Strength of Single Molecules

Introduction

Man's curiosity has driven him to understand the world that he lives in both macroscopically and microscopically. With the advent of atomic force microscopy (AFM) and chemical force microscopy (CFM), it has become possible to study the shapes of atoms and molecules. The ability to probe interfacial forces is critical to develop a molecular understanding of a variety of phenomena such as friction, adhesion, double layer forces and fracture at interfaces.

The strength of molecular systems plays a crucial role in their functions. In particular, mechanical forces play a key role in biological and polymeric systems. The understanding of these molecular systems provides a basis for interpretable mapping of various chemical functionalities. Direct information regarding the strength of molecular structures inspires development of new materials with a higher strength-to-size ratio. For example, carbon nanotubes, which have elastic modulus of the order of 1 TPa, have been utilized as nanoscale reinforcement in composites[1]. In a simpler sense, "A carbon nanotube the size of half the diameter of a pencil can bear the load of twenty full-size cars."

1. Characterization of Molecules

The key factors to be considered in the characterization of single moleculas are its energy and geometry. The energy consideration deals with the strength of the intramolecular and intermolecular forces, which has a direct bearing on the macroscopic mechanical properties such as Young's Modulus, Bending Modulus and Torsional Strength. The geometry and symmetry aspects allow manipulation of various properties according to the requirements.

The various methods used to characterize single molecules are :-

(i) TEM (Transmission Electron Microscopy)
(ii) AFM (Atomic Force Microscopy)
(iii) CFM (Chemical Force Microscopy)
(iv) Raman Spectroscopy

1.1 Transmission electron microscopy

TEM is mainly applied in determining lattice parameters using high-resolution images. It is also possible to characterize mechanical properties such as bending modulus using *in-situ* nanomeasurements[2].

1.2 Atomic force microscopy

The atomic force microscope (AFM) has been the main tool in studying the mechanical response of molecules under static load, and when in contact with surfaces. The high spatial and force resolution of AFM enables it to reproduce nano-scale images, for example, revealing topography, adhesion, friction. The main disadvantage of AFM is that it cannot provide information better than the nano-scale properties.

1.3 Chemical force microscopy

AFM cannot detect the chemical groups that are present on the molecule, which dictate the various physical properties at the molecular level. Chemically functionalized probes can be used to detect the chemical forces present in a molecule. Chemical Force Microscopy (CFM) can be used to measure the intermolecular forces, measure the surface energy at a nano scale and determine the pK values of local chemical groups[3]. Hence, it is possible to characterize the distribution of various functional groups with their ionization state throughout the molecule. For example, in acetone, the carbon of the carbonyl group is positively charged and the carbon of the methyl group is negatively charged.

2. Nanotubes

2.1.1 Molecular structure of carbon nanotubes

A single-walled carbon nanotube is described as a rolled-up tubular shell of graphene sheet (Fig. 1). The body of the tubular shell is mainly made of hexagonal rings in a sheet of carbon atoms, where as the ends are capped by a dome-shaped half-fullerene molecules. The natural curvature in the sidewalls is due to the rolling of the sheet into the tubular structure, whereas the curvature in the end caps is due to the presence of topological (pentagonal ring) defects in the otherwise hexagonal structure of the underlying lattice. The role of the pentagonal ring defect is to give a positive convex curvature to the surface, which helps in closing of the tube at the two ends[4].

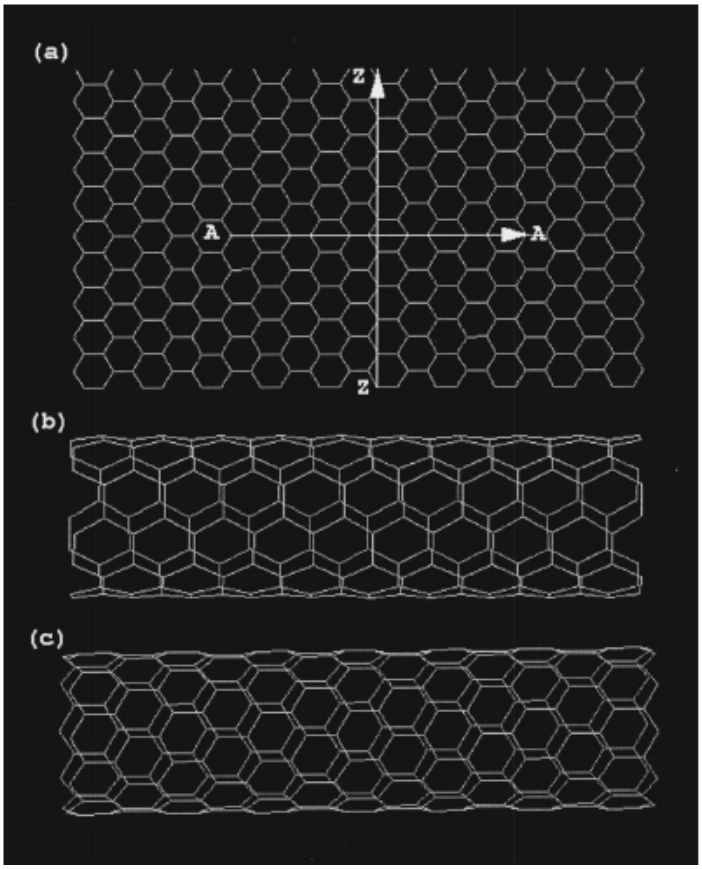

Figure 1 (a) A graphene sheet made of C atoms placed at the corners of hexagons forming the lattice with arrows AA and ZZ denoting the rolling direction of the sheet to make b) an armchair and (c) a zigzag nanotubes, respectively. [Ref: Dong Qian, Gregory J Wagner, Wing Kam Liu, Min-Feng Yu and Rodney S Ruoff, Mechanics of carbon nanotubes, Appl. Mech. Rev. vol 55, no 6, November 2002.]

2.1.2 Symmetry dependent strength of nanotubes

The elastic properties of carbon nanotubes were assumed to be independent of the chirality (helicity). The reason for this behavior is the regular isotropic nature of hexagonal two dimensional crystal. But, dislocation-theory suggests that the energetics of strength-mechanism is a function of the tube chirality. This is explained by the rotation of a C-C bond by the Stone-Wales transformation as demonstrated by molecular/dynamic simulations.[6] The dislocation theory predicts the following expression for the SW defect formation:

$$E_{sw} = A - B\varepsilon - C\sin(2\chi + \pi/6)\varepsilon$$

where A,B,C are empirical constants, ε is the tensile strain and χ is the chirality. This shows that the strength of the carbon nanotube is a function of its chirality.

A few modes of S-W transformations are illustrated in Fig.4. In the mode S_{+-} both flipping atoms depart the plane in opposite directions. In the mode S_{++}, both atoms digress from the plane in the same direction. Finally, in the mode S_{+}, only one atom buckles out[7]

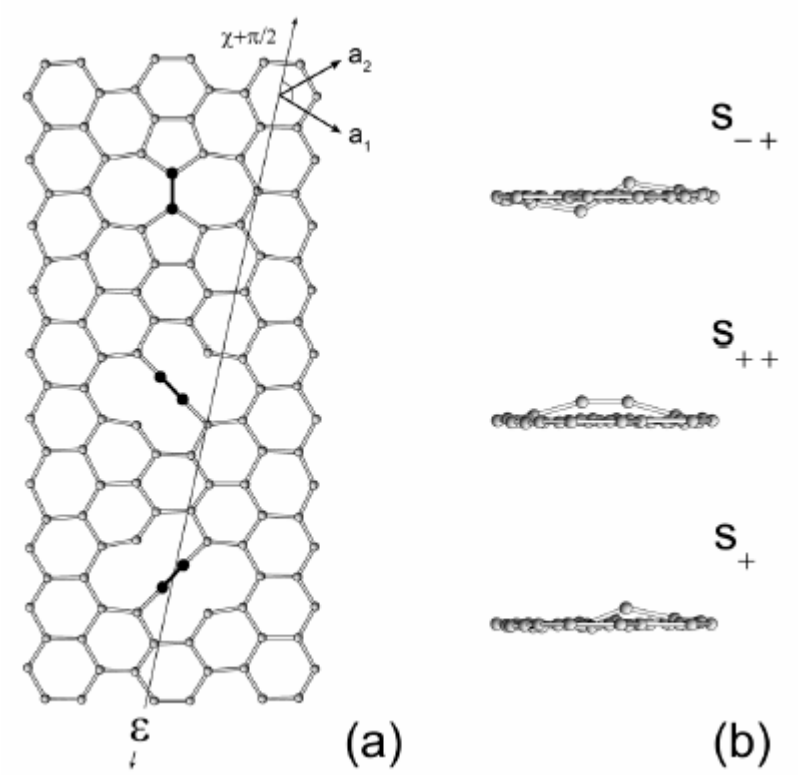

Figure 2. (a) Atomic configurations for a 5-7-7-5 defect. Corresponding transition states are aligned differently with respect to the tensile strain ε, directed at the angle $\chi + \pi/2$ from the basis vector $\mathbf{a}_1$ (in a nanotube of chirality χ). (b) Modes S_{-+}, S_{++}, and S_{+} differ in the atom excursions out of plane. [Ref: Georgii G. Samsonidze, Guram G. Samsonidze, and Boris I. Yakobson, (2002) Kinetic Theory of Symmetry-Dependent Strength in carbon nanotubes, Phy.Rev.Lett. 88(6), 1-4.]

2.1.3 Bonding mechanism

The bonding mechanism in a carbon nanotube system is similar to that of graphite. The strong sigma covalent bond that binds the atoms in the plane, and results in the high stiffness and high strength of a carbon nanotube. The pi bond determines the interlayer interaction between atoms on neighboring layers, which is weaker than those between atoms within the layer.

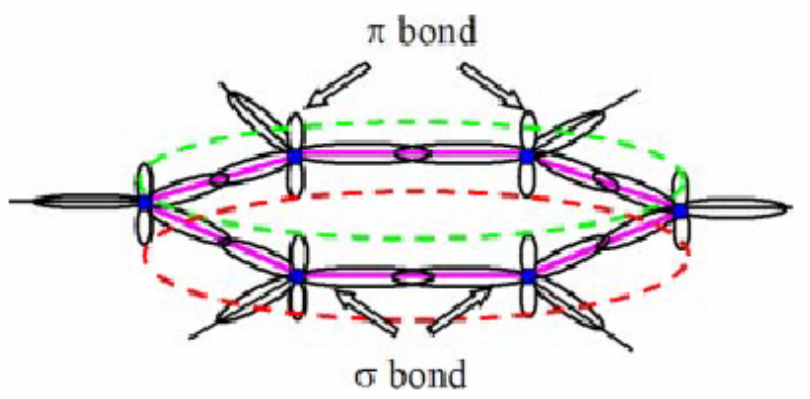

Figure 3. Basic Hexagonal bonding structure for a graphite layer

The first carbon nanotubes discovered were multi-walled carbon nanotubes as shown in Fig.4. Transmission electron microscopy studies on multi-walled carbon nanotubes suggest a Russian doll-like structure nested shells and give interlayer spacing of approximately 0.34 nm close to the interlayer separation of graphite, 0.335 nm. The analysis of energetics suggests the formation of a scroll, which may then convert into a stable multi-wall structure composed of nested cylinders.

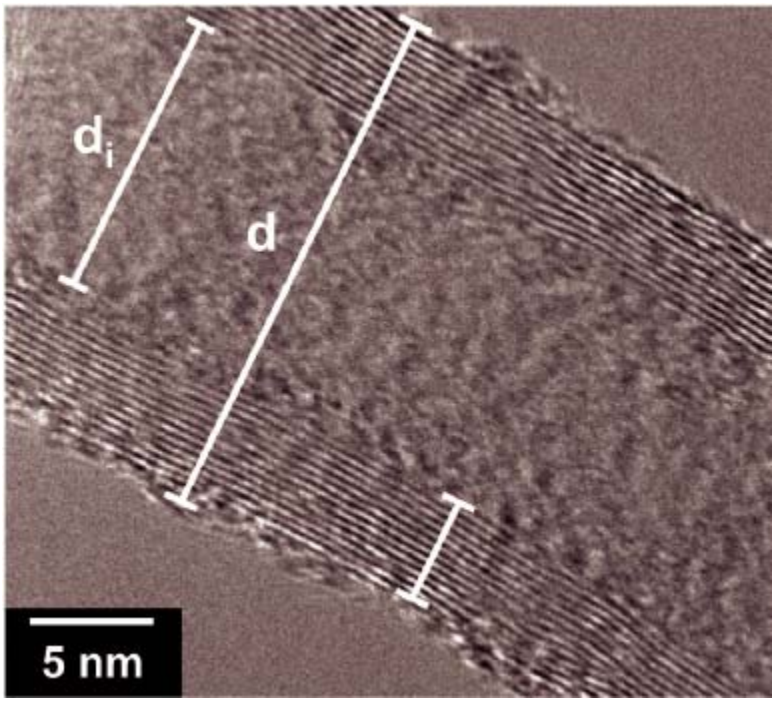

Figure 4. TEM micrograph of a multi-walled carbon nanotube with measurements of outside diameter, inside diameter and wall thickness indicated. [Ref: Z. L. Wang, P. Poncharal, and W. A. de Heer, (2000) Nanomeasurements of individual carbon nanotubes by *in-situ* TEM, Pure Appl. Chem., 72(1-2), 209–219]

2.2 Elastic properties of carbon nanotubes

2.2.1 Atomic force microscopy method

The elastic properties of nanotubes have been measured using the beam assumption. The problem of measuring mechanical properties arises due to difficulty in gripping and handling fibres that have nano-size diameters. These measurements have extensively depended on Atomic force microscopy (AFM). By deflecting of the nanofibre and holding the both the ends of the fibre fixed, the mechanical strength can be calculated by correlating the lateral displacement as a function of the applied load. This type of measurement has two limitations. The deformation of the tip was ignored and the interface sliding was also ignored[8].

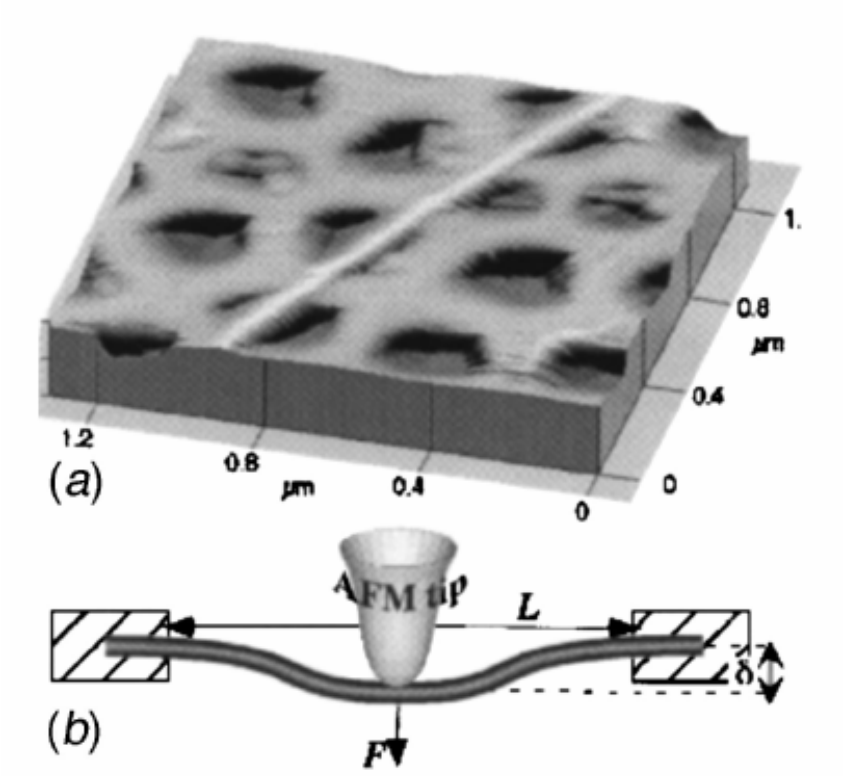

Figure 5. (a) AFM image of a SWCNT bundle adhered to the polished alumina ultrafiltration membrane, with a portion bridging a pore of the membrane; (b) Schematic of the measurement: the AFM is used to apply a load to the nanobeam and to determine directly the resulting deflection. [Ref: Dong Qian, Gregory J Wagner, Wing Kam Liu, Min-Feng Yu and Rodney S Ruoff, (2002) Mechanics of carbon nanotubes, Appl. Mech. Rev. 55(6)]

It has been shown from many methods that the strain energy of a single carbon nanotube is proportional to $1/R^2$; where R is the radius of the carbon nanotube. This goes to show that small deformation beam theory is still valid even at such nano levels for a carbon nanotube[9].

Assuming small deformations, the equation of motion for a beam is

$$\rho A \frac{\partial^2 u}{\partial t^2} + EI \frac{\partial^4 u}{\partial x^4} = q(x)$$

where u is the displacement function, ρ is the density, E Young's Modulus, A the cross sectional area and q(x) a distributed applied load. This model assumes no warpage, i.e. plane sections remain as plane sections during bending.

2.2.2 Electrostatic Bending

The carbon nanotube can be charged by an externally applied potential and the induced charge is mostly distributed at the tip of the carbon nanotube. It shows deflection under an electric field which are captured in a series of TEM images. The tips of the nanotubes attract each other, and the bright and dark contrast of the two tubes is due to the opposite charges built on the tubes. It can be bent for more than 90º, due to their flexible nature, after which it recovers its original shape[2].

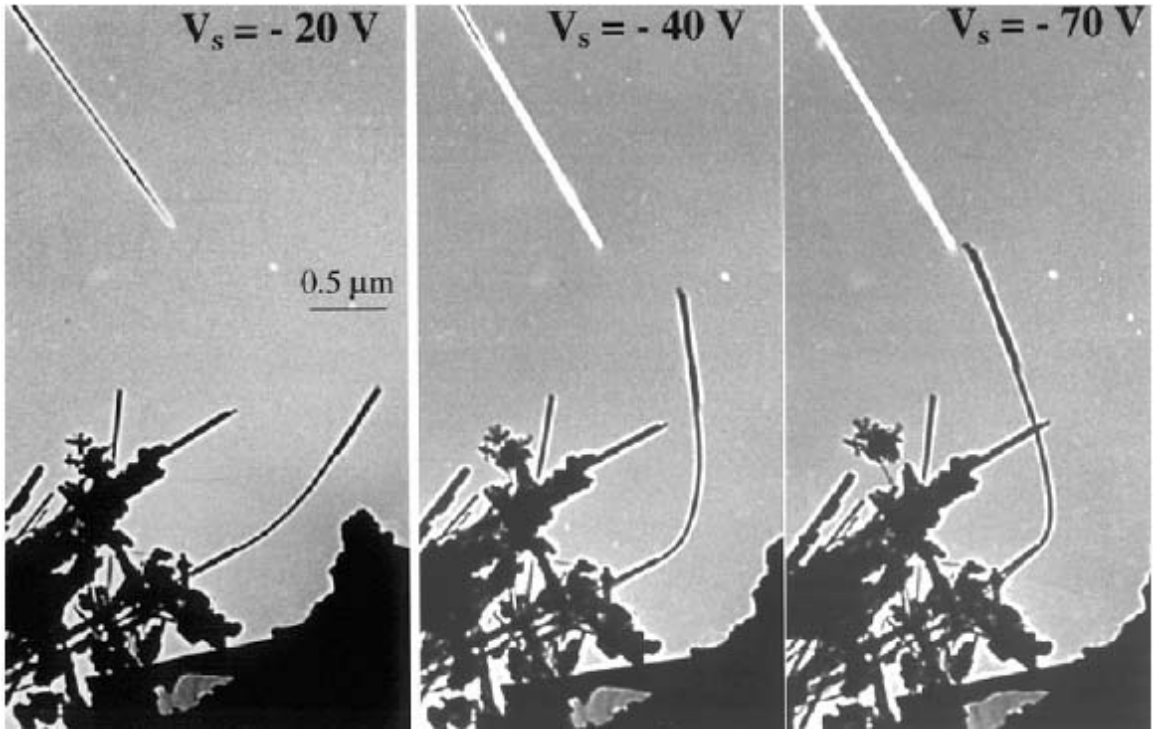

Figure. 6 Electrostatic attraction between two carbon nanotubes induced by a constant field across the electrodes. The induced charges are mainly accumulated at the tip. [Ref: Z. L. Wang, P. Poncharal, and W. A. de Heer, (2000) Nanomeasurements of individual carbon nanotubes by *in-situ* TEM, Pure Appl. Chem., 72(1–2), 209–219]

2.2.3. Bending Modulus

Although carbon nanotubes are systems with relatively high Knudsen number, it's presumed that these nanotubes have very small number of defects. A simplified model for carbon nanotubes using simple beam theory for small deflections is employed.

The natural frequency of the i^{th} mode of vibration of the beam is given by

$$\omega_i = \frac{\beta_i^2}{L^2}\sqrt{\frac{EI}{\rho A}}$$

where β_i are the roots of an equation that is dictated by the boundary conditions. For the case mentioned, the equation is

$$\cos\beta_i \cosh\beta_i + 1 = 0$$

and hence, $\beta_1 = 1.875$, $\beta_2 = 4.694$, and $\beta_3 = 7.855$.

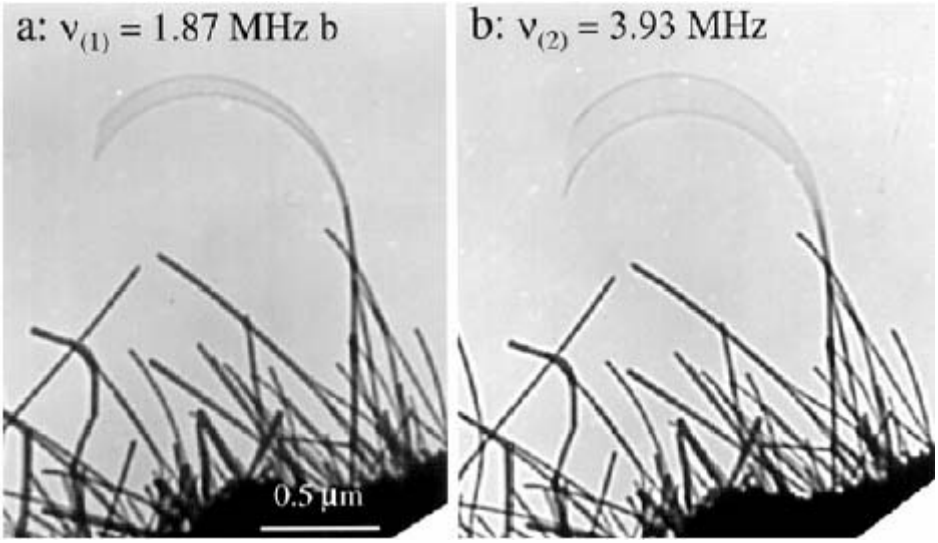

Figure. 7. Resonance of a bent carbon nanotube at (a) $\nu_1 = 1.87$ MHz, $V_0 = 2$ V and (b) $\nu_2 = 3.93$ MHz, $V_o = 5$ V, showing the multiple harmonic effect, where Vo is the amplitude of the applied voltage. [Ref: Z. L. Wang, P. Poncharal, and W. A. de Heer, (2000) Nanomeasurements of individual carbon nanotubes by *in-situ* TEM, Pure Appl. Chem., 72(1–2), 209–219]

2.2.4 Measurement of Bending Modulus

Measurements of bending modulus can be done by application of an oscillating voltage to a fixed nanotube as shown in figure 6. By tuning the frequency of the voltage applied resonance can be obtained between the voltage and the vibrating nanotube. As shown earlier, the natural vibration frequency is a function of various physical properties of the nanotube. Hence we have very selective resonance.

From *in-situ* TEM measurements we can also determine the mode of vibration of the carbon nanotube at a particular resonance frequency. The tube diameter and the length can be very accurately measured using TEM images. Using the above relation for the frequency, the Bending Modulus for the carbon nanotube is computed[2].

Material	Young's Modulus (GPa)
Wrought Iron and Steel	190-210
Silicon Carbide	450
Diamond	1050-1200
Carbon Nanotube	1000-1300

Table 1. Comparison of material strengths

3 Applications

3.1 Nano-balance

The elastic properties of carbon nanotubes can be calibrated with very high precision with the various spectroscopic methods. This can be used to find the mass of any particle attached to its tip with very high precision. Carbon nanotube attached with a mass at the tip acts like spring-mass system and hence, can be used to find out the mass of the particle.

Under the application of a known potential difference, carbon nanotube vibrates at its harmonic frequencies. A mass is attached to the tip with the help of Scanning Probe tip and the frequency of vibration is observed using the same technique as shown in Fig.7. An effective mass approach is used to calculate the moment of inertia for the mass attached balance. Using the relation between the vibrating frequency and moment of inertia of the system, the mass of particle can be calculated. This setup has been demonstrated and is the most sensitive and smallest balance in the world and can measure weights of the the order of a few femtograms.

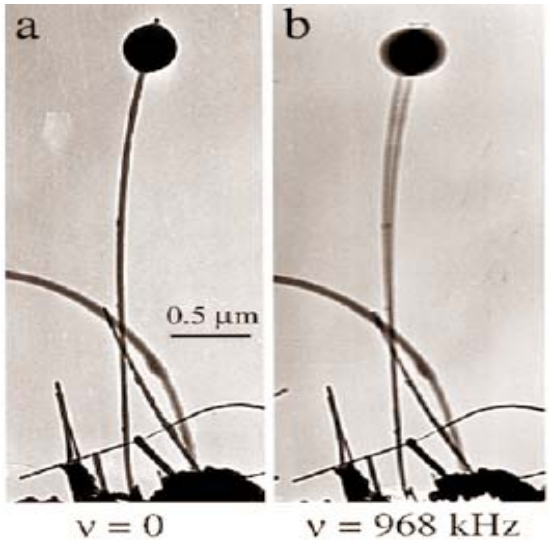

Figure. 8. A small particle attached at the end of a carbon nanotube at (a) stationary and (b) first harmonic resonance (ν = 0.968 MHz). The effective mass of the particle

measures ~22 fg (1 f = 10–15). [Ref: Z. L. Wang, P. Poncharal, and W. A. de Heer, Nanomeasurements of individual carbon nanotubes by *in-situ* TEM, (2000) Pure Appl. Chem., 72(1–2), 209–219]

3.2 Nano composites

The characterization of the carbon nanotubes has shown that their elastic moduli are of the order of a few TPa, over and above the good electrical and thermal conductivity. These properties can be harnessed by using carbon nanotubes as nanoscale reinforcements in composites.

3.2.1 Micromechanics of nanocomposites

The continuum assumptions for the fibre are made in micro-mechanics model, which are no longer valid in the nano-scale and the chemical structure and bonding need to be incorporated into the model. carbon nanotube is considered as an 'effective fibre' and the properties of the composite are determined based on micro-mechanical discontinuous fibre models.

3.2.2 Nanotube load transfer mechanism: Effective fibre properties

The structure must be taken into consideration to model the properties of nanotube-based composite. A multi-walled carbon nanotube is simply formed by concentric single-walled nanotubes, which in turn can be visualized as cylindrical graphene sheets as explained earlier. The load is transferred as shear forces at the nanotube/matrix interface. The bonding between walls of the carbon nanotubes being weak due to van der Waals nature, the load applied at the nanotube/matrix interface is almost entirely taken up by the outermost layer and there is very little load transfer between layers.

The load for the effective fibre is assumed to be acting on the whole cross-sectional area of the nanotube and an iso-strain model is adopted for the effective fibre system.

$$\varepsilon_{\mathrm{NT}} = \varepsilon_{\mathrm{eff}}$$

where the subscripts NT and eff refers to the nanotube and the effective fibre respectively.

$$E_{\mathrm{eff}} = \frac{\sigma_{\mathrm{eff}}}{\sigma_{\mathrm{NT}}} E_{\mathrm{NT}}$$

The diameter and the length of the tube and the composite are assumed to be same as shown in Fig. 8. From the above equation, the elastic properties of the nanotube and the effective fibre can be related.

$$E_{\mathrm{eff}} = \frac{4t}{d} E_{\mathrm{NT}}$$

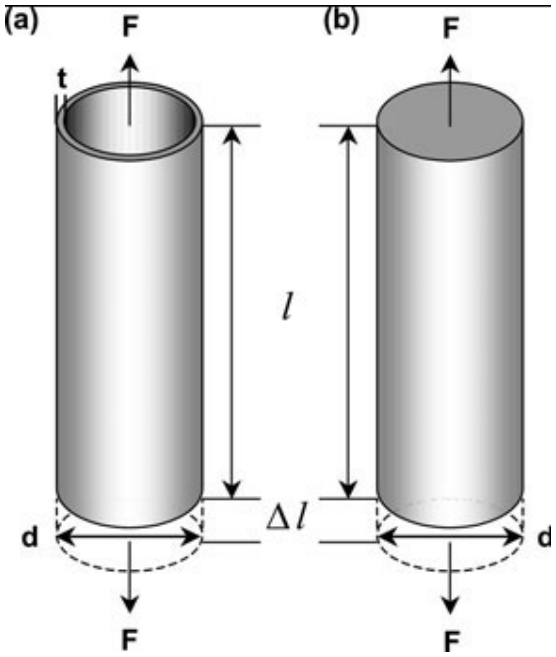

Figure 9 Schematic of (a) nanotube and (b) effective fibre used to model the elastic properties of a nanotube embedded in a composite. [Ref: Erik T Thostenson and Tsu-Wei Chou, On the elastic properties of carbon nanotube-based composites: modeling and characterization, J. Phys. D: Appl. Phys. 36 (2003) 573–582]

Using the above model and employing a nanotube diameter distribution, the strength of the nanocomposites can be simulated as a function of the volumetric fraction of the carbon nanotubes and diameter of the carbon nanotube using Double Gaussian and Double Lorentian methods.

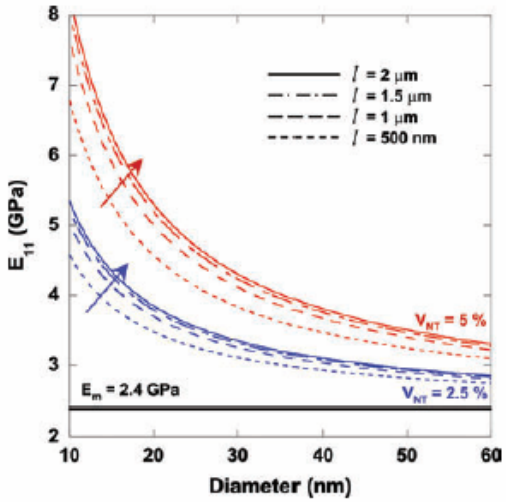

Figure 10. Influence of nanotube diameter, volume fraction and length on the elastic properties of an aligned nanocomposite system. [Ref: Erik T Thostenson and Tsu-Wei Chou, On the elastic properties of carbon nanotube-based composites: modeling and characterization, J. Phys. D: Appl. Phys. 36 (2003) 573–582]

The simulation shows that the nanocomposite elastic properties are particularly sensitive to the nanotube diameter. Nanotubes of a given diameter show better strength with a greater volume fraction, which is clear from Fig.9.

3.3 Scanning Probe Tips

Carbon nanotubes, which have high strength-weight ratios and which buckle reversibly, are ideal structures for use as tips in scanning probe microscopies, such as atomic force microscopy (AFM). Chemical Vapour Deposition method is employed for growing the carbon nanotubes on the Scanning Probe tips as it can be grown in precise regions with high precision. Alternatively, carbon nanotube can be attached to the scanning probe tip. It must be ensured that the attachment is perpendicular to achieve maximum lateral resolution[10]. The attachment is shown in Fig.11.

Carbon nanotubes show greater endurance properties than etched Si tip. Multi Walled carbon nanotube shows no tip wear after several scans whereas etched Si tip shows considerable tip wear after just a few scans. This is due to the reversible buckling phenomenon exhibited by multi-walled carbon nanotubes.

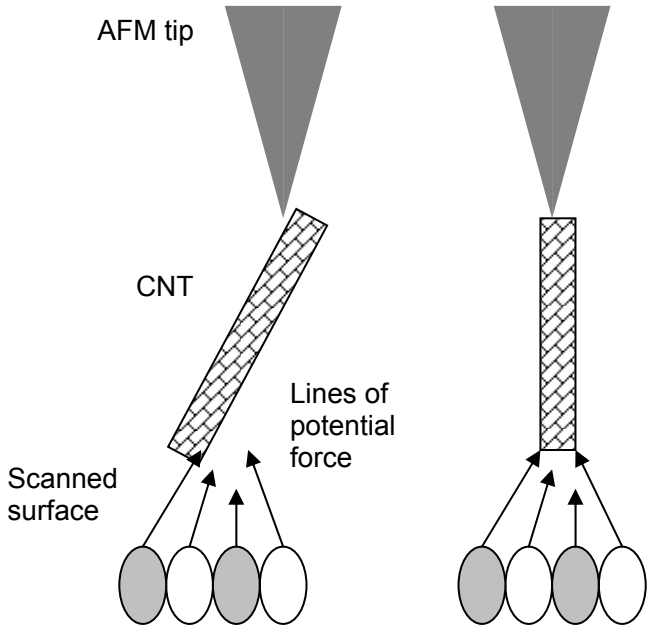

Figure 11. The attachment of carbon nanotube to an AFM tip

3.4 Nanotweezers

The single probe tips used in SPMs limit these tools' ability to manipulate objects and measure physical properties; for example, one tip cannot grab an object, and electrical measurements cannot be made without a second contact to structures. Two probes in the form of tweezers can overcome this limitation[11]. The method of making a nanotweezer is schematically represented in Fig. 12.

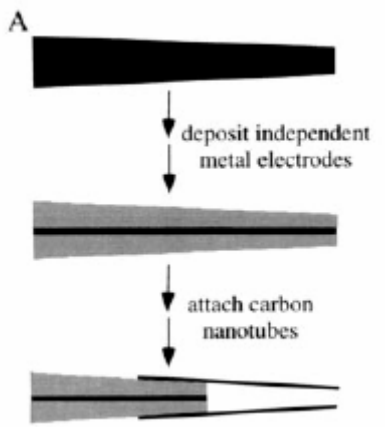

Figure 12. Schematic illustration of making a nanotweezer. [Ref: Philip Kim and Charles M. Lieber, (1999) Nanotube Nanotweezers, Science, 286 2148-2150]

The electromechanical response of nanotweezers can be investigated by applying bias voltages to the electrodes and simultaneously imaging the nanotube displacements. The ends of the tweezer arms bent closer to each other from their relaxed position as the bias voltage is increased as shown in Fig.13. These results demonstrate that the mechanical response is elastic and no plastic deformation occurs. The tweezer arms suddenly close at 8.5V. The nanotweezer arms typically remain closed after removal of the actuating voltage, because the van der Waals interaction between tubes produces a second potential minimum at contact.

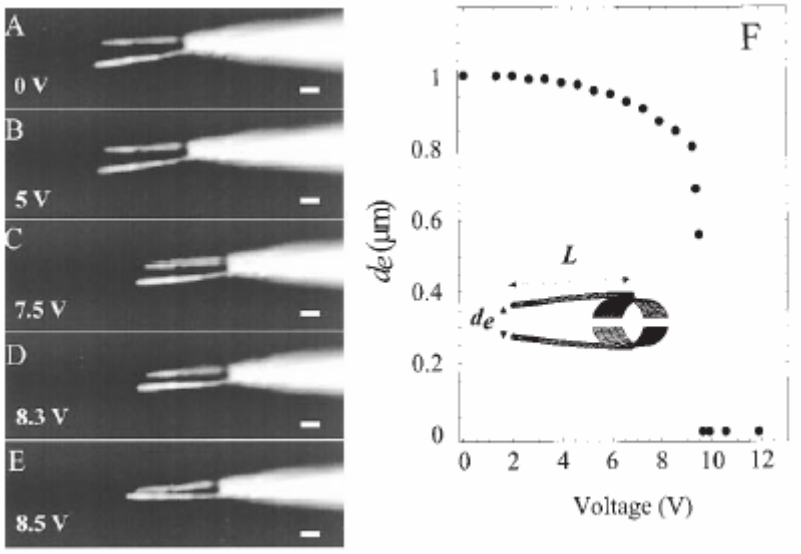

Figure 13. Electromechanical response of the nanotube nanotweezers. [Ref: Philip Kim and Charles M. Lieber, (1999) Nanotube Nanotweezers, Science, 286 2148-2150]

These nanotweezers can also be used to create new types of quantum dot and quantum wire structures. They can also be used as a two-tip STM or conducting AFM probe.

3.5 Nanoropes

Nanoropes are preferred over nanowires because of their better load transfer abilities. It has a greater structural reliability because the radial component of force gives it additional stability. For example, when one wire component breaks, the broken sections of that particular wire can still bear load transferred from the other wires through the strong friction force that is a consequence of the radial compression.

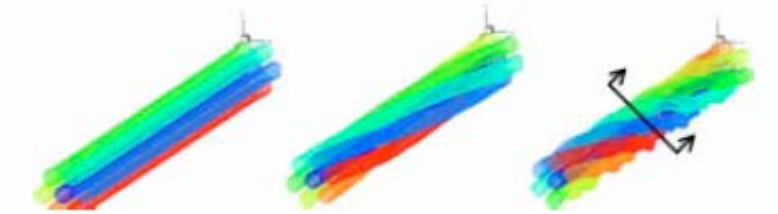

Figure 14. Twisting of the single-walled carbon nanotube bundle

The properties of nanoropes are strong functions of the twisting angle as can be seen in the Fig 15 and 16.

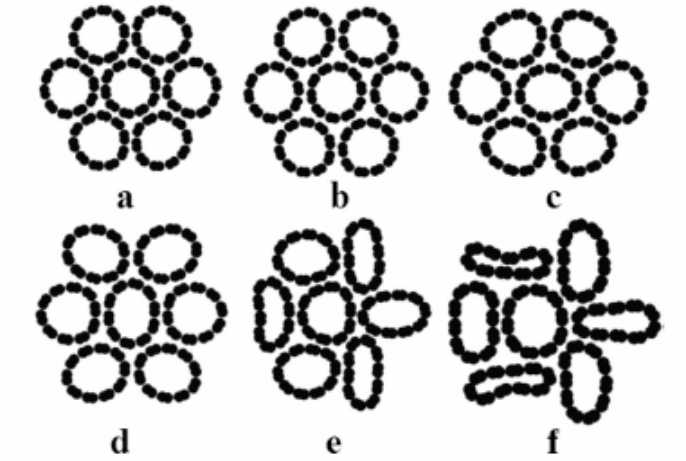

Fig. 15 Change in cross-section at the mid-point of the single-walled carbon nanotube bundle as a function of twist angle (From a–f, the twisting angles are 30, 60, 90, 120, 150, and 180˚)

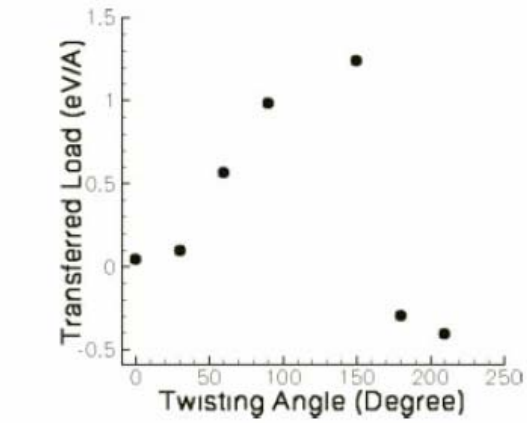

Figure 16. Transferred load as a function of twisting angle

4. Summary

The study of nanosystems is very crucial in understanding macroscopic functional evolution. The functional characterization of materials were discussed with respect to the spectroscopic techniques. The mechanical properties of carbon nanotubes can be experimentally characterized by various methods such as atomic force microscopy and electrostatic bending. The core of the work carried out in this area is largely experimental and computational studies have been briefly summarized. The applicability of continuum mechanics to the nanoscale works surprisingly well, considering the high Knudsen number. The study of nanomechanics bridges the gap between the quantum level and the continuum level. A number of applications have been described in section 3, which highlight the strength of the carbon nanotube. It is believed that carbon nanotubes will eventually make a fundamental change to technology.

5. References

[1] Thostenson E T, Ren Z F and Chou T-W, (2001) Advances in the science and technology of carbon nanotubes and their composites: a review *Compos. Sci. Technol.* **61** 1899–912.

[2] Z. L. Wang, P. Poncharal, and W. A. de Heer, Nanomeasurements of individual carbon nanotubes by *in-situ* TEM, (2000) Pure Appl. Chem., 72(1–2), 209–219.

[3] Aleksandr Noy, Dmitri V. Vezenov, and Charles M. Lieber, (1997) Chemical Force Microscopy, Annu. Rev. Mater. Sci. 27:381–421.

[4] Dong Qian, Gregory J Wagner, Wing Kam Liu, Min-Feng Yu and Rodney S Ruoff, (2002) Mechanics of carbon nanotubes, Appl. Mech. Rev. 55(6).

[5] Erik T Thostenson and Tsu-Wei Chou, (2003) On the elastic properties of carbon nanotube-based composites: modeling and characterization, J. Phys. D: Appl. Phys. 36 573–582.

[6] D. Pierson, C. Richardson, B. I. Yakobson, Symmetry-dependent strength of carbon nanotubes, Sixth Foresight Conference on Molecular Nanotechnology.

[7] Georgii G. Samsonidze, Guram G. Samsonidze, and Boris I. Yakobson, (2002) Kinetic Theory of Symmetry-Dependent Strength in carbon nanotubes, Phy.Rev.Lett. 88(6), 1-4.

[8] Salvetat JP, Briggs GAD, Bonard JM, Bacsa RR, Kulik AJ, Stockli T, Burnham NA, and Forro L, (1999) Elastic and shear moduli of single walled carbon nanotube ropes, *Phys. Rev. Lett.* 82(5), 944–947.

[9] Zhou X, Zhou JJ, and Ou-Yang ZC, (2000) Strain energy and Young's modulus of single-wall carbon nanotubes calculated from electronic energy-band theory, *Phys. Rev. B* **62(**20), 13692–13696.

[10] J. H. Hafner, C. L. Cheung, C. M. Lieber, (1999), Growth of nanotubes for probe microscopy tips, Nature, 398, 761-762.

[11] Philip Kim and Charles M. Lieber, (1999) Nanotube Nanotweezers, Science 286 2148-2150.

[12] Eric W. Wong, Paul E. Sheehan, Charles M. Lieber, (1997) Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes, Science 277 1971-1975.

[13] Deepak Srivastava, Kyeongjae Cho and Chenyu Wei, (2003) Nanomechanics of carbon nanotubes and composites, Appl Mech Rev 56(2) 215-230.

Additional Reading

[1] Carbon Nanotubes: Synthesis, Structure, Properties and Application by R.E. Smalley, Mildred S. Dresselhaus, Gene Dresselhaus.

[2] Carbon Nanotubes: Science and Applications, by M. Meyyappan

[3] Science of Fullerenes and Carbon Nanotubes : Their Properties and Applications by M. S. Dresselhaus, et al.