
Electronic, Thermal and Mechanical Properties of Carbon Nanotubes

Author(s): M. S. Dresselhaus, G. Dresselhaus, J. C. Charlier, E. Hernández

Source: *Philosophical Transactions: Mathematical, Physical and Engineering Sciences*, Vol. 362, No. 1823, Nanotechnology of Carbon and Related Materials (Oct. 15, 2004), pp. 2065-2098

Published by: [The Royal Society](#)

Stable URL: <http://www.jstor.org/stable/4142433>

Accessed: 19/09/2011 11:13

Your use of the JSTOR archive indicates your acceptance of the Terms & Conditions of Use, available at

<http://www.jstor.org/page/info/about/policies/terms.jsp>

JSTOR is a not-for-profit service that helps scholars, researchers, and students discover, use, and build upon a wide range of content in a trusted digital archive. We use information technology and tools to increase productivity and facilitate new forms of scholarship. For more information about JSTOR, please contact support@jstor.org.



The Royal Society is collaborating with JSTOR to digitize, preserve and extend access to *Philosophical Transactions: Mathematical, Physical and Engineering Sciences*.

<http://www.jstor.org>

Electronic, thermal and mechanical properties of carbon nanotubes

BY M. S. DRESSELHAUS¹, G. DRESSELHAUS², J. C. CHARLIER³
AND E. HERNÁNDEZ⁴

¹*Department of Physics and Department of
Electrical Engineering and Computer Science,*

²*Francis Bitter Magnet Laboratory, Massachusetts Institute
of Technology, Cambridge, MA 02139-4307, USA*

³*Université Catholique de Louvain, Unité de Physico-Chimie
et de Physique des Matériaux, Place Croix du Sud 1,
Bâtiment Boltzmann, 1348 Louvain-la-Neuve, Belgium*

⁴*Institut de Ciència de Materials de Barcelona (ICMAB-CSIC),
08193 Bellaterra, Barcelona, Spain (ehe@icmab.es)*

Published online 13 August 2004

A review of the electronic, thermal and mechanical properties of nanotubes is presented, with particular reference to properties that differ from those of the bulk counterparts and to potential applications that might result from the special structure and properties of nanotubes. Both experimental and theoretical aspects of these topics are reviewed.

Keywords: nanotubes; electronic properties; mechanical properties; phonon properties; Raman spectroscopy; thermal properties

1. Introduction

Carbon nanotubes (CNTs) are tubular structures that are typically of nanometre diameter and many micrometres in length. This fascinating new class of materials was first observed by Endo (1975), and later by Iijima (1991) in the soot produced in the arc-discharge synthesis of fullerenes. Because of their tiny size, these nanostructures exhibit many interesting and often unexpected properties, and hence there are many possibilities for using them in nanotechnology. Shortly after the 1991 discovery of multi-wall CNTs, single-walled nanotubes (SWNTs) with small (*ca.* 1 nm) and uniform diameters were synthesized using arc-discharge methods with transition metal catalysts (Bethune *et al.* 1993; Iijima & Ichihashi 1993). Crystalline ropes of SWNTs, with each rope containing tens to hundreds of tubes of similar diameter, closely packed into a triangular lattice, have been synthesized by a variety of methods, providing ample amounts of sufficiently characterized samples for study of the fundamental properties of the SWNTs.

In this review we present a condensed overview of the current state of knowledge on three key aspects of CNTs, namely, their electronic structure and related properties, their vibrational and thermal characteristics and their mechanical properties.

One contribution of 12 to a Theme ‘Nanotechnology of carbon and related materials’.

These different aspects are all interrelated, since both thermal and mechanical properties reflect the chemical bonding in the carbon network, which also controls their electronic structure. Thus, all three aspects ultimately reflect the unique structure of nanotubes. Other relations between these different aspects will become apparent below.

As in other fields of nanotechnology, CNTs have provided and continue to provide a wonderful opportunity for the fruitful interaction between experiment, theory and simulation, as is evident from the bibliography. This is partly due to the high level of interest generated by nanotubes during the last decade, but also because nanotubes, given their well-defined structure, are particularly amenable to theoretical and simulation studies.

The contents of this paper are as follows: §2 is devoted to the electronic properties of SWNTs, how these properties are related to their geometry and structure; the influence of structural defects such as pentagons and heptagons is also discussed, as is the possibility of fabricating nanotube-based junctions of different geometries, and their implications on nano-electronics. Section 3 reviews the vibrational properties of nanotubes. We start by describing the vibrational modes of SWNTs, particularly how they are related to (and in what way they differ from) those of graphite. Raman spectroscopy of nanotubes is discussed in some detail, as this technique has been an extensively used tool to probe the vibrational properties of nanotubes. Section 4 dwells upon the mechanical properties of nanotubes. In this section we first describe how the mechanical properties of nanoscaled objects can be characterized. Many ingenious experimental set-ups have been developed to attempt this characterization, and they are described in our review of experimental results. This is followed by a review of theoretical results on the characterization of mechanical properties. Thermal properties of nanotubes, in particular specific heat, thermal conductivity, thermal expansion and thermopower, are discussed in §5. In reviewing our present state of knowledge, the similarities and differences between the thermal properties of CNTs and two-dimensional (2D) graphite are emphasized. The paper concludes in §6 with remarks about key aspects of nanotubes that are discussed in the text, and gives an outlook on future developments in this field.

2. Electronic properties of CNTs and junctions

The nanometre dimensions of the CNTs, together with the unique electronic structure of a graphene sheet, make the electronic properties of these one-dimensional (1D) structures highly unusual. The aim of the present section is to review the relation between the atomic structure and the electronic and transport properties of SWNTs. In addition to the ideal tubes, we show how the electronic and the quantum conductance of tubes are affected by defects. Finally, the structure and the electronic properties of carbon-nanotube-based junctions are also studied. Such a rich interplay between the structural and the electronic properties of CNTs gives rise to new phenomena and the possibility of nanoscale device applications.

As illustrated in figure 1, a single-walled carbon nanotube is geometrically just a rolled up graphene strip. Its structure can be specified or indexed by its circumferential periodicity (C_h), as described using the chiral vector (AA' in figure 1), which connects two crystallographically equivalent sites (A and A') on a graphene sheet. In this way, the SWNT's geometry is completely specified by a pair of integers (n, m),

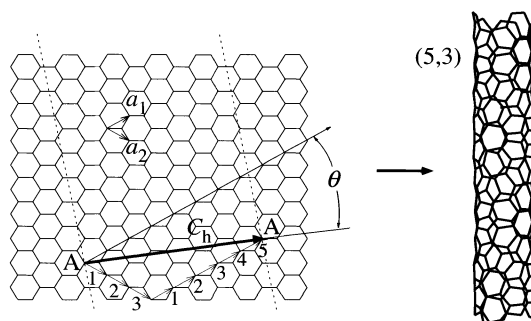


Figure 1. Schematic showing a possible wrapping of the 2D graphene sheet into a tubular form. In this example, a (5,3) nanotube is under construction and the resulting tube is illustrated on the right.

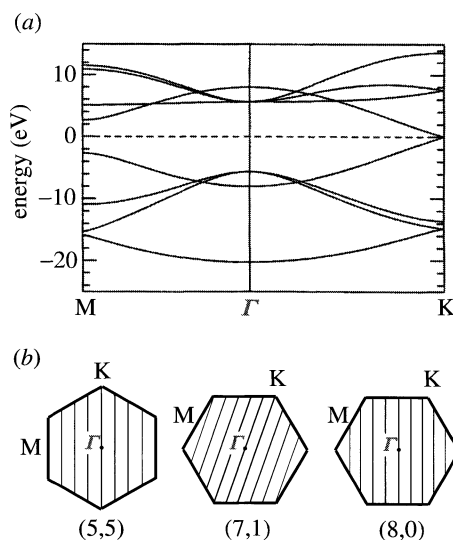


Figure 2. (a) Tight-binding band structure of graphene (a single basal plane of graphite), showing the main high symmetry points. (b) Allowed $\mathbf{k}$ -vectors of the (5,5), (7,1) and (8,0) tubes (solid lines) mapped onto the graphite Brillouin zone.

denoting the relative position $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ of the pair of atoms on a graphene strip which, when rolled onto each other, form a tube ($\mathbf{a}_1$ and $\mathbf{a}_2$ are basis vectors of the hexagonal honeycomb lattice; see figure 1). This chiral vector $\mathbf{C}_h$ also defines a chiral angle θ , which is the angle between $\mathbf{C}_h$ and the zigzag direction of the graphene sheet.

Theoretical calculations (Hamada *et al.* 1992; Mintmire *et al.* 1992; Saito *et al.* 1992) showed early on that the electronic properties of the CNTs are very sensitive to their geometric structure. Although graphene is a zero-gap semiconductor, theory has predicted that the CNTs can be metals or semiconductors with different sized energy gaps, depending very sensitively on the diameter and helicity of the tubes, i.e. on the indices (n, m) . The physics behind this sensitivity of the electronic properties of CNTs to their structure can be understood within a band-folding picture. It is due to the unique band structure of a graphene sheet, which has states crossing the

Fermi level at only two inequivalent points in k -space, and to the quantization of the electron wavevector along the circumferential direction. An isolated sheet of graphite is a zero-gap semiconductor whose electronic structure near the Fermi energy is given by an occupied π band and an empty π^* band. These two bands have linear dispersion and, as shown in figure 2, meet at the Fermi level at the K point in the Brillouin zone. The Fermi surface of an ideal graphite sheet consists of the six corner K points. When forming a tube, owing to the periodic boundary conditions imposed in the circumferential direction, only a certain set of $\mathbf{k}$ states of the planar graphite sheet is allowed. The allowed set of k values, indicated by the lines in figure 2, depends on the diameter and helicity of the tube. Whenever the allowed k include the point K , the system is a metal with a non-zero density of states at the Fermi level, resulting in a 1D metal with two linear dispersing bands. When the point K is not included, the system is a semiconductor with different sized energy gaps. It is important to note that the states near the Fermi energy in both the metallic and the semiconducting tubes are all from states near the K point, and hence their transport and other electronic properties are related to the properties of the states on the allowed lines. For example, the conduction band and valence bands of a semiconducting tube come from states along the line closest to the K point.

The general rules for the metallicity of the SWNTs are as follows: (n, n) tubes are metals; (n, m) tubes with $n - m = 3j$, where j is a non-zero integer, are very tiny-gap semiconductors; and all others are large-gap semiconductors. Strictly within the band-folding scheme, the $n - m = 3j$ tubes would all be metals but, because of tube curvature effects, a tiny gap opens for the case that j is non-zero (figure 3). Hence, CNTs come in three varieties: large gap, tiny gap and zero gap. The (n, n) tubes, also known as armchair tubes, are always metallic within the single-electron picture, independent of curvature because of their symmetry (figure 3). As the tube radius, R , increases, the band gaps of the large-gap and tiny-gap varieties decrease with a $1/R$ and $1/R^2$ dependence, respectively. Thus, for most experimentally observed carbon nanotube sizes, the gap in the tiny-gap variety, which arises from curvature effects, is so small that, for most practical purposes, all the $n - m = 3j$ tubes can be considered as metallic at room temperature. Thus, in figure 2, a $(7, 1)$ tube would be metallic, whereas a $(8, 0)$ tube would be semiconducting; the $(5, 5)$ armchair tube would always be metallic. Such a band-folding picture, based on the tight-binding approach (Hamada *et al.* 1992; Mintmire *et al.* 1992; Saito *et al.* 1992), is expected to be valid for larger-diameter tubes.

Ab initio pseudopotential local density functional calculations (Blase *et al.* 1994b) indeed reveal that sufficiently strong hybridization effects can occur in small-diameter nanotubes which significantly alter their electronic structure. Strongly modified low-lying conduction band states are introduced into the band gap of insulating tubes because of hybridization of the σ^* and π^* states. As a result, the energy gaps of some small-diameter tubes are decreased by more than 50%. For example, the $(6, 0)$ tube which is predicted to be semiconducting in the band-folding scheme is shown to be metallic. For nanotubes with diameters greater than 1 nm, these re-hybridization σ - π effects are unimportant. Recently, ultra-small-diameter SWNTs (diameter *ca.* 0.4 nm) have been produced by confining their synthesis inside inert AlPO_4 -5 zeolite channels (with inner diameter of *ca.* 0.73 nm) (Wang *et al.* 2000). The ultra-small diameter of these tubes gives them many unusual properties, such as superconductivity (Tang *et al.* 2001). Such a narrow diameter distribution

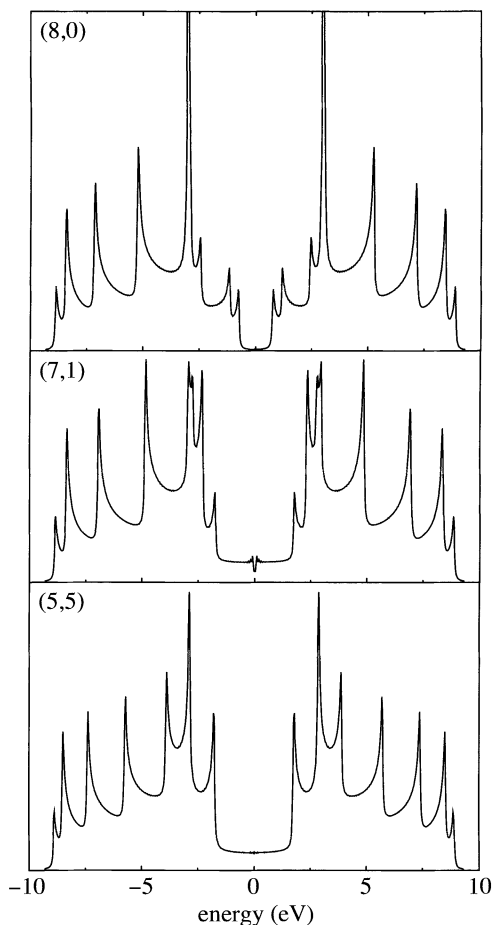


Figure 3. Electronic densities of states for the (5,5), (7,1) and (8,0) tubes showing singularities characteristic of 1D systems. The (5,5) armchair nanotube is metallic for symmetry reasons. The (7,1) chiral tube displays a tiny gap due to curvature effects, but will display a metallic behaviour at room temperature. The (8,0) zigzag tube is a large-gap semiconductor (Chico *et al.* 1996).

(*ca.* 0.4 nm) reduces the potential candidates to three: (3,3), (4,2) and (5,0). The properties of these ultra-small-diameter tubes have already been extensively investigated using *ab initio* calculations, since the small unit cell of these tubes allows such accurate calculations to be carried out (Dubay *et al.* 2002; Liu *et al.* 2002; Sanchez-Portal *et al.* 1999).

There have been many experimental studies (Bockrath *et al.* 1997; Dai *et al.* 1994; Ebbesen *et al.* 1996; Langer *et al.* 1996; Tans *et al.* 1997) based on low-temperature transport measurement on an SWNT rope in an attempt to understand its electronic properties. These results have been interpreted in terms of single-electron charging and resonant tunnelling through the quantized energy levels of the nanotubes. In addition, there have also been high-resolution low-temperature scanning tunnelling microscopy (STM) studies, which directly probe the relationship between the structural and electronic properties of the CNTs (Odom *et al.* 1998; Wildöer *et al.* 1998).

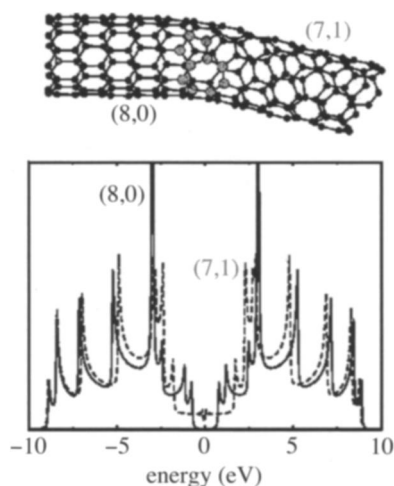


Figure 4. Atomic structure of a (8,0)/(7,1) intramolecular carbon nanotube junction. The large light-grey balls denote the atoms forming the heptagon–pentagon pair. The electron density of states related to the two perfect (8,0) and (7,1) nanotubes are illustrated by solid and dashed lines, respectively (Charlier *et al.* 2002).

In these measurements, the resolution of the measurements allowed for the identification of the individual carbon rings. From the orientation of the carbon rings and the diameter of the tube, the geometric structure of the tube was fully deduced. Measurement of the normalized conductance in the scanning tunnelling spectroscopy (STS) mode was then used to obtain the local density of states (LDOS) in very good agreement with theoretical predictions.

However, CNTs are probably not as perfect as they were once thought to be. Defects like pentagons, heptagons, vacancies or dopant species are found to modify the electronic properties of these nanosystems drastically. The electronic properties of defective nanotube-based structures are then more complex than infinitely long, perfect nanotubes. The introduction of defects into the carbon network is thus an interesting way to tailor its intrinsic properties, in order to create new potential nanodevices and to propose new potential applications in nano-electronics.

Since CNTs are metals or semiconductors depending sensitively on their structures, they can be used to form metal–semiconductor, semiconductor–semiconductor or metal–metal junctions. These junctions have great potential for applications since they are of nanoscale dimensions and are made entirely of a single chemical element. In constructing this kind of on-tube junction, the key is to join two half-tubes of different helicities seamlessly with each other, without too much cost in energy or disruption in structure. It has been shown that the introduction of pentagon–heptagon pair defects into the hexagonal network of a single carbon nanotube can change the helicity of the carbon nanotube and fundamentally alter its electronic structure (Charlier *et al.* 1996; Chico *et al.* 1996; Dunlap 1994; Lambin *et al.* 1995; Saito *et al.* 1996). Both the existence of such atomic-level structures and the measurement of their respective electronic properties have already been established experimentally (Ouyang *et al.* 2001; Yao *et al.* 1999).

The defects, however, must induce zero net curvature to prevent the tube from flaring or closing. The smallest topological defect with minimal local curvature (hence

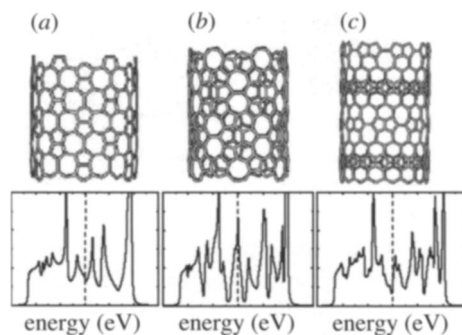


Figure 5. Non-chiral haeckelite nanotubes of similar diameter (1.4 nm). Nanotube segments: (a) containing only heptagons and pentagons paired symmetrically; (b) exhibiting repetitive units of three agglomerated heptagons, surrounded by alternating pentagons and hexagons; (c) containing pentalene and heptalene units bound together and surrounded by six-membered rings. The electronic properties of the three planar structures used to create these haeckelite tubes are illustrated below. All the respective tight-binding DOSs display a metallic behaviour. The Fermi energy is represented by a dashed line (Terrones *et al.* 2000).

the lowest energy cost) and zero net curvature is a pentagon–heptagon pair. When the pentagon is attached to the heptagon as in the aniline structure, it creates only topological changes (but no net disclination), which can be treated as a single local defect. Such a 5/7 pair will create only a small local deformation in the width of the nanotube, and may also generate a small change in the helicity, depending on its orientation in the hexagonal network.

Figure 4 depicts the connection, using a single 5/7 pair, between two nanotubes exhibiting different electronic properties. As mentioned above, the (8,0) nanotube has a 1.2 eV gap in the tight-binding approximation, and the (7,1) tube is a metal (although a small curvature-induced gap is present close to the Fermi energy).

Joining a semiconducting nanotube to a metallic one, using a pentagon–heptagon 5/7 pair incorporated in the hexagonal network can thus be proposed as the basis of a nanodiode (or molecular diode) for nano-electronics. The system illustrated in figure 4 forms a quasi-1D semiconductor–metal junction since, within the band-folding picture, the (7,1) half-tube is metallic and the (8,0) half-tube is semiconducting. This has led to the prediction that these defective nanotubes behave as the desired nanoscale metal–semiconductor Schottky barriers, semiconductor heterojunctions, or metal–metal junctions with novel properties, and that they could be the building blocks of nanoscale electronic devices.

Following the previous idea of introducing 5- and 7-rings into hexagonal networks, a novel class of perfect crystals, consisting of layered sp^2 -like carbon and containing periodic arrangements of pentagons, heptagons and hexagons, has been proposed (Terrones *et al.* 2000). These sheets are rolled up so as to generate SWNTs (figure 5), which locally resemble the radiolaria drawings of Haeckel (1862). These ‘ideally’ defective tubes exhibit intriguing electronic properties: LDOS calculations of haeckelite tubes revealed an intrinsic metallic behaviour, independent of orientation, tube diameter and chirality. Particularly, an unusual high-intensity LDOS peak at the Fermi level is noticed for the family of tubes depicted in figure 5b, thus suggesting the possible existence of superconductivity, as the electron–phonon coupling is also expected to be enhanced by the tube curvature. Considering the metallic

properties of haeckelites, they should offer advantages over CNTs in applications. If they can be manufactured, there is no necessity for diameter or helicity selection to separate metallic structures (i.e. for electronic interconnect applications). Our calculations also reveal that these haeckelite structures are more stable than C_{60} , and have energies of the order of 0.3–0.4 eV per atom with respect to graphene, allowing the potential synthesis of this new class of nanotubes. However, these ideal topologies have never been synthesized, although the structure of coiled carbon nanostructures has been recently explained by rolling up strips made of heptagons, pentagons and hexagons, with a predominance for non-hexagonal rings (Biró *et al.* 2002).

It is interesting to connect nanotubes in a network in order to correlate both their mechanical and electronic properties to their structures. Recently, the electron beam of a transmission electron microscope has been used to irradiate nanostructures locally. Covalently connected crossed SWNTs have thus been created using electron-beam welding at elevated temperatures (Terrones *et al.* 2002*a,b*). These molecular junctions of various geometries ('X-', 'Y-' and 'T'-junctions) are found to be stable after the irradiation process. To study the relevance of some of these nanostructures, various models of ideal molecular junctions have been generated. The presence of heptagons is found to play a key role in the topology of nanotube-based molecular junctions. Figure 6 depicts an ideal 'X' nanotube connection, where a (5, 5) armchair nanotube intersects a (11, 0) zigzag tube. In order to create a smooth topology at the molecular junctions, six heptagons have been introduced at each crossing point.

The calculation of the LDOSs has been performed in order to investigate the electronic properties of these molecular junctions. Both the metallic character of the (5, 5) nanotube and the semiconducting behaviour of the (11, 0) nanotube are illustrated in figure 6. The LDOS of the regions, where the two nanotubes cross, reveals an enhancement of the electronic states at the Fermi level, thus suggesting a strong metallic behaviour (figure 6). These metallic sites (tube intersections) may well behave as quantum dots when embedded in a semiconducting tubular system. It is also notable that the presence of localized donor states in the conduction band (as indicated by arrows) is caused by the presence of heptagons. The novel small peak in the valence band (also shown by an arrow), close to the Fermi energy, can probably be attributed to the high curvature of the graphitic system. The van Hove singularities (VHSs) present in the LDOSs of the two achiral nanotubes are drastically less pronounced in the junction region (figure 6), thus illustrating a clear loss of the 1D character in this region. LDOSs of junction models, as those created by electron-beam irradiation, are described to suggest their importance in electronic device applications. The results suggest a way toward the controlled fabrication of nanotube-based molecular junctions and network architectures exhibiting exciting electronic and mechanical behaviour.

Carbon nanotubes are hence a fascinating new class of materials with many unique and desirable properties. The rich interplay between the geometric and electronic structures of the nanotubes gives rise to many interesting new physical phenomena. At the practical level, these systems have the potential for many possible applications. Nanotube-based electronics is probably one of the main potential uses of nanotubes. The flexibility of the nanoscale design and the availability of both semiconducting and metallic nanotubes enable a wide variety of configurations. In the present paper, the fascinating electronic properties of carbon nanotube have been reviewed and tailored by the presence of topological defects. Junctions between semiconducting

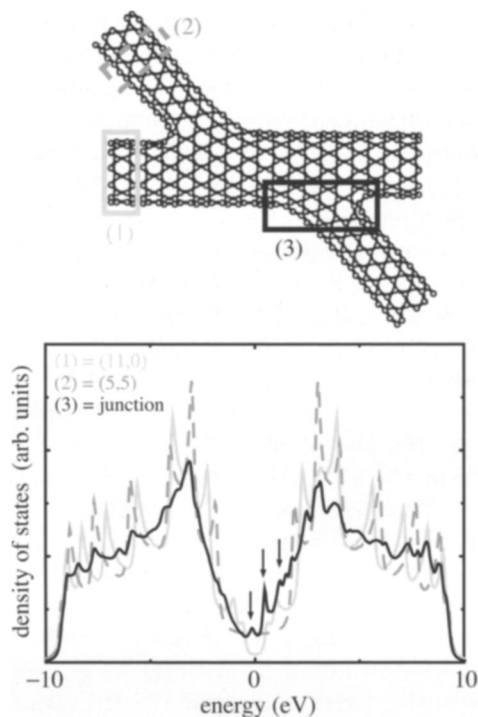


Figure 6. Electronic properties of an ideal X-junction, created by intersecting a (5,5) tube with a (11,0) tube. The graphs show the 1D electronic densities of states of a semiconducting (11,0) nanotube (light curve), a metallic (5,5) nanotube (dashed curve) and the average over the intersecting region of the molecular junction (black curve). The Fermi level is positioned at the zero of energy. Localized states due to the presence of defects are indicated by arrows (Charlier *et al.* 2002).

and metallic nanotubes can act as diodes. Junctions between two crossed nanotubes can act as rectifiers. More exotic configurations for nanoscale devices are Y-, T- or X-junctions. Although a number of early prototypical nanotube-based devices have already been made, the production and integration of nanotube components into easily reproducible device structures present many challenges. Very recently, however, several major steps toward nanotube-based circuitry have been achieved: an array of field-effect transistors has been made by selectively burning-off metallic nanotubes in SWNT ropes (Derycke *et al.* 2001), and field-effect transistors based on single nanotubes have been assembled, by several research groups, into the logic circuits that are building blocks of computers (Bachtold *et al.* 2001; Derycke *et al.* 2001; Huang *et al.* 2001). The realization of single molecule logic circuits has been a long-standing goal within molecular electronics. A bright new world of nanocircuitry may now be possible, thanks to these recent advances in nanotube electronics.

3. Phonon properties and Raman spectroscopy of CNTs

Phonons denote the quantized normal-mode vibrations that strongly affect many processes in condensed-matter systems, including thermal, transport and mechanical properties. Phonons play an important role as carriers of thermal energy in thermal

conduction processes and in thermodynamic properties, such as the heat capacity, and in scattering processes for bringing electrons into equilibrium with the lattice in various electron transport phenomena, such as electrical conductivity, magnetotransport phenomena and thermoelectricity. The vibrational spectra also determine the speed of sound, elastic properties of solids, and their mechanical properties. Phonons, through their interaction with electrons, can also mediate interactions and pairing between electrons, giving rise to superconductivity. These topics are particularly interesting in 1D systems, because of the VHSs that 1D systems exhibit in their density of states (see figure 3). These phenomena are even more interesting in SWNTs which allow these interesting 1D effects to be studied in detail.

Since an SWNT can be considered to be a 2D graphene sheet that has been rolled up seamlessly, the electron dispersion relations of SWNTs are typically related to those of 2D graphite (a graphene sheet), as is discussed in §2. A similar procedure is generally applied to obtain the phonon-dispersion relations and phonon density of states for SWNTs from those of the 2D graphene sheet (Saito *et al.* 1998), as illustrated respectively in figure 7*a, b* for a (10, 10) SWNT. The large amount of sharp structure in the phonon density of states in figure 7*b* for the (10, 10) SWNT reflects the many phonon branches and the 1D nature of SWNTs relative to 2D graphite. The phonon density of states for 2D graphite shown in figure 7*c* is obtained by summing the 1D phonon density of states for many SWNTs (Jorio *et al.* 2003; Saito *et al.* 1998). In addition to the longitudinal acoustic (LA) and transverse acoustic (TA) modes, there are two acoustic twist modes for rigid rotation around the tube axis, which are important for heat transport and charge-carrier scattering. Also important for coupling electrons to the lattice are the low-lying optical modes at the centre of the Brillouin zone $q = 0$. These modes include one with E_2 symmetry expected at *ca.* 17 cm^{-1} (the squash mode), one with E_1 symmetry, expected at *ca.* 118 cm^{-1} and the A symmetry (radial breathing mode (RBM)) expected at *ca.* 165 cm^{-1} for a (10, 10) SWNT (Saito *et al.* 1998). The RBM, where all the carbon atoms are vibrating in phase in the radial direction, is unique to SWNTs and does not occur in other carbon systems. The RBM has been of great importance in identifying the presence of SWNTs in carbon samples and in determining SWNT diameters d_t , as discussed below.

(a) Raman spectroscopy

The Raman spectra of SWNTs have been particularly valuable for providing detailed information on the vibrational modes of SWNTs (Dresselhaus & Eklund 2000), for characterizing SWNT samples (Rao *et al.* 1997), and for revealing a variety of unique phenomena in 1D systems (Dresselhaus *et al.* 2003; Samsonidze *et al.* 2003*a*). In the first report of Raman spectra on SWNTs (Rao *et al.* 1997) it was shown that, despite the large number of branches in the SWNT phonon-dispersion relations (see figure 7*a*), the Raman spectra for an SWNT bundle (see figure 8) only exhibit two dominant features, namely the RBM at 186 cm^{-1} for laser excitation energy $E_{\text{laser}} = 2.41\text{ eV}$ and the tangential band in the range from $1520\text{--}1620\text{ cm}^{-1}$. Because of the strong connection of this tangential band to the corresponding mode in 2D graphite, this higher-frequency band for SWNTs is commonly called the G band. Other lower intensity features, discussed below, also provide important and unique information about SWNTs.

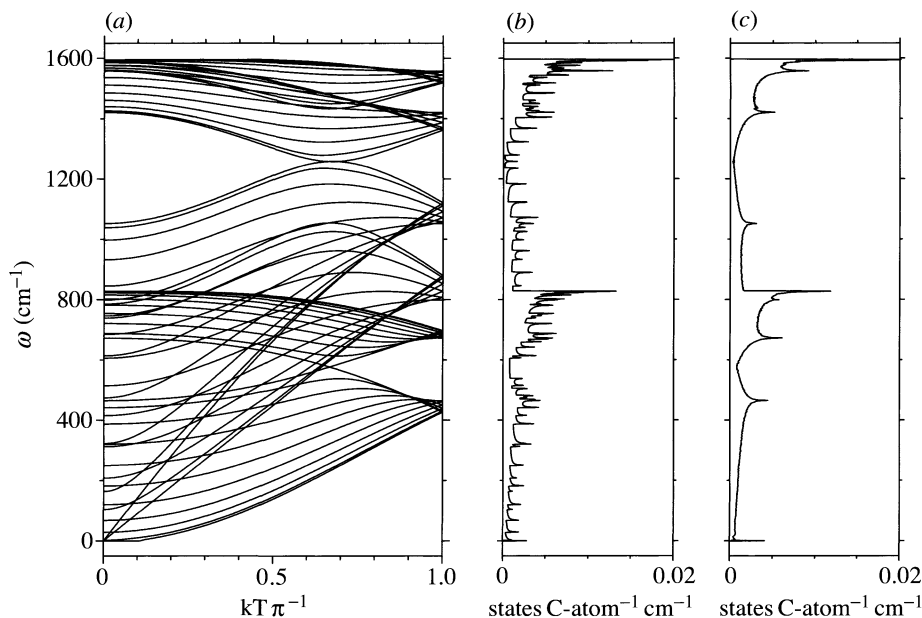


Figure 7. (a) The calculated phonon-dispersion relations of an armchair carbon nanotube with $(n, m) = (10, 10)$. The number of degrees of freedom is 120 and the number of distinct phonon branches is 66 (Saito *et al.* 1998). (b) The corresponding phonon density of states for a $(10, 10)$ nanotube. (c) The corresponding phonon density of states for a 2D graphene sheet (Jorio *et al.* 2003).

In this first paper on the Raman effect in SWNTs (Rao *et al.* 1997), the strong and non-monotonic dependence of the SWNT Raman spectra on the laser excitation energy E_{laser} established the Raman scattering to be associated with a resonance process for the excitation laser energy E_{laser} with the optical transition energy E_{ii} , between VHSs in the valence band and conduction bands (see figure 3), and therefore the E_{ii} value for a particular SWNT is dependent on its diameter. Because of the very small diameters of SWNTs (*ca.* 1 nm), the joint density of states for this optical process exhibits very large singularities, with associated large enhancements in Raman intensity, allowing the observation of spectra from one individual SWNT that is in strong resonance with E_{laser} (Jorio *et al.* 2001*a,b*).

Figure 8 indicates that the G-band feature consists of a superposition of two dominant components, shown at 1593 cm^{-1} (G^+) and at 1567 cm^{-1} (G^-), along with other lower intensity components (shown in the inset to figure 8). The G^+ feature is associated with carbon atom vibrations along the nanotube axis and its frequency ω_{G^+} is sensitive to charge transfer from dopant additions to SWNTs (upshifts in ω_{G^+} for acceptors, and downshifts for donors). The G^- feature, in contrast, is associated with vibrations of carbon atoms along the circumferential direction of the nanotube, and its line shape is highly sensitive to whether the SWNT is metallic (Breit-Wigner-Fano line shape) or semiconducting (Lorentzian line shape) (Brown *et al.* 2001; Pimenta *et al.* 1998). The smaller intensity features shown in the inset arise from phonons with E_1 and E_2 symmetry. Phonons with A , E_1 and E_2 symmetries

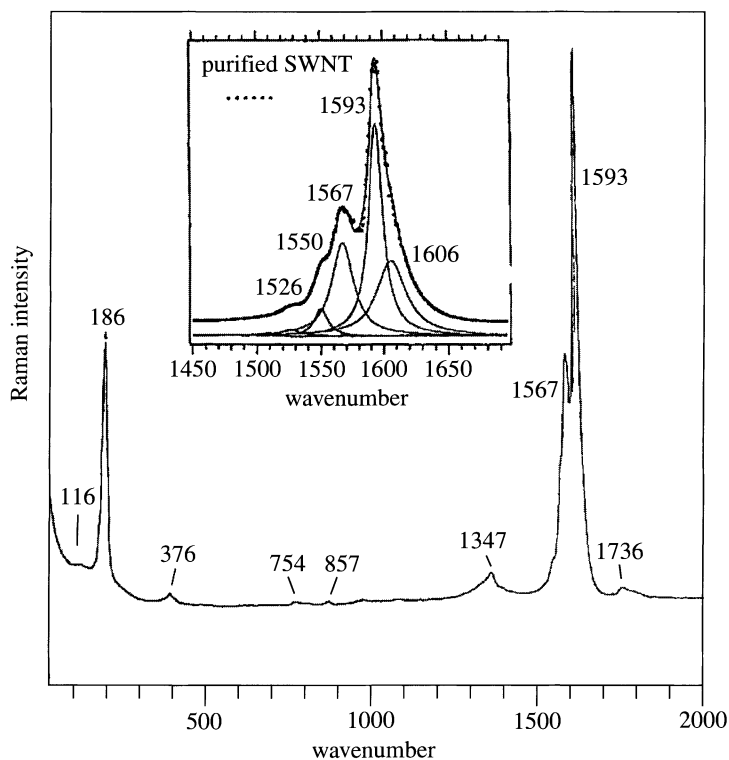


Figure 8. Experimental Raman spectrum taken with 514.5 nm (2.41 eV) laser excitation from an SWNT bundle sample with a diameter distribution $d_t = 1.36 \pm 0.20$ nm. The inset shows an expanded version of the spectra in the $1450\text{--}1700\text{ cm}^{-1}$ range (Rao *et al.* 1997).

can be distinguished from one another by their behaviour in polarization-sensitive Raman experiments (Jorio *et al.* 2000).

Also commonly found in the Raman spectra in SWNT bundles are the D band with frequency ω_D at 1347 cm^{-1} in figure 8, stemming from the disorder-induced mode in graphite, and its second harmonic, the G' band (not shown) occurring at around $2\omega_D$, both associated with a double resonance process (Thomsen & Reich 2000). Both the D band and the G' band are sensitive to the nanotube diameter and chirality, and therefore have been very important in revealing trigonal warping effects in SWNTs and in measuring their magnitudes in the dispersion relations for electrons (Saito *et al.* 2000; Souza Filho *et al.* 2002) and for phonons (Samsonidze *et al.* 2003b).

Returning to figure 8, the weak feature at 116 cm^{-1} may be due to a low-frequency E_1 symmetry SWNT mode that is not observed in graphite, while the mode at 376 cm^{-1} is likely to be the second harmonic of ω_{RBM} . The broad weak feature at 857 cm^{-1} is identified with the out-of-plane optical TO mode that is infrared active in 2D graphite, while the feature at 1736 cm^{-1} is identified with its second harmonic. Both the 857 cm^{-1} and the 1736 cm^{-1} features are commonly seen in both SWNT bundles and at the single-nanotube level, and these features are attributed to a double resonance process (Brar *et al.* 2002). The intermediate frequency feature

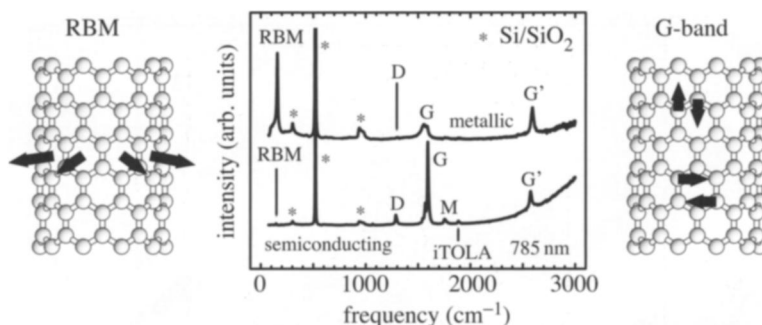


Figure 9. Raman spectra from (a) a metallic and (b) a semiconducting SWNT at the single-nanotube level using 785 nm (1.58 eV) laser excitation, showing the RBM, D-band, G-band and G' band features, in addition to weak double resonance features associated with the M band and the iTOLA second-order modes (Brar *et al.* 2002). Insets on the left and the right show atomic displacements associated with the RBM and G-band normal-mode vibrations. The isolated CNTs are sitting on an oxidized silicon substrate which provides contributions to the Raman spectra denoted by '*' which are used for calibration purposes.

at 754 cm^{-1} is a very special mode that arises in nanotubes because of the special properties of 1D phonons (Fantini *et al.* 2004).

Because of the sharp VHSs occurring in CNTs with diameters less than 2 nm, the Raman intensities for the resonance Raman process can be so large that it is possible to observe the Raman spectra from one individual SWNT (Jorio *et al.* 2001a,b), as shown in figure 9, where the differences in the G-band spectra between semiconducting and metallic SWNTs can be seen at the single-nanotube level. Because of the trigonal warping effect, every (n, m) carbon nanotube has a different electronic structure and a unique density of states (see figure 3). Therefore, the energies E_{ii} of the VHSs in the joint density of states for each SWNT are different, as shown in figure 10, for all (n, m) nanotubes in the diameter range up to 2.9 nm and for E_{ii} up to 3.0 eV. In this so-called Kataura plot (figure 10), we see that, for small-diameter SWNTs ($d_t < 1.7\text{ nm}$) and for the first few electronic transitions for semiconducting and metallic SWNTs, the E_{ii} values are arranged in bands, whose spread is determined by the trigonal warping effect (Saito *et al.* 2000). A general chiral semiconducting SWNT will have VHSs in the E_{11}^S , E_{22}^S , E_{33}^S , etc., bands, while a chiral metallic SWNT will have two vHSs in each of the E_{11}^M , E_{22}^M , etc., bands. The tight-binding approximation provides quite reliable values for the E_{ii} energies for the vHSs for SWNTs with diameters in the 1.0–2.0 nm range (to an accuracy of better than 20 meV) (Souza Filho *et al.* 2004). The Raman effect provides a determination of E_{ii} values, either by measurement of the relative intensities of the RBM frequency for the Stokes (phonon emission) and anti-Stokes (phonon absorption) processes, or by RBM relative Raman intensity measurements for the Stokes process for many SWNTs (Dresselhaus *et al.* 2002). The frequency of the RBM is used to determine the diameter of an isolated SWNT sitting on an oxidized Si surface using the relation $\omega_{\text{RBM}}\text{ (cm}^{-1}\text{)} = 248/d_t\text{ (nm)}$, and from a knowledge of the (E_{ii}, d_t) values for an individual SWNT (figure 10), the (n, m) indices for that SWNT can be determined from the Kataura plot. Not only can resonance Raman spectroscopy at the single-nanotube level determine the (n, m) indices from study of the RBM frequency and intensity, but studies of other Raman features also provide valuable information

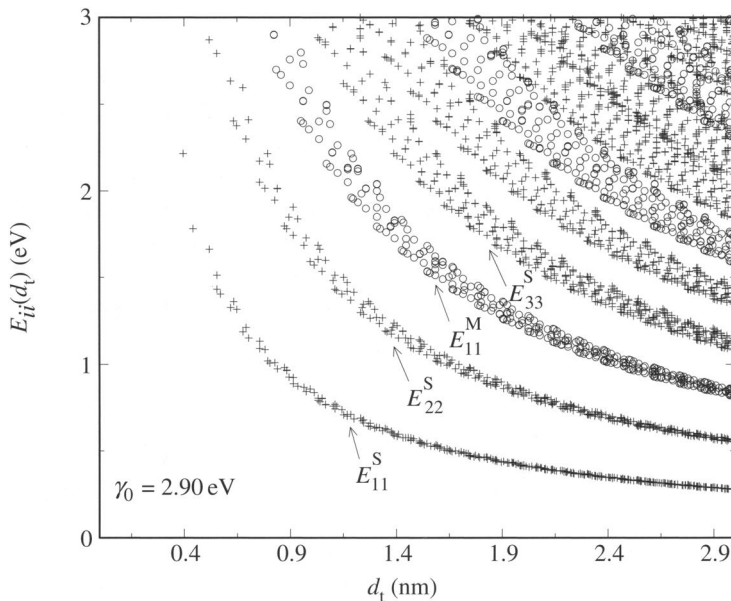


Figure 10. Calculated (Kataura *et al.* 1999) energy separations E_{ii} between VHSs i in the 1D electronic density of states of the conduction and valence bands for all possible (n, m) values versus nanotube diameter in the range $0.5 < d_t < 3.0$ nm, using a value for the carbon–carbon energy overlap integral of $\gamma_0 = 2.9$ eV and a nearest-neighbour carbon–carbon distance $a_{C-C} = 0.144$ nm for making this plot (Dresselhaus *et al.* 2000; Saito *et al.* 2000). Semiconducting (S) and metallic (M) nanotubes are indicated by crosses and open circles, respectively. The subscript $i = 1$ denotes the index of the lowest energy of a singularity in the joint density of states.

not obtainable from SWNT bundles (Dresselhaus *et al.* 2002) nor by using other characterization techniques.

Measurements on the G band at the single-nanotube level show that this feature is a first-order process, with the frequency ω_{G+} essentially independent of d_t or chiral angle θ , while ω_{G-} is only dependent of d_t and not on θ . Such diameter-dependent measurements can only be made at the single-nanotube level, and the results can be used along with many other measurements to corroborate (n, m) assignments carried out on the basis of the RBM feature. Single-nanotube measurements of the D-band and G' -band features provide information on the chirality and diameter dependence of ω_D and $\omega_{G'}$, and can be used to measure the trigonal warping effect in the electron and phonon-dispersion relations of SWNTs, providing information not readily available using other experimental techniques (Dresselhaus *et al.* 2002). Measurements of ω_D and $\omega_{G'}$ for special semiconducting SWNTs, where the *incident* photon is in resonance with one vHS (e.g. E_{44}^S) and the *scattered* photon is in resonance with another vHS (e.g. E_{33}^S), are particularly useful for corroborating specific (n, m) assignments made by the RBM mode, as well as for corroborating the (n, m) assignment procedure itself (Dresselhaus *et al.* 2002).

The ability to use a gate (Cronin *et al.* 2004), an externally applied potential (Corio *et al.* 2004) or a tunable laser (Fantini *et al.* 2004) to move the VHS for an individual SWNT into and out of resonance with the laser offers great promise for

detailed studies of the 1D physics of single-walled CNTs using resonance Raman spectroscopy.

Raman spectra of CNTs, particularly at the single-nanotube level, have been especially rich in information. Because of the simplicity of the geometrical structure of nanotubes, detailed analysis of the Raman spectra has yielded much information about the phonon-dispersion relations, such as information about their trigonal warping. Such information is not yet available for 2D graphite, but can be studied in nanotubes because of their one-dimensionality. Because of the close coupling between electrons and phonons under resonance conditions, Raman spectra have also provided valuable and detailed information about electronic structure, such as an evaluation of the magnitude of the trigonal warping effect for electrons, yielding information not readily available by the use of other probes.

4. Mechanical properties of nanotubes

The carbon–carbon chemical bond in a graphene layer is probably the strongest chemical bond in an extended system known in nature. Since CNTs are nothing but seamlessly rolled-up graphene layers (see figure 1), from the time of their discovery it has been speculated that these nanostructures have exceptional mechanical properties, and to quantify these properties has become a topic of great interest in the field of nanotechnology. Many of the envisaged applications of nanotubes, such as composite reinforcement or lubrication, are related in one way or another to their mechanical properties, and therefore a great deal of experimental and theoretical studies have been devoted to their characterization. In this section we first make some general comments on how to quantify the mechanical properties at the nanoscale, pointing out the peculiarities that arise due to the reduced dimensions of tubular nanostructures. Secondly, we review the experimental efforts aimed at a determination of the mechanical properties of nanotubes, and finally we also discuss theoretical studies along the same lines. Due to space constraints, we cannot provide an exhaustive review of the topic; we do nevertheless hope to provide a summary of the most significant results. More extensive reviews of this topic are given by Yakobson & Avouris (2001) and Quian *et al.* (2003).

The mechanical properties of a material in the linear regime are commonly specified by the definition of a series of moduli (elastic constants, Young's modulus, Poisson ratio, etc.) which have been traditionally defined in a macroscopic context, i.e. all dimensions of the material fall in the same scale, which is typically much larger than the molecular scale. One of the unusual features of nanotubes is that they simultaneously involve widely varying scales: their length can be macroscopic, up to millimetres, while their width falls in the nanoscale. In the case of SWNTs, the thickness of the nanotube shell is an ill-defined concept, for what is the thickness of a shell one-atom thick? As pointed out elsewhere (Hernández *et al.* 1998, 1999; Yakobson & Avouris 2001), the use of macroscopic concepts, such as elastic moduli, to characterize the mechanical properties of nanoscopic objects, such as nanotubes, has to be done with some care, and this generally requires the adoption of some conventions. Let us illustrate this with Young's modulus. The Young modulus along a given direction is defined as

$$Y = \frac{1}{V_{\text{eq}}} \left(\frac{\partial^2 E}{\partial \epsilon^2} \right)_{\epsilon=0}, \quad (4.1)$$

where E is the total energy of the system, V_{eq} is the equilibrium volume of the system and ϵ is the strain. As mentioned above, for an SWNT there is no unambiguous way of defining V_{eq} ; therefore, a better definition would be

$$\tilde{Y} = \frac{1}{S_{\text{eq}}} \left(\frac{\partial^2 E}{\partial \epsilon^2} \right)_{\epsilon=0}, \quad (4.2)$$

where S_{eq} is the nanotube surface area at zero strain, which can be determined unambiguously. If one insists on using equation (4.1) to characterize the response to an elastic axial deformation of an SWNT, then a convention for determining V_{eq} must be adopted. A frequently used convention is $V_{\text{eq}} = S_{\text{eq}}h$, where $h = 0.34$ nm, i.e. the interlayer spacing in graphite. It must be stressed, however, that this choice is motivated by convenience for comparison with graphite, and there is nothing fundamental about it.

Since it is expected that nanotubes find application in reinforcement of materials, their response to deformation in the elastic regime is not the only important aspect of their mechanical properties. At least equally important is their behaviour at large (tensile and compressive) strains, the yield mechanism and strength at failure and their buckling when bent, since these will ultimately determine the properties of the material. This is currently a challenging and active field of research at both the experimental and theoretical levels.

(a) *Experimental studies*

The manipulation of nanoscaled objects is a difficult and challenging task, but in spite of this, a number of direct experimental measurements of Young's modulus of nanotubes have appeared in the literature. The first study reporting the measurement of Young's modulus of multiwall nanotubes (MWNTs) was due to Treacy *et al.* (1996). The physical basis underlying these experiments is the correlation of the thermal oscillation amplitude of the free ends of anchored nanotubes as a function of temperature with Young's modulus. This correlation is possible if one regards a nanotube as a hollow cylinder with a given wall thickness; for such a system the mean-squared vibrational amplitude of the free tip is directly proportional to the temperature and inversely proportional to Young's modulus. Therefore, the latter can be obtained by plotting the mean-squared amplitude versus the temperature. Treacy and co-workers obtained the thermal amplitude for a series of anchored MWNTs using transmission electron microscopy (TEM) at different temperatures. Averaging over all observed nanotubes, they obtained a mean value of 1.8 TPa, though the values for individual nanotubes ranged from 0.4 to 4.15 TPa, reflecting the difficulties in carrying out these measurements. In spite of the uncertainties implicit in the scatter of these data, they confirmed the expectation that CNTs possessed exceptional mechanical properties. A subsequent study using the same experimental approach on SWNTs was performed by the same team (Krishnan *et al.* 1998). This time a larger sample of nanotubes was employed, and a mean value of $Y = 1.25$ TPa was obtained: a value much closer to the C_{11} graphite basal plane elastic modulus. Employing the same technique, Chopra & Zettl (1998) determined the Young modulus of boron nitride (BN) nanotubes, obtaining a value of 1.22 TPa. This result raised the expectation that BN nanotubes could be as stiff as carbon nanotubes.

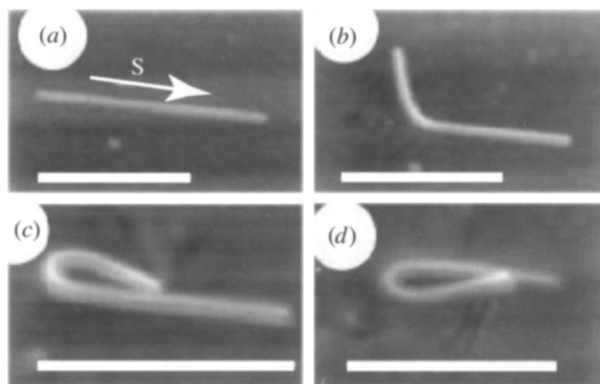


Figure 11. Series of steps in the deformation of a MWNT (Falvo *et al.* 1997). The nanotube shown has a diameter of 10.5 nm and is 850 nm long. (a) Initial configuration of the nanotube, before being distorted. (b) The nanotube is bent until it reaches the configuration shown in (c). (d) The tube has been bent all the way back until it reaches a shape that is a mirror image of that shown in (c). The scale bars at the bottom of each panel represent 500 nm.

A different experimental set-up to determine the Young modulus of MWNTs has been used by Wong *et al.* (1997). These authors used the tip of an atomic force microscope (AFM) to bend cantilevered nanotubes laterally, recording at the same time the force exerted by the bent nanotube on the AFM tip as a function of the lateral displacement. From this information, Young's modulus can be extracted, and Wong and co-workers thus reported an average value of Young's modulus of 1.28 ± 0.5 TPa. A third approach, similar in spirit to the previous one, was used by Salvétat *et al.* (1999), and consisted of placing SWNTs on an ultra-filtration membrane. Many of the tubes are then found to lie partially suspended across the holes found on such a membrane. The AFM tip was then used to apply a load on the suspended portion of the nanotube or bundle, recording simultaneously the exerted load and deflection. Assuming that attractive dispersion forces pin the nanotubes to the substrate, these authors reported a Young modulus of 0.8 ± 0.4 TPa—somewhat smaller than that found in earlier experiments. In the same work, the Young modulus of nanotubes produced by the catalytic decomposition of hydrocarbons was determined, giving values in the range 10–50 GPa, i.e. two orders of magnitude smaller than the more structurally ordered nanotubes produced by laser ablation or arc-discharge methods. This large difference presumably reflects the influence of a large density of structural defects in catalytically grown nanotubes. Falvo *et al.* (1997) also used an AFM to bend MWNTs laterally (see figure 11); the lateral distortions inflicted on the tubes were considerable, but still no failure of the nanotube structures was observed, testifying to the flexibility and capacity for reversible deformation, in other words, toughness, of these structures.

Poncharal *et al.* (1999) have observed the deflection of charged cantilevered nanotubes in external static and oscillating electric fields. They measured what they call an effective bending modulus for a series of MWNTs of different diameters. The effective bending modulus corresponds to the standard Young modulus if the nanotube bends by stretching in the outer arc and by compression in the inner arc. This appears to be the case for nanotubes with diameter $d_t < 12$ nm, where the effective bending modulus was found to have a value of *ca.* 1 TPa, in good agreement with

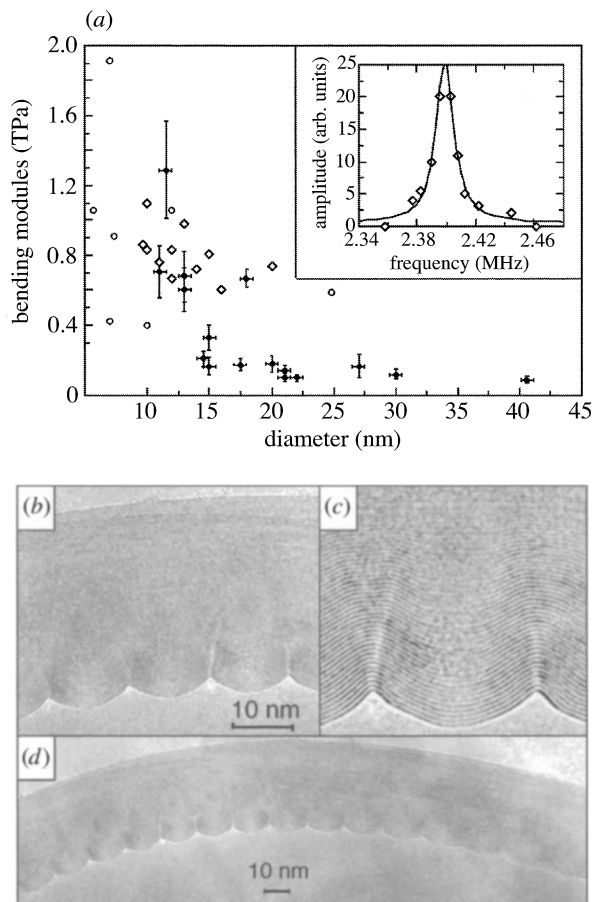


Figure 12. (a) Effective bending modulus of MWNTs as a function of tube diameter obtained from electromechanical resonance experiments (Poncharal *et al.* 1999). For small-diameter tubes (less than 12 nm), the bending modulus is high (approaching 1 TPa) and can be associated with Young's modulus. For nanotubes having larger diameters there is a dramatic drop in the effective bending modulus (to values of *ca.* 0.2 TPa), a fact attributed to the onset of a strain-relaxation mechanism, which results in the wave-like distortion illustrated in (b)–(d). The inset in (a) shows the Lorentzian shape of the electromechanical excitation of a nanotube.

the values previously obtained for Young's modulus. However, for MWNTs of larger diameters, it was found that the effective bending modulus dropped dramatically to values of *ca.* 100 GPa. High-resolution TEM images of such large-diameter nanotubes revealed a rippled or buckling distortion along the inner arc of the bent nanotubes (see figure 12). This phenomenon, which had been observed previously (Iijima *et al.* 1996; Lourie *et al.* 1998; Ruoff & Lorents 1995), reveals the onset of a strain-relaxation mechanism, which becomes more easily available for wide nanotubes than for narrow ones. Thus, only in the latter ones, the effective bending modulus reaches a value close to that of Young's modulus. These experiments, together with the earlier observations of bent nanotubes, reveal that MWNTs, while difficult to stretch axially, are easy to bend laterally, and they can reversibly withstand large lateral distortions.

The response of nanotubes to direct axial tensile strain has been measured by Yu *et al.* (2000a) for MWNTs and by Yu *et al.* (2000b) for SWNTs employing an experimental set-up, consisting of attaching a nanotube to two opposing AFM tips and using these to pull the nanotube beyond the elastic limit into the plastic regime. The experiments performed on the MWNTs showed that these break at the outermost layer, with the inner layers being pulled out like a sword from its sheath. From these experiments, the authors deduce a tensile strength of between 11 and 63 GPa for the 19 MWNTs that were studied. They were able to collect stress–strain data, from which values of Young’s modulus between 0.27 and 0.95 TPa were obtained for the outermost layer. The same experimental set-up was used to measure the tensile strength of 15 SWNT ropes (Yu *et al.* 2000b). The data resulting from these observations were best fit by a model that assumed that the tensile load is transmitted by the tubes on the outer perimeter of the bundle. The tensile strength in this case was found to be between 13 and 52 GPa, with a mean value of 30 GPa. The Young modulus for individual nanotubes was estimated to be between 0.32 and 1.47 TPa, with a mean value of 1.002 TPa. The differences observed in the various samples considered in both the MWNT and SWNT bundles presumably reflect the presence of defects and their influence on the mechanical properties. Experiments on SWNTs using an AFM tip in a similar set-up as that employed by Salvétat *et al.* (1999) have been carried out by Walters *et al.* (1999), who estimated an average strength of 45 GPa.

Another approach used to probe the mechanical properties of nanotube samples is to embed them in a matrix of another material, which is then subjected to strain, a methodology that has been frequently used in testing the mechanical properties of fibres. Using this approach, Wagner *et al.* (1998) observed the fracture of embedded MWNTs, finding a tensile strength of 55 GPa. Li *et al.* (2000) found a somewhat lower value for SWNT ropes embedded in polyvinyl chloride.

The response of CNTs to hydrostatic pressure has also been investigated, particularly in connection with Raman spectroscopy studies, as there is an interest in analysing the behaviour of the different peaks with applied pressure. Venkateswaran *et al.* (1999) observed that the RBM disappears at applied pressures of 1.5 GPa and higher—an observation which they attribute to the nanotubes undergoing a structural change at such pressures. Reich *et al.* (2000) obtained the pressure derivative of different phonon modes, and showed that the strain components are different in the circumferential and axial directions of the nanotubes.

In considering all these results on nanotube strength, it should be taken into account that the results for different samples will most likely depend on the concentration of different types of defects, experimental parameters and synthesis techniques.

(b) Theoretical studies

The most directly accessible mechanical property of nanotubes from a computational perspective, and the one to have been calculated first, is the so-called strain energy, defined as the energy difference per atom between a nanotube and an infinite flat graphene layer. It is known from continuum elasticity theory (Landau & Lifshitz 1986) that the strain energy should display a C/d_t^2 behaviour, where d_t is the nanotube diameter and C is a constant. Theoretical calculations based on empirical

potentials (Robertson *et al.* 1992), semi-empirical tight-binding methods (Hernández *et al.* 1998, 1999) and *ab initio* calculations (Blase *et al.* 1994a; Miyamoto *et al.* 1994a,b) all agree in predicting that the strain energy of nanotubes fits the continuum elasticity theory result, even for very narrow nanotubes ($d_t < 0.6$ nm). The strain-energy constant C can be related to the stiffness of the nanotubes, and indeed a correlation exists between the values of Young's modulus and the value of C for nanotubes of different compositions (Hernández *et al.* 1999). The strain energy of CNTs is the largest; BN nanotubes, for example, are predicted to have a lower strain energy, and also a lower Young modulus (Hernández *et al.* 1998, 1999).

The first thorough theoretical study of the mechanical properties of CNTs was reported by Lu (1997), who used an empirical force field to calculate Young's modulus as well as other elastic properties of MWNTs and SWNTs, the latter both as isolated tubes and in crystalline bundles. In this study it was found that the Young modulus of isolated SWNTs was insensitive to the nanotube diameter or chiral angle, having a value of *ca.* 1 TPa. For the bundles, it was found that Young's modulus decreases with increasing nanotube diameter, but this fact reflects geometrical factors rather than a degradation of the mechanical properties of the bundle or its constituting tubules with increasing diameter; as the diameter of the tubules is increased, the volume of the unit cell grows more rapidly than the number of atoms it contains, and hence, if Y is calculated via equation (4.1), its value decays with increasing tube diameter. MWNTs were found to have a value of Y of *ca.* 1.11 TPa. In a subsequent study, Hernández *et al.* (1998, 1999) performed a comparative study, based on semi-empirical tight-binding (Goringe *et al.* 1997) methods, in which Young's modulus and the Poisson ratio were calculated for C, BN, BC₂N, C₃N₄ and BC₃ SWNTs of varying diameter and chiral angle. This study confirmed that C nanotubes possess the highest Young modulus among the different materials considered, which was estimated to be *ca.* 1.26 TPa (assuming $h = 0.34$ nm) for the widest C nanotubes considered, with a diameter of *ca.* 2 nm, while BN nanotubes have a Young modulus of *ca.* 0.8 TPa, which is still quite high, but lower than that of C nanotubes. In agreement with the results of Lu (1997), it was found that Young's modulus was largely independent of the tube diameter and chiral angle, except for very narrow tubes, with diameters below *ca.* 0.6 nm, in which the strength of the C–C bonding is reduced due to the high curvature in the structure. The results of Lu (1997) and Hernández *et al.* (1998, 1999) are in rather good agreement with the experimental results of Krishnan *et al.* (1998) for SWNTs, and those of Wong *et al.* (1997).

Sanchez-Portal *et al.* (1999) also reported an extensive study of the structural, vibrational and mechanical properties of CNTs using first-principles electronic-structure methods based on density functional theory (Kohn & Sham 1965). For SWNTs in an isolated geometry and using the interlayer spacing ($h = 0.34$ nm) convention, they obtained values of Young's modulus of *ca.* 1 TPa. They also estimated this value in a bundle geometry, obtaining values that depend on the nanotube diameter (see our comments on this issue above), being 0.5 TPa for a bundle of (10, 10) nanotubes. Kudin *et al.* (2001) also have reported first-principles calculations of C and BN nanotubes, reporting values of their mechanical properties in good agreement with the earlier results. The response of nanotubes to applied hydrostatic pressure has been studied using first-principles methods by Reich *et al.* (2002). They calculated the bulk modulus and its pressure derivative up to applied pressures of 8.5 GPa; the

bulk modulus they obtained was 37 GPa—very similar to that of graphite obtained within the same level of theory.

The mechanical properties of nanotubes beyond the linear regime (i.e. in the limit of large deformations) have been studied using the shell model of continuum mechanics and with atomistic simulations based on empirical potentials. Yakobson *et al.* (1996) used both models to study the response of CNTs subject to large axial compressive strain. The energy of the nanotubes displayed slope discontinuities which occur at critical strain values, at which the nanotube buckled. The first discontinuity occurs at a compressive strain of 5%, in which the nanotube forms a neck. A second neck occurs at a strain of 7.6%, and larger strains result in more irregular distortions. Similar methods were also employed to study the bending and torsion of nanotubes in a combined experimental theoretical study by Iijima *et al.* (1996).

Simulations have also been used to investigate the behaviour of nanotubes subject to large tensile strains (Yakobson *et al.* 1997). These simulations aim at determining the strength of nanotubes under tension. Fracture of nanotubes analysed by these means reveals the formation of chains of atoms linking the two nanotube fragments. The breaking of nanotubes in these numerical experiments occurs at applied tensile strains of *ca.* 30%. Detailed atomistic simulations have also revealed how nanotubes react to and accommodate large strains. The simulations of Nardelli *et al.* (1998) show evidence for the formation of a dislocation with a 5/7/7/5 Stone–Wales pair at its core. At sufficient applied strain, the energetic barrier to the formation of this defect is reduced, and its formation precipitates further relaxation of the nanotube, which can take place in the form of either brittle fracture or plastic flow, depending on the applied stress, the structure of the tube and the temperature. These authors established that at low-temperature and high-stress conditions all tubes are brittle; at low applied stress and high temperature, narrow tubes (with diameter less than 1.1 nm) are ductile, though the behaviour of larger tubes will depend on their structure.

Determining the actual strength of nanotubes from simulation is a challenging task, due to the widely varying scales involved in fracture, both in the time and length domains. Due to computational limitations, simulations are normally too short to span the macroscopic time-scale relevant to fracture experiments; on the other hand, until multiscale simulation techniques come of age, fracture phenomena tend to be simulated using an atomistic description, which imposes severe limits on the length-scale. It is therefore not surprising that not much progress has been achieved on this front thus far. Nevertheless, a first step toward a theoretical understanding of strength in CNTs was given by Samsonidze *et al.* (2002), who studied the energies of the different possible transition states in the formation of the 5/7/7/5 Stone–Wales defect, which, as shown in the work of Nardelli *et al.* (1998), can trigger the yield of nanotubes, and they established how these energies varied as a function of strain and orientation with respect to the nanotube axis. Then, using transition state theory, they were able to determine the yield strain of nanotubes as a function of the chiral angle of the nanotube and the expected failure time. According to their results, chiral tubes have lower yield strain than either zigzag or armchair nanotubes, and, to obtain failure times of the order of 1 ms to 1 s, the necessary applied strain is predicted to be *ca.* 17%, in good agreement with experiments. More recently it has been suggested that brittle yield to tension via a bond-breaking mechanism (which, contrary to the Stone–Wales yield mechanism, is not thermally activated) may be

more relevant at room temperature, and may thus be the acting yield mechanism in tensile-test experiments (Dumitrică *et al.* 2003).

(c) Conclusion

The body of experimental and theoretical work discussed above confirms the expectation that CNTs have unique mechanical properties. The Young modulus of CNTs is larger than that of any other known material, and corresponds to the C_{11} elastic constant of graphite along the basal plane. In the linear (elastic) regime, essentially no dependence on the nanotube diameter or structure is found for the elastic moduli, although theoretical predictions indicate that Young's modulus is degraded in very narrow nanotubes due to curvature effects. Beyond the linear regime, experiments have shown that nanotubes are extremely resilient, with irreversible yield setting in only at extreme temperatures and loads. Theoretical work indicates that in this limit chiral tubes are more likely to yield at lower strain than either armchair or zigzag tubes.

5. Thermal properties

We now consider the thermal properties of CNTs, including their specific heat, thermal conductivity and thermopower. Thus far, the thermal properties of SWNTs have not been as extensively studied as the electronic, mechanical or phonon properties of SWNTs. The thermal properties of CNTs display a wide range of behaviours which stem from both their relation to a 2D graphene layer and their unique structure and tiny size. The specific heat of individual nanotubes should be similar to that of 2D graphene at high temperatures, with the effects of phonon quantization becoming apparent at lower temperatures for SWNTs of small diameter (less than 2 nm).

To study the intrinsic thermal conductivity and thermoelectric power of nanotubes, measurements must be made at the single-nanotube level. Such measurements are technically very difficult to make. Therefore, work in this area is just beginning to appear in the literature. The present status of knowledge about the specific heat, thermal conductivity, thermal expansion and thermopower of CNTs is reviewed here.

(a) Specific heat

The specific heat C of CNTs is dominated by the phonon contribution C_{ph} , as also occurs in other carbon systems, and C_{ph} is obtained by integrating over the phonon density of states with a factor that reflects the energy and occupation of each phonon state:

$$C_{\text{ph}} = \int_0^{\omega_{\text{max}}} k_{\text{B}} \left(\frac{\hbar\omega}{k_{\text{B}}T} \right)^2 \exp \left\{ \left(\frac{\hbar\omega}{k_{\text{B}}T} \right) g_{\text{ph}}(\omega) d\omega \right\} \left(\exp \left\{ \frac{\hbar\omega}{k_{\text{B}}T} \right\} - 1 \right)^{-2}, \quad (5.1)$$

where $g_{\text{ph}}(\omega)$ is the phonon density of states and ω_{max} is the highest phonon energy of the material and is related to the Debye temperature $k_{\text{B}}\Theta_{\text{D}} = \hbar\omega_{\text{max}}$. At low temperature ($T \ll \Theta_{\text{D}}$), however, $C_{\text{ph}}(T)$ is in general much simpler. In the limit of low temperature, we can take $\omega_{\text{max}} \rightarrow \infty$, and if C_{ph} is dominated by a single acoustic mode in d dimensions that obeys a dispersion relation $\omega \propto k^\alpha$, then

$$C_{\text{ph}} \propto T^{d/\alpha}, \quad T \ll \Theta_{\text{D}}, \quad (5.2)$$

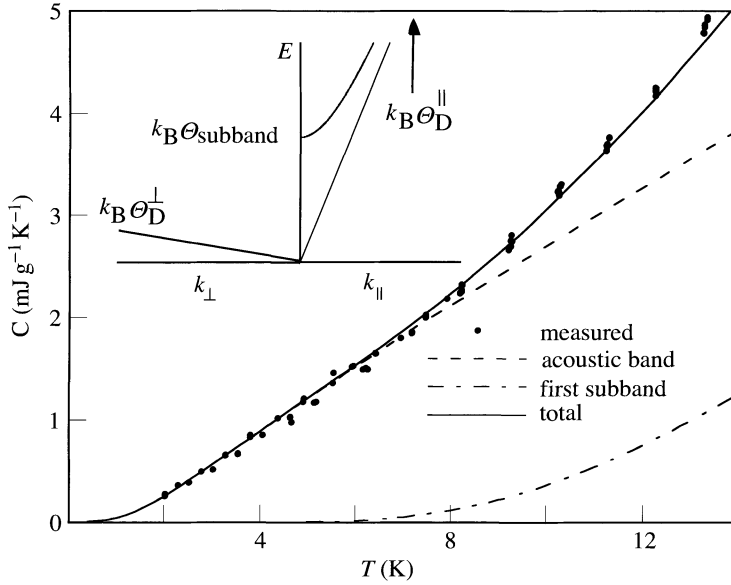


Figure 13. Measured specific heat of SWNTs compared with a two-band model with transverse dispersion (inset). The fitting parameters used are $\Theta_D^{\parallel} = 960$ K, $\Theta_D^{\perp} = 50$ K and $\Theta_{\text{subband}} = 13$ K (Hone 2001).

so that the low-temperature specific heat contains information about both the dimensionality of the system and the phonon dispersion.

At room temperature, many of the phonon subbands of the nanotube will be occupied, and the specific heat will be similar to that of 2D graphene. At low temperatures, however, both the quantized phonon structure and the stiffening of the acoustic modes will cause the specific heat of a nanotube to differ from that of graphene. In the low- T regime, only the acoustic bands will be populated, and thus the specific heat is expected to be that of a 1D system, showing a linear k dependence for the acoustic phonons $\omega(k)$. In this limit, $T \ll \hbar v/k_B R$, and equation (5.1) can be evaluated analytically, yielding a linear T dependence for the specific heat (Benedict *et al.* 1996):

$$C_{\text{ph}} = \frac{3k_B^2 T}{\pi \hbar v \rho_m} \frac{\pi^2}{3}, \quad (5.3)$$

where ρ_m is the mass per unit length, v is the acoustic phonon velocity and R is the nanotube radius. Thus the circumferential quantization of the nanotube phonons should be observable as the departure of the linear temperature dependence of C_{ph} at the lowest temperatures, to a steeper temperature dependence above the thermal energy for the first quantized phonon state (Benedict *et al.* 1996).

Figure 13 highlights the low-temperature behaviour of the specific heat, where nanotubes are expected to yield a characteristic behaviour that distinguishes nanotubes from 2D graphite. The experimental data, represented by the filled points, show a linear slope below 8 K, but the slope does not extrapolate to zero at $T = 0$, as would be expected for perfectly isolated SWNTs. This departure from ideal behaviour is most likely due to a weak transverse coupling between neighbouring tubes in the SWNT bundles. The measured data can be fitted using a two-band model, shown

in the inset of figure 13. The dashed line in figure 13 represents the contribution from a single acoustic mode, which has a high on-tube Debye temperature $\Theta_D^{\parallel}$ and a much smaller inter-tube Debye temperature $\Theta_D^{\perp}$. The dot-dashed line represents the contribution from the first (doubly degenerate) subband, with minimum energy $k_B\Theta_{\text{subband}}$. The solid line represents the sum of the two contributions, and fits the data quite well. The derived values for the on-tube and transverse Debye temperatures are $\Theta_D^{\parallel} = 960$ K (80 meV) and $\Theta_D^{\perp} = 50$ K (4.3 meV), respectively, and Θ_{subband} is 13 K (1.1 meV) (Hone 2001). Thus, accurate specific heat measurements can provide information about low-frequency optical phonons in SWNTs.

(b) *Thermal conductivity of SWNTs*

In graphite, the thermal conductivity is generally dominated by phonons, and limited by the small crystallite size within a sample. The apparent long-range crystallinity of nanotubes and long phonon mean free path led to the speculation (Ruoff & Lorents 1995) that the longitudinal thermal conductivity of nanotubes could possibly exceed the in-plane thermal conductivity of graphite—the material, together with diamond, that has the highest 3D thermal conductivity. The thermal conductivity, along with the specific heat, provides a sensitive tool for probing the interesting low-energy phonon structure of nanotubes, and also has the potential for practical applications that exploit the high thermal conductivity of these nanostructures.

Since the dominant carriers of thermal energy are the low-frequency phonons, the thermal conductivity along the nanotube axis is determined by the kinetic formula

$$\kappa_{zz} = \sum C v_z^2 \tau, \quad (5.4)$$

where C , v and τ are the specific heat, group velocity and relaxation time of a given phonon state, respectively, and the sum is over all phonon states. From equation (5.4), we see that the thermal conductivity is most sensitive to the states with the highest band velocity and the longest scattering time or largest mean free path. Since the thermal conductivity along the tube axis is at least two orders of magnitude larger than that normal to the tube axis, we would expect that the magnitude and temperature dependence of the thermal conductivity of an SWNT bundle or of an isolated MWNT should be close to those of their constituent tubes, though some inter-tube thermal conduction could occur. The thermal conductivity of ‘mat’ samples, however, is expected to be dominated by inter-tube thermal conduction processes (Hone 2001).

Measurements have been reported on the thermal conductivity of an individual SWNT bundle (Li 2002) and an individual MWNT (Small *et al.* 2003). In both cases, the nanotube sample is made by using the SWNT bundle or the MWNT to bridge the two heating pads/thermal contacts. The sample geometry thus obtained is used to measure the thermal conductance, electrical conductance and Seebeck coefficient on the same sample. For an SWNT bundle sample with a diameter range estimated to be 10–100 nm, thermal conduction measurements were made between 14.5 and 320 K with a peak observed at *ca.* 310 K (Li 2002), as shown in figure 14. Since the number of SWNTs contributing to the heat transport was not determined, the thermal conductivity could not be deduced from the measured thermal conductance. The functional form of $\kappa(T)$ exhibits a $T^{1.6}$ dependence, clearly lower than that for graphite (which exhibits a $T^{2.3}$ dependence) (Heremans & Beetz 1985), but also

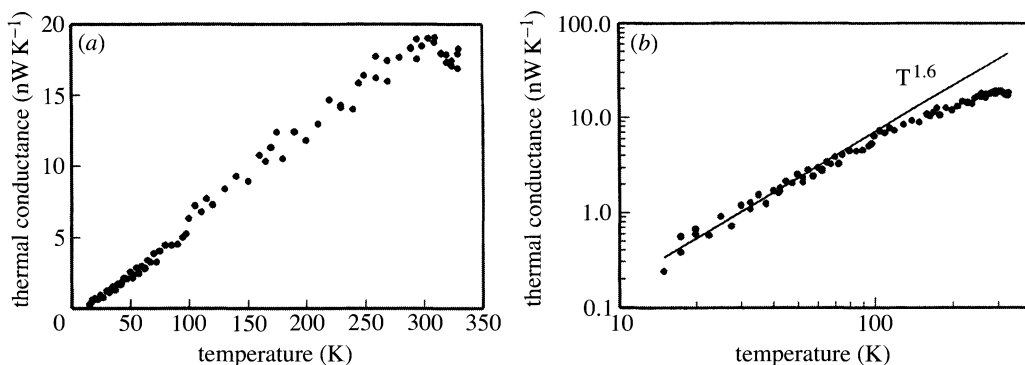


Figure 14. Measured temperature dependence of the thermal conductivity of a single bundle of SWNTs (Li 2002) from 15 K to 330 K plotted on (a) a linear T plot and on (b) a log–log plot.

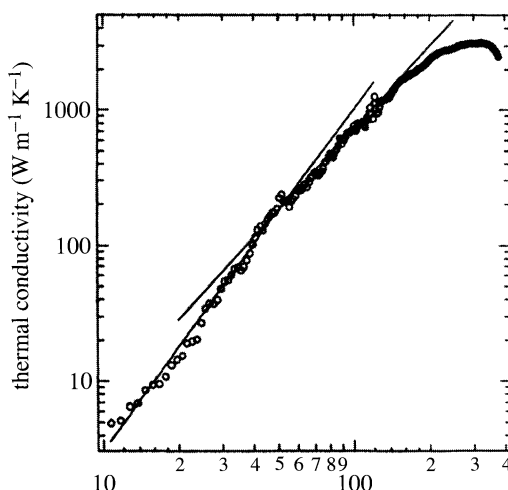


Figure 15. Measured temperature dependence of the thermal conductivity of an individual MWNT, 14 nm in diameter (Kim *et al.* 2001; Small *et al.* 2003; Yang *et al.* 2002).

greater than the linear T dependence that would be expected for a 1D system, and that previously reported for ‘mat’ SWNT samples (Hone 2001). The departure for a linear T dependence may be due to coupling to optical phonons and to tube–tube scattering/conduction processes. The peak at 310 K suggests that phonon–phonon scattering becomes important near room temperature for SWNT bundle samples, but this effect is much weaker than in graphite, possibly reflecting the much smaller number of available scattering states for a 1D system. Such a maximum in $\kappa(T)$ is not seen in the thermal conductivity measurements on SWNT ‘mat’ samples where inter-tube processes are much more important (Hone 2001).

Measurements of $\kappa(T)$ shown in figure 15 for an individual MWNT (14 nm diameter) show very high values of κ (over $3000 \text{ W m}^{-1} \text{ K}^{-1}$) and a maximum in $\kappa(T)$, which is indicative of significant phonon–phonon scattering at high T (Small *et al.* 2003). The slope of $\kappa(T)$ for the low- T data is 2.0, indicative of a 2D system, while the corresponding slope of $\kappa(T)$ at larger T (e.g. 77 K) is ~ 2.5 , indicative of the many nanotube phonons that are activated in this T range, which is to be com-

pared with a slope of 2.3 for graphite, a quasi-2D material. The much larger values of $\kappa(T)$ obtained at the single-nanotube level indicate the dominance of tube–tube thermal conduction in ‘mat’ samples of SWNTs (Hone 2001). The crossover from the T^2 to $T^{2.5}$ behaviour at 50 K provides a measure of the out-of-plane Debye temperature, while the Debye temperature along the nanotube axis is expected to be similar to that of a graphene sheet (e.g. 2480 K). As mentioned above, the magnitude of $\kappa(T)$ is sensitive to the sample structure, with the highest values (like those in the best graphite samples) achieved for measurements on individual SWNT bundles or individual MWNTs, and much lower values are found for disordered ‘mat’ samples, with $\kappa \sim 35 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K (Hone 2001), while intermediate values of $\kappa \sim 200 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K are found for ‘mat’ samples consisting of aligned SWNTs (Hone *et al.* 2000).

We have seen above that the small diameter of CNTs causes phonon quantization, which can be observed both in the heat capacity and in the thermal conductivity at low temperatures. The restricted geometry of the nanotubes suppresses the peak in the thermal conductivity and moves it to higher temperatures compared with graphite, reflecting the fact that phonon–phonon scattering should be suppressed in a 1D system, because of the unavailability of states into which to scatter (Jishi *et al.* 1993; Peierls 1955).

(c) Thermal expansion

The thermal expansion of an SWNT bundle has been measured using X-ray diffraction techniques (Maniwa *et al.* 2001), and the results are consistent with expectations based on graphite, which has an exceedingly small in-plane thermal expansion coefficient, but a large inter-planar expansion coefficient. The measurements show almost no thermal expansion along the direction of the nanotube axis ($-0.15 \pm 0.20 \times 10^{-5} \text{ K}^{-1}$), but a value of $0.75 \pm 0.25 \times 10^{-5} \text{ K}^{-1}$ is found for the expansion in the range 300–950 K along the direction of the SWNT diameter. The value for the temperature dependence of the inter-tube gap is $(4.2 \pm 1.4) \times 10^{-5} \text{ K}^{-1}$ for an SWNT bundle, which is larger than $(2.6 \pm 1.4) \times 10^{-5} \text{ K}^{-1}$ for graphite, with a significantly larger anharmonicity shown for SWNTs relative to graphite. The very tiny thermal expansion coefficient of the tube diameter reflects the strong in-plane C–C bonds in nanotubes. The various values of the thermal expansion coefficients affect the temperature dependence of the observed phonon modes. Also, considerable strain is introduced when nanotubes are mixed with other constituents to form composites for various applications, because of the very different thermal expansion properties of SWNTs and other materials.

(d) Thermopower

Early measurements of the thermopower were carried out on ‘mat’ SWNT samples exposed to air (Bradley *et al.* 2000), and the results were dominated by ensemble averaging effects, inter-tube interactions and oxygen doping effects. Subsequent studies showed the thermopower or Seebeck coefficient of SWNT bundles to be very sensitive to exposure to oxygen and other gaseous species (Sumanasekera *et al.* 2000, 2002*b*), because oxygen adsorption causes SWNTs to become p-type, and to yield quite high thermopower values. This high sensitivity of the thermopower to gas adsorption has

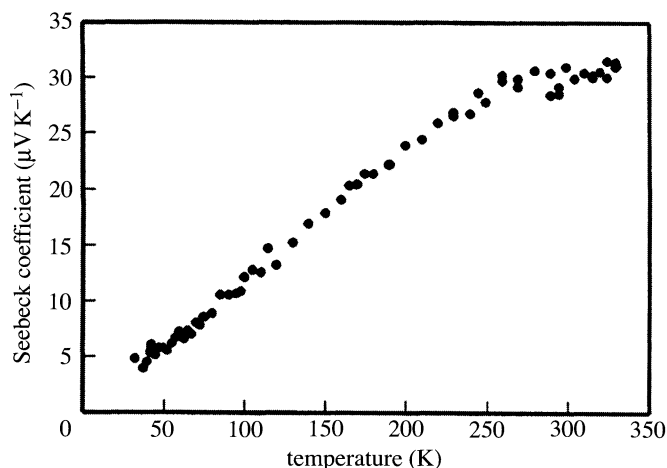


Figure 16. Measured temperature dependence of the Seebeck coefficient of a single SWNT bundle as a function of temperature (Li 2002).

potential for use as a gas sensor (Sumanasekera *et al.* 2002a). However, for quantitative measurements of the temperature dependence of the intrinsic thermopower of SWNTs, the removal of adsorbed gases is essential. The Seebeck coefficient is sensitive to charge transfer effects, motion of the Fermi level and various other effects, which can potentially be used to characterize SWNTs, but at the same time requires great care with sample preparation for the measurement of intrinsic behaviour in SWNTs. For example, the insertion of C₆₀ inside SWNTs to form peapods shows a decrease in the positive value of the Seebeck coefficient $S(T)$ for all temperatures T (Vavro *et al.* 2002), which may perhaps be related to charge transfer. Pressure-dependent studies of the $S(T)$ in SWNT ‘mats’ show a suppression of the thermopower above 50 K, which is interpreted in terms of a change in phonon population due to both temperature and pressure-dependent effects (Barišić *et al.* 2002).

Thermopower measurements for an individual SWNT bundle, de-oxygenated in high vacuum for several hours (10^{-6} – 10^{-8} Torr), have been carried out, yielding smaller values of the Seebeck coefficient (Li 2002) (see figure 16), than those reported for oxygenated samples (Bradley *et al.* 2000). Because of the large positive Seebeck coefficient observed in figure 16, it is possible that, since the SWNT bundle was not heated during the de-oxygenation process, the SWNT bundle still contained adsorbed oxygen. The measured positive Seebeck coefficient shows a linear temperature dependence in the temperature range 30–250 K and saturation behaviour at a value of *ca.* 30 $\mu\text{V K}^{-1}$ above 250 K (Li 2002). By measuring the Seebeck coefficient S , the electrical resistance R , and the thermal conductance G on the same SWNT bundle sample, the temperature dependence of the thermoelectric figure of merit ($Z \equiv S^2/RG$) was deduced (Li 2002). Because of the very high thermal conductivity of SWNTs, their thermoelectric figure of merit is quite low.

More detailed measurements of the thermopower of an individual SWNT are now in progress (P. Kim 2003, personal communication). By measuring the thermopower and electrical conductance at the same time, detailed studies of universal conductance fluctuations and Coulomb blockade phenomena can be carried out (P. Kim 2003, personal communication). The results show that the thermopower follows in detail

the universal conductance fluctuations observed in the conductance, in accordance with the Mott formula. It is further found that the phonon drag term is not important in SWNTs, and that the thermopower is dominated by the diffusion term down to low temperatures (P. Kim 2003, personal communication). The effects of the Coulomb blockade and of electron–electron interaction can be seen in metallic SWNTs. The thermopower of semiconducting SWNTs appears to be qualitatively different from that for metallic SWNTs (P. Kim 2003, personal communication).

(e) Conclusion

The demonstration of thermal measurements at the individual nanotube level, as described above, is expected to have a major impact on the direction of future studies on the thermal properties of nanotubes, especially for individual SWNTs and SWNT bundles. Single-nanotube studies will allow more detailed measurements of intertube contributions to thermal transport and to the thermopower, the tube diameter dependence of various thermal processes, differences in behaviour of thermal processes in semiconducting and metallic SWNTs, the role of optical phonons in thermal processes and the effect of specific adsorbed gases and dopants on the thermal and thermoelectric properties of nanotubes. The study of quantum thermal phenomena at low temperatures should be especially interesting regarding studies of the effect of individual selected phonons on the various thermal properties.

6. Concluding remarks

In this paper we have covered three important aspects of CNTs: their electronic, thermal and mechanical properties. The importance of these different aspects can be gauged by their relevance to practical applications. As discussed in §2, the intriguing and fascinating electronic properties of CNTs offer a huge potential for nanoelectronics and applications. However, one important issue of electronics at the nanoscale is the capacity of device components to dissipate heat and to withstand the stresses of operating conditions. Therefore, the high thermal conductivity and extraordinary mechanical properties of CNTs are especially relevant for practical applications. But nanoelectronics is only one of the many and varied fields in which nanotubes are expected to find application. Their thermal properties, combined with their capacity to absorb radiation, have lead to the expectation that nanotubes could be used to obtain stealth paints or coatings, while their high strength and low density immediately suggest their use in toughening of composite materials and in the fabrication of lightweight, strong nanotube-based fibres.

Numerous hurdles have yet to be overcome before the practical potential of nanotubes can be realized, not least finding better and cheaper synthesis and purification techniques, improving our ability to manipulate them at the nanoscale, and the development of more sensitive characterization methods. But given that their properties are so unusual, their size is so small and the scope for applications is so large, we feel confident that it is only a question of time before the promise of nanotubes is fulfilled.

J.C.C. acknowledges the financial support of the National Fund for Scientific Research (FNRS) of Belgium. This paper presents research results of the Belgian Program on Inter-university Attraction Poles (PAI5/1/1) entitled *Quantum Size Effects in Nanostructured Materials* and of

the Action de Recherche Concertée entitled *Interaction électron-phonon dans les nanostructures*, sponsored by the Communauté Française de Belgique. M.S.D. and G.D. gratefully acknowledge support from NSF grant DMR01-16042 and stimulating discussions with Professor Charles Lieber, Professor Gang Chen, Professor Arun Majumdar, Professor Peidong Yang, Professor Philip Kim, Professor Jean-Paul Issi and Dr Joseph Heremans. E.H. thanks the Spanish Ministry of Science and Technology (MCyT) for support through projects BFM2002-03278 and BFM2003-03372-C03.

References

- Bachtold, A., Hadley, P., Nakanishi, T. & Dekker, C. 2001 Logic circuits with carbon nanotube transistors. *Science* **294**, 1317–1320.
- Barišić, N., Gaál, R., Kézmárki, I., Mihály, G. & Forró, L. 2002 Pressure dependence of the thermoelectric power of single-walled carbon nanotubes. *Phys. Rev. B* **65**, 241403.
- Benedict, L. X., Louie, S. G. & Cohen, M. L. 1996 Heat capacity of carbon nanotubes. *Solid State Commun.* **100**, 177–180.
- Bethune, D. S., Kiang, C. H., de Vries, M. S., Gorman, C., Savoy, R., Vazquez, J. & Beyers, R. 1993 Cobalt-catalysed growth of carbon nanotubes with single atomic layer walls. *Nature* **363**, 605–607.
- Biró, L. P., Márk, G. I., Koós, A. A., Nagy, J. B. & Lambin, P. 2002 Coiled carbon nanotube structures with supraunitary nonhexagonal to hexagonal ring ratio. *Phys. Rev. B* **66**, 165405.
- Blase, X., Rubio, A., Louie, S. G. & Cohen, M. L. 1994a Stability and band-gap constancy of boron nitride nanotubes. *Europhys. Lett.* **28**, 335–340.
- Blase, X., Benedict, L. X., Shirley, E. L. & Louie, S. G. 1994b Hybridization effects and metallicity in small radius carbon nanotubes. *Phys. Rev. Lett.* **72**, 1878–1881.
- Bockrath, M., Cobden, D. H., McEuen, P. L., Chopra, N. G., Zettl, A., Thess, A. & Smalley, R. E. 1997 Single-electron transport in ropes of carbon nanotubes. *Science* **275**, 1922–1925.
- Bradley, K., Jhi, S.-H., Collins, P. G., Hone, J., Cohen, M. L., Louie, S. G. & Zettl, A. 2000 Is the intrinsic thermoelectric power of carbon nanotubes positive? *Phys. Rev. Lett.* **85**, 4361–4364.
- Brar, V. W., Samsonidze, G. G., Dresselhaus, G., Dresselhaus, M. S., Saito, R., Swan, A. K., Ünlü, M. S., Goldberg, B. B., Souza Filho, A. G. & Jorio, A. 2002 Second-order harmonic and combination modes in graphite, single-wall carbon nanotube bundles, and isolated single-wall carbon nanotubes. *Phys. Rev. B* **66**, 155418.
- Brown, S. D. M., Jorio, A., Corio, P., Dresselhaus, M. S., Dresselhaus, G., Saito, R. & Kneipp, K. 2001 Origin of the Breit–Wigner–Fano lineshape of the tangential G-band feature of metallic carbon nanotubes. *Phys. Rev. B* **63**, 155414.
- Charlier, J.-C. 2002 Defects in carbon nanotubes. *Acc. Chem. Res.* **35**, 1063–1069.
- Charlier, J.-C., Ebbesen, T. W. & Lambin, P. 1996 Structural and electronic properties of pentagon–heptagon pair defects in carbon nanotubes. *Phys. Rev. B* **53**, 11 108–11 113.
- Chico, L., Crespi, V. H., Benedict, L. X., Louie, S. G. & Cohen, M. L. 1996 Pure carbon nanoscale devices: nanotube heterojunctions. *Phys. Rev. Lett.* **76**, 971–974.
- Chopra, N. G. & Zettl, A. 1998 Measurement of the elastic modulus of a multi-wall boron nitride nanotube. *Solid State Commun.* **105**, 297–300.
- Corio, P., Santos, A. P., Santos, P. S., Temperini, M. L. A., Brar, V. W., Pimenta, M. A. & Dresselhaus, M. S. 2004 Characterization of single wall carbon nanotubes filled with silver and with chromium compounds. *Chem. Phys. Lett.* **383**, 475–480.
- Cronin, S. B., Barnett, R., Tinkham, M., Chou, S. G., Rabin, O., Dresselhaus, M. S., Swan, A. K., Unlu, M. S. & Goldberg, B. B. 2004 Electrochemical gating of individual single-wall carbon nanotubes observed by electron transport measurements and resonant Raman spectroscopy. *Appl. Phys. Lett.* **84**, 2052–2054.

- Dai, H., Wong, E. W. & Lieber, C. M. 1994 Probing electrical transport in nanomaterials: conductivity of individual carbon nanotubes. *Science* **272**, 523–526.
- Derycke, V., Martel, R., Appenzeller, J. & Avouris, P. 2001 Carbon nanotube inter- and intramolecular logic gates. *Nano Lett.* **1**, 453–456.
- Dresselhaus, M. S. & Eklund, P. C. 2000 Phonons in carbon nanotubes. *Adv. Phys.* **49**, 705–814.
- Dresselhaus, G., Pimenta, M. A., Saito, R., Charlier, J.-C., Brown, S. D. M., Corio, P., Marucci, A. & Dresselhaus, M. S. 2000 On the π - π overlap energy in carbon nanotubes. In *Science and Applications of Nanotubes. Proc. Int. Workshop on the Science and Applications of Nanotubes, Michigan State University, East Lansing, MI, USA, 24–27 July 1999* (ed. D. Tománek & R. J. Enbody), pp. 275–295. Dordrecht: Kluwer Academic.
- Dresselhaus, M. S., Dresselhaus, G., Jorio, A., Souza Filho, A. G. & Saito, R. 2002 Raman spectroscopy on isolated single wall carbon nanotubes. *Carbon* **40**, 2043–2061.
- Dresselhaus, M. S., Dresselhaus, G., Rao, A. M., Jorio, A., Souza Filho, A. G., Samsonidze, G. G. & Saito, R. 2003 Resonant Raman scattering on one-dimensional systems. *Indian J. Phys. B* **77**, 75–99.
- Dubay, O., Kresse, G. & Kuzmany, H. 2002 First-principles calculations of small diameter tubes. *H. Phys. Rev. Lett.* **88**, 235506.
- Dumitrică, T., Belytschko, T. & Yakobson, B. I. 2003 Bond-breaking bifurcation states in carbon nanotube fracture. *J. Chem. Phys.* **118**, 9485–9488.
- Dunlap, B. I. 1994 Relating carbon tubules. *Phys. Rev. B* **49**, 5643–5651.
- Ebbesen, T. W., Lezec, H. J., Hiura, H., Bennett, J. W., Ghaemi, H. F. & Thio, T. 1996 Electrical conductivity of individual carbon nanotubes. *Nature* **382**, 54–56.
- Endo, M. 1975 Mécanisme de croissance en phase vapeur de fibres de carbone. PhD thesis, University of Orleans, France.
- Falvo, M. R., Clary, G. J., Taylor, R. M., Chi, V., Brooks, F. P., Washburn, S. & Superfine, R. 1997 Bending and buckling of carbon nanotubes under large strain. *Nature* **389**, 582–584.
- Fantini, C., Souza, M., Jorio, A., Dantas, M. S. S., Ladeira, L. O., Pimenta, M. A., Souza Filho, A. G., Samsonidze, G. G., Dresselhaus, G., Dresselhaus, M. S. & Saito, R. 2004 Step-like dispersive behavior of the intermediate frequency Raman modes in carbon nanotubes. *Phys. Rev. Lett.* (In the press.)
- Goringe, C. M., Bowler, D. R. & Hernández, E. 1997 Tight-binding modelling of materials. *Rep. Prog. Phys.* **60**, 1447–1512.
- Haeckel, E. 1862 *Die Radiolarien (Rhizopoda Radiaria)*. Berlin: Reimer.
- Hamada, N., Sawada, S. & Oshiyama, A. 1992 New one-dimensional conductors: graphitic microtubules. *Phys. Rev. Lett.* **68**, 1579–1581.
- Heremans, J. & Beetz, C. P. 1985 Thermal conductivity and thermopower of vapor-grown graphite fibers. *Phys. Rev. B* **32**, 1981–1986.
- Hernández, E., Goze, C., Bernier, P. & Rubio, A. 1998 Elastic properties of C and $B_xC_yN_z$ composite nanotubes. *Phys. Rev. Lett.* **80**, 4502–4505.
- Hernández, E., Goze, C., Bernier, P. & Rubio, A. 1999 Elastic properties of single-wall nanotubes. *Appl. Phys. A* **68**, 287–292.
- Hone, J. 2001 Phonons and thermal properties of carbon nanotubes. In *Carbon nanotubes: synthesis, structure, properties and applications* (ed. M. S. Dresselhaus, G. Dresselhaus & Ph. Avouris), pp. 273–286. Springer Series in Topics in Applied Physics, vol. 80. Springer.
- Hone, J., Llaguno, M. C., Nemes, N. M., Johnson, A. T., Fischer, J. E., Walters, D. E., Casavant, M. J., Schmidt, J. & Smalley, R. E. 2001 *Appl. Phys. Lett.* **78**, 666–668.
- Huang, Y., Duan, X., Cui, Y., Lauhon, L. J., Kim, K. H. & Lieber, C. M. 2001 Logic gates and computation from assembled nanowire building blocks. *Science* **294**, 1313–1317.
- Iijima, S. 1991 Helical microtubules of graphitic carbon. *Nature* **354**, 56–58.
- Iijima, S. & Ichihashi, T. 1993 Single shell carbon nanotubes of 1-nm diameter. *Nature* **363**, 603–605.

- Iijima, S., Brabec, C., Maiti, A. & Bernholc, J. 1996 Structural flexibility of carbon nanotubes. *J. Chem. Phys.* **104**, 2089–2092.
- Jishi, R. A., Dresselhaus, M. S. & Dresselhaus, G. 1993 Electron–phonon coupling and the electrical conductivity of fullerene nanotubules. *Phys. Rev. B* **48**, 11 385–11 389.
- Jorio, A., Dresselhaus, G., Dresselhaus, M. S., Souza, M., Dantas, M. S. S., Pimenta, M. A., Rao, A. M., Saito, R., Liu, C. & Cheng, H. M. 2000 Polarized Raman study of single-wall semiconducting carbon nanotubes. *Phys. Rev. Lett.* **85**, 2617–2620.
- Jorio, A., Saito, R., Hafner, J. H., Lieber, C. M., Hunter, M., McClure, T., Dresselhaus, G. & Dresselhaus, M. S. 2001a Structural (n, m) determination of isolated single-wall carbon nanotubes by resonant Raman scattering. *Phys. Rev. Lett.* **86**, 1118–1121.
- Jorio, A., Souza Filho, A. G., Dresselhaus, G., Dresselhaus, M. S., Saito, R., Hafner, J. H., Lieber, C. M., Matinaga, F. M., Dantas, M. S. S. & Pimenta, M. A. 2001b Joint density of electronic states for one isolated single-wall carbon nanotube studied by resonant Raman scattering. *Phys. Rev. B* **63**, 245416.
- Jorio, A., Pimenta, M. A., Souza Filho, A. G., Saito, R., Dresselhaus, G. & Dresselhaus, M. S. 2003 Characterizing carbon nanotube samples with resonance Raman scattering. *New J. Phys.* **5**, 139.1–139.17.
- Kataura, H., Kumazawa, Y., Maniwa, Y., Umez, I., Suzuki, S., Ohtsuka, Y. & Achiba, Y. 1999 Optical properties of single-wall carbon nanotubes. *Synth. Metals* **103**, 2555–2558.
- Kim, P., Shi, L., Majumdar, A. & McEuen, P. L. 2001 Thermal transport measurements of individual multiwalled nanotubes. *Phys. Rev. Lett.* **87**, 215502.
- Kohn, W. & Sham, L. J. 1965 Self-consistent equations including exchange and correlation effects. *Phys. Rev. A* **140**, 1133–1138.
- Krishnan, A., Dujardin, E., Ebbesen, T. W., Yianilos, P. N. & Treacy, M. M. J. 1998 Young's modulus of single-walled nanotubes. *Phys. Rev. B* **58**, 14013–14019.
- Kudin, K. N., Scuseria, G. E. & Yakobson, B. I. 2001 C₂F, BN, and C nanoshell elasticity from *ab initio* computations. *Phys. Rev. B* **64**, 235406.
- Lambin, Ph., Fonseca, A., Vigneron, J. P., Nagy, J. B. & Lucas, A. A. 1995 Structural and electronic properties of bent carbon nanotubes. *Chem. Phys. Lett.* **245**, 85–89.
- Landau, L. D. & Lifshitz, E. M. 1986 *Theory of elasticity*. Oxford: Pergamon.
- Langer, L., Bayot, V., Grivei, E., Issi, J. P., Heremans, J. P., Olk, C. H., Stockman, L., Van Haesendonck, C. & Bruynseraede, Y. 1996 Quantum transport in a multiwalled carbon nanotube. *Phys. Rev. Lett.* **76**, 479–482.
- Li, D. 2002 Thermal transport in individual nanowires and nanotubes. PhD thesis, Department of Mechanical Engineering, University of California, Berkeley, CA, USA.
- Li, F., Cheng, H. M., Bai, S., Su, G. & Dresselhaus, M. S. 2000 Tensile strength of single-walled carbon nanotubes directly measured from their macroscopic ropes. *Appl. Phys. Lett.* **77**, 3161–3163.
- Liu, B. B., Sundqvist, B., Li, D. M. & Zou, G. T. 2002 Resistivity and fractal structure in carbon nanotube networks. *J. Phys. Condens. Matter* **44**, 11 125–11 129.
- Lourie, O., Cox, D. M. & Wagner, H. D. 1998 Buckling and collapse of embedded carbon nanotubes. *Phys. Rev. Lett.* **81**, 1638–1641.
- Lu, J. P. 1997 Elastic properties of nanotubes and nanoropes. *Phys. Rev. Lett.* **79**, 1297–1300.
- Maniwa, Y., Fujiwara, R., Kira, H., Kataura, H., Suzuki, S., Achiba, Y., Nishibori, E., Takata, M., Sakata, M., Fujiwara, A. & Suematsu, H. 2001 Thermal expansion of SWNT bundles: X-ray diffraction studies. *Phys. Rev. B* **64**, 241402.
- Mintmire, J. W., Dunlap, B. I. & White, C. T. 1992 Are fullerene tubules metallic? *Phys. Rev. Lett.* **68**, 631–634.
- Miyamoto, Y., Rubio, A., Louie, S. G. & Cohen, M. L. 1994a Chiral tubules of hexagonal BC₂N. *Phys. Rev. B* **50**, 4976–4979.

- Miyamoto, Y., Rubio, A., Cohen, M. L. & Louie, S. G. 1994*b* Electronic properties of tubule forms of hexagonal BC₃. *Phys. Rev. B* **50**, 18 360–18 366.
- Nardelli, M., Yakobson, B. I. & Bernholc, J. 1998 Brittle and ductile behavior in carbon nanotubes. *Phys. Rev. Lett.* **81**, 4656–4659.
- Odom, T. W., Huang, J. L., Kim, P. & Lieber, C. M. 1998 Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature* **391**, 62–64.
- Ouyang, M., Huang, J. L., Cheung, C. L. & Lieber, C. M. 2001 Energy gaps in ‘metallic’ single-walled carbon nanotubes. *Science* **292**, 702–705.
- Peierls, R. 1955 *Quantum theory of solids*. Oxford University Press.
- Pimenta, M. A., Marucci, A., Empedocles, S., Bawendi, M., Hanlon, E. B., Rao, A. M., Eklund, P. C., Smalley, R. E., Dresselhaus, G. & Dresselhaus, M. S. 1998 Raman modes of metallic carbon nanotubes. *Phys. Rev. B* **58**, 16 016–16 019.
- Poncharal, P., Wang, Z. L., Ugarte, D. & de Heer, W. A. 1999 Electrostatic deflections and electromechanical resonances of carbon nanotubes. *Science* **283**, 1513–1516.
- Quian, D., Wagner, G. J., Liu, W. K., Yu, M. F. & Ruoff, R. S. 2003 Mechanics of carbon nanotubes. In *Handbook of nanoscience, engineering and nanotechnology* (ed. W. A. Goddard III, D. W. Brenner, S. E. Lyshevski & G. J. Iafrate), pp. 19–1–19–63. Boca Raton, FL: CRC Press.
- Rao, A. M. (and 12 others) 1997 Diameter-selective Raman scattering from vibrational modes in carbon nanotubes. *Science* **275**, 187–191.
- Reich, S., Jantoljak, H. & Thomsen, C. 2000 Shear strain in carbon nanotubes under hydrostatic pressure. *Phys. Rev. B* **61**, 13 389–13 392.
- Reich, S., Thomsen, C. & Ordejón, P. 2002 Elastic properties of carbon nanotubes under hydrostatic pressure. *Phys. Rev. B* **65**, 153407.
- Robertson, D. H., Brenner, D. W. & Mintmire, J. W. 1992 Energetics of nanoscale graphitic tubules. *Phys. Rev. B* **45**, 12 592–12 595.
- Ruoff, R. S. & Lorents, D. C. 1995 Mechanical and thermal properties of carbon nanotubes. *Carbon* **33**, 925–930.
- Saito, R., Fujita, M., Dresselhaus, G. & Dresselhaus, M. S. 1992 Electronic structure of chiral graphene tubules. *Appl. Phys. Lett.* **60**, 2204–2206.
- Saito, R., Dresselhaus, G. & Dresselhaus, M. S. 1996 Tunneling conductance of connected carbon nanotubes. *Phys. Rev. B* **53**, 2044–2050.
- Saito, R., Dresselhaus, G. & Dresselhaus, M. S. 1998 *Physical properties of carbon nanotubes*. London: Imperial College Press.
- Saito, R., Dresselhaus, G. & Dresselhaus, M. S. 2000 Trigonal warping effect of carbon nanotubes. *Phys. Rev. B* **61**, 2981–2990.
- Salvetat, J. P., Briggs, G. A. D., Bonard, J. M., Bacsá, R. R., Kulik, A. J., Stockli, T., Burnham, N. A. & Forro, L. 1999 Elastic and shear moduli of single-walled carbon nanotube ropes. *Phys. Rev. Lett.* **82**, 944–947.
- Samsonidze, Ge. G., Samsonidze, G. G. & Yakobson, B. I. 2002 Kinetic theory of symmetry-dependent strength in carbon nanotubes. *Phys. Rev. Lett.* **88**, 065501.
- Samsonidze, Ge. G., Saito, R., Jorio, A., Pimenta, M. A., Souza Filho, A. G., Grüneis, A., Dresselhaus, G. & Dresselhaus, M. S. 2003*a* The concept of cutting lines in carbon nanotube science. *J. Nanosci. Nanotechnol.* **3**, 431–458.
- Samsonidze, Ge. G., Saito, R., Jorio, A., Souza Filho, A. G., Grüneis, A., Pimenta, M. A., Dresselhaus, G. & Dresselhaus, M. S. 2003*b* Phonon trigonal warping effect in graphite and carbon nanotubes. *Phys. Rev. Lett.* **90**, 027403.
- Sanchez-Portal, D., Artacho, E., Soler, J. M., Rubio, A. & Ordejón, P. 1999 *Ab initio* structural, elastic, and vibrational properties of carbon nanotubes. *Phys. Rev. B* **59**, 12 678–12 688.
- Small, J. P., Shi, L. & Kim, P. 2003 Mesoscopic thermal and thermoelectric measurements of individual carbon nanotubes. *Solid State Commun.* **127**, 181–186.

- Souza Filho, A. G. (and 11 others) 2002 Probing the electronic trigonal warping effect in individual single-wall carbon nanotubes using phonon spectra. *Chem. Phys. Lett.* **354**, 62–68.
- Souza Filho, A. G. (and 12 others) 2004 Stokes and anti-Stokes Raman spectra of small diameter isolated carbon nanotubes. *Phys. Rev. B*, **69**, 115428.
- Sumanasekera, G. U., Adu, C. K. W., Fang, S. & Eklund, P. C. 2000 Effects of gas adsorption and collisions on electrical transport in single-walled carbon nanotubes. *Phys. Rev. Lett.* **85**, 1096–1099.
- Sumanasekera, G. U., Pradhan, B. K., Adu, C. K. W., Romero, H. E., Foley, H. C. & Eklund, P. C. 2002a Thermoelectric chemical sensor based on single wall carbon nanotubes. *Molec. Cryst. Liq. Cryst.* **387**, 31–37.
- Sumanasekera, G. U., Pradhan, B. K., Romero, H. E., Adu, C. K. W. & Eklund, P. C. 2002b Giant thermopower effects from molecular physisorption on carbon nanotubes. *Phys. Rev. Lett.* **89**, 166801.
- Tang, Z. K., Zhang, L., Wang, N., Zhang, X. X., Wen, G. H., Li, G. D., Wang, J. N., Chan, C. T. & Sheng, P. 2001 Superconductivity in 4 Å SWNTs. *Science* **292**, 2462–2465.
- Tans, S. J., Devoret, M. H., Dai, H., Thess, A., Smalley, R. E., Geerligs, L. J. & Dekker, C. 1997 Individual single-wall carbon nanotubes as quantum wires. *Nature* **386**, 474–477.
- Terrones, H., Terrones, M., Hernández, E., Grobert, N., Charlier, J. C. & Ajayan, P. M. 2000 New metallic allotropes of planar and tubular carbon. *Phys. Rev. Lett.* **84**, 1716–1719.
- Terrones, M., Banhart, F., Grobert, N., Charlier, J. C., Terrones, H. & Ajayan, P. M. 2002a Molecular junctions by joining SWNTs. *Phys. Rev. Lett.* **89**, 075505.
- Terrones, M., Terrones, G. & Terrones, H. 2002b Structure, chirality and formation of giant icosahedral fullerenes and spherical graphitic onions. *Appl. Phys. A* **74**, 355–371.
- Thomsen, C. & Reich, S. 2000 Double resonant Raman scattering in graphite. *Phys. Rev. Lett.* **85**, 5214–5217.
- Treacy, M. M. J., Ebbesen, T. W. & Gibson, J. M. 1996 Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature* **381**, 678–680.
- Vavro, J., Llaguno, M. C., Satishkumar, B. C., Luzzi, D. E. & Fischer, J. E. 2002 Electrical and thermal properties of C₆₀-filled single-wall carbon nanotubes. *Appl. Phys. Lett.* **80**, 1450–1452.
- Venkateswaran, U. D., Rao, A. M., Richter, E., Menon, M., Rinzler, A., Smalley, R. E. & Eklund, P. C. 1999 Probing the single-wall carbon nanotube bundle: Raman scattering under high pressure. *Phys. Rev. B* **59**, 10 928–10 934.
- Wagner, H. D., Lourie, O., Feldman, Y. & Tenne, R. 1998 Stress-induced fragmentation of multiwall carbon nanotubes. *Appl. Phys. Lett.* **72**, 188–190.
- Walters, D. A., Ericson, L. M., Casavant, M. J., Liu, J., Colbert, D. T., Smith, K. A. & Smalley, R. E. 1999 Elastic strain of freely suspended single-wall carbon nanotube ropes. *Appl. Phys. Lett.* **74**, 3803–3806.
- Wang, N., Tang, Z. K., Li, G. D. & Chen, J. S. 2000 Materials science: single-walled 4 Å carbon nanotube arrays. *Nature* **408**, 50–51.
- Wildöer, J. W. G., Venema, L. C., Rinzler, A. G., Smalley, R. E. & Dekker, C. 1998 Electronic structure of atomically resolved carbon nanotubes. *Nature* **391**, 59–62.
- Wong, E. W., Sheehan, P. E. & Lieber, C. M. 1997 Nanobeam mechanics: elasticity, strength and toughness of nanorods and nanotubes. *Science* **277**, 1971–1975.
- Yakobson, B. I. & Avouris, Ph. 2001 Mechanical properties of carbon nanotubes. In *Carbon nanotubes: synthesis, structure, properties and applications* (ed. M. S. Dresselhaus, G. Dresselhaus & Ph. Avouris), pp. 287–327. Topics in Applied Physics, vol. 80. Springer.
- Yakobson, B. I., Brabec, C. J. & Bernholc, J. 1996 Nanomechanics of carbon nanotubes: instabilities beyond linear response. *Phys. Rev. Lett.* **76**, 2511–2514.
- Yakobson, B. I., Campbell, M. P., Brabec, C. J. & Bernholc, J. 1997 High strain rate fracture and C-chain unraveling in carbon nanotubes. *Computat. Mater. Sci.* **8**, 341–348.

- Yang, D. J., Zhang, Q., Chen, G., Yoon, S. F., Ahn, J., Wang, Q., Zhou, Q., Wang, Q. & Li, J. Q. 2002 Thermal conductivity of multiwalled carbon nanotubes. *Phys. Rev. B* **66**, 165440.
- Yao, Z., Postma, H. W. C., Balents, L. & Dekker, C. 1999 Carbon nanotube intramolecular junctions. *Nature* **402**, 273–276.
- Yu, M.-F., Lourie, O., Dyer, M. J., Moloni, K., Kelly, T. F. & Ruoff, R. S. 2000*a* Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science* **287**, 637–640.
- Yu, M.-F., Files, B. S., Arepalli, S. & Ruoff, R. S. 2000*b* Tensile loading of ropes of single-wall carbon nanotubes and their mechanical properties. *Phys. Rev. Lett.* **84**, 5552–5555.