MECHANICAL PROPERTIES OF NANOTUBES

Boris I. Yakobson* and Angel Rubio**

*Department of Mechanical Engineering and Materials Science, and Center for Nanoscale Science and Technology, Rice University, Houston, U.S.A.
**Departamento Física Teórica, Universidad de Valladolid, Spain and Donostia International Physics Center (DIPC) and Centro Mixto CSIC-UPV/EHU

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1. INTRODUCTION

While the prediction of electronic properties of carbon nanotubes required relatively subtle theoretical analysis (cf. Chapter VI), their unique mechanical behavior could be intuitively anticipated based on several features: strength of carbon bonds, their uniform arrangement within the graphitic sheet, and the seamless folding of this network into a tubule (Ross, 1991; Calvert, 1992). As a result, the research in this field was less of a discovery type, but has rather been driven by the demand for the experimental and theoretical evidence to support and quantify somewhat expected properties. This is not to say that to obtain the reliable understanding and quantitative data is easier; in opposite, that required sophisticated experimental techniques (due to difficulties to manipulate with molecular-size object) and theoretical methods (needed for treatment of multi-atomic systems and especially of their kinetic behavior). Still, for that very reason, we make an attempt of a logical (from linear elasticity to the nonlinear, further to inelastic behavior, and to fracture), rather than chronological exposition in this chapter.

1.1 Nanomechanics at a Glance

Before proceeding with the more detailed presentation, one can try to highlight the “nanomechanics at a glance”, based on the knowledge accumulated up-to-date. Carbon as well as composite boron nitride nanotubes demonstrate very high stiffness to an axial load or a bending of small amplitude, which translates in the record-high efficient linear elastic moduli. At larger strains, the nanotubes (especially, the single-walled type) are prone to buckling, kink forming and collapse, due to the hollow shell-like structure. These abrupt changes (bifurcations) manifest themselves as singularities in the non-linear stress-strain curve, but are reversible and involve no bond-breaking or atomic rearrangements. This resilience corresponds, quantitatively, to a very small sub-angstrom efficient thickness of the constituent graphitic shells. Irreversible yield of nanotubes begins at extremely high deformation (from several to dozens percent of in-plane strain, depending on the strain rate) and high temperature. The atomic relaxation begins with the edge dislocation dipole nucleation, which (in case of carbon) involves a diatomic interchange, i.e. a ninety-degree bond rotation. A sequence of similar diatomic steps ultimately leads to failure of the nanotube filament. The failure threshold (yield strength) turns out to depend explicitly on

1 Note that the temperature is an important parameter in the strength of a material since the motion of dislocations is thermally activated. Like all covalent materials, nanotubes are brittle at low temperatures. The flexibility of the nanotubes at room temperature is due to their high strength and the unique ability of the hexagonal network to distort in order to release the applied stress (for more details see Sec. 5).

2 This bond-rotation defects are more unlikely in boron nitride due to the larger energy needed to form B-B or N-N bonds. BN-nanotubes will have a different yield strength and mechanical behavior compared to carbon nanotubes (Ruoff, 2000).
nanotube _helicity_, which thus demonstrates again the profound role of symmetry for the physical properties, either electrical conductivity or mechanical strength. Finally, the manifestation of mechanical strength in the _multiwalled_ or _bundled_ nanotubes (ropes) is obscured by the poor load transfer from the exterior to the core of such larger structure. This must lead to lower apparent strength and even lower linear moduli, as they become limited by the weak lateral interaction between the tubules rather than by their intrinsic carbon bond network. The ultimate strength of nanotubes and their ensembles is an issue that requires the modeling of inherently mesoscopic phenomena, such as plasticity and fracture, on a microscopic, atomistic level, and constitutes a challenge from the theoretical as well as experimental points of view.

1.2 Research Motivations

In spite of the above mentioned complications in coupling the load to the nanotube itself, their potential utility as the strongest or stiffest elements in nanoscale devices or composite materials remains a powerful motivation for the research in this area. While the jury is still out on practical realization of these applications and large quantity synthesis of well-defined samples (cf. Chap. I), another impetus comes from the fundamental materials physics.

Indeed, fracture of materials is a complex phenomenon whose theory generally requires a multiscale description involving microscopic, mesoscopic and macroscopic modeling. Numerous traditional studies are based on a macroscopic continuum picture that provides an appropriate model except at the region of failure where a detailed atomistic description (involving real chemical bond breaking) is needed.

Classical molecular dynamics (MD) simulations using empirical potentials can be used to bridge the mesoscopic and microscopic modeling which can help to elucidate several relevant processes at the atomic level. To bridge micro-, meso- and macro- scales it is desirable to find a hierarchy of models, both for ease of computation and for conceptual understanding. When models bridging different scales are worked out one will be able to analyze and optimize materials properties at different levels of approximation, eventually leading to the theoretical understanding of materials or even design of their novel forms. In this ambitious program, nanotubes (due to their relative simplicity and atomically precise morphology) offer the opportunity of addressing the validity of different macroscopic and microscopic models of fracture and mechanical response. Contrary to crystalline solids where the structure and evolution of ever-present surfaces, grain-boundaries, and dislocations under applied stress determine the plasticity and fracture of the material, nanotubes possess simpler structure while still can show rich mechanical behavior within
elastic or inelastic brittle or ductile domain. This second, theoretical-
heuristic value of nanotube research supplements their import due to
anticipated practical applications. A morphological similarity of fullerenes
and nanotubes to their macroscopic counterparts, the engineered
architectural forms (cf. Fig. 1) makes it compelling to test the laws and
intuition of macro-mechanics in the scale ten orders of magnitude smaller.

1.3 Section Overview

In the following, Sec. 2 provides general background for the discussion of
nanotubes: basic concepts from materials mechanics (Sec. 2.1) and an
outline of relevant modeling methods (Sec. 2.2). We then detail several
aspects of nanotube behavior. Theoretical results for the elastic constants,
presented in Sec. 3.1, are followed by the discussion of experimental
measurements and obtained data (Sec. 3.2), for carbon and, more generally,
boron- nitride- carbon nanotubes. After the linear elasticity, the Sec. 4.1
outlines the non-linear buckling instabilities, and some evidence from
experiment is presented in Sec. 4.2. Going to even further deformations, in
Sec.5 we discuss irreversible changes in nanotubes, responsible for their
inelastic relaxation and failure. Fast molecular tension tests (Sec. 5.1) are
followed by the theoretical analysis of relaxation and failure (Sec. 5.2),
based on intramolecular dislocation concept and combined with the
computer simulation evidence. Then a few experimental facts, likely
related with the failure mechanisms, are discussed in Sec. 5c. Finally, we
briefly review several phenomena and studies related with mechanical
properties of nanotubes (Sec. 6): composites, cutting techniques, coupling
with electronics, potential applications, etc.

2. BASIC CONCEPTS AND METHODS IN MATERIALS MECHANICS

2.1 Basic Mechanical Properties: Stiffness, Strength, and Toughness

The mechanical properties of a solid material must ultimately depend on
its interatomic forces and the spatial arrangement of atoms. The stiffness,
or more properly the linear elastic moduli (e.g. the Young’s modulus Y of a
material) are directly related to the stiffness of the bonds and one can
write \( Y \propto k/r_0 \), where \( k \) is the spring constant of the bond and \( r_0 \) is the
interatomic distance. This distance does not vary much for different bonds
but the value of \( k \) does. For metals and ionic solids \( k \) varies between 15-100 N/m and for covalent solids spans 20-200 N/m, with the highest
known values for the carbon-carbon bond between 500-1000 N/m (Ashby,
1989). Obviously, a low mass-density is also often desirable for
applications. Most polymers are made of carbon and have low density,
however they often have weak bonds between their chains and therefore
lack stiffness. This can be improved by forming composites of polymer with other stiff materials like nanotubes.

A definition of elastic moduli for a solid implies a translational invariance (at least in average, statistical sense) of a uniform material. This is required to accurately define any intensive characteristics, and generally fails in the nanometer scale. A single nanotube lacks translational invariance, since in the radial direction a hollow center and a sequence of coaxial layers are well distinguished, with the interlayer spacing $c$ comparable with the nanotube radii, $R$. It is essentially an engineering structure, not a material. A definition of any material-like characteristic for a nanotube, while heuristically appealing, must always be accompanied with the specification of the assumptions made; without it a confusion can easily cripple the results or comparisons (see Sec. 3).

The strength of a solid material must also ultimately depend on the strength of its interatomic forces/bonds (Kelly, 1986). However, this relationship is far less direct than in the case of linear-elastic characteristics; it is greatly affected by the actual arrangement of atoms in a periodic or amorphous lattice. Even scarce imperfections in this arrangement play critical role for the material nonlinear response to the large force, a plastic yield or brittle failure. Without it, it would be reasonable to think that a piece of material would break at about 10% strain (Lindemann, 1910). Accordingly, the yield stress $\sigma_y$ would be $Y/10$.

However all single-phase solids have much lower $\sigma_y$ values, around $Y/10^4$. This is related to the present dislocations, stacking-faults, grain boundaries, voids, point defects, etc. The stress induces motion of the pre-existing defects, or a nucleation of the new ones in an almost perfect solid, and makes the deformation irreversible, permanent. The level of stress where this begins to occur at a noticeable rate determines the yield strength (Kelly, 1986).

A possible way to strengthen some materials is by introducing extrinsic obstacles that hinder or block the motion of dislocations (Hirth, 1982). There is a limit to the magnitude of strengthening that a material may benefit from, as too many obstacles will freeze (pin) the dislocations and make the solid brittle. A single-phase material with immobile dislocations or no dislocations at all breaks in a brittle fashion, with little work required. The reason is that it is energetically more favorable for a small crack to grow and propagate. Energy dissipation due to crack propagation represents materials toughness, a work required to advance the crack by a unit area, $G > 2\gamma$ (just above the doubled surface energy $\gamma$ for a brittle material, but several orders of magnitude greater for a ductile, like copper).
These concepts, similarly to linear elastic characteristics, should be applied to carbon and composite nanotubes with care. At the current stage of this research, nanotubes are either assumed to be structurally perfect or as containing few defects, also defined with atomic precision (a traditional approach of the physico-chemists, for whom a molecule is a well-defined unit, an isomer of a given exact conformation). A proper averaging of the “molecular” response to external forces, in order to derive meaningful material characteristic, represents a formidable task for theory. Our understanding of inelastic mechanical behavior of carbon, BN and other inorganic nanotubes is just beginning to emerge, and is important for the assessment of their engineering potential, as well as a tractable example of fracture physics.

2.2 Modeling methods

Due to the large number of atoms and long time-scales involved in a proper description of the mechanical properties (as well as electronic and growth mechanism, see Chaps. V and VI) of nanotubes, realistic first-principles simulations are very difficult and costly to perform and one has to resort to faster (and often less accurate) schemes. To circumvent this problem empirical and semiempirical methods (interatomic model potentials with varying accuracy and sophistication) have been developed over the years (Voter, 1996) and great experience has been gained in their application to carbon structures. More realistic models including electronic effects are obtained through tight-binding methods (Goringe, 1997) using a minimum sp-basis. The TB approximation captures part of the chemical strain through the geometry-dependence of its electronic matrix elements. However, whenever a higher accuracy is desired first-principles methods can be used.

The strong similarity of the short-range order chemical organization of carbon nanotubes to that in graphite (Dresselhaus, 1996; Ebbesen, 1997) allows theoretical analyses to be done based on empirical methodologies imported from studies on graphite. They range from the direct zone folding of the results for graphite to the quantum-mechanical studies based on tight-binding Hamiltonians fitted to graphite properties. The performance of the different techniques varies, from the qualitative picture offered by zone folding, with intrinsic deficiencies for low frequencies, to the very quantitative results of tight-binding approaches. The curvature of the tubes, however, disturbs the chemistry in a way that can cause the deviation from the graphite-based description, for narrow tubes.

In general, zone folding and force-constants neglect curvature effects, and only takes into account the new periodic conditions along the tube circumference, which allows to making important predictions about the electronic band structure (cf. Chap. VI). Model classical potentials can
account for the different distances among the atoms, as well as inter-bond angle variation, but inevitably have limited reliability. However, one needs them for many simulations that are too large for a full first-principles treatment; therein lies a love/hate relationship with the semi-empirical approach. In addition simpler models are important not only for speed but also just as much for physical insight. Another use of model potentials is in hybrid modeling. In situations where a large system contains a site of specific interest one may succeed by treating the interesting region quantum mechanically and the rest with a model potential. At larger scales, quasi-continuum models with a combination of empirical potentials and elasticity theory may be used (Tadmor, 1996).

The empirical Tersoff-Brenner (Tersoff, 1988; Brenner, 1990) potential has been widely used in the study of the structural properties of carbon nanotubes. It is based on the “bond order” ideas introduced by (Abell, 1985), i.e. the bond order (or in different words, the strength of each bond) in real systems decreases monotonically with increasing atomic coordination. The actual dependence of the bond order on coordination should be such as to yield the intermediate equilibrium coordination characteristic of covalent systems. Moreover, certain carbon bonds, i.e. the ones corresponding to the sp² and sp³ hybridization of carbon, should be favored by the potential. All these elements are built directly into the functional form of the Tersoff-Brenner potentials, which depends explicitly on both coordination and angles. It is fair to recognize that this potential does go beyond the three body potentials considered in the literature for describing covalent systems. The potential is able to reproduce the energetic, structural and elastic features of carbon over a wide range of configurations, however linear chains and ring structures, characterized by large bond angles, are not well described by this potential. The reason being that the potential favors bond angles close to 2 /3, characteristic of the sp² and sp³ hybridization of carbon. On the other hand, the melting temperature of carbon comes out 40% higher than the experimental one, then one should be careful in comparing directly MD simulations with this potential and experiments.

Different TB models have been used in the literature to study carbon and composite nanotubes. In general the TB model contains two contributions to the total energy: a so-called band-structure energy term, and a repulsive pair-potential. The band-structure energy is calculated as the sum of the eigenvalues of the occupied states of a TB Hamiltonian. Conventional TB models which have been so popular in computational materials science (Goodwin, 1989; Xu, 1992) are constructed using a minimum sp-basis set with parameters fitted to either experimental data or to data obtained from first principles calculations (structural, elastic and

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3 The Tersoff potential (Tersoff, 1988) gives a melting temperature for carbon of about 6000 K whereas the experimental value is about 4300K.
vibrational properties of different carbon phases). In contrast, the model of (Porezag, 1995) is constructed directly from first principles calculations, using a series of the well-defined approximations. A minimal basis set consisting of a single atomic-like orbital per each valence state is used. Since the basis set is not orthogonal, the calculation of the band structure energy requires the solution of a generalized eigenvalue problem. The repulsive pair potential is then constructed in such a way that the total TB energy of a reference system (usually the dimer) matches that of the full calculation with the same basis set. One of the attractive features of this TB model is that all approximations can be systematically improved upon\(^4\). An important point worth emphasizing here is the fact that no information concerning the mechanical properties of the system is used in the construction of this particular TB parameterization. We note however that the simplest and fastest orthogonal parameterization (Xu, 1992) is known to be successful in the modeling of the different allotropic forms of carbon and various carbon-based systems. In addition, molecular dynamics simulation with this parameterization contains the essential physics and chemistry of the directional carbon bonds and therefore describes both the sp, sp\(^2\) and sp\(^3\) hybridization. Furthermore, linear scaling with the number of atoms in the system can be easily achieved in this type of modeling (Goedecker, 1999) opening the way for large-scale simulations of the structure and electronic properties of nanotubes.

Let us discuss briefly the most accurate method to address the study of nanotubes that is first principles total energy calculations. These calculations provide the bonding, electronic structure and atomic arrangement, and are nowadays based on density-functional theory (DFT)\(^5\) (Kohn, 1965). This allows the calculation of the ground state and dynamic properties of a many-electron system from a simple one-electron Schrödinger equation. In this theory, the total energy, expressed as a functional of the total electron density \(n(\mathbf{r})\), is decomposed into three contributions. These are the well-known kinetic energy term of non-interacting particles, the Coulomb energy due to classical electrostatic interactions and a part that takes care of the many-electron interactions, so-called exchange-correlation energy. The effective one-electron eigenfunctions and eigenvalues allow for a formulation of bonding and

\(^4\) For example, it would be possible to include more basis functions in the treatment if a more accurate description of conduction states was found necessary. Likewise, though three-center integrals are disregarded, they could be included in a generalization of the model, should this be necessary.

structure in terms of molecular orbitals and band structure of solids. The fact that the problem has been reformulated in terms of independent electrons does not mean that correlations are ignored. This formulation is based on a self-consistent procedure in which the effective potential depends on the electron-density that also depends on the one-electron eigenfunctions. The achievement of self-consistency is one of the main technical problems in first-principles calculations (Pickett, 1989).

*Ab initio* quantum molecular dynamics simulations can be performed within this scheme by minimizing the total energy with respect to the eigenfunctions for a given ionic configuration, then computing the forces and moving the ions. This non-linear constrained minimization can be achieved by a combined preconditioning conjugate gradient technique (Payne, 1992). A different and very elegant scheme was proposed by Car and Parrinello (Car, 1985). The idea is to introduce a fictitious electronic dynamics, which keeps, during the ionic motion, the electronic wave function adiabatically close to the instantaneous eigenstates of the quantum Hamiltonian. In this approach both the ions and the eigenfunctions are treated as classical fields following the Newtonian dynamics, with the orbitals subject to the constraint of orthonormality. The trade-off in the simulations is between having smaller electronic masses, thus keeping the system close to the Born-Oppenheimer minimum and characterized by more responsive electronic degrees of freedom, and the necessity of keeping the time-step for the expensive integration of the equations of motion as large as possible, in order to simulate the dynamics for a time adequate to the atomic scales (typically from a fraction of picosecond up to several picoseconds). This technique can be used both for molecular dynamics simulations as well as for energy minimization of the DFT-functional. (See Chap. V for applications of this method to the growth mechanism of carbon nanotubes, and Sec.5.2 below, to the study of the non-linear mechanical response of nanotubes under external applied strain and/or torsion.).

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6 In principle DFT is exact but in practice one has to rely on an approximation for the exchange correlation energy (XC). The approximation most widely used is the Local Density Approximation (LDA) (Ceperley, 1985). The LDA takes the XC energy of a homogeneous electron gas at the local density $n(r)$ of the inhomogeneous system studied. The function can be decomposed in an exchange part $-3/4 (3n^{1/3} n^{-1/3})$ and a remaining correlation term that can be determined once for all by interpolating between quantum Monte Carlo calculations (Ceperley, 1985) and the appropriate asymptotic high-density limit. The rationale for this approximation is in the limit of slowly varying density. In spite of its simplicity, LDA continues to prove extremely useful in a wide and general variety of environments. Improvements over the LDA has been done in base of the generalized-gradient approximations (GGA) (Perdew, 1999) where the exchange-correlation energy density is a function not only of the density but also of its gradient. However, further improvements over the GGA functional should go in the direction of non-local or orbital-dependent functionals, in order to describe better the inhomogeneity of the XC-hole.
3. LINEAR ELASTICITY OF NANOTUBES

For a small-amplitude disturbance, the required force is proportional to the deformation, generally following the Hooke’s law of linear elasticity. Models of different level of accuracy can be exploited to calculate the values of the elastic moduli of nanotubes (Sec. 3.1), and to compare them with the analogous parameters known for graphite and with emerging experimentally measured data for single- and multi-walled nanotubes as well as nanotube bundles (Sec. 3.2).

3.1 Theoretical Results on Elastic Constants of Nanotubes

3.1.1 Elastic strain energy and $B_xC_yN_z$ nanotubes

The similarities among graphite and other $sp^2$-like bonded materials as hexagonal boron nitride and boron-carbon-nitrogen compounds, lead us to theoretical proposition that $B_xC_yN_z$ nanotubes would be stable (Rubio, 1994; Miyamoto 1994a,b). Specific synthesis of these nanotubes was achieved afterwards: boron-nitride (Chopra, 1995b; Loiseau, 1996) and $BC_2N$ and $BC_3$ (Weng-Sieh, 1995; Stephan, 1994) as well as other inorganic tubular forms of $WS_2$ and $MoS_2$ (Tenne, 1992). The predicted properties of these tubules are quite different from those of carbon with numerous possible technological applications in the fields of catalysis, lubrication, electronic and photonic devices (Miyamoto, 1994a,b).

In Fig. 3.1 we show the stability of these new composite BN and $BC_3$ single-wall nanotubes (SWNT) by means of the ab initio calculation of the strain energy per atom required to roll the planar sheets into tubules. We observe that this energy is smaller than the strain energy for carbon tubules, therefore based on simple energetic cost arguments we can expect that these tubes are likely to be formed. This fact can be related to a small value of the elastic constants in the composite tubes as compared to $7$

$^7$The electronic properties of BN nanotubes are quite different to carbon, namely: all are stable wide band-gap semiconductors independent of helicity and diameter of the nanotube and of whether the nanotube is single- or multi-walled. On the other hand, single-wall $BC_3$ tubules are found to be semiconductor with a small gap of $\sim 0.5$ eV that would disappear in the multilayer form (Miyamoto, 1994b). The inter-wall interaction for concentric tubules makes the conduction band overlap with the valence band maximum ({$\pi$}-bands). Therefore, a concentric needle of $BC_3$ tubules will have {$\pi$}-conductivity and opens the question of how many walls are necessary to give rise to conductivity in concentric $BC_3$ tubules, that is to look for a semiconductor-metal transition as a function of the number of concentric shells.
graphite. A major structural difference between BN and C and BC$_3$ tubules is that for small diameter tubules the BN system buckles with the B atoms moving inward and the N atoms toward, resulting in a dipolar double cylinder shell structure (Blase, 1994). The amount of buckling is mostly independent of the tubule helicity and decreases with increasing diameter. The driving mechanism for this structural relaxation is attributed to the fact that B tends to form sp$^2$ bonds whereas N prefers to be in a s$^2$p$^3$ environment. From the results of Fig. 3.1 we clearly see that the strain energy of C, BN and BC$_3$ nanotubes follows the D'/R$^2$ law expected from linear elasticity theory (Landau, 1975)$^8$. This dependence is satisfied quite accurately even for tubes as narrow as (4,4). All the nanotubes are energetically stable with respect to the formation of strips for diameters larger than 4 Å (Blase, 1994; Rubio, 1997). However they become unstable with respect to the formation of nanoribbons (collapsing of the tube walls due to the van der Waals attraction, see Sec.4.2 below for more details).

For armchair carbon nanotubes the constant in the strain energy equation has a value of $D' = 2.0$ eVÅ$^2$/atom (and up to 2.15 for other chiral tubes) (Sánchez-Portal, 1999). Previous calculations using Tersoff and Tersoff-Brenner potentials predict the same dependence and gave a value of $D' \approx 1.5$ eVÅ$^2$/atom and $D' \approx 1.16$ eVÅ$^2$/atom, respectively (Robertson, 1992). We note in Fig. 3.1 that the armchair (n,n) tubes are energetically more stable as compared to other chiralities with the same radius. This difference is, however, very small and decreases as the tube diameter increases. This is expected, since in the limit of large radii the same graphene is obtained, regardless of chirality. It is to some extent surprising that the predictions from elasticity theory are so closely followed by the detailed $ab\ initio$ calculations. In (Adams, 1992) an alternative explanation based on microscopic arguments is provided. They use a very simplified model in which the energetic of many different fullerene structures depend on a single structural parameter: the planarity $\Pi_0$, which is the angle, formed by the $\Pi$ orbitals of neighbour atoms. Assuming that the change in total energy is mainly due to the change in the nearest neighbor hopping interaction between these orbitals, and that this change is proportional to $\cos(\Pi_0)$, the R$^{-2}$ behavior is obtained. By using using non-selfconsistent first-principles calculations they have obtained a value of $D' = 2.12$ eVÅ$^2$/atom, similar to the self-consistent value given above.

A more complete set of calculations for carbon as well as composite nanotubes was done in (Hernández, 1998, 1999) using the TB-scheme of (Porezag, 1995) (See 2.1). It is shown that this TB model is able to

$^8$In this equation R denotes the tube radius and D' can be related to the Young modulus, the area per atom A and the thickness of the wall h as: $D' \approx Yh^3A/24$, similar to the standard flexural rigidity, cf. Sec. 4.1.
reproduce quite accurately the *ab initio* results for the strain-energy of carbon nanotubes. In this case the constant $D'$ is between 1.9-2.18 eV Å$^2$/atom, 1.36-1.42 eV Å$^2$/atom and 1.35-1.47 eV Å$^2$/atom for C, BN and BC$_3$ nanotubes, respectively. In all cases the $R^2$ behavior is reproduced, as in the *ab initio* calculations (shown in Fig.3.1).

The problem of definition of the Young modulus for a SWNT (see Sec 3.1.2 below) can now be studied from an energetic point of view by analyzing directly the elastic stiffness using the second derivative of the *ab initio* strain energy with respect to the axial strain: $d^2E/d\bar{\varepsilon}^2$. To obtain this quantity for the different tubes, we performed structural relaxation for the nanotubes, subject to deformations between -1.0% and 1.0%, at intervals of 0.13% (Sánchez-Portal, 1999). By fitting the total energies to a third order polynomial, $d^2E/d\bar{\varepsilon}^2$ was obtained from the second derivative at zero strain$^9$. The results show an average value of 56 eV. The variation between tubes with different radii and chirality is very small, and always within the limit of accuracy of the calculation. We therefore can conclude that the effect of curvature and chirality on the elastic properties is small. Furthermore, the results clearly show that there are no appreciable differences between this elastic constant as obtained for nanotubes and for a single graphene sheet (with a computed value of 60 eV).

These *ab initio* results are also in good agreement with those obtained in (Robertson, 1992) using Tersoff-Brenner potentials, who find values around 59 eV/atom, with very little dependence with radius and/or chirality. Furthermore, we can obtain an experimental estimate of this quantity using the elastic constant $c_{11}$=1.06 TPa of bulk graphite, from which we obtain $d^2E/d\bar{\varepsilon}^2 \approx c_{11}V_a = 58.2$ eV/atom (where $V_a$ is the atomic volume in graphite). This value agrees well with the computed values by either *ab initio* or semi-empirical methods.

### 3.1.2 Young modulus and Poisson ratio

Classical elasticity theory (Landau, 1975) shows that hexagonal two-dimensional crystal has only two independent elastic constant, for example the Young modulus and Poisson ratio. We discuss now how these two quantities are evaluated and afterwards, in the next section, we address the reliability of the macroscopic laws of elasticity down to the nanometer scale.

An extensive study of elastic constants of carbon nanotubes and ropes of SWNT has been reported (Lu, 1997) using an empirical pair potential$^9$. The obtained elastic properties are essentially independent of helicity and tube

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$^9$ We have estimated the numerical error of these results to be of the order of 10%.
radius, and comparable to those of graphene, with $Y = 0.97$ TPa for all tubes, smaller than TB and *ab initio* results. This difference is most likely due to the method used in this work. This model does not reflect the changing nature of the chemical bonding as the curvature is changed. To reproduce this effect, a model sensitive to the changing environment (i.e. a many-body model) is required. This is in fact achieved in either the Tersoff-Brenner potential or more complex electronic based models as the tight binding.

Other theoretical estimates of the Young modulus report values of the order of 5 TPa (Overney, 1993) based on an empirical Keating force-constant model for finite-capped (5,5)-tube. This very high value is due to the small cross-section of the aggregates used to describe the tube, with only up to 400 atoms. In a study of structural instabilities of SWNT for large deformations using Tersoff-Brenner potentials estimated the Young modulus of *the wall* to be 5.5 TPa by fitting their results to the continuum elasticity theory (Yakobson, 1996a,b). However, results for the *nanotube*, obtained with the same potential by (Robertson, 1992) report a small weakening of the stiffness of nanotubes as the diameter decreases, and therefore a Young modulus for the nanotubes smaller than the one of graphene, as in the ab-initio and TB results. The authors find a systematic dependence with the chirality which, although being small, increases with decreasing tube radius. Part of the discrepancies in the theoretical results discussed above is merely due to a different definition of the Young modulus in these systems. From the point of view of elasticity theory, the definition of the Young modulus involves the specification of the value of the thickness ($h$) of the tube wall. In this sense, the large value obtained in (Yakobson, 1996a,b) is consistent with the value of $h=0.7$ Å for the thickness of the graphene plane. It is smaller than the value used in other work (Robertson, 1992, Lu, 1997, Hernández, 1998) that simply took the value of the graphite interlayer spacing of $h=3.4$ Å. We have indicated in the previous section a way of measuring the stiffness of the SWNT by means of the second derivative of the strain energy with respect to axial strain. In what follows we present an alternative definition. The usual definition of the Young’s modulus involves the second derivative of the energy with respect to the applied strain,

$$Y = \frac{1}{V_0} \frac{\partial^2 E}{\partial \varepsilon^2}, \text{ at } \varepsilon = 0. \quad (3.1)$$

where $\varepsilon$ is the strain, $V_0$ is the equilibrium volume, and $E$ is the total energy. The second derivative measures how rapidly the energy grows as

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10 The force-constant model described by the sum of pairwise harmonic potentials between atoms up to fourth-neighbors fitted to reproduce the elastic constants and phonon frequencies of graphite.

11 Generally, for isothermal deformation it should be free energy, which differs negligibly at any realistic temperature for a rigid structure as nanotube.
the system is distorted out of its equilibrium configuration. Usually \( Y \) is given in units of pressure, however this equation presents an ambiguity in the case of SWNT (cf. Sec. 2.1), which stems from the definition of the volume \( V_0 \). This definition for a SWNT requires adopting a convention for the thickness of the carbon layer in order to define a volume for the object. Rather than adopting an *ad hoc* convention it has been introduced in (Hernández, 1998) a different magnitude to characterize the stiffness of SWNT which is independent of any shell thickness. Similarly in-plane stiffness \( C \) has been defined for nanotubes in (Yakobson, 1996a,b), see Sec. 4.1. This new definition of this elastic constant is

\[
C = \frac{1}{S_0} \Delta E / \Delta \varepsilon^2, \text{ at } \varepsilon = 0. \tag{3.2}
\]

Here \( S_0 \) is the surface area defined by the nanotube at zero strain, which is a well-defined quantity. Given that \( V_0 = S_0 h \), one can recover the usual definition by simply dividing by \( h \): \( Y = C/h \), if one wishes to adopt a particular convention.

*Ab initio* calculations (Blase, 1994, Rubio, 1997, Sánchez-Portal, 1999) have reported a slight dependence of \( C \) on the tube diameter. As the diameter becomes larger, \( C \) approaches a plateau value that corresponds to the value calculated for the flat graphene-like sheet of each nanotube composition. Interestingly, the approach to the limit value is from below, as can be expected, since bending a flat graphene sheet weakens the bonds. Given that it is the strength of the chemical bonds which determines the actual value of the Young's modulus, it is natural that small-diameter (high curvature) tubes have smaller Young's moduli, and in the limit of large diameters, the mechanical properties essentially correspond to those of the flat graphene sheet. In contrast, the results in (Lu, 1997) are largely insensitive to the tube diameter.

TB calculations of the stiffness of SWNTs has also demonstrated that the Young modulus shows a small dependence on the tube diameter and chirality for the experimental range of nanotube diameters (between 1.3 and 1.4 nm) (Hernández, 1998), in agreement with the first principles calculations reported above. It is predicted that carbon nanotubes have the highest Young's modulus of all the different types of composite tubes considered (BN, BC\(_3\), BC\(_2\)N, C\(_3\)N\(_4\), CN) (Hernández, 1999). Those results for the C and BN nanotubes are reproduced in the left panel of Fig. 3.2. Furthermore, the Young modulus approaches, from below, the graphitic limit for diameters of the order of 1.2 nm. The computed value of the Young modulus for the wider carbon nanotubes of \( C = 0.43 \) TPa nm, that corresponds to \( Y = 1.26 \) TPa modulus in our convention, is in excellent agreement with the experimental value for SWNT's of 1.25 TPa (Treacy, 1996). It is also in rather good agreement with the value of 1.28 TPa reported for multi-wall nanotubes (MWNT) (Wong, 1997). Although this
result is for MWNT the similarity between SWNT is not surprising as the intra-wall C-C bonds mainly determine the Young’s modulus. We can extend further this results and estimate the Young modulus considering two different geometries of practical relevance:

(i) multiwall like geometry, in which the normal area is calculated using the wall-wall distance as the one in MWNTs, which is approximately equal to the one of graphite,

(ii) nanorope or bundle configuration of SWNTs, where the tubes would be arranged forming an hexagonal closed packed lattice, with a lattice constant of \(2R + 0.34\), being \(R\) the tube radius in nm.

The results for these two cases are presented in the right panel of Fig.3.2. The MWNT geometry give a value that is very close to the graphitic one, however the rope geometry shows a decrease of the Young modulus with increasing the tube radius. This obvious trend is due to the quadratic increase of the effective area in this configuration, while the number of atoms increases only linearly with the tube diameter. The computed values for the SWNT ropes experimentally observed are, however, still very high (\(0.5\) TPa), even comparing with other known carbon fibers. This value is in quite good agreement with AFM experiments on anchored SWNTs ropes (Salvetat, 1998) (Y\(\sim 0.6\) TPa) and for stress-strain puller measurements of the Young modulus for aligned nanotube ropes of MWNTs (Y\(\sim 0.45\) \(\sim 0.23\) TPa) (Pan, 1999). We should remark that this apparent ‘low’ Y is not due to the presence of defects as arguments in (Pan, 1999) and can be understood in simple geometrical terms by the particular “empty” cross-sectional area of the rope geometry as being responsible for the apparent lower modulus.

For composite nanotubes, the only experimental data on mechanical properties currently available to our knowledge are the results of (Chopra, 1998), who have measured Y for BN MWNT’s. They quote a value of 1.22 TPa, which is somewhat larger than the result obtained for these tubes in the TB calculations (~0.9TPa) (Hernández, 1998), but nevertheless the agreement is close. We indicate that BN and BC\(_3\) tubes have similar values of the Young modulus, although the latter have slightly larger values. In those studies C\(_3\)N\(_4\) nanotubes are shown to be much softer than any other type of tube, the reason being that for a given amount of tube surface, there is a smaller density of chemical bonds (Hernández, 1999).

The Poisson ratio \(\nu\) is given by the variation of the radius of the SWNT resulting from longitudinal deformations along the tube axis \(\nu R/R=-\nu\). \(\nu\) The smaller Young modulus for BN compared to C-nanotubes is directly related to the difference in the experimental \(c_{11}\) elastic contants that are 0.75TPa and 1.06TPa for hexagonal- BN and graphite, respectively.

\(\nu\) The calculated average Young modulus is 0.9TPa and 0.92Tpa for BN and BC\(_3\), respectively.
where $L$ is the tube length). In all cases the computed Poisson ratio is positive: an elongation of the tube reduces its diameter. The $ab\ initio$ values are $\nu=0.14$ (from 0.12 to 0.16) for the armchair $(n,n)$ tubes, and a little larger for other chiralities: 0.19 for $(10,0)$ and 0.18 for $(8,4)$. The uncertainty of the obtained values is of the order of 10%. These results reveal a slight decrease of the Poisson ratio with the tube radius, and a stronger dependence with chirality. The computed value is close to the value $\nu=0.19$ obtained using Tersoff-Brenner potentials (Yakobson, 1996a), but considerably smaller than the value $\nu=0.28$ given by a force constant model (Lu, 1997) and $\nu=0.26$ from a tight-binding calculation (Hernández, 1998). The corresponding magnitude along the basal plane in graphite is $\nu=0.16$. In summary, the $ab\ initio$ calculations indicate that the Poisson ratio retains graphitic values except for a possible slight reduction for small radii. It shows chirality dependence: $(n,n)$ tubes display smaller values than $(10,0)$ and $(8,4)$. Similar differences are found between the $ab\ initio$ and TB calculations for BN tubes, namely for the $(6,6)$ tube the $ab\ initio$ value for the Poisson ratio is 0.23 whereas the TB one is 0.30 (Hernández, 1998).

In general, the computed $ab\ initio$ Young modulus for both C and BN nanotubes agrees well with the values obtained by the TB calculations and with the trends given by the empirical Tersoff-Brenner potential. These results support the use of the simpler models to describe the mechanical properties of nanotubes for more complex situations as nonlinear elastic and failure of tubes (see Sec. 4.1).

3.1.3 Torsion, bending and buckling: macroscopic elasticity

Recent molecular dynamics calculations based on the Tersoff potential predict that a $(10,10)$ nanotube can support an axial compression strain of 0.05 before buckling (Yakobson, 1996a) (see Sec. 4.1 for details). This limit, trough Hooke’s law corresponds to a large stress in the nanotube network (about 0.9nN/Å). In a recent experiment (Lourie, 1998) large compressive strains were applied to carbon nanotubes dispersed in a polymeric film. Two distinct deformation modes were observed (Fig.3.3): a sideways buckling of thick tubes and collapse/fracture of thin tubes without any buckling. High bending conditions introduce a wave-like deformation at the tube surface (Fig 3.3) similarly to the deformations observed by (Poncharal, 1999) in the study of electromechanical resonances in carbon nanotubes (see Fig. 3.6D below). The buckling of thick tubes is in agreement with the simulations of (Yakobson, 1996a,b) whereas discrepancies are found for the plastic collapse or fracture of thin tubes. The compressive strain is estimated to be larger than 5% and critical stress

\[\text{The compressive stress arises from polymerization shrinkage as well as for thermal effects associated with the electron beam in the TEM cell (Lourie, 1998).}\]
for inward collapse or fracture is expected to be between 100 to 150 GPa for thin tubes. In (Srivastava, 1999) a new mechanism for the collapse and plasticity of compressed thin nanotubes was reported. The relaxation of the strain energy in the collapsed section of the tube causes immediate graphitic to diamondlike bonding reconstruction at the location of the collapse. This mechanism as well as the estimated critical stress of 153 GPa are in qualitative agreement with the experimental results (Lourie, 1998). The main outcome of those studies is that both thin and thick-walled carbon nanotubes exhibit compressive strengths about two orders of magnitude higher than any other known fiber. Furthermore, MWNT can be bent repeatedly through large angles using the tip of an atomic force microscope without undergoing catastrophic failure (Falvo, 1997). The observed response at very high strain deformation indicates that nanotubes are remarkable flexible and resilient. Therefore it is desirable to address the microscopic calculation of the torsion and bending constants of nanotubes and check if continuous models can be applied.

Preliminary TB calculations have shown that the elastic constant for torsion is smaller than the bending one, indicating that torsion could be slightly more favorable than bending (in the case of the (10,10) tube the torsion and bending elastic constants are 1.73 and 2.08 keV nm, respectively). Those elastic constants are somewhat larger for armchair than chiral tubes. An interesting result appears in the calculations for finite chiral tubes, namely, the right and left twist are not equivalent, as result of the inherent chirality of the underlying atomic structure. To get further insight into the bending and torsion processes, we can estimate the energy involved in producing either a π/2 degrees twist or bend over a 1 µ-length tube (this correspond to a global small deformation of the tube per unit length). This energy involved in this deformation is below 0.2 meV/Å. The low energy needed to create this mechanical distortion provides the ‘flexibility’ of all the nanotube samples. A more detailed discussion of the two torsional modes is given in (Vacarini, 1999b).

One open question is how well macroscopic elasticity theory works in the nanoscale regime? Previous work on the behavior of carbon nanotube under large axial strain (Yakobson, 1996a,b) shows that the simple continuum shell model of macroscopic theory is able to predict and describe accurately the nonlinear mechanical response of carbon nanotubes. In what follows we have taken the computed Young modulus and Poisson ratio from (Hernández, 1998) and estimate the

\[ E = 1.73 \text{ keV nm} \\
\[ \nu = 0.3 \\
\]

In the case of the (12,8) tube the right/left twist correspond to a decrease/increase of the chiral angle of the atomic structure; the computed values are 1.46 and 1.62 keV nm) (Vacarini, 1999b).

As we compare TB calculations with macroscopic theory, we take the computed TB-values for the two independent elastic constants \( (Y, \nu) \) needed in the macroscopic equations of elasticity.
corresponding torsion $C_T$ and bending $C_B$ modulus from the equations of macroscopic elasticity (Landau, 1997):

$$C_T = \frac{\pi Y}{4(1+\nu)} \left[ (R + \frac{h}{2})^4 - (R - \frac{h}{2})^4 \right]$$

$$C_B = \frac{\pi Y}{4} \left[ (R + \frac{h}{2})^4 - (R - \frac{h}{2})^4 \right]$$

(3.3)

where $R$ is the radius of the tube, $h$ is the thickness of the graphene layer that we take to be equal to the interlayer distance in graphite (0.34 nm). These coefficients satisfy the relation, $C_T = C_B/(1+\nu)$. The estimation from Eqn. (3.3) of the torsion and bending elastic constants of carbon nanotubes are 1.77 and 2.23 keV nm, respectively, to be compared with the TB values of 1.73 and 2.08 keV nm (Vacarini, 1999b). Similar behavior is obtained using first principles calculations. The good agreement between classical macroscopic elasticity theory and the results of quantum mechanical calculations validates the use of the macroscopic theory and continuous models even at this nanoscale regime (see Secs. 4 and 5 below).

### 3.2 Measurements of the Young’s modulus

There is a growing body of experimental evidence indicating that carbon nanotubes (both MWNT’s and SWNT’s) have extraordinary mechanical properties. However, the technical difficulties involved in the manipulation of these nano-scale structures make the direct determination of their mechanical properties a rather challenging task. In spite of these difficulties, a number of experimental measurements of the Young’s modulus of carbon nanotubes have been reported. The first such study was that of (Treacy, 1996), who correlated the amplitude of the thermal vibrations of the free ends of anchored nanotubes as a function of temperature with the Young's modulus. Regarding a MWNT as a hollow cylinder with a given wall thickness, one can obtain a relation between the amplitude of the tip oscillations in the limit of small deflections, and the Young’s modulus. In fact, considering the nanotube as a graphite cylinder with the high elastic constant $c_{11}=1.06$TPa of graphite and using the standard beam deflection formula we can calculate the bending of the nanotube under applied external force. In this case, the deflection of a cantilever beam of length $L$ with a force $F$ exerted at its free end is given by

\[^{17}\text{Just recently it has been possible to directly measure the strength and breaking of MWNTs under tensile load using a “nano-stressing stage” located within a scanning electron microscope (Yu, 2000).}\]
where \( I \) the areal moment of inertia. Then by measuring the vibration frequency of tubule we can get the mechanical properties of SWNTs (note that for a tubule of on micron length the estimated fundamental vibration frequency is about 12 MHz). The basic idea behind the technique of measuring freestanding room-temperature vibrations in a TEM is to consider the limit of small amplitudes the motion of a vibrating cantilever. This limit is governed by the fourth-order wave equation:

\[
\frac{\partial^2 z}{\partial t^2} = -\frac{Y I}{\rho A} \frac{\partial^4 z}{\partial x^4}
\]

where \( A \) is the cross sectional area, \( \rho \) is the density of the rod material. For a clamped rod the boundary conditions are such that the function and its first derivative are zero at the origin and the second and third derivative are zero at the end of the rod. Thermal nanotube vibrations are essentially elastic relaxed phonons in equilibrium with the environment; therefore the amplitude of vibration changes stochastically with time. This stochastic driven oscillator model is solved in (Krishnan, 1998) to analyze the experimental results in terms of the gaussian vibrational profile with a standard deviation given by

\[
\sigma^2 = \sum_{n=0}^{\infty} \sigma_n^2 = 0.4243 \frac{L^3 kT}{Y(D_o^4 - D_i^4)}
\]

with \( D_o \) and \( D_i \) the outer and inner radii and \( L \) the rod length, \( T \) the temperature and \( \sigma_n \) the standard deviation. An important assumption is that the nanotube is uniform along its length. Therefore, the method works best on the straightest, cleanest nanotube images. Then, by plotting the mean-square vibration amplitude as a function of temperature one can get the value of the Young modulus. See (Krishnan, 1998) for a detailed discussion of the method applied to SWNT and MWNT.

As already stated this technique was first used in (Treacy, 1996) to measure the Young modulus of carbon nanotubes. They quantified the amplitude of those oscillations by means of careful TEM observations of a number of nanotubes, they were able to obtain an average value of 1.8TPa for the Young's modulus, though there was significant scatter in the data (from 0.4 to 4.15 TPa for individual tubes). Although this number is subject to large error bars, it is nevertheless indicative of the exceptional axial stiffness of these materials. More recently (Krishnan, 1999) have reported studies on SWNT's using the same technique (see Fig.3.4). A larger sample of nanotubes was used, and a somewhat smaller average value was obtained, \( Y = 1.25 \) TPa, closer to the expected value for graphite along the basal plane. The technique has also been used in (Chopra, 1998) to
estimate the Young modulus for BN nanotubes. Their results indicate that these composite tubes are also exceptionally stiff, having a value of $Y$ around 1.22 TPa, very close to the value obtained for carbon nanotubes.

Another way to probe the mechanical properties of nanotubes is to use the tip of an Atomic Force Microscope (AFM) to bend anchored SWNTs or MWNTs while simultaneously recording the force exerted by the tube as a function of the displacement from its equilibrium position, information from which the Young's modulus of the nanotube can be extracted. In this way (Wong, 1997) have reported a mean value of 1.28TPa for MWNT in agreement with the previous experimental results. Also (Salvetat, 1999) used a similar idea, which consists of depositing MWNT's on a well polished alumina ultra-filtration membrane. Many tubes are then found to lie across the holes present in the membrane, with a fraction of their length suspended. Attractive interactions between the nanotubes and the membrane clamps the tubes to the substrate. The tip of an AFM is then used to exert a load on the suspended length of the nanotube, measuring at the same time the nanotube deflection. To minimize the uncertainty of the applied force, they calibrated the spring constant of each AFM tip (usually 0.1N/m) by measuring its resonant frequency. The slope of the deflection versus force curve gives directly the Young's modulus for a known length and tube radius. In this way, the mean value of the Young's modulus obtained for arc-grown carbon nanotubes was $0.81 \pm 0.41$ TPa. The same study on disorder catalytic nanotubes obtained by the decomposition of acetylene gives values between 10 to 50 GPa. This result is likely due to the high density of structural defects present in the catalytic nanotubes.

A similar procedure has also been used by (Muster, 1998), who used an AFM to record the profile of a MWNT lying across an electrode array. The scanning force microscopy investigation revealed a significant bending of the tubes upon crossing the electrode lines. This behavior is exemplified in Fig.3.5. Obviously, the MWNT possesses a long-range flexibility and, as a consequence, the distance of the tube from the substrate has a maximum at about the middle of the electrode gap. The bending of the tube is smooth and starts at about 150 nm in front of the left electrode. In the center of the gap, the top of the tube is 24 nm above the substrate. If one subtracts the electrode height of 14 nm and assumes a constant nanotube diameter of 8 nm this leaves a surplus of 2 nm due to the convex bending. In contrast to the gradual rise in front of the left electrode, the descent after the right electrode is much more abrupt. This is ascribed to the ending of the tube at about 80 nm after crossing the electrode. We assume that on this side, the tube has a loose hanging end, which makes no contact with the substrate. In the first approach, the Young modulus of the
MWNT in Fig.3.5 was estimated by solving the classical beam elasticity equation for a nanotube absorbed on a stepped surface:\footnote{We can also use this model to estimate the energetics involved in the deformation of a nanotube over a step surface (Biró, 1997, Lambin, 1998). The nanotube will break whenever the difference of energy between the deformed nanotube and a broken one having the two halves lying flat on the surfaces exceed the energy of the carbon covalent bond. The latter can be estimated from the surface tension of graphite (\(\Gamma=0.26\text{eV/Å}^2\)) as 4 Rh (Lambin, 1998). Therefore a 100-Å height step are needed before the energy of a broken tube becomes smaller than that of the deformed one. Still, the strength of the carbon- carbon bonds represents a large barrier to overcome.}

\[
\frac{d^4z(x)}{dx^4} = \frac{K_z(z)}{YI}
\]

where \(z(x)\) is the deflection curve when loaded by the force per unit length \(K_z(z)\). For that purpose the nanotube dimensions obtained from the SFM measurement were used to calculate the moment of inertia of the cross sectional area. The attractive substrate- nanotube force per unit length was approximated by a van der Waals attraction similar to the carbon- graphite van der Waals interaction but taking into account the different dielectric constant of the SiO\(_2\) substrate (Israelachvili, 1995). Furthermore, the Poisson ratio of 0.16 is taken from \textit{ab initio} calculations (see Sec.3.2 above). With these approximations the Young modulus of the MWNT in Fig. 3.5 is estimated to be in the order of 1 TPa. This range is in good accordance with the previous experimental results and the calculated Young moduli of MWNTs. In contrast to the rather stiff MWNTs described above, SWNTs turned out to be highly flexible on a short length scale.

An alternative method to measure the elastic bending modulus of nanotubes as a function of diameter has been presented by (Poncharal, 1999). The new technique is based on a resonant electrostatic deflection of a multi-wall carbon nanotube under an external ac-field. The idea is to apply a time-dependent voltage to the nanotube adjusting the frequency of the source to resonantly excite the vibrational bending modes of the nanotube. These modes can be described by the corresponding modes of a uniform cantilever beam (Landau, 1975),

\[
v_j = \frac{\beta_j^2}{8\pi L^2} \sqrt{(D_n^2 + D_t^2)} \sqrt{\frac{E_b}{\rho}}
\]
where $D_0 (D_i)$ is the outer (inner) tube diameter, $E_b$ is the bending modulus (related to the bending elastic constant $C_B$ introduced in Sec.3.1.3), $\rho$ the density and $\beta_i$ some constants for each of the vibrational harmonics of the bending motion (for the first two modes, $\beta_1 = 1.875$ and $\beta_2 = 4.694$). $E_b$ can be directly related to the Young modulus of the sample. For small diameter tubes this modulus is about 1 TPa in quite good agreement with the theoretical estimations of previous section. However, this modulus is shown to decrease by one order of magnitude when the nanotube diameter increases (from 8 to 40 nm). This decrease has to be related to the appearance of a different bending mode for the nanotube. In fact, this corresponds to a wavelike distortion of the inner part of the bent nanotube as it is clearly shown in Fig.3.6. The amplitude of the wavelike distortion increases uniformly from essentially 0 for layers close to the nanotube center to about 2-3 nm for the outer layers without any evidence of discontinuity or defects. The non-linear results are discussed in more detail in the next section and have been observed by many authors in different contexts (Depres, 1995; Ruoff, 1995; Iijima, 1996; Lourie, 1998). Simulations also have predicted this wave-like response of bent-carbon nanotubes (Iijima, 996, Latil 2000).

4. **NONLINEAR ELASTIC BEHAVIOUR**

Large amplitude deformations, beyond the Hookean behavior, reveal nonlinear properties of nanotubes, unusual for other molecules or for the graphite fibers. Both theory-simulations and experimental evidence suggest the ability of nanotubes to significantly change their shape, accommodating to external forces without irreversible atomic rearrangements. They develop kinks or the ripples (multiwalled tubes) in compression and bending, flatten into deflated “ribbons” under torsion, and still can reversibly restore original shape. This resilience is unexpected for a graphite-like material. It must be attributed to the small dimension of the tubules, which leaves no room for the stress-concentrators – micro-cracks or dislocation piles (however, see Sec. 5.2), making a macroscopic material prone to failure.

4.1 **Atomistic Simulations and Shell Model**

Calculations of the elastic properties of carbon nanotubes confirm that they are extremely rigid in the axial direction (high-tensile strength) and more readily distort in the perpendicular direction (radial deformations), due to their high aspect ratio. The detailed studies, stimulated first by experimental reports of visible kinks in the molecules, lead one to conclude that, in spite of their molecular size, nanotubes obey very well the laws of continuum shell theory (Landau, 1975; Timoshenko, 1988;
One of the outstanding features of fullerenes is their hollow structure; built of atoms densely packed along a closed surface that defines the overall shape. This also manifests itself in dynamic properties of molecules, resembling so much the macroscopic objects of continuum elasticity known as shells. Macroscopic shells and rods have long been of interest: the first study dates back to Euler, who discovered the elastic instability. A rod subject to longitudinal compression remains straight but shortens by some fraction $\epsilon$, proportional to the force, until a critical value (Euler force) is reached. It then becomes unstable and buckles sideways at $\epsilon > \epsilon_{cr}$, while the force almost does not vary. For hollow tubules there is also a possibility of local buckling in addition to buckling as a whole. Therefore, more than one bifurcation can be observed.

In application to fullerenes, the theory of shells now serves as a useful guide (Yakobson, 1996a,b, 1997b; Cornwell, 1997; Garg, 1998; Srivastava, 1999), but its relevance for a covalent-bonded system of only a few atoms in diameter was far from being obvious. MD simulations seem better suited for objects that small. Perhaps the first MD-type simulation indicating the macroscopic scaling of the tubular motion emerged in the study of nonlinear resonance (Sumpter, 1995). Soon afterwards, results of detailed MD simulations for a nanotube under axial compression allowed one to introduce concepts of elasticity of shells and to adapt them to nanotubes (Yakobson, 1996a,b). Further MD simulations for other modes of load have also been compared with those suggested by the continuum model and, even more importantly, with experimental evidence (Iijima, 1996), (see next section and Fig.4.4).

In Fig. 4.1 we show a simulated nanotube exposed to axial compression. The atomic interaction was modeled by the Tersoff-Brenner potential (Sec. 2.2) which reproduces the lattice constants, binding energies, and the elastic constants of graphite and diamond. The end atoms were shifted along the axis by small steps and the whole tube was relaxed by conjugate-gradient method while keeping the ends constrained. At small strains the total energy [Fig. 4.1(a)] grows as $E(\epsilon)=1/2 \ E''\epsilon^2$, where $E''=59$ eV/atom (see Sec.3.1 for comparison of this values within different theoretical models). The presence of four singularities at higher strains was quite a striking feature, and the patterns (b)-(e) illustrate the corresponding morphological changes. The shading indicates strain energy per atom, equally spaced from below 0.5 eV (brightest) to above 1.5 eV (darkest). The sequence of singularities in $E(\epsilon)$ corresponds to a loss of molecular symmetry from $D_{\infty h}$.

\[19\] An addition of finite temperature up to several hundred degrees does not change the results.
to S₄, D₂h, C₂h and C₁. This evolution of the molecular structure can be put in the framework of the continuum elasticity.

The intrinsic symmetry of a graphite sheet is hexagonal, and the elastic properties of two-dimensional hexagonal structure are isotropic. A curved sheet can also be approximated by a uniform shell with only two elastic parameters: flexural rigidity D, and its resistance to an in-plane stretching, the in-plane stiffness C. The energy of a shell is given by a surface integral of the quadratic form of local deformation,

\[ E = \frac{1}{2} \int \left\{ D\left(\kappa_x^2 + \kappa_y^2\right) - 2(1 - \nu)(\kappa_x\kappa_y - \kappa_{xy}^2) \right\} + \frac{C}{(1 - n^2)} \left(\varepsilon_x^2 + \varepsilon_y^2 - 2(1 - \nu)(\varepsilon_x\varepsilon_y - \varepsilon_{xy}^2)\right) \right\} dS, \tag{4.1} \]

where \( \kappa \) is the curvature variation, \( \varepsilon \) is the in-plane strain, and \( x \) and \( y \) are local coordinates. In order to adapt this formalism to a graphitic tube, the values of \( D \) and \( C \) are identified by comparison with the detailed \textit{ab initio} and semiempirical studies of nanotube energetics at small strains (Adams, 1992; Robertson, 1992). Indeed, the second derivative of total energy with respect to axial strain corresponds to the in-plane rigidity \( C \) (cf. the definition and the values in Sec. 3.1). Similarly, the strain energy as a function of tube diameter \( d \) corresponds to \( 2D/d^2 \) in Eq. (4.1). Using the data of (Robertson, 1992), we obtain \( C = 59 \text{ eV/atom} = 360 \text{ J/m}^2 \), and \( D = 0.88 \text{ eV} \). The Poisson ratio of \( \nu = 0.19 \) was extracted from a reduction of the diameter of a tube stretched in simulations and it is close to the computed \textit{ab initio} values (cf Sec.3.1.2). A similar value is obtained from experimental elastic constants of single crystal graphite (Kelly, 1981). One can make a further step towards a more tangible picture of a tube as having wall thickness \( h \) and Young modulus \( Y_s \). Using the standard relations \( D = Y_h^3/12(1 - \nu^2) \) and \( C = Y_s h \), one finds \( Y_s = 5.5 \text{ TPa} \) and \( h = 0.067 \text{ nm} \). With these parameters, linear stability analysis (Timoshenko, 1988; Landau, 1986) allows one to assess the nanotube behavior under strain.

To illustrate the efficiency of the shell model, consider briefly the case of imposed axial compression. A trial perturbation of a cylinder has a form of Fourier harmonics, with M azimuthal lobes and N halfwaves along the tube (Fig. 4.2, inset), i.e. sines and cosines of arguments \( 2M\pi y/d \) and \( N\pi x/L \). At a critical level of the imposed strain, \( \varepsilon_c(M,N) \), the energy variation (4.1) vanishes for this shape disturbance. The cylinder becomes unstable and lowers its energy by assuming an \((M,N)\)-pattern. For tubes of \( d = 1 \text{ nm} \) with the shell parameters identified above, the critical strain is shown in Fig. 4.2. According to these plots, for a tube with \( L > 10 \text{ nm} \) the bifurcation is first attained for \( M = 1, N = 1 \). The tube preserves its
circular cross section and buckles sideways as a whole; the critical strain is close to that for a simple rod,

$$\varepsilon_c = \frac{1}{2} (\pi d/L)^2,$$  \hspace{1cm} (4.2)

or four times less for a tube with hinged (unclamped) ends. For a shorter tube the situation is different. The lowest critical strain occurs for $M=2$ (and $N \geq 1$, see Fig. 4.2), with a few separated flattenings in directions perpendicular to each other, while the axis remains straight. For such a local buckling, in contrast to (4.2), the critical strain depends little on length and estimates to $\varepsilon_c = 4d^{-1} = (2/\sqrt{3})(1-\nu^2)^{-1/2} h d^{-1}$ in the so-called Lorenz limit. For a nanotube one finds,

$$\varepsilon_c = 0.077 \text{ nm/d}.$$  \hspace{1cm} (4.3)

Specifically, for the 1 nm wide tube of length $L = 6$ nm, the lowest critical strains occur for the $M=2$ and $N=2$ or 3 (Fig. 4.2), and are close to the value obtained in MD simulations, Fig. 4.1a. This is in accord with the two- and three-fin patterns seen in Fig. 4.1b-c. Higher singularities cannot be quantified by the linear analysis, but they look like a sideways beam buckling, which at this stage becomes a non-uniform object.

Axially compressed tubes of greater length and/or tubes simulated with hinged ends (equivalent to a doubled length) first buckle sideways as a whole at a strain consistent with (4.2). After that the compression at the ends results in bending and a local buckling inward. This illustrates the importance of the "beam-bending" mode, the softest for a long molecule and most likely to attain significant amplitudes due to either thermal vibrations or environmental forces. In simulations of bending, a torque rather than force is applied at the ends and the bending angle $\theta$ increases stepwise. While a notch in the energy plot can be mistaken for numerical noise, its derivative $dE/d\theta$ drops significantly, which unambiguously shows an increase in tube compliance -- a signature of a buckling event (Allen, 1980). In bending, only one side of a tube is compressed and thus can buckle. Assuming that it buckles when its local strain, $\varepsilon = K d/2$, where $K$ is the local curvature, is close to that in axial compression, Eq. (4.3), we estimate the critical curvature as

$$K_c = 0.155 \text{ nm/d}^2.$$  \hspace{1cm} (4.4)

This is in excellent agreement (within 4%) with extensive simulations of single wall tubes of various diameters, helicities and lengths (Iijima, 1996)\(^20\)

\(^{20}\) The critical local curvature at which the tube forms a kink is independent of tube length and can be fitted to the equation $K_c=0.149/d^2[1+0.0989\cos(6\theta)/d^5]$ where $K_c$ is given in
Due to the end effects, the average curvature is less than the local one and the simulated segment buckles somewhat earlier than at $\theta_c = K_c \cdot L$, which is accurate for longer tubes.

In simulation of torsion, the increase of azimuthal angle $\phi$ between the tube ends results in changes of energy and morphology shown in Fig. 4.3. In continuum model, the analysis based on Eq. (4.1) is similar to that outlined above, except that it involves skew harmonics of arguments like $N\pi x/L \pm 2\pi m/L$ [12]. For overall beam-buckling (M=1),

$$\phi_c = 2(1+\nu)\pi$$  \hspace{1cm} (4.5)

and for the cylinder-helix flattening (M=2),

$$\phi_c = 0.055 \text{ nm}^{3/2} \frac{L}{d^{5/2}}.$$  \hspace{1cm} (4.6)

The latter should occur first for $L < 136 \text{ d}^{5/2} \text{ nm}$, which is true for all tubes we simulated. However, in simulations it occurs later than predicted by Eq. (4.6). The ends, kept circular in simulation, which is physically justifiable, by a presence of rigid caps on normally closed ends of a molecule, deter the through flattening necessary for the helix to form (unlike the local flattening in the case of an axial load).

In the above discussion, the specific values of the parameters $C$ and $D$ (or $Y$ and $h$) are chosen to achieve the best correspondence between the elastic-shell and the MD simulation within the same study, performed with the Tersoff-Brenner potential. Independent studies of nanotube dynamics under compression generally agree very well with the above description, although reveal reasonable deviations in the parameter values (Cornwell, 1997; Garg, 1998). More accurate and realistic values can be derived from the TB or the ab initio calculations (Adams, 1992; Blase, 1994; Rubio, 1997) of the elastic shell, and can be summarized in the somewhat “softer but thicker” shell (Yakobson, 1996b). Based on most recent study (Hernández, 1998) one obtains effective shell parameters $C = 415 \text{ J/m}^2$ and $D = 1.6 \text{ eV} = 2.6 \times 10^{-19} \text{ J}$, that is correspondingly $Y_s = 4.6 \text{ TPa}$ and $h = 0.09 \text{ nm}$, cf. Sec. 3.1.

Simulations of nanotubes under mechanical duress lead to shapes very different in appearance. At the same time there are robust traits in common: a deformation, proportional to the force within Hooke's law, eventually leads to a collapse of the cylinder and an abrupt change in pattern, or a sequence of such events. The presence of a snap-through buckling of nanotubes allows for a possibility of "shape memory", when in radians/nm, $\theta$ is the tube’s helicity angle and $d$ is the diameter in nm. (Iijima, 1996).
an unloading cycle the switch between patterns occurs at a somewhat lower level of strain. A small hysteresis observed in simulations is practically eliminated by thermal motion at any finite temperature. However, this hysteresis is greatly enhanced by the presence of van der Waals attraction which causes the tube walls to “stick”-flatten together after the collapse, Fig. 4.3d (Chopra, 1995a). The simulations at even a low temperature (e.g. 50 K) shows strongly enhanced thermal vibrations in the vicinity of every pattern switch, while before and after the transition only barely noticeable ripples are seen. Physically, this indicates softening of the system, when one of the eigenvalues tends to zero in the vicinity of the bifurcation.

While several reports focus on a nonlinear dynamics of an open-end SWNT, when the terminal ring atoms are displaced gradually in simulation, a more realistic interaction of a cap-closed SWNT with the (diamond or graphite) substrates has been studied recently (Garg, 1998). An inward cap collapse and/or sideways sliding if the nanotube tip along the substrate are identified, in addition to the buckling of the tubule itself. Furthermore, an interaction of a small (four SWNT) bundle and a double-wall tubule with the substrates has been also reported (Garg, 1999).

An atomistic modeling of multi-layer tubes remains expensive. It makes extrapolation of the continuum model tempting, but involves an interlayer van der Waals interaction. The flexural rigidity scales as $\sim h^3$ in case of a coherent, and as $\sim h$ for an incoherent stack of layers (Safran, 1994), sliding with respect to each other when the tube is deformed; this affects the mechanical properties and still has to be investigated.

Direct simulations of the tubules under hydrostatic pressure have not been reported to the best of our knowledge. In this scale anisotropic lateral forces in a molecular crystal packing are more plausible than a uniform pressure. An ability of a shell-tubule to bifurcate in a flattened form makes it an example of a two-level system, which manifests in the phase-transition behavior of SWNT crystal, as first described in (Tersoff, 1994) and now indicated by several experimental reports. While the faceting in the triangular crystal packing results in a partial wall flattening, a singular tubule under hydrostatic pressure can collapse completely. One can resort to continuum elasticity and estimate a pressure leading to an inward collapse.

There exist some Raman experiments under pressure for SWNTs (Venkatewaran, 1999) where it is shown that intertube interactions strongly influence the pressure dependence of the radial breathing mode (Henrard, 1999). Also transformation from circular to elliptical tube cross section is considered to be responsible for the increase of density of highly crystalline SWNTs samples with increasing pressure (Chesnokov, 1999). The measured volume compressibility is about 0.024 GPa (L.C. Qin and S. Iijima, private communication 2000). This is in agreement with semiempirical calculations based on the Tersoff potential (Tersoff, 1994).
buckling as \( p_c = 2Y(h/d)^3 \) (Allen, 1980), that is thousands of atmospheres for a nanometer tube. However, it drops fast with the diameter and is assisted by a flattening effects of twisting or bending and by van der Waals attraction between the opposite walls (Chopra, 1995a). Such collapse cannot occur simultaneously throughout the significant SWNT length, but rather propagates at a certain speed depending on the ambient over-pressure \( u \propto \sqrt{p - p_c} \). This pressure dependence (Yakobson, 1996b) is similar to the observations on macroscopic objects like underwater pipelines (Palmer, 1975).

### 4.2 Experimental Evidence of Nanotube Resilience

Collapsed forms of the nanotube (“nanoribbons”) have been observed in experiment (Fig. 4.3d) and their stability can be explained by the competition between the van der Waals attraction and elastic energy. The basic physics can be understood by noticing that the elastic curvature energy per unit length is proportional to \( 1/R \) (R, radii of the tube); however, for a fully collapsed single-wall tubule with the opposite tubule walls at the typical van der Waals contact distance \( c \), the energy per unit length would be composed of a higher curvature energy due to the edges which is independent of the initial tubule diameter, and a negative van der Waals contribution, \( \varepsilon_{vdW} \sim 0.03\text{-}0.04 \text{ eV/atom} \), that is \( \propto R \) per unit length. Collapse occurs when the latter term prevails above a certain critical tube radii \( R_c \) that depends on the number \( N \) of shells of the nanotube, \( R_c(N=1) \sim 8c \) and \( R_c(N=8) \sim 19c \) (Chopra, 1995a), and the thickness of the collapsed strip-ribbon is \( (2N-1)c \). Any additional torsional strain imposed on a tube in experimental environment also favors flattening (Yakobson, 1996a,b) and facilitates the collapse, Fig. 4.3b-c.

The bending seems fully reversible up to very large bending angles despite the occurrence of kinks and highly strained tubule regions in simulations, that are in excellent morphological agreement with the experimental images (Iijima, 1996). Similar bent-buckled shapes have been reported by several groups (Despres, 1995; Ruoff, 1995; Iijima, 1996), Fig. 4.4. This apparent flexibility stems from the ability of the \( sp^2 \) network to rehybridize when deformed out of plane, the degree of \( sp^2-sp^3 \) rehybridization being proportional to the local curvature (Haddon, 1993).

The accumulated evidence thus suggests that the strength of the carbon-carbon bond does not guarantee resistance to radial, normal to the graphene plane deformations. In fact, the graphitic sheets of the nanotubes, or of a plane graphite (Hiura, 1994) though difficult to stretch are easy to bend and to deform. A crystal-array (Tersoff, 1994) or a pair
(Ruoff, 1993) of parallel nanotubes flatten at the lines of contact between them so as to maximize the attractive van der Waals intertube interaction.

An accurate measurement with the atomic force microscope (AFM) tip detects the “failure” of a multiwall tubule in bending (Wong, 1997), which essentially represents nonlinear buckling on the compressive side of the bent tube. The estimated measured local stress is 15-28 GPa, very close to the calculated value (Yakobson, 1997c; Smalley, 1998). A variety of largely and reversibly distorted configurations of the nanotubes has been achieved with AFM tip (Falvo, 1997; Hertel, 1998). Ability of nanotube to “survive the crash” during the impact with the sample/substrate reported in (Dai, 1996) also documents their ability to reversibly undergo large nonlinear deformations.

5. STRENGTH AND FRACTURE

Mechanical properties such as tensile yield strength can be predicted with some confidence from the known elastic properties of single crystal graphite. Since the tensile load does not lead to any shell-type instabilities, it is transferred more straightly to the chemical bond network. The inherent strength of the carbon-carbon bond indicates that the tensile strength of carbon nanotubes might exceed that of other known fibers.

5.1 Atomistics of High Strain-Rate Failure

The simulations of compression, torsion, and tension described above (Sec. 4.1) do not show any bond breaking or atoms switching their positions, in spite the very large local strain in the nanotubes. Overall, the simulations show that graphitic layers remain highly elastic. Conversely, this conclusion, consistent with the recent detection of the patterns (Despres, 1995; Iijima, 1996), serves as another verification of the potential used (Tersoff, 1988; Brenner, 1990), which thus proves to be realistic at large strain. This abets the study of axial tension, where no shape transformations occur up to an extreme dilation. How strong in tension is a carbon nanotube? Experimental measurements remain complex (Sec. 5.3) due to the small size of the grown single tubes. In the meantime, some tests are being done in computer modeling, especially well suited to the fast strain rate (Yakobson, 1996a,b; 1997a,b). Indeed, a simulation of a thousand of atoms large object even with classical potential interaction between the atoms is usually limited to picoseconds up to nanoseconds of real physical time. This is sufficiently long by molecular standards, that is orders of magnitude greater than the periods of intramolecular vibrations of intermolecular collision times. However, it is still much less than a normal test-time for a material, or an engineering structure. Therefore a standard MD simulation addresses a “molecular strength” of the CNT,
leaving the true mechanisms of material behavior to the more subtle considerations (Sec. 5.2).

In MD simulation, the high-strain-rate test proceeds in a very peculiar manner. Fast stretching simply elongates the hexagons in the tube wall, until at the critical point an atomic disorder suddenly nucleates: one or a few C-C bonds break almost simultaneously, and the resulting “hole” in a tube wall becomes a crack precursor (see Fig. 5.1a). The fracture propagates very quickly along the circumference of the tube. A further stage of fracture displays an interesting feature, the formation of two or more distinct chains of atoms, \( \ldots=\mathrm{C}=\mathrm{C}=\ldots \), spanning the two tube fragments, Fig. 5.1b. The formation of the chain is similar to that observed in \( \text{C}_{60} \) cluster formation and fragmentation (Chelikowsky, 1991). The vigorous motion (substantially above the thermal level) results in frequent collisions between the chains, they coalesce, and soon only one such chain survives. A further increase of the distance between the tube ends does not break this chain, which elongates by increasing the number of carbon atoms that pop out from both sides into the necklace. This scenario is similar to the monoatomic chain unraveling suggested in field-emission experiments (Rinzler, 1995), where the electrostatic force unravels the tube like the sleeve of a sweater. Notably, the breaking strain in such fast-snap simulations is as about 30\%, and varies with temperature and the strain rate. (For a rope of nanotubes this translates in a more than 150 GPa breaking stress.) This high breaking strain value is consistent with the stability limit (inflexion point on the energy curve) of 28\% for symmetric low-temperature expansion of graphene sheet (Stumm, 2000), and with some evidence of stability of highly stresses graphene shells in irradiated fullerene onions (Banhart, 1996).

5.2 Yield Strength and Relaxation Mechanisms in Nanotubes

Fast strain rate (in the range of 100 MHz) simulations correspond to the elongation of the tubule at percents of the speed of sound. In contrast to such “molecular tension test”, materials engineering is more concerned with the static or slow tension conditions, when the sample is loaded during significantly longer time. Fracture, of course, is a kinetic process where time is an important parameter. Even a small tension, as any non-hydrostatic stress, makes a nanotube thermodynamically meta-stable and a generation of defects energetically favorable. In order to study a slow strength-determining relaxation processes, preceding the fast fracture, one should either perform extensive simulations at exceedingly elevated temperature (Buongiorno-Nardelli, 1998a,b), or to apply dislocation theory (Yakobson, 1997c,d, 1998). It has been shown that in a crystal lattice such as the wall of a CNT, a yield to deformation must begin with a homogeneous nucleation of a slip by the shear stress present. The non-
basal edge dislocations emerging in such slip have a well-defined core, a pentagon-heptagon pair, 5/7. Therefore the prime dipole is equivalent to the Stone-Wales (SW) defect (Dresselhaus, 1996), see Fig. 5.2. The nucleation of this prime dislocation dipole “unlocks” the nanotube for further relaxation: either brittle cleavage or a plastic flow. Remarkably, the latter corresponds to a motion of dislocations along the helical paths (glide “planes”) within the nanotube wall. This causes a stepwise (quantized) necking, when the domains of different chiral symmetry, and therefore different electronic structure (Chap. 3 and 6) are formed, thus coupling the mechanical and electrical properties (Yakobson, 1997c,d). It has further been shown (Yakobson, 1997c,d, 1998; Smalley, 1998; Pierson, 1998; Buongiorno-Nardelli, 1998b; Zhang, 1998) that the energetics of such nucleation explicitly depends on nanotube helicity.

Below we deduce (Yakobson, 1997c, 1998), starting with dislocation theory, the atomistics of mechanical relaxation under extreme tension. Locally, the wall of a nanotube differs little from a single graphene sheet, a two-dimensional crystal of carbon. When a uniaxial tension $\sigma$ (N/m — for the two-dimensional wall it is convenient to use force per unit length of its circumference) is applied it can be represented as a sum of expansion (locally isotropic within the wall) and a shear of a magnitude $\sigma/2$ (directed at $\pm45^\circ$ with respect to tension). Generally, in a macroscopic crystal the shear stress relaxes by a movement of dislocations, the edges of the atomic extra-planes. Burgers vector $\mathbf{b}$ quantifies the mismatch in the lattice due to a dislocation (Hirth, 1982). Its glide requires only local atomic rearrangements and presents the easiest way for strain release, provided sufficient thermal agitation. In an initially perfect lattice such as the wall of a nanotube, a yield to a great axial tension begins with a homogeneous nucleation of a slip, when a dipole of dislocations (a tiny loop in three-dimensional case) first has to form. The formation and further glide are driven by the reduction of the applied-stress energy, as characterized by the elastic Peach-Koehler force on a dislocation. The force component along $\mathbf{b}$ is proportional to the shear in this direction and thus depends on the angle between the Burgers vector and the circumference of the tube,

$$f_b = -\frac{1}{2}\sigma|\mathbf{b}| \sin 2\theta.$$  

The max $|f_b|$ is attained on two $\pm45^\circ$ lines, which mark the directions of a slip in an isotropic material under tension.

The graphene wall of the nanotube is not isotropic, its hexagonal symmetry governs the three glide planes – the three lines of closest zigzag atomic packing, oriented at $120^\circ$ to each other (corresponding to the $\{10\overline{1}l\}$ set of planes in three-dimensional graphite). At non-zero shear these directions are prone to slip. The corresponding c-axis edge dislocations
involved in such slip are indeed known in graphite (Kelly, 1981; Dresselhaus, 1988). The six possible Burgers vectors \( \frac{1}{3}a<2_{110} \) have a magnitude \( b=a=0.246 \) nm (lattice constant), and the dislocation core is identified as a 5/7 pentagon-heptagon pair in the honeycomb lattice of hexagons. Therefore, the primary nucleated dipole must have a 5/7/7/5 configuration (a 5/7 attached to an inverted 7/5 core). This configuration is obtained in the perfect lattice (or a nanotube wall) by a 90° rotation of a single C-C bond, well known in fullerene science as a Stone-Wales diatomic interchange (Dresselhaus, 1996). One is led to conclude that the SW transformation is equivalent to the smallest slip in a hexagonal lattice and must play a key role in the nanotube relaxation under external force.

The preferred glide is the closest to the maximum-shear ±45° lines, and depends on how the graphene strip is rolled-up into a cylinder. This depends on nanotube helicity (cf. Chap. III) specified by the chiral indices \((c_1, c_2)\) or a chiral angle \(\theta\) indicating how far the circumference departs from the leading zigzag motif \(a_1\). The max \(|f_b|\) is attained for the dislocations with \(b = \pm(0,1)\) and their glide reduces the strain energy,

\[
E_g = - |f_b a| = - Ca^2/2 \cdot \sin (2\theta + 60^\circ) \cdot \varepsilon, \tag{5.2}
\]

per one displacement, a. Here \(\varepsilon\) is the applied strain, and \(C=Yh=342\) N/m can be derived from the Young modulus of \(Y = 1020\) GPa and the interlayer spacing \(h=0.335\) nm in graphite; one then obtains \(Ca^2/2 = 64.5\) eV. (cf. values in Sec. 4.1). The Eq. 5.2 allows one to compare different nanotubes (assuming similar amount of pre-existing dislocations): the more energetically favorable is the glide in a tube, the earlier it must yield to applied strain.

In a pristine nanotube-molecule, the 5/7 dislocations have first to emerge as a dipole, by a prime SW transformation. Topologically, the SW defect is equivalent to either one of the two dipoles, each formed by an \(~a/2\) slip. Applying Eq. (5.1) to each of the slips one finds,

\[
E_{SW} = E_0 - A \cdot \varepsilon - B \cdot \sin (2\theta + 30^\circ) \cdot \varepsilon, \tag{5.3}
\]

The first two terms, the zero-strain formation energy and possible isotropic dilation, do not depend on nanotube symmetry. The symmetry-dependent third term, which can also be derived as a leading term in the Fourier series, describes the essential effect: SW rotation gains more energy in the armchair (\(\theta = 30^\circ\)) nanotube, making it the weakest, most inclined to SW nucleation of the dislocations, in contrast to the zigzag (\(\theta = 0\)) where the nucleation is least favorable.
Consider for example a (c, c) armchair nanotube as a typical representative (we will also see below that this armchair type can undergo a more general scenario of relaxation.) The initial stress-induced SW rotation creates a geometry that can be viewed as either a dislocation dipole or a tiny crack along the equator. Once “unlocked”, the SW defect can ease further relaxation. At this stage, both brittle (dislocation pileup and crack extension), or plastic (separation of dislocations and their glide away from each other) routes are possible, the former usually at larger stress and the latter at higher temperatures (Buongiorno-Nardelli, 1998a,b; Yakobson, 1997c,d, 1998).

Formally, both routes correspond to a further sequence of SW-switches. The 90° rotation of the bonds at the “crack tip” (Fig. 5.3, left column) will result in a 7/8/7 flaw and then 7/8/8/7 etc. This further strains the bonds-partitions between the larger polygons, leading eventually to their breakage, with the formation of greater openings like 7/14/7 etc. If the crack, represented by this sequence, surpasses the critical Griffith size, it cleaves the tubule.

In a more interesting distinct alternative, the SW rotation of another bond (Fig. 5.3, top row) divides the 5/7 and 7/5, as they become two dislocation cores separated by a single row of hexagons. A next similar SW switch results in a double-row separated pair of the 5/7’s, and so on. This corresponds, at very high temperatures, to a plastic flow inside the nanotube-molecule, when the 5/7 and 7/5 twins glide away from each other driven by the elastic forces, thus reducing the total strain energy [cf. Eq. (5.2)]. One remarkable feature of such glide is due to mere cylindrical geometry: the glide “planes” in case of nanotubes are actually spirals, and the slow thermally-activated Brownian walk of the dislocations proceeds along these well-defined trajectories. Similarly, their extra-planes are just the rows of atoms also curved into the helices.

A nanotube with a 5/7 defect in its wall loses axial symmetry and has a bent equilibrium shape; the calculations show (Chico, 1996) the junction angles <15°. Interestingly then, an exposure of an even achiral nanotube to the axially symmetric tension generates two 5/7 dislocations, and when the tension is removed, the tube “freezes” in an asymmetric configuration, S-shaped or C-shaped, depending on the distance of glide, that is time of exposure. Of course the symmetry is conserved statistically, since many different shapes form under identical conditions.

When the dislocations sweep a noticeable distance, they leave behind a tube segment changed strictly following the topological rules of dislocation theory. By considering a planar development of the tube segment containing a 5/7, for the new chirality vector $c'$ one finds,
\[(c_1',c_2') = (c_1,c_2) - (b_1,b_2), \quad (5.3)\]

with the corresponding reduction of diameter, \(d\). While the dislocations of the first dipole glide away, a generation of another dipole results, as shown above, in further narrowing and proportional elongation under stress, thus forming a neck. The orientation of a generated dislocation dipole is determined every time by the Burgers vector closest to the lines of maximum shear (±45°) cross at the end-point of the current circumference-vector \(c\). The evolution of a \((c,c)\) tube will be: \((c,c) \rightarrow (c,c-1) \rightarrow (c,c-2) \rightarrow \ldots (c,0) \rightarrow (c-1,1) \rightarrow (c-1,0) \rightarrow (c-2,1) \rightarrow (c-2,0) \rightarrow [(c-3,1) \text{ or } (c-2,-1)] \rightarrow (c-3,0) \text{ etc.}\) It abandons the armchair \((c,c)\) type entirely, but then oscillates in the vicinity of zigzag \((c,0)\) kind, which appears a peculiar attractor. Correspondingly, the diameter for a \((10,10)\) tube changes stepwise, \(d = 1.36, 1.29, 1.22, 1.16\) nm, etc., the local stress grows in proportion and this quantized necking can be terminated by a cleave at late stages. Interestingly, such plastic flow is accompanied by the change of electronic structure of the emerging domains, governed by the vector \((c_1,c_2):\) The armchair tubes are metallic, others are semiconducting with the different band gap values (Chap. 6). The 5/7 pair separating two domains of different chirality has been discussed as a pure-carbon heterojunction (Chico, 1996; Charlier, 1996) and argued to cause the current rectification detected in a nanotube nanodevice (Collins, 1997) and can be used to modify, in a control way, the electronic structure of the tube (Crespi, 1998). Here we see how this electronic heterogeneity can arise from a mechanical relaxation at high temperature: if the initial tube was armchair-metallic, the plastic dilation transforms it into a semiconducting type irreversibly.

*Computer simulations* have provided a compelling evidence of the mechanisms discussed above. By carefully tuning the tension in the tubule and gradually elevating its temperature, with extensive periods of MD annealing, the first stages of the mechanical yield of CNT have been observed (Buongiorno-Nardelli, 1998a,b). In simulation of tensile load the novel patterns in plasticity and breakage, just described above, clearly emerge.

Classical MD simulations have been carried out for tubes of various geometries with diameters up to 13 nm. Such simulations, although limited by the physical assumptions used in deriving the interatomic potential, are still invaluable tools in investigating very large systems for the time scales that are characteristic of fracture and plasticity phenomena. Systems containing up to 5000 atoms have been studied for simulation times of the order of nanoseconds. The ability of the classical potential to correctly reproduce the energetics of the nanotube systems
has been verified through comparisons with TB and \textit{ab initio} simulations (Buongiorno-Nardelli, 1998a,b).

Beyond a critical value of the tension, an armchair nanotube under axial tension releases its excess strain via spontaneous formation of a SW defect through the rotation of a C-C bond producing two pentagons and two heptagons, \(5/7/7/5\) (Fig. 5.4). Further, the calculations (Buongiorno-Nardelli, 1998a,b) show the energy of the defect formation, and the activation barrier, to decrease approximately linear with the applied tension; for \((10,10)\) tube the formation energy can be approximated as 
\[E_{\text{sw}}(\text{eV}) = 2.3 - 40\varepsilon.\]
The appearance of a SW defect represents the nucleation of a (degenerate) dislocation loop in the planar hexagonal network of the graphite sheet. The configuration \(5/7/7/5\) of this primary dipole is a \(5/7\) core attached to an inverted \(7/5\) core, and each \(5/7\) defect can indeed further behave as a single edge dislocation in the graphitic plane. Once nucleated, the dislocation loop can split in simulations into two dislocation cores, \(5/7/7/5 \leftrightarrow 5/7 + 7/5\), which are then seen to glide through successive SW bond rotations. This corresponds to a plastic flow of dislocations and gives rise to possible ductile behavior. The thermally activated migration of the cores proceeds along the well-defined trajectories (Fig. 5.5) and leaves behind a tube segment changed according to the rules of dislocation theory, Eq. (5.3). The tube thus abandons the armchair symmetry \((c, c)\) and undergoes a visible reduction of the diameter, a first step of the possible quantized necking in “intramolecular plasticity” (Yakobson, 1997c,d, 1998).

The study, based on the extensive use of classical, tight-binding and \textit{ab initio} MD simulations (Buongiorno-Nardelli, 1998b), shows that the different orientations of the carbon bonds with respect to the strain axis (in tubes of different symmetry) lead to different scenarios. Ductile or brittle behaviors can be observed in nanotubes of different indices under the same external conditions. Furthermore, the behavior of nanotubes under large tensile strain strongly depends on their symmetry and diameter. Several modes of behavior are identified, and a map of their ductile- vs-brittle behavior has been proposed, Fig. 5.6. While graphite is brittle, carbon nanotubes can exhibit plastic or brittle behavior under deformation, depending on the external conditions and tube symmetry. In the case of a zig-zag nanotube (longitudinal tension), the formation of the SW defect is strongly dependent on curvature, i.e., on the diameter of the tube and gives rise to a wide variety of behaviors in the brittle- vs-ductile map of stress response of carbon nanotubes (Buongiorno-Nardelli, 1998b). These are summarized in Fig. 5.6 where a map for the ductile vs brittle behavior of a general \((c_1,c_2)\) carbon nanotube under an axial tensile load is presented. In particular, the formation energy of the off-axis \(5/7/7/5\) defect (obtained via the rotation of the C-C bond oriented 120° to the tube axis) shows a crossover with respect to the diameter. It is negative for \((c,0)\)
tubes with \( c < 14 \) (\( d < 1.1 \) nm). The effect is clearly due to the variation in curvature, which in the small-diameter tubes makes the process energetically advantageous. Therefore, above a critical value of the curvature a plastic behavior is always possible and the tubes can be ductile.

Overall, after the nucleation of a first 5/7/7/5 defect in the hexagonal network either brittle cleavage or plastic flow are possible, depending on tube symmetry, applied tension and temperature. Under high strain and low temperature conditions, all tubes are brittle. If, on the contrary, external conditions favor plastic flow, such as low strain and high temperature, tubes of diameter less than approximately 1.1 nm show a completely ductile behavior, while larger tubes are moderately or completely brittle depending on their symmetry. These possibilities are summarized in Fig. 5.6.

5.3 Attempts of Strength Measurements

Reports on measurements of carbon nanotube strength are scarce, and remain the subject of continuing effort. A nanotube is too small to be pulled apart with standard tension devices, and too strong for tiny “optical tweezers”, for example. The proper instruments are still to be built, or experimentalists should wait until longer nanotubes are grown.

A bending strength of the MWNT has been reliably measured with the AFM tip (Wong, 1997), but this kind of failure is due to buckling of graphene layers, not the C-C bond rearrangement. Accordingly, the detected strength, up to 28.5 GPa is twice lower than 53.4 GPa observed for non-laminated SiC nanorods in the same series of experiments. Another group (Falvo, 1997) estimates the maximum sustained tensile strain on the outside surface of a bent tubule as large as 16%, which (with any of the commonly accepted values of the Young’s modulus) corresponds to 100-150 GPa stress. On the other hand, some residual deformation that followed such large strain can be an evidence of the beginning yield and the 5/7- defects nucleation. A detailed study of the failure via buckling and collapse of matrix-embedded carbon nanotube must be mentioned here (Lourie, 1998), although again this compressive failure mechanisms are essentially different than the bond-breaking yield processes in tension (as discussed in Sec.3.1 above).

Actual tensile load can be applied to the nanotube immersed in matrix materials, provided the adhesion is sufficiently good. Such experiments, with stress-induced fragmentation of carbon nanotube in polymer matrix has been reported, and an estimated strength of the tubes is 45 GPa, based on a simple isostrain model of the carbon nanotube-matrix. It has to be
also reminded that the authors (Wagner, 1998) interpret the contrast bands in HRTEM images as the locations of failure, although the imaging of the carbon nanotube through the polymer film limits the resolution in these experiments.

While a singular single-wall nanotube is extremely difficult object for mechanical tests due to its small molecular dimensions, the measurement of the “true” strength of SWNT in a rope-bundle arrangement is further complicated by the weakness of inter-tubular lateral adhesion. External load is likely to be applied to the outmost tubules in the bundle, and its transfer and distribution across the rope cross-section obscures the interpretation of the data. Low shear moduli in the ropes (1GPa) indeed has been reported (Salvetat, 1999).

Recently, a suspended SWNT bundle-rop e was exposed to a sideways pull by the AFM tip (Walters, 1999). It is reported to sustain reversibly many cycles of elastic elongation up to 6%. If this elongation is actually transferred directly to the individual constituent tubules, the corresponding tensile strength then is above 45 GPa. This number is in agreement with that for multiwalled tubes mentioned above (Wagner, 1998), although the details of strain distribution can not be revealed in this experiment.

A direct tensile, rather than sideways pull of a multiwall tube or a rope has clear advantage due to simpler load distribution, and an important step in this direction has been recently reported (Yu, 2000). In this work tensile-load experiments are performed for MWNTs reporting tensile-strengths in the range of 11 to 63 GPa with no apparent dependence on the outer shell diameter. The nanotube broke in the outermost layer (“sword in sheath” failure) and the analysis of the stress-strain curves indicates a Young modulus for this layer in between 270 and 950 GPa. Moreover, the measured strain at failure can be as high as 12% change in length.

In spite of significant progress in the experimenting with the nanotube strength, that makes some important data available, a direct and reliable measurement remains an important challenge for nanotechnology and materials physics.

6. MISCELLANEOUS PHENOMENA

Mechanical behavior is often coupled with other physico-chemical phenomena, which of course broadens the import of mechanical properties. Below we discuss briefly several examples where the role of mechanical properties seems more prominent but many others are expected to appear in the near future.
6.1 Elasto-electronics

Coupling with electrical properties can manifest itself both ways, where either deformation affects the charge distribution or transport, or an additional charge can cause visible deformation, thus making an actuator. Change in the bandgap of nanotubes with strain and torsion has been discussed (Kane, 1997)\textsuperscript{22}. This variation could have some implications for nanoscale electro-mechanical devices (Joachim, 1997). We can estimate based on a simple one-electron picture the role of a small tensile or torsional strain in the electronic structure of carbon nanotubes. To do so, we need to realize that the mechanical deformation induces a change of the bond-length and therefore a change in the value of the hopping parameters between carbon atoms in the unit cell. Working only with nearest-neighbor interactions we consider three different hopping parameters for each neighbor atom with the usual $1/r^2$ dependence of the hopping with distance (Harrison, 1989). This model can be solved analytically for a strained graphene sheet that can be directly translated to the nanotube by considering the appropriate periodic boundary conditions along the tube circumference (Hamada, 1992) we get the energy dispersion for a (n,m) nanotube strained tube (strain $\varepsilon$),

$$E(k_z) = t_1^2 + t_2^2 + t_3^2 + 2t_1t_2 \cos \left( \frac{\pi q}{C} \frac{n+m}{2} C \frac{1}{k_z (1+\varepsilon)} \right) + 2t_1t_3 \cos \left( \frac{\pi q}{C} \frac{2n+m}{2} C \frac{1}{k_z (1+\varepsilon)} \right) + 2t_2t_3 \cos \left( \frac{\pi q}{C} \frac{n-m}{2} C \frac{1}{k_z (1+\varepsilon)} \right)$$

where $C$ is the circumference of the tube in units of the equilibrium lattice vectors, $C=(n^2+m^2+nm)^{1/2}$, $k = k_x \mathbf{u}_c + k_z \mathbf{u}_z$, and the condition for quantization of the $k$-vector along the circumference is $kC = 2q$. Taking now all the hopping integrals equal $t_i=2.7$ eV (i=1,2,3), the previous equation reproduces the results obtained for SWNTs (Hamada, 1992). From this expression we can easily compute the change of band gap with applied strain or torsion can be deduced (Yang, 2000). In all cases the derivative of the band gap follows the $(n-m)$ mod 3 rule (Hamada, 1992) and can even change sign as a function of the applied strain (Yang, 1998). For zig-zag tubes the absolute value of the band-gap derivative is constant equal to $3t_0$ and continuously decreases as we change the chirality from zig-zag to armchair. The metallic character of armchair tubes does not change as we applied strain to the tube, however it opens a gap for a torsional deformation (Kane, 1997). Under torsional strain the absolute value of the band-gap change is constant for armchair tubes (equal to $3t_0$) and

\textsuperscript{22} The coupling between the conduction electrons and long wavelength twistons, i.e. torsional shape vibrations is relevant for understanding the transport properties at low temperatures, namely, the relevance for the peculiar linear dependence of the of the electrical resistivity with temperature in the metallic armchair tubes.
continuously decreases going from armchair to zig-zag chirality (Yang, 2000).

Furthermore, bending of a carbon nanotube introduces an increased mixing of \( \uparrow \) and \( \downarrow \)-states that leads to an enhanced density of states at the Fermi energy region and to a charge polarization of the carbon-carbon bond in the deformed region (Rochefort, 1999). The transport properties of bent tubes depend on the chirality of the tube; indeed, armchair tubes keep their metallic character irrespective of the deformation but this is not the case for chiral metallic tubes where local-electronic barriers arise from the bending of the tube (Buongiorno-Nardelli, 1999). This calculations are in agreement with recent experimental transport data of individual carbon nanotubes supported on a series of electrodes (Bezryadin, 1998).

Mechanical stretching has been proposed as a method for inducing chiral conductivity in these carbon nanotubes when doped (Miyamoto, 1996). The essence of chiral conduction is symmetry breaking on tubule walls upon mechanical stretching. Calculations of the transport properties of mechanically stretched doped-carbon nanotubes show that stretching induces chirality on the tubule current, being the most efficient geometry for the induced chirality an arm-chair like atomic arrangement. If a nanocoil is subjected to an external frequency-dependent electric field the effective inductance varies with respect to AC-frequency different to the inductances of ordinary coils. This induced current chirality is most likely for geometrically chiral nanotube having helical pitches close to those of armchair tubules. By solving Maxwell's equations for chiral conducting nanotubes (nanocoils) it is found that the self-inductance and the resistivity of nanocoils should depend on the frequency of the alternating current even when the capacitance of the nanocoils is not taken into account (Miyamoto, 1999). This is in contrast to elementary treatment of ordinary coils. This fact is useful to distinguish nanocoils by electrical measurements.

An interesting manifestation of electro-mechanical coupling in nanotubes has recently emerged as carbon nanotube actuators (Baughman, 1999). By changing the applied voltage and therefore injecting the electrons or holes one causes either an expansion or contraction of carbon nanotube, or a graphene sheet. A separate contribution of a purely quantum-mechanical change in band structure and in orbital occupancy and the role of electrochemical double-layer are not completely understood, the experimental evidence is quite convincing. Nanotube sheets adhered to the opposite sides of insulating film make a cantilever sensitive to the voltage applied between the sheets: a small elongation on one side and a

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23 The basic physics behind this phenomenon is that in a nanocoil the chiral angle of the current is frequency dependent whereas in a classical coil this is fixed by the pitch of the winding of the wires in forming the coil.
contraction on the other results in significant bending of the bilayer cantilever. The limit of the gravimetric work capacity, $\frac{1}{2}Y\varepsilon^2/\rho$, is expected to be much higher than for other materials, like ferroelectrics, due to great values of modulus $Y = 1$ TPa, strain range $\varepsilon = 1\%$, and the low density $\rho = 1.3$ g/cm$^3$ for carbon nanotube bundles.

6.2. Composite tube-polymer

Different to traditional graphitic fibers, nanotubes combine, as we have shown all through the present chapter, combine high flexibility and high strength with high stiffness. These properties open the way for a new generation of high performance light-weight polymer composites useful for structural reinforcement. This has triggered a lot of research looking at the ability of nanotubes to stiffen and strengthen a polymer (Schadler, 1998; Ajayan, 1997, 1999). The reinforcement will depend on how load is transferred to the nanotube aggregates such as single-walled nanotube bundles. If the adhesion between the matrix and the nanotubes is not strong enough to sustain high loads, the benefits of the high tensile strength of carbon nanotubes are lost. Load transfer in carbon nanotube epoxy composites was studied in both tension and compression (Schadler, 1998). Under tension it seems that only the outermost nanotube is loaded due to weak interlayer bonding. This could be related to the absence of registry between graphene layers that makes adhesion and friction reduced (Falvo, 1999).

Furthermore, in the case of SWNTs epoxy composites, it is shown that individual SWNTs can easily pull out of nanotube bundles, making load transfer difficult (Ajayan, 1999; Yakobson, 2000). It is unclear, however, if the failures observed in MWNT and SWNT composites are failures of the nanotubes or local instabilities of the aggregates. Clearly in the case of SWNT, the failure could be either individual nanotubes pulling out of a bundle or actual fracture of a SWNT. The shear strength to pull out a nanotube can also be estimated through the shear modulus of graphite (4.5 GPa). This is to be compared with the Young modulus of the order of 1TPa, therefore it is much easier to slide a nanotube out of the bundle than break it. However, the entangled structure of the nanotube sample helps in providing toughness to the composite (Ajayan, 1999). Two striking observations were seen in the epoxy composites on the application of stress and composite-fracture. A typical fracture surface consists of a network of SWNT bundles that cover the surface (Fig. 6a). From the morphology of the nanotube network, it looks as if the tube bundles were pulled out of the matrix during the fracture of the composites and collapsed back onto the surface as a loose network. This can be contrasted to other areas of the fracture surface where the nanotubes are not entirely pulled out but fully stretched (Fig. 6b). It seems here that the local
deformation was not enough to pull out the tube bundles. The stretched nanotube bundles look well aligned. This is a clear indication that stretching can align nanotube bundles, as reported in earlier work (Ajayan, 1994). This particular case corresponds to cracks of the order of 1 μm (Fig. 6b). In the intermediate case, when the crack width is several tens to few hundred nanometers, most nanotubes are seen curved and looped (Fig. 6c); few are seen stretched since the crack separation is not uniform. This is due to the fact that the crack opens, stretches the nanotubes and subsequently closes somewhat (relaxes) removing the load on nanotubes. Therefore, the curving and stretching emphasizes the high flexibility of the nanotube bundles experienced over localized areas of the composite and their ability to damp the applied deformation. This behavior might be of importance in increasing the toughness of the composite because the nanotubes could pull out from many directions without failing. In fact, this effect would increase the effectiveness of the pullout and crack bridging contributions to toughness (Ajayan, 1999).

Recent bending experiments of the elastic behavior of epoxy-nanotube composite (Vacarini, 1999a) gives a value of Young modulus of 3.35 GPa for 9% weight of nanotubes (as compared to the 2.4 GPa of the pristine epoxy sample). This corroborates the previous results and shows some limiting behavior in the load transfer in polymer/nanotube composites. More work is needed to understand the mechanical behavior of these complex systems and to address the potential application of nanotubes as reinforcement in polymers, liquid resins and for ceramics- matrix and metals composites. The exceptional mechanical properties of nanotubes will manifest themselves in composites once a good load transfer between the matrices and outer surface of the nanotubes is achieved.

6.3 Cutting tubes with STM:

Recently it has been found that tubes can be effectively cut by applying voltage pulses of 1 ms to the tip of a scanning tunneling microscope (STM) located just above a nanotube (Venema, 1997). A threshold for the voltage during a pulse of 3.8 ± 0.2 V is found for cutting nanotubes, independent on polarity, feedback tunnel current or voltage. Both SWNT (either semiconducting or metallic) as well as nanotubes in bundles can be cut with this technique. It has been shown that the STM-electronic induced strain can lead to the cutting of a SWNT (Rubio, 2000) through the formation of topological Stone- Wales defects (cf. Sec.5.2 for a detailed description of the dynamics of this defects in carbon nanotubes). Molecular dynamics simulations of strain-induced defect and plastic-brittle behaviour using a tight binding parameterization, show that at high applied strain and low temperature all tubes are brittle. The simulation time scale for the formation and evolution of these defects is of the order of nanoseconds, much shorter than the applied voltage pulse of 1 ms.
Therefore, we expect that these defects nucleates under the tip of the STM. The critical strain for defect formation varies from 5% for a (10,10) nanotube to 12% for a (12,0) nanotube. Above this critical value the defect density increases rapidly with length (Zhang, 1998). Furthermore the activation barrier for the formation of defects is lowered by the external applied tension. Indeed the activation barrier for bond rotation in a (10,10) nanotube reduces from 5.6 eV at zero strain to 3 eV at 10% strain; similar reduction is observed for the barrier for separation of the pentagon-heptagon dislocation cores.

In conclusion, the cutting process is triggered by the inelastic electron excitation involving transitions of localized \(\pi\)-states at about 4 eV. This could account for the threshold voltage found in the experiments. The carbon-carbon bonds are further weakened by the mechanical stress induced by the large electric-field between tip and sample. The carbon network releases part of the electronic-induced mechanical-stress by forming topological defects (that act as nucleation center for the formation of dislocations). Under the continuous applied stress the dislocations dynamically propagate towards bond breaking triggering the cutting process.

6.4. Applications

The understanding of the mechanical response of nanotubes to external forces is of relevance for the application of nanotubes as a composite material reinforcement as well as in electronic devices, where the deformation of the tubes induced by the substrate alter locally the electronic properties of the nanotube. A broad discussion of potential applications of the nanotube can be found in existing reviews (Ebbesen, 1997; Ajayan, 1997; Yakobson, 1997b; Bernholc, 1997), also outlining the challenges of implementation. There are two already actual applications, where the carbon nanotube can commercially compete with other materials units, and the mechanics of carbon nanotube plays either central or an important secondary role in both cases.

Nanotubes are ideal proximal tips because they do not plastically deform during tip crashes on the surfaces as conventional tips often do. Instead they elastically deform, buckle and slip. The recovering mechanism has to be taken into account when analyzing the data from AFM measurements using the nanotubes as tips. The enhanced capability of a scanning force microscope using carbon nanotube has been already demonstrated (Dai, 1996). Nanotube tips have also been used as pencils for writing 10-nm-width structures on silicon substrates. The robustness of the nanotube tips permits a writing rate 0.5 mm/sec, five times faster than was possible with older AFM tips. The way the nanotube writes is for an electric field, emanating from the nanotube, to remove hydrogen atoms from a layer of
hydrogen atop a silicon base. The exposed silicon surface oxidizes; thus the "writing" consists of narrow SiO$_2$ track.

The development of new tools to manipulate and analyze the nanoworld relies in extending traditional macroscopic techniques down to the nanoscale. Just recently it has been probed that the mechanical robustness and electrical conductivity of nanotubes can be used to build electromechanical-tweezers (Kim, 1999). The nanotubes are attached to a metal electrode. This tweezers not only allow to grab and manipulate mesoscopic silicon-carbide dots and gallium-arsenide wires but also can be used to probe electronic properties across the structure (transport). Many other applications can be envisioned, for example, the manipulation of biological structures and to measure the weight of viruses and other organic (and inorganic) individual molecules$^{24}$. Applications as actuators were discussed in a previous subsection 6.6.1.

A full-sealed field emission full-color display has been recently reported by the group at Samsung Corporation (Choi, 1999) who used a relatively disordered conglomeration of SWNT embedded in a composite nitrocellulose substrate, in combination with closely-placed (200 µm) phosphorous layer$^{25}$. At the SWNT density of only 1-3/µm$^2$, the current density is stable for hours and high enough to induce bright light. In this important example, mechanical robustness of the carbon network in the tips prevents them from deterioration and ensures stable performance. The combined electronic and mechanical behavior of carbon nanotubes have been also used to demonstrate that nanotubes act as molecular chemical sensors (Kong, 2000)$^{26}$. The nanotube sensors exhibit a fast response and substantially higher sensitivity to gaseous molecules (as NO$_2$ or NH$_3$) than existing solid-state sensors at room temperature. As the research in this fascinating field is evolving really fast, we envision many more applications to be reported in the very near future.

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$^{24}$ The nanobalance is based on the resonant electrostatic deflection of a carbon nanotube under an external ac-field. By knowing the response of the isolated tube and measuring the change in resonant frequency of the tube plus the molecule we can get a direct measure of the molecule weight (Poncharal, 1999).

$^{25}$ A full-color 11.4 cm display that appears to be durable enough to provide 10000 hours-lifetime. The power consumption is smaller than traditional liquid-crystal displays (LCD) for the same brightness. The main disadvantage is the actual manufacturing price of nanotubes as compared to LCD.

$^{26}$ The electrical resistivity of SWNT samples changes dramatically by exposing the nanotube sample to gaseous molecules. This effect provides the high sensitivity of nanotubes as chemical sensors.
7. Acknowledgements

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FIGURE CAPTIONS:

Fig. 1.1: Buckyball $C_{60}$ and other fullerenes owe their name to the author of Expo dome (Montreal, 1967, top left). Similarly, the nanotubes resemble an architectural design of the towers, like in the Gaudi’s Sagrada Familia chapel, growing in Barcelona since 1884. A scaling factor of $10^{10}$, separating the objects on the left and right columns does not prevent the validity of macroscopic engineering insight in the molecular world.

Fig. 3.1: Ab initio results for the total strain energy in eV per atom as a function of the tubule diameter, $d$, for C- (solid circle), BC$_3$- (solid triangle) and BN- (open circle) tubules. The data points are fitted to the classical elastic function $1/d^2$. The inset shows in a log plot more clearly the $1/d^2$ dependence of the strain energy for all these tubes (see text for discussion). We note that the elasticity picture holds down to subnanometer scale. The three calculations for BC$_3$ tubes corresponds to the (3,0), (2,2) and (4,0) tubes (adapted from (Blase, 1994, Miyamoto, 1994a,b, Rubio, 1994,1996)).

Fig. 3.2: Left: Young modulus for armchair and zig-zag carbon and BN nanotubes. The values are given in the proper unit of TPa nm for SWNTs (left axis), and converted to TPa (right axis) by taking a value for the graphene thickness of 0.34nm. The experimental values for carbon nanotubes are reported on the right-hand-side: (a) 1.28 TPa (Wong, 1997); (b) 1.25 TPa (Krishnan, 1998); (c) 1 TPa for MWNTs (Muster, 1998). Right: Young modulus versus tube diameter in different arrangements. Open symbols correspond to the multi-wall geometry (10-layer tube with an interlayer distance of 0.34 nm), and solid symbols for the single-wall-nanotube crystalline-rope configuration. In the MWNT geometry the value of the Young modulus does not depend on the specific number of layers. The experimental value of the $c_{11}=1.06$ TPa elastic constant of graphite is also shown (adapted from (Sánchez- Portal, 1999)).

Fig. 3.3. TEM micrographs of multiwall carbon nanotubes under compression. The slender tube behaves as a classical rod that under the applied force buckles forming bends (a) and loops (b). (c) For high bending, the nanotube collapse to form kinks on the internal compressed side of the bent (From (Lourie, 1998) with permission.)
**Fig. 3.4:** A) Bright field TEM images of free-standing multi-wall carbon nanotubes showing the blurring of the tips due to thermal vibration (from 300 to 600 K). Detailed measurement of the vibration amplitude is used to estimate the mechanical properties of the nanotubes. B) Same micrographs for single-wall nanotubes at room temperature. Inserted with each micrograph is the simulated image corresponding to the best-squares fit adjusting the tube length $L$, diameter $d$ and vibration amplitude $\tilde{d}$. The results are a) $\tilde{d} = 0.33$ nm, $L = 36.8$ nm, $d = 1.5$ nm, $Y = 1.33 \pm 0.2$ TPa; b) $\tilde{d} = 0.18$ nm, $L = 24.3$ nm, $d = 1.52$ nm, $Y = 1.20 \pm 0.2$ TPa; c) $\tilde{d} = 0.30$ nm, $L = 23.4$ nm, $d = 1.12$ nm, $Y = 1.02 \pm 0.3$ TPa. The averaged measured Young modulus for tubes ranging between 1.0 to 1.5 nm in diameter is 1.25 TPa. (From Treacy, 1996; Krishnan, 1998) with permission.

**Fig. 3.5:** SFM image of a MWNT with a length of 850 nm and a height of 8 nm. By assuming an inner tube diameter between 0.7 nm and 2 nm and a shell distance of 0.34 nm, the number of shells is estimated to 8 - 10. The bending of the tube over the two electrodes is stressed by the corresponding 3-dimensional plot. The electrode lines are 100 nm apart, 80 nm wide and 14 nm in height. A cross sectional analysis along the tube axis is given in Fig. 4c (full line), with the broken line representing the profile of the underlying electrodes (Adapted from (Muster, 1998) with permission.)

**Fig. 3.6:** A) Bending modulus ($E_b$) for multi-wall nanotubes as a function of diameter for carbon nanotubes measured by the resonant response of the nanotube to an alternating applied potential (the inset shows the Lorentzian line-shape of the resonance). The dramatic drop in $E_b$ is attributed to the onset of a wavelike distortion, which is the favorable bending mode for thicker nanotubes. D) High-resolution TEM of a bent nanotube with a curvature radii of 400 nm exhibiting a characteristic wavelike distortion. (B and C) are magnified views of a portion of D (from Poncharal, 1999) with permission.

**Fig. 4.1:** Simulation of a (7,7) nanotube exposed to axial compression, $L = 6$ nm. The strain energy (a) displays four singularities corresponding to shape changes. At $\epsilon_1 = 0.05$ the cylinder buckles into the pattern (b), displaying two identical flattenings—"fins" perpendicular to each other. Further increase of $\epsilon$ enhances this pattern gradually until at $\epsilon_2 = 0.076$ the tube switches to a three-fin pattern (c), which still possesses a straight axis. In a buckling sideways at $\epsilon_3 = 0.09$ the flattenings serve as hinges, and only a plane of symmetry is preserved (d). At $\epsilon_4 = 0.13$ an entirely squashed asymmetric configuration forms (e). From (Yakobson, 1996a).
Fig. 4.2: The critical strain levels for a continuous, 1 nm wide shell-tube as a function of its scaled length L/N. A buckling pattern (M,N) is defined by the number of halfwaves 2M and N in y and x directions, respectively, e.g., a (4,4)-pattern is shown in the inset. The effective moduli and thickness are fit to graphene. From (Yakobson, 1996a).

Fig. 4.3: Simulation of torsion and collapse (Yakobson, 1996b). The strain energy of a 25 nm long (13,0) tube as a function of torsion angle $\phi$ (a). At first bifurcation the cylinder flattens into a straight spiral (b) and then the entire helix buckles sideways, and coils in a forced tertiary structure (c). Collapsed tube (d) as observed in experiment (Chopra, 1995).

Fig. 4.4: HREM images of bent nanotubes under mechanical duress. (a) and (b) single kinks in the middle of SWNT with diameters of 0.8 and 1.2 nm, respectively. (c) and (d) MWNT of about 8nm diameter showing a single and a two-kink complex, respectively (From (Iijima, 1996), with permission.) The critical local curvature at which the kink forms is independent of the length of the tube.

Fig. 5.1: High strain rate tension of a two-wall tube begins from the outmost layer, nucleating a crack precursor (a), where the atomic size is reduced to make the internal layer visible. Eventually it leads to the formation of monoatomic chains (b). From (Yakobson, 1997a).

Fig. 5.2: Stone-Wales (SW) dipole imbedded in a nanotube hexagonal wall (Terrones, 1996).

Fig. 5.3: SW-transformations of an equatorially oriented bond into a vertical position creates a nucleus of relaxation (top left corner). It evolves further as either a crack – brittle fracture route, left column – or as a couple of dislocations gliding away along the spiral slip “plane” (plastic yield, top row). In both cases only SW rotations are required as elementary step. The stepwise change of the nanotube diameter reflects the change of chirality, bottom right image (causing the corresponding variations of electrical properties). Formation of a next SW defect can continue the necking process, unless the dislocations pile-up at insufficient temperature.

Fig. 5.4. (Color) Kinetic mechanism of 5/7/7/5 defect formation from an ab-initio quantum mechanical molecular dynamics simulation for the (5,5) tube at 1800 K (Buongiorno-Nardelli, 1998). The atoms that take part in the Stone-Wales transformation are highlighted in red. The four snapshots show the various stages of the defect formation, from top to bottom: system in the ideal configurations (t = 0 ps); breaking of the first
bond \( t = 0.10 \text{ ps} \); breaking of the second bond \( t = 0.15 \text{ ps} \); the defect is formed \( t = 0.20 \text{ ps} \).

**Fig. 5.5.** (Color) \( T = 3000 \text{ K}, \) strain 3\%, plastic flow behavior (about 2.5 ns). The shaded area indicates the migration path of the 5/7 edge dislocation.

**Fig. 5.6.** (Color) Red area: region of complete ductile behavior, where the formation of 5/7/7/5 defects is always favored under sufficiently large strain. White area: moderately ductile region, where tubes are ductile but the plastic behavior is limited by the brittle regions near the axes. The initial ductile behavior will eventually change the indexes to the vicinity of the zig-zag symmetry, where the tubes are completely brittle. Green area: the formation energy of the 5/7/7/5 defect is still negative, but other cracks are observed during molecular dynamics simulations. Blue area the 5/7/7/5 defect always has a positive formation energy and no plastic flow of dislocations is energetically favored to occur (from Buongiorno-Nardelli, 1998).

**Fig. 6.1:** SEM micrograph of a) network of SWNT aggregates collapsed on the surface of a fractured nanotube-epoxy composite. b) SWNT bundles stretched across cracks observed in a nanotube-carbon composite pellet for a certain critical crack width of about 1 micron. c) Curved bundles of SWNT that are no longer under load, as observed in a SEM image. (from Ajayan, 2000) with permission.
Torque $\phi$, radians

a)

b)

c)
plastic flow possible
armchair tubes
brittle region A
brittle region B
completely ductile region
moderately ductile region
zig–zag tubes
The graph shows the relationship between armchair and zig-zag tubes in terms of plastic flow possible. The graph is divided into regions:

- **Completely ductile region** (red)
- **Moderately ductile region**
- **Brittle region A** (green)
- **Brittle region B** (blue)

The x-axis represents the m index, and the y-axis represents the n index. The diagonal line indicates the boundary between armchair and zig-zag tubes. The shaded areas represent regions where plastic flow is possible.
Fig. 2: Treacy, Ebbesen & Gibson