resistance exhibits a broad transition around the superconducting transition temperature of the contacts and becomes zero at lower temperature as seen in figure 1. The transition is shifted to lower temperature when a magnetic field is applied in the plane of the contacts and perpendicular to the tube axis. Above 2 T all signatures of superconductivity disappear: the resistance becomes field independent and slightly increases when the temperature is lowered below 0.2 K. The critical field, can be extracted as the inflection point of the magnetoresistance depicted in figure 1, its value of the order of 1 T for all samples is surprisingly high and is ten times larger than the measured critical field of the contact (0.1 T). It is possible that these high values of critical field are due to local modifications of the bilayer Ta/Au film in the contact region due to the laser pulse, in particular the melted upper gold film is probably much thinner than the original one. It is, however, important to note that the critical fields are nearly the same for the various samples measured and all vary linearly with temperature down to \( T_c \).

The most striking signature of proximity induced superconductivity is the existence of Josephson supercurrents
Figure 1. Temperature dependence of the resistance of three different single tubes ST1, 2, 4, mounted on TaAu measured for different values of the magnetic field perpendicular to the tube axis in the plane of the contacts. Bottom inset: transmission electronic microscopy picture of the nanotube ST1 suspended between the two TaAu contacts. Top inset: field dependence of the transition temperature (defined as the inflection point of $R(T)$).

Figure 2. Typical $I(V)$ characteristics for the suspended individual SWNT ST1 measured at 100 mK. The transition between the superconducting state (zero voltage drop through the sample) and the dissipative (resistive) state is quite abrupt and displays hysteresis. It is characterized by a critical current $i_c = 0.14 \, \mu A$ near zero temperature. The value of the product $R_d i_c$ at $T = 0$, for the three samples depicted in figure 1, varies between 1.6 and 3.5 mV, it is of the order but significantly larger than the expected value of the order of the gap of pure tantalum $\Delta_{Ta} = 0.7$ mV in the short junction limit.

Observation of a strong proximity effect indicates that phase coherent transport takes place in carbon nanotubes on a micrometre scale. However, the surprisingly high values of critical currents measured cannot be described by the theory of SNS junctions where the normal part $N$ is a LL with repulsive interactions [20, 21].

Our data could, on the other hand, be explained by the existence of superconducting fluctuations intrinsic to SWCNT [22, 23]. For an infinite nanotube, because of its 1D character, these fluctuations are not expected to give rise to a superconducting state at finite temperature. However, the superconducting state could be stabilized by the macroscopic superconductivity of the contacts. In such a situation, it is conceivable to expect the supercurrent to be enhanced compared with its value in a conventional SNS junction and to be equal to the critical current of a superconducting filament which reads $i_c = (4e^2/h) \Delta$, determined by the value of the superconducting pairing amplitude $\Delta$, inside the wire and independent of the normal state resistance of the nanotube (in the limit where the mean free path is larger than the superconducting coherence length). We see in the next section that the observation of intrinsic superconductivity in suspended ropes of SWCNT corroborates this scenario.

2.2. Sensitivity to mechanical vibrations: nanotubes as superconducting nano-electromechanical resonators

We show in the following that it is possible to take advantage of the extreme sensitivity of proximity-induced superconductivity to dephasing events in the nanotubes and detect their transverse low frequency vibrational modes (bending modes) from transport measurements. The experiment consists of exciting vibrations on the tubes by applying a radio-frequency (rf) electromagnetic field via...
harmonics, at 110 mK and for different applied rf powers.

contacts. (line shapes of the sixth harmonics with the temperature of the tube, under an electron microscope [24]. When the tubes are not uniformly distributed on the tube, the excitation of strain along this long rope, leading to weak coupling of the fundamental mode to an homogeneous excitation) or may be an intrinsic origin (for instance the non-homogeneity of the superconducting, the mechanical vibrations induce a loss of phase coherence which is detected via a reduction in the critical current and the onset of finite resistance at large enough rf power excitation and can simply be detected via a transport experiment as shown in figure 3. The experimentally observed resonance frequencies are approximately multiples of 300 MHz which is the value expected for the transverse vibrations of a slightly stretched rope [26]. The fundamental frequency is, however, not observed. This absence may have an intrinsic origin (for instance the non-homogeneity of the strain along this long rope, leading to weak coupling of the fundamental mode to an homogeneous excitation) or may be simply due to the particularly small coupling to the antenna in this frequency range.

The mechanical origin of the resonances has been confirmed by the shift to lower frequencies caused by deposition of nitrogen molecules on the nanotubes. The quality factors of these resonances were found to be of the order of 1000 at 1 K and to increase approximately as 1/T at low temperature. We have also observed non-linear effects at high RF excitation power which have not yet received clear explanations [26].

Since these preliminary experiments, mechanical resonances of carbon nanotubes have been explored in various experimental setups [27, 28], however, only in the normal state. It is also interesting to note that the high quality factor values we have observed (probably due to the superconducting contacts) were only reproduced very recently in the strongly Coulomb blocked regime. Superconducting nano-electromagnetic resonators have also been recently investigated theoretically [29] in the interesting regime where the Josephson frequency coincides with eigenmechanical modes in the system and deserve further experimental studies.

2.3. Tunable supercurrents in gated carbon nanotubes

Proximity induced superconductivity was also explored in devices in which the number of electrons in the nanotube can be adjusted with a gate voltage. Evidence was shown of a strong modulation of conductance at bias voltages lower than the superconducting gap, but in most cases no supercurrent was observed [30–32]. More recently, tunable supercurrents could be detected in the resonant tunnelling conduction regime, where the transmission of the contacts approaches unity [33]. In this regime, the discrete spectrum of the nanotube is still preserved and the maximum value of supercurrent is observed when the Fermi energy of the electrodes is at resonance with ‘the-electron-in-a-box’ states of the nanotube.

A superconducting quantum interference device was also fabricated with carbon nanotubes as Josephson junctions: supercurrent $\pi$ phase shifts occurred when the number of electrons in the nanotube dot was changed from even to odd [34] corresponding to the transition from a singlet (non-magnetic) to a doublet magnetic state of the dot. Sharp discontinuities in the critical current at this 0–$\pi$ transition in relation with the even–odd occupation number of the nanotube quantum dot were also observed in single nanotube junction devices [35]. It was pointed out in the SQUID experiment [34] that a Josephson current can be observed in the Kondo regime, when the Kondo temperature is large compared with the superconducting gap, confirming theoretical predictions [36–41] and previous experiments [31, 42] with no determination of supercurrents though, indicating that Kondo effect and proximity induced superconductivity can cooperate in favouring the coherent transfer of Cooper pairs through the nanotube, provided that Kondo correlations are strong enough with $T_K > \Delta$. We have recently investigated this competition between Josephson and Kondo physics by monitoring on the same device the bias dependence of the differential conductance in the normal state.

Figure 3. (a) Effect of an rf electromagnetic radiation on the dc voltage across a 1.6 $\mu$m long suspended rope of carbon nanotubes connected to superconducting electrodes when it is run through by a dc current below the critical current. (b) Evolution of the resonance line shapes of the sixth harmonics with the temperature of the contacts. (c) Resistance of the rope versus frequency near the sixth harmonics, at 110 mK and for different applied rf powers.
and the Josephson current in the superconducting state as a function of the gate voltage [43]. A supercurrent is observed (for an odd number of electrons on the nanotube) when both energy level spacing and Kondo temperature are sufficiently high compared with the superconducting gap $\Delta$ and when the asymmetry of the transmission of the electrodes is not too large. This is understood considering that the formation of a coherent, non-magnetic, resonant Kondo singlet state on the tube prior to the onset of the BCS superconducting order favours the transmission of Cooper pairs through the island. The induced superconducting BCS gap is only a minor perturbation in the transmission of Cooper pairs through the island. The induced superconducting gap is related to the magnetic spin remains unscreened at all temperatures leading to a sign reversal of the Josephson current phase relation ($\pi$-junction) with a very low transmission of Cooper pairs.

We have also explored [43] the intermediate regime where the Kondo temperature can be tuned with the gate voltage via the position of the energy levels with respect to the Fermi energy, from a value slightly below the superconducting gap at half filling to a value slightly below the superconducting gap. This transition does not exist when $T_K > T_C$ along the whole Kondo ridge (ridge C) [43].

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These results displayed in figure 5 show that disordered ropes of carbon nanotubes can be considered as anisotropic diffusive conductors, which in contrast to individual tubes in our experiments on suspended tubes discussed above. It has been argued that uncontrolled dissipative electromagnetic environments could be responsible for this strong supercurrent reduction. It is also possible that the presence in all these experiments of a strongly doped underlying Si substrate (used as a backgate) covered by an oxide layer contributes to electromagnetic noise at high frequency. In the case of suspended nanotubes, however, we will see in the following that their suspended character seems to favour intrinsic superconducting fluctuations on normal contacts which could explain an enhancement of supercurrents in the proximity induced superconductivity regime.

3. Intrinsic superconductivity in ropes of carbon nanotubes

3.1. Normal state transport in ropes of SWCNT

A rope of SWCNTs is made of ordered parallel tubes with different helicities, but with a narrow distribution of diameters [2, 44]. The centre of the tubes forms a triangular lattice so that there is for each metallic tube in a rope on average two neighboring tubes which are also metallic. In the absence of disorder within the tubes, the intertube electronic transfer, defined as the matrix element of the transverse coupling between two neighbouring tubes, integrated over spatial coordinates, is negligible because of the longitudinal wave vector mismatch between tubes of different helicities [45]. The rope can then be considered to be made of independent nanotubes in parallel. The transport is ballistic and the dimensionless conductance (in units of the quantum conductance $G_Q = 2e^2/h$) of the rope is two times the number of its metallic tubes. However, it has been shown [45, 46] that disorder within the tubes favours intertube scattering by relaxing the strict orthogonality between the longitudinal components of the wave functions.

Using a very simple model in which disorder is treated perturbatively, we have shown [47] that the intertube scattering time can be shorter than the elastic scattering time within a single tube. In tubes longer than the elastic mean free path, this intertube scattering provides thus additional conducting paths to electrons which would otherwise be localized in isolated tubes. In the limit of localized transport along the tubes it is possible to show that the longitudinal localization length of a rope is not a monotonic function of disorder and increases at moderate disorder. In order to go beyond these simple analytical results we have performed numerical simulations on a tight binding model of coupled 1D chains with different longitudinal hopping energies $t_{ij}$ [47]. This model mimics the physics of transport in a rope of carbon nanotubes in the sense that in the absence of disorder the electronic motion is localized within each chain. Transverse delocalization as a function of disorder was investigated through the sensitivity of eigenenergies to a change of transverse boundary conditions from periodic to antiperiodic [48].
Figure 5. Transverse delocalization by disorder: evolution of $\delta\epsilon_{\text{perp}}$ with the amplitude of disorder for 10 coupled chains of 100 sites, $W$ corresponds either to on site disorder (black dots), or to bond disorder (open circles). The situation of identical values of $t_\parallel$ on all chains, corresponding to $\delta t_\parallel = 0$, upper curves exhibit expected disorder induced localization, whereas the situation with different values of $t_\parallel$ where $\delta t_\parallel/t_\parallel = 0.2$ shows a regime of disorder induced transverse delocalization. The transverse hopping energy is chosen to be $t_\perp = 0.06 t_\parallel$. $\nu$ is the density of states (inverse nearest level spacing) [47].

exhibit a localization length that can be much greater than the elastic mean free path. As a consequence, ropes of SWCNT contacted using the laser nano-soldering technique present a much wider range of resistance values than individual tubes: the resistances vary between less than 100 $\Omega$ and $10^5$ $\Omega$ at 300 K. There is also no systematic relation between the diameter of a rope and the value of its resistance. This may indicate that in certain cases only a small fraction of the tubes within a rope are well connected on both contacts. In contrast to individual nanotubes, the ropes seem to verify the Thouless criterion [49]: they strongly localize when their resistance is above 10 k$\Omega$ at room temperature and stay quasi-metallic otherwise. This behaviour is very similar to phase coherent quasi-1D metallic wires. The temperature dependence of low resistance ropes ($R < 10$ k$\Omega$) is found to be very weak. Moreover, it is not monotonic, in contrast to individual tubes: the resistance decreases linearly as temperature decreases between room temperature and 30 K (see figure 6) indicating the freezing-out of ‘twiston phonon modes’ [50] and then increases as $T$ is further decreased, as in individual tubes.

3.2. Sub-kelvin superconductivity in suspended ropes of SWCNT on normal contacts

In the following we discuss the low temperature transport (below 1 K) of suspended ropes of SWCNT connected to normal electrodes. The electrodes are trilayers of sputtered Al$_2$O$_3$/Pt/Au of respective thicknesses 5, 3 and 200 nm.

As shown in figure 7, sample dependent behaviours are observed for the temperature dependence of the resistance measured in the linear response regime. The resistance of some samples ($R_{3\text{PtAu}}$ and $R_{6\text{PtAu}}$) increases weakly and monotonically as $T$ is reduced, whereas the resistance of others ($R_{1\times2}, R_{2\times4}, 5\text{PtAu}$) drops over a relatively broad temperature range, starting below a temperature $T^*$ between 0.4 and 0.1 K ($T^*_1 = 140$ mK, $T^*_2 = 550$ mK, $T^*_4 = 100$ mK). The resistance of $R_{1\text{PtAu}}$ is reduced by 30% at 70 mK and that of $R_{4\text{PtAu}}$ by 75% at 20 mK. In both cases no inflection point in the temperature dependence is observed. On the other hand the resistance of $R_{2\text{PtAu}}$ decreases by more than two orders of magnitude, and becomes independent of magnetic field. These data suggest that the ropes 1, 2, 4 and 5 (first cool down) present intrinsic superconducting fluctuations.

In the temperature and field range where the zero-bias resistance drops, the differential resistance is strongly current-dependent, with lower resistance at low current, see figure 8. The differential resistance displays a large number of peaks whose density increases with the value of the current and the resistance of the sample. They can be attributed to the formation of small normal regions around defects (phase slip
Earlier experiments in nanowires [51–54] dealt with at least wires having less than one hundred conduction channels. That this is the first observation of intrinsic superconductivity being normal.

of the existence of a finite residual resistance due to the contacts a few thousand channels. We therefore expect a strong rope) and resistance jumps occur in the d curves.

Figure 7. Resistance as a function of temperature for various ropes of carbon nanotubes connected to non-superconducting electrodes. Note the absence of transition on the rope R5 after a thermal cycling which resulted in an increase in its resistance.

centres) when the current is increased [14]. The density of phase slips is found to be much higher in disordered ropes such as R2PtAu compared with ballistic ones. Note also the major difference between these data and what is measured on SWCNTs connected to superconducting contacts [13, 14]: the V (I), dV/dI(I) curves do not show any supercurrent because of the existence of a finite residual resistance due to the contacts being normal.

Before analysing the data further we wish to emphasize that this is the first observation of intrinsic superconductivity in wires having less than one hundred conduction channels. Earlier experiments in nanowires [51–54] dealt with at least a few thousand channels. We therefore expect a strong 1D behaviour for the transition. In particular, due to large fluctuations of the superconducting order parameter in reduced dimension the resistance drop extends on a wide range of temperature starting at the 3D transition temperature $T^*$ down to zero temperature. In the following we will attribute the variety of behaviours observed taking to several essential features: the large normal contacts, together with the finite length of the samples compared with relevant mesoscopic and superconducting scales, the number of tubes within a rope, the amount of disorder and intertube coupling and finally the suspended character of the tubes. We first assume that all ropes are diffusive conductors but we will see that this hypothesis is probably not valid in the most ordered ropes.

3.2.1. Normal contacts and residual resistance. We first recall that the conductance of any superconducting wire measured through normal contacts is limited by $N_c / R_0$, where

$N_c$ is the number of conducting channels of the superconductor in contact with the normal reservoir. A metallic SWCNT, with two conducting channels, has a contact resistance of half the resistance quantum, $R_0/2$ even if it is superconducting. A rope of $N_m$ parallel metallic SWCNTs will have a minimum resistance of $R_0/(2N_m)$ in the S state. Therefore we use the residual resistance $R_r$ measured at the lowest temperature, to deduce a lower bound for the number of metallic tubes in the rope $N_m = R_0/2R_r$. From the residual resistances of 74 $\Omega$ in sample R2PtAu and less than 170 $\Omega$ in R4PtAu we deduce that there are at least $\approx 90$ metallic tubes in R2PtAu (which contains 300 tubes) and $\approx 40$ in R4PtAu (which contains 50 tubes). In both cases that means that a large fraction of tubes take part in the conduction and justifies a posteriori the hypothesis that ropes are multichannel possibly diffusive conductors.

3.2.2. Destruction of superconductivity by the normal contacts. What are the parameters characterizing the superconductivity in the ropes? Assuming that the BCS relation holds we get for the superconducting gap $\Delta = 1.76 k_B T^*$: $\Delta \approx 85 \mu eV$ for R2PtAu. We can then deduce the superconducting coherence length along the rope in the diffusive limit:

$$\xi = \sqrt{h v_F l_e / \Delta},$$

where $l_e$ is the elastic mean free path which characterizes the amplitude of disorder and can be deduced from the high temperature value of the resistance of the rope and the number of contacted metallic tubes. This expression yields $\xi_2 \approx 0.3 \mu m$, where $v_F$ is the longitudinal Fermi velocity $8 \times 10^5 m s^{-1}$. We now estimate the superconducting coherence length of the other samples, to explain the extent or the absence of observed transition. Indeed, investigation of the proximity effect at high-transparency NS interfaces has shown that superconductivity resists the presence of normal contacts only if the length of the superconductor is much greater than $\xi$ [55]. This condition is nearly fulfilled in R2PtAu ($\xi_2 \approx L_2/3$). Taking the same value of $\Delta$ for all samples, we find $\xi_1 \approx L_1/2$, $\xi_4 \approx L_4/2$, $\xi_5 \approx 2L_4$ and $\xi_6 \approx 2L_6$. These values express qualitatively the reduced transition temperature of R1PtAu and R4PtAu and the absence of a transition for R3PtAu.
and $R_{\text{SWCNT}}$, see figure 7. It is, however, not possible to explain the behaviour of sample 5 with the same kind of argument, since the same expression yields a coherence length $\xi_s$ much shorter than the length of the sample, and nonetheless no complete transition is seen. We believe that this is due to the strong disorder in this sample which is very close to the localization limit. These results emphasize also the particular role of disorder which on one hand favours superconductivity by reducing $l_c$ and accordingly the ratio $\xi/L$, but on the other hand leads to localization if it is too important.

3.2.3. Number of tubes. Another $a$ priori important parameter is the number of tubes in a rope: the fewer tubes in a rope, the closer the system is to the strictly 1D limit and the weaker the transition. If we compare the ropes $R_2$ and $R_4$ in figure 7, it is clear that the transition both in temperature and magnetic field is much broader in rope $R_4$ with only 40 tubes than in rope $R_2$ with 350 tubes. Moreover, there is no inflexion point in the temperature dependence of the resistance in the thinner rope, typical of a strictly 1D behaviour. We also expect a stronger screening of e–e interactions in a thick rope compared with a thin one, which could also favour superconductivity as we will discuss below.

3.2.4. Disorder and intertube coupling. As is clear from expression (1) for the superconducting coherence length, disorder is at the origin of a reduction in the superconducting coherence length in a diffusive sample compared with a ballistic one and can in this way also decrease the destructive influence of the normal contacts. More subtle and specific to the physics of ropes, we have seen that disorder also enhances intertube coupling, so it can increase the dimensionality of the superconducting transition: weakly disordered ropes such as $R_1$ and $R_4$ will be more 1D-like than the more disordered rope $R_2$. Of course disorder must always be sufficiently small so as not to induce localization. These considerations may explain the variety of behaviours observed and depicted in figure 7.

Finally, disorder is also the essential ingredient which reveals the difference between the normal state and the superconducting state. In a ballistic rope we would not expect to observe a variation of the resistance over the superconducting transition because in both cases the resistance of the rope is just the contact resistance.

To gain insight into the transport regime, we have performed shot noise measurements of ropes $R_1$, $3$, $4$, $6_{\text{SWCNT}}$ in the normal state (higher level of 1/$f$ noise in the more resistive ropes $R_2$, $5_{\text{SWCNT}}$ made the analysis of shot noise impossible in those samples) between 1 and 15 K. The shot noise power of these low resistive ropes in the normal state was found to be of the order of $S_f = 2eI/100$, much less than the shot noise power $S_f = 2eI/3$ expected for a coherent diffusive sample. Such a large reduction could be the signature of ballistic transport through the rope [56] and implies that all the tubes in these ropes are either completely ballistic or completely localized [56]. This is in apparent contradiction with the observation of the superconducting transition of $R_4_{\text{SWCNT}}$, with a 60% resistance drop.

It is, however, possible to explain a resistance decrease in ballistic ropes turning superconducting, if the number of conducting channels is larger for Cooper pairs than for individual electrons. In his theoretical investigation of superconductivity in ropes of SWCNT, Gonzalez [57] has shown the existence of a finite intertube transfer for Cooper pairs, even between two tubes of different helicities which have no possibility of single electron intertube transfer. This Cooper pair delocalization could lead to the opening of new channels when a rope, containing a mixture of insulating and ballistic tubes not all connected to the electrodes, becomes superconducting.

3.2.5. Suspended character of the tubes. In order to investigate the importance of the suspended character of the SWCNT ropes, we have gradually coated a suspended rope of SWCNTs with organic materials. We observed that superconductivity was gradually destroyed. Parallel Raman experiments on other samples showed that radial breathing modes (RBMs) are affected by coating, thereby hinting to these modes as playing a major role in the superconductivity of carbon nanotubes.

The sample whose superconductivity we have altered is a rope containing roughly 40 SWCNTs (sample $R_4_{\text{SWCNT}}$). The number of conducting SWCNTs is determined from the normal state resistance, given that the two wire resistance of a SWCNT is at least $h/4e^2 \approx 6.5$ kΩ. In the normal state, transport proceeds via ten ballistic tubes. It is likely that the ten tubes through which current flows in the normal state are those at the circumference of the rope. But in the superconducting state, Cooper pairs can delocalize over all the superconducting tubes since their total momentum is zero [57].

The sample was then modified in successive steps. We first (stage (b)) coated it at room temperature with a drop of benzene diethanol. In step (c), we coated the rope with polymethyl methacrylate (PMMA) which is more viscous than benzene diethanol. In stage (d) more PMMA was added, so that the entire slit was covered with PMMA. The trend upon successive coatings, presented in figure 9, is to have a slightly modified normal state (high temperature) resistance, which varies between 550 and 750 Ω, and more spectacularly a superconducting transition which weakens as the nanotube rope is coated. The transition temperature $T^*$, defined as the temperature at which the resistance starts to decrease, which would be the transition temperature of a (hypothetical) corresponding 3D superconductor, shifts from 120 to 60 mK in curves 9 (a) to (c). In curve (d), the coating is so important that no transition is visible down to less than 15 mK. The resistance even increases by 0.5% between 200 and 16 mK.

The gradual weakening of the rope’s superconductivity is also clearly seen in the differential resistance curves with a disappearance of any detectable low bias anomaly in the coated rope.

To understand the link between the weakening of superconductivity and the effect of coating on the phonon modes of these ropes, we have investigated the effect of PMMA deposition on the Raman response of other suspended
nanotubes [58]. We compared the relative intensity of the RBM with respect to the tangential modes (TM). In the uncoated sample, the intensity of the RBM peak at 200 cm\(^{-1}\) is much greater than the intensity of the TM at 1600 cm\(^{-1}\). This is due to the fact that the tubes are suspended, and therefore do not interact through Van Der Waals interaction with the substrate [59]. With a coating we find that the RBM intensity becomes much smaller (at least an order of magnitude) than the intensity of the TM. After removal of the PMMA coating with acetone, the overall Raman intensity is recovered, as is the large intensity of the metallic RBM relative to the TM.

The fact that the absolute RBM signal is much larger for suspended tubes than for tubes on a substrate has also been observed in recent scanning tunnelling microscopy experiments on suspended nanotubes [60]. The authors found spectroscopic signature of the RBM modes only on the suspended portions of the tubes, and not on the contact regions. But our experiment also shows that coating tubes with PMMA suppresses their RBM much more than the TM. In the transport experiment on the rope containing 40 tubes, it is therefore likely that the RBM of the tubes on the surface of the rope are suppressed because they are coated by PMMA. The disappearance of superconductivity could therefore be explained by the fact that the blocking of the RBM of the 10 connected outer tubes causes the suppression of their superconducting transition. Although the inner tubes which are uncoated by PMMA could still be superconducting, the superconducting transition would not be seen in a transport experiment since there is barely any electronic transfer between normal external tubes and inner tubes in a rope with little disorder [57].

We have thus shown that coating nanotubes with polymers suppresses the RBM of individual SWCNTs and suppresses the superconducting transition of a suspended rope of 40 SWCNTs. This suggests that the RBM could be the phonon responsible for the phonon mediated attractive interaction responsible for the superconductivity of carbon nanotubes.

Figure 9. Temperature dependence of the resistance of the 10 nm wide, 1 \(\mu\)m long rope containing 40 SWCNTs. (a) Before coating. (b) After benzenedithiol deposition. (c) After additional coating with PMMA. (d) After completely covering the rope and the slit with PMMA. Lines are a guide to the eye.

3.3. Magnetization measurements: Meissner effect in ropes of carbon nanotubes

Beside transport, it is also essential to investigate thermodynamic signatures such as the Meissner effect of this unusual superconductivity. The geometry of carbon nanotubes, which are very narrow 1D cylinders, is \textit{a priori} not favourable for efficient magnetic flux expulsion. Nevertheless, magnetization measurements performed on very small (0.4 nm) diameter SWCNTs revealed a diamagnetic contribution increasing at low temperature, below 6 K, [62] which was interpreted as superconducting fluctuations.

We have also addressed this question of flux expulsion (i.e. Meissner effect) by measuring the magnetization of ropes of SWCNTs similar to those previously studied in transport measurements [63]. The magnetic signal contains unfortunately an important contribution coming from residual catalyst iron particles in the purified ropes of carbon nanotubes. They mostly give rise to a hysteretic contribution which does not change with temperature below 35 K. At low temperature, it was thus possible to decompose the magnetic signal into a \(T\) independent contribution attributed to frozen large magnetic particles and into a temperature dependent part which is reversible. We have shown [63] that beside this contribution of unfrozen superparamagnetic particles, it is possible to identify the presence of a diamagnetic low field dependent contribution growing below 0.4 K which provides a strong indication of the existence of a Meissner contribution in ropes of SWCNTs, in agreement with the onset of superconductivity observed in transport measurements realized on similar samples, see figure 10. From the partial alignment of the tubes in the samples, it was also possible to probe the anisotropy of the Meissner effect.

Figure 10. Temperature dependence of the magnetization of an assembly of ropes of carbon nanotubes after subtraction of the superparamagnetic contribution of the catalyst particles. Inset: reconstitution of the field dependence of the diamagnetic contribution for various temperatures. Note the small values of critical field (related to the breaking of Josephson coupling between the tubes within a rope) compared with the much larger value in the tesla range observed in transport experiments.
3.4. Conclusion on experiments on ropes of SWCNTs

Data depicted in the previous section show the existence of intrinsic superconductivity in ropes of 1.2 nm diameter carbon nanotubes comprising between 40 and 400 nanotubes. The question of the existence of superconducting correlations in the limit of the individual tube cannot be answered yet. It is of course tempting to consider the high supercurrent measured on superconducting contacts as a strong indication that superconducting fluctuations are present also in individual carbon nanotubes. However, since unscreened Coulomb repulsive interactions in these samples are expected to suppress superconductivity, precise investigations of individual carbon nanotubes on normal contacts are necessary. It is essential to conduct experiments on sufficiently long samples (such as ropes presently studied) so that intrinsic superconductivity is not destroyed by the normal contacts. The experiments conducted down to low temperature to this day outline the stringent requirements to observe superconductivity: nanotubes should not be coated with polymers, and should be suspended. They should be long enough in order to avoid the inverse proximity effect, which causes the proximity to normal contacts to destroy the superconductivity in the tubes. Finally, there should be efficient screening of the repulsive interaction in nanotubes, so that superconductivity should develop the most in tubes that are assembled in a rope.

4. Signatures of superconductivity at ‘high’ temperature in small diameter tubes and doped multiwall carbon nanotubes (MWCNTs)

Other experiments have also shown evidence of intrinsic superconductivity in carbon nanotubes at temperatures as high as 10 K. This was first the case in magnetization experiments which strongly supported the existence of anisotropic superconducting fluctuations below 6 K in very small diameter (0.4 nm) individual tubes grown in zeolites. Very recent transport experiments both in linear and non-linear regimes confirm this superconducting behaviour. The high value of $T_c$ observed explained by the very small diameter of the tubes leading to a breathing mode at much higher energies is compared with the 1.2 nm diameter nanotubes we have investigated (see next section).

Resistance and magnetization measurements performed on arrays of MWCNTs have also been shown to exhibit a transition around 12 K. The transport experiments have, however, been found to strongly depend on the way the nanotubes were connected, indicating that only small diameter internal shells were exhibiting superconductivity. It was then shown that these samples were doped with boron and that this doping was playing an essential role in stabilizing the superconductivity. This was recently confirmed by magnetization experiments on intentionally boron doped arrays of SWCNTs constituting thin films. For boron concentrations between 1 and 3 at% the low field dependent magnetization is compatible with a Meissner effect at temperatures below 12 K and magnetic field below 0.4 T. Finally, even more surprising, superconducting fluctuations (resistance drop below 20 K) have been observed in individual gated SWCNT’s in good contact with normal electrodes. These fluctuations were found only for fairly high values of gate voltages indicating the importance of carrier doping also in these experiments. It is suggested (like in previous experiments) that it may be possible to enter a regime where the Fermi energy is aligned with a Van Hove singularity characteristic of the band structure of a SWCNT.

5. What is the mechanism of superconductivity in carbon nanotubes?

We now discuss what could be the relevant mechanism for superconductivity in carbon nanotubes. Observation of superconductivity in carbon based compounds was reported a long time ago. First in graphite intercalated with alkali atoms (Cs, K), superconducting transitions were observed between 0.2 and 0.5 K. Much higher temperatures were observed in alkali-doped fullerenes and more recently in graphite intercalated with Ca or Yb. Like in these systems, a phonon-mediated BCS-type attractive interaction is expected to be at the origin of superconductivity in carbon nanotubes. Nevertheless, a purely electronic coupling mechanism has also been shown to induce superconducting fluctuations in carbon nanotubes expected to behave like coupled double chain systems such as ladders. The very small order of magnitude for the energy scale of these superconducting fluctuations does not seem, however, to be compatible with experimental findings. These results point towards a purely phononic mechanism for superconductivity. However, like in doped fullerene molecules, the question of the relevant phonons for superconductivity in carbon nanotubes is still unsettled. Whereas Sediki et al consider the coupling to optical phonons, De Martino and Egger conjecture that attractive interactions can be mediated by low energy phonon modes specific to the structure of carbon nanotubes, in particular the RBM, which is compatible with our experimental results depicted above. They find that the attractive interaction may be strong enough to overcome the repulsive interactions in SWCNTs, especially in ropes of SWCNTs where the Coulomb interaction can be screened because the SWCNTs are packed so closely together. Their theory also could reproduce the temperature dependence of the superconducting transition observed in ropes as well as its dependence on the number of tubes.

Another important question concerns the influence of doping. In all experiments on fullerenes and graphite it was essential to chemically dope the system to observe superconductivity. There are no such chemical dopants in the ropes of carbon nanotubes discussed in section 3 but there is some possibility of hole doping of the tubes by the gold metallic contacts whose electronic work function is larger than that of the tubes. However, although this doping could slightly depopulate the highest occupied energy band, it is very unlikely that it is strong enough to depopulate other lower energy subbands for a tube with a diameter in the nanometre range. We have seen on the other hand, in section 4, that intentionally doped carbon nanotubes, either
chemically or using a strongly biased electrostatic gate, exhibit superconducting fluctuations at much higher temperatures than what we have observed, indicating in particular the importance of Van Hove singularities in the density of states of carbon nanotubes.

In conclusion, the physical picture which comes out from these findings is that superconductivity in carbon nanotubes results from a delicate balance between several antagonist mechanisms either in favour or against superconductivity, yielding a transition temperature which is strongly sample dependent. These mechanisms are strong electron–phonon interactions and unscreened electron–electron interactions together with the 1D character of transport and the tunable carrier density. It is an important challenge to learn how to master all these parameters in order to obtain reproducible and predictable results in the future.

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