Carbon Nanotubes Literature Review

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Introduction

This annotated bibliography has been created to summarize a collection of articles in the area of carbon nanotubes. The focus of this work has been on the mechanical properties of carbon nanotubes and their use in polymer composites; however, sections on fabrication, atomistic models, electrical properties, and other phenomena have been included for completeness. The last section contains miscellaneous notes collected from the readings included in this work. In most instances, these documents have been grouped according to the primary thrust of the article. In some cases, an article may be referenced under more than one heading.

These article summaries were compiled from notes taken from the readings, and in many cases are biased according to the research interests of the author. The authors take no responsibility for these annotations, and readers are encouraged to use this list only as a way to identify relevant literature for their personal research.

Fabrication of carbon nanotubes

Cui, Zhou and Stoner. 2000.

Table of most common NT production methods.

Arc discharge method	Chemical vapor deposition	Laser ablation (vaporization)
Ebbesen and Ajayan, NEC, Japan 1992	Endo, Shinshu University, Nagano, Japan	Smalley, Rice, 1996
Connect two graphite rods to a power supply, place them millimeters apart, and throw switch. At 100 amps, carbon vaporizes in a hot plasma.	Place substrate in oven, heat to 600 C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield = 30%	20 to 100 %	Up to 70%
Can produce SWNT and MWNTs with few structural defects	Easiest to scale to industrial production; long length	Primarily SWNTs, with a large diameter range that can be controlled by varying the reaction temperature
Tubes tend to be short with random sizes and directions	NTs are usually MWNTs and often riddled with defects	By far the most costly, because requires expensive lasers

Shi, Lain, Liao, Zhou, Gu et al. 2000.

NTs can be grown efficiently by the catalytic decomposition of a reactive gas that contains carbon, with iron often being used as the catalyst. The process has two advantages:

1. NTs obtained at a much lower temperature (although at the cost of lower quality).
2. Catalyst can be grown on a substrate, allowing novel structures to be obtained.

It is now known that the Young's modulus should approach 1.25 TPa. This is true for both SWNT and MWNTs, and is determined mostly by the carbon-carbon bonds in the nanotubes. Salvetat and coworkers found modulus of arc-grown NTs about 1 TPa, whereas those grown by catalytic decomposition of hydrocarbons are smaller by 1 or 2 orders of magnitude.

Gennett, Dillon, Alleman, Jones, Hasoon et al. 2000.

Deposition of aligned bamboo-like carbon nanotubes via microwave plasma enhanced chemical vapor deposition. Their research is in the area of field emission and field-enhanced ionization properties of the CNTs. Their work suggests that CNTs form via a continual growth and renucleation mechanism that is taking place. There appear to be two competing processes: the growth of the multiwalled segments, and renucleation of subsequent segments

Smith, Benes, Luzzi, Fischer, Walters et al. 2000.
Large-scale synthesis of SWCNT by the arc discharge method yielded quantities of tens of grams a day under arc conditions of 40~60 A d.c. and helium pressures of 500 to 700 torr. Results show that helium atmosphere strongly affects the yield of SWNTs, and that the diameter distribution of the SWNTs is affected by the catalyst.

Peng, Wang, Zheng, Lifshitz, Kulik et al. 2000.
SWNTs exist in a random tangle because of the conditions under which they are synthesized and purified; they are formed within the high temperature plasma and then rapidly quenched. They found that through ultrasound and polar solvents it is possible to unwind the intertwined SWNT bundles. This results in realignment and collapse of the SWNTs into the much larger superbundle configuration. Superbundles are between 0.4 and 1.0 μm in diameter (roughly 30 times greater than previously observed) and 5-10 μm in length. The superbundle configuration evidently arises from the minimization of the interactions between hydrophobic SWNT surfaces and the polar solvent such that the VDW interactions along the axial length of the tunes are maximized. They estimate that virtually all of the tubes are aligned within 20 degrees, and a vast majority are aligned within 10 degrees. The degree of alignment is expected to improve as the density is increased. In a superbundle the number of NTs in a pure bundle was increased from several hundred to several thousand.

Bower, Zhu, Jin and Zhou. 2000.
Thick films of aligned SWNT and ropes have been produced by filtration/deposition from nanotube suspensions in strong magnetic fields. Aligned films are denser than ordinary filter-deposited films, and much denser than as-grown materials. Ropes in these films lie preferentially in the plane of the film, while the addition of the strong magnetic field introduces a preferred direction in the plane, as verified in SEM images. Found that 30% of the aligned NT material is empty volume, a much smaller percentage than it typically found in aligned buckypaper (~70-90 %) or in compacts of as-grown material (~95%). The important point is that partial alignment about two axes should produce a large density increase with respect to no alignment (which would also be true for NT-reinforced polymers).

Vigolo, P nicaud, Coulon, Sauder, Pailler et al. 2000.
MASS-SELECTED CARBON ION BEAM DEPOSITION (MSIBD) is a newer technique that takes place at an elevated temp, but much lower than used in conventional methods. Combination of the stress induced by the ion impact and the C migration formed graphitic sheets with their normal (c axis) parallel to the surface of the silicon substrate. Some sheets closed to form MWNTs – the smallest diameter of the innermost tube was found to be 0.4 nm. The smallest diameter of carbon NTs reported (very recently) is 0.5 nm, which corresponds to a C36 molecule. Theoretical calculations indicate that carbon NTs with a diameter of 0.4 nm are possible since they have lower energies than the graphene sheet. This diameter matches a C20 fullerene.

The advantages of this (MSIBD) method over conventional methods, not including mechanical properties:
1. high purity with no catalyst needed
2. simple applicability to most surfaces without pretreatment
3. low deposition temperature
4. simple controllability of the NT size, structure, and orientation
5. patterning and writing options

Conventional methods of carbon NT production (all performed at high temperatures (~800-1000 C) and are difficult to directly apply on a surface to control):
1. Arc discharge (Ebbesen 1992)
2. Thermal deposition (Endo, 1995)
3. Chemical vapor deposition (Qin 1997, Kong, 1998)

Wei, Zhang, Ramanath and Ajayan. 2000.

Uniform films of well-aligned CNTs grown using microwave plasma-enhanced CVD. CNTs can be grown on contoured surfaces. The alignment is induced by the electrical self-bias, so switching the plasma field off leads to a transition between straight and curvy NTs. NTs grew at a rate of 100 nm/s. NTs grew about 30 nm in diameter, and about 12 μm long. Spacing between islands measured to be 150 nm, corresponding to a density of NTs of 4.4×10^9 NTs/cm^2. NTs aligned to within 8% of the surface normal. Show the growth of NTs on an optical fiber (diameter of 125 μm). NT grows from the base (i.e. like human hair). Nucleation and growth of CNTs via microwave plasma chemical vapor deposition. Figure 1 shows that you get very different MWNTs depending on the thickness of the catalytic (cobalt) islands – from thin, uniform tubes to thick, short, curvy MWNTs. It is essential to have NT materials with controlled diameter, length, orientation, location, and microstructure. Although laser ablation method can produce high quality SWNTs with some control in diameter and electronic props, the process is not compatible with conditions required for device fabrication. Their results suggest that maybe SWNTs could be produced if the islands could be made small enough. NTs were typically composed of 20-40 concentric graphene sheets. Many of the NTs had "bamboo-like" defects along their length (~50%).

Cohen, Rein, Vaykhansky and Porter. 1999.

Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes; they show incredible pictures of large tubes showing actually tied in knots! Process: disperse NTs in a surfactant solution, re-condense the NTs in the flow of a polymer solution to form a NT mesh, collating this mesh to a NT fiber. Flow-induced alignment may lead to preferential orientation of the NTs in the mesh. The process uses SDS (sodium dodecyl sulfate), a surfactant that absorbs at the surface of the NT bundles. At low concentrations, the amount that was used was too low to produce an efficient coating and induce electrostatic repulsions that could counterbalance the vdW interactions. At too high of concentrations, suspensions occurred and the material was multiple phase. At intermediate concentrations, the SWNTs were homogeneously dispersed and formed a single phase. Ribbons were washed and the additives desorbed. From this material they made fibers with diameters ranging from a few micrometers to 100 μm. The SWNT

fibers exhibit plastic flow at RT before they break, possibly from the displacement of the NTs within the fibers. In the elastic regime found that the E ranged from 9 to 15 GPa – although far weaker than the modulus of individual NTs, an order of magnitude greater than that of high-modulus bucky paper.

Che, Lakshmi, Martin and Fisher. 1998.

Controlled synthesis of vertically aligned carbon nanotube patterns, grown under patterned metal layers on silicon substrates by combining chemical-vapor deposition and conventional lithography. We show that the metal patterns lift up by vertically aligned nanotubes during growth. This lift-up growth links the thin-film metal patterns and the silicon substrate via nanotube assemblies, giving the possibility of creating nanotube architectures in 3 dimensions.

Dresselhaus, Dresselhaus, Eklund and Saito. 1998.

An economic way to produce massive CNT arrays is the CVD process using a precursor of a carbon source and a metal catalyst containing metallocene. This method does NOT require predeposition of the catalyst and tubes grow everywhere on the substrates. If one needs to adapt this method to growing NTs in well-specified locations on the substrate (for example, for field emission and other device applications), then the idea of substrate-site selectivity needs to be explored.

Journet, Maser, Bernier, Loiseau, de la Chapelle et al. 1997.

Developed a new approach for preparing graphitic carbon nanofiber and nanotube ensembles entailing chemical vapor deposition (CVD) based synthesis of carbon within the pores of an alumina template membrane, with or without a Ni catalyst. CVD is a versatile process in which gas-phase molecules are decomposed to reactive species, leading to film or particle growth. Two advantages of CVD methods are the ability to controllably create films of widely varying stoichiometry, and to uniformly deposit thin films of materials, even onto non-uniform shapes. The authors' primary interest is in the production of a material that could be used as the anode in a rechargeable lithium nanobattery.

Yakobson and Smalley. 1997.

Rice group used laser vaporization of carbon target, with a cobalt-nickel catalyst, and achieved 70-90% efficiency. They used two laser pulses 50 ns apart so that the growth conditions can be maintained over a larger volume and for a longer time. This method of NT production has had the largest impact on the field.

Thess, Lee, Nikolaev, Dia, Petit et al. 1996.

Electric-arc technique to make SWNTs close-packed in bundles. High-yields (70-90%) of SWNTs close-packed in bundles can be produced by laser ablation of carbon targets. The method (electric-arc) used here is cheaper and easier, but previously had only low

yields of NTs. They show that it can generate large quantities of SWNTs with characteristics similar to those obtained by laser ablation. Synthesis times for their method is 2 minutes. Fig 1 shows large amounts of entangled carbon filaments in the collar deposit, homogeneously distributed over large areas (here at least a few millimeters) and with diameters ranging from 10 to 20 nm. Average length between entanglement point is several μm (although they are not sure of the nature of the crosslinks). Say that the bundle formation is the same as that made using the Thess (with Smalley, Rice) technique, but they don't compare the mechanical properties.

Smith and Luzzi. 2000.

Although various fullerenes can be produced using different ways of vaporizing carbon, followed by condensation of the tiny clusters, the presence of an electric field in the arc discharge seems to promote the growth of the long tubules. In addition, a small amount of transition metal powder (i.e. cobalt, nickel, or iron) seems to favor growth of SWNTs. Here the metal clearly serves as a catalyst, preventing the growing tubular structure from wrapping around and closing into a smaller fullerene cage. The presence of the catalyst also allows one to lower the operating temperature.

The carbon atoms in an NT, neglecting the ends, have 99.4% of the cohesive energy that they would have in perfect crystalline graphite. This is far better than the amount of cohesive energy that would be found in C60. If feeding a cheap hydrocarbon such as ethylene to the NT ever becomes possible, buckyropes will grow, and grow inexpensively, in industrial laboratories.

Salvetat, Kulik, Bonard, Briggs, St ckli et al. 1999.

Fullerene SWNTs were produced in yields of more than 70% by condensation of a laser-vaporized carbon-nickel-cobalt mixture at 1200C . X-ray diffraction and electron microscopy showed that these SWNTs are nearly uniform in diameter and that they self-organize into "ropes", which consist of 100 to 500 SWNTs in a 2D triangular lattice with a lattice constant of 17A. The optimum diameter of the nanotube is determined by competition between the strain energy of curvature of the graphene sheet and the dangling-bond energy of the open edge, where growth occurs. With only a single laser, the yield was typically only 50 to 60%. When looking at the edge of an NT rope, all of the NTs end within a few nm of each other length-wise; this could possible be because of VDW forces at the ends or due to the growth mechanism. The results led them to propose the scooter method of nanotube growth.

Structure of carbon nanotubes

Venkateswaran, Rao, Richter, Menon, Rinzler et al. 1999.

C60 molecules are seen to deposit on the surfaces of SWNTs from the gas phase and to enter the tubes, ostensibly via defects. They subsequently self-assemble into VDW interacting chains, called bucky-peapods. Material was PLV (pulse-laser vaporized). They exist naturally, albeit in low concentrations. Large (~3nm) diameter tubes are observed to contain irregularly arranged clusters of C60 near their ends, because for the large diameter NTs the energy is minimum at the interior walls. It is conceivable that at the higher temperatures, neighboring C60 molecules have a reasonable probability of colliding with sufficient kinetic energy to cause them to coalesce within the time frame of the experiment. The surrounding 1.4nm NT thus acts as a reaction container, templating the fused product into a 0.7nm diameter NT. The process has min and max temperature; 325 because C60 needs to diffuse within the NT in a reasonable time scale, and a maximum temperature because the C60 needs to be on the surface of the NT long enough to find a defect to enter the interior. Thus need to soak the SWNTs at a middle temperature. This may be useful to get other types of interior species.

Setlur. 1999.

Point defects may be present in the graphitic planes, but they should be removed to a great extent by high temperature annealing. The advantage of the catalytic process is that it can yield an almost continuous production of long nanofibers. However, catalytic reactions may produce only ordered NTs containing structural defects, which are expected to have weaker the mechanical properties. We found that although the elastic properties of NTs are scarcely affected by the presence of point defects, extended stacking defects and disorder can reduce the elastic modulus by orders of magnitude. Furthermore, since point defects are believed to be present in as-grown MWNTs, arc-grown tubes were also studied after high temperature annealing at 2500C to investigate the influence of the reduced point defect density on the elastic modulus. Disordered NTs were produced by catalytic methods; in this case, the NTs show a high density of structural defects. Furthermore, there is no apparent difference between the annealed and unannealed NTs, suggesting that point defects, if present at all, do not affect the mechanical properties of the MWNT. This is in strong contrast to the values measured for the catalytic NTs: E ranged from 10 to 50 GPa. The disorder in the NTs thus considerably influences the elastic properties. Note that the annealing of catalytic disordered tubes at 2500C yields well-ordered MWNTs with a structure similar to those obtained by the arc-discharge method. Measurements performed on such samples revealed a strong increase in the elastic modulus of at least an order of magnitude - although the results not included in this paper, because the MWNT was so stiff that couldn't get measurable deflection. They chose to work with particularly poorly disordered NTs, but people are working on CVD methods with fewer defects and hence better mechanical properties.

Smith, Monthioux and Luzzi. 1999.

Probing the single-wall carbon nanotube bundle using Raman scattering under high pressure. Looked at change in the Raman scattering cross section due to a hexagonal distortion in the cylindrical cross section of the tubes in the bundles under compression. Material: Both the pulsed vaporization and electrical arc technique used to produce SWNT bundles (or ropes) consisting of several hundred SWNT arranged in a 2D triangular lattice. A comparison of our MD calculations and the experimental data suggest that the intertube VDW coupling and the details of the hexagonal distortion in the tube cross section play an important role in determining the frequency and pressure dependence of the R mode in SWNT bundles. Also, the reappearance of the vibrational modes upon releasing the pressure indicates that the SWNT bundles are resilient under compression to at least 5 GPa.

Kiang, Endo, Ajayan, Dresselhaus and Dresselhaus. 1998.

SWNT ropes are typically closest packed, although there are situations where there are missing tubes. They tend to self-assemble into these ropes (or bundles) due to the van der Waal interactions between individual ropes within the bundle. Arc discharge is the most common method of MWNT production. Current production rates about 10 g/day. But the arc is a batch process; you need to replace the anode and collect the deposit from the cathode, and there are many extra products that need to be filtered away.

Venema, Wild er, Dekker, Rinzler and Smalley. 1998.

Report of elongated fullerene capsulates contained within an SWNT. These encapsulates may give properties (particularly transverse properties) different from that of the bulk tube. The limit of the SWNT as the inner capsulate major axis goes to infinity is a MWNT.

Saito, Yoshikawa, Bandow, Tomita and Hayashi. 1993.

Study of the intershell spacing using high-resolution TEM images; spacing found to range from 0.34 to 0.39 nm, increasing with decreasing tube diameter. Larger spacing for smaller diameter is attributed to the high curvature, resulting in an increased repulsive force, associated with the decreased diameter of the NT shells. Equation for the intershell spacing:

$$\hat{d}_{002} = 0.344 + 0.1e^{-D/2}$$

Size effect is most profound in the small diameter region (D < 10 nm), where each additional shell results in a measurably different spacing. This could also result in different physical and chemical properties – for example, NTs of larger intershell spacing should be less stable and, therefore, more reactive.

Yu, Kowalewski and Ruoff. xxxx.

Obtained atomically resolved STM images of individual SWCNTs. The interpretation of the apparent lattice is nontrivial, in most cases they observed a triangular lattice instead of the expected hexagonal carbon lattice. They are also able to determine the chirality of the tubes, something that has not been done before. It is well known that the hex lattice of bulk graphite often appears triangular in STM images, although this effect is

attributed to multiple layers and 3D stacking. But after separation of the 3D layers, hex lattice is observed; this can't be the case for a SWNT since there are no layers. This issue left unresolved in this article.

Ru. 2000b.

The value of 0.34nm spacing in the bulk graphite crystal is *approximately* that of the NTs. But a closer study revealed that the mean value of the interlayer spacings is 0.3444 ± 0.001 nm; the values in NT are larger, by a few percent, than those in the bulk graphite crystal.

Mechanical properties of carbon nanotubes

Yu, Kowalewski and Ruoff. 2000.
Collapsed section of a MWCNT significantly more flexible than the uncollapsed section and advanced 120 nm within one month due to thermal activation. The ability of the CNT to deform radially is in contrast with their high axial rigidity, which is why they can be reversibly beyond the point of buckling.

Gao, Wang, Bai, de Heer, Dai et al. 2000.
The bending modulus of CNTs from aligned arrays grown by pyrolysis was measured by in situ electromechanical resonance in TEM. Bending modulus of NTs with point defects was approximately 30 GPa, and that of NTs with volume defect was about 2-3 GPa. Also demonstrated a fentogram nanobalance (10^{-15} g). There is strong evidence that all layers of a MWCNT are stressed in compression, whereas only the outer walls are stressed in tension.

Wang, Poncharal and de Heer. 2000.
Experimental values of the Young's modulus in the radial direction: 0.3 to 4 GPa. This is on the order of magnitude of semicrystalline polymers such as low density PE (E = 0.2 GPa) and polyamide (E = 1.9 GPa). This is related to the value of C_{33} in graphite of 36.5 GPa, where C_{33} refers to the response to a load perpendicular to the basal plane, i.e. the transverse direction. This value is smaller than that for graphite because it is hollow.

Li, Cheng, Bai, Su and Dresselhaus. 2000.
Bending modulus of pyrolytically grown CNTs with point defects was about 30 GPa. For CNTs with volume defects, bending modulus was 2-3 GPa. From earlier work, NTs with diameters larger than 30 nm had a bending modulus of about 200 GPa. For the chemically grown NTs, they found a bending modulus of about 30 GPa, mainly due to point defects in the latter. Also saw really good creep properties of the CNTs, there was no visible change in behavior with 2.575×10^9 cycles.

Harris. 1999.
There are 3 keys in the development of nanoscience and nanotechnology: materials preparation, property characterization, and device fabrication. MATERIAL: NTs produced by arc-discharge technique, with diameters of 5-50 nm and lengths 1-20 μm. Resonance is NT selective because the natural vibration frequency depends on the tube diameter, length, density, and bending modulus. One problem is that this assumes that the tube is isotropic. The resonance frequency drops by up to 40% with the addition of a small mass at the tip. The bending modulus has been measured as a function of its diameter. It is as high as 1.2 TPa (as strong as diamond) for NTs with diameters < 8 nm, and it drops to as low as 0.2 TPa for those diameters > 30 nm. A decrease in

bending modulus as the increase of the tube diameter is the result of the rippling effect of the NT.

Pan, Xie, Lu, Chang, Sun et al. 1999.

Tensile strength (not modulus) of 20 mm long ropes consisting of soundly aligned SWNT ropes, made by catalytic decomposition of hydrocarbons, were employed in direct tensile strength measurements. The average tensile strength of SWNT rope composites is as high as 3.6 ± 0.4 GPa, similar to that of carbon fibers. The tensile strength of SWNT bundles was extrapolated to be 2.3±0.2 to 14.2±1.4 GPa by taking into account the volume fraction of SWNT bundles in the mini-composite. Tensile strengths of single SWNT estimated to be as high as 22.2±2.2 GPa. The ropes consist of roughly aligned bundles, which consist of well-aligned SWNTs. They impregnated the aligned SWNT ropes with PVC resin to form a mini-composite structure with a gage length of 10 mm. The mechanical properties of the SWNTs were characterized through a combination of experimental measurements and modeling prediction for the composite material. Results indicate that SWNT ropes, in fact, have a very high strength, similar to carbon fibers, even though the bonding between the bundles is quite poor. A SWNT bundle can be regarded as a triangular crystal and the distance between the SWNTs is 0.315 nm.

Zhang, Lammert and Crespi. 1998.

Graphite whiskers have diameters of approximately 5 µm, lengths up to 3 cm, 20 GPa tensile strength, and 800 GPa Young's modulus. However, there is a high cost and low yield, so they are hardly used in practice. They are not closed structures like nanotubes, but are more scroll-like in structure.

For catalytically grown carbon fibers, you can readily see the size effect:

Diameter	Tensile Strength (GPa)	Young's modulus (GPa)
40 µm	1	170
10 µm	25	350

Wagner, Lourie, Feldman and Tenne. 1998.

Directly measured the E and tensile strength of MWCNTs made by CVD by pulling on very long (~2 mm) ropes with a tensile tester. Found E of 0.45 ± 0.23 and tensile strength of 1.72 ± 0.64 GPa. The "ropes" (not the same sense as usually used in the literature, these are more like strands, many of which are not initially taut) contain tens of thousands of well-separated parallel tubes. The tubes had an ID and OD of 12 and 30 nm, respectively, and spacing of about 100 nm between the tubes. To account for this spacing, they use the effective cross sectional area. They treat the NTs (because isolated) as parallel resistors of conductance 1/R – by measuring this value, they estimate the rate at which the tubes break. They measured the tensile strength of the ropes to be an order of magnitude lower than that of graphite whiskers. They simplify the stress transfer; even though the fiber breaks, it can still transfer the stress; it only matters when the tubes start breaking at the same "location" so that there are too few

at a given x to hold the load, and they all break. Once an NT breaks, it can still be useful away from the break.

Lu. 1997.

Although the elastic properties of a carbon nanotube are nearly independent of wrapping indices, we show that the onset of plastic deformation depends very strongly on the wrapping index. An (n,0) NT has an elastic limit nearly twice that of an (n,n) tube with the same radius. If the tube is under stress, defects relieve strain and constitute a fundamental mode of plastic deformation. The efficiency of this strain release depends on the alignment between the defect and the tube axis. For example, virtually no strain is relieved if the bond is initially orientated $\pi/4$ from the circumference. They use tight-binding MD to investigate the plastic deformation of carbon NTs under strain. Just as the critical force s very sensitive to the wrapping angle, so the critical strain varies from about 6% for a (6,6) tube to 12% extension for a (12,0) tube. The defect concentration increases most rapidly in the (n,0) tubes, since in these tubes each individual defect is less efficient in relieving strain. This work suggests that there is a big difference in the way that tubes of different chirality may deform plastically.

Schadler, Giannaris and Ajayan. 1998.

Experimentally estimated that the tensile stress at fracture in the NT was ~ 55 GPa, based on polymer-NT specimens and assuming that the stress is transferred to the NT via the interface shear mechanism. Recent unpublished experiments provide estimates of 150 GPa for the compressive strength of MWCNTs.

Wong, Sheehan and Lieber. 1997.

There is the possibility of very high tensile strength of CNTs, maybe as high as 200 GPa *Falvo, Clary, Taylor II, Chi, Brooks Jr et al. 1997.*, or the order of 100 GPa. For comparison, the tensile strength of high-strength tool steel is 2.345 GPa. Another exciting possibility is that the spacing is 1.42A in graphene (lattice spacing in SWNT crystal), whereas it is 1.54A in diamond. This suggests that NTs could be stronger than diamond. However, the problem is that the NTs are hollow. So a possibility is that you get the same overall properties, only that NTs have a smaller density because they are hollow. Maybe this is why RIBBONS will make the best for mechanical properties, because they are not hollow.

Chopra, Benedict, Crespi, Cohen, Louie et al. 1995.

Lateral displacement via AFM of nanomaterials (SiC nanorods and MWCNTs) along a substrate to determine the mechanical properties. MWCNTs twice as stiff, and had an elastic buckling process. But because of buckling, the ultimate strength of MWCNTs was LESS than that of the SiC, suggesting the use of MWCNTs as uniquely tough energy absorbing material. Found E of MWCNTs to be 1.38 $\pm$ 0.59 TPa, as compared to 610 GPa for the SiC. Bending strengths of 14.2 $\pm$ 8.0 GPa for MWCNTs, with a maximum of

28.5 GPa. For SiC the largest bending strength was 53.4 GPa, which is approaching the predicted maximum of 0.1 E.

Ruoff and Lorents. 1995.

Although the high stiffness of CNTs is predicted to provide an improvement over existing materials, it is the NT's unusual strength that is its most distinguishing property. This arises from its high stiffness combined with extraordinary flexibility and resistance to fracture. Also show a nice picture of a tube being bent through 180°. Maximum strain found in the samples was 16%, with no failure.

Tersoff and Ruoff. 1994.

The material used was carbon NTs that were prepared by a carbon-arc discharge method. Every fully collapsed NT that we observe contains at least one twist. This may be evidence that the twists are the origin of tube collapse. Alternatively, it may be that the NTs are prone to twisting, much as any flat ribbon is more prone to twisting than a hollow cylindrical tube of the same material. In this paper, they estimate the energy per unit length of the VDW interaction as ~ 0.20 eV/Å^2.

Stahl, Appenzeller, Martel, Avouris and Lengeler. 2000.

Suggested that the thermal expansion of CNTs will be largely isotropic, which is different than conventional graphite fibers, which are strongly anisotropic. This may be beneficial for carbon-carbon composites. It is expected that low-defect CNTs will have very low coefficients of thermal expansion. Finds that classical continuum theory applied to NTs is quite reliable for predicting the mechanical and some of the thermal behavior of the tubes. Will probably want to use SWNTs in a composite, rather than MWCNTs, because want greater surface contact between the CNTs and the matrix. Bulk modulus of an ideal SWNT crystal proportional to $D^{1/2}$ for tubes of less than 1 nm diameter. For larger tubes, bulk modulus is independent of tube diameter and is quite low.

Chen, Xia, Peng, Li and Xie. 2000.

They discuss the ordered condensed phase of CNTs (as called in 1994); these are now known as ropes or bundles. Tubes 10Å and less in diameter behave as rigid cylinders. For diameters over 25Å, the tubes flatten against each other under the VDW attraction, forming a honeycomb structure. This structure exhibits an anomalous rigidity, which does not decrease as expected with increasing tube diameter, i.e. the rigidity doesn't decrease with decreasing density. Their calculations use a valence-force model to treat the atomic interactions within each tube. Because of the hex symmetry of a graphite sheet, its elastic properties are 2D isotropic, and so the helicity plays no significant role; this is a significant simplification. The cohesive energy of the NTs would control their tendency to unbind and disperse in the matrix, rather than stay together as bundles. For small D, one can understand this behavior in terms of VDW forces. At large D, however, this is not the case. You get strengthening as the CNTs deform into a more hexagonal shape. The modulus of the material is also highly nonlinear. Under

compression, the density decreases and so the modulus rapidly increases. For example, for a 40Å tube, a 1% linear compression gives a 20% decrease in density. This corresponds to a factor of 2 increase in the modulus.

Nanoelectronics and carbon nanotubes

Satishkumar, Thomas, Govindaraj and Rao. 2000.
Interesting paper that studied the coupling between individual tubes in a SWNT rope by introducing defects into the top tubes in the bundle and studying the effect on the resistance of the entire rope. Electronic structure usually characterized using scanning tunneling microscopy. One possible use of the NT is as a diode. They think that they obtained defects on the order of 1 defect per 1000 atoms (or, a distance of 5-10 nm along the tubes) via ion beam sputtering.

Hannson, Paulsson and Stafstr m. 2000.
Interested in coating CNTs via electroless plating. They put cobalt on the surface, useful for bonding with metal matrices; could also be useful in changing the electrical and magnetic properties. Material: MWNT via CVD; 10-30 nm diameter; 10 concentric tubes; ID and OD of 4.5 and 14 nm, respectively.

Andriotis, Menon and Froudakis. 2000.
Carbon nanotubes with junctions are considered to be of potential value in nanoelectronics; for such applications, it is important to be able to connect the NTs of different chirality and diameters. Nanotube fabrication was via a pyrolysis method.

Collins and Avouris. 2000.
For moderate bending, the overall current remains essentially unaffected. But for large bending, the π electron system becomes more disturbed, resulting in a marked decrease in the conductivity along the tube. Thus the electrical and mechanical behavior of the NT are coupled. A single carbon vacancy in the NT is shown to have a very small effect on the conductivity in the center of the metallic band, whereas by increasing the defect concentration the conductivity decreases in the same way as for strongly bent tubes.

Cumings and Zettl. 2000.
Bonding of the transition metal atoms on a single-wall CNT depends on the detailed contact conditions. They suggest that the early 3-elements (Sc, Ti, and V) can be expected to be good candidates for making metal-SWCNTs contacts of low resistance, while late 3-d elements are expected to exhibit large contact resistance. Work suggests that with the appropriate choice of the transition metal and the growing conditions of the TMA on the SWCNT, one may be able to prepare metal-SWCNT contacts with the desired value of contact resistance.

Yu, Kowalewski and Ruoff. 2000.
In a graphite sheet, one particular state (the Fermi state) gives graphite almost all of its conductivity; none of the electrons in the other states are free to move about. But you need the right combination of diameter and helicity to include this special Fermi point in

the subset of allowed states; if this is the case, you have metallic nanowires (1/3 of NTs). The other remaining 2/3rds are semiconductors – they do not pass current easily without an additional boost of energy. But this energy can be a burst of light or a voltage to knock electrons from valence states into conductance states that can move about freely. The amount of energy needed depends on the separation between the two levels and is the so-called band-gap of a semiconductor.

Theorists predict that a truly nanoscale switch could run at clock speeds of one terahertz or more – 1000 times as fast as the processors of today. Can also make diodes, where current only flows in one direction, by joining metallic and semiconducting NTs. Theorists have predicted that NTs would conduct heat nearly as well as diamond or sapphire, and preliminary results seem to confirm these predictions. Thus NTs could be used to cool electronic devices by drawing away heat. Latest measurements show that a bundle on NTs one square cm in cross section could conduct about 1 billion amps. Such high current would vaporize copper of gold.

Experimental properties of carbon nanotubes

Yu, Yakobson and Ruoff. 2000.
In some situations in SEM one can see the diameter of the tube changes as a function of length. This could be due to either shell separation in a MWNT, or due to tube-bundle separation in an NT rope. In the first case, this is termed "sword and sheath" failure (has also been seen in traditional carbon fibers), and has been hypothesized for use as extremely low-friction linear bearings. They have also demonstrated the vdW energy-based retraction force, which sucks an extended inner shell back into the MWNT. This force is independent of the contact area, such that it's a constant-force spring. Could be used to make super fast switches. Always see sliding between the same two shells, suggesting a self-selection process where the most perfect two shells slide with respect to one another.

Yu, Lourie, Dyer, Moloni, Kelly et al. 2000.
Tapping force AFM found reversible radial deformability up to 40%. Also hypothesized that they can use to figure out how many walls in a MWNT. Lots of work on tensile properties, but not many on the radial properties, although this may affect their electrical properties. Found that the kinks were much stiffer than the main parts of the tube.

Yu, Files, Arepalli and Ruoff. 2000.
Realize the sliding between nested shells, and estimated the shear strength between the individual and the surface energy shells estimated. Interface force F_i = 85 nN. Static shear interaction strength value of τ = 0.30 MPa; for comparison, that of graphite between 0.25 and 0.75 MPa.

Ajayan, Schadler, Giannaris and Rubio. 2000.
Tested the sword-and-sheath failure, and found that tensile strength from 11 to 63 GPa for 19 MWNTs. E of the outermost layer from 270 to 950 GPa. If assume that the 5-7-7-5 defect mechanism is used to release strain, the tensile strength will be a function of chirality because of how these defect structures are aligned relative to the tube axis. Also found an inverse relationship between Young's modulus and tensile strength, an affect that is also seen in conventional fibers.

Xie, Li, Pan, Chang and Sun. 2000.
Tensile loading of SWCNT ropes. Eight of them broke at strain values of 5.3% or *lower*. Force-strain data fit well by a model that assumes that the load is carried by the SWCNTs on the perimeter. Based on this model, the range of breaking strengths is (13,52) GPa with a mean of 30 GPa; for Young's modulus the range is (320,1470) GPa with a mean of 1002 GPa. They found that to maximize the number of perimeter

SWCNTs relative to interior ones, the ropes should have 10 SWCNTs per bundle. They see the diameter of the rope change, suggesting that not all tubes broke at the same time.

Poncharal, Wang, Ugarte and de Heer. 1999.

NTs were excited at the fundamental frequency and higher harmonics as revealed by their deflection contours, which correspond closely to those determines for cantilevered elastic beams. Estimate the lower limit of the shear modulus of SWNT rope (~1 GPa), in good agreement with recent AFM experiments on NT bundles.

Salvetat, Briggs, Bonard, Basca, Kulik et al. 1999.

Aligned and very long carbon NTs were prepared by CVD on various substrates. Large quantities of CNTs can now be produced by either the arc-discharge method or thermal decomposition of hydrocarbon. MATERIAL: CNTs with diameters of 7-30 nm, 20 µm in diameter, 1.95 mm total length, 0.92 mm free length. Most CNTs are straight, and others are curved due to the defects resulting from the low temperature (~700 C) growth of the tubes. Y and tensile strength of the thinner "ropes" of aligned MWNTs were obtained by pulling long (~ 2 mm) ropes contains ten thousands of aligned NTs with a specially designed puller. Note that these are not bundles, thus you get some "free" elongation because the NTs are not taut. It is well known that the strength probability distribution of the tubes in the rope obeys the Weibull distribution law. From this, the average strength of the tubes and the expected value of the tubes can be derived. Thus they find final values of Y ~ 0.45 TPa and tensile strength of 3.6 TPa. These are somewhat lower than those measure previously; defects in the tube walls and interwall slides within the MWNT may be responsible.

Salvetat, Kulik, Bonard, Briggs, St ckli et al. 1999.

NTs excited at the fundamental frequency; behavior closely approximates that of cantilevered beams. E found to sharply DECREASE with increasing diameter (8 to 40 nm). Found that a 20 nm tube can be bent elastically to a radius as small as 80 nm. Even with large amplitude cycling for 30 min (>10^9 cycles), found frequency drift < 1%. Different bending modes become prevalent at larger diameters, which is why there is a significant reduction in the bending modulus at higher diameters. Work (not here) has shown that 200 keV electron irradiation has increased the resonance frequencies (i.e. made the NT stiffer by introducing cross-linking).

Salvetat, Bonard, Thomson, Kulik, Forr et al. 1999.

By using AFM and a special substrate, the elastic and shear moduli of SWNT ropes measured to be on the order of 1 TPa and 1 GPa, respectively. This shear value for ropes is much less than that of MWNTs. Show that the SWNT ropes CANNOT be modeled as an assembly of free tubes, because gives huge values for the modulus; rather, the ensemble of tubes should be considered as an anisotropic beam. In nanoropes, we can expect a non-negligible contribution of shear even for long beams,

which will increase the deflection and lower the apparent value of E. From their model they obtained a decrease in G as the diameter increases (where they measure E and then back out G), because large diameter ropes may contain even more imperfections that smaller ropes. Would greatly increase the properties to be able to cross-link the individual tubes in the rope.

Salvetat, Kulik, Bonard, Briggs, St ckli et al. 1999.

Furthermore, there is no apparent difference between the annealed and unannealed NTs, suggesting that point defects, if present at all, do not affect the mechanical properties of the MWNT. This is in strong contrast to the values measured for the catalytic NTs: E ranged from 10 to 50 GPa. The disorder present in the NTs thus influences considerably the elastic properties. MWNTs are expected to be anisotropic in their elastic properties. For ordered arc-grown tubes, the radial elastic constant c11 was calculated to be about 1/3 of the axial elastic constant c33. In contrast, the elastic behavior of disordered tubes may involve shear deformation, which is sensitive to defects and dislocations. For a perfect graphite crystal, c44 equals 4.5 GPa, but it can also be as low as 0.18 GPa for pyrolytic graphite due to glissile basal plane dislocations.

Salvetat, Bonard, Thomson, Kulik, Forr et al. 1999.

Tapping mode AFM experimental work, found that the average E for 11 tubes was 810 ± 410 GPa, which should be taken as a minimum value.

Yu, Dyer, Skidmore, Rohrs, Lu et al. 1999.

Ruoff group has developed a 3D testing stage using scanning electron microscopy. SEM has several advantages over the more traditional atomic force microscopy (AFM method) without compromising the positional resolution. The AFM method is 2D, so it cannot evaluate the mechanical properties in real time, and is restricted to sample surfaces (so that you cannot probe the properties around the circumference of the tube).

Treacy, Ebbesen and Gibson. 1996.

Table 1 gives some values for length, ID, OD, and E from experimental tests on CNTs, but doesn't specify if they are SWNT or MWNT. The data is from 1996, measuring their intrinsic thermal vibration.

Atomistic models of carbon nanotubes

Girifalco, Hodak and Lee. 2000.

Looked at the VDW interaction between different graphitic materials (C60, NTs, etc.) All of these interactions fall on the same curve when graphed with respect to certain reduced parameters, suggesting a universal graphitic potential. Differentiates between two types of LJ models: the continuum model and the discrete atom model. Considering the typical high length of NTs, the total VDW interaction between tubes becomes very strong. Because of this effect, the NTs in the samples will orient themselves to be parallel whenever possible, therefore forming crystalline ropes.

Xin, Jianjun and Zhong-can. 2000.

Strain energies in straight and bent SWCNTs are calculated by taking account of the total energy of all occupied band electrons (without potentials?). The wall thickness of the SWNT comes completely from the overlap of electronic orbitals and is approximately of the extension of the π-orbital of carbon atoms. Both Young's modulus and wall thickness are independent of the radius and the helicity of the SWNT, and insensitive to the fitting parameters. Among most calculations, many depend on the empirical potential between carbon atoms, such as the Tersoff-Brenner potential. But they use a simple method of calculating the strain energy of straight and bent SWNTs *without* empirical potentials. Results show that classical elasticity theory can well describe the bending of SWNTs, and that the Young's modulus and the wall thickness are independent of diameter and helicity. They found E = 5.1 TPa, with wall thickness ~ 0.74A, the size of a carbon atom (similar to Bernholc – this formulation more useful in that it also describes bending behavior). Important distinction: in curved SWNTs, the bond length is nearly that of the graphite sheet, since the distortion that is creating the bending nature of the curved tube is topologically relaxed by the inclusion of 5- and 7-fold rings. However, the application of an external force moment at the two ends gives a different deformation. Thus, "curved SWNT" means an SWNT grown with pent/hept defects, whereas a "bent SWNT" is an SWNT that bends with outer-stretching and inner-compression deformations under external load. In a related work, Ou-Yang has developed a macroscopic continuous elastic model to calculate the curved SWNT. In their work, the strain energy of the curved SWNT comes from the angular change of the bonds or curvature of the tubes. However, in the case of bent SWNTs, the bond-length effect will contribute the main part of the strain energy.

Bharadwaj, Berry and Farmer. 2000.

Molecular dynamics simulation study of norbornene-POSS polymers. An appealing goal of polymer science is the development of polymer materials reinforced on the spatial scale of a few nanometers. They get Tg by plotting occupied volume versus Temperature (which may be pretty easy to do in a molecular dynamics simulation). All of their MD work used the Discover program employing the Compass force-field. They also look at predicting the mechanical properties using MD. Stiffening of the polymer

matrix is to be expected based on the higher Tg and the slowing of the conformational dynamics in the presence of the anchor-like entities.

Peters, McNeil, Lu and Kahn. 2000.

Interesting article. Authors use CELIUS2 software for MD work, to investigate the structural phase transition in CNT bundles under pressure. Material: SWNT laser ablation. Found that high-pressure effects are reversible, but only slowly.

Nardelli, Fattebert, Orlikowski, Roland, Zhao et al. 2000.

They can identify the full variety of elastic responses in strained NTs. They have a figure that shows different regions of elastic and plastic behavior depending on values for *n* and *m* of the chiral vector. They also talk about the effects of addimers, which may be present in small amounts or deposited with an STM tip or other method. While very high strain rates must lead to failure, NTs with (n,m) < 14 can display plastic flow under suitable conditions. This plastic flow occurs through the formation of a 5-7-7-5 defect, which then splits into two 5-7 pairs. This could potentially lead to metal-semiconductor junctions.

Yildirim, Gulseren, Kili and Ciraci. 2000.

Authors predict new forms of carbon consisting of one and two-dimensional networks of interlinked SWCNTs. The physical properties of CNTs can be altered by intertube interactions between NTs packed in hexagonal lattices, as so called "nanoropes", thus nanoropes consisting of interlinked SWNT will be significantly stronger than nanoropes composed of VDW packed NTs. This two-D interlinked structure is about 4 times stiffer than the 1D interlinked phase and 16 times stiffer than the vdW nanoropes. Looking at the electronic structure, the vdW nanoropes found to be metallic even though the individual tubes making up the nanorope are insulating or semiconducting with a small band gap.

Pan, Yang and Yang. 2000.

Tight-binding calculations are presented for the formation energies of a type of topological defect called the 5-7-7-5 defect in achiral NTs. This defect results in the transformation of 4 nearby hexagons into a pair of heptagons having a common side and the separation of two pentagons, a process that is termed direct exchange. Calculations show that the defect formation energy is dependent on the chirality and radius of the tube as well as the different orientations of the 5-7-7-5 defect in a tube. People found that the breathing mode frequency of a CNT is inversely proportional to the tube diameter and independent of chirality, thus the diameter of a tube can be estimated from the measured breathing mode from the Raman experiment.

Hannson, Paulsson and Stafstr m. 2000.

One group that looked at using MD to model effect of bending on electronic behavior of NTs. To obtain realistic values of the "new bond length", the semi-empirical Austin model one (AM1) was used to optimize the geometry of the NT at various bending angles. The optimization is performed on a (5,5) NT with 160 carbon atoms. To model bending, the atoms at the end are fixed as a chosen bending angle, and the positions of the other atoms are optimized.

S nchez-Portal, Artacho, Soler, Rubio and Ordej n. 1999.

Studied *ab initio* structural, elastic, and vibrational properties of carbon nanotubes of SWCNT with different radii and chirality. Young moduli are found to be very similar for graphite and do not exhibit systematic variation with either radius or chirality. The Poisson ratio also retains graphitic values except for a possible slight reduction for small radii. However, unlike the modulus, the Poisson ratio does display chirality dependence. Thus, it is important to use have potentials that don't depend on the properties of graphite. The data follows the behavior expected from classical elasticity theory, where the strain energy per atom (relative to the graphene sheet) is $E_{st} = C/r^2$, where C is a constant that depends on the Young modulus and the thickness of the wall in a model tube: $C = Yh^3a/24$. In order to get around the difficulty with defining the thickness of the tube, we have analyzed our results on the elastic stiffness of the NT using the second derivative of the strain energy with respect to the axial strain:

$$\frac{d^2E}{d\varepsilon^2}$$

Thus, the total energies for a deformation in the interval (-0.75%, 0.75%) were fitted to a 3rd order polynomial, and then the derivative taken and evaluated at zero strain to get the Young modulus. From table I, see that the average value in the tubes is 56 eV. Also found that the effect of curvature (radius) and chirality on the elastic properties is small. *Specifically, the effect of curvature on Y is small down to radii of the order of, at least, 2.8 Å*. They defined the Poisson ratio for a NT defined as:

$$\frac{\Delta r}{r} = -\nu\frac{\Delta l}{l}$$

where *l* is the tube length. Always found that n is positive – an elongation of the tube reduces the diameter. These results also show a slight decrease in the Poisson ratio with the tube radius, and a stronger dependence with the chirality. Other values of *v* are: 0.19 (Yakobson, using Brenner potential), 0.28 (Lu using constant force model), 0.26 from a tight bonding calculation, and 0.16 (basal plane in graphite)

Che, Cagin and Goddard III. 1999a.

Generalized extended empirical bond-order dependent **(GEEBOD)** force fields including nonbond interactions. Describe a general approach that properly describes multiple bonds at small distances while describing nonbond (Coulomb and VDW) interactions at long distances. For many important problems, it is essential to describe the dissociation and formation of chemical bonds, something that is not done is a standard force field analysis. Results for DWNT show that the Brenner FF leads to a stiffness 28% lower than that of the GEEBOD FF. This is because the Brenner FF missed the extra resistance to deformation due to NB interactions between tubes. Values of E found using various force fields:

- E = 944 GPa for GEEBOD FF
- E = 931 GPa for GraFF
- E = 740 GPa for Brenner FF

Type	C-C	C-H	H-H
ε_0 (kcal/mol)	0.0692	0.0324	0.0
σ (Angstrom)	3.805	3.50	3.195

Table 2 – Lennard-Jones 12-6 parameters. The C-C VDW parameters come from GraFF; the H-H and C-H parameters come from the Drieding FF except that $\varepsilon_{H\text{-}H} = 0$.

Che, Cagin and Goddard III. 1999b.

Extended bond-order potential, it not only captures the advantages of the bond order potentials (simulating bond forming and breaking), but also systematically includes non-bond contributions to energy and forces. Use to study the structure and thermal properties of C60, as well as the elastic properties and plastic deformation processes of SWNT and DWNT. Empirical bond order potentials have an advantage in that they can describe the chemical bonding. Among various empirical bond order potentials, the Brenner potential is parameterized specifically for various forms of carbon and hydrocarbon systems. For a SWNT, uniaxial stretching mostly involves covalent bond stretching and angle bending. In general, chemical bonds are orders of magnitude stronger than NB interactions.

Nardelli, Yakobson and Bernholc. 1998.

In strained NTs at high T, spontaneous formation of pentagon-heptagon defect pairs. These are energetically preferred at strains > 5%. These strains mark the onset of "plastic" deformation of the CNT. But in reality, this is really the onset of "non-elastic" behavior (i.e. buckling). The system is able to recover some (if not most) of its original hexagonal network, such that it is probably best described as elasto-plastic with zero hysteresis.

Gao, Cagin and Goddard III. 1998.

Employing an accurate interaction potential derived from quantum mechanics, looking at isolated CNTs up to a radius of 170 A. Found three different stability regions for SWNTs:

1. Below 10A, only the circular cross-section tubules are stable
2. Between 10A and 30A, both circular and collapsed are possible, although the circular are favorable
3. Beyond 30A, the collapsed form becomes more favorable

Used a classical thin-plate approximation and variation of strain energy as a function of curvature to calculate the bending modulus of CNTs. Found on the order of 960 GPa. Calculated the Young's modulus to be approximately 640 GPa. They modeled the basic energetics of the NT by approximating the tube as a membrane with a curvature 1/R and a bending modulus of κ.

Hern ndez, Goze, Bernier and Rubio. 1998.

Using a non-orthogonal tight-binding potential, predict that CNTs have higher modulus than other nanotubes, of the same order as defect-free graphene sheets. These results are in good agreement with experimental results. Applications of NTs as field tip emitters, nanoscale electronic devices, and hydrogen storage, but probably the highest potential is in connection with the exceptional electronic properties. After graphitic NTs, proposed that other compounds forming laminar graphite-like structures could also form nanotubes, such as BN, BC_2N, BC_3, and CN. One difficulty is that no empirical potentials exist such as that used for carbon, which is why not as much work done. For CNTs they find that $Y \sim 1.22$ TPa, and $\nu \sim 0.27$; they list specific values for a list of geometries in Table 1. They also discuss the dependence of Y on tube diameter, backing up their argument with some pretty clear results.

Lu. 1997.

Elastic properties of carbon NTs and nanoropes are investigated using an empirical force-constant method. For single and MW NTs the elastic moduli are shown to be insensitive to structural details such as the helicity, radius, and number of walls. The tensile Young's modulus and torsion shear modulus of tubes are comparable to that of diamond, while the bulk modulus is smaller that that of diamond. In an empirical force-constant model, the atomic interactions near the equilibrium structure are approximated by the sum of pairwise harmonic potentials between atoms. In the most successful models for graphite interactions, up to fourth-order neighbor in-plane and out-of-plane interactions are included. Tables 1-3 give nice summaries for the properties of SWNT, MWNT, and NT ropes. They conclude that:

- Elastic moduli are insensitive to size and helicity of the tube (SWNT)
- Young's and shear moduli are comparable to that of diamond (SWNT)
- SWNTs are stiff in both the axial direction and the basal plane (SWNT)
- Elastic moduli vary little with number of walls (MWNTs)
- Interwall vdW interactions do not affect significantly the elastic moduli (MWNTs)
- Large anisotropy in elastic properties in both SW and MW NTs (MWNTs)

Their value (Y~1 TPa) is smaller than others report, a discrepancy that may be due to the large uncertainty in how to estimate the Young's modulus from experiment. Also, in their models an isotropic model was assumed. Their results show large anisotropy, and perhaps this should be taken into account for experimental data.

From their nanoropes simulations:

1. Nanoropes are extremely anisotropic. The basal plane is soft (small c11) whereas the axial direction is very stiff (large c33). This unique property is in sharp contrast to graphite and makes nanoropes superior to conventional carbon fibers in making strong composite materials.
2. Young's modulus is about 1/2 that of diamond, and decreases with NT radius. However, per unit mass the nanorope is still stiffer than diamond.
3. Nanoropes possess the ideal qualities of high tensile strength and light weight.

Yakobson and Smalley. 1997.

The observed buckling resemble the instabilities well known in macroscopic elasticity of the hollow objects, such as thin shells. A synergism of atomistic and macroscopic structural mechanics was achieved with the proper choice of parameters of the continuum shell: a Young's modulus of elasticity (Y) of 5 TPa, and an effective thickness of 0.07 nm. The small thickness reflects the fact that flexing is much easier than stretching. This is consistent with the modulus of graphite being 1TPa and a thickness of 0.34 nm, where Y(h/c)=1 TPa.

Srivastava and Barnard. 1997.

MD simulations on shared-memory architecture; article is more a piece on computer storage, but a little on NTs. Bond rearrangements occur at the kink sites, leading to formation of topological defects, preventing the tube from fully relaxing back to its original configuration.

NASA's primary interest in NTs derive from:

- A SWNT can be either metallic or semiconducting, depending on its chiral vector
- NTs have very good elasto-mechanical properties because the 2D arrangement of C atoms in a graphene wall allows large out-of-plane distortion, while the strength of in-plane C-bonds keeps the graphene sheet exceptionally strong against any in-plane fracture or distortion
- Since NTs are hollow, they have been proposed as lightweight packing material for hydrocarbon fuels, as nanoscale containers for molecular drug-delivery, and as casting structures for making metallic nanowires and nanocapsulates.

Simulations often not extended to MWNTs for two reasons:

1. Number of atoms for MWNTs increases rapidly with system size
2. MWNTs require long-range VDW interactions to describe the intershell interactions under compressive strain

The simulations of MWNTs require a reactive potential because the bonding structure of the molecule may change when the elastic limit is reached. The VDW interaction, along with the nesting of NTs, is expected to lead to more stiffness and to prevent buckling. The major distinguishing feature of Brenner's potential is that the short-range bonded interactions are reactive, meaning that bonds can form and break during the course of the simulation. The set (5n, 5n) where n=4 to 7 was chosen because the experimentally observed MWNTs are generally of larger diameter than the diameter of experimentally observed SWNTs (which typically correspond to a (10,10) NT.

Iljima, Brabec, Maiti and Bernholc. 1996.

Interesting paper combining the experimental electron microscopy work of Iijima with the computational work of Bernholc. Using both, show that the bending and kink formation is fully reversible up to very large bending angles (about 110°). In this work they provide a formula for the critical curvature of the tube for kink formation:

$$C_c = \frac{1.49}{d^2}\left[1 + \frac{9.89}{d^5}10^3 \cos(6h)\right]$$

Brabec, Maiti, Roland and Bernholc. 1995.

Uses MD to study the growth of CNTs. Modeled the carbon atoms using a 3-body potential of Tersoff's form, with parameters from Brenner. Pentagons introduce a large amount of curvature at the tube-tip, so that the tube begins to close with additional deposits. Tubes need to be above a certain diameter to stay open during growth – found this diameter to be approximately 3 nm. For narrower tubes, the all-hexagonal structures are highly strained and structures involving adjacent pentagonal rings are favorable. (Maybe why always see 1.4 nm SWNTs.) A hexagonal structure, once formed, is found to be very stable against bond-switching processes, even at high temperatures.

Rapp , Casewit, Colwell, Goddard III and Skiff. 1992.

A detailed discussion of how they obtained the values that they use in the universal force field (UFF). The potential energy of an arbitrary geometry is written as a superposition of various 2, 3, and 4 body interactions in the form:

$$E = Er + E\theta + E\phi + E\omega + EvdW + Eel$$

where Er is bond stretching, $E\theta$ is bond angle bending, $E\phi$ is dihedral angle torsion, $E\omega$ is inversion terms, and EvdW and Eel are vdW and electrostatic terms, respectively. UFF is capable of reproducing most structural features across the periodic table with errors less than 0.1Å in bond distances and 5 to 10 degrees in angle bend

Brenner. 1990.

Brenner developed an empirical many-body potential potential-energy expression that can model intramolecular chemical bonding. The model is based on Tersoff's covalent bonding formalism with additional non-local terms. The potential is short-termed and quickly evaluated. This model includes bond breaking and forming.

Mechanics models of carbon nanotubes

Ru. 2000a.

Look at column buckling of MWNTs, and show that the critical strain can be overestimated in certain cases if the VDW forces aren't strong enough. In that case, each tube acts independently, and the smallest diameter tube fails first; others follow. It is known that actual bending stiffness of carbon SWNTs is low – about 25 times lower than that predicted by the elastic shell model if a representative thickness of 0.34 nm is used. However, there is the possibility of using MWNTs to improve bending strength.

Ru. 2000b.

Elastic model to study infinitesimal buckling of a double-walled CNT under compression. Show that CET (classical elasticity theory) works well, but existing CET models cannot be used directly for CNTs, because of the lack of study of a vdW interaction. They use the Airy stress function. Finds that adding an inner tube cannot increase the critical axial strain, although it can increase the force because it is changing the cross section.

Ru. 2000c.

Owing to their single atom-layer structure, the bending stiffness of SWCNTs is much lower than that given by the elastic shell model if the commonly defined representative thickness is used. Thus it is proposed that the effective bending stiffness of a SWNT should be regarded as an independent material parameter not related to the representative thickness by the classical bending stiffness formula. In contrast to SWNTs, bending stiffness of MWNTs is found to be well estimated by the classical bending stiffness formula when adjacent NTs are squeezed severely so that the induced high friction barrier prevents interlayer slips. To apply the elastic shell theory to CNTs, a basic quantity that has to be defined appropriately is the representative thickness of SWNTs. Most of all work has used the equilibrium interlayer spacing (0.34 nm) as the representative thickness. One of the advantages of this definition is that multilayer graphite and MWNTs can be treated as a solid block or hollow cylinder without any interior gap. Using this assumption, it is tacitly assumed that

$$D = \frac{Eh^3}{12\left(1-\nu^2\right)}$$

The above equation predicts that the bending stiffness is proportional to the cube of the thickness. However, as pointed out by Yakobson et al, the actual bending stiffness of a SWNT is much lower than if the usual 0.34 nm is used. The thickness which gives the appropriate value for the bending is 0.066 nm. His proposal is that a SWNT should be treated as a single-layer elastic shell with an effective bending stiffness DIFFERENT from that in the above equation. This doesn't change the other parts of elastic shell theory; in effect, you are treating the bending stiffness as a separate material parameter. This consideration highlights the noncontinuum character of the carbon NTs. It is known that bending of an originally circular tube causes the ovalization of the cross section, which eventually leads to as much as a 20% change in the diameters when local buckling

occurs. He suggests that this will happen for a MWNT, causing the interlayer to shrink and now friction can occur.

Ru. 2000d.

In this paper the definitions of Yakobson et al of a SWCNT with a thickness of SWNT of to = 0.0666 nm, with a corresponding E of 5.5 TPa, will be used. The predicted critical pressure stays unchanged if the representative thickness of t = 0.34 nm and E = 1.1 TPa are used. So the small thickness doesn't change many of the mechanical parameters, only the bending behavior. Pressure dependence in SWNT ropes: in CNTs, the nearest intertube spacing is almost uniform and around 0.34 nm. Under high pressure, the flattening of the circular walls of the CNTs will lead to a regular honeycomb. The intertube spacing will still remain 0.34 nm, as the change in intertube distance because of high pressure is small because the hard-core component of the inter-atomic interaction is repulsive and strongly resists significant reduction of the intertube spacing. For a non-loaded SWNT rope, the intertube interaction between adjacent tubes is usually so low that any two adjacent walls could slide to each other, thus bending deformation is independent of the opposing wall. Since the intertube wall spacing doesn't change, there is no VDW effect here; this feature of SWNT ropes makes them susceptible to elastic buckling under high pressure.

Salvetat, Bonard, Thomson, Kulik, Forr et al. 1999.

A really nice summary paper about the experimental and theoretical work completed to date with CNTs. Elastic constants follow a simple fourth order power law with lattice parameter; thus small variations in lattice can have a large impact on modulus. Due to thermal expansion, the C_{33} parameter of graphite is very dependent on temperature.

Govindjee and Sackman. 1999.

Often the equations of continuum beam theory are used to interpret the mechanical response of NTs, specifically, using the Bernoulli-Euler equation for the Young's modulus. Reports that show explicit dependence of "material" properties on system size when a continuum cross-section is assumed. Report that the super-high values of E reported are because of the breakdown of the continuum hypothesis. Other modes can be used to define E, and we should expect that the value of E is not dependent on the mode of deformation. If E is different in tension and compression, then you have to look at how this would affect the bending stiffness!

Yakobson, Campbell, Brabec and Bernholc. 1997.

The intrinsic symmetry of a graphite sheet is hexagonal, and a 2D hexagonal structure is isotropic. Thus, it can be represented by a uniform shell with only 2 elastic parameters: resistance to in-plane bending (in-plane stiffness C) and flexural rigidity D. They quote another reference to get C = 59 eV/atom = 360 J/m^2, and D = 0.85 eV. They estimate Poisson ratio to be 0.19 based on simulation, and this corresponds to the experimental value for single crystal graphite. Claim that using Y = 5.5 TPa and h = 0.066 nm gives

the correct values for the modulus and flexural rigidity. Choosing a more "natural" value for h (say 0.34 nm, the graphite interlayer spacing) really overshoots the rigidity. Found it useful to use these values for the shell continuum model. They estimate that the bulk modulus is slightly higher than diamond, and significantly higher than graphite.

Zhong-can, Su and Wang. 1997.

A model using the string equation to describe the possible existing shapes of the axial curve of MWCNTs; could be incorporated into a model looking at curved/bent NTs (or perhaps how NTs would curve/bend under applied load). They show that under certain geometric conditions the shape formation energy of a straight NT becomes negative, i.e. the straight NT is unstable and a bent/twisted NT is favored.

Yakobson, Brabec and Bernholc. 1996.

With properly chosen parameters, the continuum shell model provides a remarkably accurate "roadmap" of NT behavior beyond Hooke's law. They model the NT using a realistic many-body Tersoff-Brenner potential and MD, and then show that these transformations can be modeled with a continuous tubule model. Using this, they can model the behavior beyond the linear response (i.e. buckling).

Ruoff, Tersoff, Lorents, Subramoney and Chan. 1993.

Most models assume that the CNTs will have perfect cylindrical shape. But Ruoff showed that the NTs will deform due to vdW interactions; this will particularly be of interest in SWNT ropes. Found that it was measurable for SWNTs as small as 20 nm is diameter, so maybe it wouldn't be necessary for ropes, because they are SO small in diameter. Found that nesting of the tubes (MWNT) causes a moderate reduction in the change in shape of the tube.

Use of carbon nanotubes in composite materials

Lozano and Barrera. 2001.

Carbon nanofibers are those produced by the vapor-grown carbon method and have an average diameter of 100 nm. These hollow-core nanofibers are an ideal percursor system to working with SWNT and MWNT for composite development. Matrix was polypropylene. Incorporation of the NFs raised the working temperature range of the composite by 100 C (which can be explained by restrictions on the mobility of the macromolecules imposed by the VGCFs). Although the tensile strength of the composite was unaltered with NF concentration, the dynamic modulus increased by 350%. The thermoplastic matrix PP (polypropylene) was selected because thermoplastics are now receiving increased interest due to their manufacturing versatility, high strength, and stiffness. They are also recyclable. In particular, polypropylene is a nonpolar semicrystalline polymer with low surface tension. Little has been done to see whether the nanoscale reinforcement produces different behaviors in crystallization processes of the polymer matrix, especially since *the NFs have 2 to 4 orders of magnitude more surface area*. In short, dispersed NFs may well alter the polymer crystallinity to grossly affect the polymer matrix properties. Given the size of the NFs, it is possible that the amorphous phase will be immobilized by the NFs, resulting in a stiffer, less flow-resistant material. At 2% VGCF concentration, they see an increase in the degree of crystallinity, which they attribute to enhanced mobility of the PP macromolecular chains, leading to a better alignment of the crystal lattice (unclear?). They also see a significant increase in E', even with as low as 2% VGCF. Although a direct enhancement of tensile strength has not been observed for these composites, possibly associated with a more brittle matrix condition, a detrimental strength condition also hasn't been seen, suggesting that NFs play a small role in strength enhancement. However, they do see a large decrease in the ultimate strain of the composite. Table 3 shows what appears to be an inverse quadratic relationship between tensile strength and NT concentration, suggesting that there is an optimal % of NT for strength considerations.

Ajayan, Schadler, Giannaris and Rubio. 2000.

Fabrication of epoxy-SWCNT bundles (5% wt), loaded in tension and compression and looked at the Raman spectroscopy results as a function of applied strain. Hypothesize that the transfer between matrix and NT may be limited, because the NTs are slipping within the bundles. Failure that they see at large crack distances is not tube failure, but rather bundles falling apart. They get this result because of constant values of the Raman peaks (indicating that the individual tubes are not being strained). They also looked at CNT-carbon composite pellets. Show some results of the CNTs on the fracture surface, but really don't discuss much.

Gong, Liu, Baskaran, Voise and Young. 2000.

Looked at the role of an ionic surfactant in CNT-polymer composite processing. Without surfactant, modest improvements in the composite behavior compared to that of the

pure matrix. However, with the surfactant, 1% wt CNT increases Tg from 63 to 88 C and increases the modulus by 30%. This paper gives both G' and G'' data (Figure 1). Claim that the most likely role of the surfactant is as a dispersing agent. Without the agent, the NTs were long, wavy, and lumped together.

Qian, Dickey, Andrews and Rantell. 2000.

MWNT homogeneously dispersed by simple solution/evaporation method in polystyrene to form a 0.4mm thick composite; found that 1% wt CNT (0.487% volume fraction) resulted in approximately 36-42% and 25% increase in elastic modulus and break stress, respectively. Found good agreement between their model and experimental results. To get this kind of mechanical improvement using conventional carbon fibers, would need 5% volume (10% wt) carbon fibers inclusions. Found that during fracture of the CNT-containing composite, the CNTs align perpendicular to the crack surface, and provide closure stress. When the crack exceeds 800 nm, the CNTs were seen to start to pull out of the matrix.

Collins and Avouris. 2000.

"Superstrong materials." Embedded into a composite, NTs have enormous resilience and tensile strength, and could be used to make cars that bounce in a wreck or buildings that sway rather than crack in an earthquake. The problem is that NTs cost 10-1000 times more than carbon fibers now used in composites, and that they are so smooth that they slip out of the matrix, allowing it to fracture easily.

Chen, Shaffer, Coleby, Dixon, Zhou et al. 2000.

High resolution electron microscopy (HREM) revealed that the individual NTs are uniformly coated with Ppy (polypyrrole), which formed bridges between the NTs to give dense composite films. Electronically conducting films have been the focus of many intensive research programs over the past two decades. Simple ECPS (typically Ppy, polyaniline, and polythiophene), can be prepared either chemically in a bulk quantity or electrochemically as a thin film. They show interesting physiochemical properties exploitable for batteries, sensors, light-emitting diodes, and electrochromic displays. Need sufficiently high loadings must be achieved within the composite in order to enable percolation.

Lordi and Yao. 2000.

A key issue for these types of composites is obtaining good interfacial adhesion between the phases. They use force-field based molecular mechanics calculations to determine binding energies and sliding frictional stresses between pristine carbon NTs and a range of polymer substrates, in an effort to understand the factors governing interfacial adhesion. Surprisingly, they found that binding energies and frictional forces play only a minor role in determining the strength of the interface, but that helical polymer conformations are essential. Previous works have only examined bulk properties

of NT-polymer composites; here they will examine the mechanisms of adhesion at the molecular level. Various factors can affect this, including:

1. chemical bonds between phases
2. VDW adhesion between the phases
3. frictional forces enhanced by protrusions on the fiber surface.

Chemical bonding of NTs to the matrix may be detrimental to the fiber properties as defects in the graphene network must be introduced. Likewise, functionalizing the NT to increase surface friction or to promote bonding would destroy its structure. Thus they focus on VDW forces, which are dependent on the choice of the matrix and the conformation of the polymer.

Also did a calculation for a double-wall CNT to determine the interlayer friction. Found that the sliding friction between any two walls is MUCH lower than between NT and matrix. This substantiates previous concern about using MWNTs in composites because of interlayer slippage; the same of which can happen between SWNTs in a bundle. Thus, isolation of SWNT for a composite is highly desirable. In conclusion, found that the strength of the interface may be mostly due to molecular-level entanglement of the two phases and forced long-range ordering of the polymer.

Haggenmueller, Gommans, Rinzler, Fischer and Winey. 2000.

Production of SWNT-polymer composites with enhanced mechanical and electrical properties and exceptional alignment. A combination of solvent casting and melt mixing used to disperse the SWNT materials in poly(methyl methacrylate) (PMMA). Composite films showed higher conductivity along the flow direction then perpendicular to it. PMMA, a thermoplastic, was chosen for the matrix to facilitate both the dispersion of the SWNTs and the alignment of the SWNTs using established polymer melt processing methods. Specifically, PMMA has good fiber spinning qualities and is soluble in dimethylformaminde (DMF). The melt-spinning process successfully produced fibers with draw ratios from 60 to 3600, i.e. NT fibers with diameters from 10 to 75 μm. The elastic modulus increased with SWNT content: for $\lambda = 70$, Y = 3.1, 3.3, 5, and 6 GPa for 0, 1, 5, and 8% wt purified soot. The modulus increases a little with draw ratio, while the tensile strength increases MORE with draw ratio. Melt mixing promoted NT dispersion and should be applicable to most thermoplastic matrix polymers.

Wood, Zhao, Frogley, Meurs, Prins et al. 2000.

Nanotubes (SWNT, 0.1% wt) were embedded in an ultraviolet curable urethane acrylate polymer. At this low NT concentration, tensile tests revealed that there was no significant improvement in the mechanical properties of the films with respect to the pure polymer. Claim that "the shape of the curve is a potential reason for the low performance of NT-reinforced composites, which have, so far, not shown the expected improvements in mechanical properties above that of the base polymer." Recent mechanical data using DMTA on NT-reinforced composites (and on polymers reinforced with cellulose fibers) exhibit small improvements in the modulus below Tg, but large retention of modulus above the Tg of the polymer matrix, possibly because the Tg of the composite is higher than that of the polymer. This may be the case especially since

the NTs are so small that they can really be distributed in there, and really affect polymer chain movement. In view of the stress-strain curve produced here, we suggest that NTs have the potential to reinforce the matrix provided that the higher mechanical strains are applied, possibly above the Tg.

Jia, Wang, Xu, Liang, Wei et al. 1999.

Study on poly(methly methacrylate)/carbon nanotube composites. Good paper that shows that processing of the polymer can improve CNT/polymer composite behavior. Without processing the composite behavior is somewhat poor, because you're not improving the interface. Experimental results show that CNTs can be initiated by AIBN to open their π-bonds, which imply that CNTs may participate in PMMA polymerization and form a strong combining interface between CNTs and the PMMA matrix. Through the use of an improved *in situ* process, the mechanical properties and heat deflection temperatures of composites rise with the increase in CNTs. Found an "improved" process by starting PMMA polymerization for a certain period of time BEFORE adding the CNTs. The as-synthesized CNTs (untreated) exist in large masses, whereas the "grounded" CNTs had better distribution. The untreated NTs result in a poor dispersion ratio of CNTs in the PMMA matrix and rather low mechanical properties of the composite.

Shaffer and Windle. 1999.

The stiffness of the composites measured at RT was relatively low and was interpreted using short-fiber composite theory; the high temperature properties showed considerable promise. The electrical conductivity of these composites shows the type of percolation behavior observed in other fiber-filled systems. MATERIAL: catalytically grown NTs, despite a higher defect concentration. Average length of 1.1 µm. Different loadings of NTs (0-60%). Use a value for the density of the CNTs of 1.75 g/cm^3. In the samples examined, the NTs were found to be evenly dispersed and voids were only found in the 60% wt composites. Tensile elastic modulus and damping properties of the composite films were assessed in a dynamic mechanical thermal analyzer (DMTA) as a function of NT loading and T. The low effective length of the NTs, as fit to the Krenchel equation, is seen as a reflection of both the NT curvature and the reduced efficiency of shear stress transfer. The best fit to the experimental data for the in-plane stiffness of the composite films, as a function of NT concentration, was obtained using values of 150 MPa for the axial modulus and a reduced effective length of 35 nm. Not sure whether this is due to the weakness of THESE catalytically grown NTs, or whether it relates to a fundamental difficulty of shear stress transfer between the shells of MWNTs. Above the Tg of the matrix, the NTs had a much more significant, resulting in the retention of a large portion of the stiffness seen below Tg, although the NTs didn't change the location of the peak of the tan δ curve. In this case it is likely that those PVOH segments near to the NT surface were less mobile and showed an increased Tg. (But the authors aren't clear why didn't this affect the location of the Tg peak?) Nice plots of the real component of modulus and loss tan versus temperature for different values of NT concentration. Also, the electrical conductivity of the composites was measured using impedance spectroscopy. The percolation threshold for these composites between 5 and 10%

Srivastava, Brenner, Schall, Ausman, Yu et al. 1999.

Srivastava terms this "kinky chemistry"; locally controlled deformation can enhance chemical reactivity by as much as 1.6 eV. Also discusses how pristine NTs are preferentially reactive at the end caps due to curvature, causing a loss of spatial overlap of the atomic π-orbitals that contribute to conjugation and a shift in the hybridization from sp^2 to sp^3. However, the end cap functionalization is unlikely to affect bulk properties because of the large aspect ratio. Has some pictures of how hydrogen atoms would attack the strained NT.

Bower, Rosen, Lin, Han and Zhou. 1999.

Experimental investigation of NT/thermoplastic composite. Estimated the onset of buckling strain and fracture strain at 5% and 18%, respectively. Fracture strains estimated to be 10-100 times better than those of carbon fibers. See better load transferring efficiency when NT composite loaded in compression vs. tension. Uniaxial alignment of NTs achieved by mechanically stretching the composite above the Tg of the polymer and then releasing the load. Buckling of NTs in the composite – possibly due to compressive/bending forces caused by shrinkage as cooled from 100 C to RT. A TEM of the fracture surface showed really good adhesion between the NT and the matrix.

Lourie, Cox and Wagner. 1998.

Experimental observations of deformation and fracture modes of SWCNT in a thin epoxy film. The SWNTs were not aligned. Compressive strength of thin and thick-walled SWCNTs is two orders of magnitude higher than any known fiber (approximately 0.5 GPa range). Discuss *K*, the foundation modulus, which reflects the fiber/matrix interaction. Found that the presence of the matrix results in a 30% increase in the critical stress for compressive buckling, due to support of the matrix. Estimate the compressive strength of the film to be ~ 60 GPa.

Jin, Bower and Zhou. 1998.

Alignment of CNTs in a thermoplastic matrix by mechanical stretching at elevated (95C) temperatures. Found that the degree of alignment was a function of the stretching ratio and the NT concentration (perhaps a case similar to physical aging, where too many NTs decreases the effective mobility?) Unfortunately, no mechanical data, although some nice pictures showing good adhesion and a strong interface between the NT and the polymer.

Lourie and Wagner. 1998b.

Experimental paper in TEM showing well-aligned SWCNT bundles under tensile stress. Good wetting and adhesion; tensile failure of the tube and not at the interface.

Suggests that the matrix-fiber stress transfer mechanism is relatively well described by either the Cox or the Kelly-Tyson model, although for the latter there are several parameters that are not well understood. Nice pictures of a SWCNT bundle bridging a ellipsoidal hole.

Wagner, Lourie, Feldman and Tenne. 1998.

Report the observation of single NT fragmentation, under tensile stress, in an NT-polymer film. The MWNT-polymer stress transfer efficiency is estimated to be at least one order of magnitude LARGER than in conventional fiber-based composites. They used the Kelly-Tyson formula for the interfacial shear strength, τ_{NT}, via

$$\tau_{NT} = \frac{\sigma_{NT}(l_c)}{2(l_c / D_{NT})}\left(1 - \frac{d_{NT}^2}{D_{NT}^2}\right)$$

where is the $\sigma_{NT}(l_c)$ is the strength of a nanotube fragment of length l_c (the saturation length), and d_{NT} and D_{NT} are the inner and outer tube diameters. They found that the interface appears stronger than both the NT and the matrix in terms of sustaining shear. Strong curvature, as well as the presence of multiple concentric graphene planes, are likely to enhance the reactivity of CNTs towards double-bonds containing polymeric chains, upon UV radiation.

Schadler, Giannaris and Ajayan. 1998.

Tension/compression tests in an epoxy matrix. Found that the load transfer is much greater in compression. Raman peak shifted in compression, but not in tension, indicating strain in carbon bonds under compressive loading. Paper has good data for an MT-type analysis, with epoxy and composite data.

Lourie and Wagner. 1998a.

Evaluation of Young's modulus of a with graphite inclusions (SWNT, MWNT, and also a high modulus graphite fiber) in an epoxy matrix. SWNT average diameter of 1.4 nm; arc-discharge MWNTs 10-20 nm diameter; pitch-based CF with a diameter of 9.9 μm. Quenched the composite to induce compressive stresses in the composite. Measure this via micro-Raman spectroscopy, which they relate to the compression of the C-C bonds. Young's modulus of the matrix was 2 GPa.

Tang, Wang, Chan and Ho. 1996.

Paper that talks about the influence of the NTs in the PPA chains. NTs are wrapped helically by the chains – also found that alignment can be induced by mechanical force. NTs exhibit a strong photostabilization effect, protecting the polymer chains from photo-degradation under harsh laser irradiation, suggesting another possible use of the NTs, although I'm not sure if this happens for normal carbon fibers. Material: well-ground MWNTs, short in length. They're interested in optical properties. They get a peak in the high molecular weight region that wasn't there for the pure PPA, believed to be caused by the presence of the NTs; this would tend to increase the Tg. Also noted

the effect of the NTs on processing – seemed to be “stealing” species necessary for the reaction.

Ajayan, Stephan, Colliex and Trauth. 1994.

A simple technique (1994) is described that produces aligned arrays of carbon NTs. The method is based on cutting thin slices (50 to 200 nm) of a NT-polymer composite. MWNT were prepared by the arc-discharge method and dispersed randomly in a liquid epoxy resin by mechanical mixing. Images of slices < 200 nm thick show that the tubes were preferentially orientated during the cutting process. But this does not happen for thicknesses greater than that. They saw that all of the longer and thinner tubes have been orientated, whereas the thicker and shorter tubes and the nanoparticles still have the random orientation; when the thickness of the slice increases over 0.3 to 0.5 µm, the aligning affect becomes less pronounced, disappearing about 1 µm. But they do have a problem with the TEM of the thicker samples; may only be imaging NTs on the surface. They present a model to explain the orientation, which resembles the pullout of fibers from a rigid matrix when a fiber composite is mechanically loaded. The directional cutting process creates shear that induces flow in the material. As the thickness of the section increases, the cross section over which the forces are distributed also increases, decreasing the stress and the ability to deform and align tubes.

Related nanotube work

Cuenot, Demoustier-Champagne and Nysten. 2000.
Elastic modulus of polypyrrole (type of polymer) nanotubes. Diameters between 35 and 160 nm. Stronger behavior when the surface to volume ratio is higher (because chains are better orientated along the surface). Tested in 3-pt bending. OD > 100 nm, E = (1.2, 3.2) GPa – order of polypyrrole thin films. 70<OD<100 nm, E increases slowly to 5 GPa. OD < 70 nm, strongly increases up to 60 GPa for an OD of 35 nm. Is this the same size effect that is being demonstrated with carbon fibers?

Choi, Kim, Park, Lee, Bae et al. 2000.
Catalytic grown of ß-Ga_2O_3 nanowires by arc discharge. It is desirable to have a large surface area / volume ratio for use as an oxygen sensor.

Golberg, Bando, Bourgeois, Kurashima and Sato. 2000.
Paper on the structure of a BN (boron nitride) nanotube. Very stable insulating properties with ultimate strength. Usually thought to be a structural analog of CNTs.

Wang, Dai, Gao, Bai and Gole. 2000.
Side-by-side SiC – Silica nanowires. See a structural transformation between a biaxial and a coaxial configuration. The nanowires were between 50-80 nm in diameter, and lengths up to 100 µm. Tables 1 and 2 give experimentally measured properties for biaxial and coaxial nanowires.

Peigney, Laurent, Flahaut and Rousset. 2000.
Looks at using NTs in a ceramic matrix, with metal added to improve the catalysis method. Mechanical properties obtained show that the additive effect expected with the addition of the CNTs was not observed (i.e. minimal increase in fracture strength). It appeared that the cohesion between the CNT bundles and the matrix was rather poor.

Jin, Sun, Xu, Goh and Ji. 2000.
Previous investigations showed that MWNTs possess optical-limiting properties with a broadband response covering the visible to infrared spectrum; this is also seen with SWNTs. Such nonlinear optical effects (NLO) have potential applications in the protection of optical sensors from high-intensity laser beams. Coating the NTs with the polymer did not alter the NLO properties.

Kuzumaki, Hayashi, Miyazawa, Ichinose, Ito et al. 1998.
Paper on the mechanical behavior of carbon NT / C_{60} composite. Shear strength of a carbon fiber - C_{60} composite estimated to be 4.4 x 10^{-2} MPa, with easy pullout between the NT and the C_{60} matrix. Carbon fiber / C_{60} composites have been shown to exhibit large elongation.

Miscellaneous notes (carbon nanotubes)

Nanotubes were discovered in 1991. The archtypical example of aerospace composite is an epoxy resin reinforced with 60% (volume) continuous fiber. *Calvert. 1992.*

For a typical 1.0 nm NT, the stiffness is about 800 GPa, or about 75% of the ideal. As a practical means of estimating the yield strengths, Bacon used the estimate $Y_{max} = ß E$, where ß ranges from 0.05 to 0.1. Bacon used the value of 0.025 for graphite whiskers. Most of the experimental SWCNTs are determined to be of type (n,n), where *n* is between 8 and 11. Coulson's statement: "The C-C bond in graphite is the strongest bond in nature." TEM shows SWCNTs with aspect ratios exceeding 1000; a typical number for the aspect ratio is 100-300. *Ruoff and Lorents. 1995.*

Tensile strength of *graphite whiskers* is on the order of 20 GPa. Average Young's modulus of macroscopic vapor-grown fibers of 680 GPa. Carbon whiskers made by Bacon in the 1960s had a modulus of 800 GPa. *Treacy, Ebbesen and Gibson. 1996.*

Individual SWNT exhibiting small band gaps on the order of 10 meV observed for the first time in electron transport measurements; will have nontrivial consequences to the electrical properties of SWNTs. *Zhou, Kong and Dai. 2000.*

NTs are claimed to have "excellent resistance to bending". But this statement primarily refers to MWNTs, where there are in the inner tubes that act as additional constraints. SWNTs are very susceptible to bending. *Nardelli, Yakobson and Bernholc. 1998.*

Calculations of the strain at tensile failure estimate values around 40%. However, experimental results have shown values of approximately 16%. Work suggests that the nanotubes that show more "irreversible" mechanical strains are possibly not single tubes, but is rather a nanotube rope, where the irreversibility is due to the relative sliding of individual ropes within the bundle. The new geometry is maintained by the strong van der Waals attraction between the tubes in the rope. *Yu, Dyer, Skidmore, Rohrs, Lu et al. .*

The chemical reactivity of sp^3 is more reactive than the planar sp^2. The graphite basal plane, also known as graphene, is a hexagonal network of sp^2 covalently bonded carbon atoms. Interesting, CNTs seem to be highly flexible, in contrast with the brittleness of graphite. *Yakobson, Brabec and Bernholc. 1996.*

In-plane modulus of graphite is 1.06 TPa. The modulus of diamond, one of the stiffest materials known, is 1.2 TPa.

For some applications, use of SiC nanorods may be better reinforcing materials (SiC for stiff matrices, CNTs for more flexible composites). *Wong, Sheehan and Lieber. 1997.*

For strong fibers used in the composite materials field, compressive-to-tensile strength is 0.1 to 0.3. But this ratio may be closer to one for perfect microstructures like CNTs. (However, it is interesting that with CNTs they find that the compressive strength of the NTs is higher.) *Wagner, Lourie, Feldman and Tenne. 1998.*

Interfacial energies are normally about ~50-300 J/m^2 when chemical bonds are present, but only ~50-350 mJ/m^2 is only vdW interactions are assumed. *Lu, Huang, Nemchuk and Ruoff. 1999.*

Use TEM to determine the morphological, structural, and chemical information. Raman spectroscopy is used to determine the structure of the carbon materials. By analyzing first order Raman peaks, it is possible to determine the extent of sp^2 and sp^3 bonding. Can also use this to measure the defect density. Conversion of carbon materials to graphite typically occurs through the progressive removal of defects. *Setlur. 1999.*

8-year record of smallest diameter was 0.7nm, matching that of a C_{60} buckyball. New experimental evidence suggests that diameters of 0.5 and 0.33 nm exist; 0.5nm diameter can be closed with a C_{36} cage. Talk about growing these super-small NTs as junctions; can be grown on NTs of any helicity. *Peng, Zhang, Xue, Wu, Gu et al. 2000.*

A free carbon atom has the structure $(1s)^2(2s)^2(2p)^2$. In order to form covalent bonds, one of the 2s electrons is promoted to 2p, and the orbitals are hybridized. In graphite, one of the 2s electrons hybridizes with two of the 2p's to give three sp^2 orbitals at 120 degrees. The sp^2 orbitals form the strong σ bonds between carbon atoms in the graphite planes, while the π orbitals provide weak vdW bonds between the planes. In diamond, each carbon atom is joined to four neighbors in a tetrahedral structure; the bonding here is sp^3 and results from mixing one 2s with three 2p orbitals. Thus diamond is less stable than graphite, and is converted to graphite at a temperature of 1700 C at normal pressure. In C60, the bonding carbon atom is joined to three neighbors, so the bonds are essentially sp2, although there could be some sp^3 at areas of curvature; this is true for NTs in general. *Harris. 1999.*

In graphite, each carbon atom has a coordination of 3. Due to the conjugation, each bond has approximately 1/3 double bond and 2/3 single bond character. (Note that carbon has a valence of 4.) *Brenner. 1990.*

When all of the dimensions of an atomic-scale object are small, it is possible to use purely computational methods to understand its behavior. But when one dimension is larger, purely atomistic methods become time consuming. *The existence of a nanoscale dimension is in the authors' opinion not a reason by itself to reject continuum theory.* Another nanotube that is similar to a CNT is Bacteriophage T4, whose cylindrical tail is one atomic layer thick with a pseudo-triclinic structure. Under certain conditions the tail undergoes a spontaneous martensitic phase transformation resulting in a sudden lengthening of the tube, a feature that it employs to invade its host. *Friesecke and James. 2000.*

Load transfer depends on interfacial shear stress between fiber and the matrix; a high interfacial shear will transfer the applied load to the fiber over a short distance. Hypothesize three methods of load transfer: micromechanical inter-locking, chemical bonding between NTs and the matrix (which was estimated that it could be as high as 500 GPa), and weak vdW bonding between fiber and the matrix. Found that NTs remained curved and interwoven in the composite. Another possible benefit of the NTs over carbon fibers is the ease of processing, and especially the lack of inclusion breakdown during processing. *Schadler, Giannaris and Ajayan. 1998.*

Fracture strains of NTs estimated to be 10-30%, 10-100 times better than traditional carbon fibers. *Bower, Rosen, Lin, Han and Zhou. 1999.*

While NTs are "good" in hydrostatic pressure, they are sensitive to inward buckling and collapse. *Yakobson, Campbell, Brabec and Bernholc. 1997.*

Graphite has a very high level of anisotropy. Van der Waals forces are weak (typically about1 eV), whereas covalent bonds are much stronger. Young's modulus is the 2nd derivative of the strain energy, divided by the equilibrium volume. CET predicts a $1/R^2$ variation of the strain energy, and a bunch of *ab initio* studies have shown that only a small correction is needed for the NTs. *Salvetat, Bonard, Thomson, Kulik, Forr et al. 1999.*

Temperature could have a huge affect on the tensile behavior (ductile or brittle) of the NT; providing the thermal energy for the defects to move and bonds to reform. Probably not a concern in a polymer composite, because the temperature would have to be so high as to degrade most polymers.

There is usually an inverse relationship between strength and modulus for carbon fibers.

Most work uses a carbon-carbon bond distance of 1.44 Angstroms (.144 nm).

An increase of the interfacial strength with Young's modulus is observed in graphite fibers, but it has not been strictly demonstrated that this will be the case for CNTs. *Lourie and Wagner. 1998b.*

In general case, can superpose deflection of beams (involving both bending and shear):

$$\delta = \delta_{\text{bending}} + \delta_{\text{shear}} = \frac{FL^3}{192EI} + \frac{f_s FL}{4GA}$$

Conversion factor:1 eV = 12.235 GPa.

W = 2.62 A^2/atom is the occupied area per carbon atom in SWNTs. *Xin, Jianjun and Zhong-can. 2000.*

A typical nanoscale system has from tens to millions of atoms. For a SWNT, uniaxial stretching mostly involves covalent bond stretching and angle bending. In general, chemical bonds are orders of magnitude stronger than NB interactions.

The tensile strength of high-strength tool steel is 2.345 GPa.

The chiral angle of an (n,m) tube is defined as: *Pan, Yang and Yang. 2000.*

$$\chi = \arctan\frac{\sqrt{3}m}{2n+m}$$

Graphite is normally formed at temperatures over 2500 C. At lower decomposition temperatures, the degree of ordering can be considerably less.

Dual-component systems and Tg: Gordon and Taylor for copolymers, whereas Kelley and Bueche is for polymer-diluent systems.

L-J 6-12 potential describing van der Waals interactions between two atoms:

$$u(x) = -\frac{A}{x^6} + \frac{B}{x^{12}}$$ LJ potential for two atoms

$$x_o = 2^{1/6}\sigma = \left(\frac{2B}{A}\right)^{1/6}$$ equilibrium distance

$$\varepsilon = \frac{A^2}{4B}$$ well depth

where A and B are the attractive and repulsive constants in the Lennard-Jones potential. *Girifalco, Hodak and Lee. 2000.*

Electromechanical actuators based on sheets of single-walled CNTs were shown to generate higher stresses than natural muscle and higher strains than high-modulus ferroelectrics. The direct conversion of electrical energy to mechanical energy through a material response is critically important for such diverse needs as robotics, optical fiber switches, optical displays, prostetic devices, sonar projectors, and microscopic pumps. *Ferroelectric and electrorestrictive materials are especially useful for direct energy conversion.* The material they used was hexagonally packed bundles of CNTs with a diameter of 12 to 14 A, an intertube separation within a bundle of ~17 A, and an average bundle diameter of ~100 A. In addition to having a large displacement, a high-performance actuator material should have both a high strength and high modulus. Predict a volumetric work capacity that is ~ 29 times higher than has been tabulated for the best known ferroelectric, electrorestrictive, or magnetorestrictive materials. Could also run in reverse and convert mechanical energy to electrical energy. NTs could provide high currents at low voltages, which is desirable for remote sensors. This could ultimately lead to such applications as the conversion of the mechanical energy of ocean waves to electrical energy. *Baughman, Cui, Zakhidov, Iqbal, Barisci et al. 1999.*

The diameter of a carbon nanotube of helicity (a,b) is given by $D=0.78(a^2+ab+b^2)$ (need to check this) *Thess, Lee, Nikolaev, Dia, Petit et al. 1996.*

NT radius is given by

$$R = a_o\frac{\sqrt{3\left(n_1^2+n_2^2+n_1n_2\right)}}{2\pi}$$

where a_o is the C-C bond length, 1.42A. The density of the SWNT ropes, 1.3 g/cm^3, is only half that of graphite, and 1/3 that of diamond. Although it should be noted that many different values for the density of these ropes have been used. *Lu. 1997.*

What makes NTs so stable is the strength with which carbon atoms bond to one another, which is also what makes diamond so hard. In diamond, the atoms link into 4-sided tetrahedra, but in NTs they are in hexagonal rings like chicken wire.

Nanotechnology is predicted to spark a series of industrial revolutions in the next two decades that will transform our lives to a far greater extent than silicon microelectronics did in the 20th century. Carbon NTs could play a pivotal role in this upcoming revolution is their electrical and mechanical properties can be exploited. *Jamieson. 2000.*

SWNTs are also expected to be very strong and to resist fracture under extension, just as carbon fibers commonly used in the aerospace industry. However, unlike the latter, the CNTs wouldn't fracture under compression, rather they form kink-like ridges that can relax elastically when the stress is released. *Dresselhaus, Dresselhaus, Eklund and Saito. 1998.*

NMD – nanomemory device – capsule and a shuttle. The buckyball contains a potassium ion (K^+) which gives the shuttle its charge. The VDW forces between the tube and the shuttle will tightly bind the shuttle to one end of the tube, giving a binary value. Discuss the possibility of terahertz switching speeds. Also, each bit could require as little as 2 square nm. This density that would meet the that "required" well past 2030. Writing to the NMD is the easy part; reading is much more challenging. Somehow the state of the device must be sensed. *Brehob, Enbody, Kwon and Tom nek. .*

Carbon atoms in diamond are tetrahedrally bonded to their 4 nearest neighbors, forming the rigid 3D lattice that gives diamond its unparalleled hardness. By contrast, the 2D arrangement of atoms in graphene NT wall permits some out-of-plane flexibility. Combined with the strength of the constituent bonds, this promises spectacular properties. There is good reason to suggest that a macroscopic one-inch-thick rope, where 1014 parallel buckyropes are all holding together, to be almost as strong as theory predicts, because defects don't propagate as in the theory of internal flaws and Griffith cracks. Instead of changing smoothly with applied voltage, currents in NTs increase and decrease in a stepwise fashion, revealing the grainy nature of such quantum wires. The use of crash-proof tips in scanning microscopy (because so easy to bend) exploits the mechanical resilience and conductivity of the CNTs. *Yakobson and Smalley. 1997.*

Asbestos is also about 10 nm in diameter and a few µm long; there is the possibility that there could be the same type of health risks involved. Euler's law is that a hexagonal lattice of any size or shape can only form a closed structure by the inclusion of precisely 12 pentagons. At present, the smallest features on commercial chips have dimensions of 0.35 µm. May be able to get to 0.1 µm with current (photolithography) techniques, but will then hit a wall. The current cost of NTs is about $20 per gram. For carbon fibers, the cost about a few dollars per kg, and the carbon fibers are considered to be too expensive! *Harris. 1999.*

References

1. Ajayan, P., L. Schadler, C. Giannaris and A. Rubio (2000). "Single-walled carbon nanotube-polymer composites: strength and weakness." Advanced Materials **12**(10): 750-753.

2. Ajayan, P., O. Stephan, C. Colliex and D. Trauth (1994). "Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite." Science **265**: 1212-1214.

3. Andriotis, A., M. Menon and G. Froudakis (2000). "Various bonding configurations of transition-metal atoms on carbon nanotubes: their effect on contact resistance." Applied Physics Letters **76**(26): 3890-3892.

4. Baughman, R., C. Cui, A. Zakhidov, Z. Iqbal, J. Barisci, et al. (1999). "Carbon nanotube actuators." Science **284**: 1340-1344.

5. Bernholc, J. (1999). "Computational materials science: the era of applied quantum mechanics." Physics Today: 30-35.

6. Bharadwaj, R., R. Berry and B. Farmer (2000). "Molecular dynamics simulation study of norbornene-POSS polymers." Polymer **41**: 7209-7221.

7. Bower, C., R. Rosen, J. Lin, J. Han and O. Zhou (1999). "Deformation of carbon nanotubes in nanotube-polymer composites." Applied Physics Letters **74**(22): 3317-3319.

8. Bower, C., W. Zhu, S. Jin and O. Zhou (2000). "Plasma-induced alignment of carbon nanotubes." Applied Physics Letters **77**(6): 830-832.

9. Brabec, C., A. Maiti, C. Roland and J. Bernholc (1995). "Growth of carbon nanotubes: a molecular dynamics study." Chemical Physics Letters **236**: 150-155.

10. Brehob, M., R. Enbody, Y.-K. Kwon and D. Tománek "The potential of carbon-based memory systems." unpublished.

11. Brenner, D. (1990). "Empirical potential for hydrocarbons for use in simulating the chemical vapor deposition of diamond films." Physical Review B **42**(15): 9458-9471.

12. Calvert, P. (1992). "Strength in disunity." Nature **357**: 365-366.

13. Che, G., B. Lakshmi, C. Martin and E. Fisher (1998). "Chemical vapor deposition based on synthesis of carbon nanotubes and nanofibers using a template method." Chemistry of Materials **10**: 260-267.

14. Che, J., T. Cagin and W. Goddard III (1999a). "Generalized extended empirical bond-order dependent force fields including nonbond interactions." Theoretical Chemistry Accounts **102**(346-354).

15. Che, J., T. Cagin and W. Goddard III (1999b). "Studies of fullerenes and carbon nanotubes by an extended bond order potential." Nanotechnology **10**: 263-268.

16. Chen, G., M. Shaffer, D. Coleby, G. Dixon, W. Zhou, et al. (2000). "Carbon nanotube and polypyrrole composites: coating and doping." Advanced Materials **12**(7): 522-526.

17. Chen, X., J. Xia, J. Peng, W. Li and S. Xie (2000). "Carbon-nanotube metal-matrix composites prepared by electroless plating." Composites Science and Technology **60**: 301-306.

18. Choi, Y., W. Kim, Y. Park, S. Lee, D. Bae, et al. (2000). "Catalytic growth of ß-Ga_2O_3 nanowires by arc discharge." Advanced Materials **12**(10): 746-750.

19. Chopra, N., L. Benedict, V. Crespi, M. Cohen, S. Louie, et al. (1995). "Fully collapsed nanotubes." Nature **377**: 135-138.

20. Cohen, Y., D. Rein, L. Vaykhansky and R. Porter (1999). "Tailoring the interface in polyethylene fiber/matrix composites: surface-entangled interfacial layer." Composites: Part A **30**: 19-25.

21. Collins, P. and P. Avouris (2000). "Nanotubes for electronics." Scientific American: 62-69.

22. Cuenot, S., S. Demoustier-Champagne and B. Nysten (2000). "Elastic modulus of polypyrrole nanotubes." Physical Review Letters **85**(8): 1690-1693.

23. Cui, H., O. Zhou and B. Stoner (2000). "Deposition of aligned bamboo-like carbon nanotubes via microwave plasma enhanced chemical vapor deposition." Journal of Applied Physics **88**(10): 6072-6074.

24. Cumings, J. and A. Zettl (2000). "Low-friction nanoscale linear bearing realized from multiwall carbon nanotubes." Science **289**: 602-604.

25. Dresselhaus, M., G. Dresselhaus, P. Eklund and R. Saito (1998). "Carbon nanotubes." Physics World(January).

26. Falvo, M., G. Clary, R. Taylor II, V. Chi, F. Brooks Jr, et al. (1997). "Bending and buckling of carbon nanotubes under large strain." Nature **389**: 582-584.

27. Friesecke, G. and R. James (2000). "A scheme for the passage from atomic to continuum theory for thin films, nanotubes, and nanorods." Journal of the Mechanics and Physics of Solids **48**: 1519-1540.

28. Gao, G., T. Cagin and W. Goddard III (1998). "Energetics, structure, mechanical and vibrational properties of single-walled carbon nanotubes." Nanotechnology **9**: 184-191.

29. Gao, R., Z. Wang, Z. Bai, W. de Heer, L. Dai, et al. (2000). "Nanomechanics of individual carbon nanotubes from pyrolytically grown arrays." Physical Review Letters **85**(3): 622-625.

30. Gennett, T., A. Dillon, J. Alleman, K. Jones, F. Hasoon, et al. (2000). "Formation of single-wall carbon nanotube superbundles." Chemical Materials **12**: 599-601.

31. Girifalco, L., M. Hodak and R. Lee (2000). "Carbon nanotubes, buckyballs, ropes, and a universal graphitic potential." Physical Review B **62**(19): 13104-13110.

32. Golberg, D., Y. Bando, L. Bourgeois, K. Kurashima and T. Sato (2000). "Insights into the structure of BN nanotubes." Applied Physics Letters **77**(16): 1979-1981.

33. Gong, X., J. Liu, S. Baskaran, R. Voise and J. Young (2000). "Surfactant-assisted processing of carbon nanotube/polymer composites." Chemistry of Materials **12**: 1049-1052.

34. Govindjee, S. and J. Sackman (1999). "On the use of continuum mechanics to estimate the properties of nanotubes." Solid State Communications **111**: 227-230.

35. Haggenmueller, R., H. Gommans, A. Rinzler, J. Fischer and K. Winey (2000). "Aligned single-wall carbon nanotubes in composites by melt processing methods." Chemical Physics Letters **330**: 219-225.

36. Hannson, A., M. Paulsson and S. Stafström (2000). “Effect of bending and vacancies on the conductance of carbon nanotubes.” Physical Review B **62**(11): 7639-7644.

37. Harris, P. (1999). Carbon nanotubes and related structures: new materials for the 21st century. Cambridge, Cambridge University Press.

38. Hernández, E., C. Goze, P. Bernier and A. Rubio (1998). “Elastic properties of C and $B_xC_yN_z$ composite nanotubes.” Physical Review Letters **80**(20): 4502-4505.

39. IIjima, S., C. Brabec, A. Maiti and J. Bernholc (1996). “Structural flexibility of carbon nanotubes.” Journal of Chemical Physics **104**(5).

40. Jamieson, V. (2000). “Carbon nanotubes roll on.” Physics World **June**.

41. Jia, Z., Z. Wang, C. Xu, J. Liang, B. Wei, et al. (1999). “Study on poly(methly methacrylate)/carbon nanotube composites.” Materials Science and Engineering A **271**: 395-400.

42. Jin, L., C. Bower and O. Zhou (1998). “Alignment of carbon nanotubes in a polymer matrix by mechanical stretching.” Applied Physics Letters **73**(9): 1197-1199.

43. Jin, Z., X. Sun, G. Xu, S. Goh and W. Ji (2000). “Nonlinear optical properties of some polymer/multi-walled carbon nanotube composites.” Chemical Physics Letters **318**: 505-510.

44. Journet, C., W. Maser, P. Bernier, A. Loiseau, M. de la Chapelle, et al. (1997). “Large-scale production of single-walled carbon nanotubes by the electric-arc technique.” Nature **388**: 756-758.

45. Kiang, C.-H., M. Endo, P. Ajayan, G. Dresselhaus and M. Dresselhaus (1998). “Size effects in carbon nanotubes.” Physical Review Letters **81**(9): 1869-1872.

46. Kuzumaki, T., T. Hayashi, K. Miyazawa, H. Ichinose, K. Ito, et al. (1998). “Discussion on the mechanical behavior of carbon nanotube/C60 composite based on observation of interfacial structure.” Materials Transactions, JIM **39**(5): 578-581.

47. Li, F., M. Cheng, S. Bai, G. Su and M. Dresselhaus (2000). “Tensile strength of single-walled carbon nanotubes directly measured from their macroscopic ropes.” Applied Physics Letters **77**(20): 3161-3163.

48. Lordi, V. and N. Yao (2000). “Molecular mechanics of binding in carbon-nanotube-polymer composites.” Journal of Materials Research **15**(12): 2770-2779.

49. Lourie, O., D. Cox and H. Wagner (1998). “Buckling and collapse of embedded carbon nanotubes.” Physical Review Letters **81**(8): 1638-1641.

50. Lourie, O. and H. Wagner (1998a). “Evaluation of Young's modulus of carbon nanotubes by micro-Raman spectroscopy.” Journal of Materials Research **13**(9): 2418-2422.

51. Lourie, O. and H. Wagner (1998b). “Transmission electron microscopy observations of fracture of single-wall carbon nanotubes under axial tension.” Applied Physics Letters **73**(24): 3527-3529.

52. Lozano, K. and E. Barrera (2001). “Nanofiber-reinforced thermoplastic composites. I. Thermoanalytical and mechanical analyses.” Journal of Applied Polymer Science **79**: 125-133.

53. Lu, J. (1997). “Elastic properties of carbon nanotubes and nanoropes.” Physical Review Letters **79**(7): 1297-1300.

54. Lu, X., H. Huang, N. Nemchuk and R. Ruoff (1999). “Patterning of highly orientated pyrolytic graphite by oxygen plasma etching.” Applied Physics Letters **75**(2): 193-195.

55. Nardelli, M., J.-L. Fattebert, D. Orlikowski, C. Roland, Q. Zhao, et al. (2000). “Mechanical properties, defects, and electronic behavior of carbon nanotubes.” Carbon **38**: 1703-1711.

56. Nardelli, M., B. Yakobson and J. Bernholc (1998). “Mechanism of strain release in carbon nanotubes.” Physical Review B **57**(8): 4277-4280.

57. Pan, B., W. Yang and J. Yang (2000). “Formation energies of topological defects in carbon nanotubes.” Physical Review B **62**(19): 12652-12655.

58. Pan, Z., S. Xie, L. Lu, B. Chang, L. Sun, et al. (1999). “Tensile tests of ropes of very long aligned multiwalled carbon nanotubes.” Applied Physics Letters **74**(21): 3152-3154.

59. Peigney, A., C. Laurent, E. Flahaut and A. Rousset (2000). “Carbon nanotubes in novel ceramic matrix nanocomposites.” Ceramics International **26**: 677-683.

60. Peng, H., N. Wang, Y. Zheng, Y. Lifshitz, J. Kulik, et al. (2000). “Smallest diameter carbon nanotubes.” Applied Physics Letters **77**(18): 2831-2833.

61. Peng, L., Z. Zhang, Z. Xue, Q. Wu, Z. Gu, et al. (2000). “Stability of carbon nanotubes: how small can they be?” Physical Review Letters **85**(15): 3249-3252.

62. Peters, M., L. McNeil, J. Lu and D. Kahn (2000). “Structural phase transition in carbon nanotube bundles under pressure.” Physical review B **61**(9): 5939-5944.

63. Poncharal, P., Z. Wang, D. Ugarte and W. de Heer (1999). “Electrostatic deflections and electromechanical resonances of carbon nanotubes.” Science **283**: 1513-1516.

64. Qian, D., E. Dickey, R. Andrews and T. Rantell (2000). “Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites.” Applied Physics Letters **76**(20): 2868-2870.

65. Rappé, A., C. Casewit, K. Colwell, W. Goddard III and W. Skiff (1992). “UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations.” Journal of the American Chemical Society **114**(25): 10024-10035.

66. Ru, C. (2000a). “Column buckling of multiwalled carbon nanotubes with interlayer radial displacements.” Physical Review B **62**(24): 16962-16967.

67. Ru, C. (2000b). “Effect of van der Waals forces on axial buckling of a double-walled carbon nanotube.” Journal of Applied Physics **87**(10): 7227-7231.

68. Ru, C. (2000c). “Effective bending stiffness of carbon nanotubes.” Physical Review B **62**(15): 9973-9976.

69. Ru, C. (2000d). “Elastic buckling of single-walled carbon nanotube ropes under high pressure.” Physical Review B **62**(15): 10405-10408.

70. Ruoff, R. and D. Lorents (1995). “Mechanical and thermal properties of carbon nanotubes.” Carbon **33**(7): 925-930.

71. Ruoff, R., J. Tersoff, D. Lorents, S. Subramoney and B. Chan (1993). “Radial deformation of carbon nanotubes by van der Waals forces.” Nature **364**: 514-516.

72. Saito, T., T. Yoshikawa, S. Bandow, M. Tomita and T. Hayashi (1993). “Interlayer spacings in carbon nanotubes.” Physical Review B **48**(3): 1907-1909.

73. Salvetat, J.-P., J.-M. Bonard, N. Thomson, A. Kulik, L. Forró, et al. (1999). “Mechanical properties of carbon nanotubes.” Applied Physics A **69**(255-260).

74. Salvetat, J.-P., G. Briggs, J.-M. Bonard, R. Basca, A. Kulik, et al. (1999). “Elastic and shear moduli of single-walled carbon nanotube ropes.” Physical Review Letters **82**(5): 944-947.

75. Salvetat, J.-P., A. Kulik, J.-M. Bonard, G. Briggs, T. Stöckli, et al. (1999). “Elastic modulus of ordered and disordered multiwalled carbon nanotubes.” Advanced Materials **11**(2): 161-165.

76. Sánchez-Portal, S., E. Artacho, J. Soler, A. Rubio and P. Ordejón (1999). “*Ab initio* structural, elastic, and vibrational properties of carbon nanotubes.” Physical Review B **59**(19): 12678-12688.

77. Satishkumar, B., P. Thomas, A. Govindaraj and C. Rao (2000). “Y-junction carbon nanotubes.” Applied Physics Letters **77**(16): 2530-2532.

78. Schadler, L., S. Giannaris and P. Ajayan (1998). “Load transfer in carbon nanotube epoxy composites.” Applied Physics Letters **73**(26): 3842-3844.

79. Setlur, A. (1999). The growth of empty and filled graphitic nanostructures. Materials Science and Engineering. Evanston, IL, Northwestern University**:** 132.

80. Shaffer, M. and A. Windle (1999). “Fabrication and characterization of carbon nanotube/poly(vinyl alcohol) composites.” Advanced Materials **11**(11): 937-941.

81. Shi, Z., Y. Lain, F. Liao, X. Zhou, Z. Gu, et al. (2000). “Large scale synthesis of single-wall carbon nanotubes by arc-discharge method.” Journal of Physics and Chemistry of Solids **61**: 1031-1036.

82. Smith, B., Z. Benes, D. Luzzi, J. Fischer, D. Walters, et al. (2000). “Structural anisotropy of magnetically aligned single wall carbon nanotube films.” Applied Physics Letters **77**(5): 663-665.

83. Smith, B. and D. Luzzi (2000). “Formation mechanism of fullerene peapods and coaxial tubes: a path to large scale synthesis.” Chemical Physics Letters **321**: 169-174.

84. Smith, B., M. Monthioux and D. Luzzi (1999). “Carbon nanotube encapsulated fullerenes: a unique class of hybrid materials.” Chemical Physics Letters **315**: 31-36.

85. Srivastava, D. and S. Barnard (1997). “Molecular dynamics simulation of large-scale carbon nanotubes on a shared-memory architecture.” Proceedings of SuperComputing 97.

86. Srivastava, D., D. Brenner, J. Schall, K. Ausman, M.-F. Yu, et al. (1999). “Predictions of enhanced chemistry reactivity at regions of local conformational strain on carbon nanotubes: kinky chemistry.” Journal of Physical Chemistry B **103**(21): 4330-4337.

87. Stahl, H., J. Appenzeller, R. Martel, P. Avouris and B. Lengeler (2000). “Intertube coupling in ropes of single-wall carbon nanotubes.” Physical Review Letters **85**(24): 5186-5189.

88. Tang, M., C. Wang, C. Chan and K. Ho (1996). “Environment-dependent tight-binding potential model.” Physical Review B **53**(3): 979-982.

89. Tersoff, J. and R. Ruoff (1994). “Structural properties of a carbon-nanotube crystal.” Physical Review Letters **73**(5): 676-679.

90. Thess, A., R. Lee, P. Nikolaev, H. Dia, P. Petit, et al. (1996). “Crystalline ropes of metallic carbon nanotubes.” Science **273**: 483-487.

91. Treacy, M., T. Ebbesen and J. Gibson (1996). “Exceptionally high Young's modulus observed for individual carbon nanotubes.” Nature **381**: 678-680.

92. Venema, L., J. Wildöer, C. Dekker, G. Rinzler and R. Smalley (1998). “STM atomic resolution images of single-wall carbon nanotubes.” Applied Physics A **66**: 153-155.

93. Venkateswaran, V., A. Rao, E. Richter, M. Menon, A. Rinzler, et al. (1999). “Probing the single-wall carbon nanotube bundle: Raman scattering under high pressure.” Physical Review B **59**(16): 10928-10934.

94. Vigolo, B., A. Pénicaud, C. Coulon, C. Sauder, R. Pailler, et al. (2000). “Macroscopic fibers and ribbons of oriented carbon nanotubes.” Science **290**: 1331.

95. Wagner, H., O. Lourie, Y. Feldman and R. Tenne (1998). “Stress-induces fragmentation of multiwall carbon nanotubes in a polymer matrix.” Applied Physics Letters **72**(2): 188-190.

96. Wang, A., Z. Dai, R. Gao, Z. Bai and J. Gole (2000). “Side-by-side silicon carbide-silica biaxial nanowires: synthesis, structure, and mechanical properties.” Applied Physics Letters **77**: 3349.

97. Wang, Z., P. Poncharal and W. de Heer (2000). “Measuring physical and mechanical properties of individual carbon nanotubes by in situ TEM.” Journal of Physics and Chemistry of Solids **61**: 1025-1030.

98. Wei, B., Z. Zhang, G. Ramanath and P. Ajayan (2000). “Lift-up growth of aligned carbon nanotubes.” Applied Physics Letters **77**(19): 2985-2987.

99. Wong, E., P. Sheehan and C. Lieber (1997). “Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes.” Science **277**: 1971-1975.

100. Wood, J., Q. Zhao, M. Frogley, E. Meurs, A. Prins, et al. (2000). “Carbon nanotubes: from molecular to macroscopic sensors.” Physical Review B **62**(11): 7571-7575.

101. Xie, S., W. Li, Z. Pan, B. Chang and L. Sun (2000). “Mechanical and physical properties on carbon nanotube.” Journal of Physics and Chemistry of Solids **61**: 1153-1158.

102. Xin, Z., Z. Jianjun and O.-Y. Zhong-can (2000). “Strain energy and Young's modulus of single-wall carbon nanotubes calculated
103. from electronic energy-band theory.” Physical Review B **32**: 13692.

104. Yakobson, B., C. Brabec and J. Bernholc (1996). “Nanomechanics of carbon tubes: instabilities beyond linear response.” Physical Review Letters **76**(14): 2511-2514.

105. Yakobson, B., M. Campbell, C. Brabec and J. Bernholc (1997). “High strain rate fracture and C-chain unraveling in carbon nanotubes.” Computational Materials Science **8**: 341-348.

106. Yakobson, B. and R. Smalley (1997). “Fullerene nanotubes: $C_{1,000,000}$ and beyond.” American Scientist **July-August**.

107. Yildirim, T., O. Gulseren, Kiliç and S. Ciraci (2000). “Pressure-induced interlinking of carbon nanotubes.” Physical Review B **62**(19): 12648-12651.

108. Yu, M., M. Dyer, G. Skidmore, H. Rohrs, X. Lu, et al. (1999). “Three-dimensional manipulation of carbon nanotubes under a scanning electron microscope.” Nanotechnology **10**(3): 258-262.

109. Yu, M., T. Kowalewski and R. Ruoff (xxxx). “Structural analysis of collapsed, and twisted and collapsed, multi-walled carbon nanotubes by atomic force microscopy.” Physical Review Letters (submitted) **xx**(xx): xxxx.

110. Yu, M., O. Lourie, M. Dyer, K. Moloni, T. Kelly, et al. (2000). “Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load.” Science **287**: 637-640.

111. Yu, M., B. Yakobson and R. Ruoff (2000). “Controlled sliding and pullout of nested shells in individual multiwalled carbon nanotubes.” Journal of Physical Chemistry B **104**: 8764-8767.

112. Yu, M.-F., B. Files, S. Arepalli and R. Ruoff (2000). “Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties.” Physical Review Letters **84**(24): 5552-5555.

113. Yu, M.-F., T. Kowalewski and R. Ruoff (2000). “Investigation of the radial deformability of individual carbon nanotubes under controlled indentation force.” Physical Review Letters **85**(7): 1456-1459.

114. Zhang, P., P. Lammert and V. Crespi (1998). “Plastic deformations of carbon nanotubes.” Physical Review Letters **81**(24): 5346-5349.

115. Zhong-can, O.-Y., Z.-B. Su and C.-L. Wang (1997). “Coil formation in multishell carbon nanotubes: competition between curvature elasticity and interlayer adhesion.” Physical Review Letters **78**(21): 4055-4058.

116. Zhou, C., J. Kong and H. Dai (2000). “Intrinsic electrical properties of individual single-walled carbon nanotubes with small band gaps.” Physical Review Letters **84**(24): 5604-5607.