

PHYSICS OF MULTIWALLED CARBON NANOTUBES

CHRISTIAN SCHÖNENBERGER

*Institute of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel,
Switzerland*

E-mail: Christian.Schoenenberger@unibas.ch

LASZLO FORRÓ

*Institute de Génie Atomique, École Polytechnique Fédérale de Lausanne, CH-1015
Lausanne*

E-mail: Laszlo.Forró@epfl.ch

We briefly review a couple of highlights in multiwalled carbon nanotube research. We will emphasize mechanical properties of nanotubes in general and then focus on electrical properties of multiwalled nanotubes in particular. The material is supposed to be accessible to a broad readership.

1 Introduction

Imagine being a tailor in the nanoworld with the task of tailoring a robust drinkstraw for a virus. You might come to the idea of taking a sheet of graphite (known as graphene), cutting out a long slice which is then rolled up and stitched together to form a carbon tube. These single-wall carbon nanotubes are reality, but rather than sewing the borders together, Nature forms these tubes seamless with a typical diameter of 1-2 nm. Sumio Iijima at NEC Fundamental Research Laboratory in Tsukuba discovered these giant molecules in 1991 when he studied the soot created by a direct-current arc discharge between carbon electrodes with high resolution transmission electron microscopy. What Iijima found were nanotubes consisting of several concentrically arranged single-wall carbon tubes nested into each other like a russian doll (see Fig. 1). These multishell nanotubes have outer diameters typically in the range of 10-50 nm and are now referred to as multiwall carbon nanotubes (MWNTs). Later, SWNT were discovered too and an efficient method for their production was found by Thomas Ebbesen and coworkers, also at NEC. Today, nanotubes can also efficiently be grown by catalytic decomposition of a carbon containing reaction gas. For a review, see Ref. 1.

Carbon nanotubes can be viewed as giant buckyball molecules, also called fullerenes. The basic buckyball is a 60 carbon atom soccer ball. If sliced into two halves a ring of 10 atoms can be added to get a rugby-ball. Repeating this will result in cylindrical molecules capped by half a buckyball at both ends. This is in

fact also true for well ordered MWNTs, for which all shells are capped. Multishell fullerenes are also known and called carbon onions. A multiwall nanotube is therefore a cylindrical onion or a carbon leek. Apart from these different shapes, the physics of carbon nanotubes depends on the direction of the tube axis relative to the lattice of the graphite sheet. There are many possible choices to roll a slice of graphene into a seamless cylinder. If bent into a nanotube the hexagons may spiral around the cylinder. Depending on this "chirality" carbon nanotubes can be metals with high electrical conductivity, or semiconductors with a relatively large band gap. Nanotubes have other remarkable properties: they are robust, very stiff with record elastic modulus, but at the same time not brittle at all. They can snap from one shape to the other if strongly compressed to finally resume their original perfect straightness if relaxed. These mechanical properties can, for example, be exploited for reinforcement, for nanomanipulators (tweezers) and for high-resolution scanning probe tips. Being composed of carbon only, nanotubes have a low specific weight, too. Furthermore, carbon nanotubes are hollow tubes and may be used in the future as nanopencils in which the capillary is used to deliver "ink" on the nanometer scale.

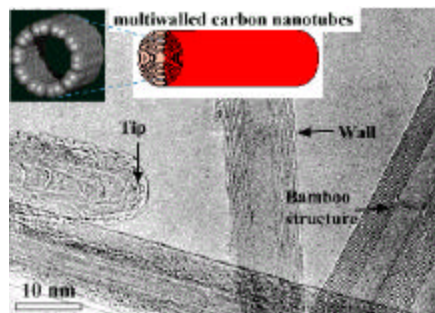


Figure 1. Multiwall carbon nanotubes (MWNTs) are composed of a set of single-wall tubes concentrically stacked into each other with a typical outer diameter of 20nm. Such a structure is clearly seen in the high-resolution transmission-electron microscopy (TEM) image of a well ordered MWNT grown in an arc-discharge.

2 Mechanical Properties

In 1996 Treacy, Ebbesen and Gibson from NEC Princeton and the University of Illinois studied MWNTs, which were rigidly supported on one side, in a transmission-electron microscope (TEM) [2]. The free ends of the nanotubes appeared considerably blurred. These nanotube levers do vibrate, stimulated by thermal excitations, causing the observed blurring. From the measured vibration amplitude, an exceptionally high elastic modulus (Young's modulus E) of order E

= 1 Tpa was derived. For a comparison, steel has a five times lower modulus. It is now known that for tubes with a radius larger than 1 nm, the Young's modulus should approach a value of 1.25 Tpa. This is true both for MWNT and SWNT because the modulus is mainly determined by intra-shell carbon bonds. This value has recently been confirmed. Charles Lieber and coworkers from Harvard University used a scanning-force microscope (SFM) to intentionally bend nanotubes which were dispersed on a substrate and mechanically fixed on one side [3]. The scanning-force microscope not only allowed to image and manipulate the tubes, but could also be employed to measure the force needed to bend the tubes. Similar values for E were obtained. Another technique to explore the bending stiffness was developed by Jean-Paul Salvetat and coworkers from the EPFL in Switzerland [4]. It involves depositing nanotubes from a suspension in liquid onto well-polished alumina ultrafiltration membranes with a pore size of about 200 nm. By chance, carbon nanotubes occasionally span the pores. The deflection of these supported tubes is then deduced from atomic-force microscopy (AFM) images operating at various normal loading force. The thus measured deflection is inversely proportional to the Young's modulus. Salvetat and coworkers compared the modulus of MWNTs grown by arc-discharge and catalytic decomposition of hydrocarbons. E is found to be approximately 1 Tpa for the former, while for the catalytic ones a much lower -- by one to two orders of magnitudes -- modulus was found. This result demonstrates that only highly ordered and well graphitized nanotubes have a stiffness comparable to graphite.

Charles Lieber and coworkers not only studied the elastic behaviour of nanotubes for small deflections (linear regime) but went on to explore what happens for large deformations. They also compared carbon nanotubes with nanorods made from silicon-carbide (SiC), another very strong material. There was a surprise: Whereas the continuous bending of the carbide nanorods ultimately led to fracture, MWNTs could be bent over large angles without fracturing. Instead buckling was observed. This elastic buckling has now been confirmed in several experiments, in which the nanotubes are either bent or axially compressed. Axial compression without any relaxation is possible up to limit, which has been calculated by the great mathematician Euler. Beyond this Euler-limit the initially straight tube or rod will flip into a curved form. If this experiment is performed with a drinking straw at constant load, the straw will suddenly develop kinks. These kinks are not elastic, but rather plastic deformations. The kinks remain if the load is removed. The carbon nanotubes are magic in this respect. If the force exceeds the bending strength, or the Euler limit if axially loaded, they first bend over surprisingly large angles, start to ripple and buckle to finally develop kinks as well. The amazing thing is that all these deformations are elastic and disappear completely if the load is removed. If combined with energy-absorbing materials, these mechanical properties of nanotubes may be usefull not only for cars but also,

for example, for light bulletproof vests and earthquake-resistant buildings. For additional reading, see Ref. 5-7.

The high strength of carbon nanotubes makes them promising candidates in reinforcement applications. There are many outstanding problems to be overcome before composite materials can be fabricated, which reflect the exceptional mechanical properties of the individual nanotubes. As well as optimizing the material properties of the individual tubes, the tubes must be bonded to a surrounding matrix in an efficient way to enable load transfer from the matrix to the tubes. In addition, efficient load bearing within the tubes themselves needs to be accomplished in such a way that shearing is prevented.

3 Electrical Properties

Carbon nanotubes are giant molecular wires in which the electrons can freely propagate, as in an ordinary metal. This strongly contrasts with conventional "conducting" polymers (like, for example, polythiophene) where the electrons localize. These molecules are actually insulators and become conductors only if heavily doped. Furthermore, conducting polymers have considerably shorter conjugation lengths. Each carbon atom of the graphene honeycomb lattice has four valence electrons of which three are strongly bound to neighbours giving graphene its in-plane rigidity. The fourth electron is delocalized and shared by all the atoms allowing for electrons to conduct. However, it turns out that a single sheet of graphite (graphene) is electronically a hybrid: it is neither a semiconductor, nor a metal. Graphene is a semimetal or a "zero-gap" semiconductor. This peculiarity renders the electronic states very sensitive to additional boundary conditions, as the periodic boundary condition along the circumference of a carbon nanotube. A stationary electron wave can only develop, if the circumference of the tube is a multiple of the electron wavelength. This condition removes the peculiarity of graphene and turns nanotubes into either true metals or semiconductors [1]. For MWNTs one expects a more complicated and richer dependence, because of a possible additional electronic coupling between adjacent shells. For a review, see Ref. 8. Combining different nanotubes and sublementing these with gate electrodes a large variety of electronic components ranging from wires, bipolar devices to field-effect transistors can be embodied in nanotubes. On the fundamental side, a perfect metallic nanotube is supposed to be a ballistic conductor. A ballistic conductor is the best (normal electron) conductor an engineer can dream of, only beaten by a superconductor. If an electron is injected from a contact into a ballistic wire with ideal contacts, the electron will end at the drain contact with certainty. There is no back-scattering in the wire, which is the source of intrinsic electric

resistance and leads to Ohm's law. A defectless carbon nanotube is like an optical fibre with two propagating modes, which results in to an electrical conductance (the inverse of the resistance) that is twice as large as the fundamental conductance unit G_0 ($G_0=2e^2/h$). Note, that the resistance is not zero as it would be for a superconductor. But quite in contrast to classical resistors and to Ohm's law, the resistance is independent of the length of the wire.

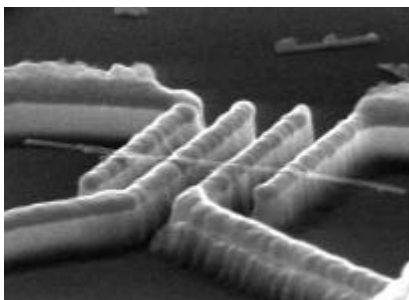


Figure 2. SEM image of a MWNT lying across four Au electrodes, which were fabricated by state-of-the-art electron-beam lithography prior to the deposition of the nanotube.

In 1998 Walt de Heer and his colleagues from the Georgia Institute of Technology invented an ingenious way for measuring the electrical conductance of single MWNTs [7]. A macroscopic fibre of MWNTs was fixed on a manipulator which allowed to steer the fibre above a drop of liquid metal (for example mercury). Because individual MWNTs stick out from the fibre, a single MWNT can now easily be contacted by gently lowering the fibre into the conducting liquid. By dipping the nanotubes to different depths it is possible to determine the resistance per unit length, which should be zero in an ideal ballistic wire. This method of contacting a nanotube is very different to, for example, the structuring of metal electrodes to nanotubes using high-resolution sub-micron fabrication technology (an example is shown in Fig. 2). Reasonably low-ohmic contacts, both for multiwall- and single-wall nanotubes, were very difficult to achieve in previous experiments. It is important to emphasize that the quantized conductance can only be observed if ideal contacts are realized. These early experiments showed that MWNTs are far from being ballistic. In contrast, strong evidence was found that electrons scatter in nanotubes, so that transport is more appropriately characterized as diffusive. Taken these early experiments the results of de Heer and coworkers were very surprising. First, these researchers showed that all MWNTs have nearly the same conductance corresponding to one conductance quantum. Secondly, the length dependent resistance was found to be very low. These two results suggest that MWNTs are ballistic conductors, despite the many shells that may be expected to interact.

Because MWNTs consist of several concentrically arranged SWNTs, one would expect that MWNTs do not qualify as one-dimensional conductors. If adjacent carbon shells interact as in graphite, electrons may not be confined to one shell only. The results of de Heer and coworkers suggest however that the current mainly flows through the outermost shell only. Our own investigation has proven that this is indeed the case. In this respect, studying electric transport in MWNTs is somewhat similar to studying transport in a large diameter SWNT. The nanotube core solely acts as a mechanical support for the electrically active outermost shell. Note, that this is no longer true, if we would find a way to contact the bulk, or even were able to selectively address inner shells. MWNTs have certain specific advantages over SWNTs: their large diameter favours low-ohmic contacts, because of the larger contact area. Arc-discharge grown MWNTs do not contain magnetic impurities, which is important for spintronics, in which the spin of the electrons is used for magnetic-sensing or switching applications or even for computation. Their large diameter enables to investigate quantum-interference phenomena in magnetic field.

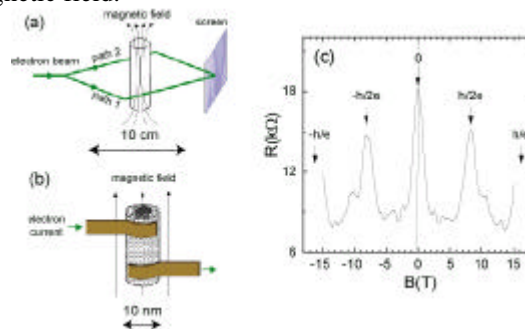


Figure 3. (a) Illustration of the Aharonov-Bohm (AB) effect. The flux through the solenoid changes the relative phase of the electron-waves in path 1 and path 2 of this two-beam electron interferometer. This affects the intensity modulation on the screen (the interference pattern). Similarly, the electron waves in a carbon nanotube are modified by the magnetic flux threading the interior of the tube (b). The change in interference pattern in (a) translates into a change of the electric resistance in (b). (c) shows the measured resistance R as a function of parallel magnetic field. The arrows point to multiple flux-quanta $h/2e$.

The most profound quantum-interference effect is the Aharonov-Bohm (AB) effect. The illustration of Fig. 3 shows what happens if an electron beam is split into two partial beams following different paths, but merge together on a screen on which the electron intensity is measured. One observes an intensity modulation in the form of a periodic stripe pattern. Such a pattern is called interference pattern. Its observation demonstrates that in this experiment a single electron does not choose either path but behaves as an extended wave which has amplitude on both paths simultaneously. The two paths form a closed loop threaded by a magnetic flux. Though electrons need never come in "contact" with the magnetic field, the

interference pattern changes periodically with flux with a period given by the magnetic-flux quantum $\Phi_0 = h/e$. This is the Aharonov-Bohm effect. Now imagine a carbon nanotubes (a single wall for simplicity) placed in a magnetic field parallel to the tube axis (Fig. 3b). Since nanotubes are cylindrical conductors the electrons that propagate on the cylinder can circle around the tube in either the clockwise or counter-clockwise direction. These two "paths" interfere, as in the example discussed before, resulting in a periodic modulation of the electrical resistance with magnetic flux through the hollow. In this case the period is half the flux-quantum. This effect is relatively robust and can even be observed if transport in nanotube is diffusive. For an ideal ballistic nanotube, a much more dramatic effect is expected. Whether a nanotube is a semiconductor or a metal depends only on the relative phase of the wavefunction around the tube circumference. Since the magnetic flux changes the phase, a metallic NT should continuously evolve into a semiconducting one and vice versa. We have placed single electrically contacted MWNTs in a parallel field and studied both the temperature and flux dependence of the electrical resistance [10]. Fig. 3c displays the main result. There is a resistance peak at zero magnetic field. This peak reappears at approximately ± 8.5 Tesla, although with reduced amplitude. If this increase is caused by the AB effect, resistance peaks should appear equidistantly. The additional resistance increase at the highest field of 15 Tesla agrees with this expectation. The magnetic field at the peak position can be related to the diameter of the nanotube, which turns out to be equal to the geometric outer diameter of the NT measured independently. This demonstrate unambiguously, that the electric current is carried by the outermost tube only. We would like to mention here, that in order to observe the first peak in a similar experiment with SWNTs would require a magnetic field of 1000 Tesla because of the small tube radius. The peak separation in Fig. 3c corresponds to half Φ_0 suggesting that transport is not ballistic in our MWNTs. If it were ballistic a much larger effect should have been observed, since the metallic NT would be turned into a semiconductor with a gap much larger than the measuring temperature. This and other magneto-resistance measurements have allowed to deduce the scattering length and the length dependent resistance. We found that transport is diffusive. A large variation in scattering length have been deduced, ranging from 3 nm (very diffusive) to 100 nm (quasi-ballistic, i.e. intermediate between diffusive and ballistic). That the observed metal-to-semiconductor transition has not been observed is a puzzle which needs to be solved, as we have to find an explanation for the large variation in scattering length, from near infinity (de Heer et al.) to a couple of nanometers. Although transport in our MWNTs is best characterized as diffusive, large electric currents (up to 1mA) can be passed through the nanotubes, demonstrating that the electrons couple only weakly, if at all, to the lattice. All magnetoresistance measurements can very well be understood in the Fermi liquid framework assuming two-dimensional diffusive

transport. However, recent measurements of the tunneling DOS in MWNTs have revealed anomalies quite similar to feature seen in SWNT which were assigned to Luttinger liquid behaviour.

Maybe the most exciting (and controversial) recent finding is the claim for *intrinsic superconductivity* in ropes of SWNTs. A transition to a seemingly superconducting state below approx. 0.4 K has been observed by Yu Kasumov, H. Bouchiat and coworkers in nanotubes contacted by a special laser tool enabling to achieve very low-ohmic contacts [11].

4 Outlook

Carbon nanotubes have shown a wealth of phenomena. Some results we firmly understand already, others are controversial today. Nanotubes are great molecules and good conductors with a wide range of interesting properties useful for applications. The future for nanotube looks very bright: Nanotubes are interesting model systems for fundamental studies of one-dimensional systems, but they are equally well (or even more) attractive to applied researchers and industries due to the large variety of potential applications.

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