

CARBON NANOTUBES

Nanotubes are ideal systems for studying the transport of electrons in one dimension, and have commercial potential as nanoscale wires, transistors and sensors

Single-wall carbon nanotubes

Paul L McEuen

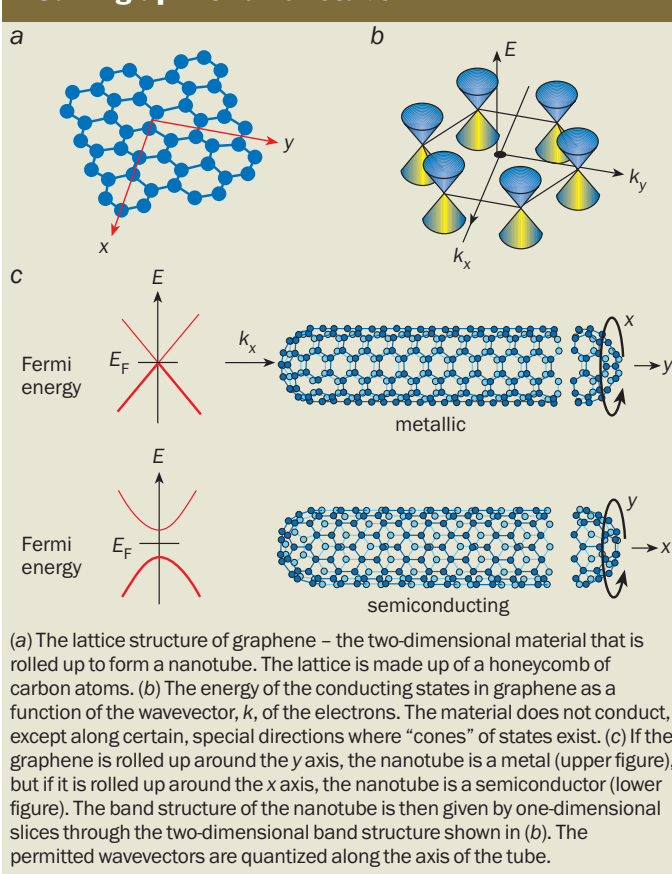
SOLID-STATE devices in which electrons are confined to two-dimensional planes have provided some of the most exciting scientific and technological breakthroughs of the last 50 years. From metal-oxide-silicon field effect transistors to high-mobility gallium-arsenide heterostructures, these devices have played a key role in the microelectronics revolution and are critical components in a wide array of products from computers to compact-disk players. From a more parochial perspective, the study of electrons in two-dimensional systems has also been responsible for two Nobel prizes in physics – to Klaus von Klitzing in 1985 and to Robert Laughlin, Horst Störmer and Daniel Tsui in 1998. This is testimony to the basic as well as applied interest of such devices (see Heiblum and Stern in further reading).

However, 1-D systems are also proving to be very exciting. For many years, studies of quasi 1-D systems, such as conducting polymers, have provided a fascinating insight into the nature of electronic instabilities in one dimension. In addition, 1-D devices such as “electron waveguides” – in which electrons propagate through a narrow channel of material – have been created. Experiments on these devices have shown, for example, that the conductance of “ballistic” 1-D systems – in which electrons travel the length of the channel without being scattered – is quantized in units of e^2/h , where e is the charge on the electron and h is the Planck constant.

These systems, however, have been limited by the fact that they are inherently complex and/or difficult to make. What has been lacking is the perfect model system for exploring one-dimensional transport – a 1-D conductor that is cheap and easy to make, can be individually manipulated and measured, and has little structural disorder. Single-wall carbon nanotubes fit this bill remarkably well. These thin, hollow cylinders of carbon were discovered in 1993 by groups led by Sumio Iijima at the NEC Fundamental Research Laboratory in Tsukuba, Japan, and by Donald Bethune at IBM’s Almaden Research Center in California – and were first mass-produced in 1995 by Rick Smalley’s group at Rice University in Texas. Since then, this new type of 1-D conductor has been the focus of amazingly intense study. Here I will describe just a small part of that activity: the creation of tiny nanoelectronic devices in which nanotubes are the active element.

As we will see, some nanotubes are semiconductors. They can therefore be used to construct devices that are one-

1 Curling up with a nanotube

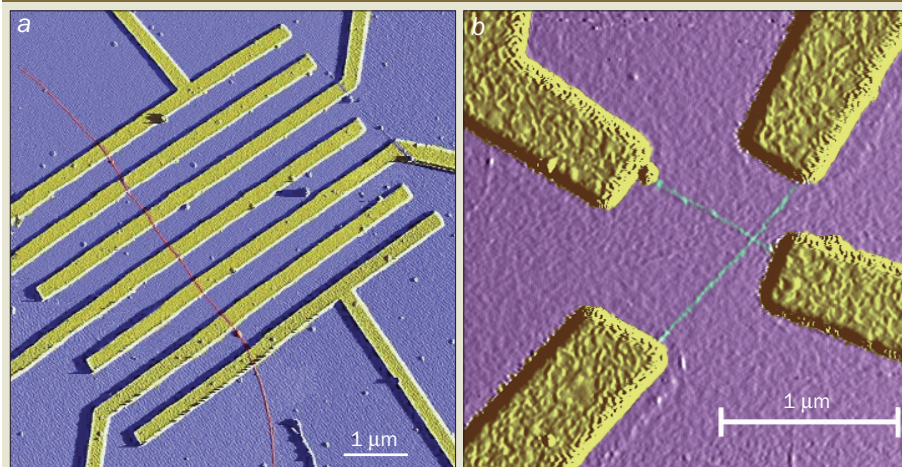


dimensional analogues of metal-oxide-silicon field effect transistors, in which the electrons move along the surface of a thin two-dimensional layer. Other nanotubes, in contrast, are nearly perfect metallic conductors, and are a new “laboratory” for studying the motion of electrons in one dimension. Both semiconducting- and metallic-nanotube devices are likely to have significant technological applications.

Electronic structure of nanotubes

The remarkable electrical properties of single-wall carbon nanotubes stem from the unusual electronic structure of “graphene” – the 2-D material from which they are made.

2 Measuring the conductance of nanotubes



To find out how nanotubes conduct electricity, we have to attach electrodes to them. Electron-beam lithography is normally used to fabricate the electrodes, which are then connected to either a single tube or a bundle of tubes. (a) An atomic force microscope (AFM) image of a single nanotube device made by researchers at the Delft Institute of Technology. The nanotube is the tiny red line running from the bottom centre to the top left. (b) An AFM image of a nanotube “cross”, made in my lab at the University of California at Berkeley. The two nanotubes are the green lines that join the electrodes. In both cases, the devices are fabricated on an conducting substrate covered with an insulating oxide layer. (c) The substrate acts as a gate to allow the charge density of the nanotube to be varied.

to form a tube (figure 1c). The resulting periodic boundary conditions on the wavefunction quantizes k_n , the component of k perpendicular to the axis of the tube: in the simplest case, $k_n = 2\pi n/C$, where C is the circumference of the tube and n is an integer. The component of k along the length of the tube, meanwhile, remains a continuous variable.

If the tube axis is chosen to point in the y direction, the energy as a function of k (i.e. the band structure) is a slice through the centre of the cone. The tube then acts as a 1-D metal with a Fermi velocity that is similar to most metals. However, if the tube axis points in different directions, such as along the x axis, then the band structure has a different conic section. This typically results in a semi-conducting 1-D band structure, with an energy gap between the filled hole states and the empty electron states.

The bottom line is that a nanotube can be either a metal or a semiconductor, depending on how the tube is rolled up. This remarkable theoretical prediction has been verified using a number of measurement techniques. Perhaps the most direct was carried out by Cees

Graphene is simply a single atomic layer of graphite, the material that makes up pencil lead. Graphene has a two-dimensional “honeycomb” structure, made up of sp^2 -bonded carbon atoms (figure 1a). Its conducting properties are determined by the nature of the electronic states near the Fermi energy, E_F , which is the energy of the highest occupied electronic state at zero temperature. The energy of the electronic states as a function of their wavevector, k , near E_F is shown in figure 1(b). This “band structure”, which is determined by the way in which electrons scatter from the atoms in the crystal lattice, is quite unusual. It is not like that of a metal, which has many states that freely propagate through the crystal at E_F . Nor is the band structure like that of a semiconductor, which has an energy gap with no electronic states near E_F due to the backscattering of electrons from the lattice.

The band structure of graphene is instead somewhere in between these extremes. In most directions, electrons moving at the Fermi energy are backscattered by atoms in the lattice, which gives the material an energy band gap like that of a semiconductor. However, in other directions, the electrons that scatter from different atoms in the lattice interfere destructively, which suppresses the backscattering and leads to metallic behaviour. This suppression only happens in the y direction and in other directions that are 60° , 120° , 180° and 240° from y (figure 1b). Graphene is therefore called a “semi-metal”, since it is metallic in these special directions and semi-conducting in the others.

Looking more closely at figure 1(b), the band structure of the low-energy states appear to be a series of cones. At low energies, graphene resembles a two-dimensional world populated by massless fermions.

To make a 1-D conductor from this 2-D world, we follow the lead of string theorists and curl one of the extra dimensions

Dekker’s group at the Delft University of Technology in the Netherlands and by Charles Lieber’s group at Harvard University in the US. The Delft and Harvard researchers used scanning tunnelling microscopy to determine the atomic structure of a particular tube – out of the many types of tube that are produced when a sample is grown – before probing its electronic properties with the microscope. Their measurements confirmed the relationship between the structure of a nanotube and its electronic properties as outlined above.

Nanotubes: how they conduct

Before we can measure the conducting properties of a nanotube, we have to wire up the tube by attaching metallic electrodes to it. The electrodes, which can be connected to either a single tube or a “bundle” of up to several hundred tubes, are usually made using electron-beam lithography. The tubes can be attached to the electrodes in a number of different ways. One way is to make the electrodes and then drop the tubes onto them (figure 2a). Another is to deposit the tubes on a substrate, locate them with a scanning electron microscope or atomic force microscope, and then attach leads to the tubes using lithography (figure 2b). More advanced techniques are also being developed to make device fabrication more reproducible and controlled. These include the possibility of growing the tubes between electrodes (see the article by Dai on page 43), or by attaching the tubes to the surface in a controllable fashion using either electrostatic or chemical forces.

The “source” and “drain” electrodes – so named in analogy to standard semiconducting devices – allow the conducting properties of the nanotube to be measured. In addition, a third terminal – called a “gate” – is often used (figure 2c). The gate and the tube act like the two plates of a capacitor, which means that the gate can be used to electrostatically induce

carriers onto the tube. A negative bias on the gate induces positive charges onto the tube, and a positive bias induces negative charges.

When the conductance of the tube is measured as a function of the gate voltage (and hence as a function of the charge per unit length of the tube), two types of behaviour are observed, corresponding to metal and semiconducting tubes. Individual metallic single-walled nanotubes were first studied in 1997 by Dekker's group at Delft and by the author's group at the University of California at Berkeley, both in conjunction with Smalley's group at Rice. Semiconducting behaviour was then reported by the Delft group in 1998.

Since then, many groups have made and measured the properties of similar devices. Indeed, most major universities and industrial laboratories, such as IBM, now have at least one group studying these materials for a variety of electronic applications. Although the data presented in this article are taken entirely from the Berkeley group led by Alex Zettl, Steven Louie, Marvin Cohen and me, they should be viewed as representative of the field. In most cases, similar results have also been obtained by other researchers.

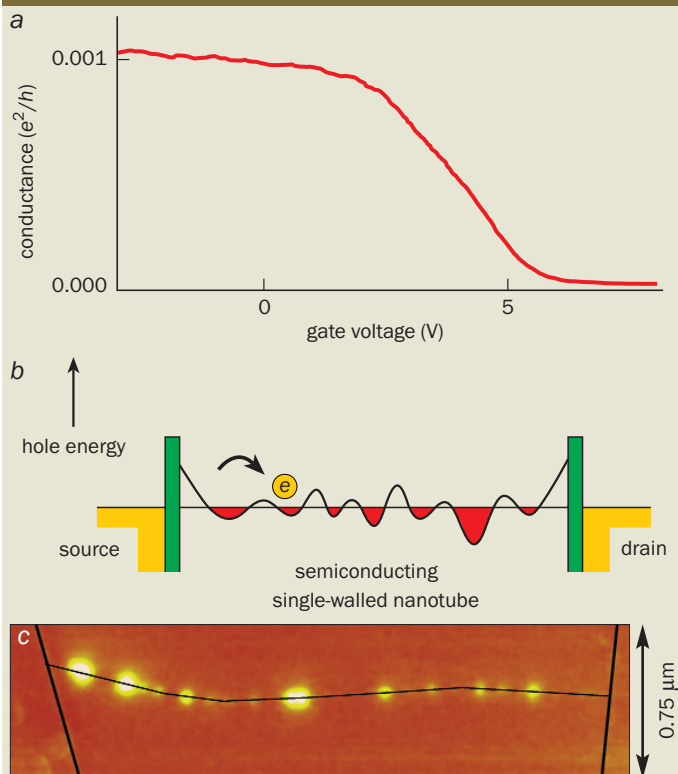
Nanotube transistors

Semiconducting nanotubes can work as transistors. The tube can be turned "on" – i.e. made to conduct – by applying a negative bias to the gate, and turned "off" with a positive bias (figure 3a). A negative bias induces holes on the tube and makes it conduct. Positive biases, on the other hand, deplete the holes and decrease the conductance. Indeed, the resistance of the off state can be more than a million times greater than the on state. This behaviour is analogous to that of a p-type metal-oxide-silicon field effect transistor (MOSFET), except that the nanotube replaces silicon as the material that hosts the charge carriers.

But why is the tube p-type? After all, one might expect an isolated semiconducting nanotube to be an "intrinsic" semiconductor – in other words, the only excess electrons would be those created by thermal fluctuations alone. However, it is now believed that the metal electrodes – as well as chemical species adsorbed on the tube – "dope" the tube to be p-type. In other words, they remove electrons from the tube, leaving the remaining mobile holes responsible for conduction. Indeed, recent experiments by Hongjie Dai's group at Stanford University and by the group at Berkeley show that changing a tube's chemical environment can change the level of doping, significantly changing the voltage at which the device turns on. More dramatically, tubes can even be doped n-type by exposing the tube to elements such as potassium that donate electrons to the tube.

The semiconducting device of the type shown in figure 3 is, in many ways, truly remarkable. First, it is only one nanometre wide. While much work has been done to create ultra-small semiconducting devices from bulk semiconductors, such devices have always been plagued by "surface states" – electronic states that arise when a three-dimensional crystal is interrupted by a surface. These surface states generally degrade the operating properties of the device, and controlling them is one of the key technological challenges to device miniaturization. Nanotubes solve the surface-state problem in an elegant fashion. First, they are inherently two-dimensional materials, so the problem of a 3-D lattice meeting a surface does not exist. Second, they avoid the problem of

3 Nanotubes as transistors



(a) The conductance of a semiconducting carbon nanotube as a function of gate voltage. The tube can be turned "on" by applying a negative voltage, and turned "off" with a positive voltage. The device turns on at negative voltages because holes are added to the tube. (b) The potential profile seen by these holes due to disorder in the structure of the nanotube and imperfect contacts between the electrodes and the tube. The holes must hop through the barriers in this profile if the nanotube is to conduct. (c) The tip of a scanning probe microscope can be used to map the barriers to conduction. The horizontal line indicates the location of the nanotube and the vertical lines indicate the contact boundaries. The conductance of the tube is measured as the positively biased tip is scanned over the sample. The bright spots are where the tip decreased the conductance, with greater intensity corresponding to a greater change in the conductance.

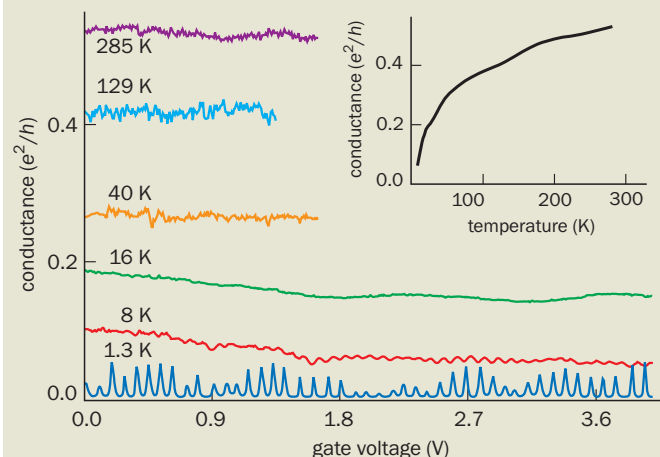
edges – because a cylinder has no edges!

Looking more closely at the conductance of semiconducting nanotubes, we see that initially it rises linearly as the gate voltage is reduced, conducting better as more and more holes are added from the electrode to the nanotube. The conductance is limited only by any barriers that the holes see as they traverse the tube. These barriers may be caused by structural defects in the tube, by atoms adsorbed on the tube, or by localized charges near the tube. The holes therefore see a series of peaks and valleys in the potential landscape, through which they must hop if the tube is to conduct (figure 3b). The resistance of the tube will be dominated by the highest barriers in the tube.

Recent experiments by the Berkeley and Delft groups confirm this simple picture. The researchers used the tip of a scanning probe microscope to identify the major scattering sites, thus enabling a map of the barriers to conduction to be produced (figure 3c).

At lower gate voltages, the conductance eventually stops increasing and becomes constant, because the contact resistance between the metallic electrodes and the tube can be quite high. Unfortunately, this contact resistance can vary by several orders of magnitude between devices, probably due

4 Nanotubes as metals



The conductance of a metallic nanotube at six different temperatures as a function of gate voltage. At low temperatures the conductance oscillates as individual electrons are added to the tube. This indicates that the nanotube acts like a long and narrow quantum dot, with electronic states that extend over the entire length of the tube. The average conductance of the tubes slowly decreases as the temperature is lowered (see insert). The functional form is consistent with the power-law behaviour predicted for tunnelling into a Luttinger liquid.

to mundane issues such as surface cleanliness. To improve the consistency of nanotube transistors, many groups are therefore trying to improve the quality of these contacts by developing new cleaning and annealing procedures – with some significant success.

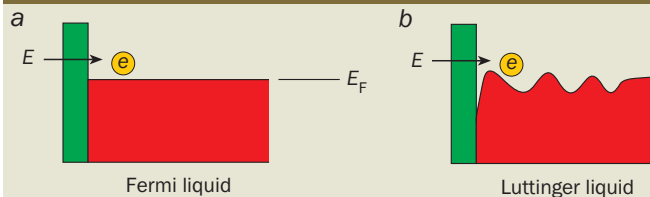
These tiny MOSFET-like devices will probably just be the first in a host of new semiconducting-device structures based on carbon nanotubes. Other devices, such as nanotube p–n junction diodes and bipolar transistors, have been discussed theoretically and are likely to be realized soon.

Nanotubes as one-dimensional metals

In dramatic contrast to semiconducting nanotubes, the conductance of some other nanotubes near room temperature is not noticeably affected by the addition of a few carriers. This behaviour is typical of metals, which have a large number of carriers and have conducting properties that are not significantly affected by the addition of a few more carriers. The conductance of these metallic nanotubes is also much larger than the semiconducting-nanotube devices, as expected. Indeed, a number of groups have made tubes with conductances that are between 25% and 50% of the value of $4e^2/h$ that has been predicted for perfectly conducting ballistic nanotubes. This result indicates that electrons can travel for distances of several microns down a tube before they are scattered. Several measurements support this conclusion, including those carried out by our group using scanning probe microscopy. These measurements also show that the contact resistance between the tube and the electrodes can be substantial, just as it is with semiconducting tubes.

Further evidence for the near-perfect nature of these tubes comes from the way they behave at low temperatures. The conductance is observed to oscillate as a function of gate voltage (figure 4). These ‘‘Coulomb oscillations’’ occur each time an additional electron is added to the nanotube. In essence, the tube acts like a long box for electrons, often called a ‘‘quantum dot’’ (see Kouwenhoven and Marcus in further reading). The

5 Electrons in one dimension



(a) An electron tunnelling from a metal electrode into a Fermi liquid leaves other electrons in the Fermi sea relatively undisturbed. (b) An electron finds it less easy, however, to tunnel into a Luttinger liquid, because collective excitations in the electron liquid must be excited. Calculations show that the Luttinger liquid has a tunnelling conductance that decreases in proportion to $(E - E_F)^\alpha$ where E is the energy of the electron, E_F is the Fermi energy and α is a power. The excess energy of the tunnelling particle is provided by either an applied temperature or voltage.

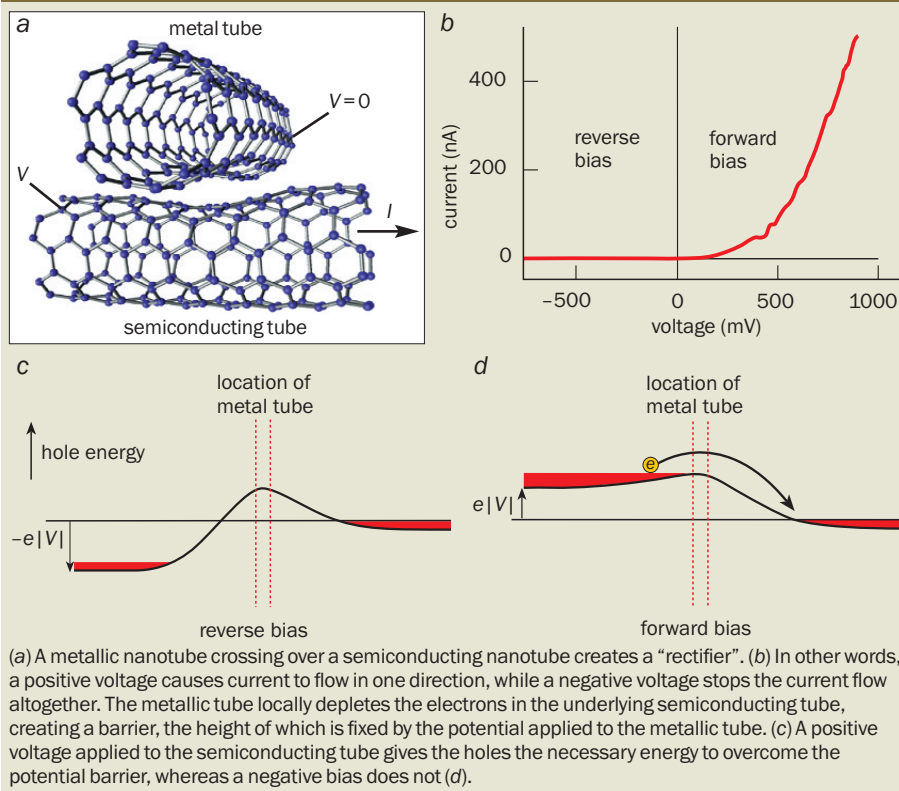
electronic and magnetic properties of these nanotube quantum dots reveal a great deal about the behaviour of electrons in nanotubes. For example, the fact that the oscillations are quite regular and periodic indicates that the electronic states are extended along the entire length of the tube. If, however, there was significant scattering in the tube, the states would become localized and the Coulomb oscillations would be less regular. Nanotube quantum dots that are as long as 10 μm have been found to exhibit these well-ordered oscillations, again indicating that the mean free path can be very long.

The experiments described above indicate that electrons can travel for long distances in nanotubes without being backscattered. This is in striking contrast to the behaviour observed in traditional metals like copper, in which scattering lengths from lattice vibrations are typically only several nanometres at room temperature. The main reason for this remarkable difference is that an electron in a 1-D system (like a nanotube) can only scatter by completely reversing its direction, whereas electrons in a 2-D or 3-D material can scatter by simply changing direction through a tiny angle. Phonons – long-wavelength lattice vibrations that scatter electrons in both 2-D and 3-D materials at room temperature – do not have enough momentum to reverse the direction of a speeding electron in a 1-D nanotube. They therefore do not influence its conductance, at least not at low voltages.

Recent experiments by Dekker’s group at Delft have shown that at high voltages (greater than 0.15 V), electrons can emit high-momentum phonons that can scatter electrons in 1-D nanotubes. This leads to a dramatic reduction in the conductance at high voltages, causing the current to saturate at about 25 microamps for a single nanotube. Still, this is a remarkably macroscopic current to be carried by such a nanoscopic system!

The fact that a metallic nanotube acts like a near-perfect 1-D conductor at low voltages makes it an ideal system to test some ideas about electrons in one dimension that have been around for half a century. Starting in the 1950s, a series of papers by Sin-Itiro Tomonaga, Joaquin Luttinger and later Duncan Haldane made it clear that a 1-D electron system should behave very differently from its 2-D and 3-D counterparts when the repulsive Coulomb interactions between neighbouring electrons are taken into account. Under ordinary conditions, a 2-D or 3-D metallic conductor behaves as a ‘‘Fermi liquid’’, even when the electrons interact with each other via the Coulomb force. The electrons in such materials fill the low-energy states up to the Fermi energy, creating what

6 Nanotubes as rectifiers



is known as a “Fermi sea” of electrons. The low-energy excitations (or “quasiparticles”) of this system act almost like completely free electrons, moving entirely independently of one another. In other words, an excited state looks very much like a single extra electron above the Fermi sea.

In 1-D systems, on the other hand, the low-energy excitations are collective excitations of the entire electron system. The electrons move in concert, rather than as independent particles of a Fermi liquid. This system is referred to as a “Tomonaga–Luttinger liquid” (or, more simply, a Luttinger liquid) to emphasize its difference from the standard Fermi-liquid behaviour of 2-D and 3-D metals.

One way to test this prediction is to see if an electron can tunnel into the system from the outside world – for example from a metallic contact. If the low-energy excitations are simple quasiparticles, then an electron will have no difficulty tunnelling into the system (figure 5a). The tunnelling conductance would not be expected to change with temperature or bias voltage. If, on the other hand, the low-energy excitations are collective in nature, the other electrons in the tube must move in concert with the tunnelling electron to make room for it. The electron must literally make a “splash” when it jumps into the Luttinger liquid (figure 5b). If the energy, E , of the tunnelling electron is much higher than the Fermi energy, E_F , then this “splash” is not a problem. As the electron tunnels in with less and less excess energy, however, it has less and less energy to push the other electrons out of the way.

Calculations show that the Luttinger liquid has a tunnelling conductance that decreases in proportion to $(E - E_F)^\alpha$, where α is a particular power. The value of α depends on the strength of the Coulomb interaction between the electrons. It also depends on whether the electron tunnels into the middle of a tube, the end of a tube, or between the ends of two tubes.

Theorists have been able to estimate these powers fairly accurately for nanotubes, resulting in very specific predictions that experimentalists can test.

Our group at Berkeley tested these predictions by measuring the tunnelling conductance into a nanotube from a metallic electrode as a function of the temperature and bias. In this case, the poor contacts worked to our advantage, serving as the tunnel barriers between the tube and the electrode. The average conductance decreases slowly as a function of temperature (figure 4). The relationship is described by a power law that agrees well with theory. The group has also measured the powers for electrons tunnelling into the middle and ends of a tube, while our colleagues at Delft have done the same for electrons tunnelling from the end of one nanotube into the end of another. All of these results agree well with the theoretical predictions.

These experiments clearly demonstrate that interacting 1-D metals behave very differently to 2-D and 3-D metals. This is perhaps not so surprising – to use a traffic analogy, car–car interactions are much more important on a one-lane highway than they are in a 2-D parking lot, where a car can move more-or-less independently of the other cars. What is surprising, however, is how long it took before these predictions were tested in detail. While previous measurements of other systems had shown evidence for Luttinger behaviour, nanotubes represent perhaps the clearest and most straightforward realization of Luttinger-liquid physics to date.

New devices and geometries

While the above experiments demonstrate that many of the basic properties of single-wall carbon nanotubes are now understood, there is an almost limitless number of new geometries and topics waiting to be explored and all manner of new structures to be created. Indeed, researchers are developing a host of new techniques that creatively combine lithography, chemistry and nanoscale manipulation, for example by growing tubes on prefabricated structures or by pushing them around with the tips of atomic force microscopes. It is quite remarkable how far the field has come since the first measurements were made in 1997 – and this progress shows no sign of slowing.

For example, new devices can be created by the intersection of two nanotubes, such as a metallic tube crossing over a semiconducting tube (figure 6). The metallic tube locally depletes the holes in the underlying p-type semiconducting tube. This means that an electron traversing the semiconducting tube must overcome the barrier created by this metal tube. Biasing one end of the semiconducting tube relative to the metal tube leads to rectifying behaviour. In other words, the barrier is overcome in one bias direction, but not in the other. This structure is just one of many possibilities for nanotube devices waiting to be explored.

Meanwhile, Phaedon Avouris and co-workers at IBM’s T J

CARBON NANOTUBES

Watson Research Center in New York have made “nanotube coils”, in which an individual tube loops back on itself to form a ring-like structure. Such coils might be used as tiny solenoids to create magnetic fields or to study quantum interference phenomena. Superconducting contacts have also been attached to nanotubes by several groups to study the behaviour of superconductors connected by a 1-D conductor.

Nanotubes also offer great promise as the active elements in “nano-electromechanical” systems. Their remarkable mechanical and electronic properties make them excellent candidates for applications such as high-frequency oscillators and filters. Many groups have now created devices in which the substrate beneath the nanotube is removed, leaving the nanotube suspended in free space between the two contacts. The tube is therefore free to vibrate like a guitar string, and researchers are starting to investigate the interactions between the mechanical and electronic degrees of freedom (see article by Dai on page 43).

The future lies in tubes

Single-nanotube devices have come a long way, but how far they will go is anyone’s guess. Clearly, they will be part of the scientific landscape for years to come as a model system for studying physics at the nanometre scale.

Many commercial applications have also been proposed, from molecular electronics to sensing. Whether these will pan out is more difficult to assess (see article by de Heer and Martel on page 49). If these real-world applications of nanotubes are to succeed, we must find ways of successfully integ-

rating them into existing microelectronic products and techniques. But if we manage to develop the technology to fabricate nanotubes of a particular type, length and diameter in a controlled fashion – and to incorporate the tubes into lithographic circuits at particular places with efficiencies approaching 100% – then the sky is, indeed, the limit.

While this is a challenging goal, there appear to be no fundamental barriers to achieving it. A proper marriage of physics, chemistry and electrical engineering may be up to the task. Electronics may begin to go the way of biology and use the carbon atom as its backbone.

Further reading

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The Nanotube Site www.pa.msu.edu/cmp/csc/nanotube.html

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